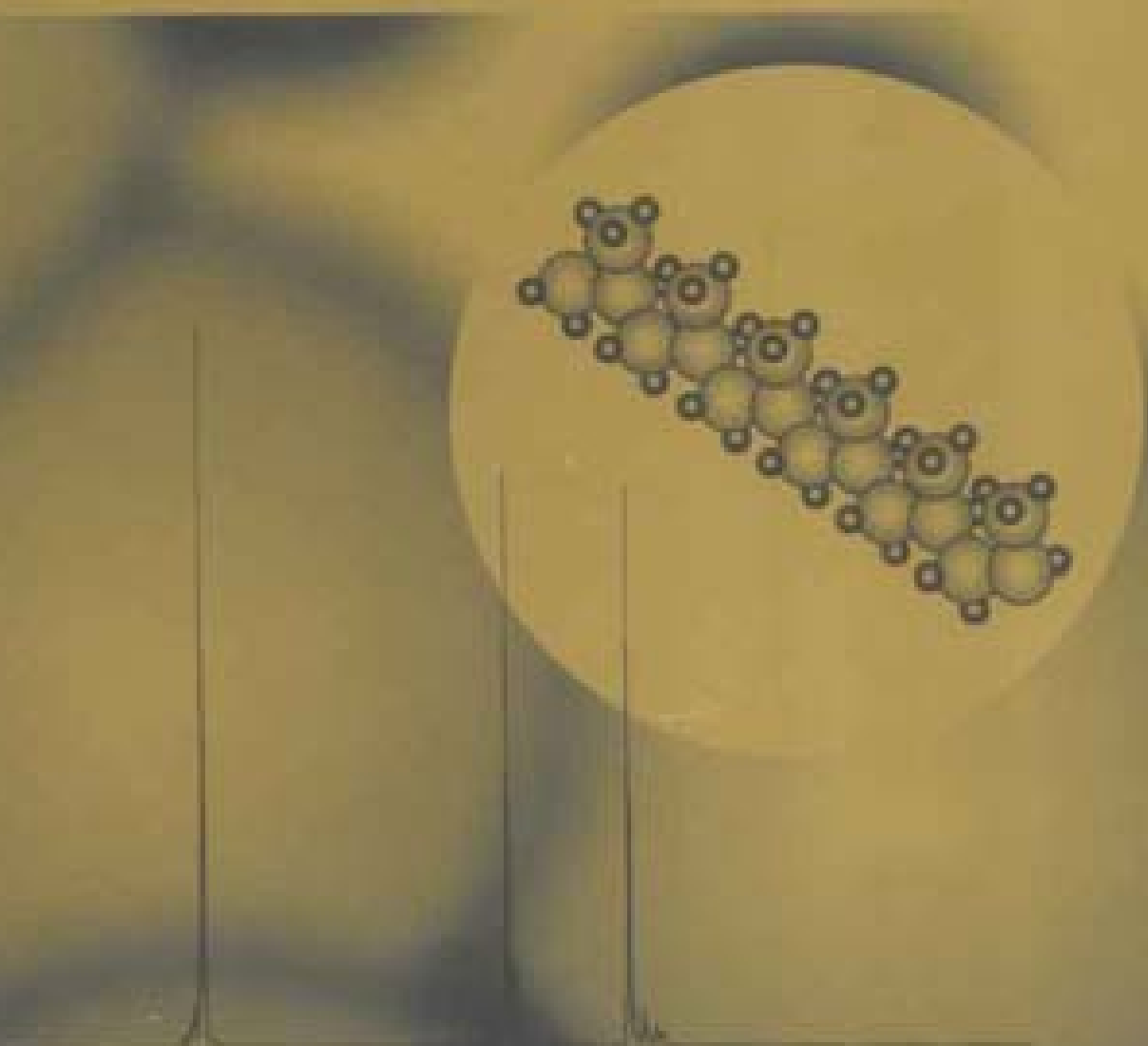


NMR Spectra of Polymers and Polymer Additives



Anita J. Brandolini
Deborah D. Hills

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Mobil Chemical Company
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Preface

Polymers are all around us. We have grown accustomed to the ubiquity of synthetic materials in our lives—in packaging, household products, clothing, and medical products, to name a few. When one also considers the occurrence of natural polymers, such as paper, wood, cotton, and wool, the prevalence of repetitive macromolecular structures becomes even more apparent. The identification and characterization of such large molecules has become an important goal for manufacturers of consumer goods, foods, pharmaceuticals, coatings, adhesives, and other products, as well as for plastics producers. High-resolution nuclear magnetic resonance (NMR) spectroscopy is one of the chemist's most versatile tools for characterizing molecular structure, and its application to polymer solutions has provided unparalleled qualitative and quantitative information about these materials.

While the interpretation of NMR spectra of polymer solutions generally follows the same approach as for smaller molecules, the characterization of commercial materials can be a more complicated task. Chemical-shift calculations, spectral editing techniques, and comparison to published data can all be used to assign the observed resonances, but a full explication of the spectrum often requires an understanding of materials formulations as well. Many polymers exhibit inherent structural complexities, such as stereoisomerism and comonomer incorporation, but commercial products are often blends of two or more polymers and may include additives at relatively high concentrations. One of our goals in collecting these spectra has been to provide not just a compilation of chemical-shift data for nearly 300 polymers and polymer additives but also pragmatic advice relevant to acquiring and interpreting NMR spectra of these materials. We hope that the result will be useful to NMR specialists who need information about the spectral characteristics of polymers, and to polymer scientists who may not be familiar with the subtleties of NMR.

In selecting the materials to be included in this compilation, we have striven first and foremost for utility. They are, for the most part, the commercially significant polymers with the exception of those that are insoluble, such as thermosetting resins. The data are predominantly ^{13}C spectra, but, where useful, spectra of other nuclei (^1H , ^{19}F , ^{29}Si , and ^{31}P) were recorded as well. With the exception of the ^{19}F data, all were acquired on our trusty JEOL GX400/Eclipse 400 spectrometer equipped with a 10-mm broadband probe. Each entry is accompanied by molecular structure(s), peak assignments, experimental parameters, literature references, and comments that include synonyms, trade names, likely blend components and additives, important end uses, and other practical background information. The polymers are grouped according to the chemical structure of the backbone (aliphatic hydrocarbons, unsaturated hydrocarbons, ethers, esters and amides, and miscellaneous) and by the nature of any pendant groups (aliphatic hydrocarbons, aromatic hydrocarbons, esters and amides, and miscellaneous). Each chapter includes an introduction that surveys samples preparation, characteristic spectral features, and typical analyses for the polymers in that group.

As with any work of this type, there are many people who contributed to our efforts. In particular, we thank all those friends and colleagues who encouraged (or, in some cases, mercilessly nagged) us over the years we have worked on this project. We extend our particular gratitude to Dr. Michael Frey of JEOL USA (Peabody, MA), who recorded the ^{19}F spectra found in Chapter V. Our coworker, Patricia Nelson, of Mobil Chemical, recorded the photomicrographs shown in Chapter I. Scientific Polymer Products (Ontario, NY) donated many of the polyacrylates and methacrylates characterized in Chapter IV, and Genesee Polymers (Flint, MI) most of the silicone materials in Chapter IX. Samples were received from many of our

former colleagues at Mobil Chemical's Edison Research Laboratory—Dr. Ellen Brandes, Dr. Robert Duttweiler, Dr. Hitesh Fruitwala, Dr. Binnur Gunesin, Dr. Yury Kissin, and Dr. Michael Krause—and from other associates: Dr. H. N. Cheng (Hercules), Professor Cecil Dybowski (University of Delaware), Dr. Richard Eckman (formerly of Exxon Chemical), Jackie Morris (Ciba Specialties), Dr. Joe Ray (formerly of Amoco), Dr. Nitu Sekhon (formerly of Montell), Dr. Mark Stachowski (University of Connecticut), Dr. Laurie Weddell (DuPont), and Professor Adolfo Zambelli (Università di Salerno). Helpful discussions with Dr. Connie Ace (Ethicon), Professor Frank Blum (University of Missouri–Rolla), Dr. Laurie Galya (DuPont), and Professor Lon Mathias (University of Southern Mississippi) are also acknowledged. The support of our management at Mobil Chemical's Edison Research Laboratory, particularly of Dr. Herbert Spannuth, is greatly appreciated. Finally, we thank Moraima Suarez of Marcel Dekker, Inc., for her helpful suggestions.

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I— Introduction

I.A— Structure-Property Relations in Polymers

Plastic garbage bags, medical implants, textile fibers, bulletproof vests—these are just a few of the diverse applications of modern polymeric materials [1]. This breadth of applicability is possible because of the wide range of properties these substances can exhibit. Although the ubiquity of polymers has largely resulted from the development of synthetic materials, natural macromolecules (cellulose and derivatives and natural fibers, such as wool and silk) also continue to be important. Polymers, which are composed of one or more repeating subunits called monomers, belong to a wide variety of chemical classes: hydrocarbons, esters, amides, ethers, and others. The chemical identity and stereochemical configuration of the long polymer molecules govern the intra- and interchain interactions that ultimately lead to the bulk properties that suit the material to a specific use [2,3].

High-resolution nuclear magnetic resonance (NMR) spectroscopy of solutions has proved to be a powerful aid in the structural characterization of all types of chemical compounds [4–7]. NMR is also an invaluable tool for the qualitative and quantitative analyses of polymers, enabling description of subtle molecular details. Spectra of either carbon or hydrogen nuclei are the most generally useful, but, in appropriate cases, other nuclides (e.g., fluorine, phosphorus, silicon, or nitrogen) can provide information not available from the more common nuclei [8,9]. The chemical shift is the NMR parameter most often used for structure determination, although analysis of coupling patterns, relaxation behavior, or nuclear Overhauser enhancements can supply additional details. The multidimensional NMR approach [10–12] allows complex chemical structures to be described even more fully by facilitating correlation of various spectral parameters. The applicability of NMR spectroscopy extends even beyond chemical characterization, to the investigation of various physical phenomena: kinetics, dynamics and morphology.

This introductory chapter will overview the application of high-resolution, solution-state NMR spectroscopy to the study of polymers. Insoluble materials necessitate the use of special techniques, such as dipolar decoupling and magic-angle spinning, to obtain a solid-state spectrum; these will not be described here [13–16]. Structure-property relations will be discussed first, because they are a key to defining the ultimate usefulness of the material. This introduction will show how NMR can help elucidate these salient details of polymer molecular structure. Neither polymer science nor NMR spectroscopy can be covered comprehensively in a few pages; the interested reader is referred to other sources for further information on polymers [1–3], NMR [4–12], or more specifically, NMR of polymers [17–23].

I.B— An Overview of Polymer Structures

Commercially important synthetic polymers belong to many different classes of chemical compounds: hydrocarbons, esters, amides, dienes, and so on. Polymers are products of a controlled chain reaction of smaller molecules called monomers. Generally speaking, one can form polymers by: (1) opening a multiple bond or ring; or (2) reacting difunctional monomers. The resulting molecules are long (molecular weights can exceed 10^6), and have final properties quite different from those of the constituent monomers. These properties depend on details of molecular structure, such as stereochemistry or degree of branching. By manipulating these details, the bulk properties of these materials can be tailored to fit an intended application.

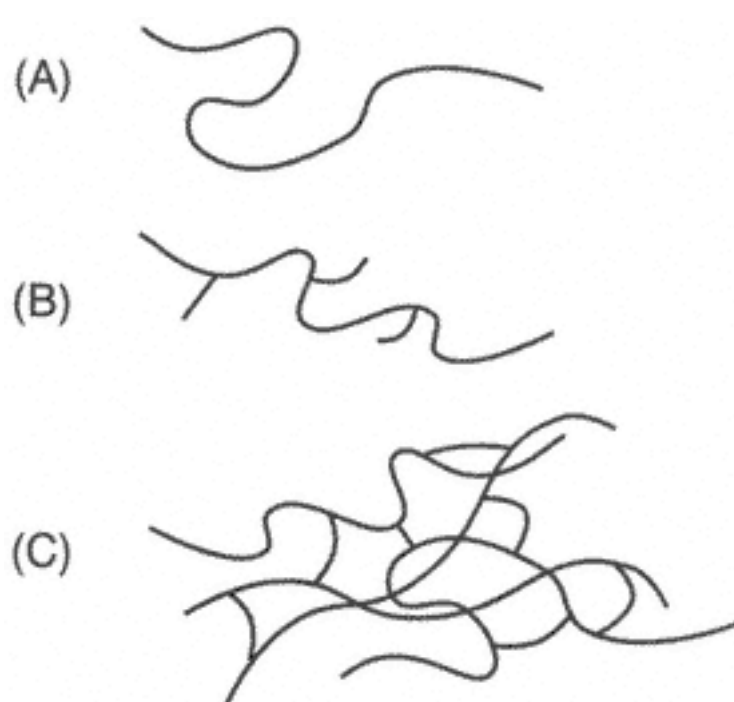


Figure I.1
Molecular architecture of of polymer
molecules: (A) linear; (B) branched; (C) cross-linked.

The overall molecular architecture of a polymer chain can be linear, branched, or cross-linked, as shown in Figure I.1. Most linear and slightly branched materials melt and flow; these are called thermoplastics. The cross-linked, or network, polymers are referred to as thermosets.

I.B.1— Polymerization Reactions

One commercially important polymer produced by breaking multiple bonds is polyethylene (PE), which is manufactured from gaseous ethylene:



I.A

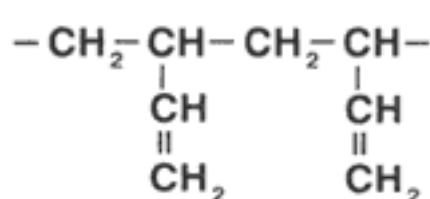
This reaction can be initiated by either a free-radical generator (such as a peroxide) or by an organometallic catalyst [1]. The free-radical process results in a highly branched polymer; catalytic routes tend to produce a more linear material. Each form of PE has distinct properties that will be discussed in detail in Section I.B.3. Many other familiar polymers [such polypropylene, polystyrene, poly(vinyl chloride), and the acrylics] are made from unsaturated monomers in this way (see Chapters II–V).

Polymers produced from dienes may retain some unsaturation. For example, polymerization of 1,4-butadiene results in a polymer with residual unsaturation in the backbone (1,4 addition):



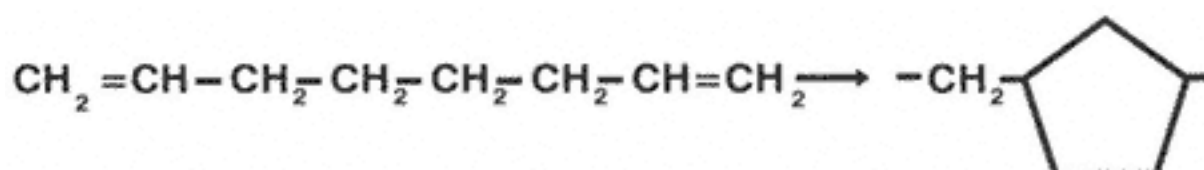
I.B

(both *cis* and *trans*) or with pendant vinyl groups (1,2 addition):



I.C

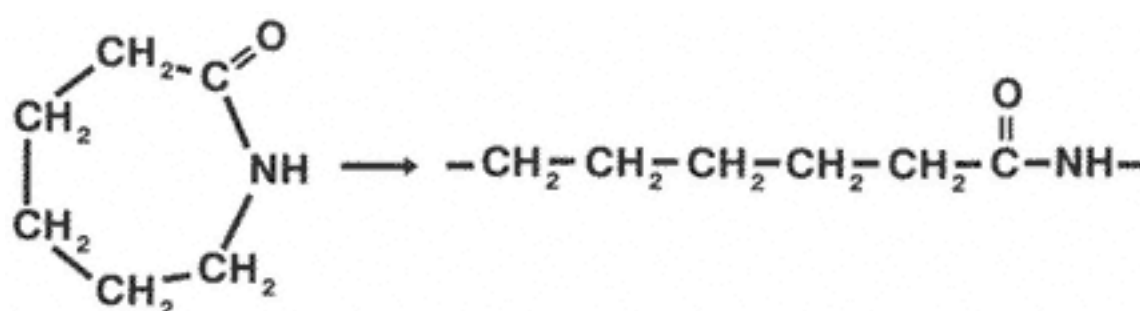
Not all dienes behave in this way, however. For example, on polymerization, 1,6-hexadiene forms in-chain cyclopentyl rings:



I.D

with both *cis* and *trans* isomers.

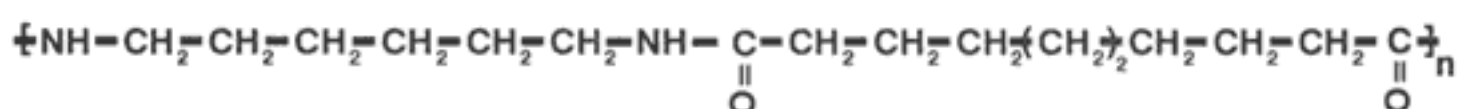
A polymer that results from a ring-opening reaction is polycaprolactam (or, as more commonly known, Nylon 6):



I.E

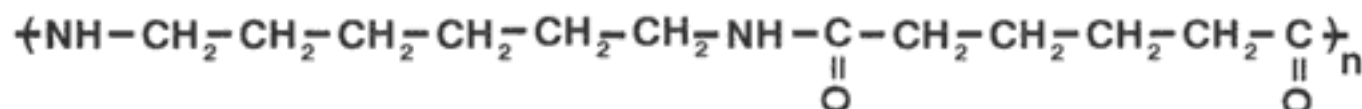
Polycaprolactam is classified as a polyamide, after the repeating amide linkage.

Another possible route to polyamides is a condensation reaction between two difunctional monomers, such as hexamethylenediamine and decanedioic (sebacic) acid, which react to give poly(hexamethylene decanediamide), or Nylon 6/10:



I.F

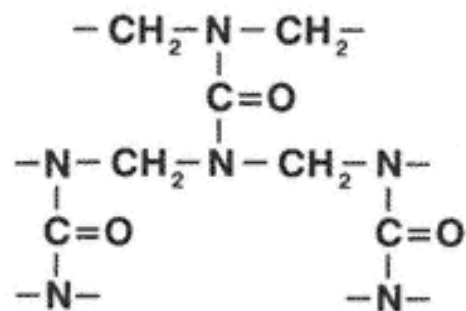
Other condensation polymers include polyesters and polyethers (see Chapters VI and VII). The polymers that result from such reactions are usually linear, but their bulk properties can be varied by changing the constituent monomers. For example, if hexanedioic (adipic) acid replaces nonanedioic acid in reaction **I.F**, poly(hexamethylene hexanediamide), or Nylon 6/6, is produced:



I.G

which has a melting point fully 40°C below that of Nylon 6/10.

If monomers with tri- or higher functionality are used, the resulting polymer is a network, as in a urea-formaldehyde resin:



I.H

for which the molecular weight is extremely high, approaching infinity. In general, these materials are polymerized in situ (i.e., the monomers are mixed together where needed and allowed to react). Except at very low molecular weights (MWs), these materials are insoluble in most solvents. Other examples of network polymers are epoxies and melamine-formaldehyde resins.

I.B.2—

Chemical Structure of Polymers

The most fundamental molecular structural feature affecting polymer properties is the molecular weight (MW). In most polymerization processes, termination steps occur somewhat randomly, leading to a statistical distribution of chain lengths, which can be described by an average molecular weight and by a molecular weight distribution (MWD) (Fig. I.2). The average MW can be calculated in several ways. The number-average MW, M_n , is given by:

$$M_n = \frac{N_i M_i}{N_i} = \frac{\text{weight of system}}{\text{no. of molecules}} \quad (\text{I.1})$$

where N_i represents the number fraction of molecules of mass M_i . The weight-average MW, M_w , is defined as:

$$M_w = \frac{W_i M_i}{W_i} \quad (\text{I.2})$$

where W_i is the weight fraction of molecules of mass M_i . The ratio M_w/M_n , the polydispersity index, indicates the breadth of the MW distribution. Some polymerization processes lead to monodisperse distributions (i.e., all chains are the same length), and for such systems, the polydispersity index is nearly 1.

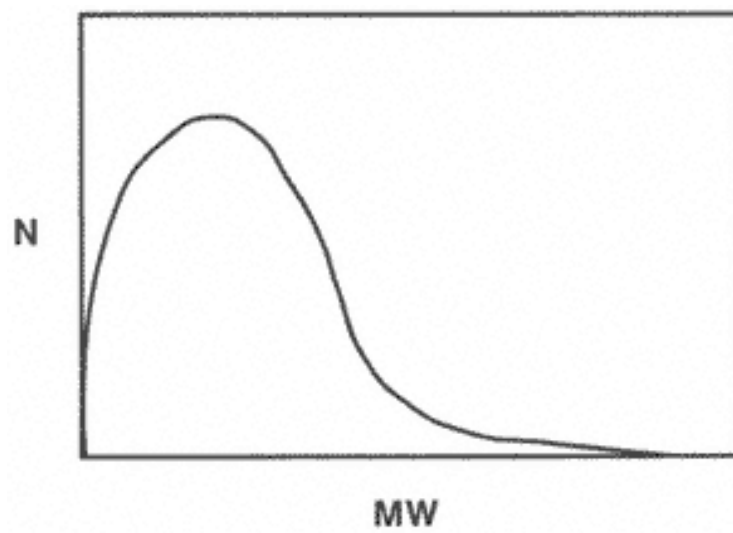
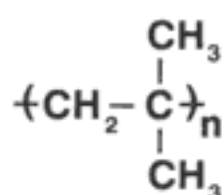


Figure I.2
Molecular weight distribution curve.

The effect of MW on properties can be easily seen for the case of polyisobutylene (PIB):

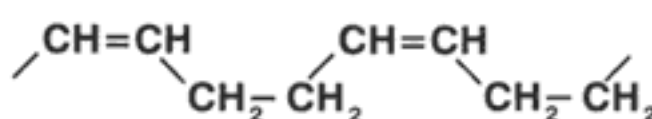


I.I

which is a viscous liquid in its low-MW form and an elastomer (rubber) at higher MWs. The liquid polymers are used as tackifying agents in the production of cling films, whereas the elastomers form the basis of the butyl rubber used to make, among other things, O-rings and gaskets [1].

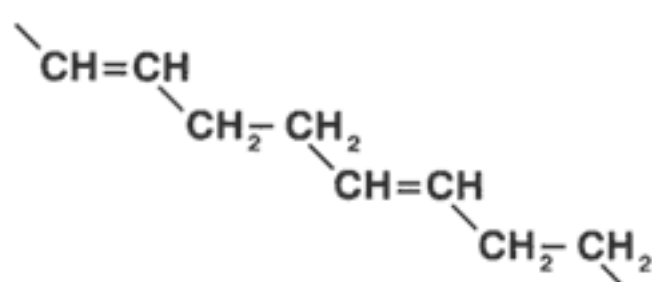
It is often the more subtle details of molecular structure, not simply the chemical classification or even the molecular weight, that ultimately account for a material's bulk properties. For example, branched PE has properties quite different from the linear form, and the density of branched PE is significantly less than that of linear (0.90 g/cm³ versus 0.95 g/cm³). In fact, branched PE is commonly called low-density polyethylene (LDPE); the linear form, high-density polyethylene (HDPE).

Some polymer structures can exhibit either geometric or stereoisomerism, which also affects polymer properties. For example, polybutadiene (PBd) has two major geometric isomers, the *cis*:



I.J

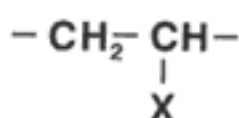
and the *trans*:



I.K

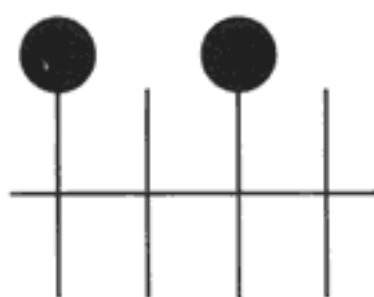
High-*cis* and high-*trans* content PBd are strikingly different materials. The high-*cis* form is a rubber at room temperature, the high-*trans* form is crystalline, and a polymer chain containing approximately equal amounts of both isomers is also elastomeric.

Another type of isomerism that strongly influences a polymer's properties is stereoisomerism, or tacticity. This effect is especially important in polymers with the general structure:



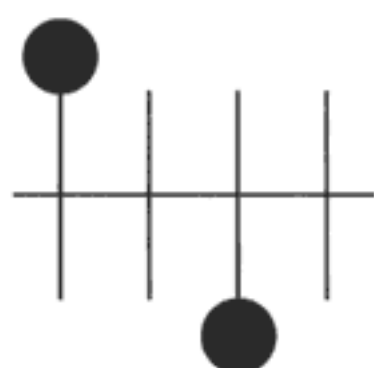
I.L

where X can be any one of a number of pendant groups, such as a chlorine atom for poly(vinyl chloride), a methyl group for polypropylene, or a phenyl ring for polystyrene. A simple ball-and-stick drawing illustrates that a pair of pendant groups (designated by the black circle) may be situated on one "side" of the polymer backbone in a *meso* (m) configuration:



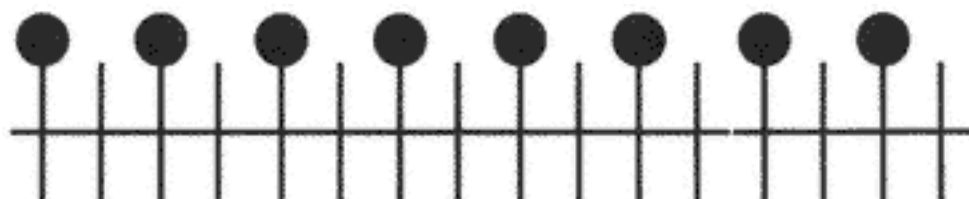
I.M

or on alternate "sides", in a *rac meic* (r) arrangement:



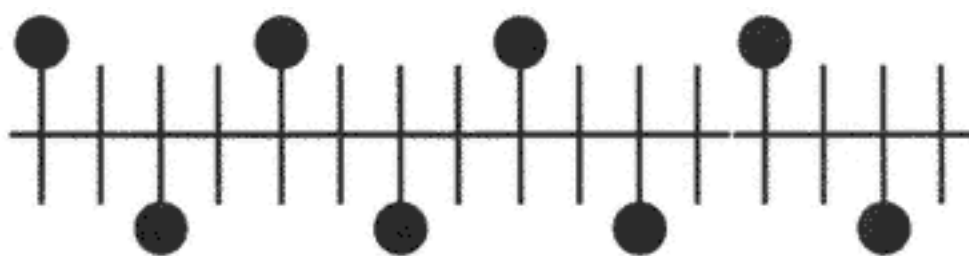
I.N

A length of the polymer chain may be viewed as a series of pairs, or dyads. Long sequences may be isotactic (-mmmmmm-):



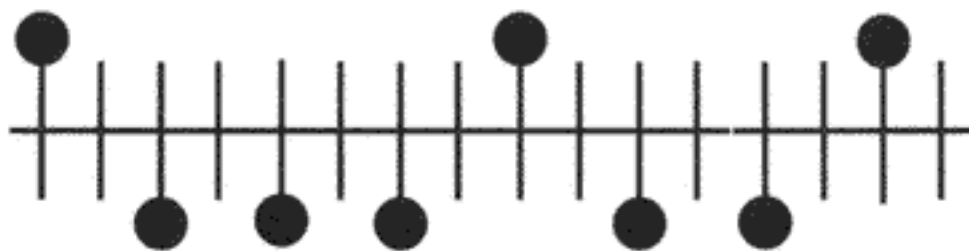
I.O

syndiotactic (-rrrrrr-):



I.P

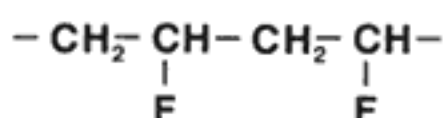
or atactic (-rmmrrmr-):



I.Q

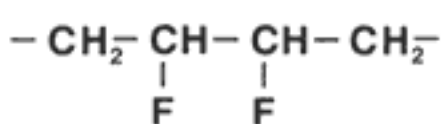
Polypropylene (PP) is a polymer for which the iso- and syndiotactic forms melt well above room temperature (160 and 135°C, respectively). In contrast, the atactic form is soft and weak at room temperature.

Yet another form of isomerism observed in some polymers is regioselectivity [17–21], the directionality of addition along a polymer chain. Monomers such as vinyl fluoride can add in either a head-to-tail:



I.R

or in a head-to-head fashion:



I.S

In most such systems, the head-to-tail configuration is strongly preferred on steric grounds. The structures of polymers with many head-to-head inversions are quite complex, because tacticity is superimposed on regioirregularity, resulting in a myriad of structures: *meso* head-to-head, *racemic* head-to-head, *meso* head-to-tail, and *racemic* head-to-tail.

Even more control over polymer characteristics can be achieved by production of copolymers, which are made by reacting two or more different monomers called comonomers. The resulting polymer structure may be blocky:

AAAAAAAAAAAAABBBBBBBBAAAAAAAAAAAA

I.T

alternating:

ABABABABABABABABABABABABABABAB

I.U

or random:

ABBAAAABBABABBBAAABABBBABBBBAABBAAA

I.V

or a second chain can be grafted onto the first:

AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
B
B
B
BBBBBBBBBBBBBBBBBB

I.W

Blocky and random copolymers are the most common. In block copolymers, the length of the block segments can influence properties. In "random" copolymers, the exact distribution of the comonomers (called the sequence distribution) is a consequence of the polymerization conditions. The sequences can be statistically random (Bernoullian), for which the distribution is a function only of the relative amount of each comonomer, or they can deviate predictably from randomness

(Markovian), in which the identity of the next unit added is influenced by the identity of the comonomer at the end of the growing chain [18].

I.B.3—

Physical Structure and Properties of Polymers

Although many of the physical properties of polymers are similar to those of lower-MW compounds, others are unique to macromolecules and arise from their large size. Some polymer molecules crystallize, others have amorphous structures, and still others possess combination, or "semicrystalline" morphologies. Thermal or mechanical treatment can alter these structures. This variety gives rise to very complex thermodynamic behavior, with many materials exhibiting several different transition temperatures. The chemical and physical structural features of a material also affect the way it can be processed into a final product, as well as the mechanical properties that the product will have.

High- and low-density polyethylene (HDPE; LDPE) demonstrate the effect of molecular structure on polymer morphology. Each is "semicrystalline," with both ordered (crystalline) and disordered (amorphous) domains (Fig. I.3; 24). The layers (called lamellae) are made up of folded PE chains. The regions around the lamellae are amorphous, composed of randomly coiled chains. The greater structural irregularity of LDPE (because of its branches) inhibits crystallization, resulting in a material with a higher proportion of amorphous chains, and with less perfectly formed crystals (Fig. I.4). Many materials, such as atactic polystyrene, poly(methyl methacrylate), and polyisobutylene exhibit no crystalline structure at all. Their chains all adopt the randomly coiled, amorphous conformation.

Polymer morphology gives rise to complex thermal behavior. For example, the more regular crystalline domains of HDPE melt at 135°C; the less ordered crystallites of LDPE melt at 110°C. This melting transition does not involve the amorphous regions of the material. Instead, amorphous polymers exhibit a secondary transition characterized by the glass-transi-

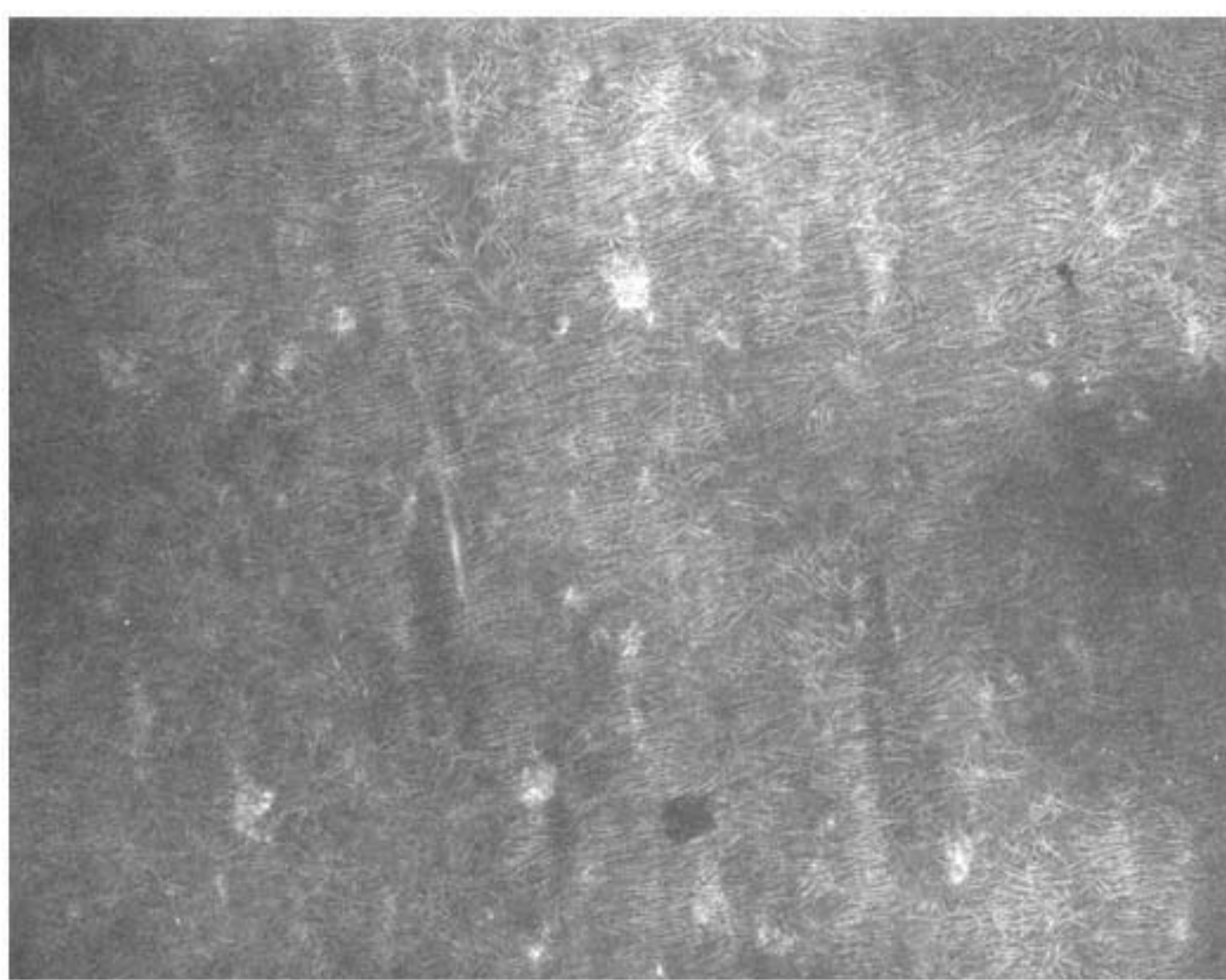


Figure I.3
Electron micrograph of high-density polyethylene, showing well-defined lamellae.
(From Ref. 24.)

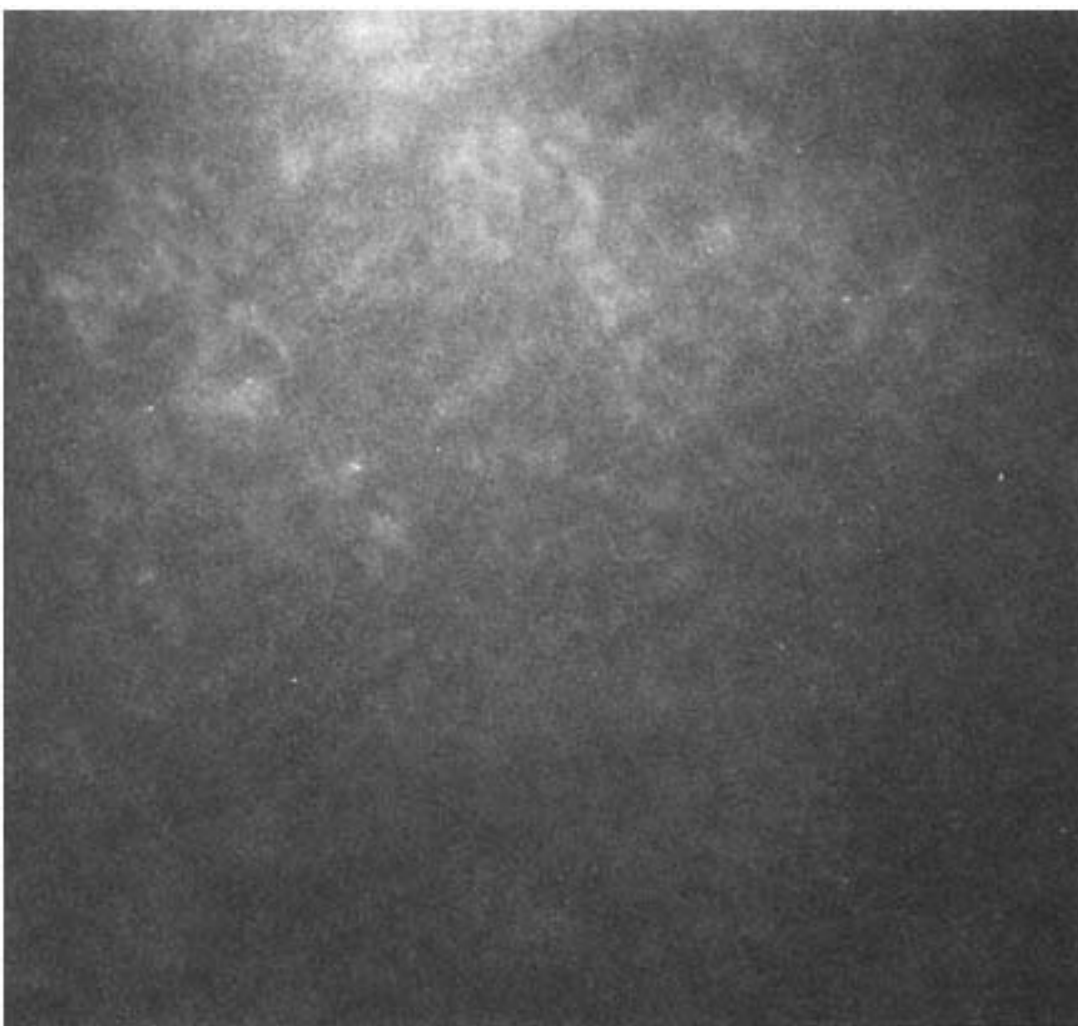


Figure I.4
Electron micrograph of low-density polyethylene, showing poorly defined lamellae.
(From Ref. 24.)

tion temperature T_g . Below T_g , the material is elastomeric; above T_g , it is brittle. For example, at room temperature, polyisoprene (natural rubber) is an elastomer; at liquid nitrogen temperatures, it shatters easily. Not all T_g s are subambient. Atactic polystyrene has a T_g of 160°C; hence, it is brittle at room temperature.

Many different processing techniques are employed to turn polymers into useful products. Much of this processing is done with the material in a fluid state (higher than T_m for semicrystalline polymers or higher than T_g for glassy polymers). For example, during injection molding, molten polymer is first forced into a mold. After cooling, the part is removed. Obviously, the polymer must flow easily and crystallize (solidify) rapidly to be useful as an injection-molding resin. On the other hand, when a fiber is spun from the melt, the material must not flow too easily, or the fiber's integrity will not be maintained during the spinning process. Because fibers are also stretched as they are produced to align the molecules for improved strength, crystallization should not occur too rapidly. These "rheological" (flow) properties can be tailored by adjusting the molecular structural parameters, such as molecular weight and MWD, or by incorporating an appropriate comonomer.

Polymeric materials exhibit complex behavior when they are subjected to stress, as shown in Figure I.5, which displays a typical relation between stress and strain during elongation. Stress, σ , is the applied force/unit area; strain, ϵ , is the resulting change in length, l/l_0 . In the elastic region (A), there is a simple, linear relation between σ and ϵ :

$$\sigma = E\epsilon \quad (1.3)$$

where the proportionality constant E is known as the Young's or elastic modulus. In this part of the σ - ϵ curve, all deformation is recoverable (i.e., if the stress is removed, the material returns to its original length). An elastomer exhibits this behavior up to the breaking point. On a molecular level, elastic deformation corresponds to small displacements or conformational changes of chemical bonds. For a thermoplastic material, such as PE, there is a "knee" in the σ - ϵ curve, called the

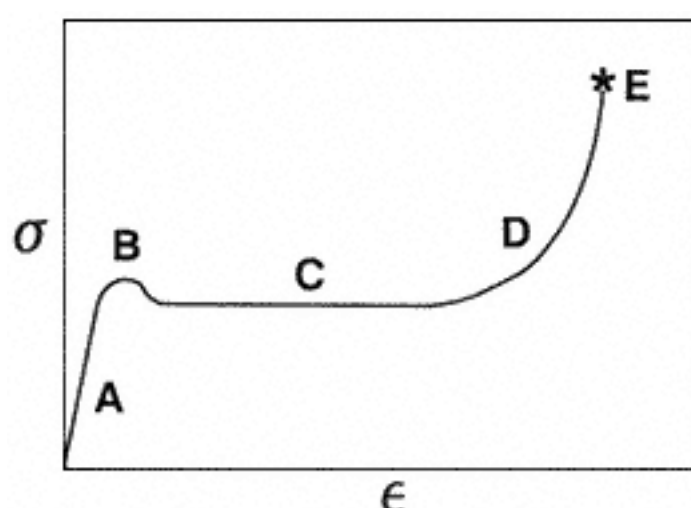


Figure I.5

Stress–strain curve for a typical polymeric material: (A) elastic region; (B) yield point; (C) flow; (D) strain hardening; (E) failure point.

yield point (B), above which elongation requires relatively little additional force (i.e., the material flows; C.). Above the yield point, morphological changes occur, with the crystalline regions reorienting, aligning themselves along the stretch axis. This process continues until the stress can no longer be accommodated by reorientation. The slope of the σ – ϵ curve then increases again. The material becomes more difficult to elongate, and strain-hardening sets in. Ultimately, the material cannot withstand further stress (D).

The rather complicated behavior illustrated in Fig. I.5 results from a very simple type of uniaxial applied stress. In real-world applications, polymeric materials undergo even more complex modes of deformation: impact, bending, twisting, tearing. Tests have been devised to evaluate the effect of these different types of mechanical stress. For example, polymers intended for applications requiring toughness, such as appliance housings, are subjected to a dart-drop test to simulate the effect of a sudden, sharp impact. Materials used in garbage bags, on the other hand, are checked for tear resistance, by measuring the force required to propagate a small notch.

I.B.4—

Multicomponent Polymer Systems

The foregoing sections have illustrated that a polymer's chemical and physical structures can be very complex. Many of these details can be manipulated, at least to some extent, to produce a material that has a desired set of characteristics. Physical blending of two or more resins is yet another strategy for tailoring polymer properties. Some blends exhibit characteristics of each component; in other blends, the properties are intermediate. For example, polystyrene homopolymer is very brittle and prone to sudden failure. When it is blended with polybutadiene, however, the resulting material, called high-impact polystyrene, is much tougher and more resistant to crack propagation. This blend can be used in certain applications (e.g., appliance housings) for which pure polystyrene is unsuitable. Sometimes, the end use may require properties intermediate between those of a low- and a high-cost resin. In such instances, the higher-cost material may be "diluted" with the lower-cost. Not all combinations of polymers mix equally well. Whereas some combine on a molecular level (such as some polyethylenes), others appear to be uniform, but actually form discrete domains on a microscopic scale (such as high-impact polystyrene). Still other combinations of polymers do not form stable blends, at some or all concentrations. Occasionally, this difficulty can be overcome through use of a compatibilizing agent, which promotes miscibility. These agents are very often block copolymers of the monomers in the each blend component.

Additives can also be used to confer desired properties. Pure poly(vinyl chloride) (PVC), for example, is rigid, brittle, and glassy at room temperature. To produce a soft material suitable for waterproof clothing or furniture covering, the T_g is lowered by addition of a few percent of a plasticizer, often a phthalate ester, which turns the base polymer into a more useful, ductile material (1). Other additives used at relatively high levels aid in processing, or confer either slipperiness or tackiness to the surface. Many other additives, such as antioxidants and light stabilizers, are blended into the polymer matrix at

parts-per-million (ppm) levels. These stabilizing additives help maintain the material's properties by limiting processing or environmental damage.

I.C— NMR Spectroscopy of Polymers

This section will assume a basic understanding of the Fourier-transform NMR experiment, and will deal only with the application of NMR spectroscopy to polymer structural analysis. For a more complete treatment, several excellent references are available [4–12]. Most of the discussion will focus on ^{13}C NMR, although other nuclei will be mentioned as appropriate.

I.C.1— The Zeeman Interaction

The source of nuclear magnetic resonance is the Zeeman interaction (i.e., the interaction between the magnetic moment of a nuclear spin and a static magnetic field):

$$\omega = \gamma H_0 \quad (1.4)$$

where ω denotes the resonant (Larmor) frequency, γ is the gyromagnetic ratio, a fundamental property of a nuclide, and H_0 is the static magnetic field. Only nuclei with nonzero spin are observable by NMR; this excludes many abundant nuclides, such as ^{12}C or ^{16}O . These elements do have NMR-active isotopes, although they occur naturally only at low concentrations (1.1% for ^{13}C ; 0.04% for ^{17}O).

The consequence of the simple relation in Eq. (1.4) is that ^{13}C , ^1H , ^{31}P , or any other NMR-active nucleus, has a unique frequency at which it can be observed. Most elements in the periodic table have at least one NMR-active nucleus [8,9]; Table I.1 summarizes the NMR properties of several commonly studied nuclei. For organic systems, ^{13}C and ^1H provide the most useful information. Unfortunately, the NMR properties of many other potentially interesting nuclei (such as ^{17}O or ^{15}N) are not favorable. Furthermore, many nuclides are quadrupolar (i.e., their spins are $> 1/2$), which generally leads to relatively broad resonance lines. NMR's ability to observe only one nuclide, without an interfering background signal from any others, can be useful. For example, many phosphorus-containing chemicals are used as antioxidants in polymers, typically at levels of 0.05–0.5 wt%. It can be difficult to identify the additive, or to study its degradation pathways, by other spectroscopic techniques, because the bands attributable to the additive are lost among those from the base polymer. ^{31}P NMR signals, however, arise only from the additive, permitting study of the additives' chemistry in situ [25].

I.C.2— Chemical Shift

The greatest strength of NMR is its sensitivity to subtle details of chemical structure. The Larmor equation (Eq 1.27) reveals the approximate resonant frequency for a particular nuclide, but slight variations from that basic frequency result from differences in chemical structure. The exact resonant position, or chemical shift, primarily depends on the electronic environment around the nucleus, with effects being observed over several bond lengths. Electronic deshielding, with resulting higher chemical shifts, occurs in, for example, halogenated, olefinic, and aromatic species. Because the effect of chemical shift is

TABLE I.1 NMR Properties of Selected Nuclei

Nucleus	Spin	Natural abundance (%)	Larmor frequency (MHz)
^1H	1/2	99.99	100.0
^{19}F	1/2	100	94.1
^{31}P	1/2	100	40.5
^{13}C	1/2	1.11	25.1
^{29}Si	1/2	4.70	19.9
^2H	1	0.02	15.4
^{17}O	5/2	0.04	13.6
^{15}N	1/2	0.37	10.1

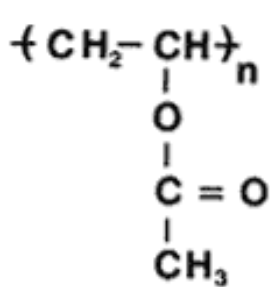
TABLE I.2 Chemical Shift Calculations^a

Substituent	¹³ C shift = -2.3 + α + β + γ + δ			
	α	β	γ	δ
>C<	9.1	9.4	-2.5	0.3
—O—	49.0	10.1	-6.0	0.3
—N<	28.3	11.3	-5.1	0.3
—S—	11.0	12.0	-5.1	-0.5
—C ₆ H ₅	22.1	9.3	-2.6	0.3
—F	66.0–70.1	7.8	-6.8	0.0
—Cl	31.1–43.0	10.0	-5.1	-0.5
—CN	3.1	2.4	-3.3	-0.5
>C=O	22.5	3.0	-3.0	0.0
—COOH	20.1	2.0	-2.8	0.0
—COO—	24.5	3.5	-2.5	0.0
—COO—	22.6	2.0	-2.8	0.0
(C-bonded)				
—COO—	54.5–62.5	6.5	-6.0	0.0
(O-bonded)				
—C=C—	21.5	6.9	-2.1	0.4

^a Some steric corrections are also required.

Source: Ref. 25.

predictable, calculational schemes, based on substituent effects, can estimate shifts for a particular molecule [5,6,26]. This is particularly true for ¹³C, the most commonly observed nucleus; one such scheme is summarized in Table I.2. This approach can be very helpful in a first attempt to assign the peaks in a spectrum. For example, Table I.3 compares calculated and observed chemical shifts for poly(vinyl acetate):



I.X

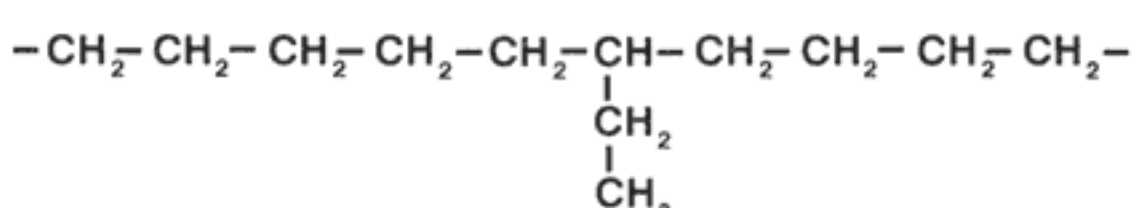
TABLE I.3 Comparison of Experimental and Calculated ¹³C Chemical Shifts for Poly(vinyl acetate)

Carbon	$\begin{array}{c} \text{A} \quad \text{B} \\ \text{-CH}_2\text{-CH-} \\ \\ \text{O} \\ \\ \text{C=O} \\ \\ \text{C CH}_3 \end{array}$	
	Experimental	Calculated
A	38.2	41.4
B	66.5	66.6
C	20.3	18.1

Although these calculation schemes give approximate shift positions, they do not account for the full variety of structural features observable by NMR. NMR spectroscopy would still be a useful, if somewhat limited, tool in polymer analysis if simple structural identification were its only application. However, it is also an extremely powerful technique for determining the microstructural details of polymer chemical structure. The NMR spectrum is sensitive to both geometric and stereoisomeric structure. The presence of both *cis*- and *trans*-isomers in PBd (see Structures I.J and I.K) is easily detected in the spectrum of Figure I.6. Tacticity, which has such a marked effect on a polymer's physical properties, is clearly observed in the NMR spectrum of Figure I.7, which contrasts the spectra of isotactic, syndiotactic, and atactic polypropylene.

NMR is also a useful tool in copolymer analysis. In addition to the low- and high-density forms of polyethylene, there is a third, commercially important type of PE, the linear low-density polyethylenes (LLDPEs), which are actually copolymers of ethylene and a few mole percent of a 1-olefin, usually 1-butene, 1-hexene, 1-octene, or 4-methyl-1-pentene [1]. The LLDPEs have a linear backbone, with side branches, the length of which are determined by the choice of comonomer (ethyl branches result from 1-butene, butyl branches from 1-hexene, and so on). These materials combine the advantages of the properties of HDPE with the better impact strength of LDPE. LLDPE products of various densities are available, and their properties are governed by the branch type, the branching concentration, and the way in which the branches are distributed along the backbone.

The chemical shifts observed in the ^{13}C spectrum of an LLDPE fall into a very narrow range ($\sim 10\text{--}40$ PPM), as in the spectrum of poly(ethylene-co-1-butene) copolymer (Fig. I.8) [27]:



I.Y

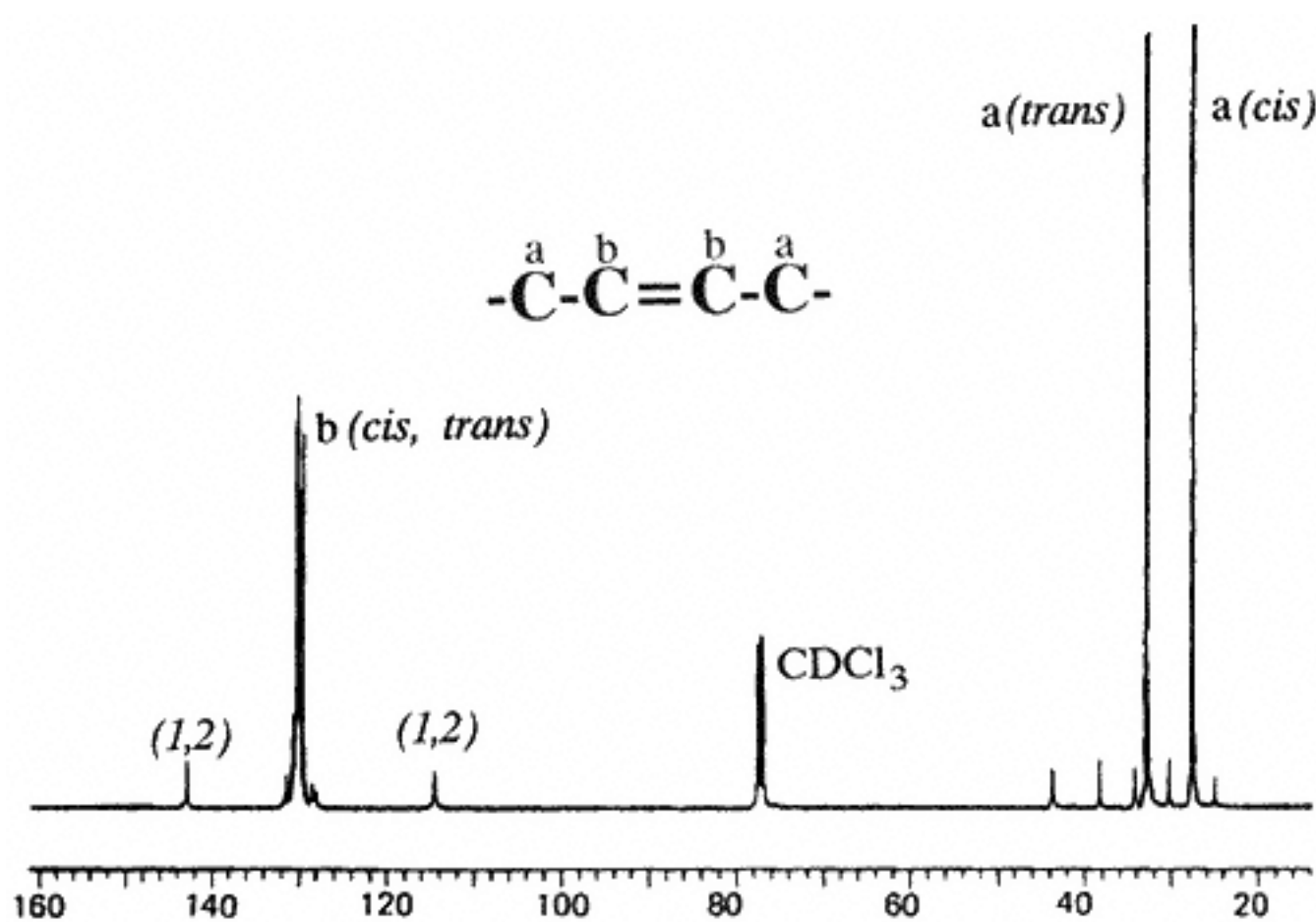


Figure I.6
 ^{13}C NMR spectrum of polybutadiene.

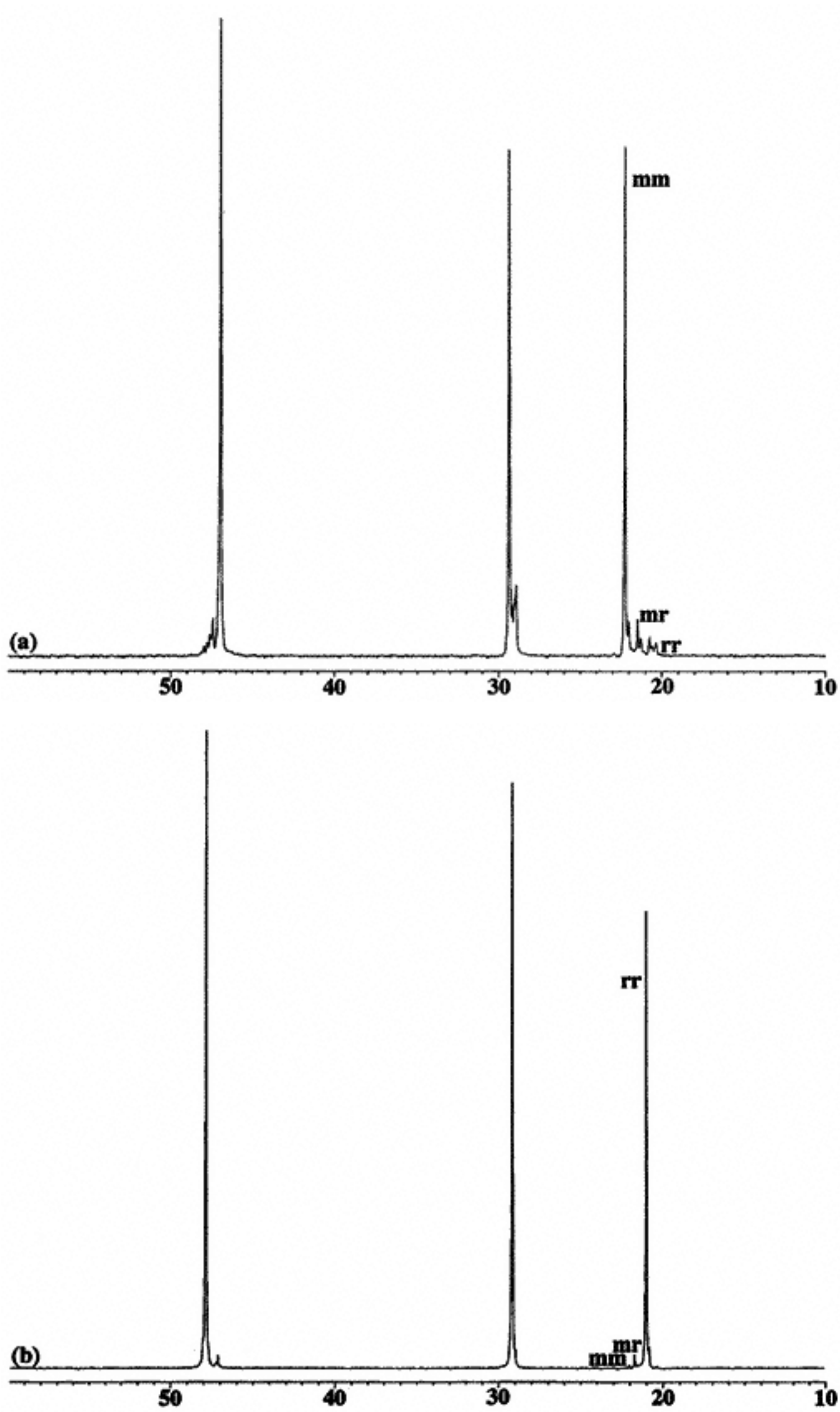


Figure I.7

Comparison of ^{13}C NMR spectra of (a) isotactic, (b) syndiotactic, and (c) atactic polypropylene.

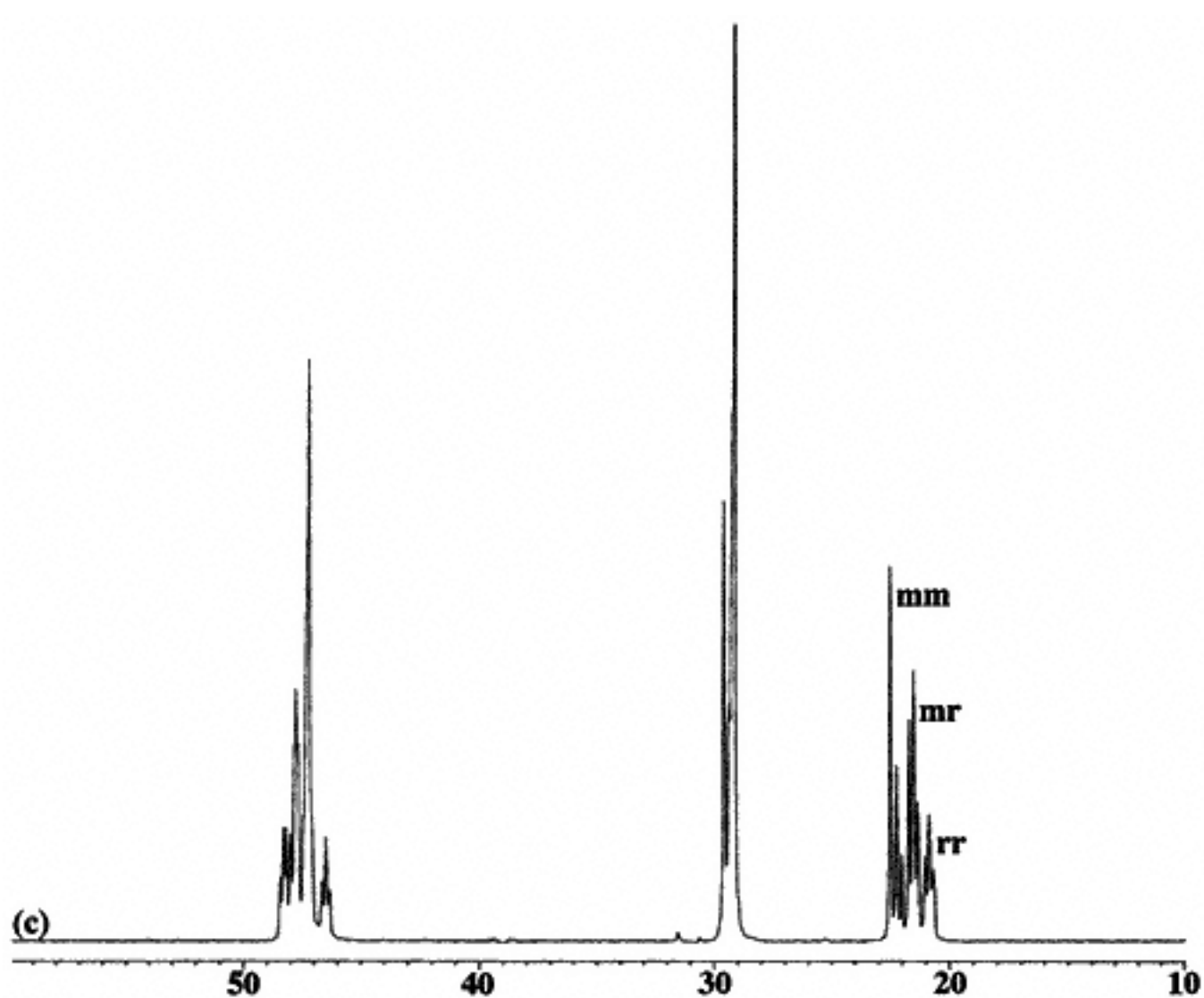


Figure I.7
(continued)

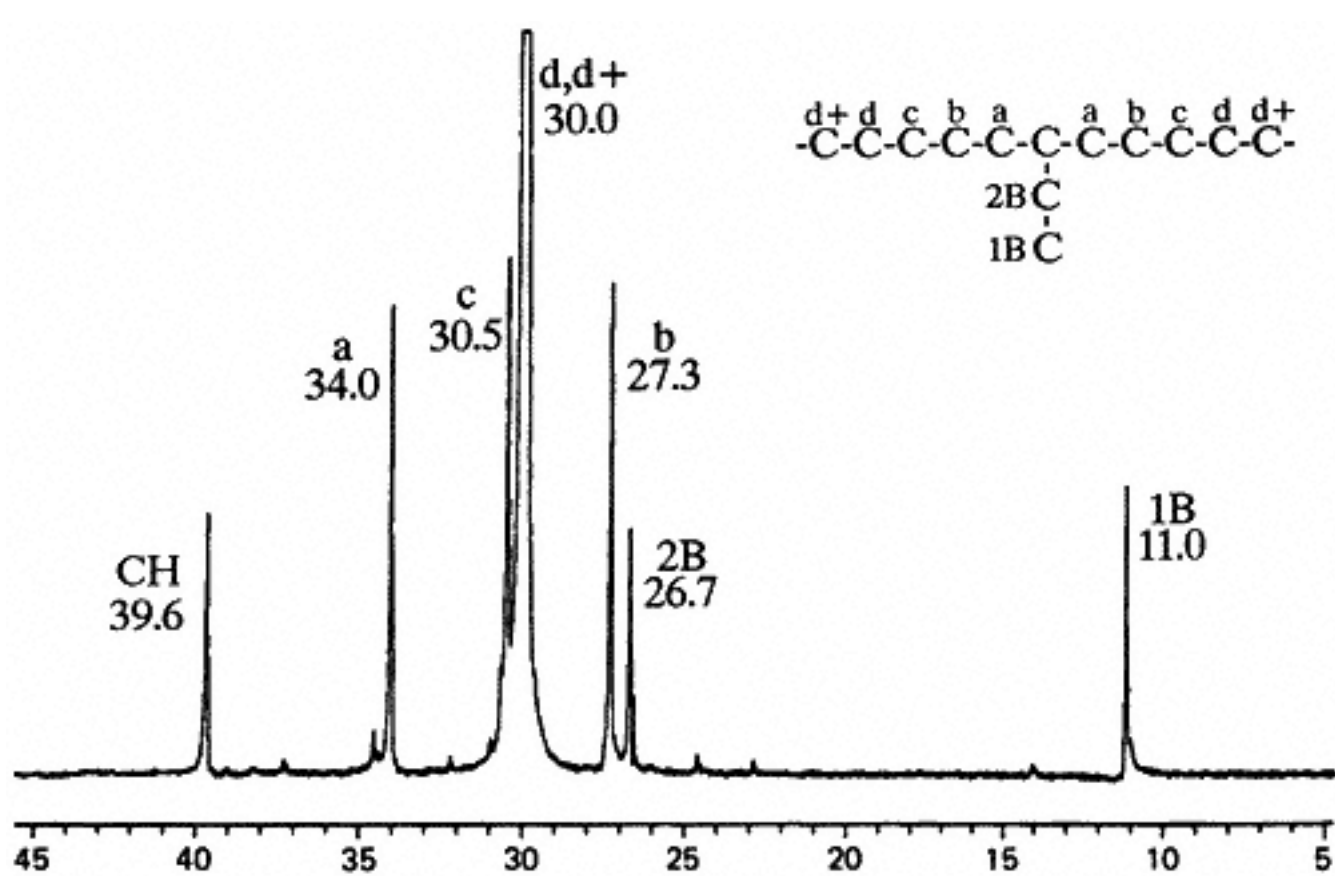
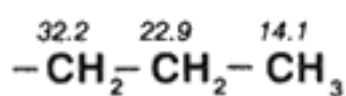


Figure I.8
 ^{13}C NMR spectrum of poly(ethylene-co-1-butene).

The main resonance at 30 ppm is due to backbone carbons far from a branch point. The secondary branch resonances in the spectrum arise from isolated branches (i.e., branches separated by at least two ethylene units). Because the butene concentration of this LLDPE is low (~3 mol%), most of the branches are isolated. Spectra of other LLDPEs, such as ethylene-1-hexene [28], ethylene-1-octene [29,30], and ethylene-4-methyl-1-pentene [30], have similarly distinctive peak patterns. Even under nonquantitative experimental conditions, these patterns can readily be used to identify the 1-olefin comonomer in an LLDPE.

Figure I.8 also has resonances that cannot be attributed to isolated branches. Some of them arise from groups at the ends of polymer chains [27] (from which M_n can be estimated),



I.Z

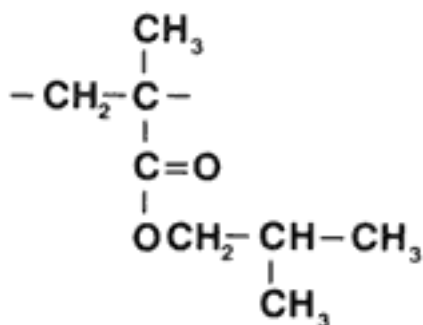
whereas others are attributable to nonisolated branches [27] arising from nearby 1-olefin groups. When spectra of such polymers are recorded under quantitative conditions, it is possible to calculate the distribution of comonomer sequences and to derive other parameters, such as the average length of ethylene and 1-olefin runs, n_E and n_B [27]. For example, the spectrum of Figure I.8 leads to values of 26.3 for n_E and 1.04 for n_B .

Analysis of comonomer sequences and tacticity distributions can provide insight into polymerization mechanisms. Simple statistical models can be applied to investigate whether Bernoullian (random) or Markovian (end-effect) statistics [31,32] best reflect the sequence or tacticity distribution. It is not possible to describe the resulting distributions by such simplistic models for many commercial polymerization processes. For example, many polymerization catalysts have more than one active site; hence, the resulting material has two or more components, each of which can be described by its own characteristic sequence or tacticity distribution [32,33]. Other compositional heterogeneities can arise from process-related variables (i.e., variation of comonomer levels, feed rate, temperature, or agitation speed) during the reaction [32]. NMR has been used to study all these effects.

I.C.3—

Dipolar and Scalar Coupling

Interactions among nuclei in a sample induce coupling of their nuclear spins, which results in a broadening or splitting of the resonances. In NMR spectra of small molecules, these interactions are averaged to zero by rapid, isotropic tumbling. However, in polymer solutions, molecular motion is slow enough that these couplings can contribute significantly to the spectrum. This problem is particularly severe for abundant spins, as in the ^1H spectrum of poly(isobutyl methacrylate)



I.AA

shown in Figure 1.9, illustrates. This broadening can, in fact, obscure other, more complex coupling patterns. For nuclei with spin $> 1/2$ (such as ^{27}Al , ^{14}N , or ^2H), another source of peak broadening is the quadrupolar interaction. In general, however, quadrupolar nuclei are not used in polymer analysis.

Scalar, or J, couplings can be homonuclear, such as those among ^1H s, or heteronuclear, such as those between ^{13}C s and ^1H s. Homonuclear J couplings can result in very complex splitting patterns, although these patterns are often obscured by the relatively strong homonuclear dipolar interactions present in polymer solutions. ^{13}C — ^1H coupling results in simpler splitting patterns. As shown in Figure I.10 for the spectrum of poly(isobutyl methacrylate), the observed multiplicity is $N + 1$, where N is the number of protons directly bonded to a carbon. This is useful information, but most ^{13}C signals are recorded with ^1H decoupling to simplify the spectrum. There are several experimental schemes for recovering

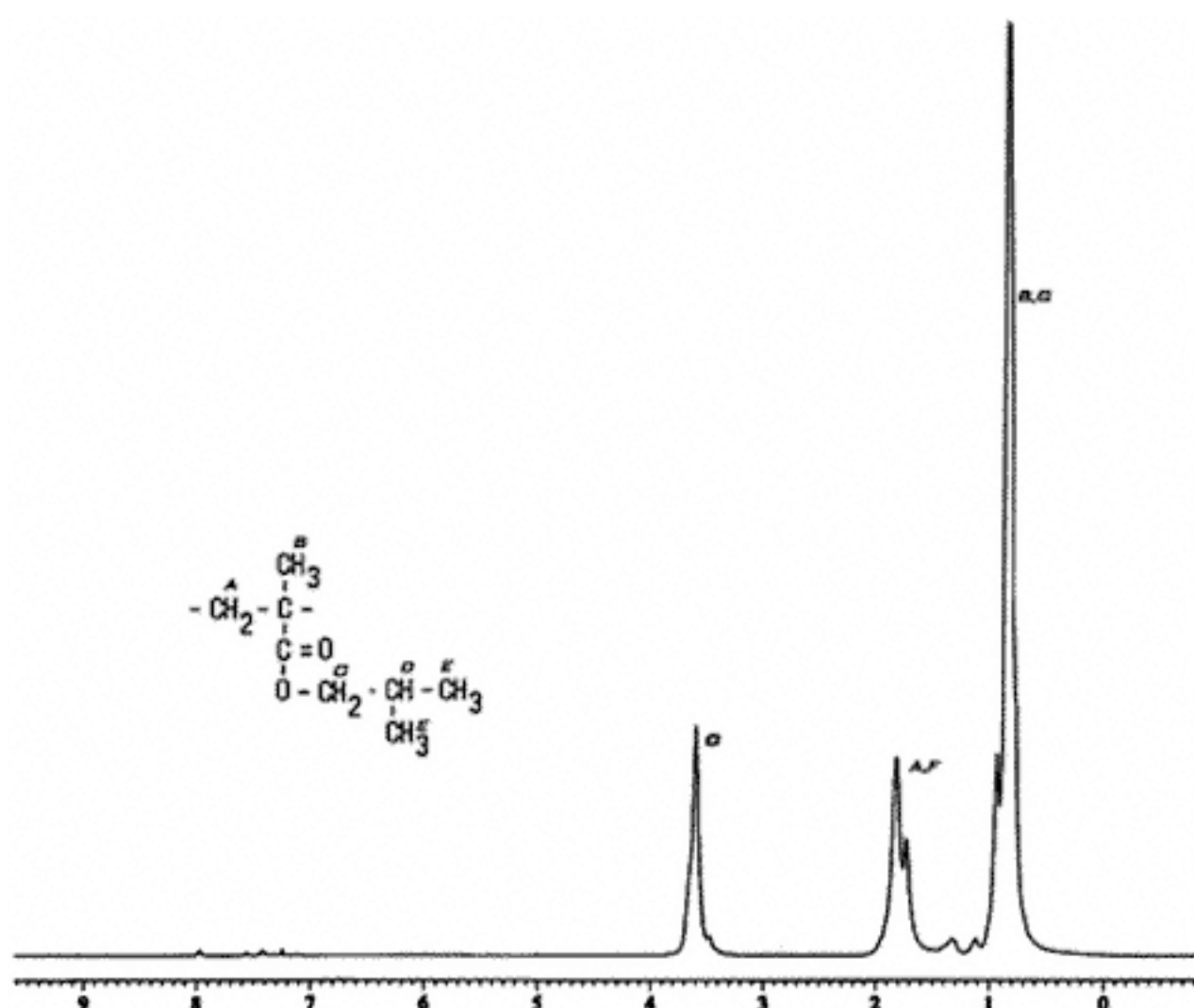


Figure I.9
 ^1H NMR spectrum of poly(isobutyl methacrylate).

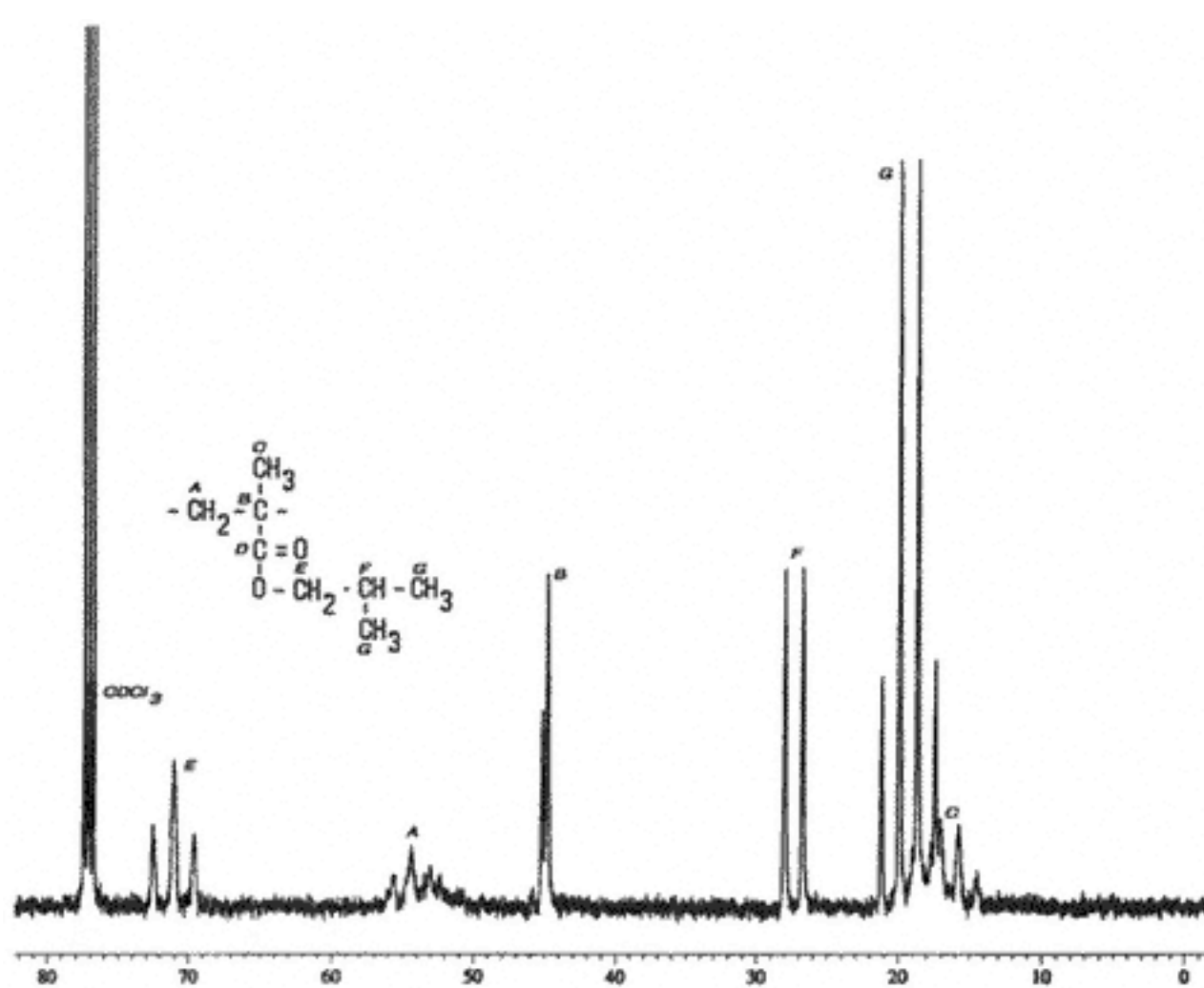


Figure I.10
 ^{13}C NMR spectrum of poly(isobutyl methacrylate), recorded without ^1H decoupling,
 revealing ^{13}C - ^1H splitting patterns.

^{13}C peak multiplicities without overly complicating the spectrum. Adjustment of the decoupling frequency can reduce the magnitude of the splitting, and other approaches, such as DEPT, INEPT, and APT, have been devised which selectively invert or null particular multiplicities [4–7].

I.C.4—

Nuclear Relaxation

The behavior of nuclei during the pulsed, or Fourier-transform, NMR experiment is time-dependent. The equilibrium magnetization is perturbed by the radiofrequency excitation pulse used. After the pulse, relaxation occurs by various processes, each of which is governed by a characteristic relaxation time. The effect of spin–spin relaxation, the time constant of which is designated T_2 , is observed in the free-induction decay signal (Fig. I.11). A more rapid decay implies a shorter T_2 , or faster relaxation, which is reflected by broadened peaks in the final spectrum. T_2 is related to the rate of molecular reorientations, with a shorter T_2 indicating slower motion. In general, large polymer molecules move more slowly (and therefore exhibit shorter T_2 s) than small molecules. T_2 is most sensitive to motions in the kilohertz (kHz) frequency regime, which usually correspond to short-range segmental reorientations. Although the average rate of polymer chain motion can be increased by reducing the solution concentration or raising the sample temperature, there is often an inherent limit on the achievable spectral resolution for polymer solutions.

A second relaxation process is spin–lattice relaxation, characterized by T_1 . The rate of spin–lattice relaxation is influenced by relatively rapid (MHz regime) motions, such as methyl group rotation. This process governs the frequency with which the pulsed experiment can be repeated. To ensure that the spin system has returned to equilibrium, it is necessary to wait many (five to ten) T_1 s between scans. Polymer solutions tend to have short T_1 s, which means that pulsed experiments can be repeated more rapidly than for most small molecules; this reduces the total experiment time.

The measurement of relaxation times, such as T_1 and T_2 , is a useful approach for studying the molecular dynamics of polymer solutions or polymeric liquids. Relaxation times can, for example, be related to rheological (flow) properties of a material [33].

I.C.5—

Nuclear Overhauser Enhancement

A secondary effect of the use of ^1H irradiation to remove J couplings is the nuclear Overhauser effect (NOE), which results in altered signal intensities. The maximum enhancement factor attainable through the NOE is governed by the gyromagnetic ratios of the coupled spins I and S:

$$\text{NOE} = \frac{\gamma_I}{2\gamma_S} \quad (\text{I.5})$$

For the ^{13}C – ^1H pair, this value is 2.988, which means that ^{13}C signals can be enhanced up to threefold. For nuclei with negative γ_S , such as ^{29}Si , the signal can be attenuated, rather than increased.

For ^{13}C , the extent of NOE observed is generally related to the number of directly bonded ^1H nuclei; that is



I.BB

and is governed by the proportion of spin–lattice (T_1) relaxation that is due to dipolar effects. As discussed in Section I.C.3., polymer solutions have strong dipolar interactions, so that a maximal NOE (threefold enhancement) is realized for most protonated carbons. Nonprotonated carbons, such as carbonyls or quaternaries, do not exhibit the full effect.

I.C.6—

Multidimensional NMR

Straightforward NMR experiments can provide much detail about polymer structure; however, on occasion, they cannot provide the necessary answer. More sophisticated experiments, such as multidimensional spectroscopy, facilitate correlation between two or more different NMR parameters. Table I.4 lists several such experiments. A discussion of the application of multidimensional NMR to polymer systems is beyond the scope of this introduction [7–12,34].

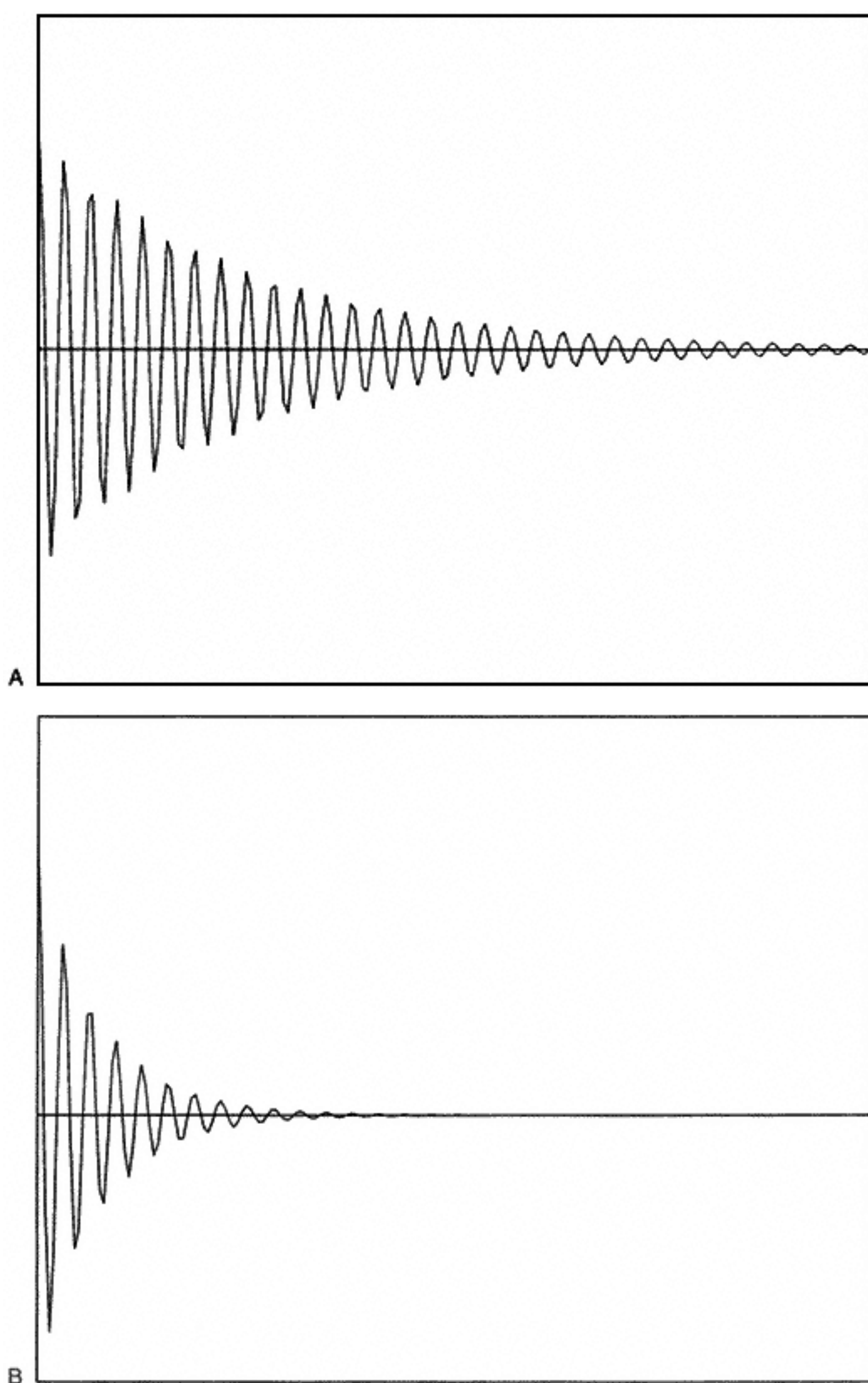


Figure I.11
Typical free-induction decays (FIDs) for NMR signal, with (A) long and (B) short T_2 .

TABLE I.4 Some Common Two-Dimensional NMR Experiments

Name of experiment	Correlated parameters
Homonuclear J-resolved	^1H chemical shift
	^1H – ^1H J-coupling
Heteronuclear J-resolved	^{13}C chemical shift
	^{13}C – ^1H J-coupling
Homonuclear correlated spectroscopy (COSY)	^1H chemical shift
	^1H chemical shift
Heteronuclear correlated spectroscopy (COSY)	^{13}C chemical shift
	^1H chemical shift
Double-quantum exchange spectroscopy (inadequate)	^{13}C chemical shift
	^{13}C chemical shift

I.D—**Practical Considerations for NMR of Polymers**

Because of the large size of a polymer chain relative to that of a typical organic molecule, the sample preparation procedure and spectrometer parameters used in acquiring the NMR spectra of polymers are slightly different from those used for small molecules. These operational concerns are particularly important if the spectral intensities are to be interpreted quantitatively.

I.D.1—**Sample Preparation**

Preparation of a polymer solution for NMR analysis is not always a simple matter. Some polymers, such as polystyrene, are soluble in many common solvents (e.g., chloroform or benzene), whereas others, such as poly(1,4-butadiene), swell in the presence of these solvents [35]. In either case, the ^{13}C NMR spectrum can be obtained easily at room temperature. Other polymers, such as polyethylene or polypropylene, dissolve in solvents, such as 1,2-dichlorobenzene, only near the crystalline melting point. The specific temperature at which the spectra are to be recorded must be chosen carefully. If it is too high, thermal decomposition of the sample may occur while data are being acquired. If it is too low, the restricted polymer-chain motion and possible residual crystallinity may cause a degradation of spectral resolution. Because of the high viscosity of most polymer solutions, sample homogeneity can be a problem. Care must be taken to minimize concentration gradients and to ensure that no air bubbles are present. The simplest way to accomplish this is to let the samples stand for several hours, with or without heating. Another potential problem (for colored samples) arises from pigments that may contain paramagnetic impurities. This is particularly troublesome for beige, brown, or orange materials, which often contain iron oxide. During spectral accumulation, these magnetic particles migrate, causing fluctuations in the magnetic field, which leads to an extremely broad, often uninterpretable spectrum.

I.D.2—**Instrumental Conditions**

When a quantitative solution ^{13}C NMR spectrum is required, careful attention must be given to several of the spectrometer settings: pulse width, repetition rate, and ^1H -decoupling mode [4–7]. When using a 90° ^{13}C radiofrequency pulse for data acquisition, it is necessary to wait at least five times the longest spin–lattice relaxation time T_1 [4–7] between data acquisitions to ensure that the spin system returns to equilibrium with the external magnetic field before the next transient is recorded. If a flip angle of less than 90° is used, a correspondingly shorter pulse delay may be used. Fortunately, polymers tend to have relatively short T_1 s, so that pulse delays of less than 1 min are usually adequate to ensure accurate quantitation [22]. Gating of the ^1H -decoupling (on, during data acquisition; off, during pulse delay) is commonly recommended to circumvent the potential problem of unequal NOEs [4–7]. This applies particularly to nonprotonated carbons, such as carbonyls [3–5]. When all carbons are protonated, the NOEs are all maximized (i.e., a nearly threefold intensity enhancement is obtained), and the peak areas are relatively correct under continuous ^1H decoupling. If ^{13}C NMR spectroscopy is to be used as a routine tool for quantitative analysis, there is a distinct advantage to using continuous decoupling when possible because an NOE of 1.988 reduces the total accumulation time by a factor of 4. Quantitative ^1H spectra can be obtained much more

quickly than quantitative ^{13}C spectra, because the natural abundance of ^1H is much higher (essentially 100% versus 1.1% for ^{13}C), and because ^1H T_1 are shorter, permitting faster pulsing.

I.E—

Concluding Remarks

Nuclear magnetic resonance is an extremely powerful tool for the study of polymers, with its ability to probe both chemical structure and molecular dynamics in great detail. The first step in applying this technique to polymers is to understand the spectral features, particularly the origin of each resonance observed. This collection of polymer spectra strives to provide a ready reference for such peak assignment, by presenting fully assigned solution-state spectra of over 300 polymers. A compilation of solid-state polymer spectra is also available [36]. We have made an effort to collect as many commercially available materials as possible, and to include some interesting newer polymers. The spectra have been organized into categories according to molecular structure. Each chapter is preceded by a brief introduction which includes relevant information about sample preparation, spectral interpretation, and quantitative analyses for each type of polymer. Most entries are ^{13}C spectra, because generally, this nucleus is the most common. Occasionally, ^1H or other heteronuclear spectra are included, if they are particularly useful for that material. Experimental conditions are provided for each spectrum. Furthermore, most entries list synonyms, summarize the most common applications of the material, and cite literature references.

The polymers have been organized primarily by backbone structure, and secondarily by the type of pendant group: Chapter 2, saturated hydrocarbon backbone; aliphatic pendant groups; Chapter 3, saturated hydrocarbon backbone; aromatic pendant groups; Chapter 4, saturated hydrocarbon backbone: ester pendant groups; Chapter 5, saturated hydrocarbon backbone: miscellaneous pendant groups; Chapter 6, unsaturated hydrocarbon backbone; Chapter 7, ether backbone; Chapter 8, ester or amide backbone; Chapter 9, miscellaneous; Chapter 10, polymer additives.

Copolymers are included with the predominant monomer, even when the common name lists the lesser comonomer first. For example, the spectrum of poly(styrene-co-butadiene) (5% styrene) is located in Chapter 6 with the other polybutadienes, whereas poly(styrene-co-butadiene) (95% styrene) is included in Chapter 2 with the polystyrenes. The same categorization applies to blends.

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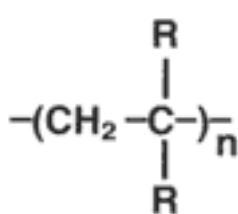
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II—

Aliphatic Backbones: Aliphatic Pendant Groups

This group of polymers has the general chemical structure:



A

where R is either a hydrogen atom or an aliphatic group such as methyl or ethyl. Copolymers in this category may carry some other functionality, such as an ester group, in the secondary component, but the structure of the predominant monomer (> 50%) is as shown.

This group includes (A) polyethylene and ethylene copolymers and derivatives; (B) polypropylene and propylene copolymers and derivatives; and (C) polymers and copolymers based on other 1-olefins. Many of these polymers, particularly those in categories (A) and (B) are commodity resins, with 1994 U.S. production topping 35 billion lb (15.9 billion kg) [1]. Most are semicrystalline and exhibit distinct melting points. Others are *thermoplastic elastomers*, which are poorly crystalline or completely amorphous. The density of unpigmented resin is usually less than 1.0 g/cm³, and the fact that many of these materials float on water serves as a quick identification test. These polymers are typically used to make films (e.g., food wrap and bags) and molded products (e.g., bottles and containers) [2]. Polymers in this group are commonly found blended with other resins, in an attempt to improve or modify properties, or to reduce material costs. Multilayer products are also often encountered, particularly in packaging applications.

II.A—

Sample Preparation and Spectral Acquisition

High molecular weight (MW) samples of most of the polymers included in this group are insoluble in common deuterated solvents at room temperature. In these cases, the best sample preparation procedure involves melting the sample in the presence of an appropriate solvent, such as 1,2-dichlorobenzene-d₄ (ODCB) or 1,1,2,2-tetrachloroethane-d₂ [3]. Because of the high viscosity of the molten polymer, extra care must be taken to ensure that the sample is homogeneous (i.e., that no air bubbles or concentration gradients are present). If the melt is transparent, this can be simply accomplished by visual inspection of the molten sample. For pigmented samples, or those with additives that render the melt opaque, it is often necessary to leave the sample at temperature for many hours, perhaps even overnight. Spectra of these polymers are typically recorded at high temperature (120–150°C) to ensure high-resolution spectra. Lower-MW samples are often soluble at room temperature in solvents such as chloroform-d or benzene-d₆ [3], and their spectra can be acquired at ambient to moderate (50–60°C) temperatures.

It is fairly easy to achieve quantitative ¹³C spectral accumulation conditions for this group of polymers. The relatively high molecular weight of most specimens slows down overall molecular motion, and the high degree of protonation equal-

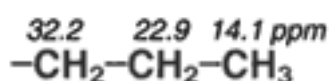
izes most nuclear Overhauser effects (NOEs) [4]. Accordingly, a pulse (relaxation) delay of 15 s following a 90° pulse is sufficient to give correct relative ^{13}C intensities for all but highly mobile nuclei (e.g., methyl groups) or nonprotonated (e.g., carbonyls in some copolymers) carbons [5]. Quantitative spectra can usually be acquired with continuous ^1H decoupling because the NOEs of all protonated carbons are equivalent. Quantitative ^1H spectra can generally be recorded with a 5-s pulse delay following a 90° pulse.

II.B— Spectral Features

The main resonances of polymers in this group lie at ^{13}C chemical shifts between 10 and 60 ppm, and at ^1H shifts between 0.8 and 2 ppm. In general, ^{13}C is the preferred nucleus for identification of unknown polymers, because the larger chemical-shift range permits differentiation among subtle structural variations. In favorable cases, ^1H NMR is useful for rapid quantitative analyses, such as comonomer contents; several examples will be discussed later. If the chemical structure of the comonomers is similar, then ^{13}C is the better alternative for quantitation.

II.B.1— Ethylene Polymers and Copolymers

Ethylene copolymers of relatively high ethylene content are most easily recognized by the dominant ^{13}C resonance at 30 ppm, which arises from long (more than four) sequences of methylene carbons [6]. In purely linear (high-density) ethylene homopolymer {II-A-1}, for example, the only other observed ^{13}C resonances are due to alkyl end groups [4]:

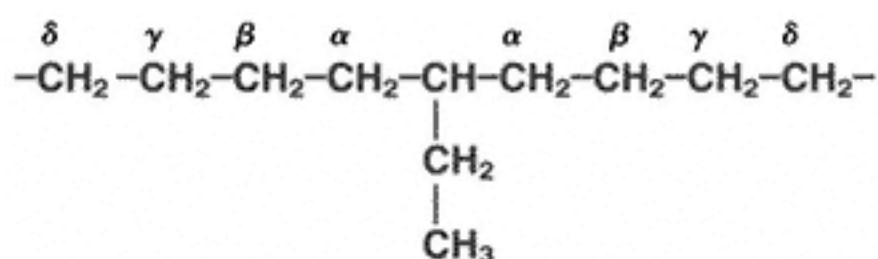


B

In most ethylene polymers and copolymers, chain branching occurs, which complicates the spectrum. In branched (low-density) ethylene homopolymer {II-A-3}, pendant alkyl groups vary in length. Those from methyl (C_1) through butyl (C_4) can be unambiguously identified from the ^{13}C spectrum; pendant groups of six carbons and longer usually give rise to indistinguishable peak patterns [6,7]. Ethylene homopolymers are sometimes derivatized (chlorinated or chlorosulfonated) to improve their properties. This considerably complicates the spectrum, as the substitution pattern is random. A few examples are included in this chapter {see II-A-5 and II-A-6}.

Many materials generically referred to as "polyethylene" are, in fact, ethylene-based copolymers. One such example is the family of linear, low-density polyethylenes (LLDPEs), which are produced by copolymerization of ethylene with a few mole% of a 1-olefin, usually 1-butene, 1-hexene, 4-methyl-1-pentene, or 1-octene. The resulting polymer has primarily a linear structure, with the unsaturated carbons from the 1-olefin incorporated into the backbone. The remaining carbons of the 1-olefin give rise to pendant branches of fixed length (ethyl from 1-butene, butyl from 1-hexene, and hexyl from 1-octene). The ^{13}C NMR spectra of these materials {II-A-7, II-A-10, II-A-11, II-A-13, II-A-15 through II-A-20} have distinct patterns that can be used to readily identify the comonomer type in an unknown resin [6]. Chemical shifts for the common LLDPE products are summarized in Table II-1.

^{13}C NMR provides the best method for calculating the branch content (i.e., the comonomer content) of an LLDPE, particularly if the comonomer is unknown. For example, in the spectrum of poly(ethylene-co-1-butene) (5%B) included in this chapter {II-A-10}, the average, per-carbon area for a branch resonance, \mathbf{A}_B , is 1.5. This value is calculated from the total area of the observed peaks, other than the one at 30 ppm and the methyl peak at 11.2 ppm, which is nonquantitative under the experimental conditions used to record the spectrum. This area contains contributions from six distinct carbon types (one branch CH_2 , one branch point CH , two $\alpha\text{-CH}_2$ s, and 2 $\beta\text{-CH}_2$ s):



C

TABLE II.1 ^{13}C NMR Chemical Shifts for Some Ethylene Copolymers
$$\begin{array}{ccccccc} & \text{A1} & \text{A2} & \text{A3} & \text{A4} & & \\ \dots & \text{---CH} & \text{---CH}_2 & \text{---CH}_2 & \text{---CH} & \dots & \\ & | & & & & & \\ & \text{C} & & & & & \\ & \text{---} & & & & & \\ & \text{B1} & & & & & \end{array}$$

Polymer	A1	A2	A3	A4	B1	B2	B3	B4	B5	B6
Poly(ethylene-co-propylene)	33.3	37.6	27.4	31.0	20.1	—	—	—	—	—
Poly(ethylene-co-1-butene)	39.8	34.2	27.3	30.5	26.7	11.1	—	—	—	—
Poly(ethylene-co-1-pentene)	38.0	34.6	27.3	30.5	37.1	20.4	14.3	—	—	—
Poly(ethylene-co-1-hexene)	38.2	34.6	27.3	30.5	34.2	29.4	23.4	14.5	—	—
Poly(ethylene-co-4-methyl-1-pentene)	36.1	34.8	27.2	30.6	44.9	26.0	23.2	—	—	—
Poly(ethylene-co-1-octene)	38.2	34.6	27.4	30.5	34.7	27.4	30.0	32.3	22.9	14.1
Poly(ethylene-co-norbornene)	50.9, 47.0, 54.4	35.2, 37.0	29.7	29.7	39.9	31.8	29.9– 31.0	—	—	—
Poly(ethylene-co-styrene)	45.9	36.0	27.6	29.7	146.7	133.9	133.4	125.8	—	—
Poly(ethylene-co-vinyl acetate)	74.6	33.7	25.7	30.0	169.4	20.8	—	—	—	—
Poly(ethylene-co-acrylic acid)	45.6	32.5	29.5	30.6	180.1	—	—	—	—	—
Poly(ethylene-co-methyl acrylate)	46.1	32.9	27.8	30.0	175.9	50.9	—	—	—	—
Poly(ethylene-co-ethyl acrylate)	45.6	32.2	26.8	30.5	175.8	59.1	14.0	—	—	—
Poly(ethylene-co-butyl acrylate)	45.7	32.7	27.2	30.5	175.6	63.5	30.0	18.9	13.9	—
Poly(ethylene-co-methacrylic acid), Na ⁺	47.0	40.0	25.3	30.6	183.2	22.4	—	—	—	—
Poly(ethylene-co-vinyl alcohol)	72.5	38.6	26.2	30.0	—	—	—	—	—	—

If the area of the main resonance at 30 ppm is set to equal 100, the branch content, in ethyl branches per 1000 carbons, B_{Et} , is given by:

$$B_{Et} = \frac{1000A_B}{100 + (7A_B)} \quad (\text{II.1})$$

Copolymers of ethylene and non-1-olefin comonomers, such as vinyl acetate, methyl acrylate, or acrylic acid, are produced for special applications. Many of these are available in a wide concentration range, from nearly 100% ethylene to nearly 100% comonomer. These copolymers are manufactured in a high-pressure process, such as that used for low-density polyethylene, so the resulting materials exhibit the same distribution of branch lengths observed in LDPE, as well as unique resonances attributable to the specific comonomer used. Chemical shifts for many such copolymers are also summarized in Table II-1.

In addition to the primary resonances seen in the ^{13}C spectra of ethylene copolymers, smaller peaks due to comonomer sequences (see Sec. I. B.2) are also observed, particularly at higher comonomer levels. The distribution of comonomer sequences can reveal details of the polymerization mechanism and conditions [8]. Resonances arising from sequences are noted in the following spectra, but specific assignments are not made. These assignments can be found in the reference(s) listed for each spectrum.

^1H spectra of ethylene homopolymers and copolymers such as the LLDPEs are not particularly informative, because all resonances overlap in a very narrow chemical-shift range. Certain copolymers, however, are amenable to ^1H analysis of comonomer content (Table II-2). For example, poly(ethylene-co-vinyl acetate) {II-A-25H} exhibits a well-resolved ^1H resonance at 5.4 ppm, owing to the proton at the backbone branch point:

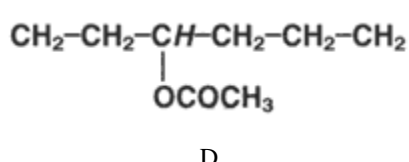


TABLE II.2 ^1H NMR Chemical Shifts for Some Ethylene Copolymers

Polymer	$\begin{array}{c} \text{H1} \quad \text{H2} \quad \text{H3} \\ \dots - \text{CH} - \text{CH}_2 - \text{CH}_2 - \dots \\ \vdots \\ \text{CH}_n - \dots \\ \text{H4} \end{array}$						
	H1	H2	H3	H4	H5	H6	H7
Poly(ethylene-co-vinyl acetate)	5.40	1.50	1.29	1.90	—	—	—
Poly(ethylene-co-acrylic acid)	2.38	1.62	1.27	9.55	—	—	—
Poly(ethylene-co-methyl acrylate)	2.29	1.58	1.29	3.56	—	—	—
Poly(ethylene-co-ethyl acrylate)	2.23	1.55	1.27	4.03	0.80	—	—
Poly(ethylene-co-butyl acrylate)	2.27	1.27	1.27	4.02	1.27	1.27	0.87
Poly(ethylene-co-vinyl alcohol)	4.62	2.05	1.47	3.59	—	—	—

A spectrum suitable for measurement of vinyl acetate (VA) contents > 0.5 wt% can be acquired very quickly (less than 10 min); the corresponding ^{13}C spectrum would take several hours. If the areas of the of the ^1H peak at 4.8 ppm and the main resonances between 0.8 and 2.0 ppm are integrated, the VA content can be easily calculated:

$$\text{VA (mol\%)} = \frac{A(4.8 \text{ ppm})}{A(4.8 \text{ ppm}) + A(0.8-2.0 \text{ ppm})} \quad (\text{II.2})$$

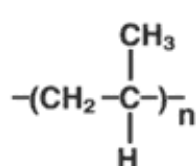
This value can be easily converted to units of wt%, which are generally used. A similar approach works well for ^1H spectra of many non-1-olefin copolymers {II-A-27H through II-A-30H, II-A-33H}.

The properties of ethylene homopolymers and copolymers are frequently modified by blending different materials. For example, high-density polyethylene film is stiff, but lacks toughness (i.e., it tends to tear easily). Addition of a few weight-percent of an elastomer can greatly reduce the film's propensity to split. In other cases, a less expensive resin may be blended with a costly material. If the properties of the blend are still suitable for the intended application, this reduces the cost of the final product. Identification of blends of different types of polyethylene can be difficult, even by ^{13}C NMR, because many of the blend components have overlapping resonances. For example, as discussed in the foregoing, branched, LDPE contains some butyl branches. Therefore, an ethylene-co-1-hexene LLDPE component contributes no unique resonances to the spectrum of an LDPE/LLDPE blends {II-A-39}. The only way that this combination can be identified as a blend by NMR is to note that the relative ratios of the branch peaks have changed. The peaks attributable to LLDPE are enhanced (compare, for example, the relative intensities of the peaks at 23.4 and 22.9 in {II-A- 3, II-A-16, and II-A-39}). This effect can generally be readily observed only for LLDPE/LDPE blend compositions greater than about 20/80. If the LLDPE content is exceeds 20%, the effects may be too subtle to be detected by visual inspection alone. Blends of linear, high-density polyethylene and LLDPE, or blends of two different LLDPE resins containing the same comonomer, are indistinguishable based on the ^{13}C NMR spectrum.

II.B.2—

Propylene Polymers and Copolymers

In polypropylene, one of the R groups shown in Structure A is a methyl group; the other is hydrogen:



The main ^{13}C spectral features of polypropylene and propylene copolymers are three dominant resonances at approximately 48, 30, and 23 ppm, attributable to the CH_2 , CH , and CH_3 carbons, respectively. Striking tacticity effects are seen in the spec-

tra of these materials; this is particularly noticeable for the methyl carbon at 20–23 ppm. This resonance typically splits into three groups of resonances, which correspond to *mm*, *mr*, and *rr* triads, as discussed in Section I.B.2. The tacticity effect is less obvious, but still observable, for the other two carbons. The most commonly encountered commercial polypropylene resins are "isotactic" (85–99% *mm*) {II-B-1}. An *isotactic* index can be calculated from the ¹³C spectrum by dividing the methyl peak area into *mm*, *mr*, and *rr* contributions. This index is given by either %*mm* or %*m*, where

$$\%m = \%mm + \%mr \quad (\text{II.3})$$

Syndiotactic polypropylene (> 95% *rr*) {II-B-3} is emerging as another commercially important material. Atactic polypropylene (*mm*, *mr*, and *rr* triads in the ratio 1:2:1) {II-B-4} is sometimes used as an adhesive. The ¹³C spectra of some polypropylenes also exhibit regioregularity effects, such as "head-to-head," or "tail-to-tail," or both insertions of the monomer units in the polymer backbone (see Sec. I.B.2) [9].

Poly(propylene-co-ethylene), poly(propylene-co-1-butene), and poly(propylene-co-ethylene-co-1-butene) are common propylene copolymers. The presence of these comonomers can be detected based on their distinct pattern of resonances.

II.B.3—

Polymers and Copolymers of Other 1-Olefins

There are also commercially available homopolymers and copolymers made from higher 1-alkenes, such as 1-butene, 3-methyl-1-propene (isobutylene), and 4-methyl-1-pentene. Although they are manufactured in lower volumes than the ethylene- and propylene-based polymers and copolymers, they do find some specific applications. ¹³C spectra of poly(1-olefins) are usually straightforward, with *n* major resonances, where *n* is the number of chemically distinct carbons in the polymer repeat unit [10], and tacticity effects are usually evident, especially in the case of poly(1-butene).

References

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2. H. Ulrich. *Introduction to Industrial Polymers*. Munich: Hanser Publishers, 1993.
3. J. Brandrup and E. H. Immergut. *Polymer Handbook*. New York: Wiley, 1975.
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SATURATED HYDROCARBON BACKBONE; ALKYL PENDANT GROUPS**List of Spectra***A. Polymers and Copolymers of Ethylene*

II-A-1	Polyethylene, linear or high-density
II-A-1H	Polyethylene, linear or high-density
II-A-2	Polyethylene, ultrahigh-molecular weight
II-A-3	Polyethylene, branched or low-density
II-A-3H	Polyethylene, branched or low-density
II-A-4	Polyethylene, oxidized
II-A-5	Polyethylene, chlorinated
II-A-6	Polyethylene, chlorosulfonated
II-A-7	Poly(ethylene-co-propylene) [~5%P]
II-A-8	Poly(ethylene-co-propylene) [~40%P]
II-A-9	Poly(ethylene-co-propylene-co-5-ethylidene-2-norbornene) [~40%P;~2%ENB]
II-A-10	Poly(ethylene-co-1-butene) [~5%B]
II-A-11	Poly(ethylene-co-1-butene) [~0.1%B]
II-A-12	Polybutadiene, hydrogenated
II-A-13	Poly(ethylene-co-1-butene-co-1-hexene)
II-A-14	Poly(ethylene-co-1-butene-co-styrene)
II-A-15	Poly(ethylene-co-1-pentene)
II-A-16	Poly(ethylene-co-1-hexene) [~5%H]
II-A-17	Poly(ethylene-co-1-hexene) [~0.1%H]
II-A-18	Poly(ethylene-co-1-hexene) [~0.1%H], Cr-catalyzed
II-A-18H	Poly(ethylene-co-1-hexene) [~0.1%H], Cr-catalyzed
II-A-19	Poly(ethylene-co-4-methyl-1-pentene)
II-A-20	Poly(ethylene-co-1-octene)
II-A-21	Poly(ethylene-co-norbornene)
II-A-22	Poly(ethylene-co-styrene)
II-A-23	Poly(ethylene-co-1,5-hexadiene)
II-A-24	Poly(ethylene-co-vinyl acetate) [~3% VA]
II-A-25	Poly(ethylene-co-vinyl acetate) [~25% VA]
II-A-25H	Poly(ethylene-co-vinyl acetate) [~25% VA]
II-A-26	Poly(ethylene-co-acrylic acid) [~5% AA]
II-A-27	Poly(ethylene-co-acrylic acid) [~15% AA]
II-A-27H	Poly(ethylene-co-acrylic acid) [~15% AA]
II-A-28	Poly(ethylene-co-methyl acrylate)
II-A-28H	Poly(ethylene-co-methyl acrylate)
II-A-29	Poly(ethylene-co-ethyl acrylate)
II-A-29H	Poly(ethylene-co-ethyl acrylate)
II-A-30	Poly(ethylene-co-butyl acrylate)
II-A-30H	Poly(ethylene-co-butyl acrylate)
II-A-31	Poly(ethylene-co-methacrylic acid), Na ⁺ salt
II-A-32	Poly(ethylene-co-methacrylic acid), Zn ²⁺ salt
II-A-33	Poly(ethylene-co-vinyl alcohol)
II-A-33H	Poly(ethylene-co-vinyl alcohol)
II-A-34	Poly(ethylene-co-carbon monoxide)
II-A-35	Polyethylene, branched/poly(ethylene-co-propylene) [40%P], 90/10 blend
II-A-36	Poly(ethylene-co-1-butene)/polyethylene, branched, 80/20 Blend
II-A-37	Poly(ethylene-co-1-butene)/poly(ethylene-co-propylene) [40%P], 90/10 blend
II-A-38	Poly(ethylene-co-1-butene)/poly(ethylene-co-vinyl acetate) [14%VA], 80/20 blend

II-A-39	Poly(ethylene-co-1-hexene)/polyethylene, branched, 80/20 Blend
II-A-40	Poly(ethylene-co-1-hexene)/poly(ethylene-co-propylene) [40%P], 90/10 blend
II-A-41	Poly(ethylene-co-1-hexene)/poly(ethylene-co-vinyl acetate) [14% VA], 80/20 blend
II-A-42	Poly(ethylene-co-1-octene)/polyethylene, branched, 80/20 blend
II-A-43	Poly(ethylene-co-1-octene)/poly(ethylene-co-propylene) [40%P], 90/10 blend
II-A-44	Poly(ethylene-co-1-octene)/poly(ethylene-co-vinyl acetate) [14% VA], 80/20 blend

B. Polymers and Copolymers of Propylene

II-B-1	Polypropylene, isotactic
II-B-1H	Polypropylene, isotactic
II-B-2	Polypropylene, stereoblock
II-B-3	Polypropylene, syndiotactic
II-B-4	Polypropylene, atactic
II-B-5	Poly(propylene-co-ethylene)
II-B-6	Poly(propylene-co-1-butene)
II-B-7	Poly(propylene-co-1-butene-co-ethylene)
II-B-8	Poly(propylene-co-ethylene)/poly(ethylene-co-propylene) [40%P], 80/20 blend

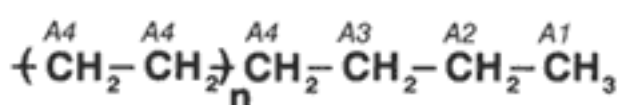
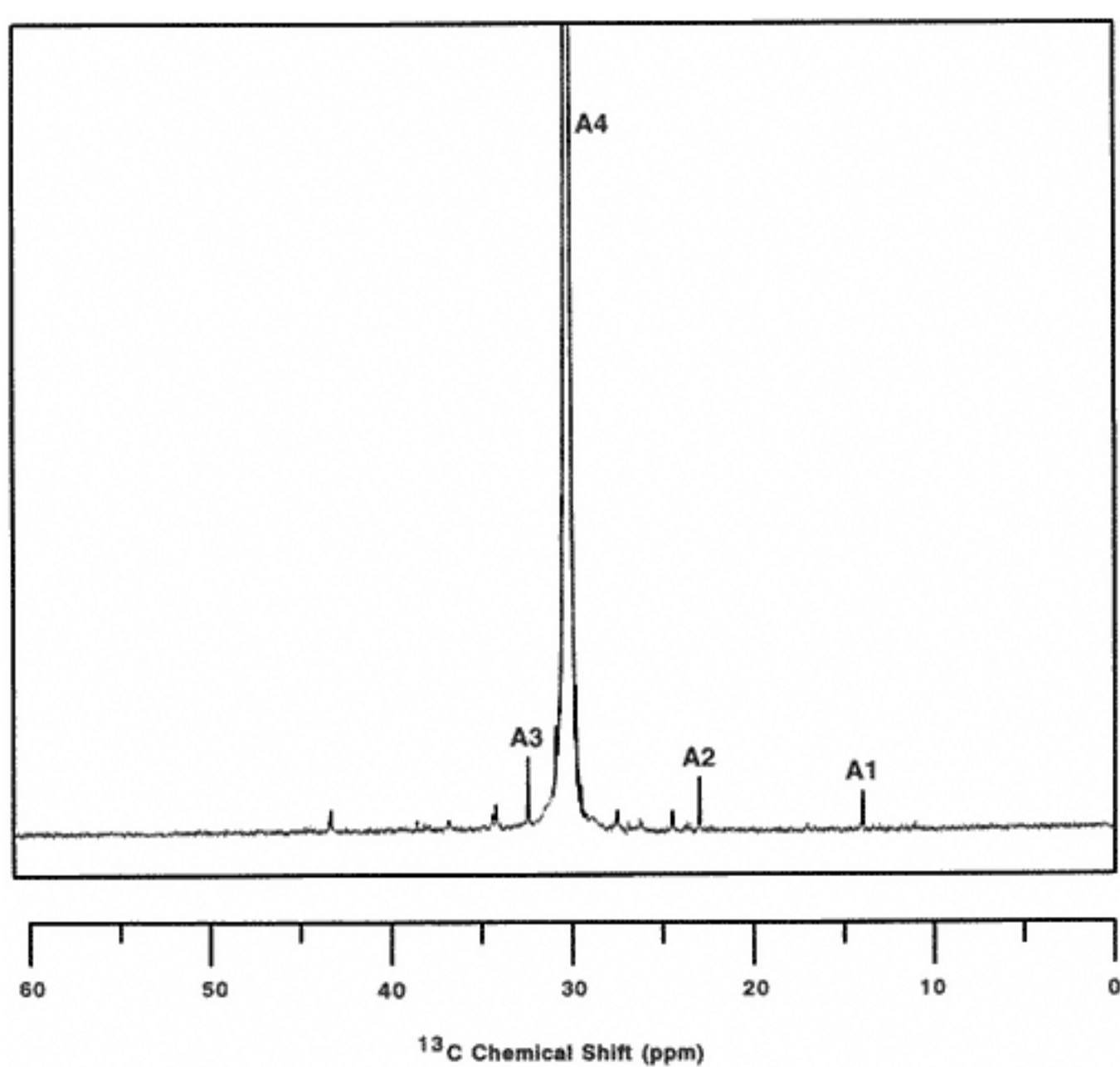
C. Polymers and Copolymers of Other 1-Olefins

II-C-1	Poly(1-butene)
II-C-2	Polyisobutylene
II-C-3	Poly(isobutylene-co-isoprene)
II-C-4	Poly(isobutylene-co-isoprene), chlorinated
II-C-5	Poly(isobutylene-co-isoprene), brominated
II-C-6	Poly(4-methyl-1-pentene)
II-C-7	Poly(1-hexene), isotactic
II-C-8	Poly(1-hexene), atactic
II-C-9	Poly(1-decene)

**II-A-1—
Polyethylene, Linear or High-Density (LPE or HDPE)**

Comments

The primary resonances arise from chain-backbone carbons; secondary peaks are due to saturated end groups. This material is also known as low-pressure polyethylene; its density is greater than 0.94 g/cm³. It is a hard, stiff plastic produced by Ziegler-Natta or other organometallic catalyst, and is commonly used for pipe, containers, films, and bottles. It melts at ~140°C.



Code	Shift (ppm)
A1	14.1
A2	22.9
A3	32.2
A4	30.0

Experimental Parameters

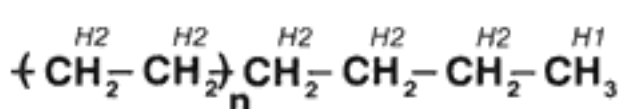
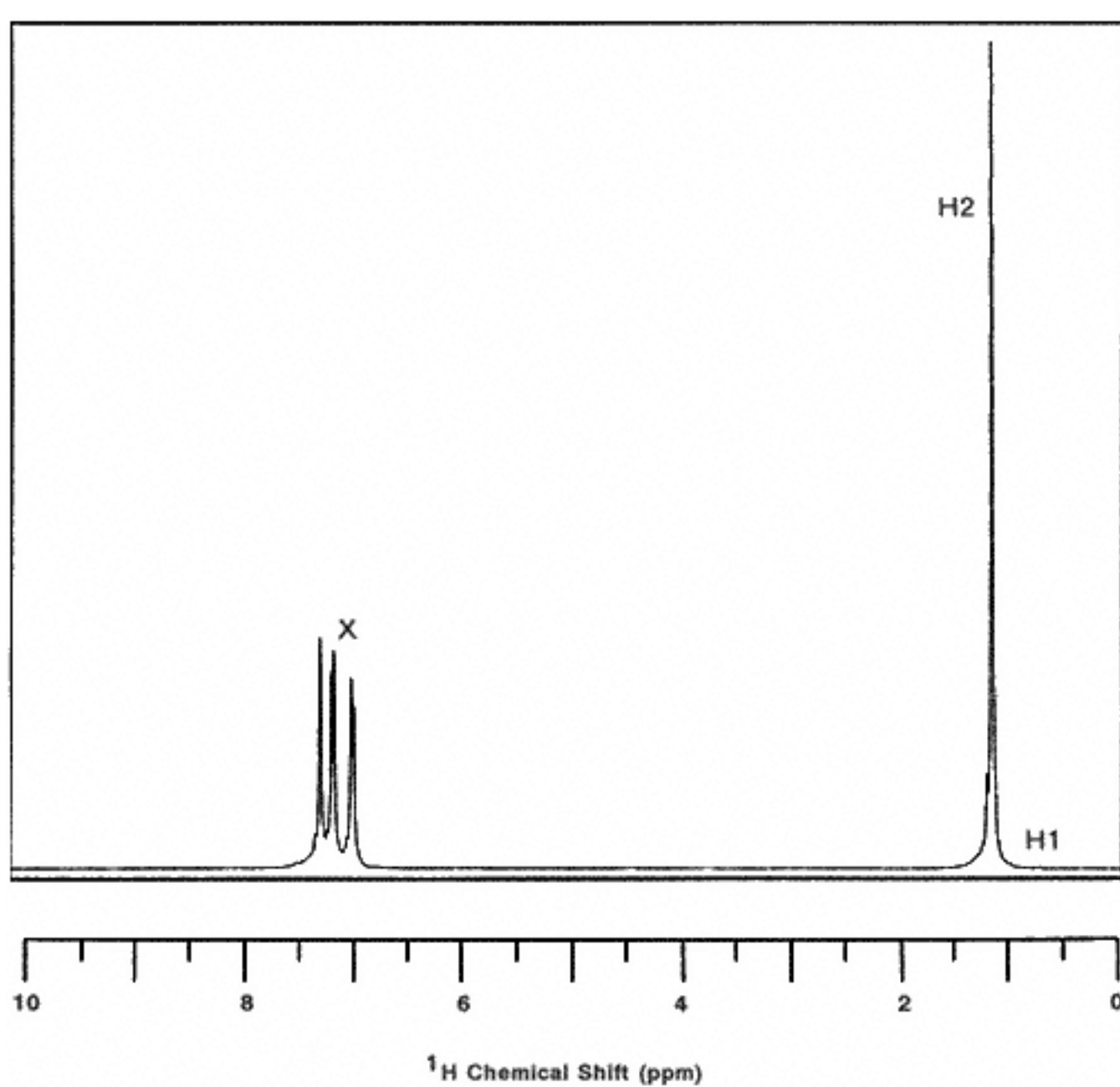
Nucleus: ¹³ C (100.4 MHz)	Temperature: 130°C
Solvent: ODCB-d ₄ /TCB (3/1 v/v)	Concentration: 30% w/w
Scans: 20,000	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 2 s

Reference

A. Kaji, Y. Akimoto, and A. Murano. *J. Polym. Sci. A Polym. Chem.* 29:1987, 1991.

II-A-1H—**Polyethylene, Linear or High-Density (LPE or HDPE)****Comments**

The primary resonance is from backbone methylenes; the very small secondary peak arises from end-group methyls. Solvent resonances are marked by **X**. This material is also known as low-pressure polyethylene; its density is greater than 0.94 g/cm³. It is a hard, stiff plastic produced by Ziegler-Natta or other organometallic catalysts, and is commonly used for pipe, containers, films, and bottles. It melts at ~140°C.



Code	Shift (ppm)
H1	0.84
H2	1.27

Experimental ParametersNucleus: ¹H (400 MHz)

Temperature: 130°C

Solvent: ODCB-d₄/TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 100

Spectral width: 8 kHz

Data points: 4096

Pulse width: 30°

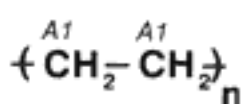
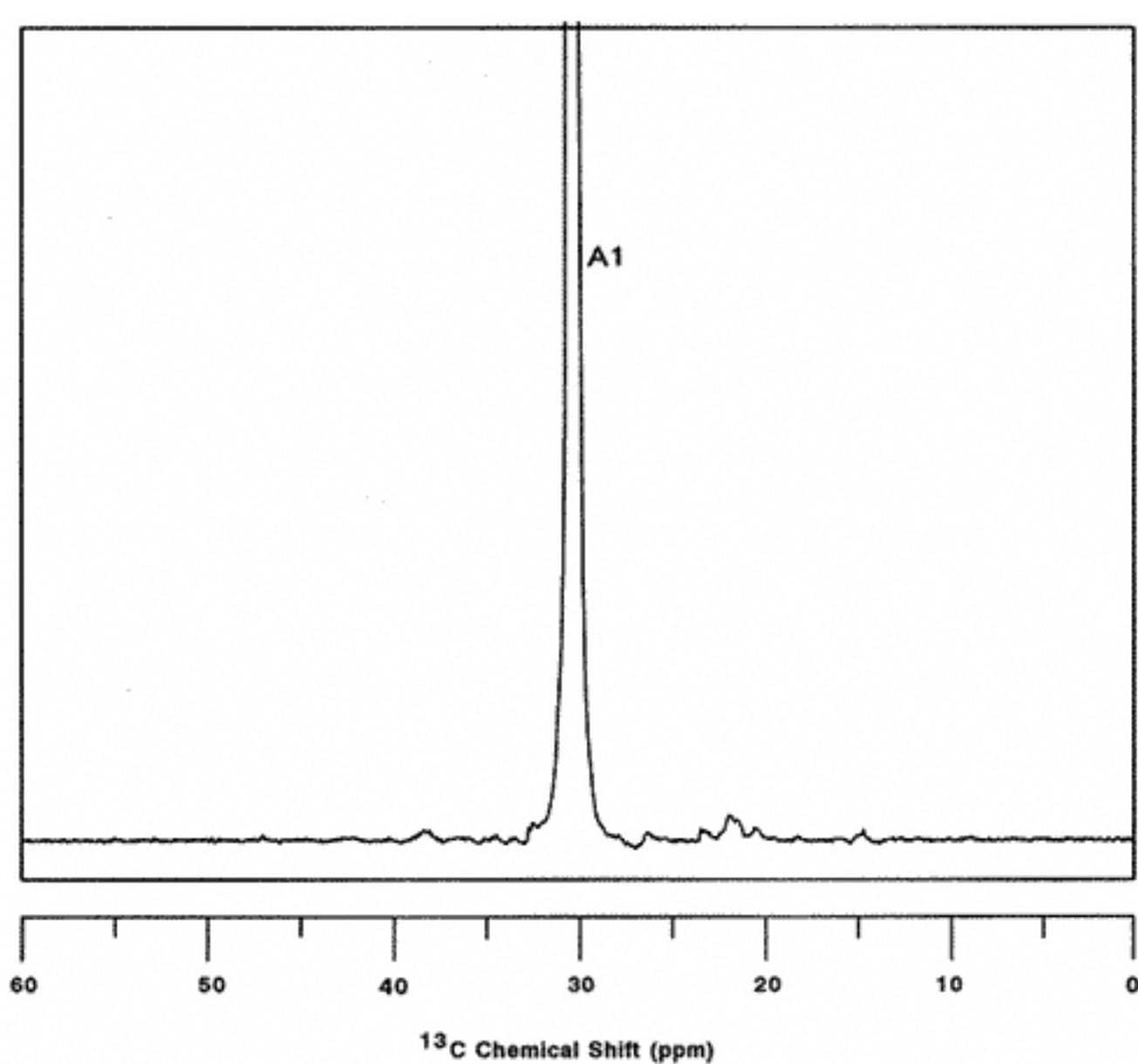
Broadening: 5 Hz

Pulse delay: 5 s

**II-A-2—
Polyethylene, Ultrahigh Molecular Weight (UHMWPE)**

Comments

Because the MW > 10⁶, only main-chain carbons are visible under normal spectral acquisition conditions. This material has high-impact strength, good abrasion resistance, and a low coefficient of friction, making it suitable for applications in bearings and chutes. It melts at ~145°C.



Code	Shift (ppm)
A1	30.0

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB-d₄/TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 20,000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

Reference

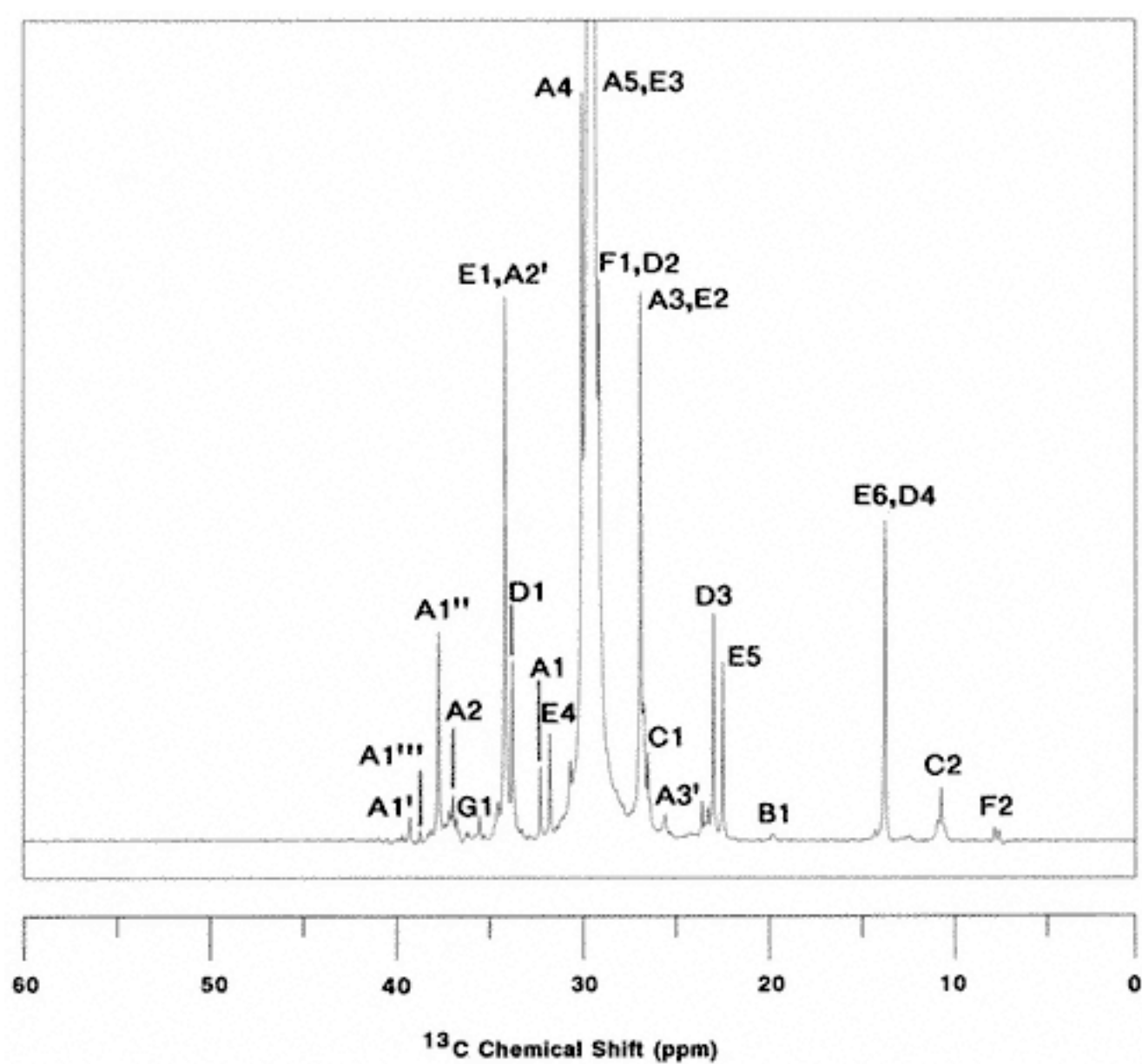
A. Kaji, Y. Akimoto, and M. Murano. *J. Polym. Sci. A Polym. Chem.* 29:1987, 1991.

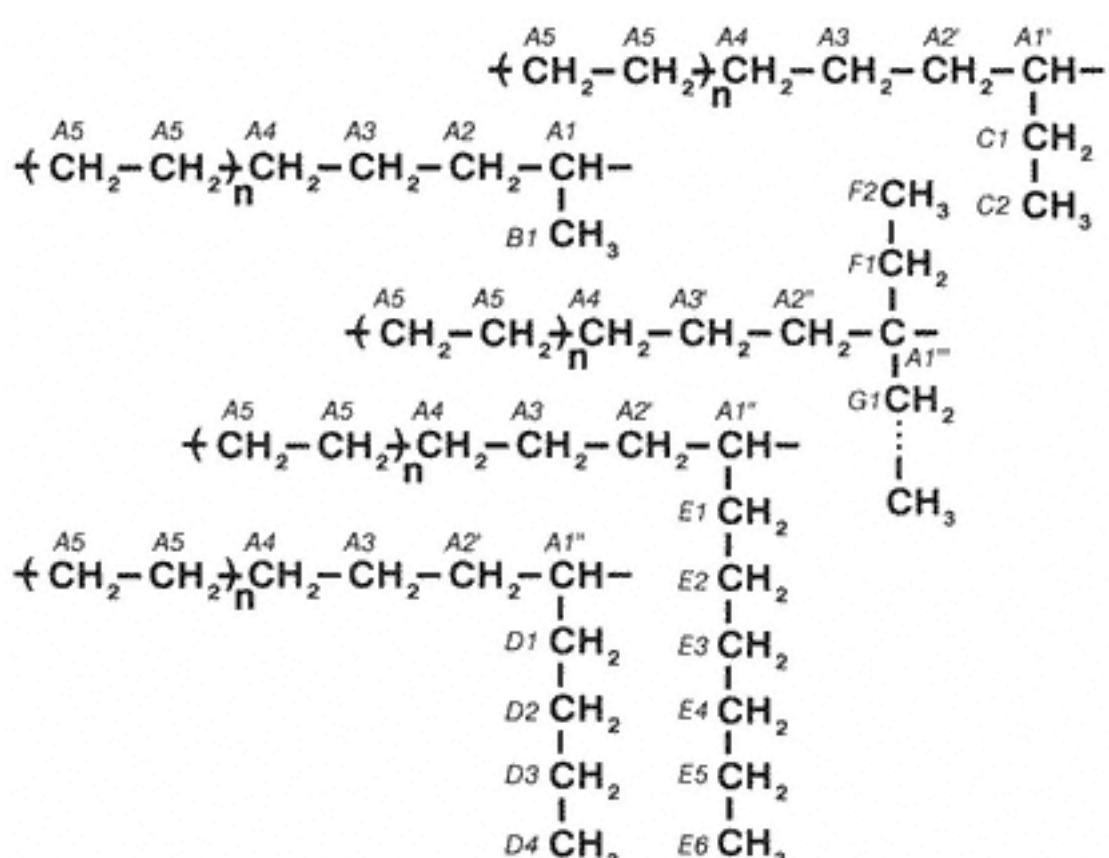
II-A-3

**II-A-3—
Polyethylene, Branched or Low-Density (BPE or LDPE)**

Comments

The primary resonance arises from backbone methylenes; secondary resonances are due to a distribution of short- (C_1 , C_2 , C_4) and long-chain ($>C_4$) branches. This material is also known as high-pressure polyethylene. It is produced by a peroxide-initiated, free-radical polymerization; its density is approximately 0.91 g/cm^3 . This soft, flexible plastic is commonly used for film and other packaging applications. It melts at $\sim 110^\circ\text{C}$.





Code **Shift (ppm)**

A1	32.8
A1'	39.8
A1''	38.2
A1'''	39.2
A2	37.4
A2'	34.6
A2''	37.4
A3	27.2
A3'	25.9
A4	30.6
A5	30.0
B1	20.1
C1	27.0
C2	10.9
D1	34.3
D2	27.3
D3	23.3
D4	14.0
E1	34.6
E2	27.2
E3	30.0
E4	32.3
E5	22.8
E6	14.0
F1	29.5
F2	8.1
G1	36.0

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 2000

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

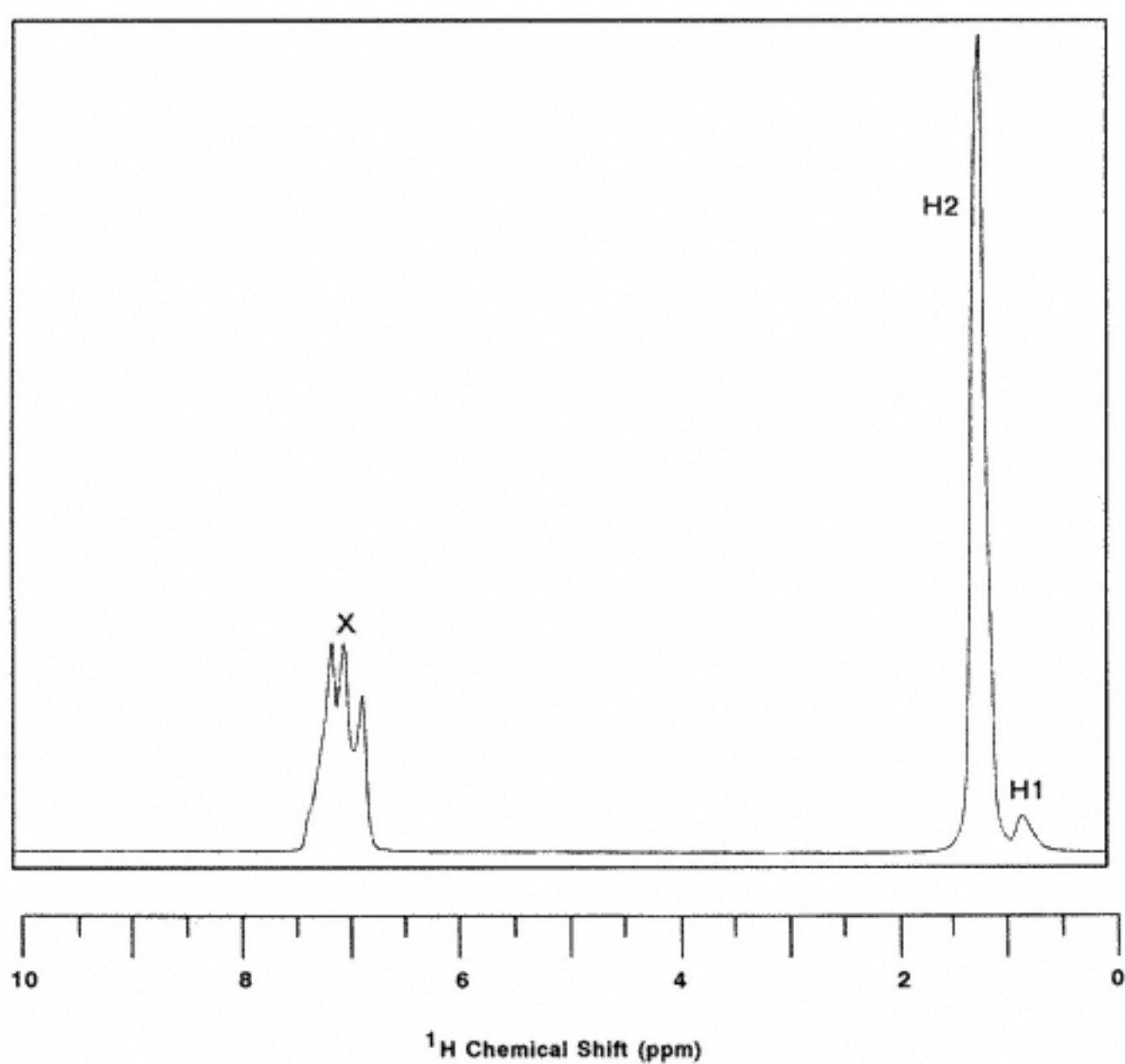
Reference

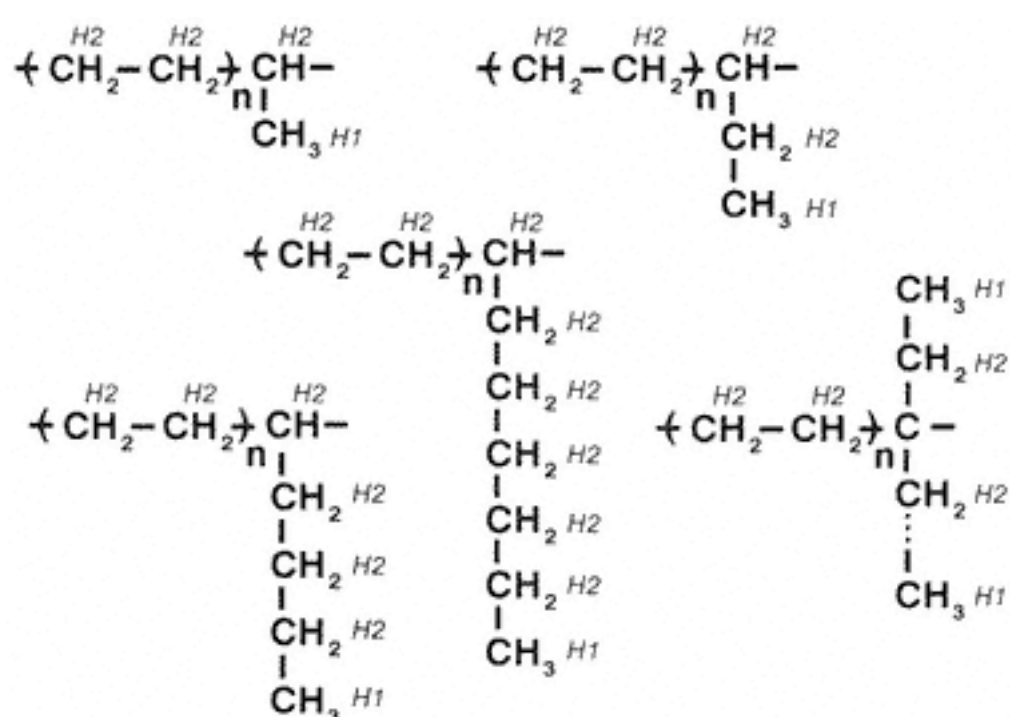
J. C. Randall. *J. Polym. Sci. Polym. Phys. Ed.* 11:275, 1973.

II-A-3H—
Polyethylene, Branched or Low-Density

Comments

The primary resonance arises from backbone methylenes; secondary resonances are due to methyl protons in branches and chain ends. Solvent resonances are marked by **X**. This material is also known as high-pressure polyethylene. It is produced by a peroxide-initiated, free-radical polymerization; its density is approximately 0.91 g/cm³. This soft, flexible plastic is commonly used for film and other packaging applications. It melts at ~110°C.





Code	Shift (ppm)
H1	0.89
H2	1.29

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 100

Spectral width: 8 kHz

Data points: 4096

Pulse width: 30°

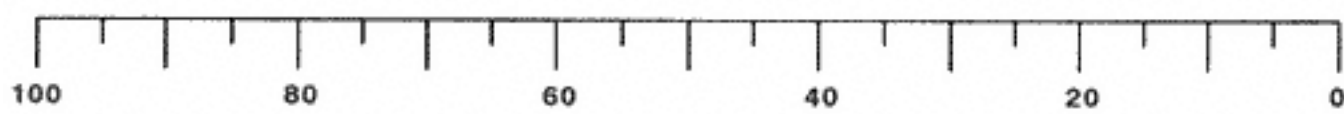
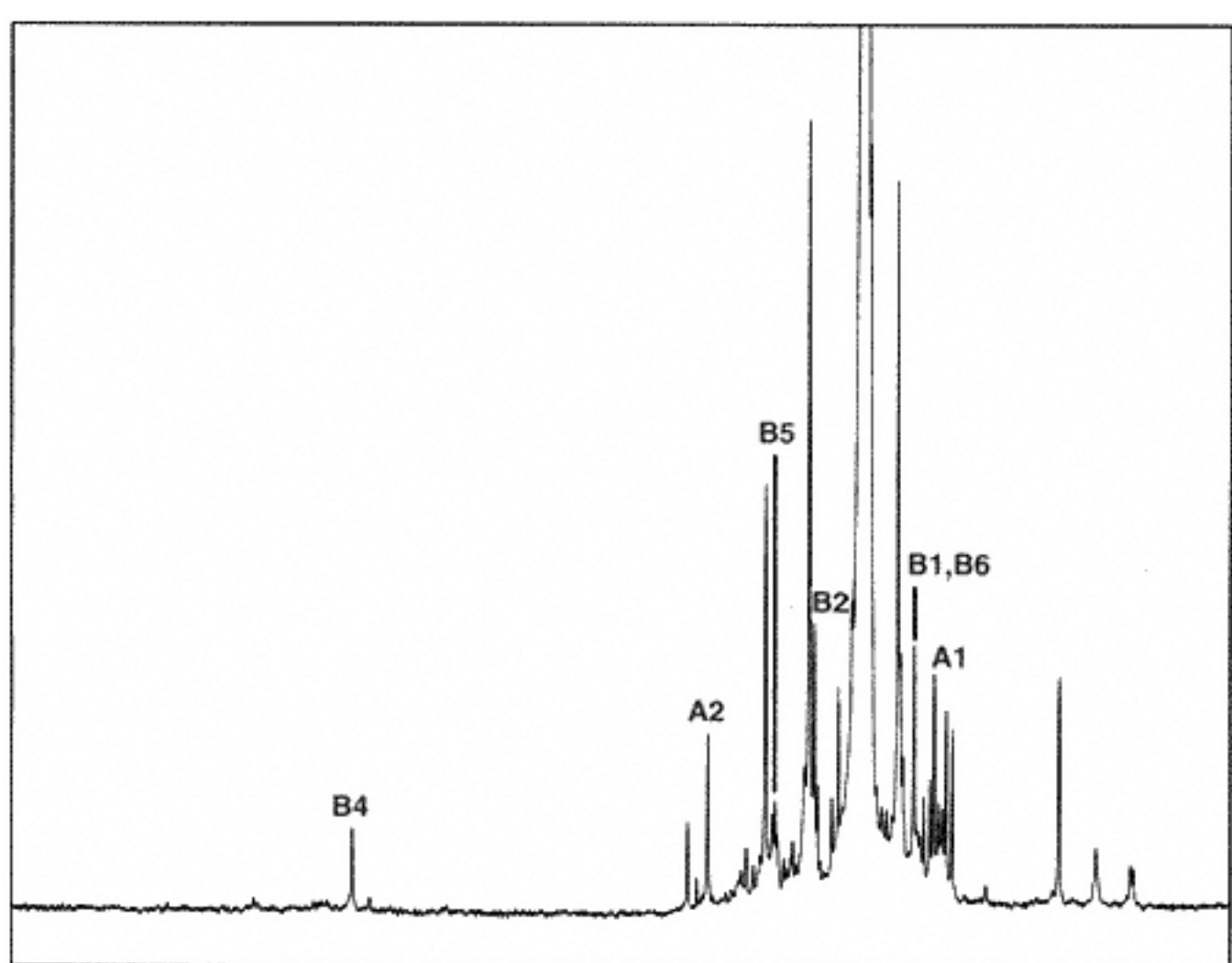
Broadening: 3 Hz

Pulse delay: 5 s

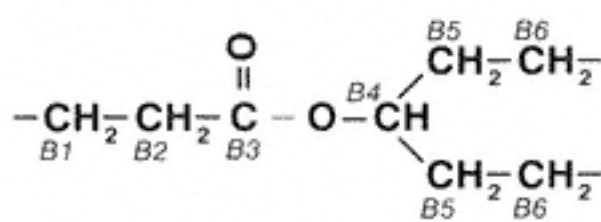
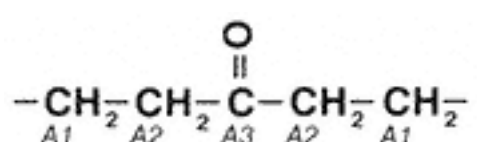
II-A-4— Polyethylene, Oxidized

Comments

Oxidation of polyethylene can lead to formation of species such as acids, secondary alcohols, esters, and lactones. The relative amounts depend on the conditions under which degradation occurred. Unintentional oxidation can be caused by aging or heat exposure (during processing, transportation, storage, or use), and is usually accompanied by yellow or brown discoloration and deterioration of properties.



^{13}C Chemical Shift (ppm)



Code	Shift (ppm)
A1	24.0
A2	44.5
A3	208.4
B1	26.0
B2	34.5
B3	175.9
B4	72.0
B5	37.2
B6	26.0

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

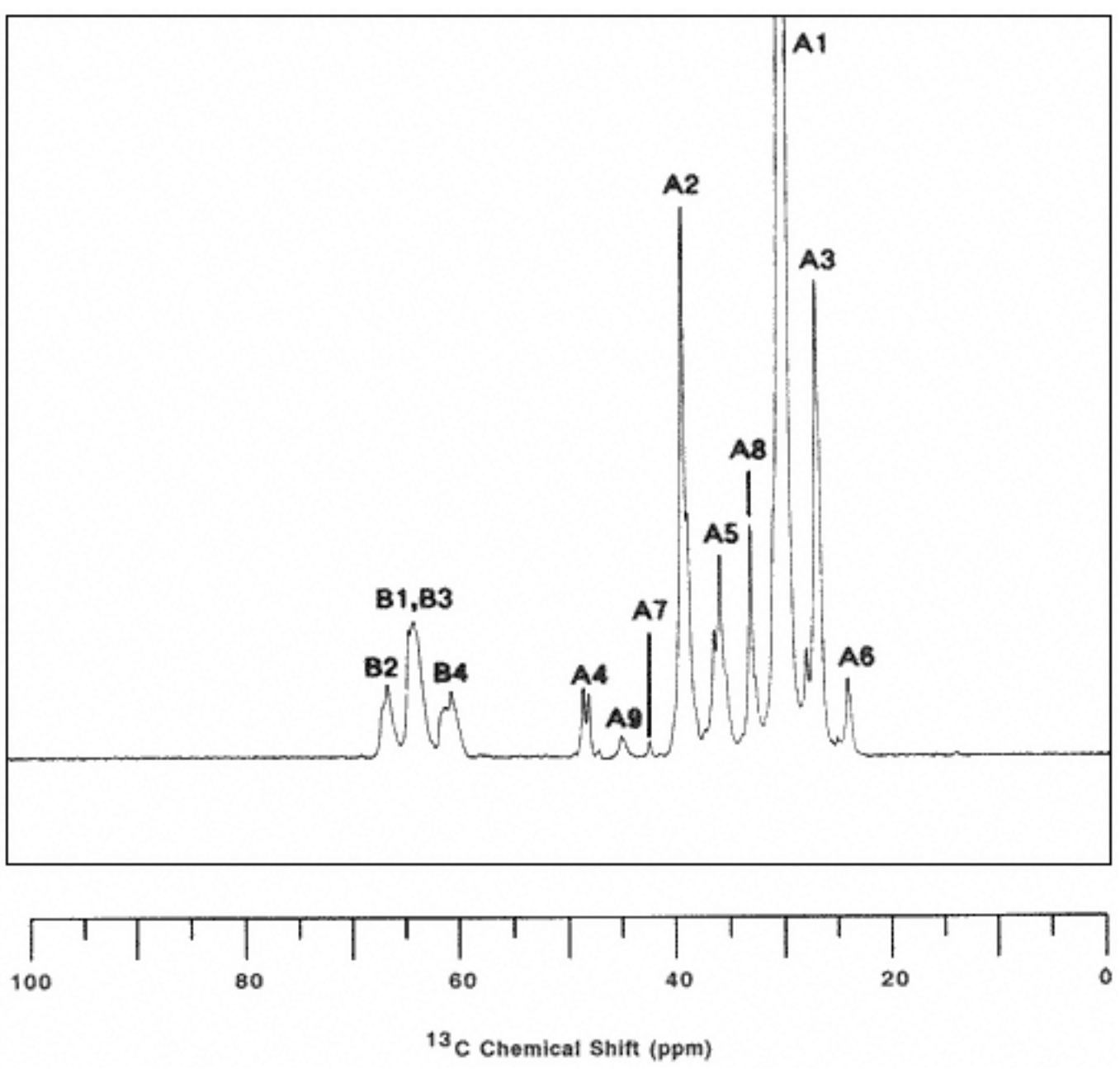
References

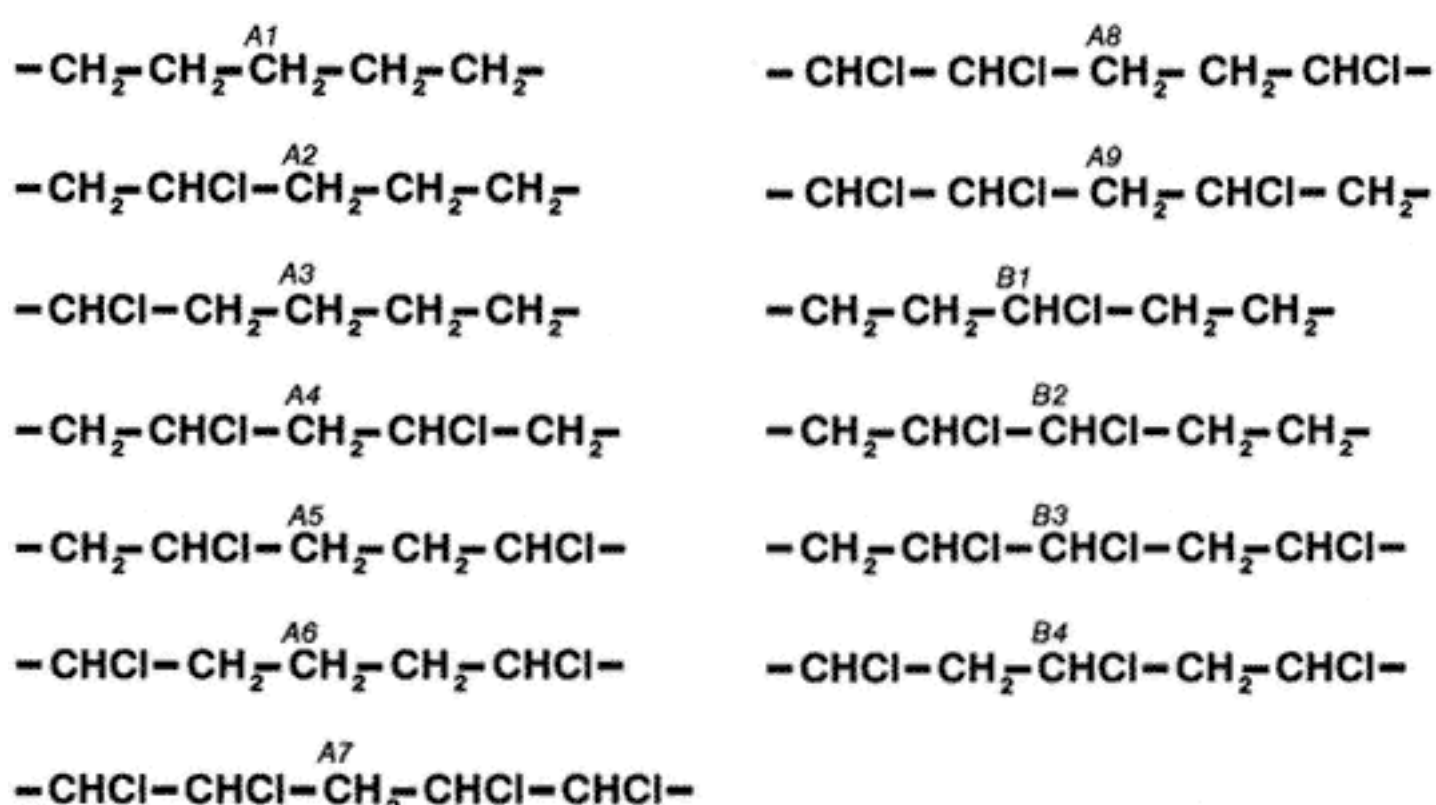
T. Kuroki, T. Sawaguchi, S. Niikuni, and T. Ikemura. *J. Polym. Sci. Polym. Chem. Ed.* 21:703 1983; H. N. Cheng, F. C. Schilling, and F. A. Bovey. *Macromolecules* p 363, 1976.

**II-A-5—
Polyethylene, Chlorinated [25% Cl] (CIPE)**

Comments

A wide distribution of resonances is observed, because of the many possible chlorination patterns. Treatment of HDPE with Cl₂ produces an elastomeric material, which can be vulcanized to further improve its properties. It is used primarily for wire and cable jacketing.





Code	Shift (ppm)
------	-------------

A1	30.0
----	------

A2	38.9
----	------

A3	26.8
----	------

A4	47.9
----	------

A5	35.5
----	------

A6	23.8
----	------

A7	41.9
----	------

A8	32.7
----	------

A9	44.5
----	------

B1	63.4
----	------

B2	65.8
----	------

B3	63.4
----	------

B4	59.9
----	------

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 2000

Spectral Width: 25kHz

Data point: 8192

Pulse Width: 90°

Broadening: 3Hz

Pulse delay: 2 s

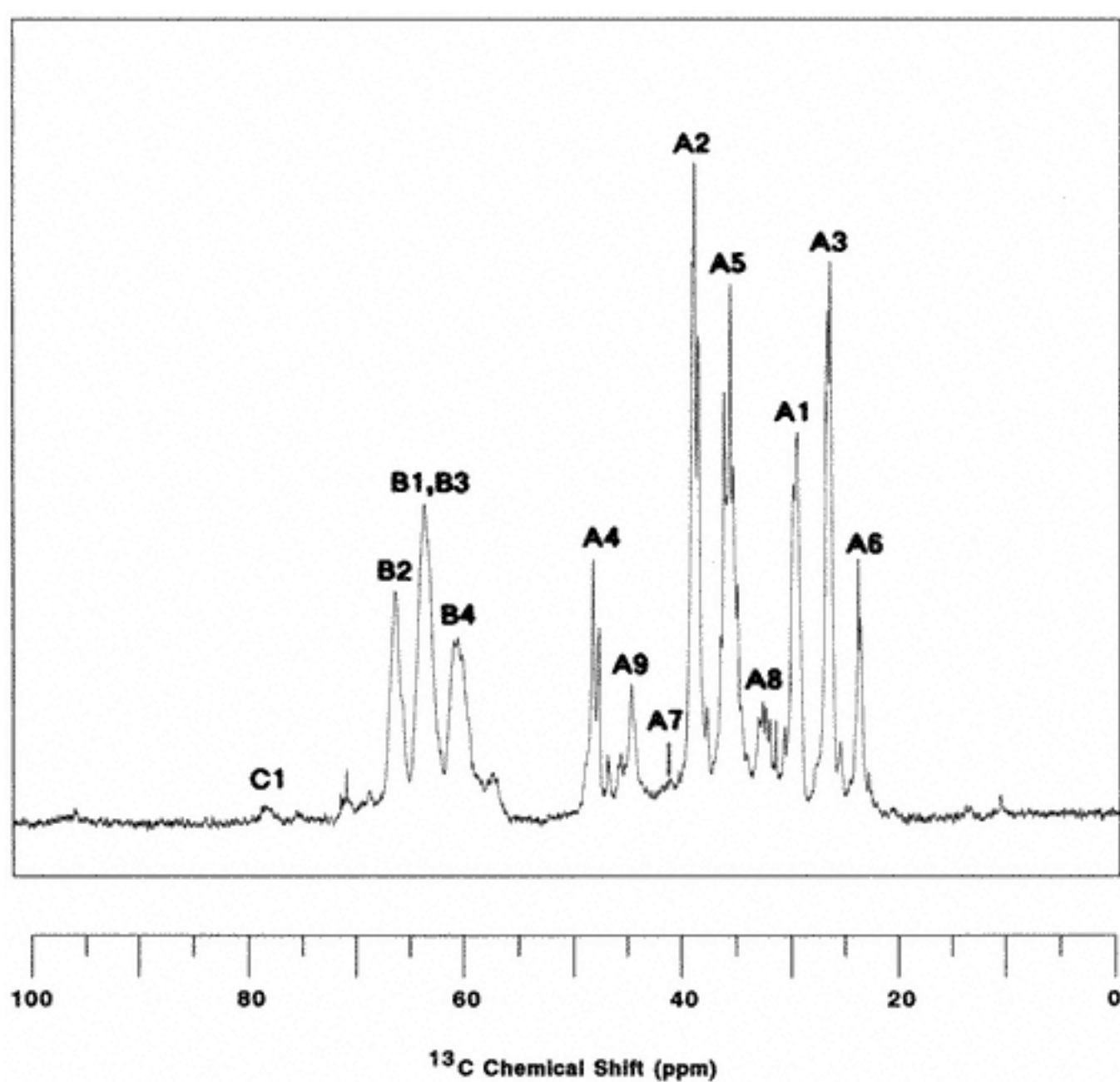
Reference

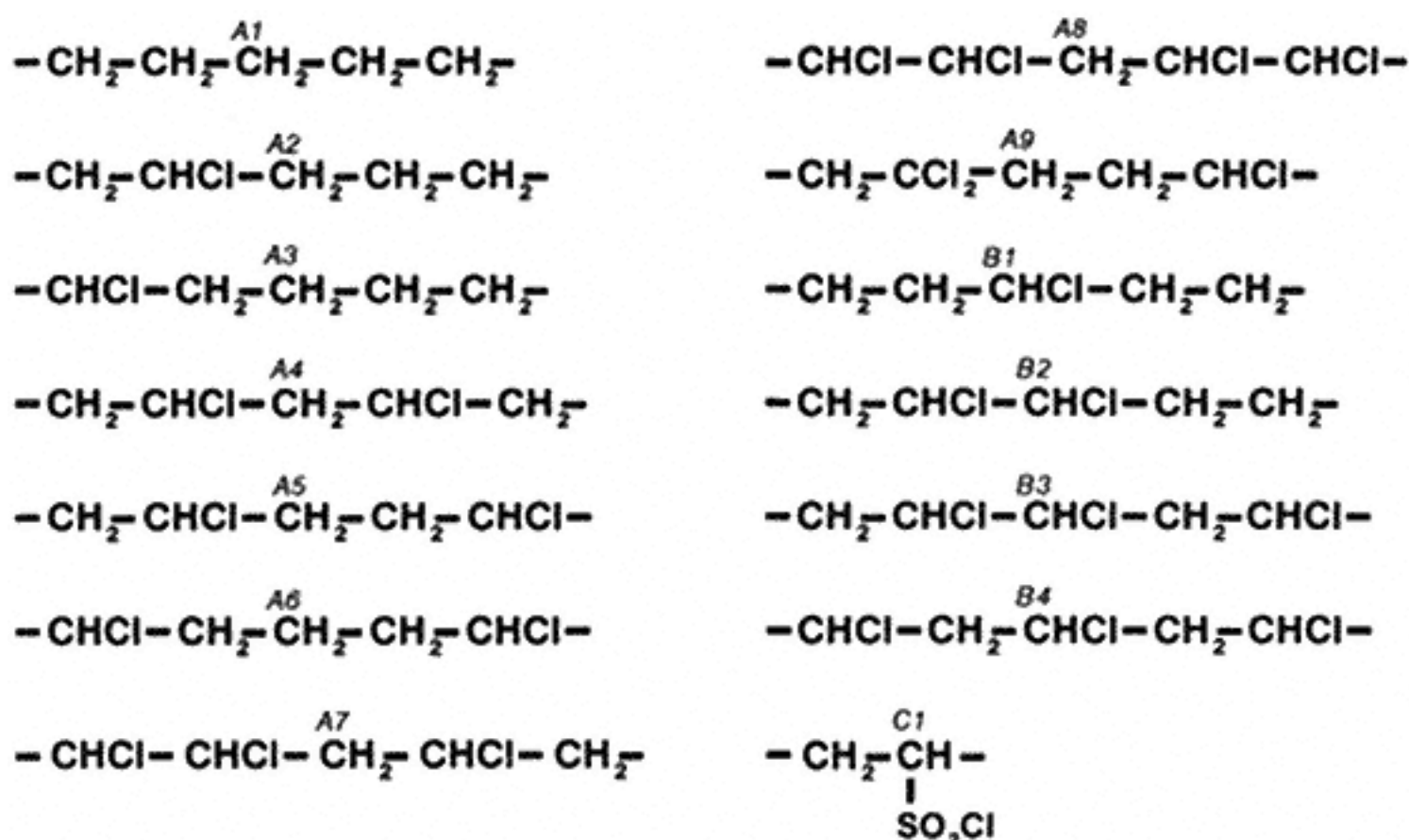
B. Hoeselbarth, F. Keller, M. Findeisen. *Acta Polym.* 40:351, 1989.

**II-A-6—
Polyethylene, Chlorosulfonated**

Comments

The pattern of resonances is similar to that of chlorinated PE {II-A-5}. Treatment of HDPE with Cl_2 and SO_2 produces an elastomer, which can be vulcanized to further improve its properties. It is found in automotive, wire, cable, and liner applications.





Code	Shift (ppm)
------	-------------

A1	30.0
----	------

A2	38.9
----	------

A3	26.8
----	------

A4	47.9
----	------

A5	35.5
----	------

A6	23.8
----	------

A7	41.9
----	------

A8	32.7
----	------

A9	44.5
----	------

B1	63.4
----	------

B2	65.8
----	------

B3	63.4
----	------

B4	59.9
----	------

C1	76.8
----	------

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB-d4/TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 2000

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

Reference

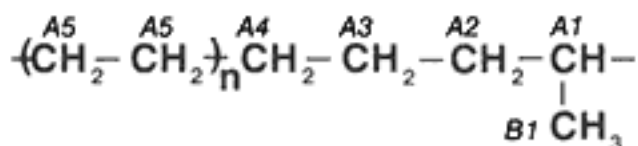
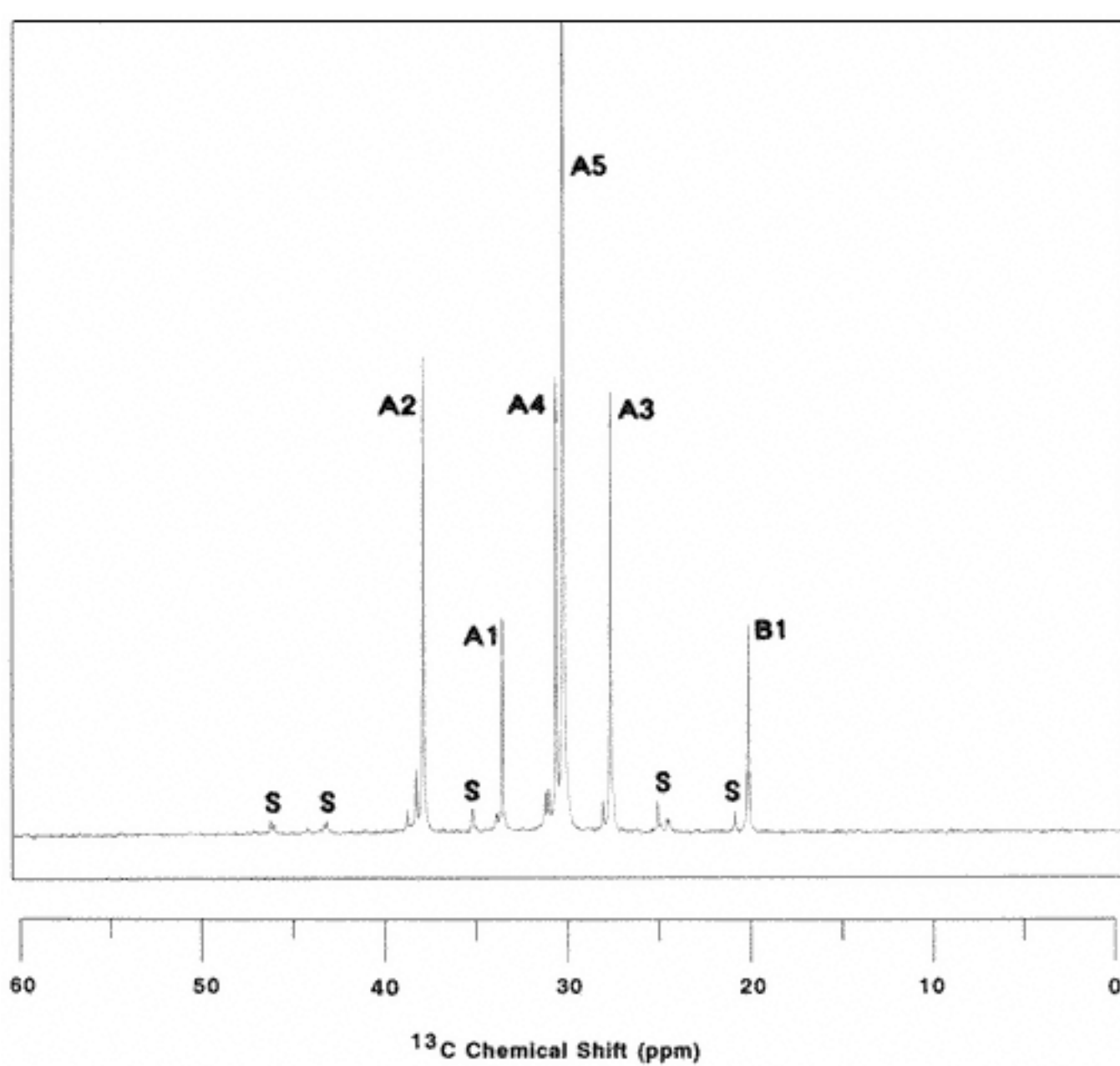
B. Hoeselbarth, F. Keller, and M. Findeisen. *Acta Polym.* 40:371, 1989.

II-A-7—

Poly(Ethylene-Co-Propylene) [~5%P]

Comments

The polymer-chain structure is primarily linear, with pendant methyl branches created by incorporation of propylene into the backbone. Because of the relatively low propylene content, the methyl branches are mostly isolated. Resonances from comonomer sequences, marked by **S**, increase in intensity with propylene content.



Code	Shift (ppm)
A1	33.3
A2	37.6
A3	27.4
A4	31.0
A5	30.0
B1	20.1

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

References

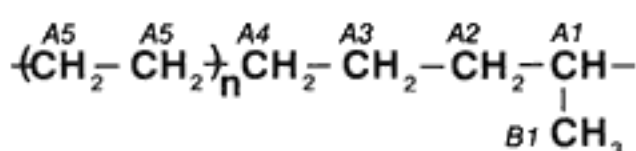
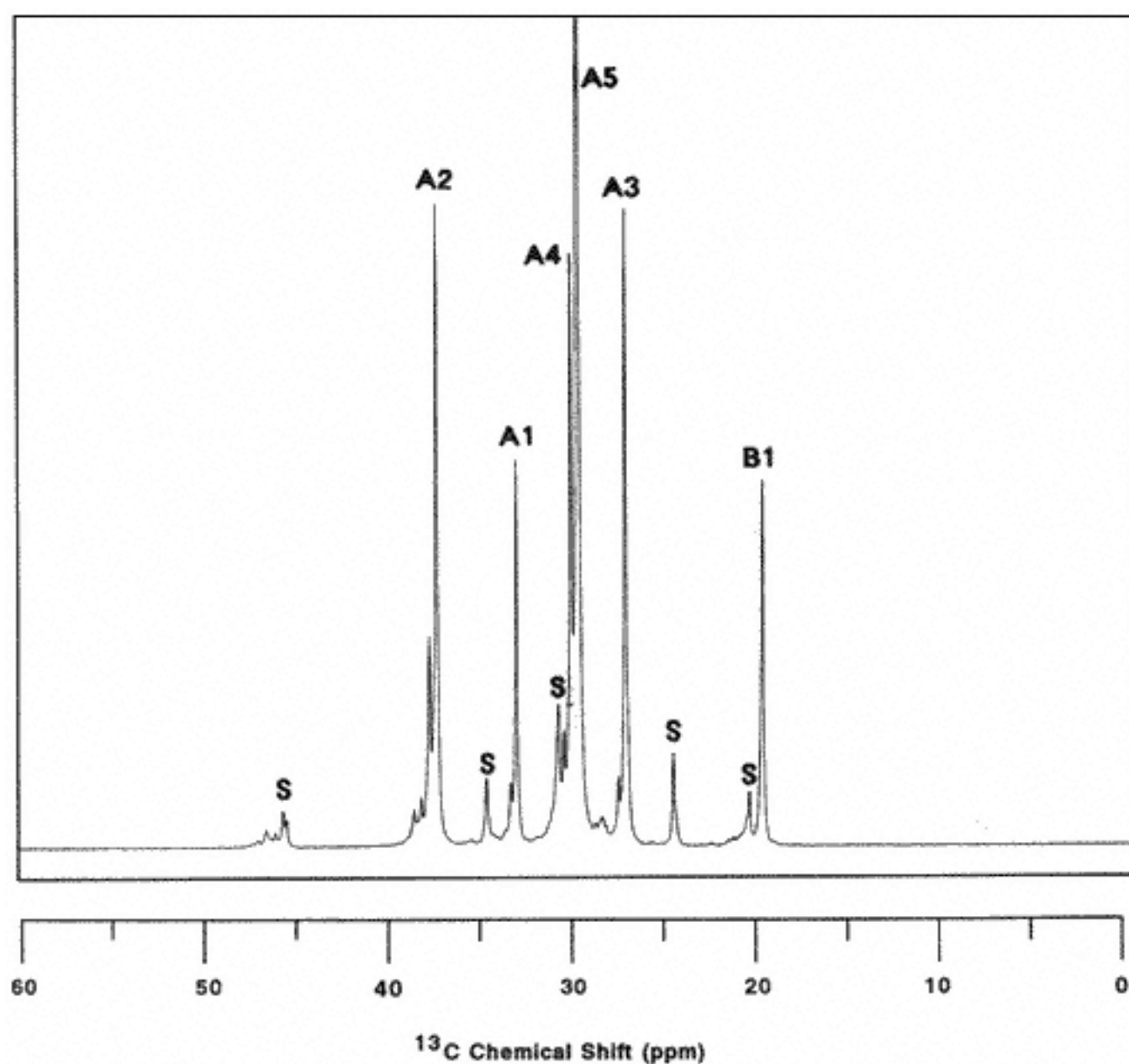
J. C. W. Chien and B. Xu. *Makromol. Chem. Rapid Commun.* 14:109, 1993; H. N. Cheng and D. A. Smith. *Macromolecules* 19:2065 1986; H. N. Cheng. *Macromolecules* 17:1950, 1984.

II-A-8—

Poly(Ethylene-Co-Propylene) [~40%P] (EPR)

Comments

Although the general pattern of resonances is similar to that of poly(ethylene-co-propylene) [~5%P] {II-A-7}, the higher level of propylene comonomer leads to more clusters of branches; peaks arising from such sequences are denoted by **S**. This material is also known as ethylene-propylene rubber (EPR). It is a thermoplastic elastomer that is often blended with polyethylene or polypropylene to improve toughness {II-A-34, II-A-36, II-A-39, and II-A-42}. Its primary uses are hoses, gaskets, and as a viscosity-index improver for lubricants.



Code	Shift (ppm)
A1	33.3
A2	37.6
A3	27.4
A4	31.0
A5	30.0
B1	20.1

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

References

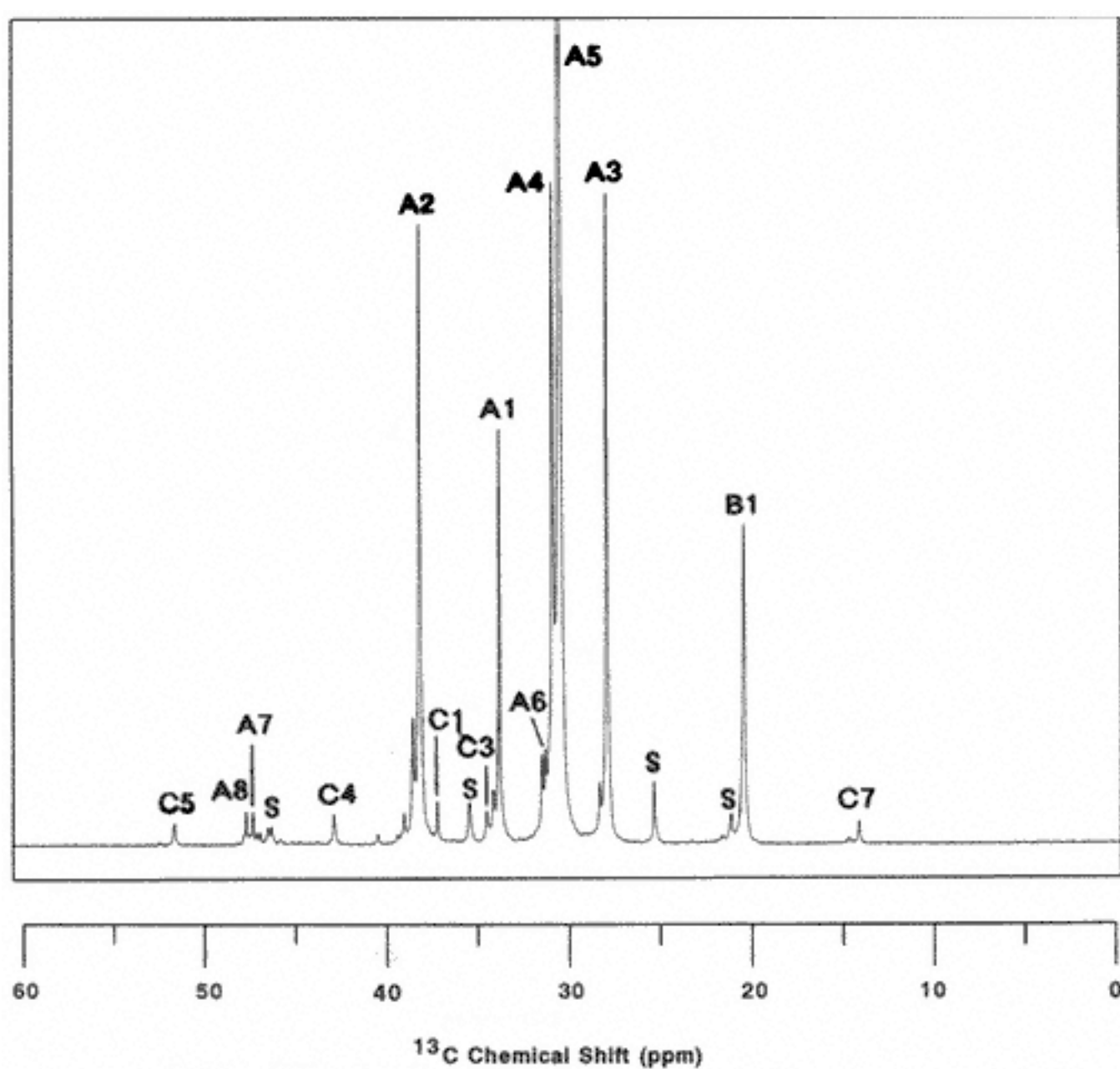
J. C. W. Chien and B. Xu. *Makromol. Chem. Rapid Commun.* 14:109, 1993; H. N. Cheng and D. A. Smith. *Macromolecules* 19:2065, 1986; H. N. Cheng. *Macromolecules* 17:1950, 1984.

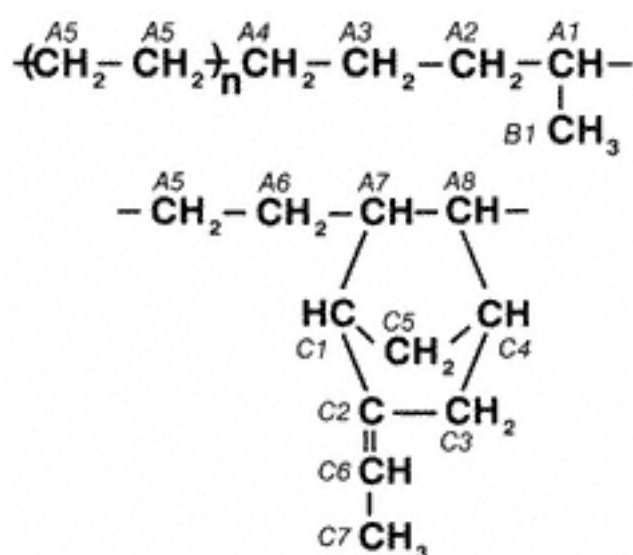
II-A-9—

Poly(Ethylene-Co-Propylene-Co-5-Ethylidene-2-Norbornene) (EPDM)

Comments

The general pattern of resonances is similar to that of poly(ethylene-co-propylene) [~5%P] {II-A-7} and EPR {II-A-8}; sequences are again denoted by S. Pendant unsaturated groups are potential cross-linking sites. This material is also known as ethylene-propylene-diene (EPDM) copolymer. It is a thermoplastic elastomer that is often blended with polyethylene or polypropylene to improve toughness; it is also used for hoses, gaskets, and viscosity index improvers in lubricants.





Code	Shift (ppm)
A1	33.3
A2	37.6
A3	27.4
A4	31.0
A5	30.0
A6	31.3
A7	46.3
A8	47.1
B1	20.1
C1	36.7
C2	147.5
C3	34.0
C4	42.3
C5	50.7
C6	111.7
C7	13.8

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB-d₄/TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

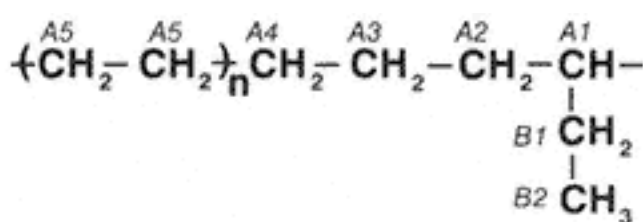
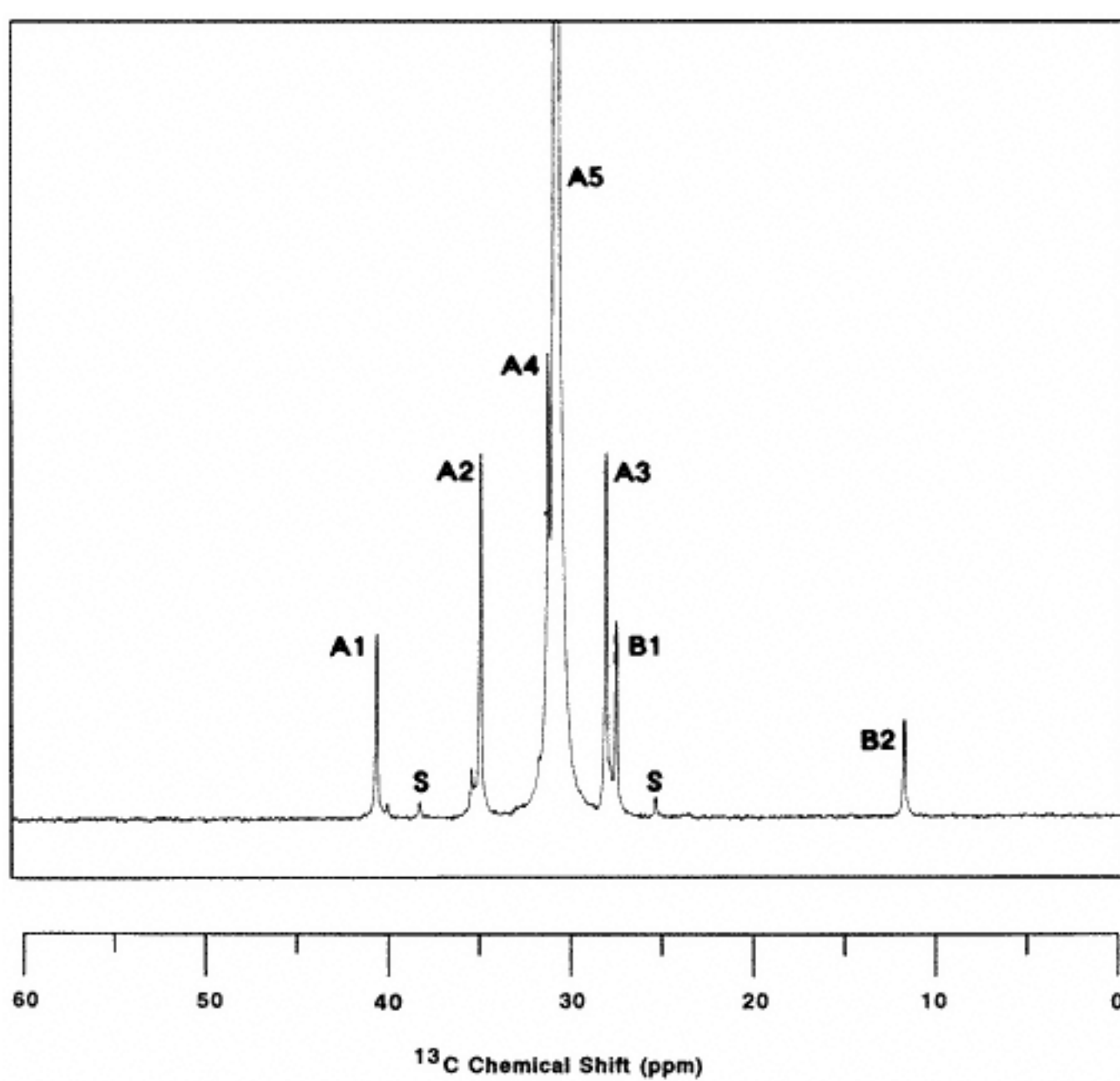
Pulse delay: 2 s

II-A-10—

Poly(Ethylene-Co-1-Butene) [~5%B] (EB-LLDPE)

Comments

The polymer-chain structure is primarily linear, with pendant ethyl branches created by incorporation of 1-butene into the backbone. Because of the relatively low 1-butene content, these ethyl branches are mostly isolated. Resonances caused by comonomer sequences, marked by **S**, increase in intensity with butene content. Poly(ethylene-co-1-butene) is one of the materials known as linear, low-density polyethylene (LLDPE), which are produced by an organometallic-catalyzed low-pressure process similar to that used for HDPE {II-A-1}. These copolymers typically contain 1–10% wt% 1-butene; their density ranges from 0.91 to 0.94 g/cm³. They are used in film, bag, and liner applications. This particular material melts at ~125°C; the melting point of these copolymers increases as the 1-butene content decreases.



Code	Shift (ppm)
A1	39.8
A2	34.2
A3	27.3
A4	30.5
A5	30.0
B1	26.7
B2	11.1

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

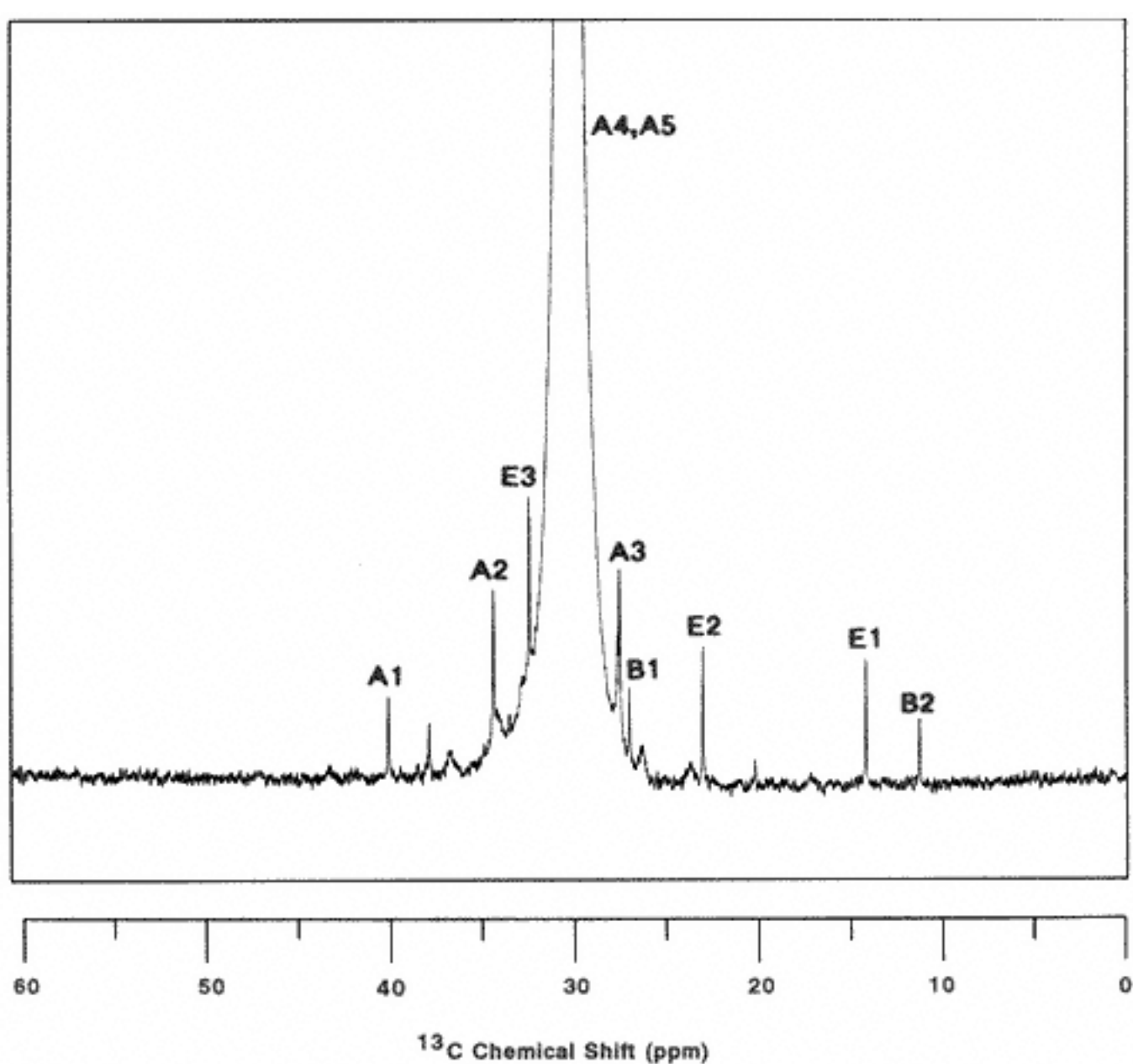
ReferenceE. T. Hsieh and J. C. Randall. *Macromolecules* 15:353, 1982.

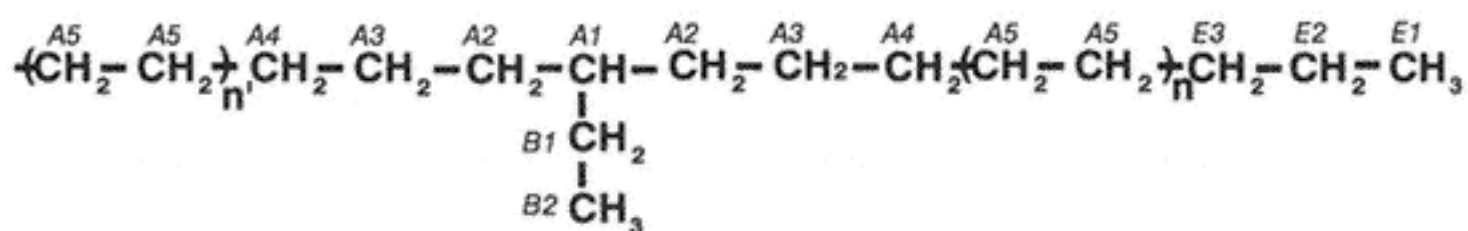
II-A-11—

Poly(Ethylene-Co-1-Butene) [-0.1%B] (EB-HDPE)

Comments

The polymer-chain structure is primarily linear, with pendant ethyl branches created by incorporation of 1-butene into the backbone. Because of the extremely low 1-butene content, the peaks from the chain ends are approximately the same intensity as those from the ethyl branches. This copolymer is produced by an organometallic-catalyzed low-pressure process similar to that used for HDPE {II-A-1}. The density of these low-butene copolymers is $> 0.94 \text{ g/cm}^3$, and their principal uses are for films and bottles. This particular material melts at $\sim 135^\circ\text{C}$; the melting point of these copolymers decreases as the 1-butene content increases.





Code	Shift (ppm)
A1	39.8
A2	34.2
A3	27.3
A4	30.5
A5	30.0
B1	26.7
B2	11.1
E1	14.1
E2	22.9
E3	32.2

Experimental Parameters

Nucleus: ^{13}C (100.4MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

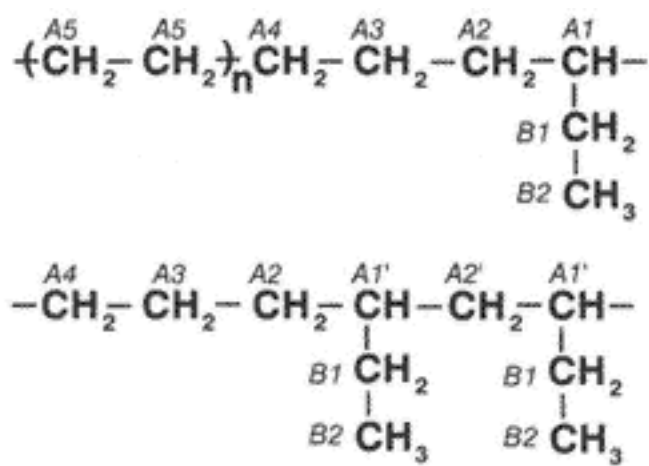
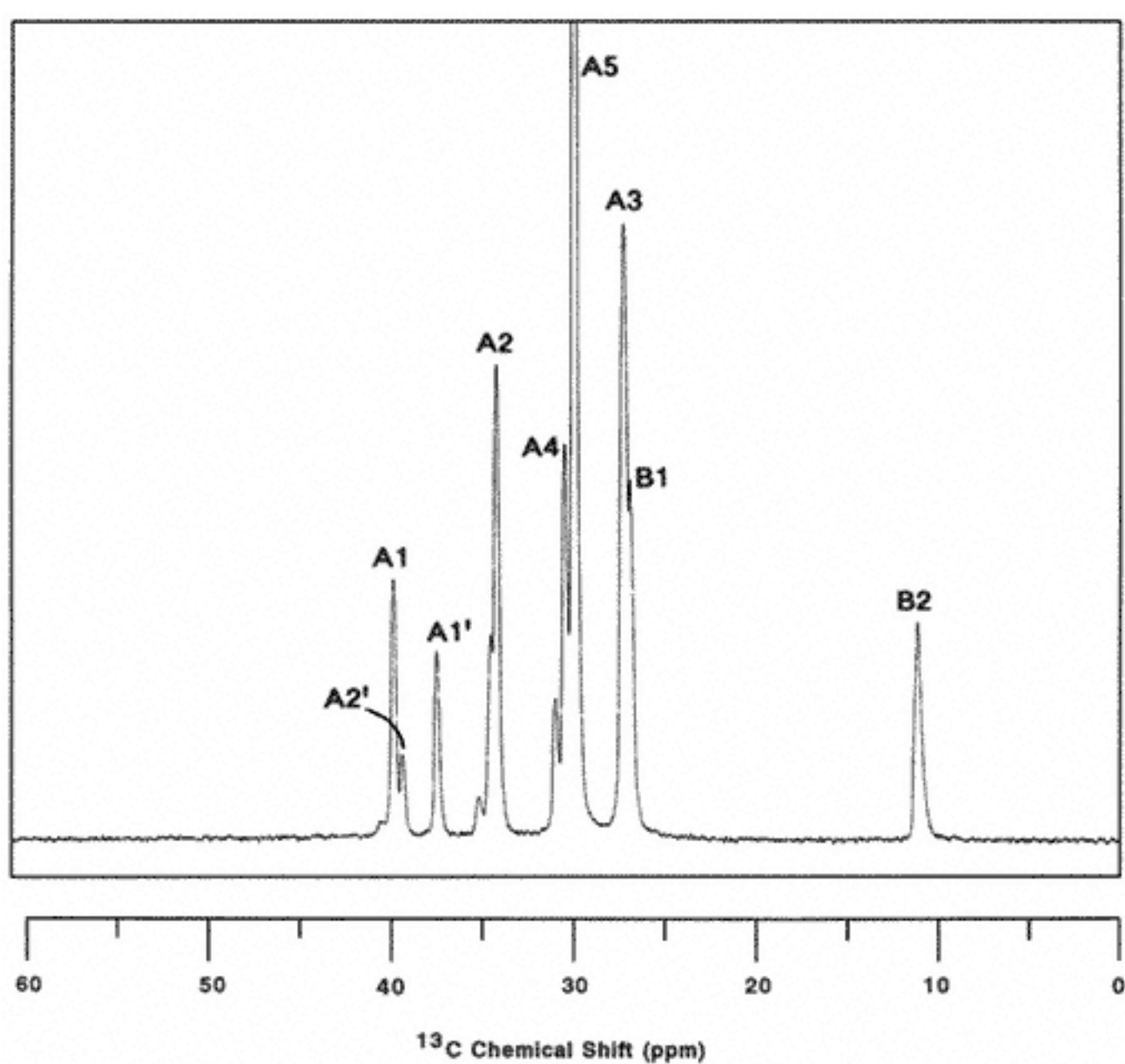
Reference

E. T. Hsieh and J. C. Randall. *Macromolecules* 15:353, 1982.

II-A-12—
Polybutadiene, Hydrogenated

Comments

Hydrogenation of polybutadiene (PBd) {IV-B-1} yields a polymer that is structurally similar to poly(ethylene-co-1-butene); the ethyl branches arise from the pendant vinyl groups in the original material. This material exhibits improved oxidation and weathering resistance over the original PBd because the unsaturation has been removed.



Code	Shift (ppm)
A1	39.8
A1'	37.5
A2	34.2
A2'	39.4
A3	27.3
A4	30.5
A5	30.0
B1	26.7
B2	11.1

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

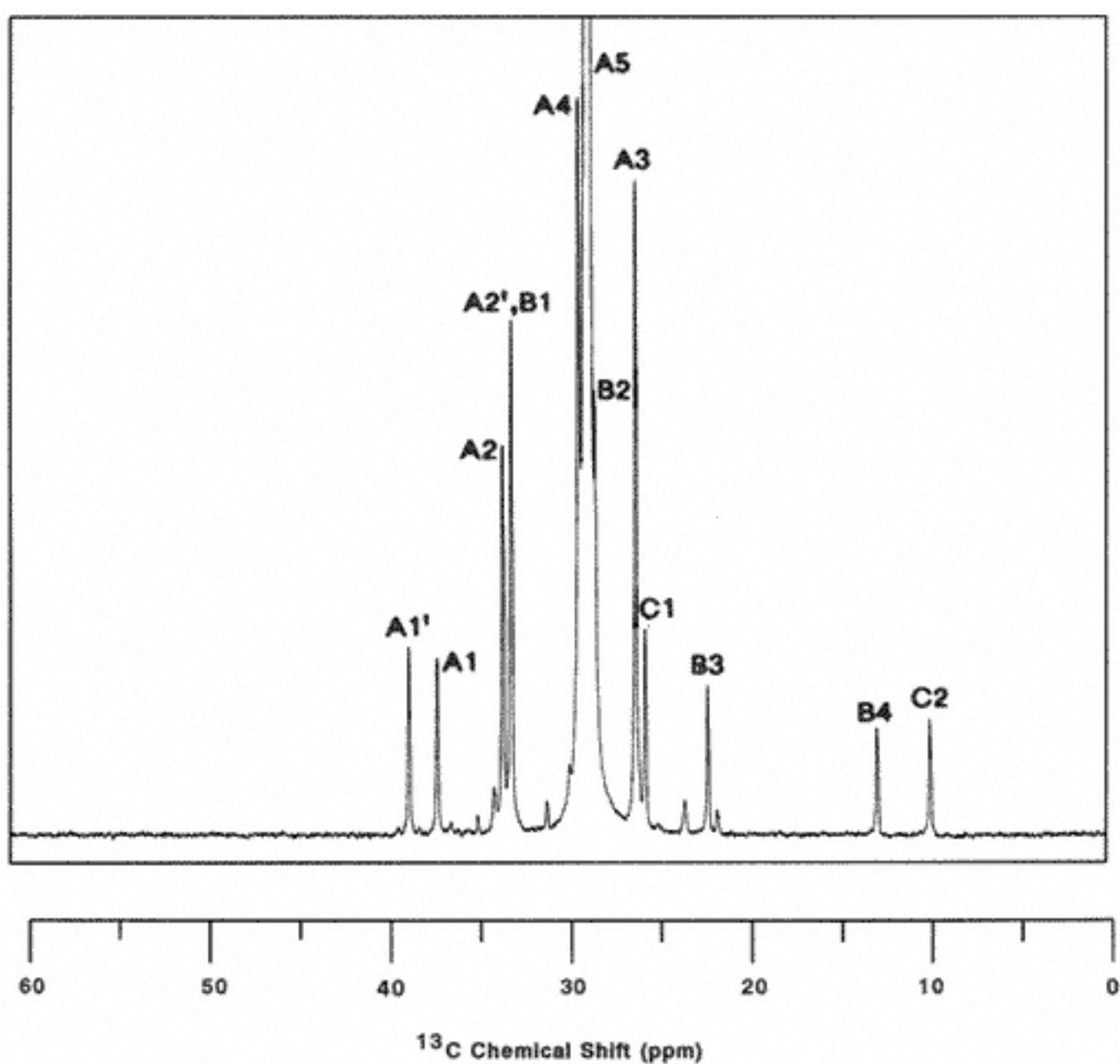
ReferenceE. T. Hsieh and J. C. Randall. *Macromolecules* 15:353, 1982.

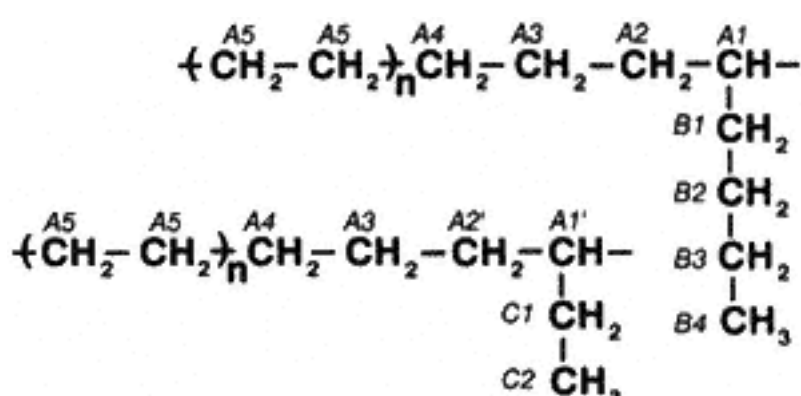
II-A-13—

Poly(Ethylene-Co-1-Butene-Co-1-Hexene) [~5%B, ~5%H]

Comments

The polymer-chain structure is primarily linear, with pendant ethyl and butyl branches created by incorporation of 1-butene and 1-hexene, respectively, into the backbone. Poly(ethylene-co-1-butene-co-1-hexene) is one of the materials known as linear, low-density polyethylene (LLDPE), which is produced by an organometallic-catalyzed low-pressure process similar to that used for HDPE {II-A-1}. The density of these copolymers is 0.91–0.94 g/cm³, and their principal uses are for films and bottles.





Code	Shift (ppm)
A1	38.1
A1'	39.8
A2	34.6
A2'	34.2
A3	27.3
A4	30.5
A5	30.0
B1	34.2
B2	29.4
B3	23.4
B4	14.1
C1	26.7
C2	11.1

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

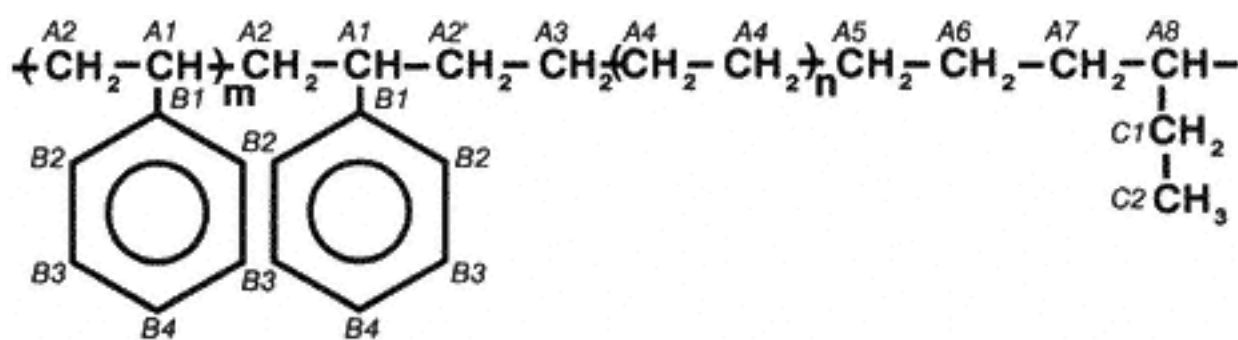
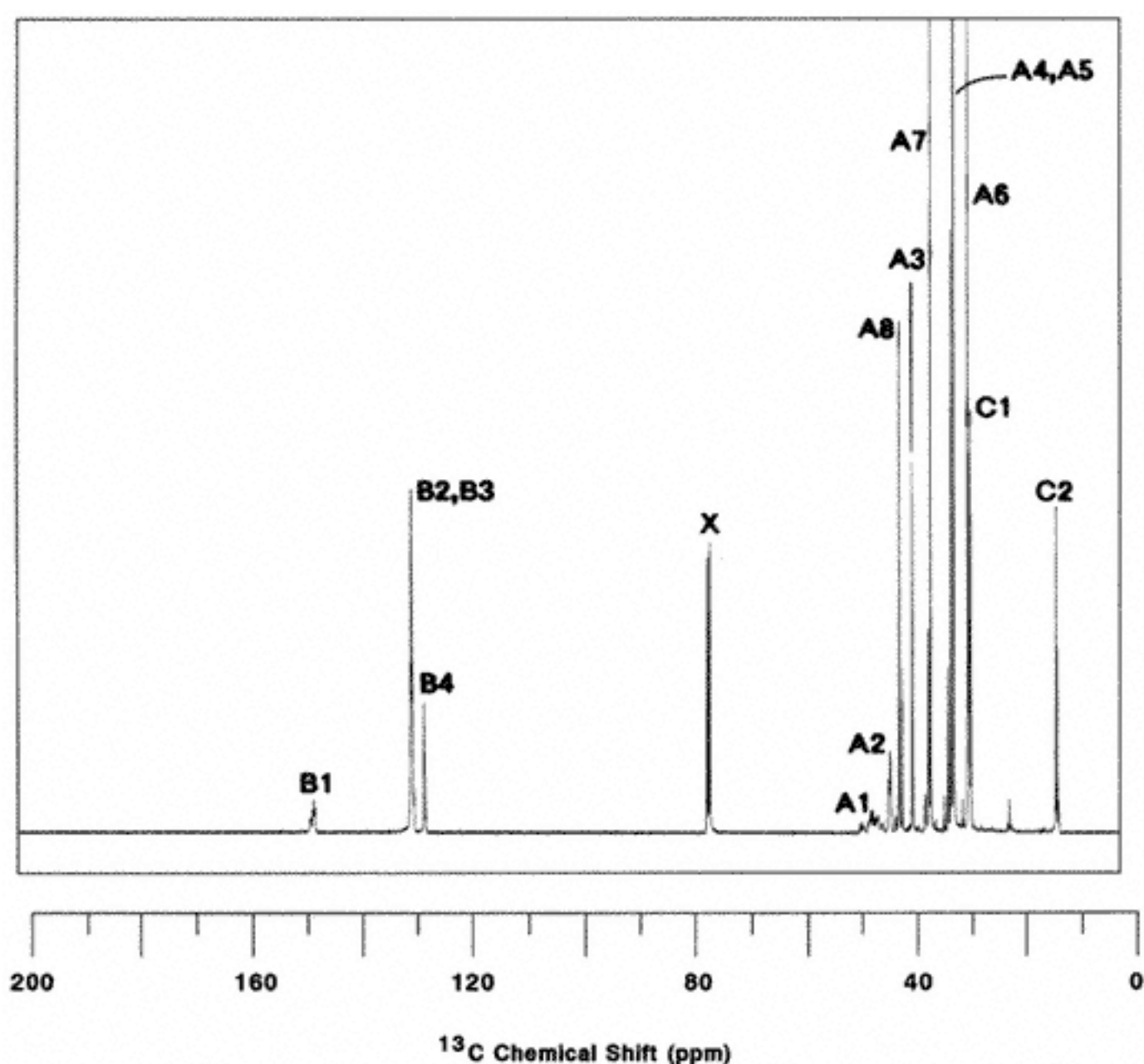
Reference

E. T. Hsieh and J. C. Randall. *Macromolecules* 15:353, 1982.

II-A-14— Poly(Ethylene-Co-1-Butene-Co-Styrene)

Comments

Hydrogenation of poly(styrene-*b*-butadiene) (SBS) {III-A-6} yields a polymer with blocks of polystyrene and blocks similar to poly(ethylene-co-1-butene), in which the ethyl branches arise from the pendant vinyl groups in the original material. Solvent resonances are marked by X. This material exhibits improved oxidation and weathering resistance over the original SBS because the unsaturation has been removed.



Code	Shift (ppm)
A1	45.2
A2	42.0
A3	38.0
A4	34.7
A5	34.7
A6	27.8
A7	34.7
A8	40.3
B1	146.6
B2	128.9
B3	128.9
B4	126.5
C1	27.4
C2	11.6

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

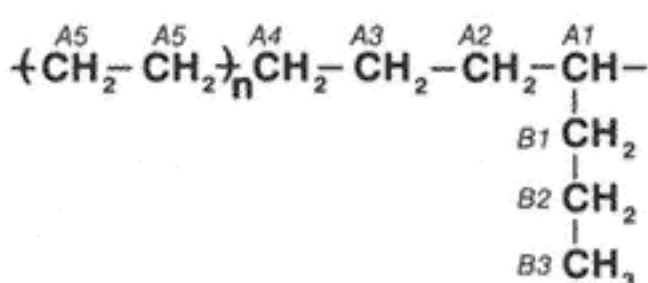
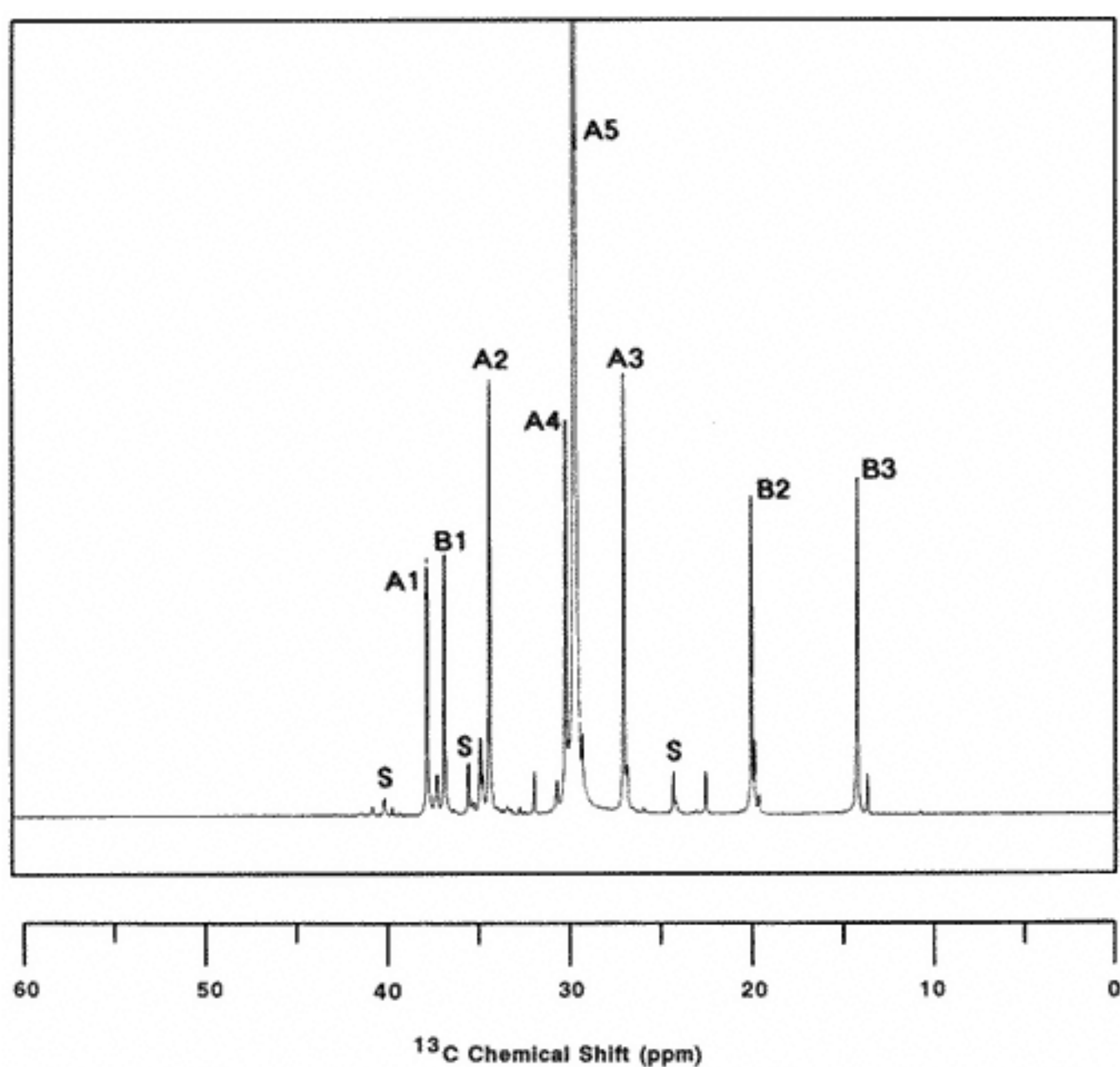
Pulse delay: 2 s

II-A-15—

Poly(Ethylene-Co-1-Pentene)

Comments

The polymer-chain structure is primarily linear, with pendant propyl branches created by incorporation of 1-pentene into the backbone. Because of the relatively low 1-pentene content, these propyl branches are mostly isolated. Resonances caused by comonomer sequences, marked by **S**, increase in intensity with pentene content. Poly(ethylene-co-1-pentene) is not currently commercially available, but exhibits properties similar to those of poly(ethylene-co-1-hexene), and is produced by an organometallic-catalyzed low-pressure process similar to that used for HDPE {II-A-1}. These copolymers typically contains 1–15% wt% 1-olefin; their density ranges from 0.91 to 0.94 g/cm³. This particular material melts at ~125°C; the melting point of these copolymers increases as the 1-pentene content decreases.



Code	Shift (ppm)
A1	38.0
A2	34.6
A3	27.3
A4	30.5
A5	30.0
B1	37.1
B2	20.4
B3	14.3

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 2,000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

Source

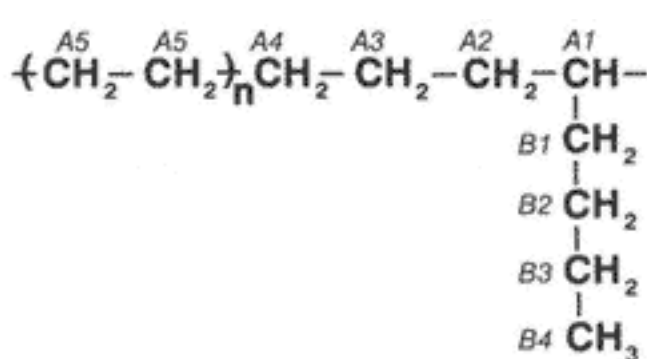
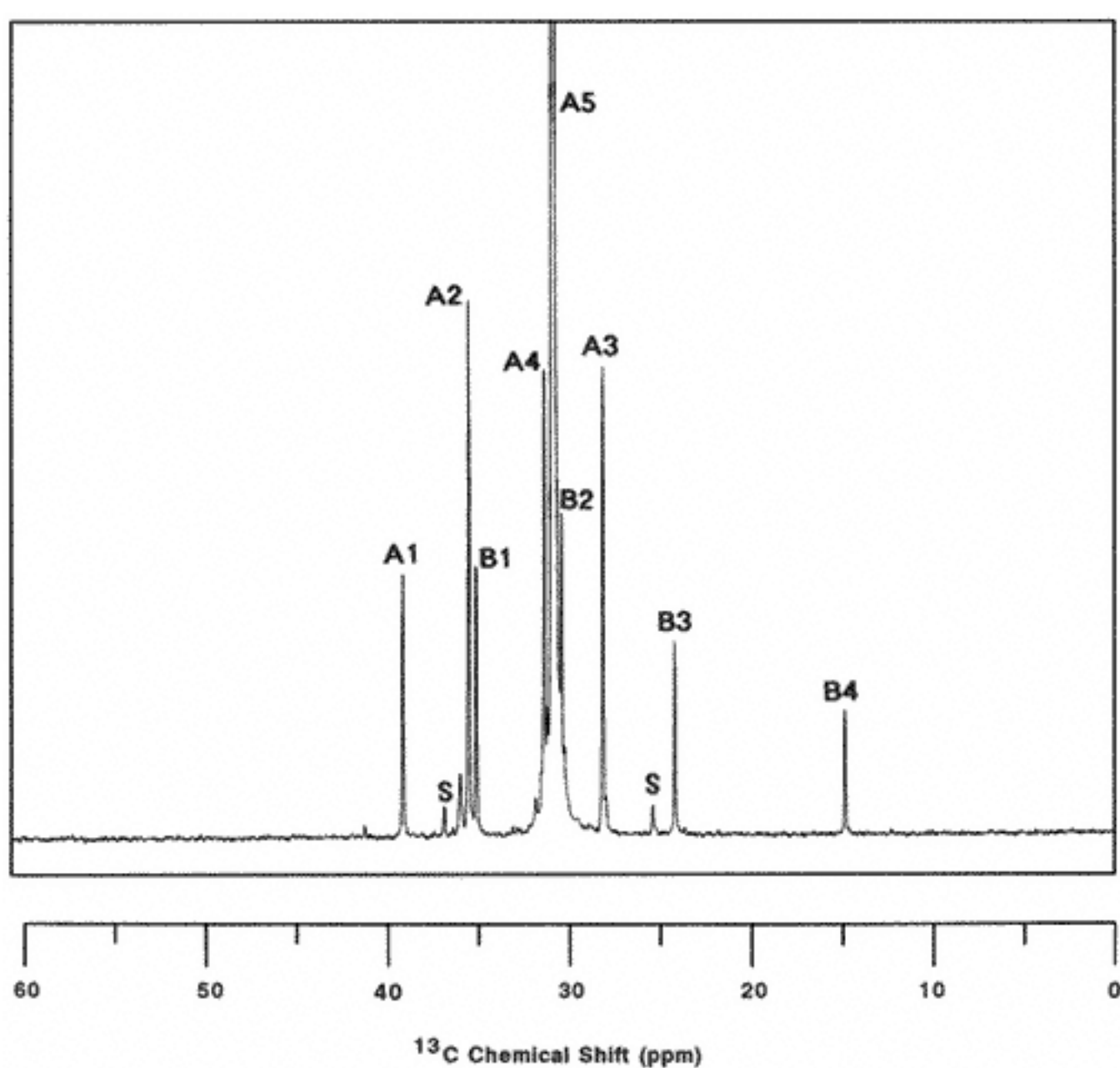
Y.V. Kissin, Mobil Chemical Company, Edison, NJ.

II-A-16—

Poly(Ethylene-Co-1-Hexene) [5% H]

Comments

The polymer-chain structure is primarily linear, with pendant butyl branches created by incorporation of 1-hexene into the backbone. Because of the relatively low 1-hexene content, these butyl branches are mostly isolated. Resonances caused by comonomer sequences, marked by **S**, increase in intensity with hexene content. Poly(ethylene-co-1-hexene) is one of the materials known as linear, low-density polyethylene (LLDPE), which are produced by an organometallic-catalyzed, low-pressure process similar to that used for HDPE {II-A-1}. These copolymers typically contains 1–15% wt% 1-hexene; their density ranges from 0.91 to 0.94 g/cm³. They are used in film, bag, and liner applications. This particular material melts at ~125°C; the melting point of these copolymers increases as the 1-hexene content decreases.



Code	Shift (ppm)
A1	38.2
A2	34.6
A3	27.3
A4	30.5
A5	30.0
B1	34.2
B2	29.4
B3	23.4
B4	14.5

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

References

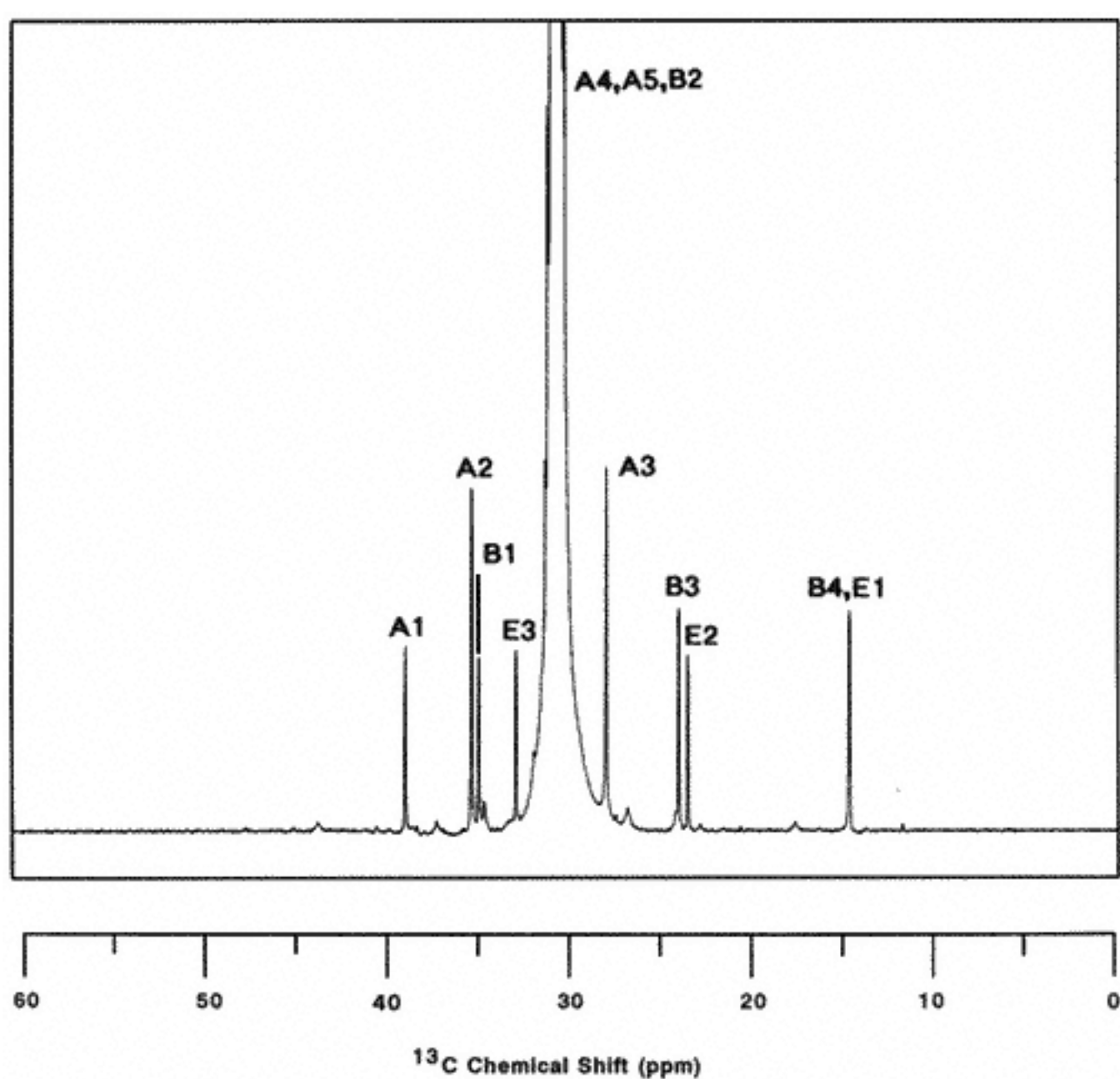
H. N. Cheng. *Polym. Bull.* 26:325, 1991; E. T. Hsieh and J. C. Randall. *Macromolecules* 15:1402, 1982.

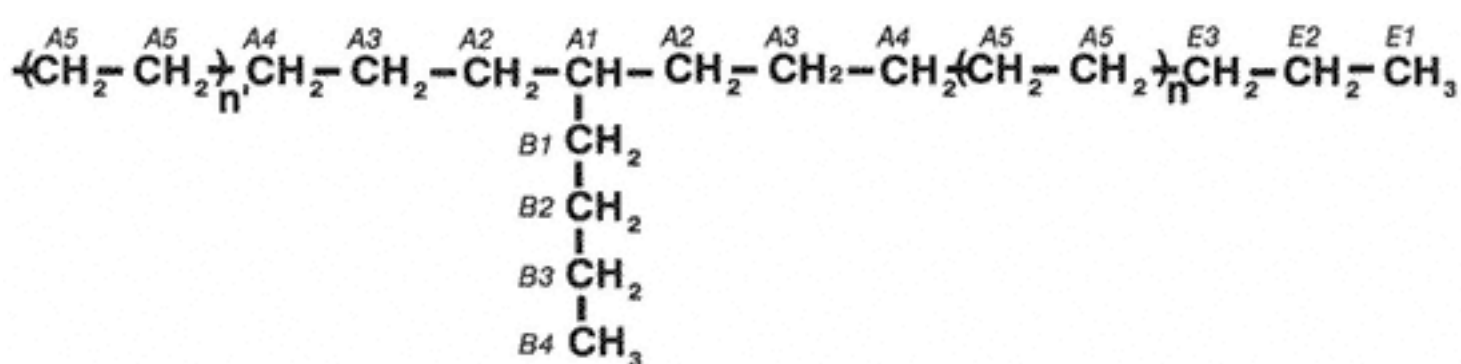
II-A-17—

Poly(Ethylene-Co-1-Hexene) [0.1% H]

Comments

The polymer-chain structure is primarily linear, with pendant butyl branches created by incorporation of 1-hexene into the backbone. Because of the extremely low 1-hexene level, the peaks from the chain ends are approximately the same intensity as those of the butyl branches. This copolymer is produced by an organometallic-catalyzed, low-pressure process similar to that used for HDPE {II-A-1}. The density of these low-hexene copolymers is $> 0.94 \text{ g/cm}^3$, and their principal uses are for films and bottles. This particular material melts at $\sim 135^\circ\text{C}$; the melting point of these copolymers decreases as the 1-hexene content increases.





Code	Shift (ppm)
A1	38.2
A2	34.6
A3	27.3
A4	30.5
A5	30.0
B1	34.2
B2	29.4
B3	23.4
B4	14.5
E1	14.5
E2	22.9
E3	32.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

Reference

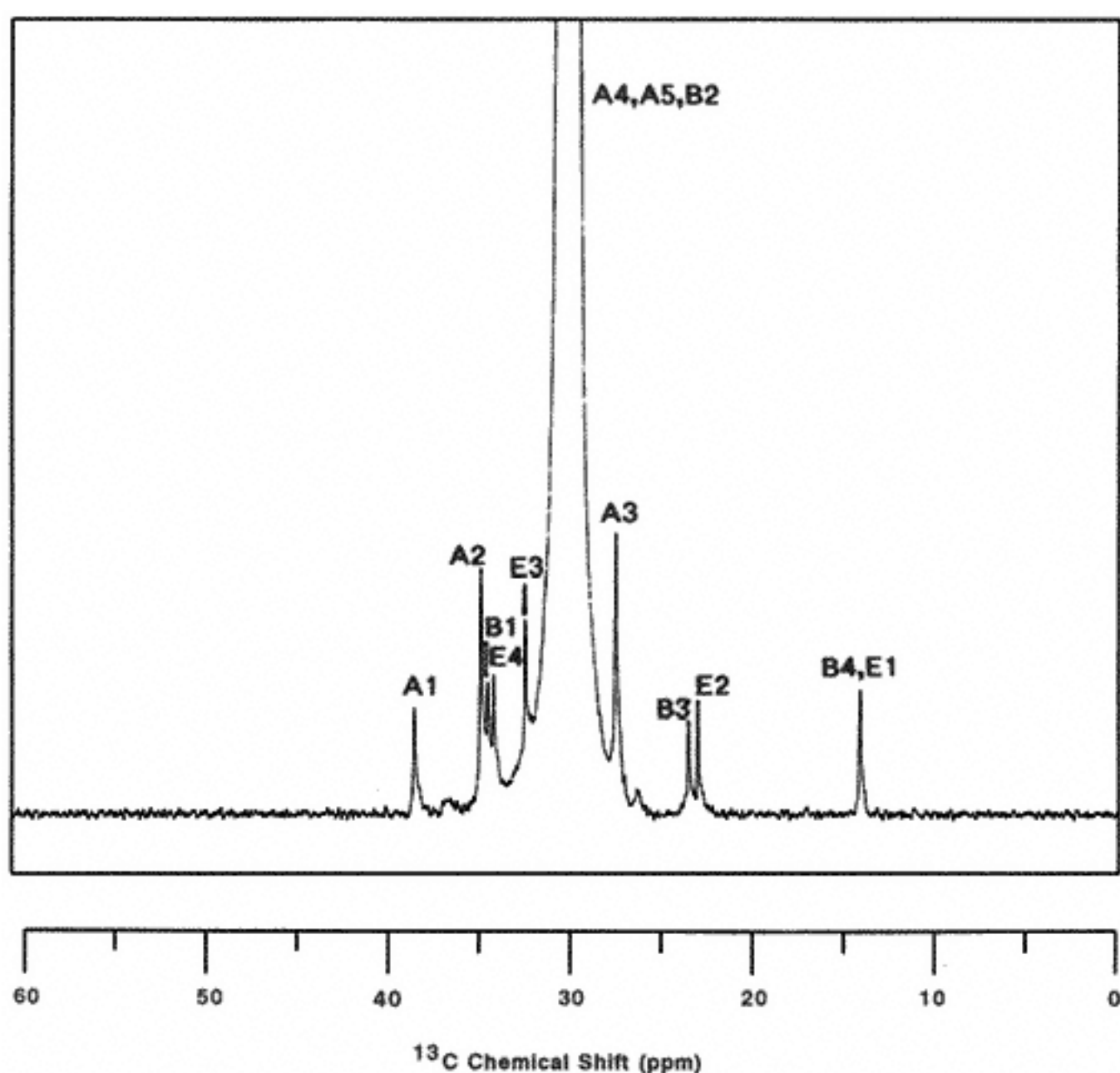
E. T. Hsieh and J. C. Randall. *Macromolecules* 15:1402, 1982.

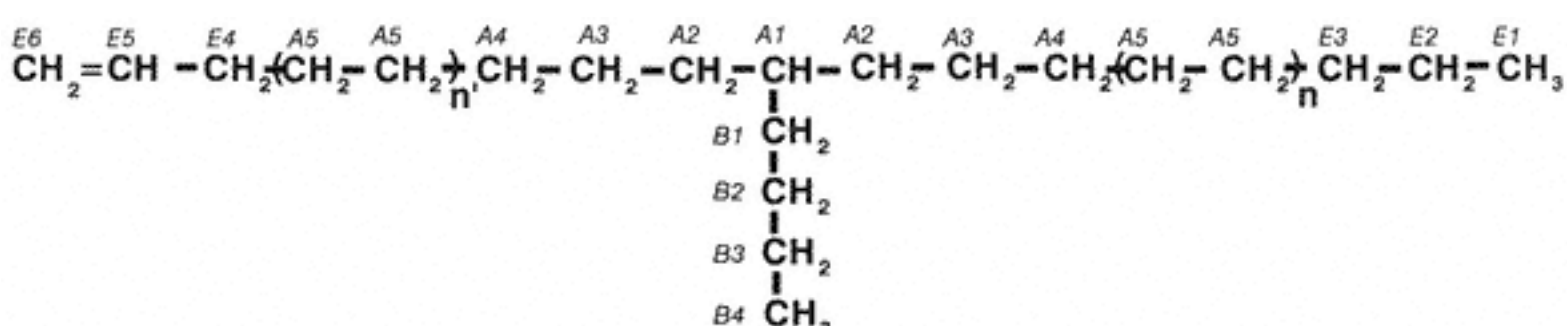
II-A-18—

Poly(Ethylene-Co-1-Hexene) [0.1% H], Cr-Catalyzed

Comments

The polymer-chain structure is primarily linear, with pendant butyl branches created by incorporation of 1-hexene into the backbone. Because of the extremely low 1-hexene content, the peaks of the saturated and unsaturated chain ends are approximately the same intensity as those of the butyl branches. This copolymer is produced in a chromium oxide-catalyzed low-pressure process, similar to that used for HDPE {II-A-1}, which results in polymer chains with one alkyl, and one vinyl, end group. Ethylene-1-butene copolymers can also be produced by these catalytic systems. The density of these low-hexene copolymers is $> 0.94 \text{ g/cm}^3$, and their principal uses are for films and bottles. This particular material melts at $\sim 135^\circ\text{C}$; the melting point of these copolymers decreases as the 1-hexene content increases.





Code	Shift (ppm)
A1	38.2
A2	34.6
A3	27.3
A4	30.5
A5	30.0
B1	34.2
B2	29.4
B3	23.4
B4	14.5
E1	14.5
E2	22.9
E3	32.2
E4	33.8
E5	138.9
E6	114.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

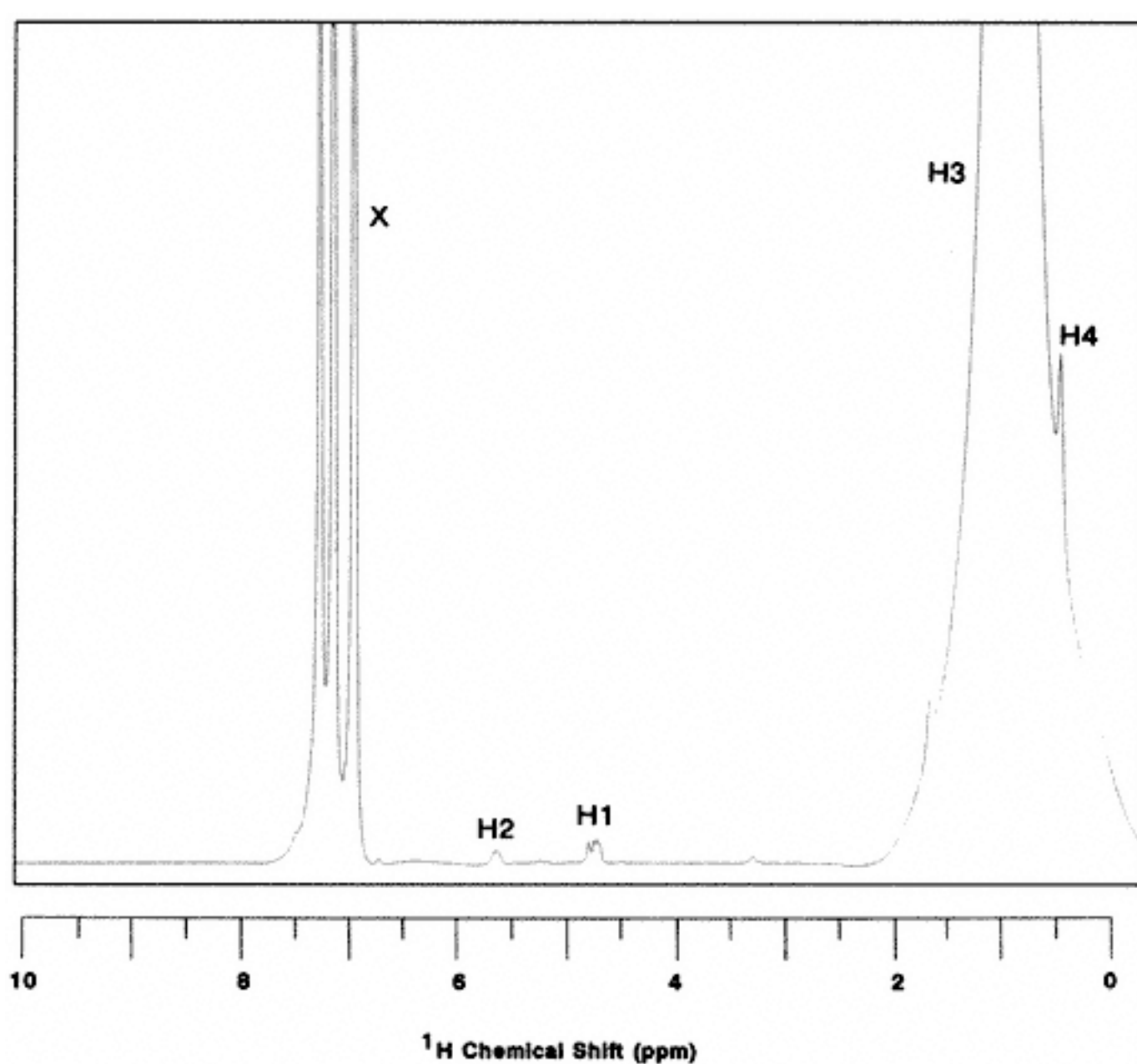
Reference

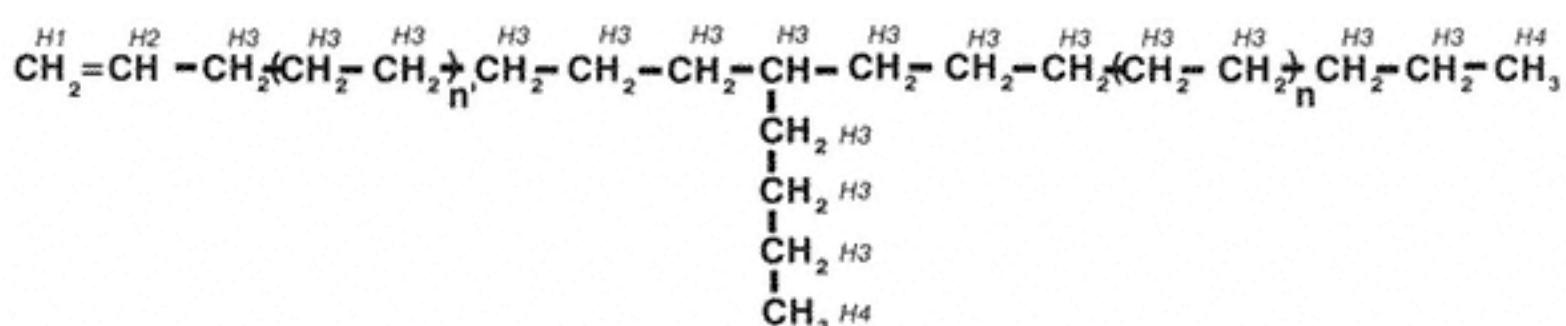
E. T. Hsieh and J. C. Randall. *Macromolecules* 15:1402, 1982.

II-A-18H—
Poly(Ethylene-Co-1-Hexene) [0.1% H], Cr-Catalyzed

Comments

The polymer-chain structure is primarily linear, with pendant butyl branches created by incorporation of 1-hexene into the backbone. Because of the extremely low 1-hexene content, the peaks from the saturated and unsaturated chain ends are approximately the same intensity as those of the butyl branches. Solvent resonances are marked by **X**. This copolymer is produced in a chromium oxide-catalyzed, low-pressure process, similar to that used for HDPE {II-A-1}, which results in polymer chains with one alkyl, and one vinyl, end group. Ethylene-1-butene copolymers can also be produced by these catalytic systems. The density of these low-hexene copolymers is $> 0.94 \text{ g/cm}^3$, and their principal uses are for films and bottles. This particular material melts at $\sim 135^\circ\text{C}$; the melting point of these copolymers decreases as the 1-hexene content increases.





Code	Shift (ppm)
H1	4.87
H2	5.73
H3	1.27
H4	0.86

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 100

Spectral width: 8 kHz

Data points: 4096

Pulse width: 30°

Broadening: 3 Hz

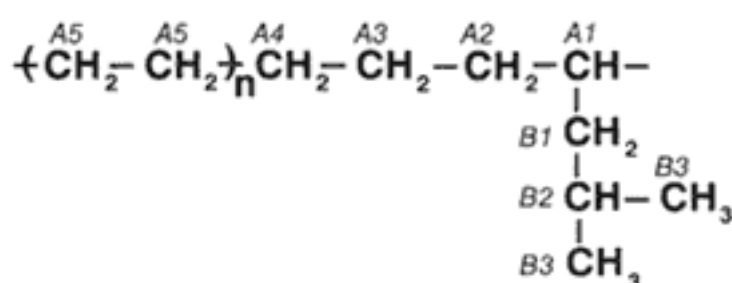
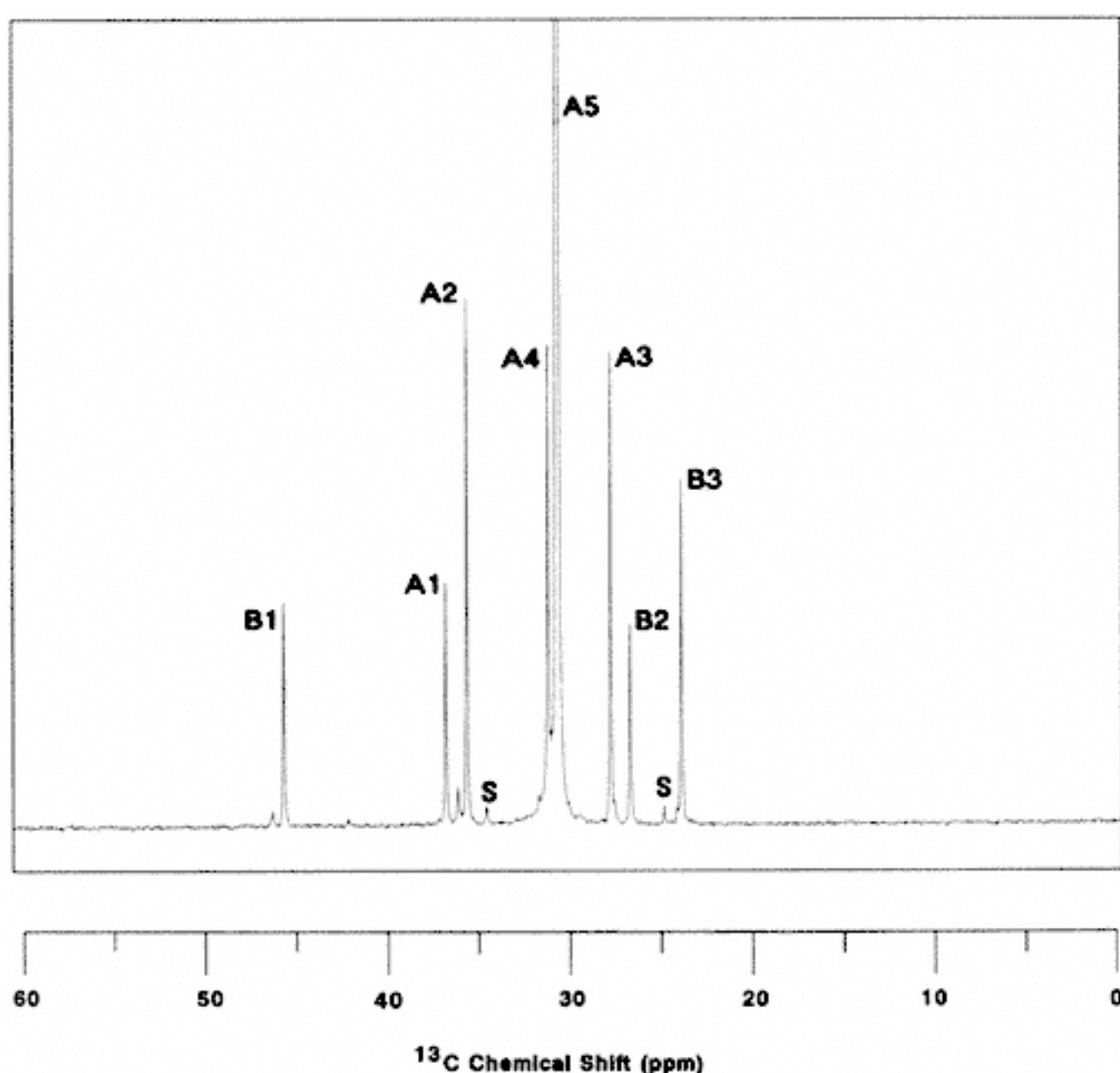
Pulse delay: 5 s

II-A-19—

Poly(Ethylene-Co-4-Methyl-1-Pentene)

Comments

The polymer-chain structure is primarily linear, with pendant isobutyl branches created by incorporation of 4-methyl-1-pentene into the backbone. Because of the relatively low 4-methyl-1-pentene content, these isobutyl branches are mostly isolated. Resonances caused by comonomer sequences, marked by **S**, increase in intensity with 4-methyl-1-pentene content. Poly(ethylene-co-4-methyl-1-pentene) is one of the materials known as linear, low-density polyethylene (LLDPE), which are produced by an organometallic-catalyzed, low-pressure process similar to that used for HDPE {II-A-1}. These copolymers typically contains 1–10% 4-methyl-1-pentene; their density ranges from 0.91 to 0.93 g/cm³. They are used in film, bag, and liner applications. This particular material melts at ~125°C; the melting point of these copolymers increases as the 4-methyl-1-pentene content decreases.



Code	Shift (ppm)
A1	36.1
A2	34.8
A3	27.2
A4	30.6
A5	30.0
B1	44.9
B2	26.0
B3	23.2

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

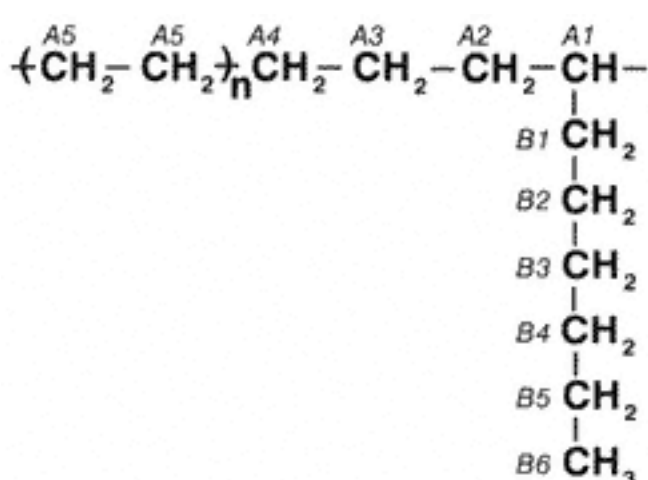
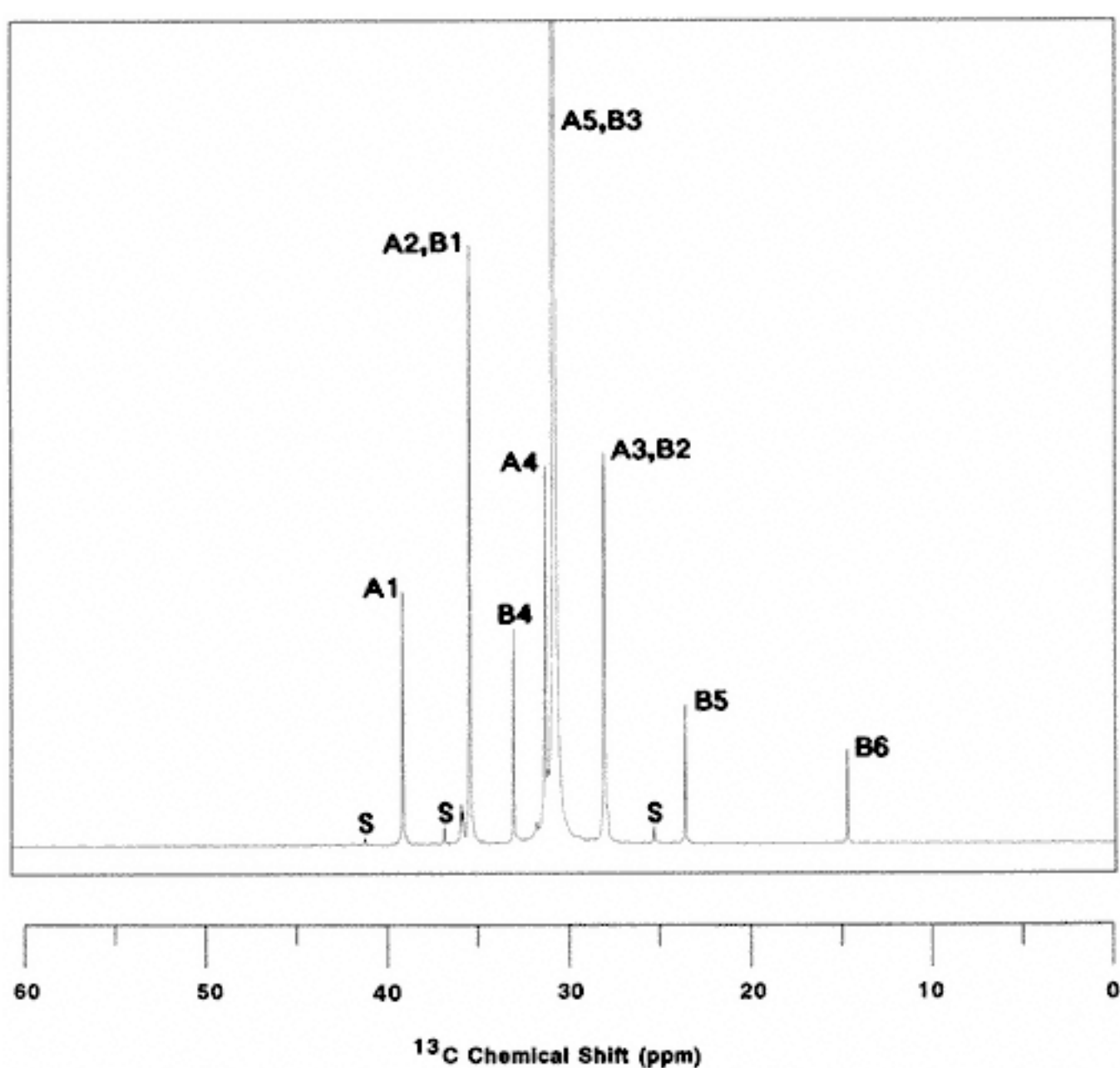
Pulse delay: 2 s

ReferenceK. Kimura, S. Yuasa, and Y. Maru. *Polymer* 25:441, 1984.

**II-A-20—
Poly(Ethylene-Co-1-Octene)**

Comments

The polymer-chain structure is primarily linear, with pendant *n*-hexyl branches created by incorporation of 1-octene into the backbone. Because of the relatively low 1-octene level, these *n*-hexyl branches are mostly isolated. Resonances due to comonomer sequences, marked by **S**, increase in intensity with octene content. Poly(ethylene-co-1-octene) is one of the materials known as linear, low-density polyethylene (LLDPE), which are produced by an organometallic-catalyzed, low-pressure process similar to that used for HDPE {II-A-1}. These copolymers typically contains 1–10% 1-octene; their density ranges from 0.91 to 0.93 g/cm³. They are used in film, bag, and liner applications. This particular material melts at ~125°C; the melting point of these copolymers increases as the 1-octene content decreases.



Code	Shift (ppm)
A1	38.2
A2	34.6
A3	27.4
A4	30.5
A5	30.0
B1	34.7
B2	27.4
B3	30.0
B4	32.3
B5	22.9
B6	14.1

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2s

References

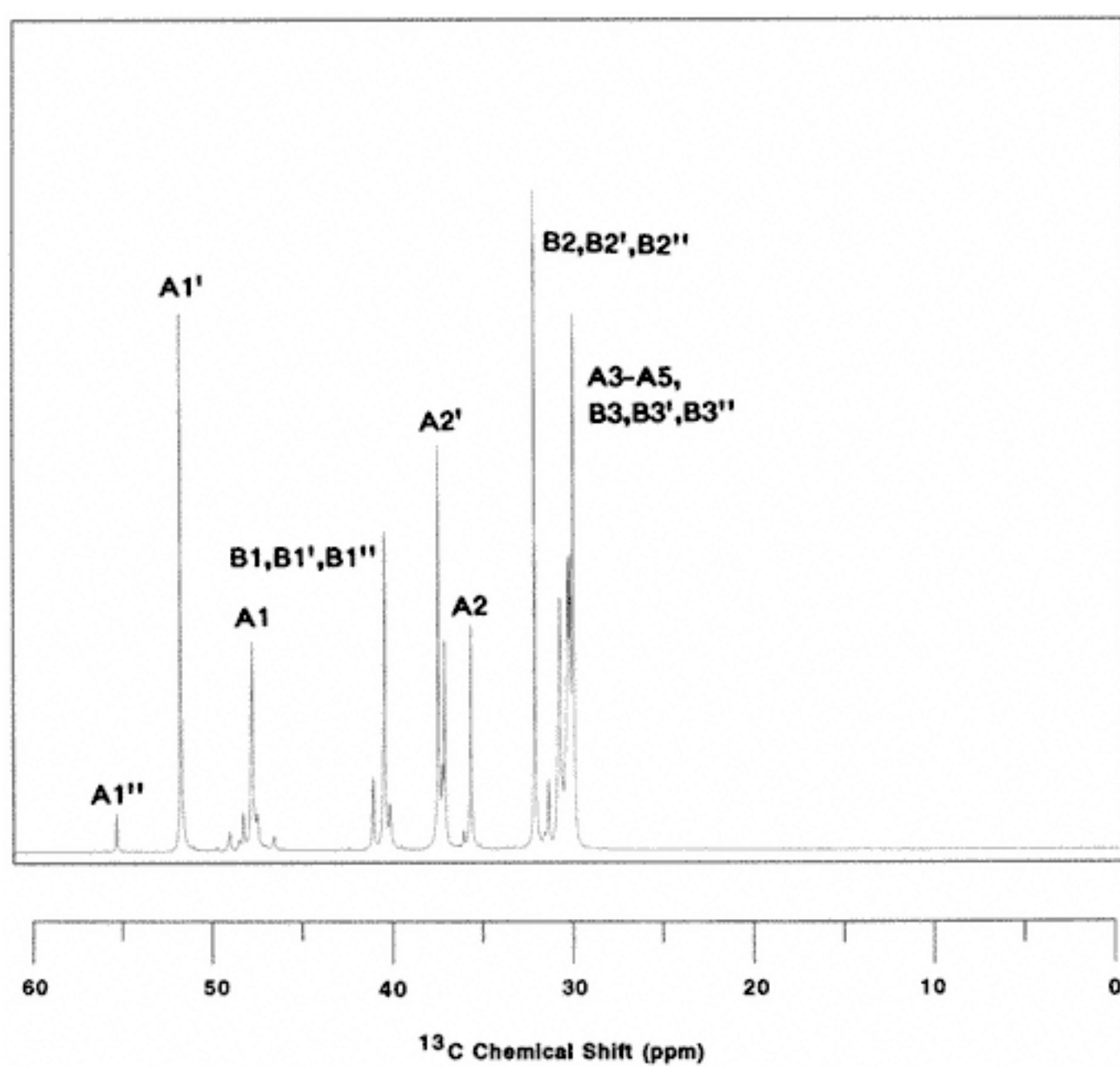
K. Kimura, S. Yuasa, and Y. Maru. *Polymer* 25:441, 1984; H. N. Cheng. *Polym. Commun.* 25:99, 1984.

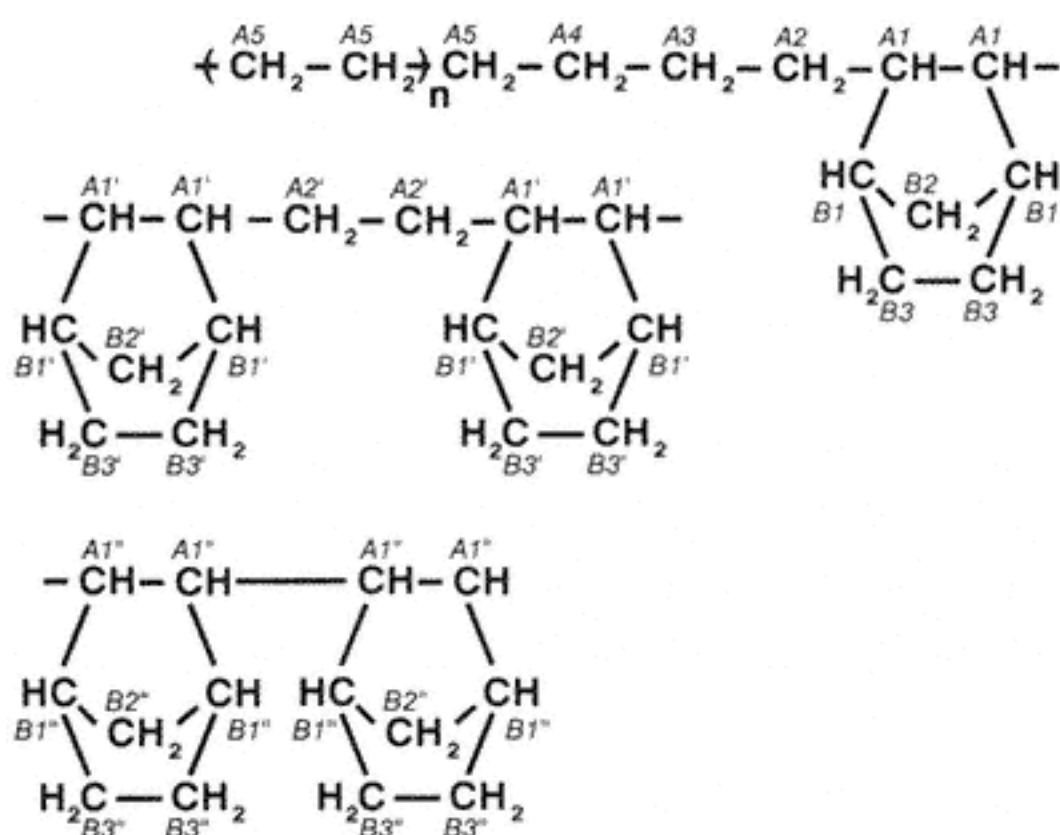
II-A-21—

Poly(Ethylene-Co-Norbornene)

Comments

Also known as cyclic olefin copolymer (COC). The norbornene ring conformations are predominantly *exo*. Because of the relatively high norbornene (N) to ethylene (E) ratio in this material, resonances due to NEN and NN sequences are pronounced. COC exhibits excellent barrier properties.





Code	Shift (ppm)
A1	50.9
A1'	47.0
A1''	54.4
A2	35.2
A2'	37.0
A3	29.7
A4	29.7
A5	29.7
B1	39.9
B1'	39.9
B1''	39.9
B2	31.8
B2'	31.8
B2''	31.8
B3	29.9–31.0
B3'	29.9–31.0
B3''	29.9–31.0

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 2000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2s

Reference

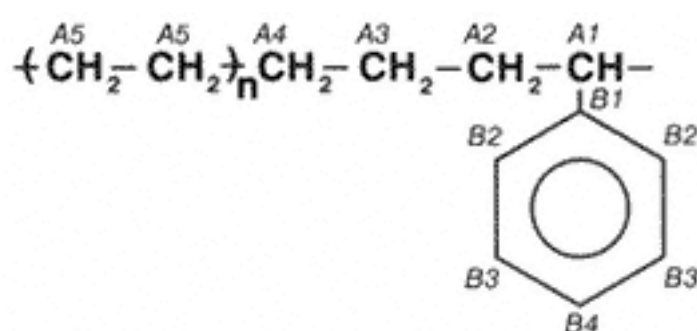
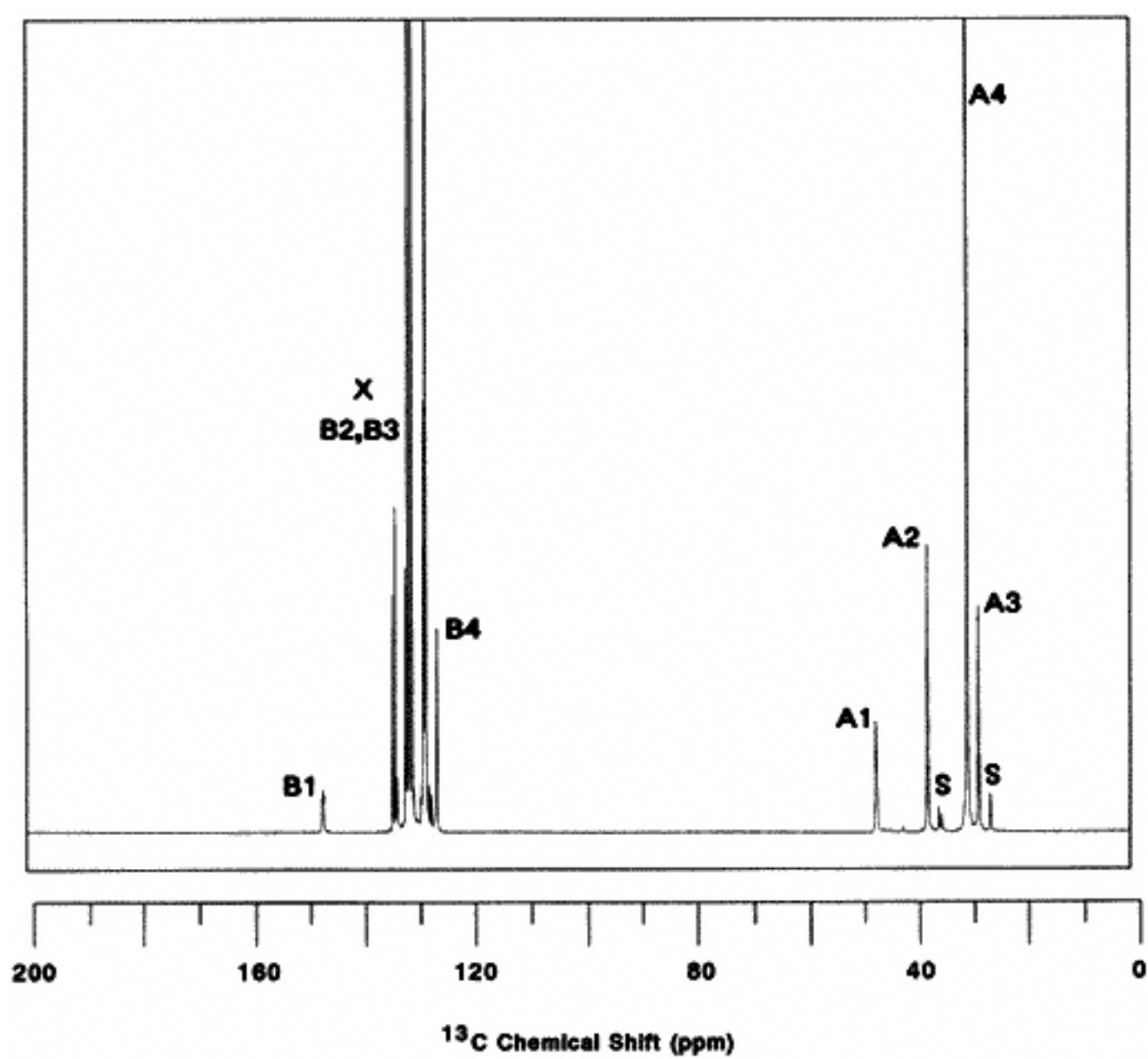
C. H. Bergstrom, B. R. Sperlich, J. Ruotoisenmaki, and J. V. Seppala. *J. Polym. Sci. A Polym. Chem.* 36:1633, 1998.

II-A-22—

Poly(Ethylene-Co-Styrene)

Comments

Random (not blocky) copolymer of ethylene and styrene. Resonances caused by comonomer sequences are marked by S, solvent peaks by X.



Code	Shift (ppm)
A1	45.9
A2	36.0
A3	27.6
A4	29.7
A5	30.0
B1	146.7
B2	133.9
B3	133.4
B4	125.8

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2s

ReferenceP. Longo, A. Grassi, and L. Oliva. *Makromol. Chem.* 191:2387, 1990.**Source**

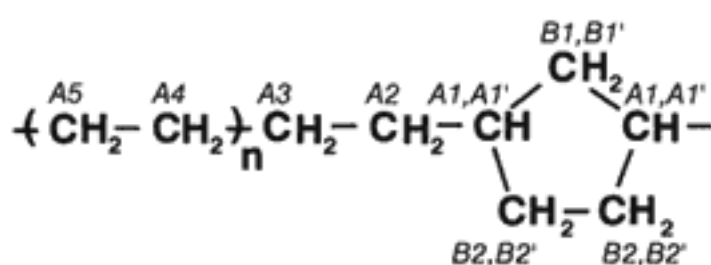
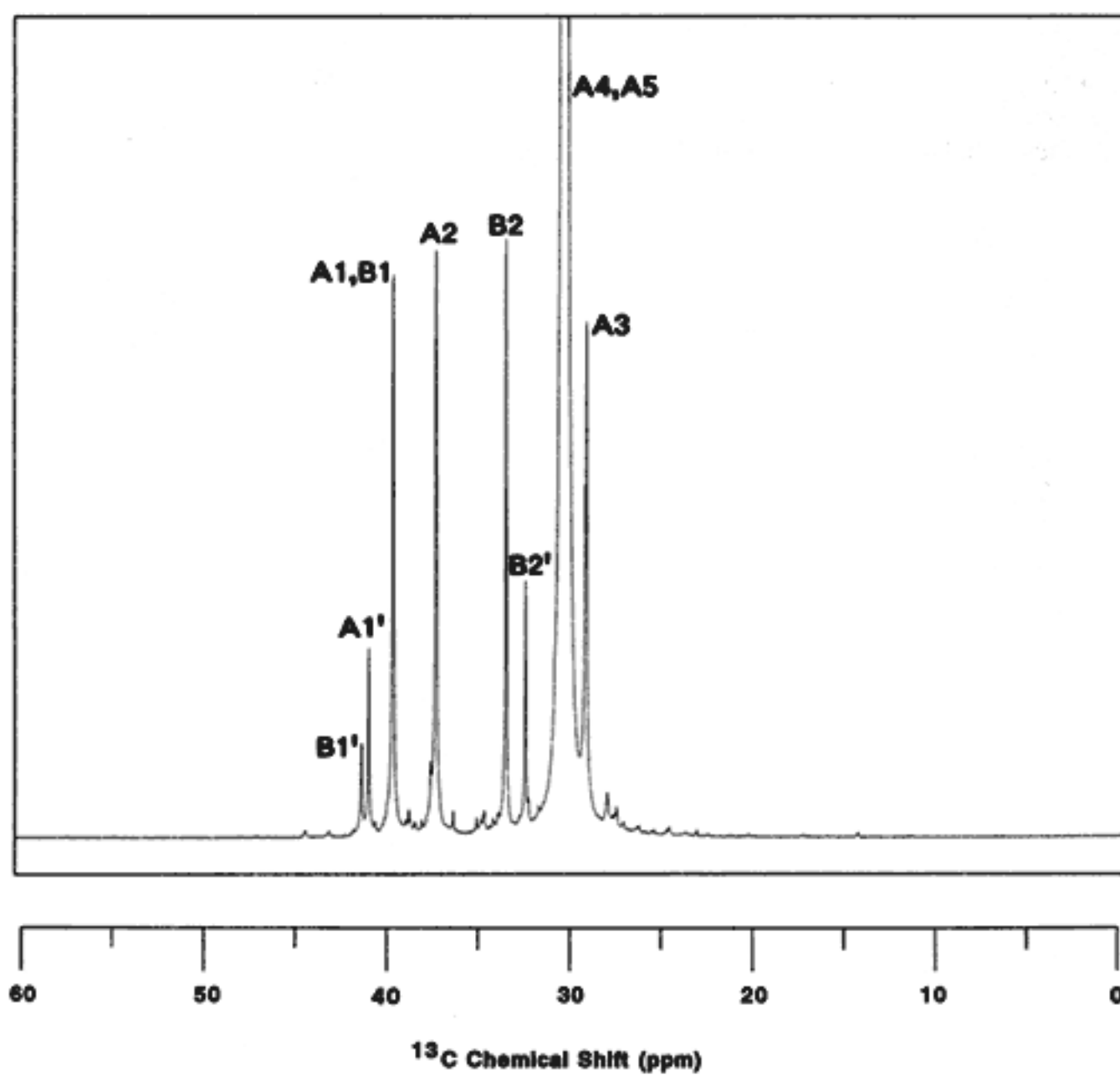
Prof. A. Zambelli, Université di Salerno, Salerno, Italy.

II-A-23—

Poly(Ethylene-Co-1,5-Hexadiene)

Comments

During polymerization, the 1,5-hexadiene comonomer cyclizes. These rings exhibit both *cis*- and *trans*-forms. This material is not currently available commercially.



Code	Shift (ppm)
A1 <i>cis</i>	39.8
A1' <i>trans</i>	41.2
A2	37.5
A3	29.3
A4	30.0
A5	30.0
B1 <i>cis</i>	39.8
B1' <i>trans</i>	41.6
B2 <i>cis</i>	33.8
B2' <i>trans</i>	32.7

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

Source

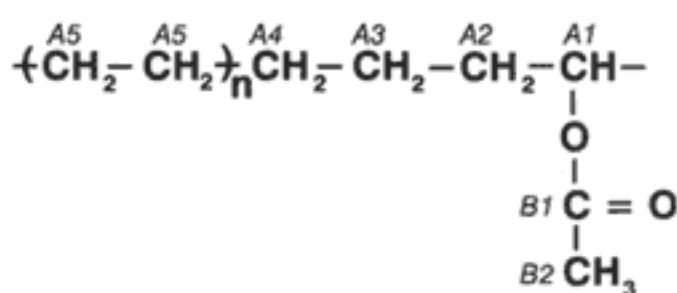
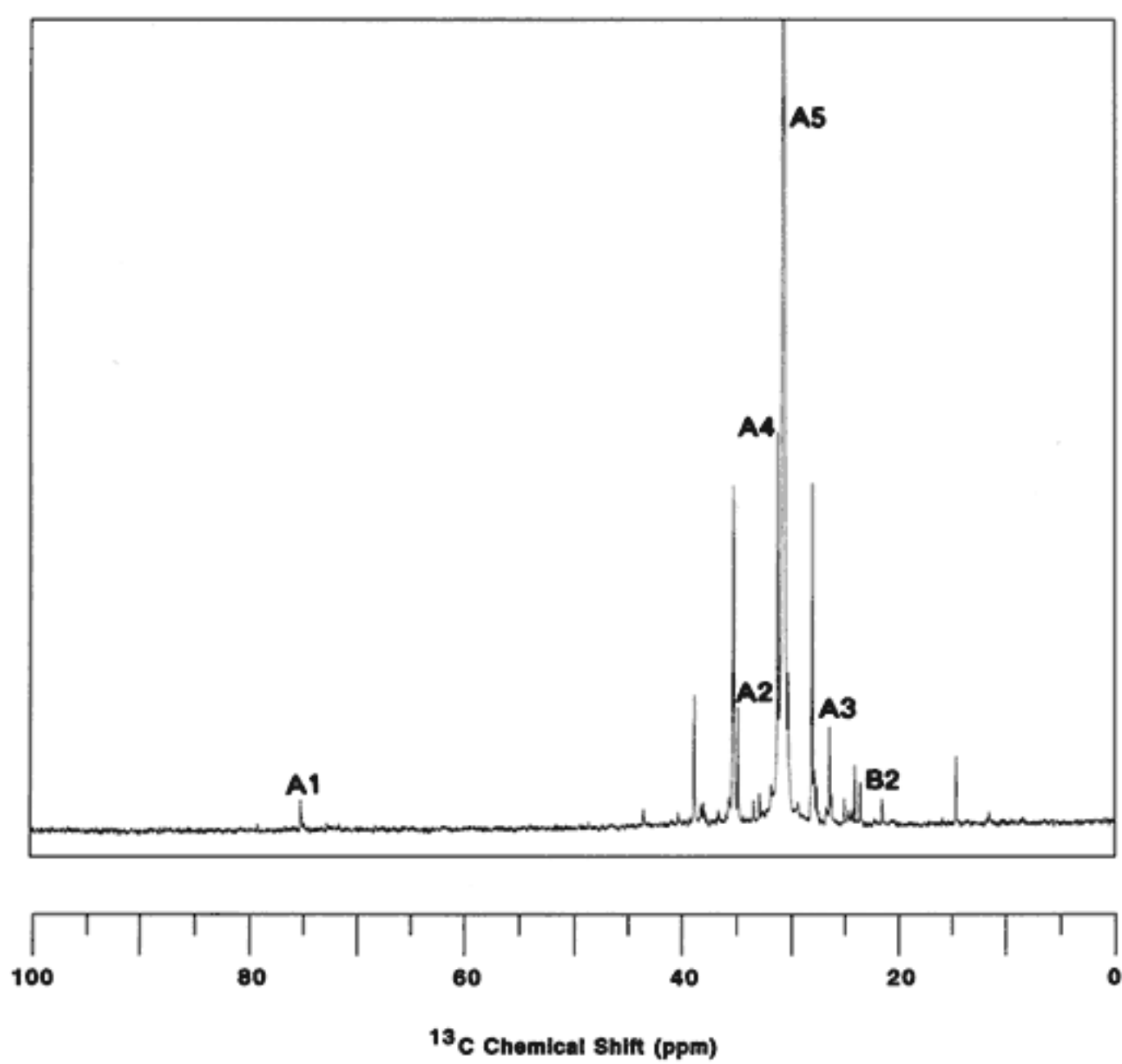
M. J. Krause, Mobil Chemical Company, Edison, NJ.

II-A-24—

Poly(Ethylene-Co-Vinyl Acetate) [~3% VA] (EVA)

Comments

Distinctive resonances arising from incorporation of vinyl acetate are listed below. Because this material is produced by a low-pressure, free-radical process, it also exhibits an alkyl-branching pattern similar to that of LDPE (II-A-3); refer to this entry for detailed assignments. EVA is a soft, flexible material with excellent clarity and heat-seal characteristics; it is used primarily in film and bag applications where these properties are important. EVA melts between 95 and 115°C; the melting point of these copolymers increases as the vinyl acetate content decreases.



Code	Shift (ppm)
A1	74.6
A2	33.7
A3	25.7
A4	30.0
A5	30.0
B1	169.4
B2	20.8

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

References

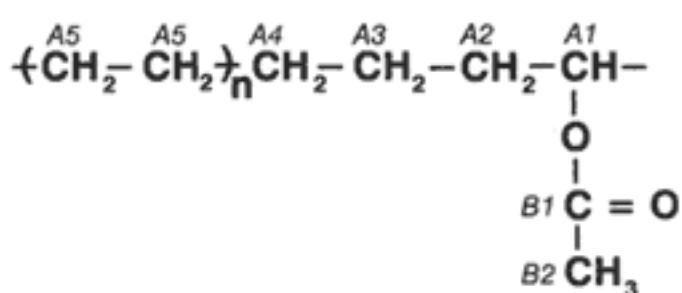
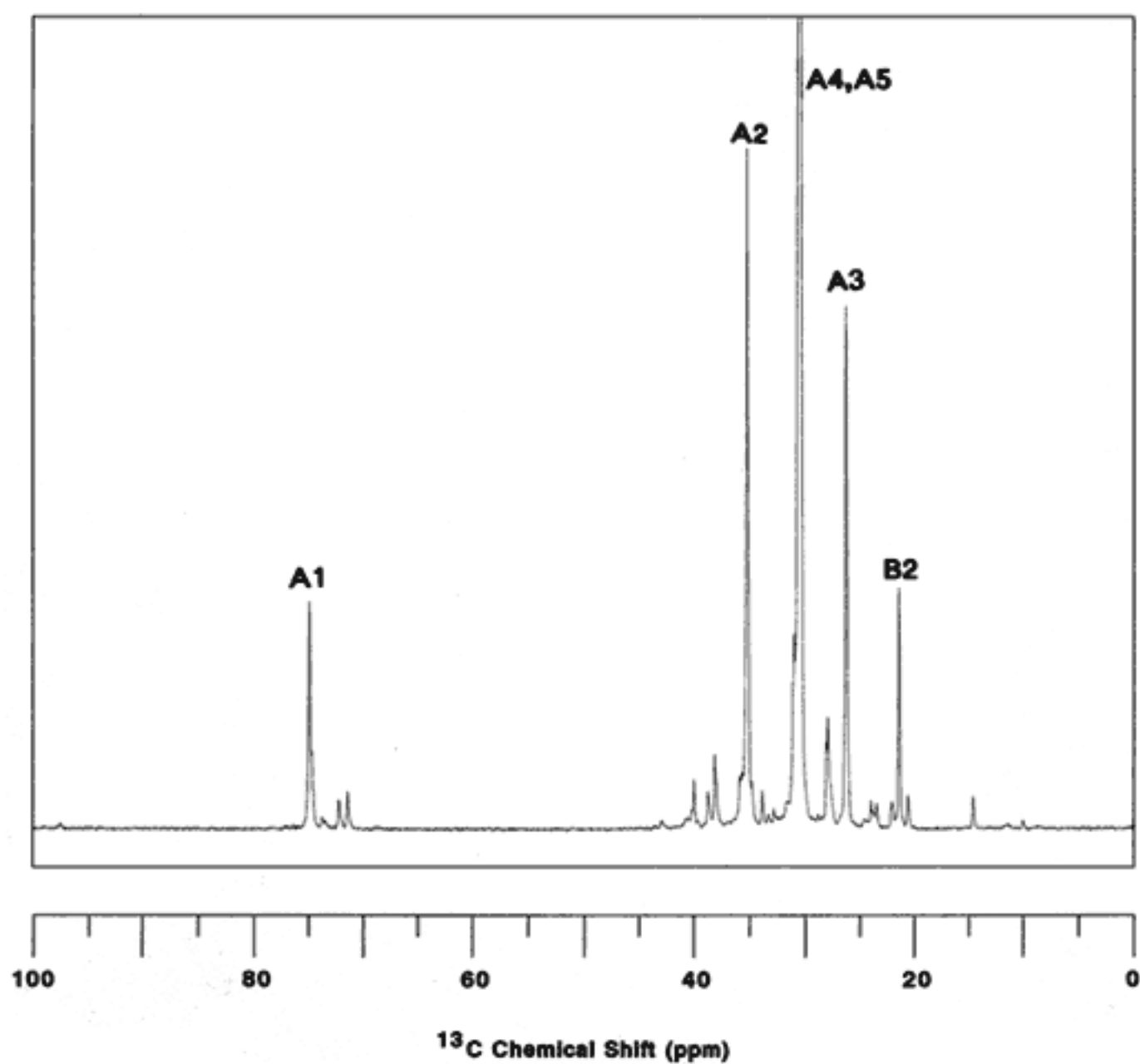
H. N Cheng and G. H. Lee. *Polym. Bull.* 19:89 (1988); H. N. Cheng and G. H. Lee. *Macromolecules* 21:3164, 1988; H. N. Sung and J. H. Noggle. *J. Polym. Sci. Polym. Phys. Ed.* 19:1493, 1981.

II-A-25—

Poly(Ethylene-Co-Vinyl Acetate) [~25% VA] (EVA)

Comments

Distinctive resonances arising from incorporation of vinyl acetate are listed below. Because this material is produced by a low-pressure, free-radical process, it also exhibits an alkyl-branching pattern similar to that of LDPE {II-A-3}; refer to this entry for detailed assignments. EVA is a soft, flexible material with excellent clarity and heat-seal characteristics; it is used primarily in film and bag applications where these properties are important. Higher levels of VA lead to lower melting points and more elastomeric characteristics. EVA melts between 95 and 115°C; the melting point of these copolymers increases as the vinyl acetate content decreases.



Code	Shift (ppm)
A1	7.6
A2	33.7
A3	25.7
A4	30.0
A5	30.0
B1	169.4
B2	20.8

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

References

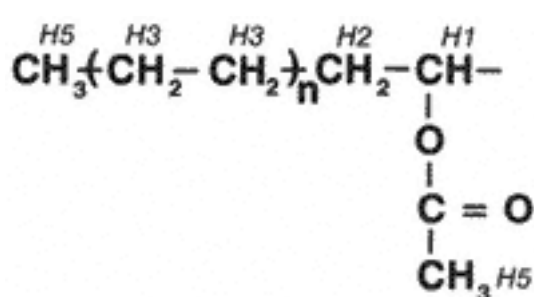
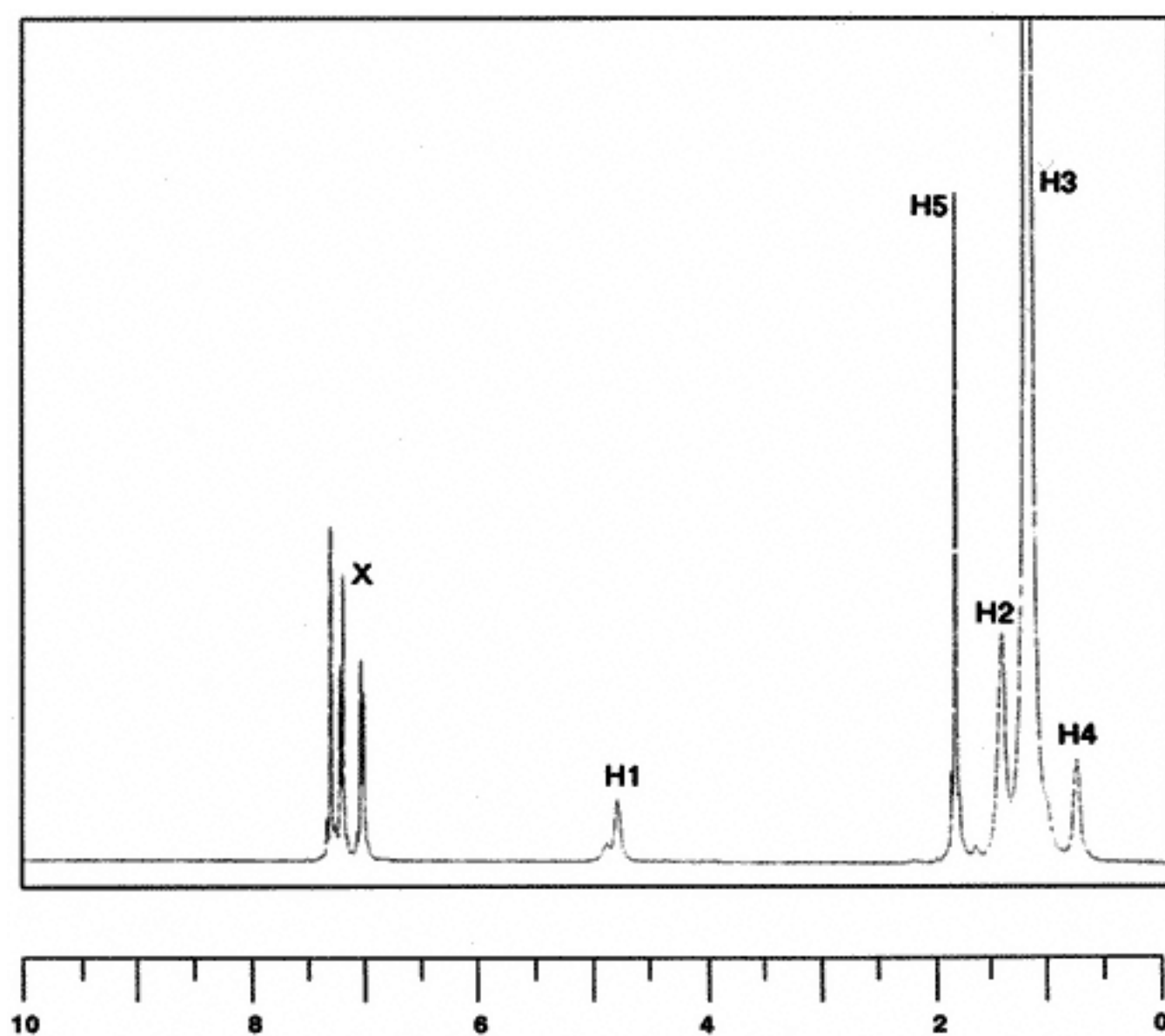
H.N. Cheng and G. H. Lee. *Polym. Bull.* 19:89, 1988; H. N. Cheng and G. H. Lee. *Macromolecules* 21:3164, 1988; H. N. Sung and J. H. Noggle. *J. Polym. Sci. Polym. Phys. Ed.* 19:1493, 1981.

II-A-25H—

Poly(Ethylene-Co-Vinyl Acetate) [25% VA]

Comments

A distinct resonance arising from incorporation of vinyl acetate appears at 4.8 ppm; this peak can readily be used to quantify the material's VA content. Solvent resonances are marked by X. EVA is a soft, flexible material with excellent clarity and heat-seal characteristics; it is used primarily in film and bag applications where these properties are important. Higher levels of VA lead to lower melting points and more elastomeric characteristics. EVA melts between 95 and 115°C; the melting point of these copolymers increases as the vinyl acetate content decreases.



Code	Shift (ppm)
H1	4.83
H2	1.50
H3	1.29
H4	0.85
H5	1.90

Experimental ParametersNucleus: ^1H (400 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 100

Spectral width: 8 kHz

Data points: 4096

Pulse width: 30°

Broadening: 3 Hz

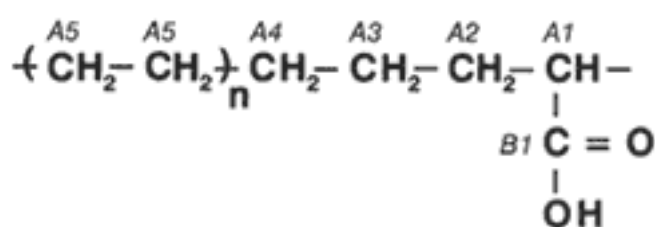
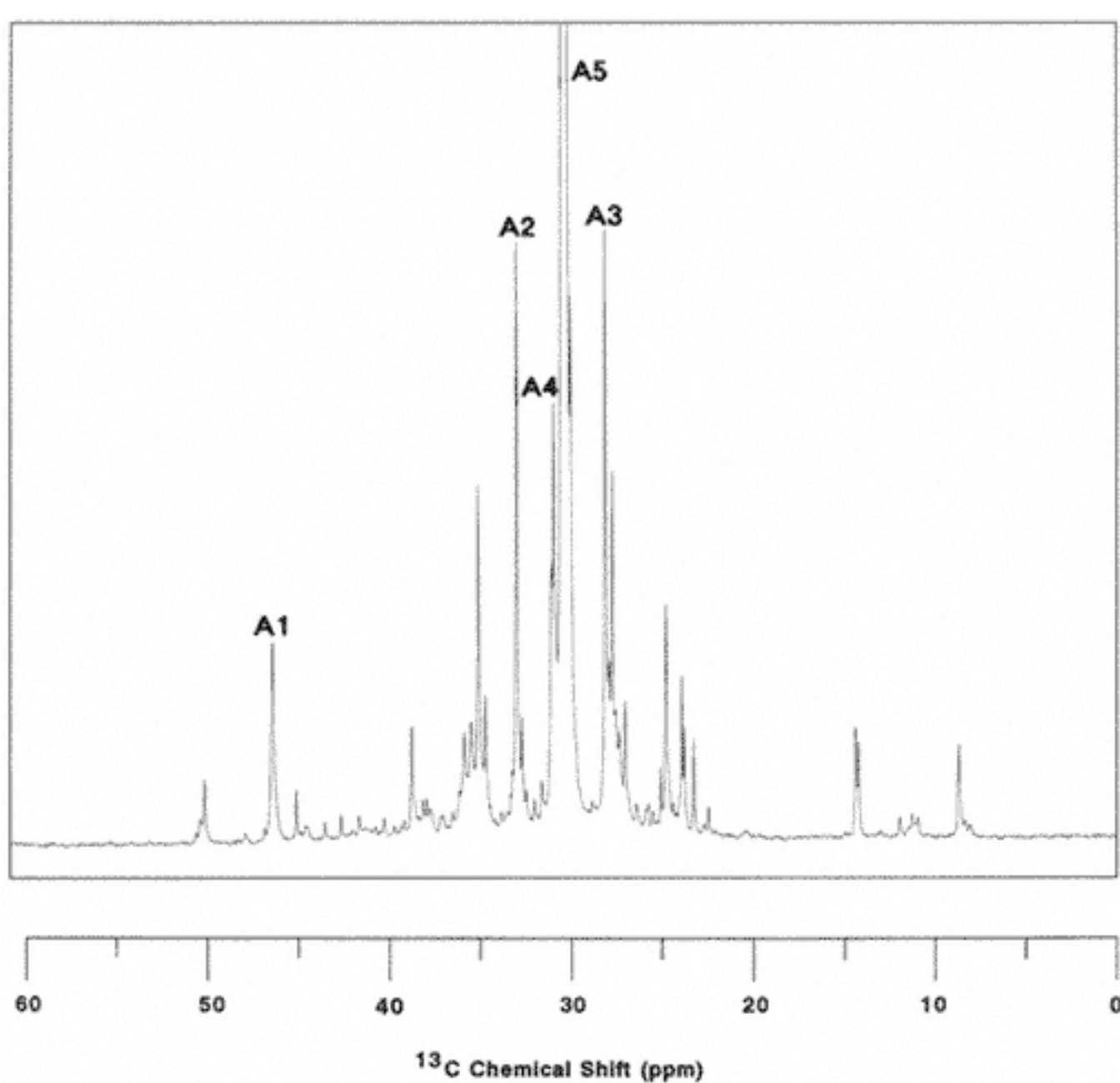
Pulse delay: 5 s

II-A-26—

Poly(Ethylene-Co-Acrylic Acid) [5% AA] (EAA)

Comments

Distinctive resonances arising from incorporation of acrylic acid are listed. Because this material is produced by a low-pressure, free-radical process, it also exhibits an alkyl-branching pattern similar to that of LDPE {II-A-3}; refer to this entry for detailed assignments. EAA is commonly found as a component layer in laminated films; it improves adhesion to metals. EAA melts between 95 and 115°C; the melting point of these copolymers increases as the acrylic acid content decreases.



Code	Shift (ppm)
A1	45.6
A2	32.5
A3	29.5
A4	30.6
A5	30.0
B1	180.1

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

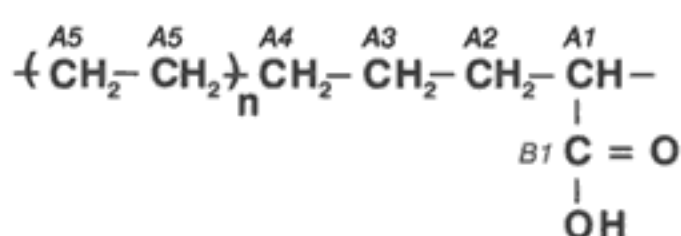
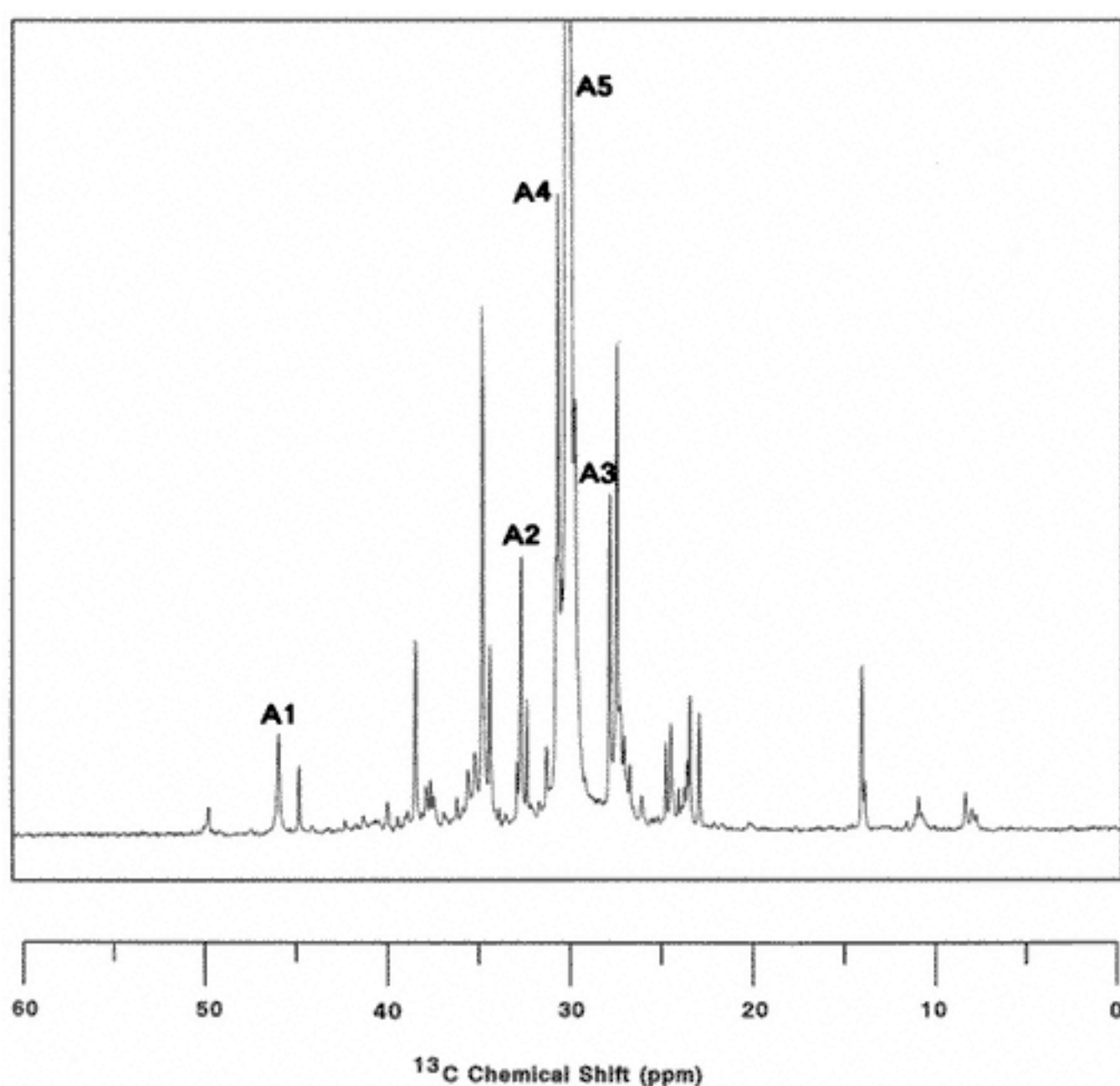
Pulse delay: 2 s

II-A-27—

Poly(Ethylene-Co-Acrylic Acid) [15% AA] (EAA)

Comments

Distinctive resonances arising from incorporation of acrylic acid are listed. Because this material is produced by a low-pressure, free-radical process, it also exhibits an alkyl-branching pattern similar to that of LDPE {II-A-3}; refer to this entry for detailed assignments. EAA is commonly found as a component layer in laminated films; it improves adhesion to metals. EAA melts between 95 and 115°C; the melting point of these copolymers increases as the acrylic acid content decreases.



Code	Shift (ppm)
A1	45.6
A2	32.5
A3	29.5
A4	30.6
A5	30.0
B1	180.1

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

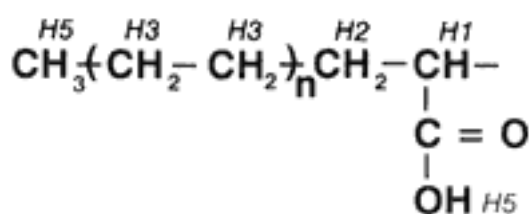
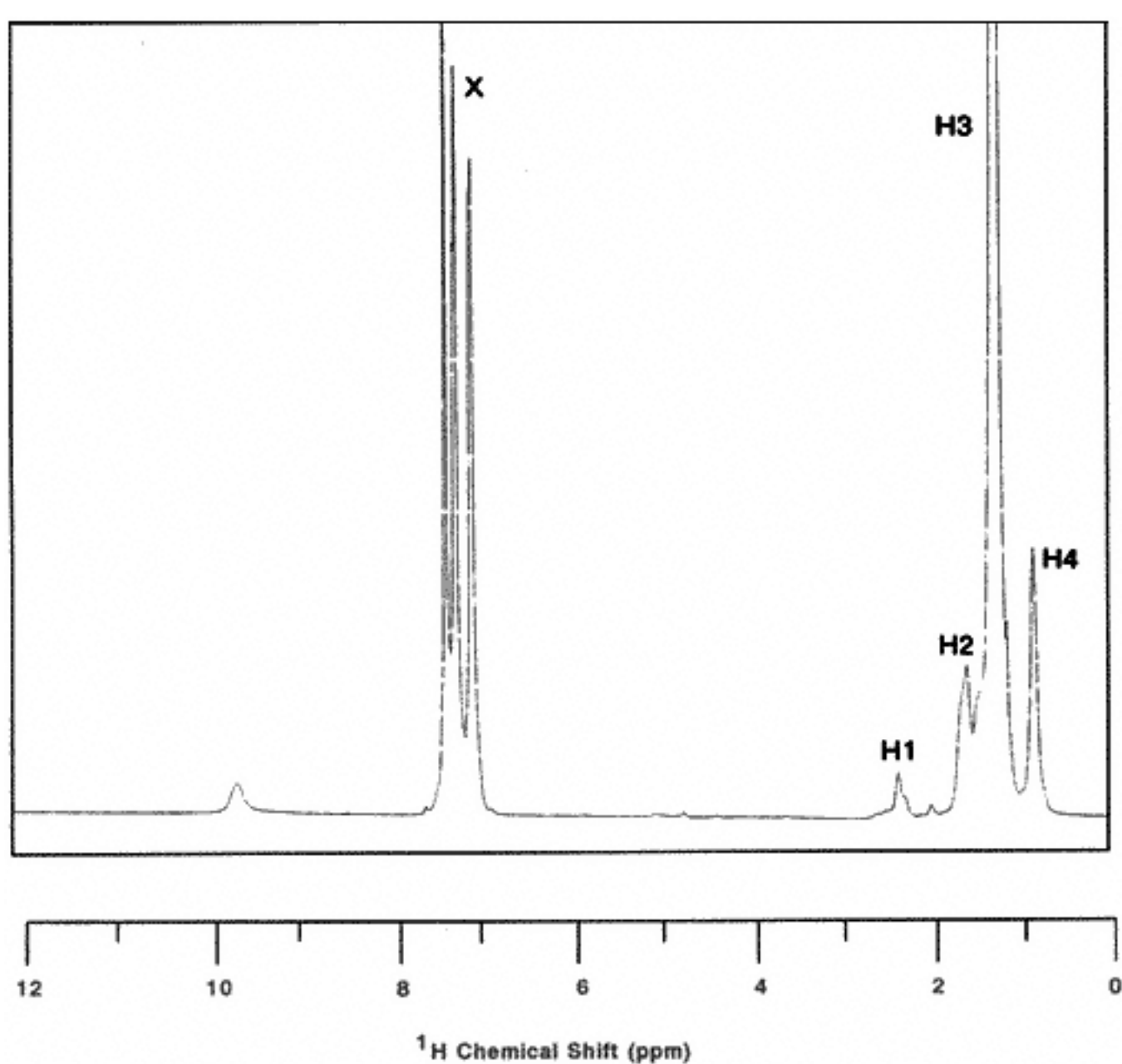
Pulse delay: 2 s

II-A-27H—

Poly(Ethylene-Co-Acrylic Acid) [15% AA] (EAA)

Comments

A distinctive resonance arising from incorporation of acrylic acid appears at 9.6 ppm; this peak can easily be used to quantify the AA content. Solvent resonances are marked by **X**. EAA is commonly found as a component layer in laminated films; it improves adhesion to metals. It melts between 95 and 115°C; the melting point of these copolymers increases as the acrylic acid content decreases.



Code	Shift (ppm)
H1	2.38
H2	1.62
H3	1.27
H4	0.89
H5	9.55

*Experimental Parameters*Nucleus: ^1H (400 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 100

Spectral width: 8 kHz

Data points: 4096

Pulse width: 30°

Broadening: 3 Hz

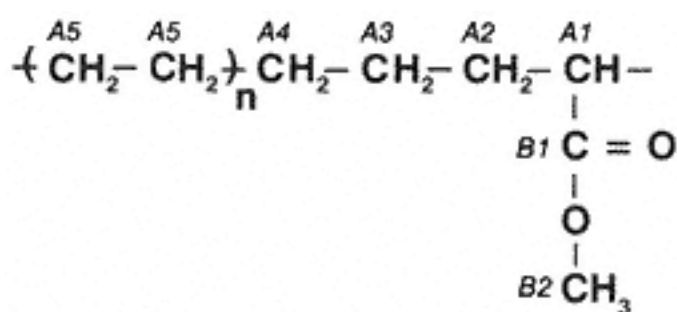
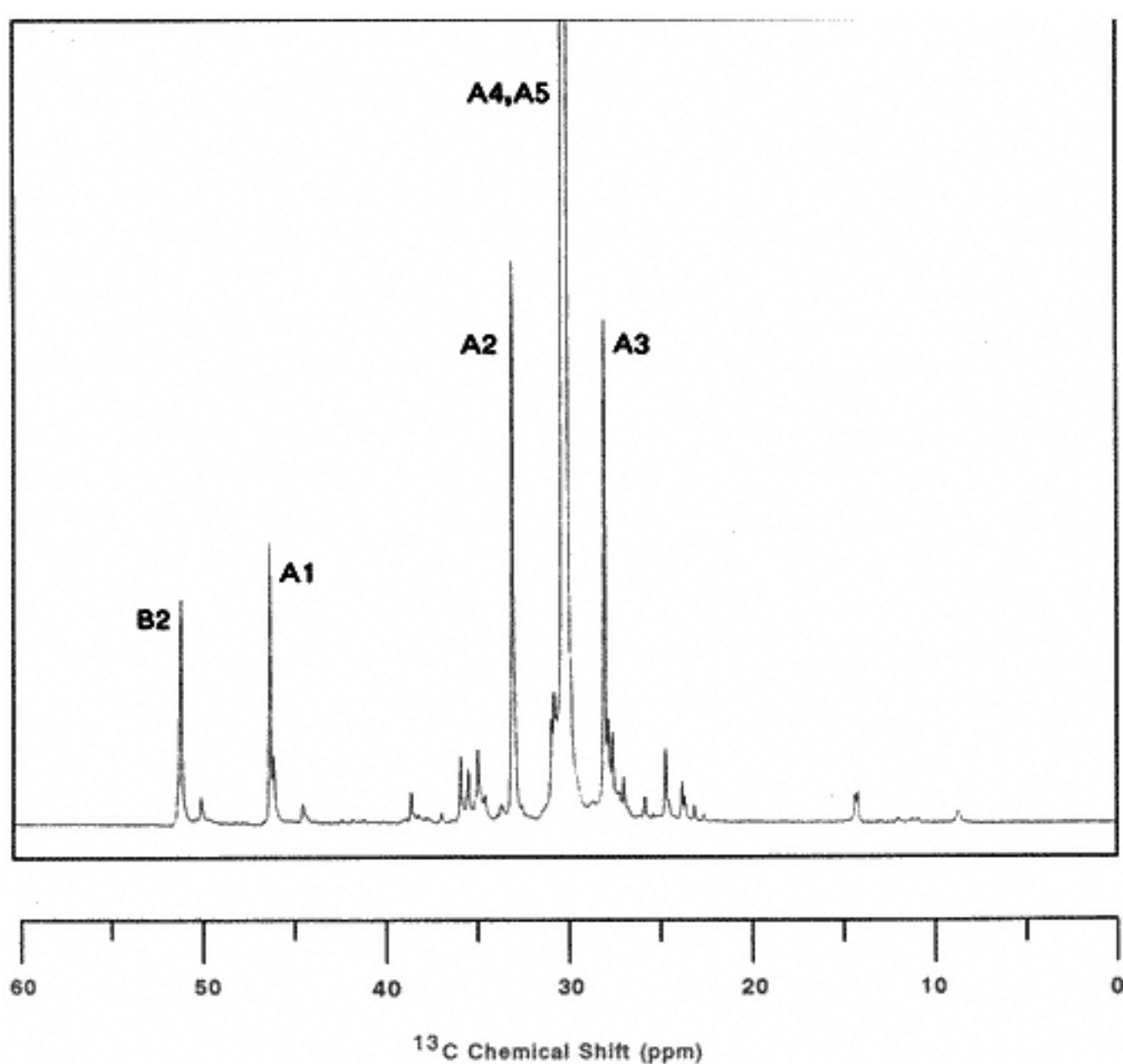
Pulse delay: 5 s

II-A-28—

Poly(Ethylene-Co-Methyl Acrylate) (EMA)

Comments

Distinctive resonances arising from incorporation of methyl acrylate are listed. Because this material is produced by a low-pressure, free-radical process, it also exhibits an alkyl-branching pattern similar to that of LDPE {II-A-3}; refer to this entry for detailed assignments. EMA is used for medical packaging and to manufacture gloves. When blended with polyethylene, it improves impact resistance, heat-seal characteristics, and toughness. It melts between 95 and 115°C; the melting point of these copolymers increases as the methyl acrylate content decreases.



Code	Shift (ppm)
A1	46.1
A2	32.9
A3	27.8
A4	30.0
A5	30.0
B1	175.9
B2	50.9

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

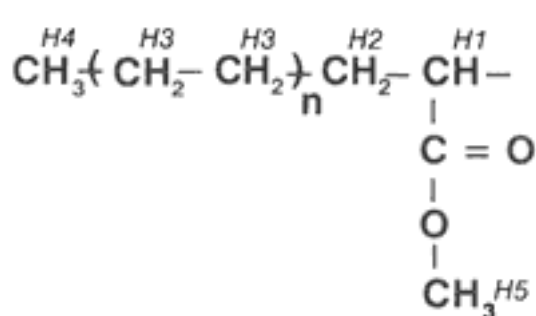
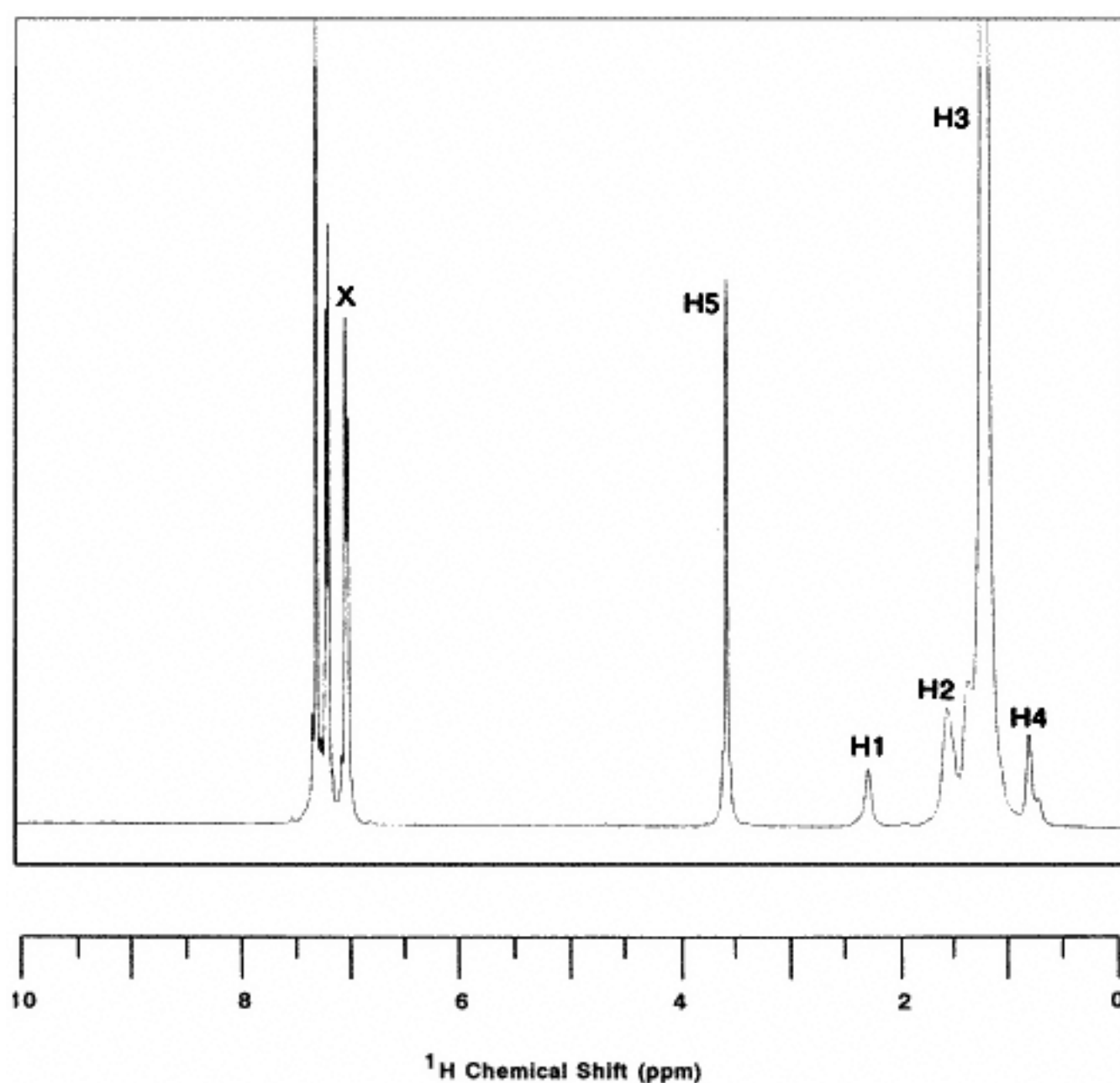
Pulse delay: 2 s

II-A-28H—

Poly(Ethylene-Co-Methyl Acrylate) (EMA)

Comments

A distinct resonance arising from incorporation of methyl acrylate appears at 3.6 ppm; this peak can easily be used to quantify the MA content. Solvent resonances are marked by **X**. EMA is used for medical packaging and to manufacture gloves. When blended with polyethylene, it improves impact resistance, heat-seal characteristics, and toughness. It melts between 95 and 115°C; the melting point of these copolymers increases as the methyl acrylate content decreases.



Code	Shift (ppm)
H1	2.29
H2	1.58
H3	1.29
H4	0.84
H5	3.56

*Experimental Parameters*Nucleus: ^1H (400 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 100

Spectral width: 8 kHz

Data points: 4096

Pulse width: 30°

Broadening: 3 Hz

Pulse delay: 5 s

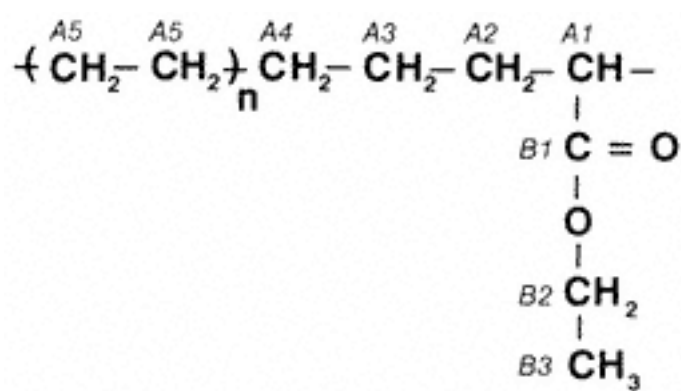
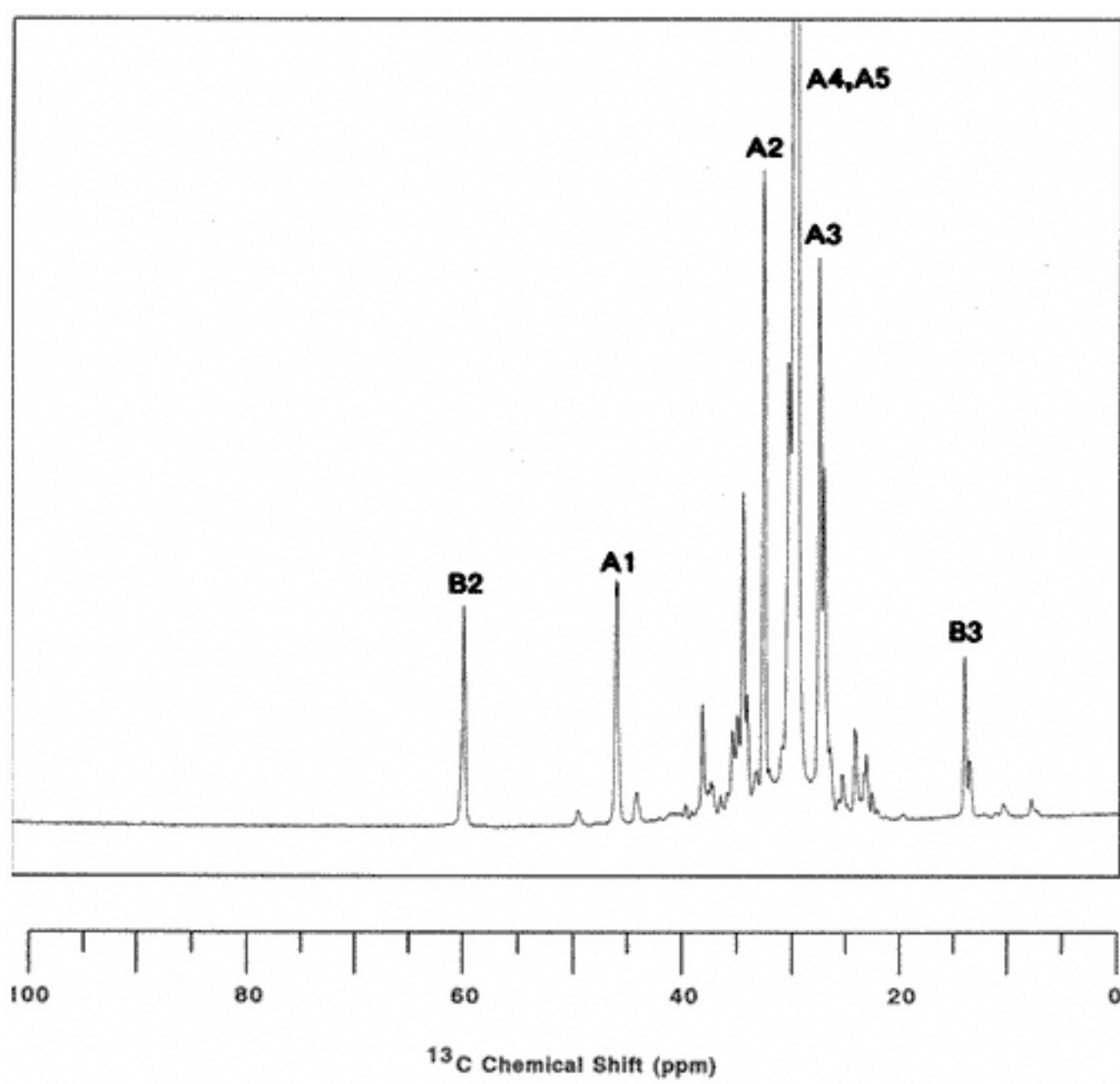
II-A-29

II-A-29—

Poly(Ethylene-Co-Ethyl acrylate) [18%EA] (EEA)

Comments

Distinctive resonances arising from incorporation of ethyl acrylate are listed. Because this material is produced by a low-pressure, free-radical process, it also exhibits an alkyl-branching pattern similar to that of LDPE (II-A-3); refer to this entry for detailed assignments. EMA is used for hoses, films, tubing, and adhesives. When blended with polyethylene, it improves impact resistance, heat-seal characteristics, and toughness. It melts between 95 and 115°C; the melting point of these copolymers increases as the ethyl acrylate content decreases.



Code	Shift (ppm)
A1	45.6
A2	32.2
A3	26.8
A4	30.5
A5	30.0
B1	175.8
B2	59.1
B3	14.0

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

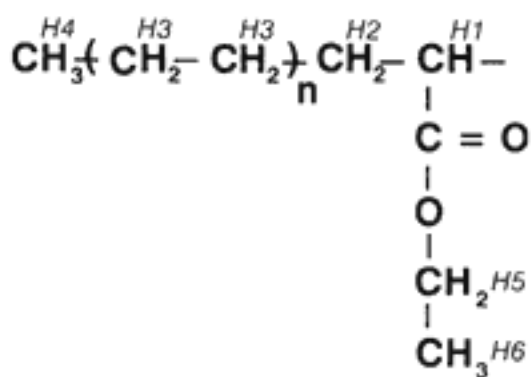
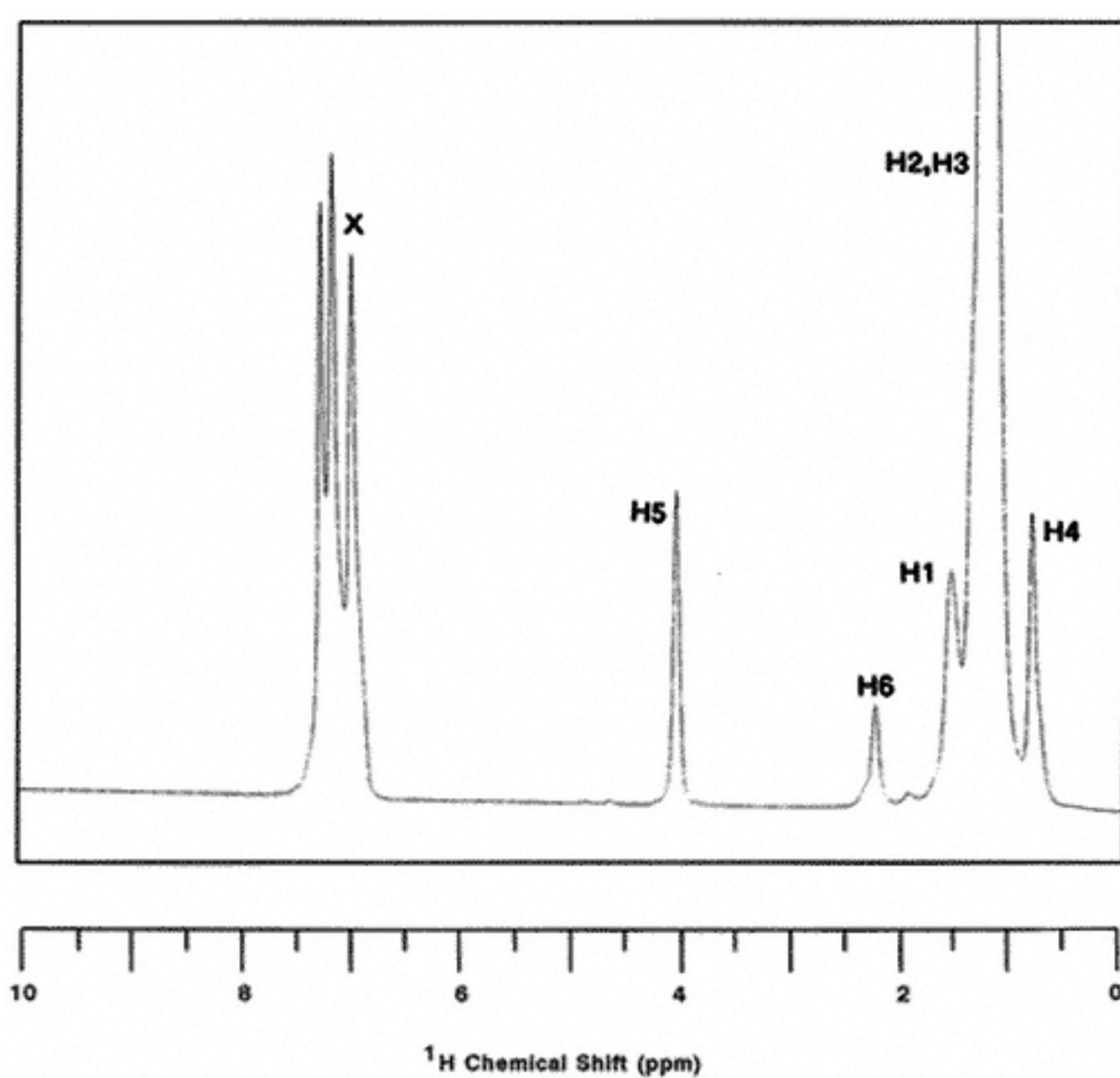
Pulse delay: 2 s

II-A-29H—

Poly(Ethylene-Co-Ethyl Acrylate) [18%EA] (EEA)

Comments

A distinct resonance arising from incorporation of ethyl acrylate appears at 4.0 ppm; this peak can easily be used to quantify the EA content. Solvent resonances are marked by **X**. EEA is used for hoses, films, tubing, and adhesives. When blended with polyethylene, it improves impact resistance, heat-seal characteristics, and toughness.



Code	Shift (ppm)
H1	2.23
H2	1.55
H3	1.27
H4	0.80
H5	4.03
H6	0.80

*Experimental Parameters*Nucleus: ^1H (400 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 100

Spectral width: 8 kHz

Data points: 4096

Pulse width: 30°

Broadening: 3 Hz

Pulse delay: 5 s

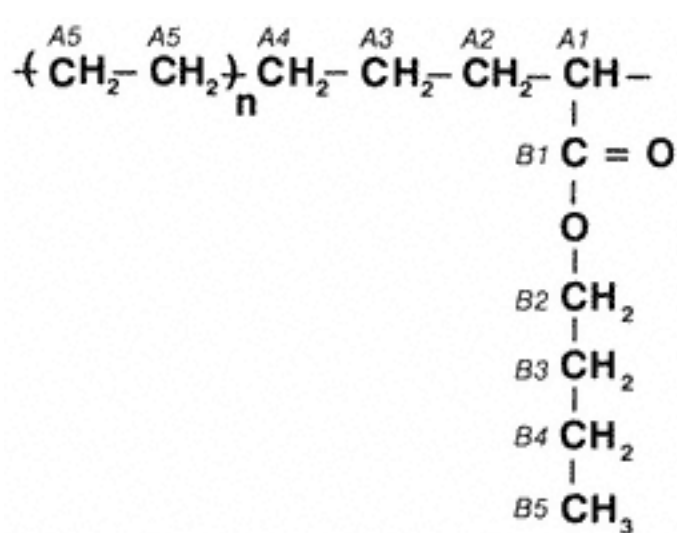
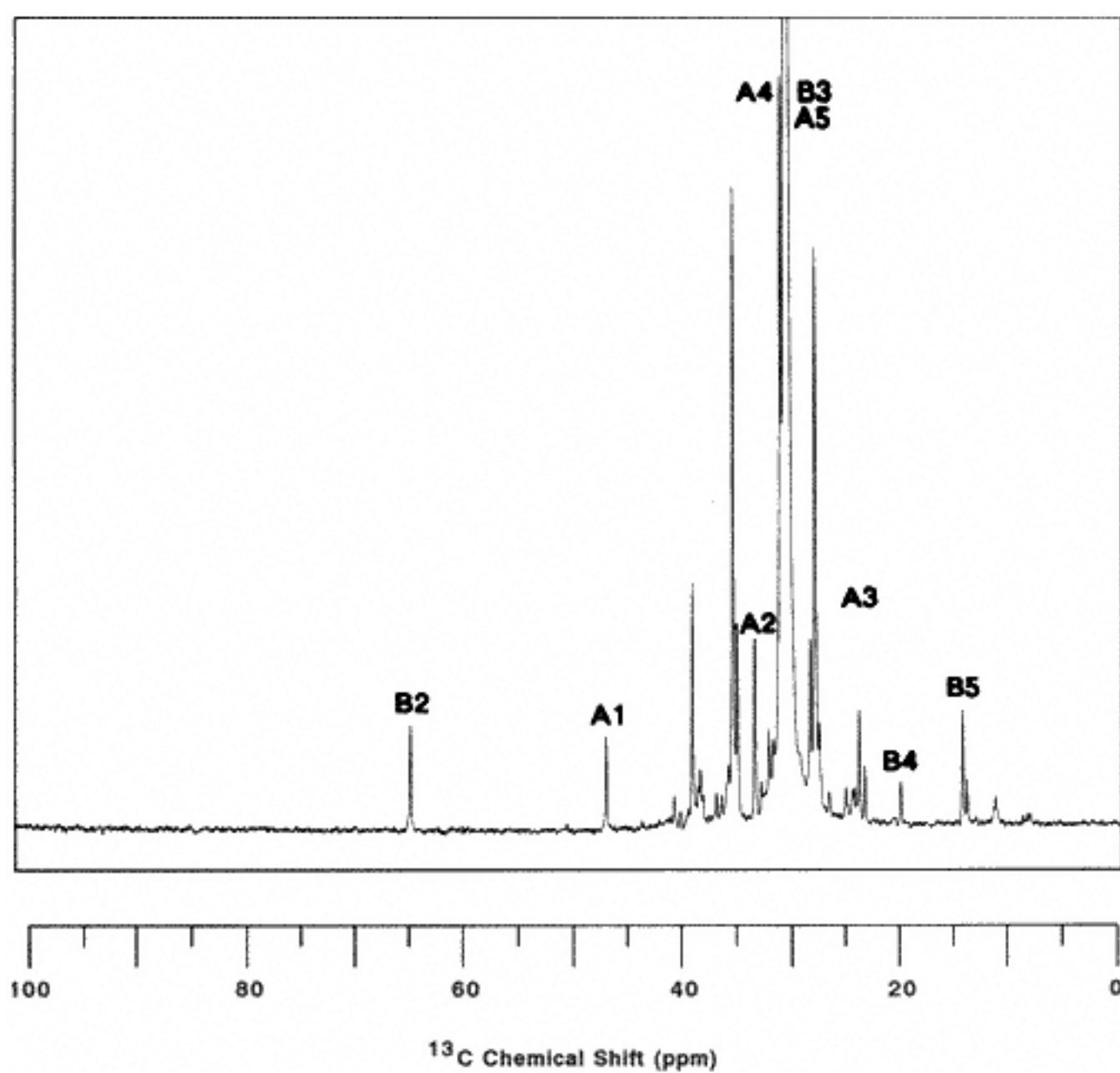
II-A-30

II-A-30—

Poly(Ethylene-Co-Butyl Acrylate) (EBA)

Comments

Distinctive resonances arising from incorporation of butyl acrylate are listed. Because this material is produced by a low-pressure, free-radical process, it also exhibits an alkyl-branching pattern similar to that of LDPE {II-A-3}; refer to this entry for detailed assignments. When blended with polyethylene, EBA improves impact resistance, heat-seal characteristics, and toughness. EBA melts between 95 and 115°C; the melting point of these copolymers increases as the butyl acrylate content decreases.



Code	Shift (ppm)
A1	45.7
A2	32.7
A3	27.2
A4	30.5
A5	30.0
B1	175.6
B2	63.5
B3	30.0
B4	18.9
B5	13.9

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

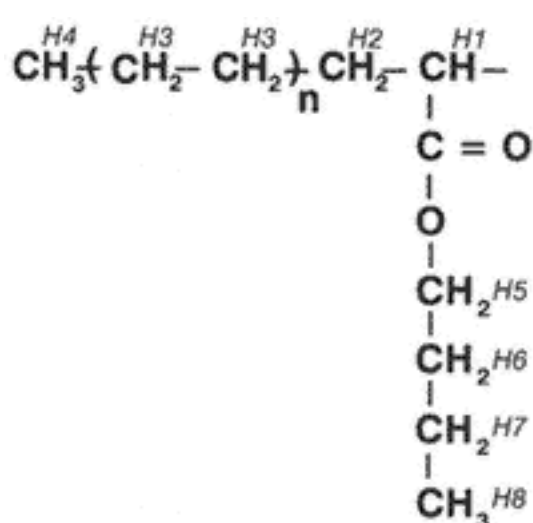
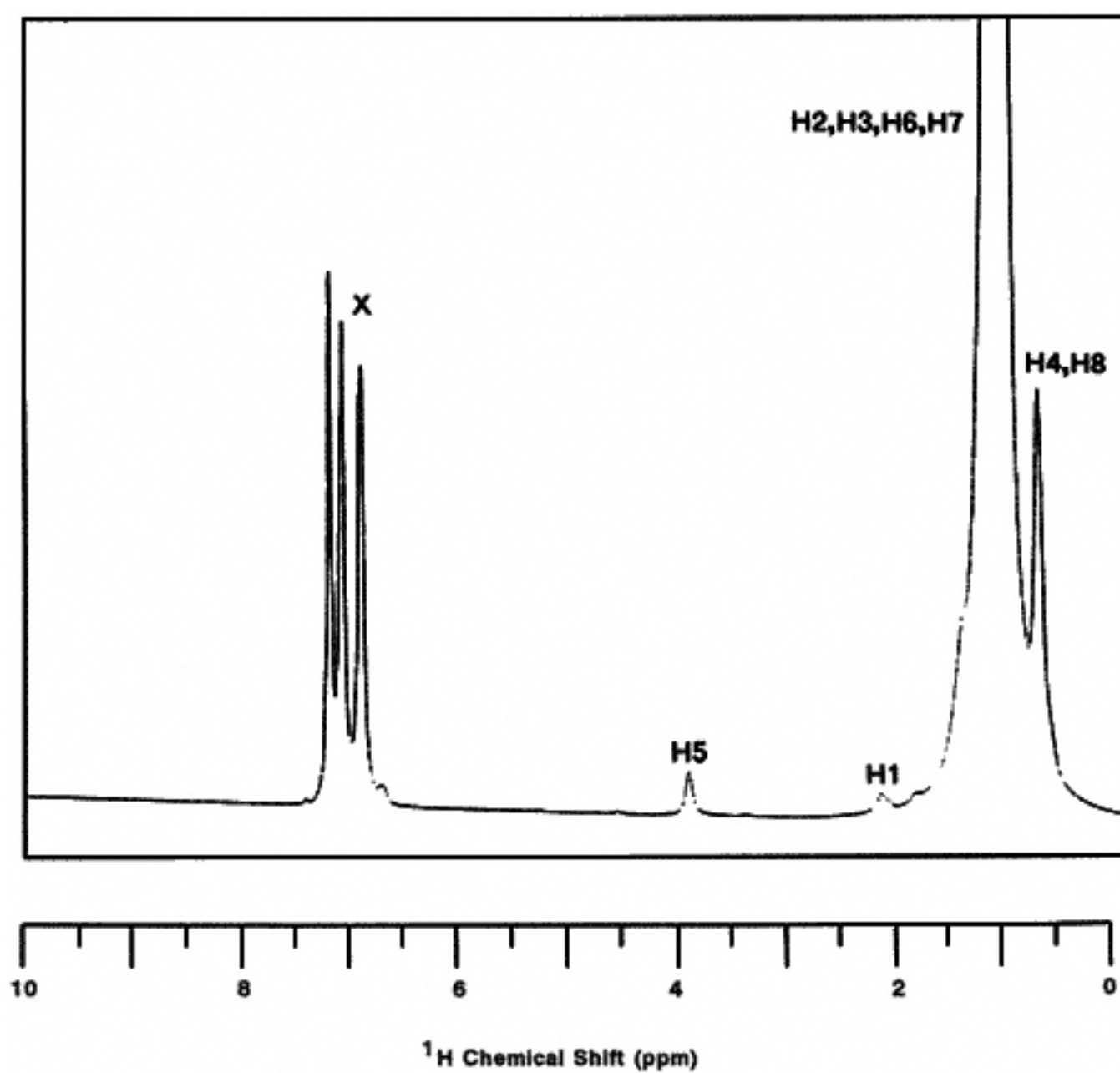
Pulse delay: 2 s

II-A-30H—

Poly(Ethylene-Co-Butyl Acrylate) (EBA)

Comments

A distinct resonance arising from incorporation of butyl acrylate appears at 4.0 ppm; this peak can easily be used to quantify the BA content. Solvent resonances are marked by X. When blended with polyethylene, EBA improves impact resistance, heat-seal characteristics, and toughness. EBA melts between 95 and 115°C; the melting point of these copolymers increases as the butyl acrylate content decreases.



Code	Shift (ppm)
H1	2.27
H2	1.27
H3	1.27
H4	0.87
H5	4.02
H6	1.27
H7	1.27
H8	0.87

Experimental ParametersNucleus: ^1H (400 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 100

Spectral width: 8 kHz

Data points: 4096

Pulse width: 30°

Broadening: 3 Hz

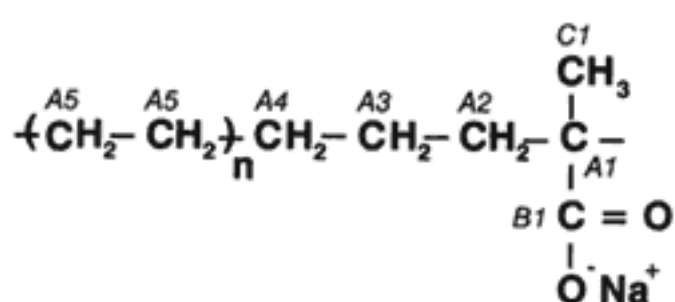
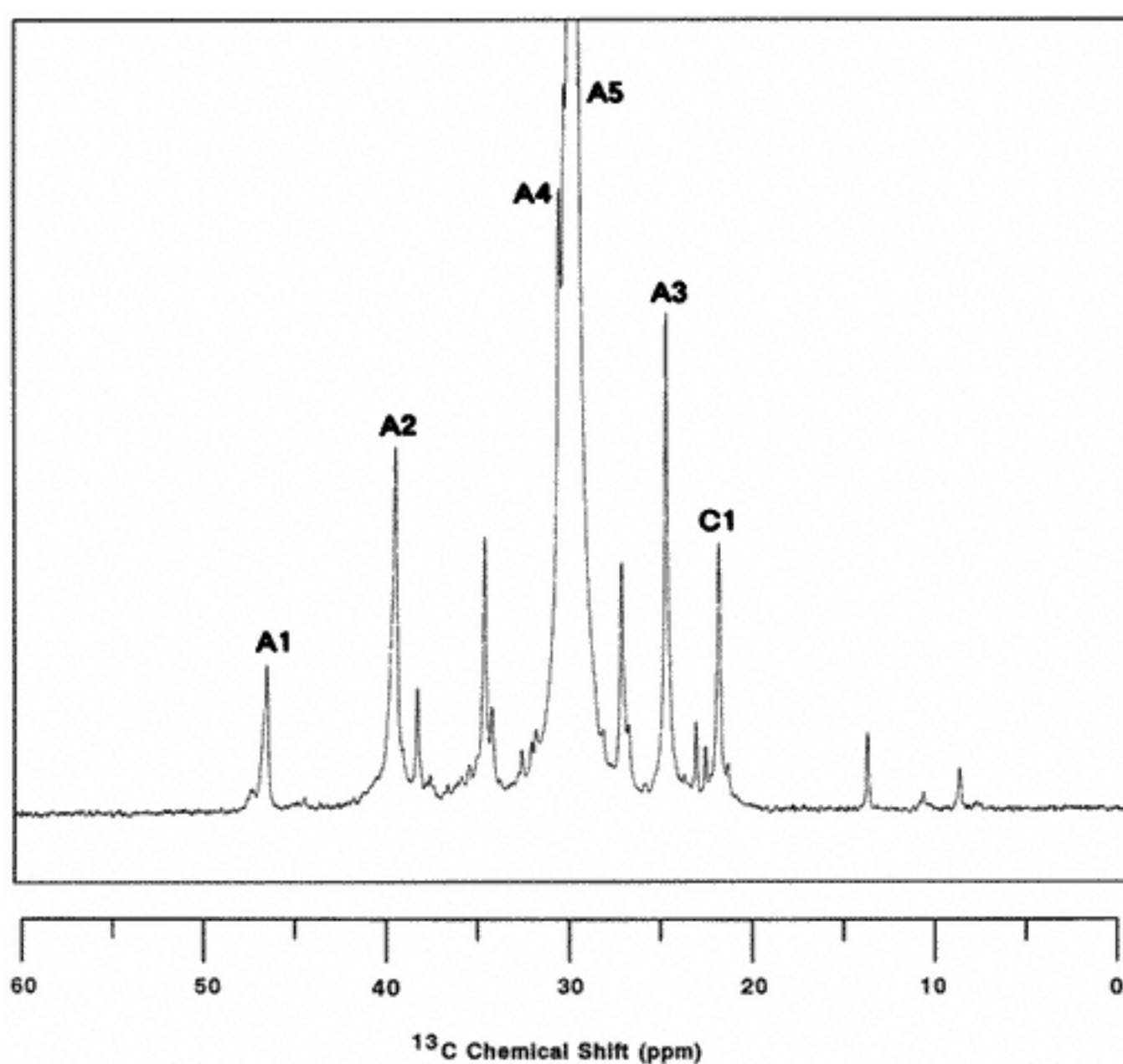
Pulse delay: 5 s

II-A-31

Poly(Ethylene-Co-Methacrylic Acid), Na⁺ Salt (EMAA)

Comments

Distinctive resonances arising from incorporation of methacrylic acid are listed. Because this material is produced by a low-pressure, free-radical process, it also exhibits an alkyl-branching pattern similar to that of LDPE {II-A-3}; refer to this entry for detailed assignments. Because of the presence of ionic groups, this material is called an *ionomer*; these groups promote interchain bonding and act as cross-links. The material is transparent and highly resistant to solvents; it also exhibits good abrasion resistance and favorable electrical properties. EMAA melts between 95 and 115°C; the melting point of these copolymers increases as the methacrylic acid content decreases.



Code	Shift (ppm)
A1	47.0
A2	40.0
A3	25.3
A4	30.6
A5	30.0
B1	183.2
C1	22.4

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

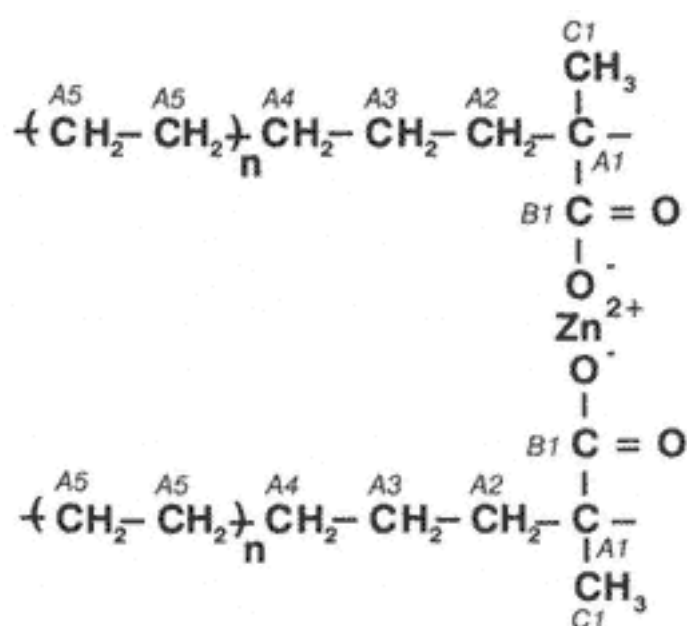
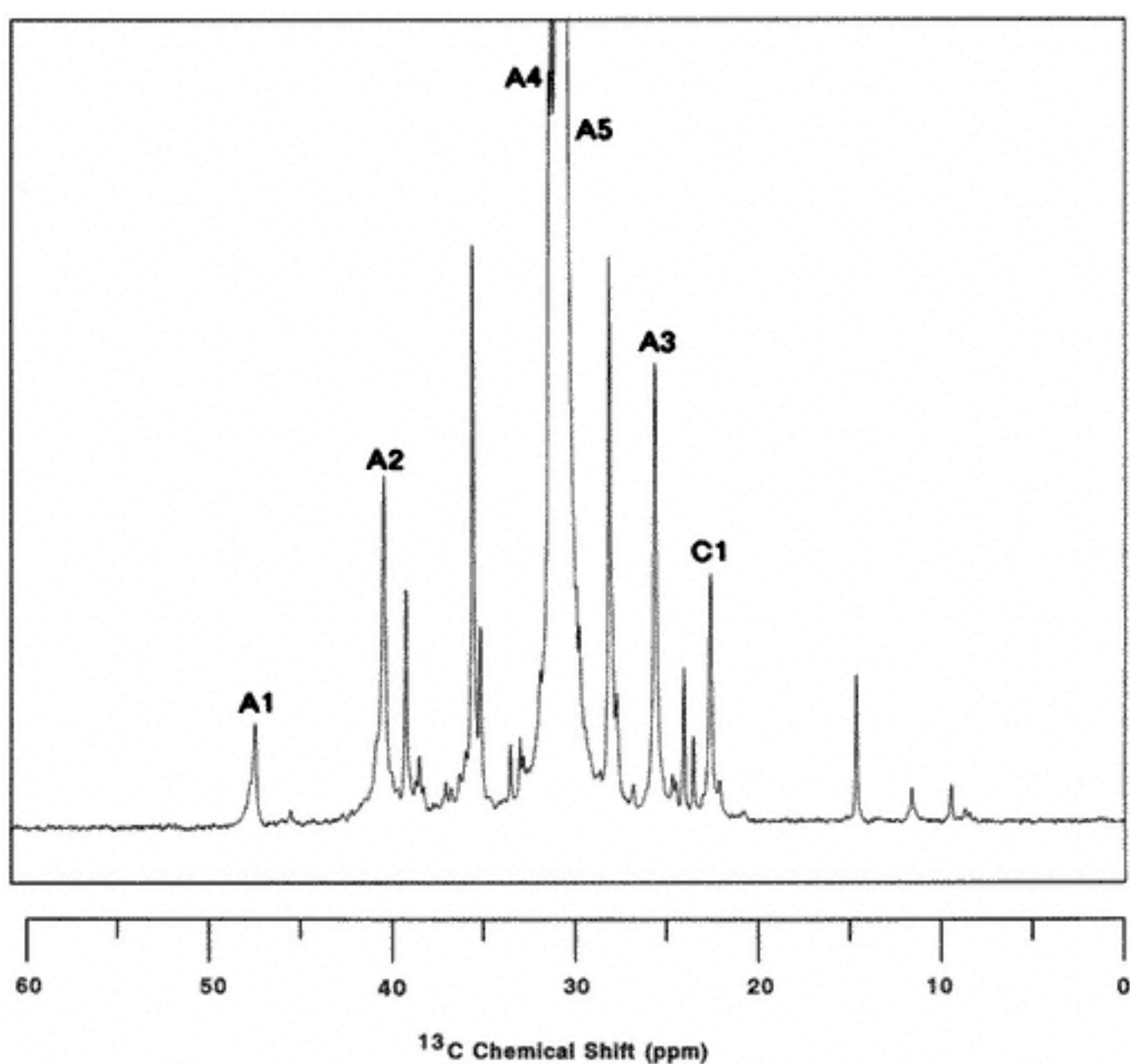
Pulse delay: 2 s

II-A-32

Poly(Ethylene-Co-Methacrylic Acid), Zn²⁺ Salt (EMAA)

Comments

Distinctive resonances arising from incorporation of methacrylic acid are listed. Because this material is produced by a low-pressure, free-radical process, it also exhibits an alkyl-branching pattern similar to that of LDPE {II-A-3}; refer to this entry for detailed assignments. Because of the presence of ionic groups, this material is called an *ionomer*; these groups promote interchain bonding and act as cross-links. The material is transparent and highly resistant to solvents; it also exhibits good abrasion resistance and favorable electrical properties. EMAA melts between 95 and 115°C; the melting point of these copolymers increases as the methacrylic acid content decreases.



Code	Shift (ppm)
A1	47.0
A2	40.0
A3	25.3
A4	30.6
A5	30.0
B1	183.2
C1	22.4

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

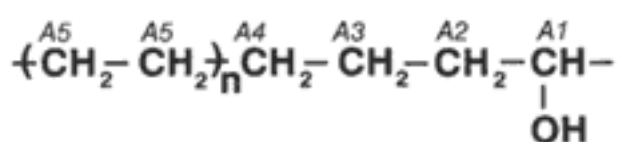
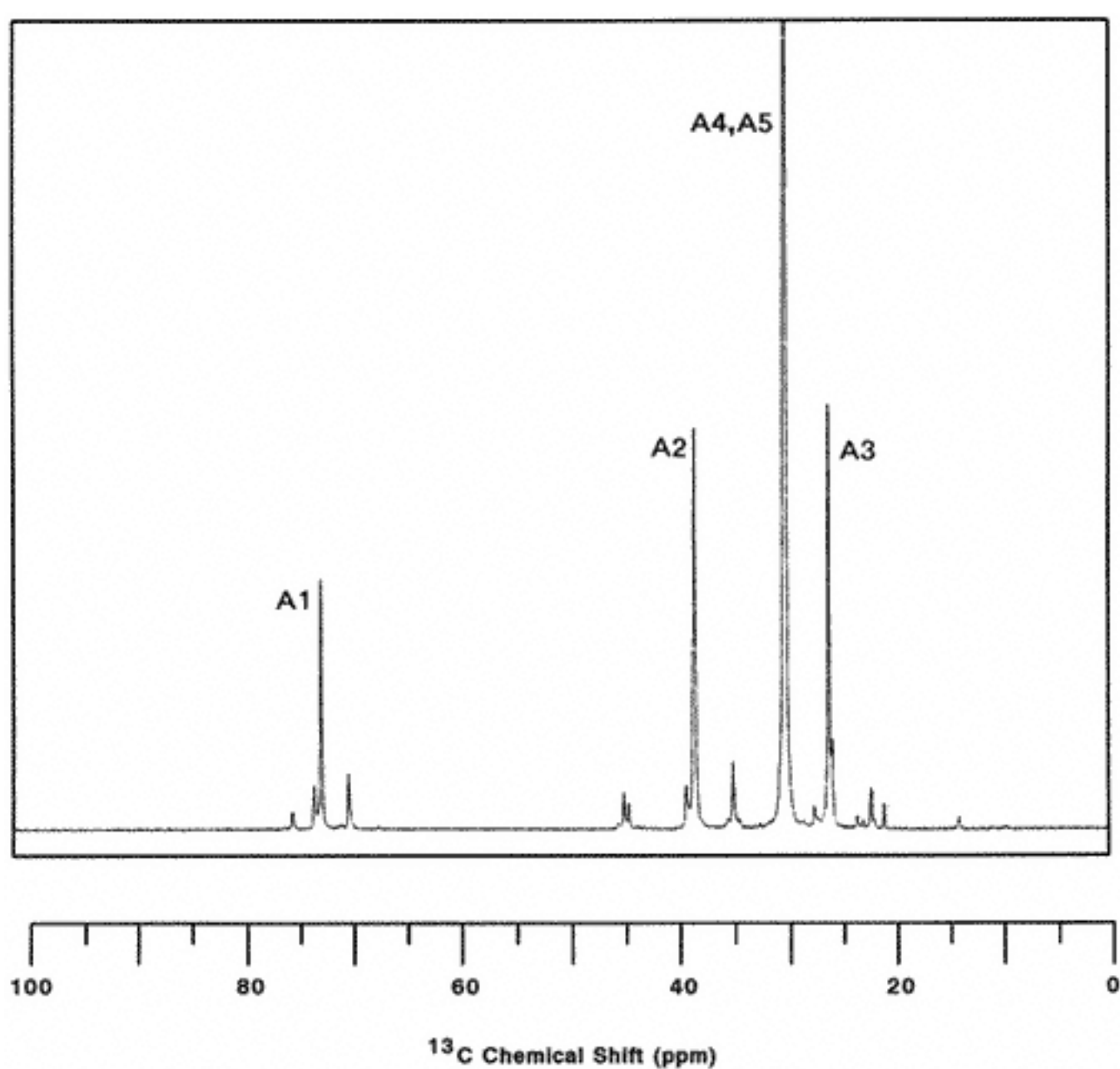
Pulse delay: 2 s

II-A-33—

Poly(Ethylene-Co-Vinyl Alcohol) [25% VOH] (EVOH, EVA1)

Comments

Distinctive resonances arising from presence of vinyl alcohol are listed. Because this material is produced by a low-pressure, free-radical process, it also exhibits an alkyl-branching pattern similar to that of LDPE {II-A-3}; refer to this entry for detailed assignments. This material is produced by hydrolysis of poly(ethylene-co-vinyl acetate) (EVA) {II-A-22, II-A-23}, so some residual EVA is usually observed. EVOH is used in barrier films because of its hydrophilicity. It melts between 95 and 115°C; the melting point of these copolymers increases as the vinyl alcohol content decreases.



Code	Shift (ppm)
A1	72.5
A2	38.6
A3	26.2
A4	30.0
A5	30.0

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

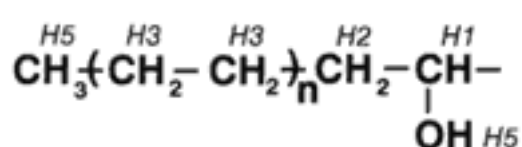
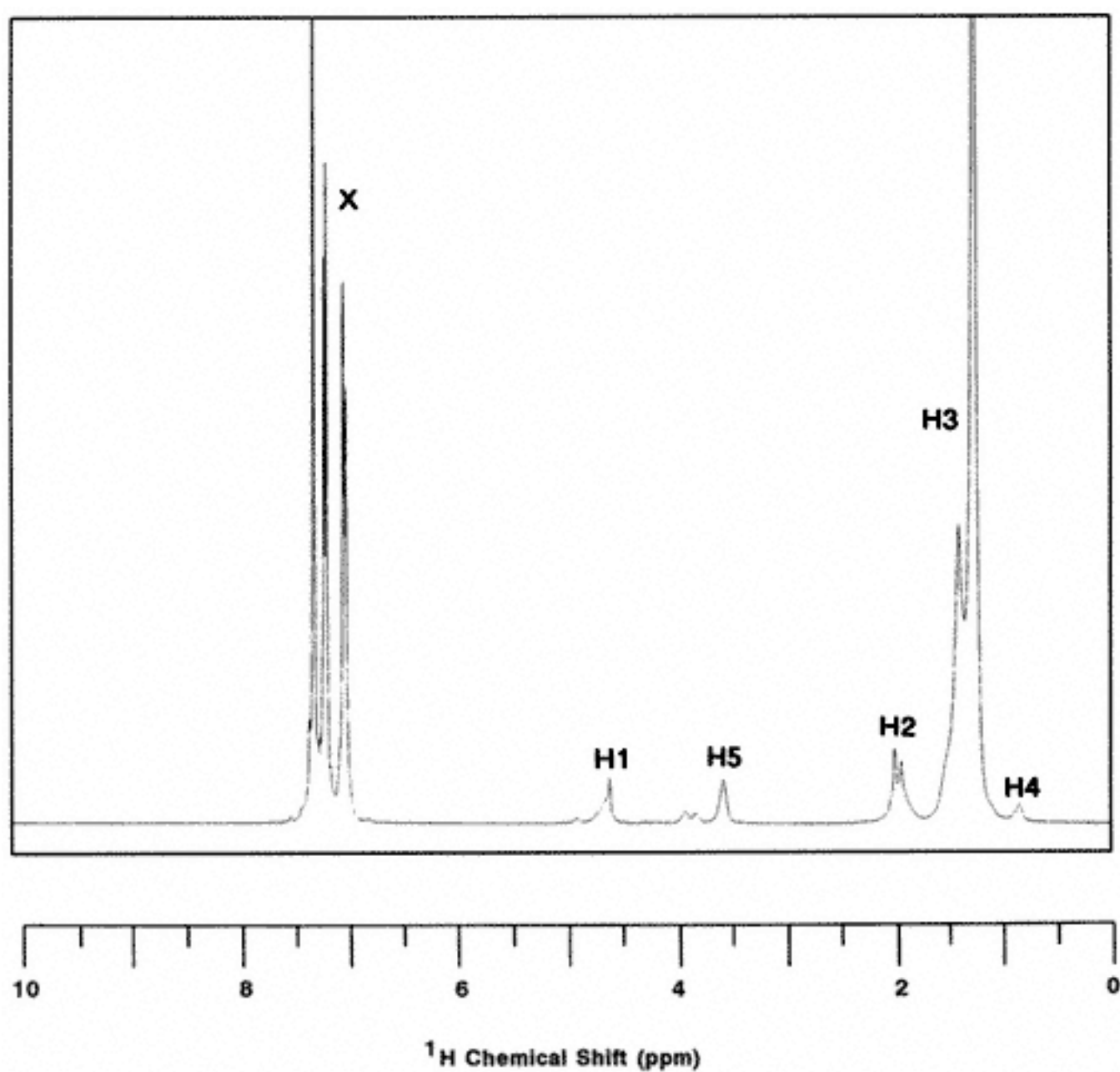
Pulse delay: 2 s

References

H. N. Cheng and G. H. Lee. *Macromolecules* 21:3164, 1988; H. Ketels, J. Beulen, and G. van der Velden. *Macromolecules* 21:2032, 1988.

II-A-33H—**Poly(Ethylene-Co-Vinyl Alcohol) [25% VOH] (EVOH, EVA1)****Comments**

A distinct resonance arising from presence of vinyl alcohol appears at 3.6 ppm; this peak can easily be used to quantify the VOH content. Solvent resonances are marked by **X**. This material is produced by hydrolysis of poly(ethylene-co-vinyl acetate) (EVA) {II-A-22, II-A-23}, so some residual EVA is usually observed. EVOH is used in barrier films because of its hydrophilicity. It melts between 95 and 115°C; the melting point of these copolymers increases as the vinyl alcohol content decreases.



Code	Shift (ppm)
H1	4.62
H2	2.05
H3	1.47
H4	0.92
H5	3.59

Experimental ParametersNucleus: ^1H (400 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 100

Spectral width: 8 kHz

Data points: 4096

Pulse width: 30°

Broadening: 3 Hz

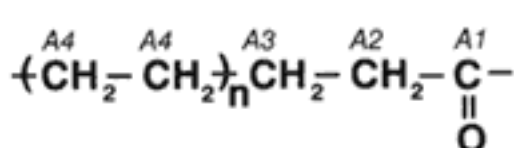
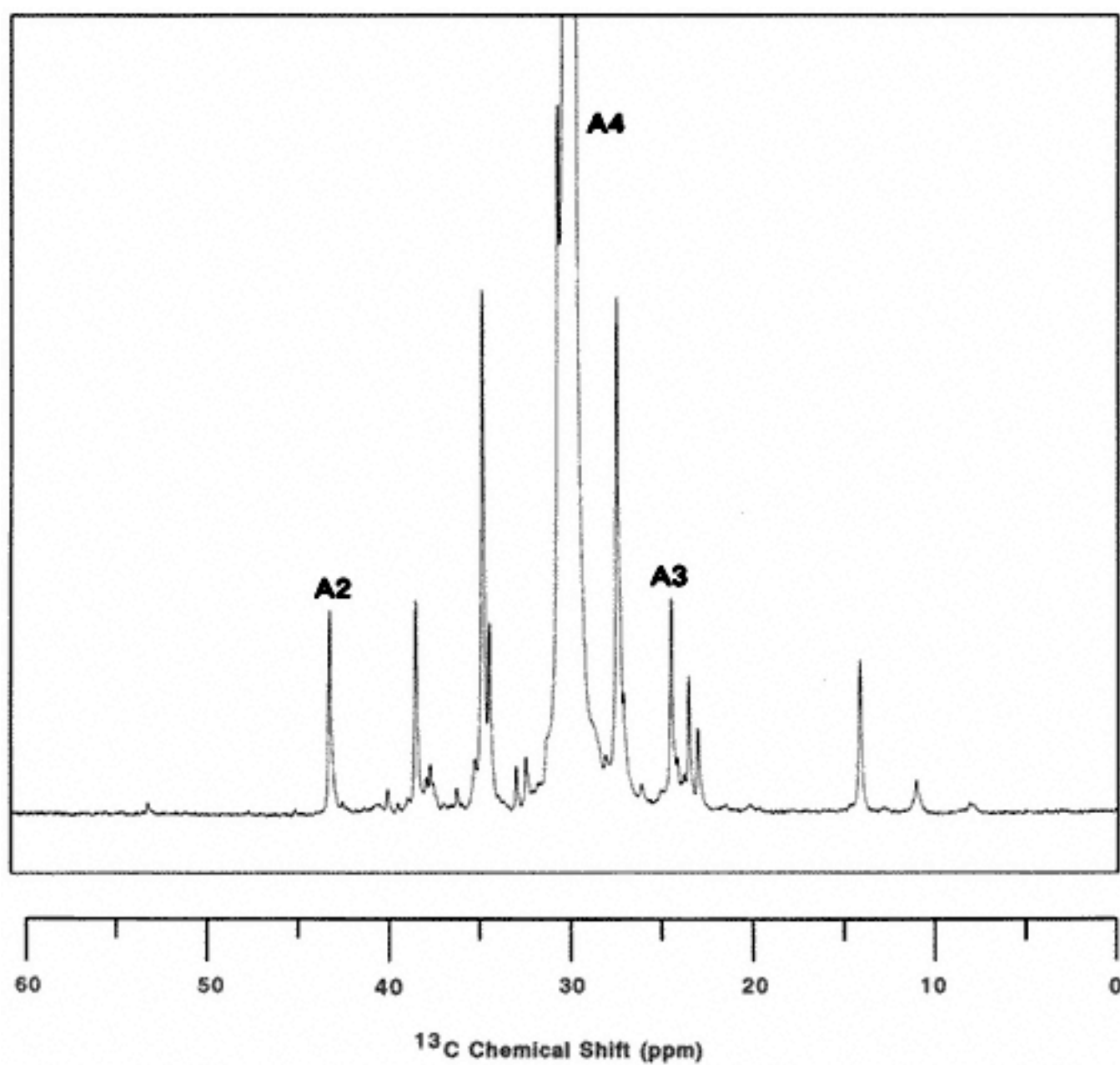
Pulse delay: 5 s

II-A-34—

Poly(Ethylene-Co-Carbon Monoxide) (ECO)

Comments

Distinctive resonances arising from the incorporation of carbon monoxide in the backbone are listed. Because this material is produced by a low-pressure, free-radical process, it also exhibits an alkyl-branching pattern similar to that of LDPE {II-A-3}; refer to this entry for detailed assignments. ECO is a biodegradable material, which is used for beverage six-pack rings. ECO melts between 95 and 115°C; the melting point of these copolymers increases as the carbon monoxide content decreases.



Code	Shift (ppm)
A1	207.9
A2	42.8
A3	24.2
A4	30.0

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

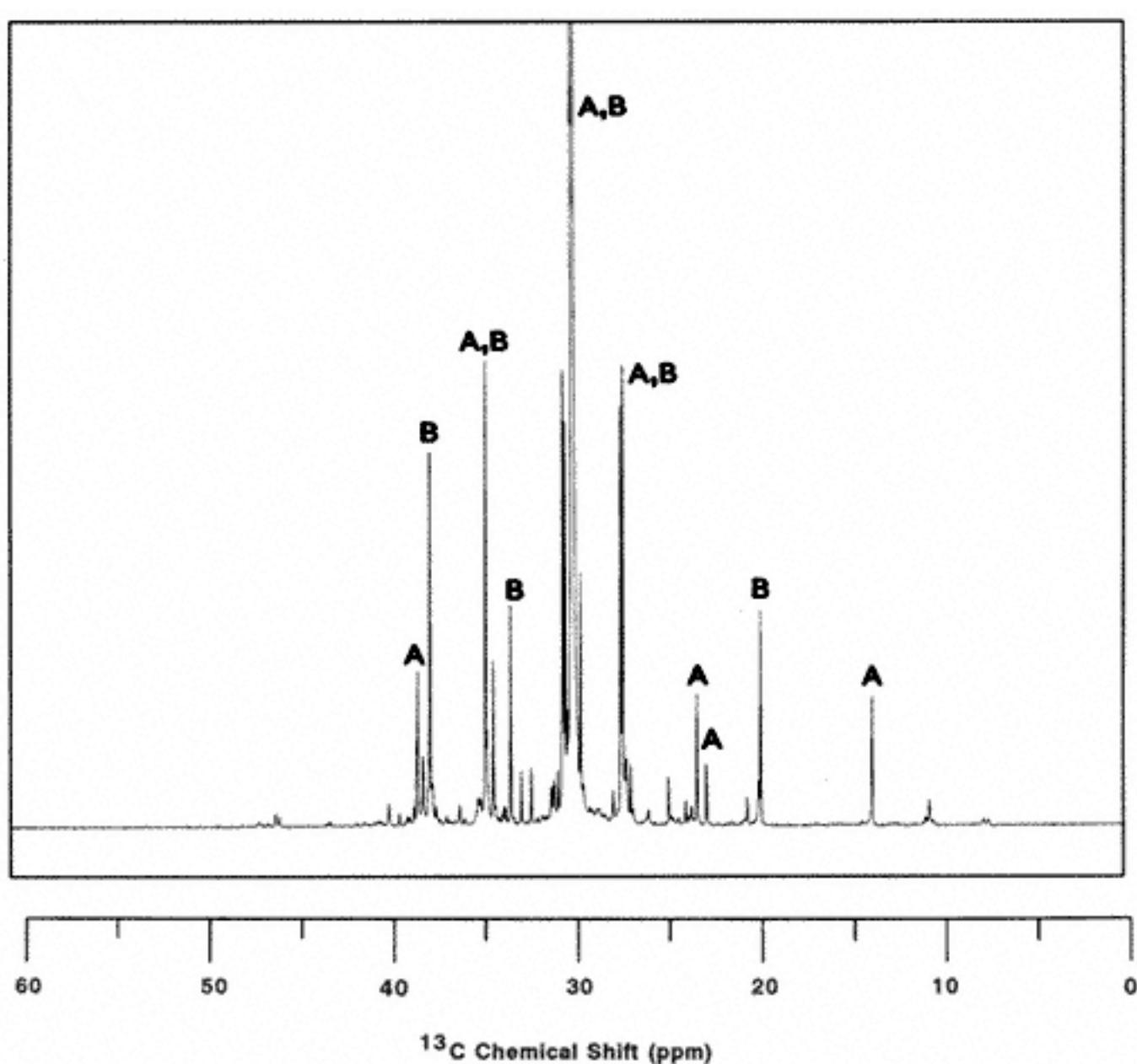
Pulse delay: 2 s

II-A-35—

Polyethylene, Branched/Polyethylene-Co-Propylene) (40%P), 90/10 Blend

Comments

The set of observed resonances is the weighted sum of the component polymers, LDPE {II-A-3} (denoted by **A**) and EPR {II-A-8} (denoted by **B**); see these entries for detailed assignments. The relative intensities of these peaks will vary according to the exact blend ratio. The addition of EPR improves the toughness of the base polymer.



Code	Shift (ppm)
A (LDPE)	38.2
B (EPR)	37.6
A,B	34.6
B	33.3
A,B	30.0
A,B	27.3
A	23.3
A	22.9
B	20.1
A	14.1

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

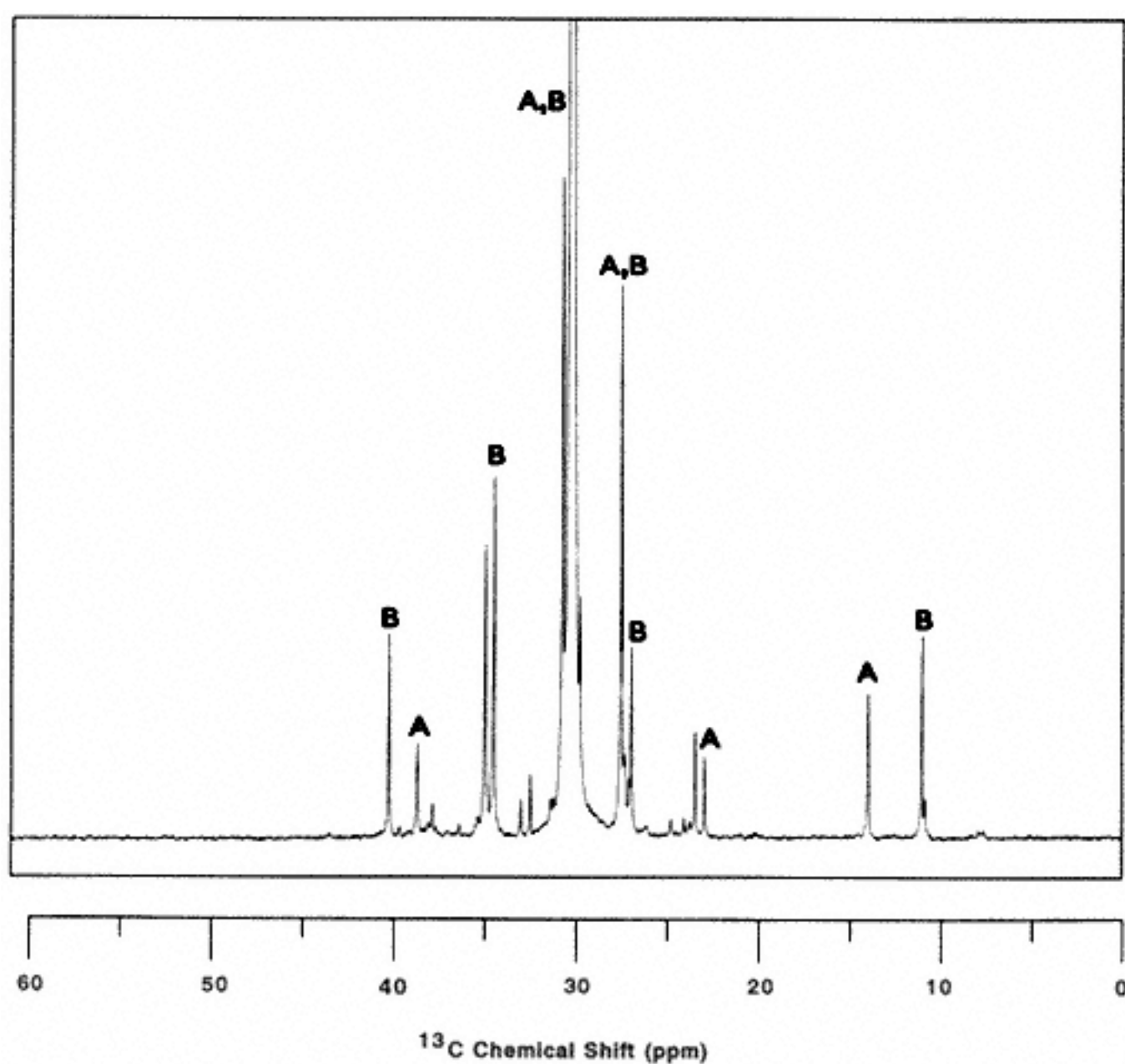
Pulse delay: 2 s

II-A-36—

Poly(Ethylene-Co-1-Butene)/Polyethylene, Branched, 80/20 Blend

Comments

The set of observed resonances is the weighted sum of the component polymers, butene-LLDPE {II-A-10} (denoted by **A**) and LDPE {II-A-3} (denoted by **B**); see these entries for detailed assignments. The relative intensities of these peaks will vary according to the exact blend ratio and 1-butene content of the LLDPE component; in some cases, LDPE may be the dominant component. These resins are often blended to produce materials of intermediate properties.



Code	Shift (ppm)
B (EB)	39.8
A (LDPE)	38.2
A	34.6
B	34.2
A,B	30.0
A,B	27.3
B	26.7
A	23.3
A	22.9
A	14.1
B	11.1

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

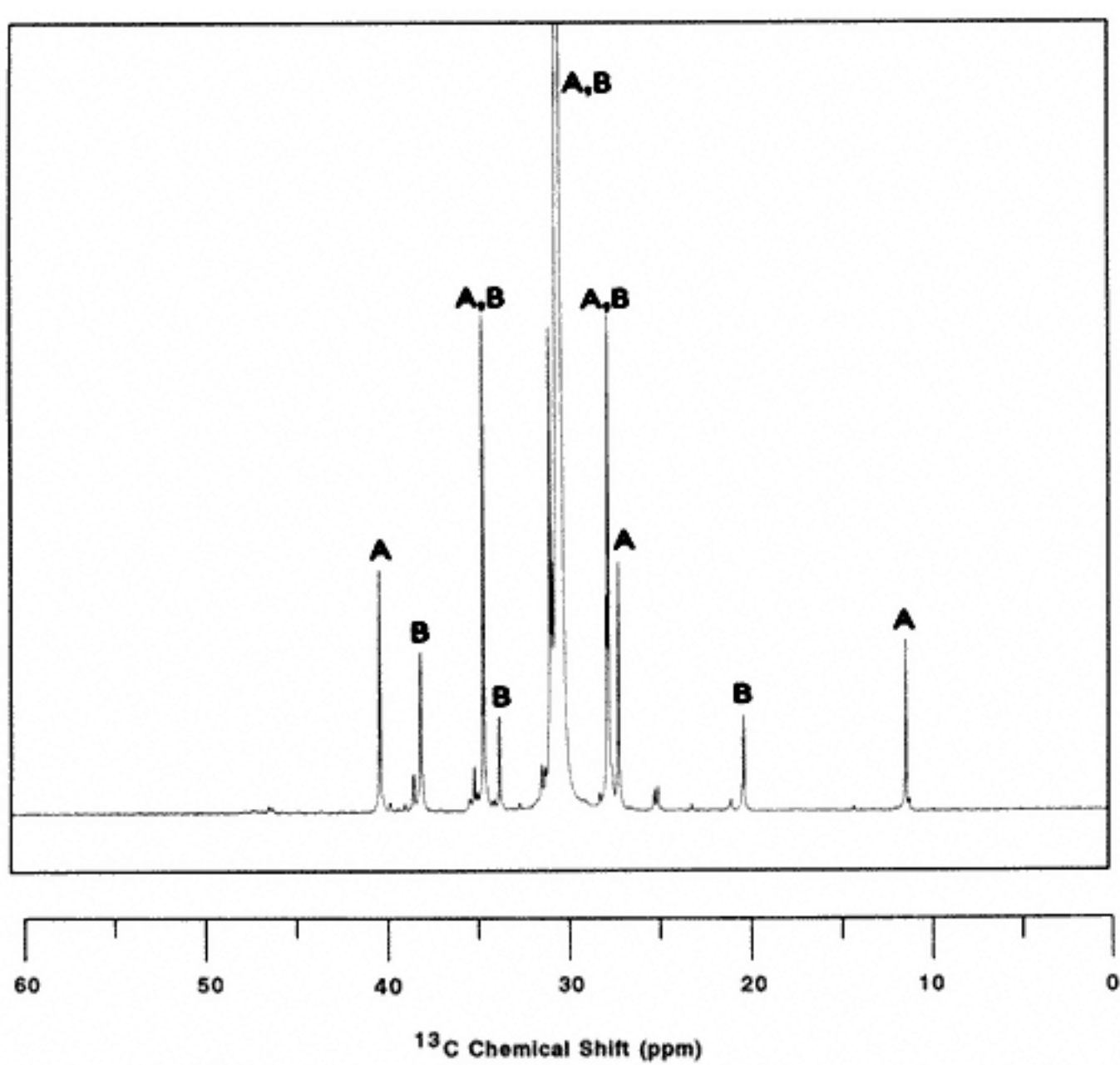
Pulse delay: 2 s

II-A-37—

Poly(Eethylene-Co-1-Butene)/Poly(Eethylene-Co-Propylene) (40%E), 90/10 Blend

Comments

The set of observed resonances is the weighted sum of the component polymers, butene-LLDPE {II-A-10} (denoted by **A**) and EPR {II-A-8} (denoted by **B**); see these entries for detailed assignments. The relative intensities of these peaks will vary according to the exact blend ratio and 1-butene content of the LLDPE component. The addition of EPR improves the toughness of the base polymer.



Code	Shift (ppm)
A (EB)	39.8
B (EPR)	37.6
A,B	34.6
B	33.3
A,B	30.0
A,B	27.3
A	26.7
B	20.1
A	11.1

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

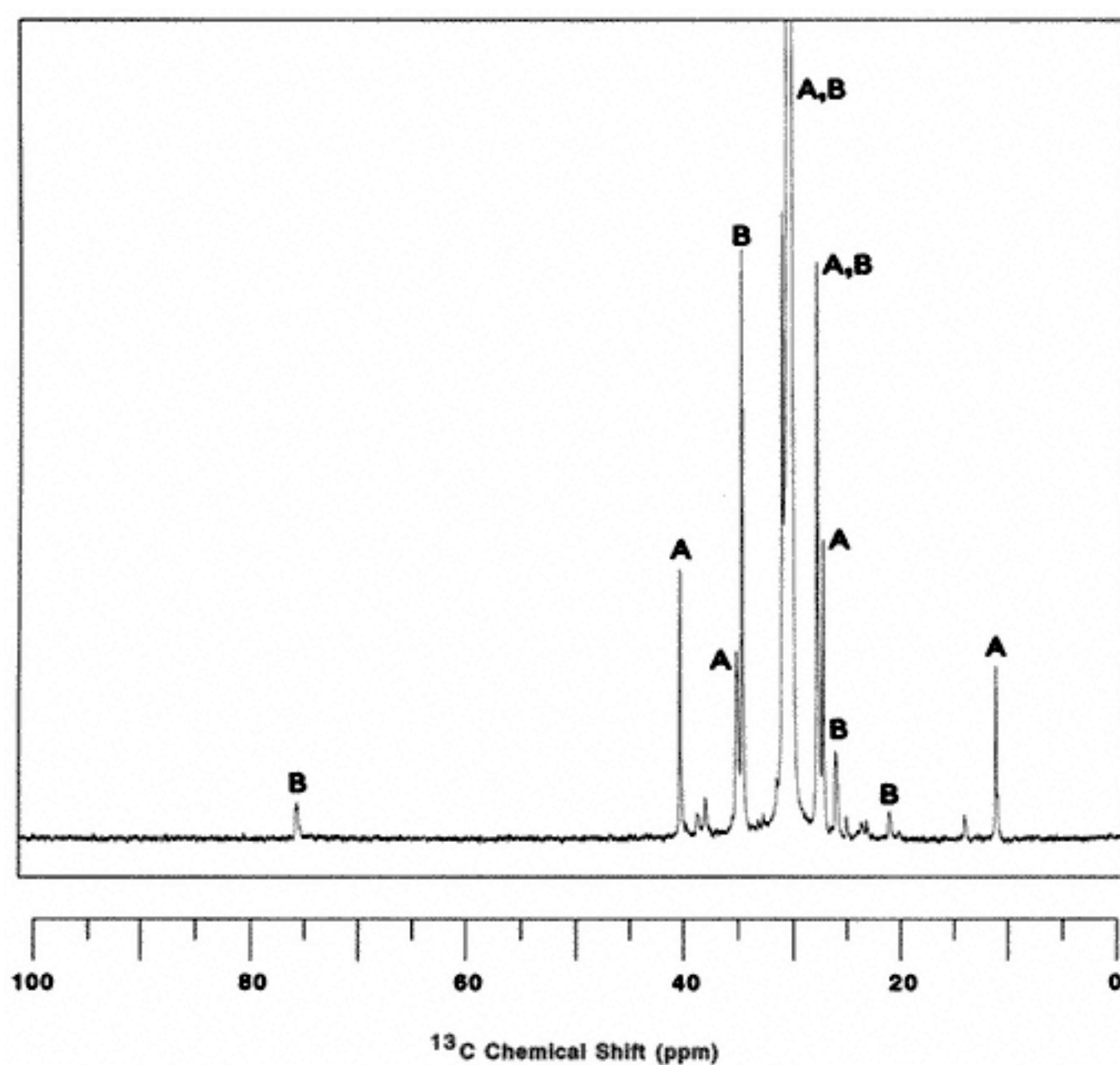
Pulse delay: 2 s

II-A-38—

Poly(Ethylene-Co-1-Butene)/Poly(Ethylene-Co-Vinyl Acetate)(14% VA), 80/20 Blend

Comments

The set of observed resonances is the weighted sum of the component polymers, butene-LLDPE {see II-A-10} (denoted by **A**) and EVA {see II-A-24} (denoted by **B**), refer to these entries for detailed assignments. The relative intensities of these peaks will vary according to the exact blend ratio and 1-butene content of the LLDPE component; in some cases, EVA may be the dominant component. These resins are often blended to produce materials of intermediate properties, and to improve the toughness and heat-seal properties of the base polymer.



Code	Shift
B (EVA)	74.6
A (EB)	39.8
A	34.6
B	34.2
A,B	30.0
A,B	27.3
A	26.7
B	25.7
B	20.8
A	11.1

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

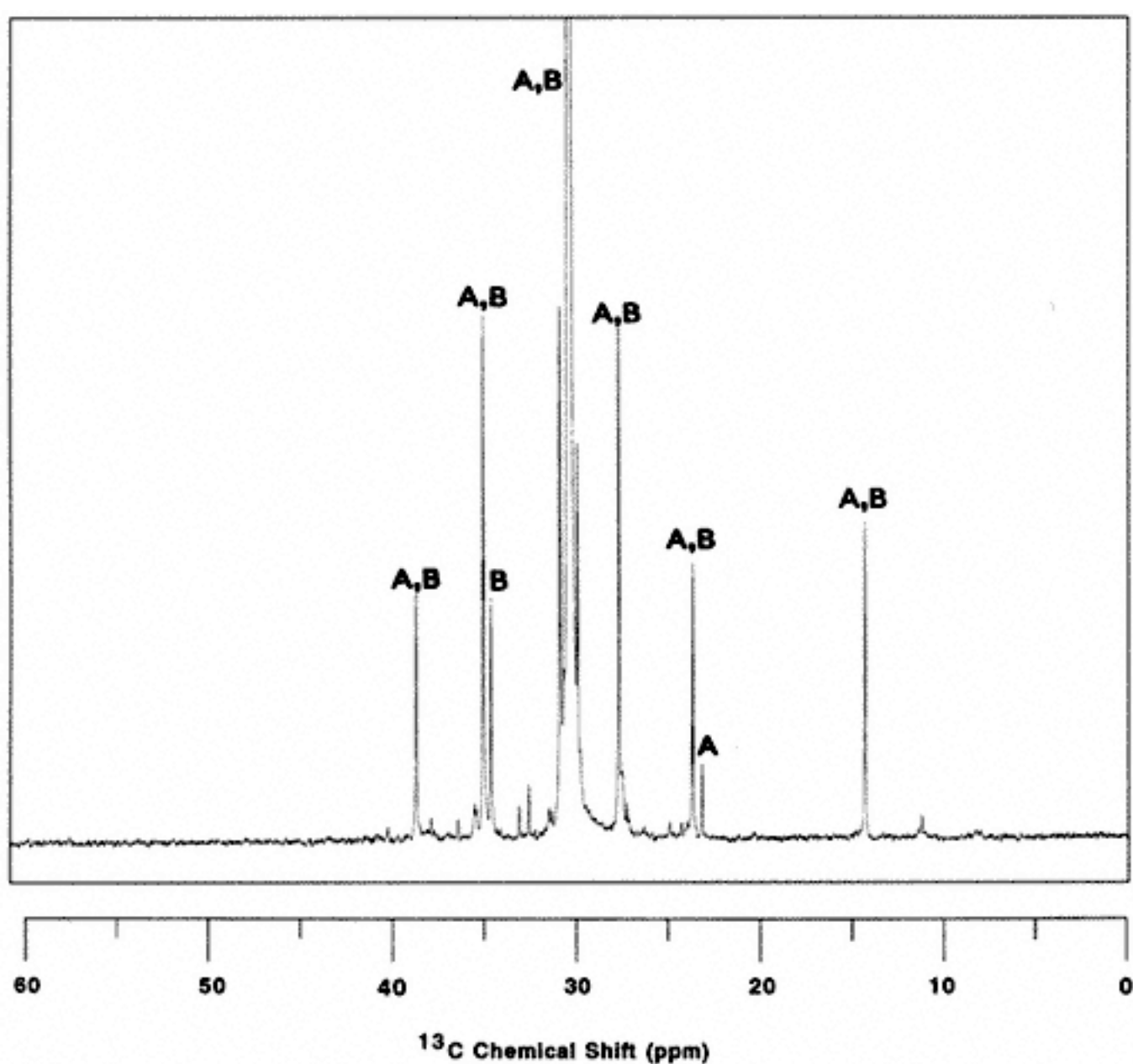
Pulse delay: 2 s

II-A-39—

Poly(Ethylene-Co-1-Hexene)/Polyethylene, Branched, 80/20 Blend

Comments

The set of observed resonances is the weighted sum of the component polymers, hexene-LLDPE {II-A-16} (denoted by **A**) and LDPE {II-A-3} (denoted by **B**); see these entries for detailed assignments. The relative intensities of these peaks will vary according to the exact blend ratio and 1-hexene content of the LLDPE component; in some cases, LDPE may be the dominant component. These resins are often blended to produce materials of intermediate properties.



Code	Shift (ppm)
A,B	38.2
A,B	34.6
B (EH)	34.2
A,B	30.0
A,B	27.3
A,B	23.3
A (LDPE)	22.9
A,B	14.1

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

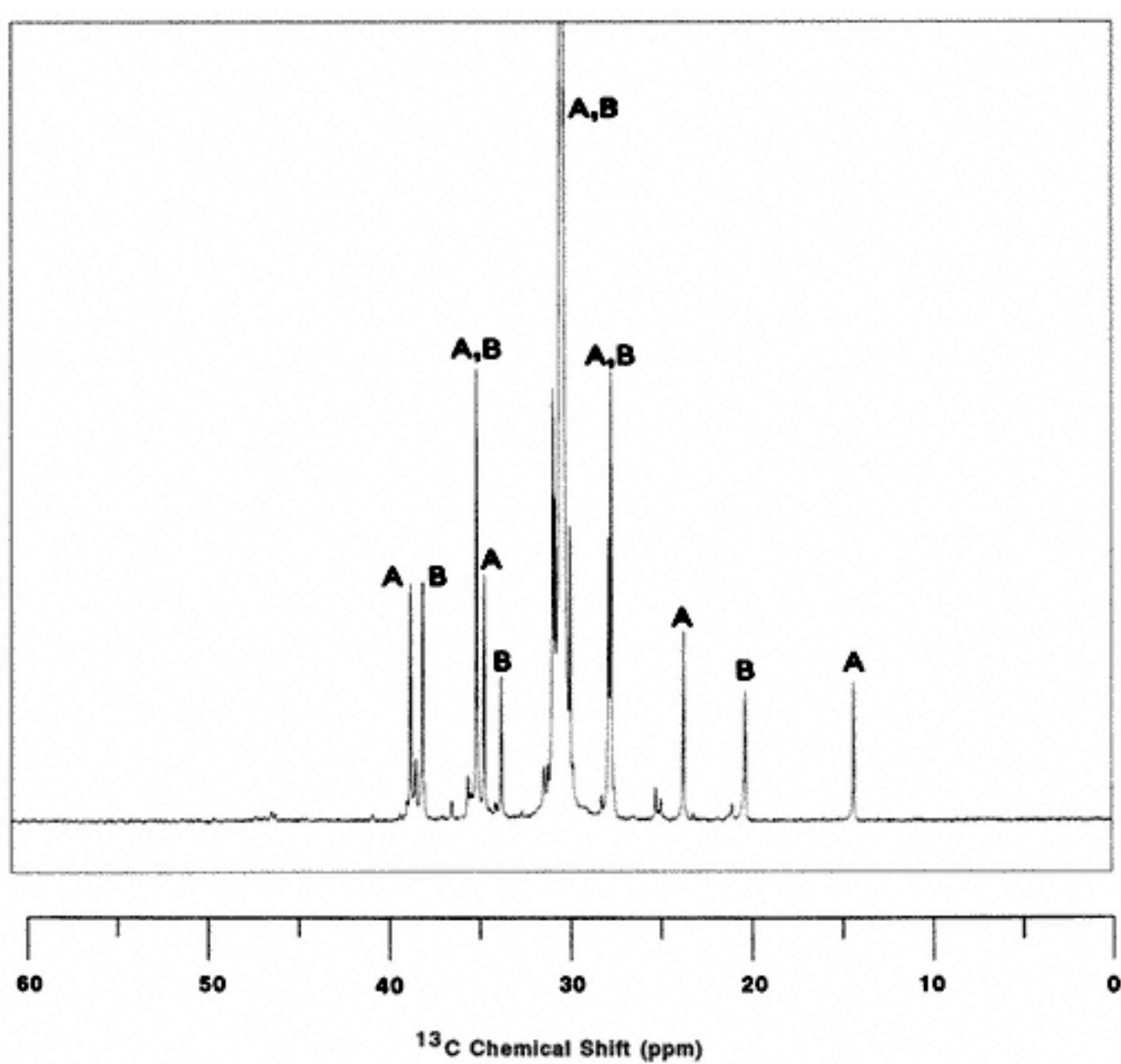
Pulse delay: 2 s

II-A-40—

Poly(Ethylene-Co-1-Hexene)/Poly(Ethylene-Co-Ppropylene)(60% E), 90/10 Blend

Comments

The set of observed resonances is the weighted sum of the component polymers, hexene-LLDPE {II-A-16} (denoted by **A**) and EPR {II-A-8} (denoted by **B**); see these entries for detailed assignments. The relative intensities of these peaks will vary according to the exact blend ratio and 1-hexene content of the LLDPE component. The addition of EPR improves the toughness of the base polymer.



Code	Shift (ppm)
A (EH)	38.2
B (EPR)	37.6
A,B	34.6
A	34.2
B	33.3
A,B	30.0
A,B	27.3
A	23.2
B	20.1
A	14.1

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

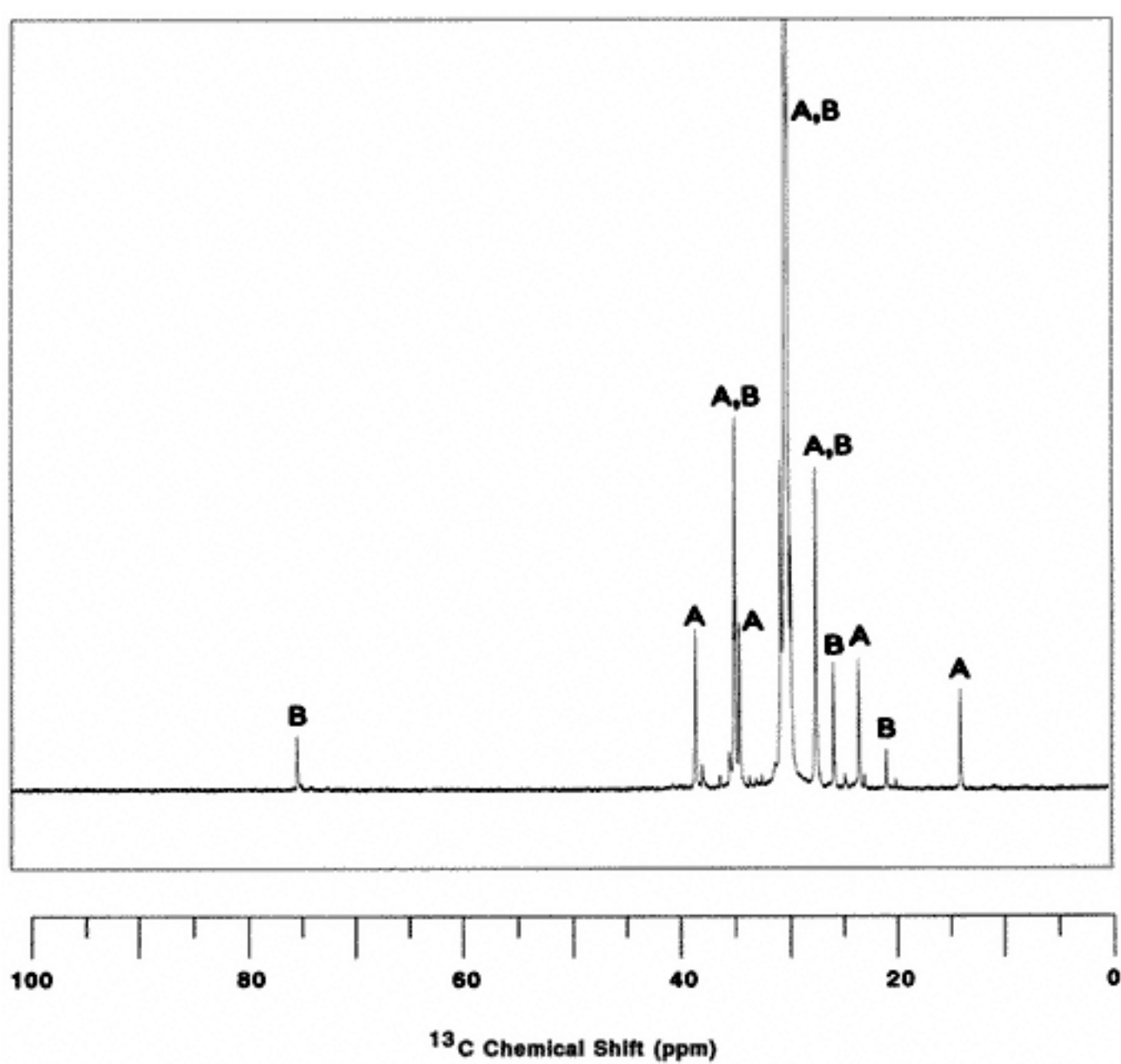
Pulse delay: 2 s

II-A-41—

Poly(Ethylene-Co-1-Hexene)/Poly(Ethylene- Co-Vinyl Acetate)(14% VA), 80/20 Blend

Comments

The set of observed resonances is the weighted sum of the component polymers, hexene-LLDPE {II-A-16} (denoted by **A**) and EVA {II-A-24} (denoted by **B**); see these entries for detailed assignments. The relative intensities of these peaks will vary according to the exact blend ratio and 1-hexene content of the LLDPE component; in some cases, EVA may be the dominant component. These resins are often blended to produce materials of intermediate properties.



Code	Shift (ppm)
B (EVA)	74.6
A (EH)	38.2
A,B	34.6
A	34.2
A,B	30.0
A,B	27.3
B	25.7
A	23.4
B	20.8
A	14.1

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

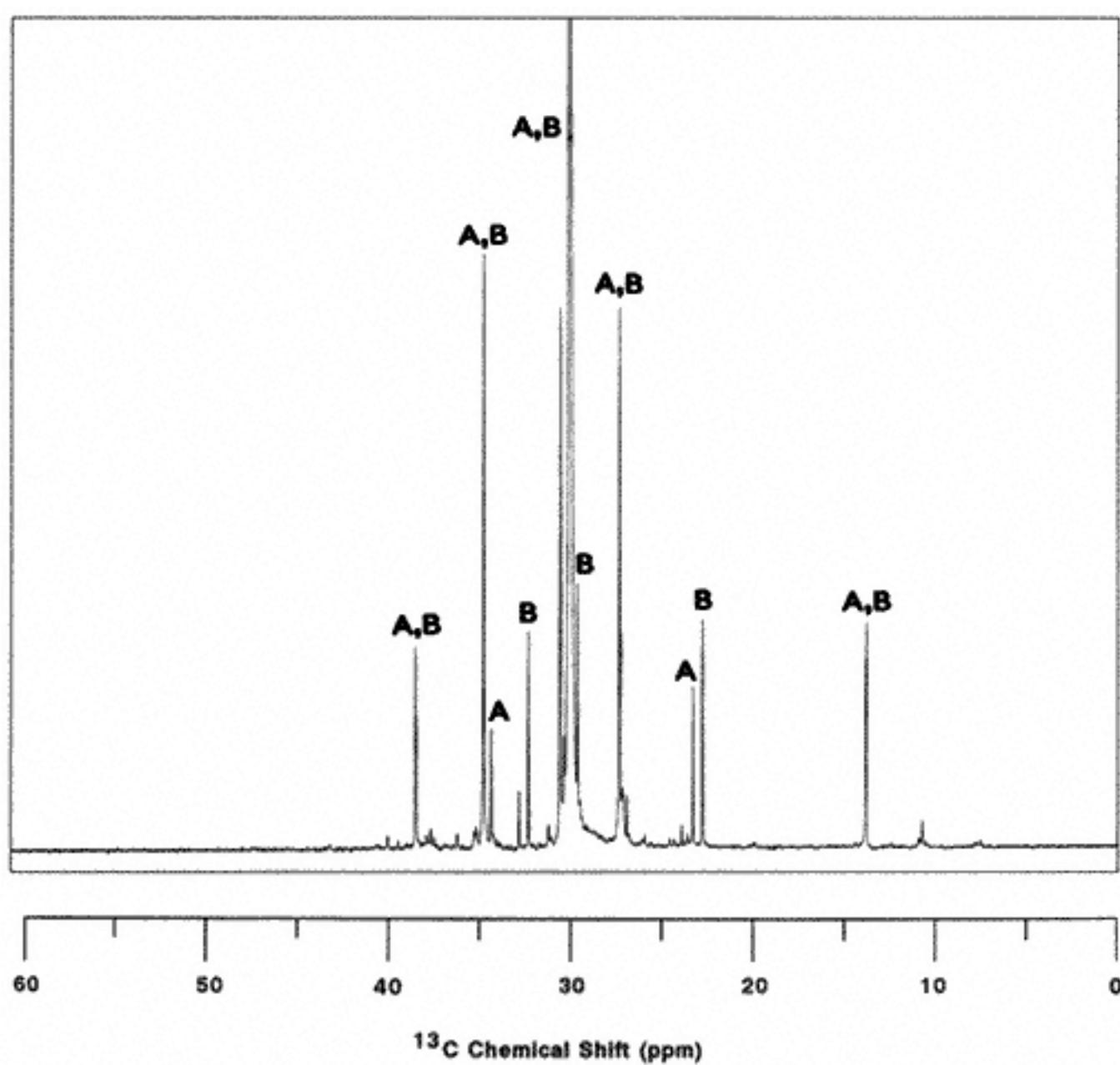
Pulse delay: 2 s

II-A-42—

Poly(Ethylene-Co-1-Octene)/Polyethylene, Branched, 80/20 Blend

Comments

The set of observed resonances is the weighted sum of the component polymers, octene-LLDPE {II-A-20} (denoted by **A**) and LDPE {II-A-3} (denoted by **B**); see these entries for detailed assignments. The relative intensities of these peaks will vary according to the exact blend ratio and 1-octene content of the LLDPE component; in some cases, LDPE may be the dominant component. These resins are often blended to produce materials of intermediate properties.



Code	Shift (ppm)
A,B	38.2
A,B	34.6
B (EO)	34.2
B	32.2
A,B	30.0
A,B	27.3
A (LDPE)	23.3
A,B	22.9
A,B	14.1

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

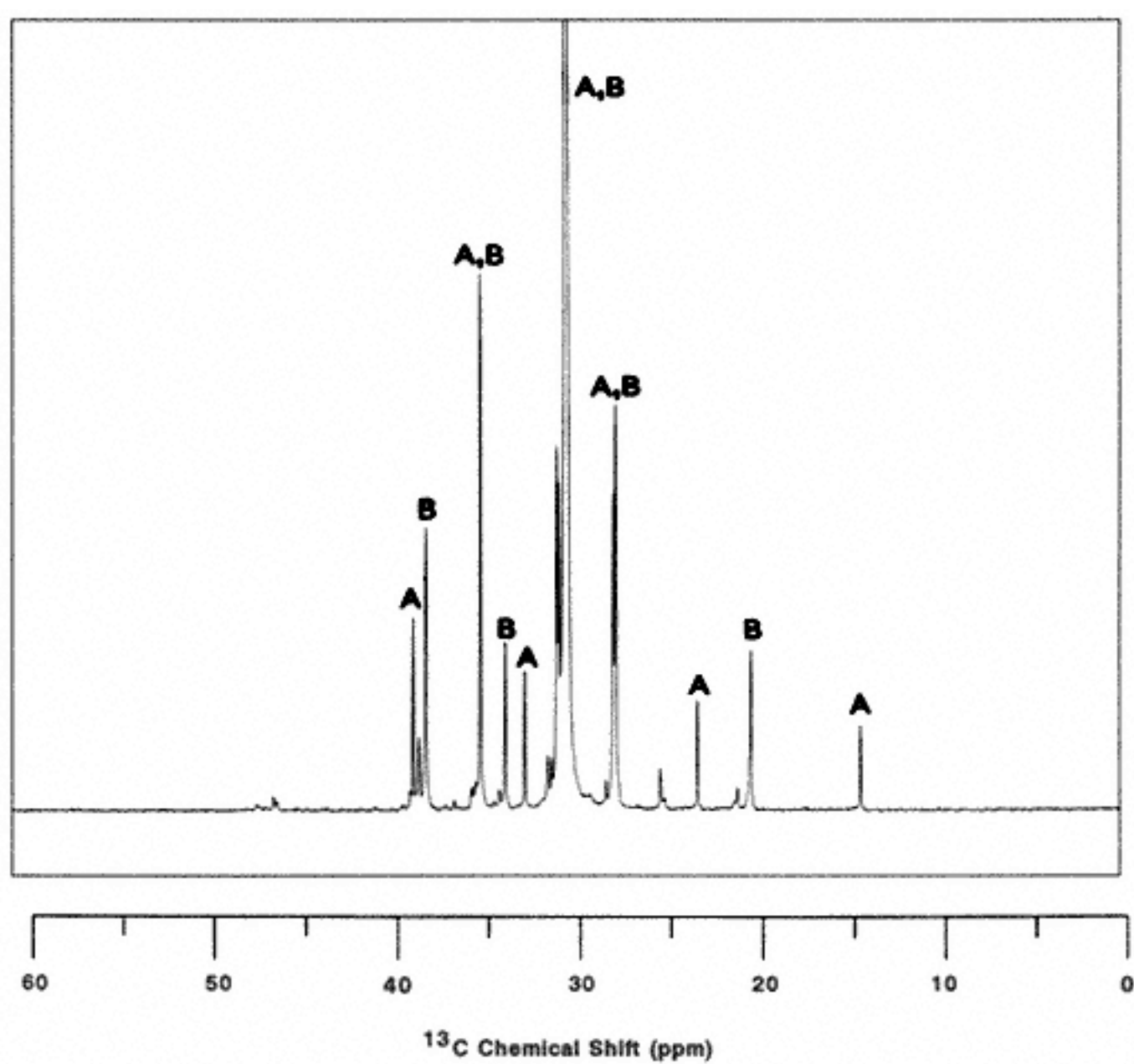
Pulse delay: 2 s

II-A-43—

Poly(Ethylene-Co-1-Octene)/Poly(Ethylene-Co-Propylene)(60% E), 90/10 Blend

Comments

The set of observed resonances is the weighted sum of the component polymers, octene-LLDPE {II-A-20}, (denoted by **A**), and EPR {II-A-8}, (denoted by **B**); see these entries for detailed assignments. The relative intensities of these peaks will vary according to the exact blend ratio. The addition of EPR improves the toughness of the base polymer.



Code	Shift (ppm)
A (EO)	38.2
B (EPR)	37.6
A,B	34.6
B	33.3
A	32.2
A,B	30.0
A,B	27.3
A	22.9
B	20.1
A	14.1

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

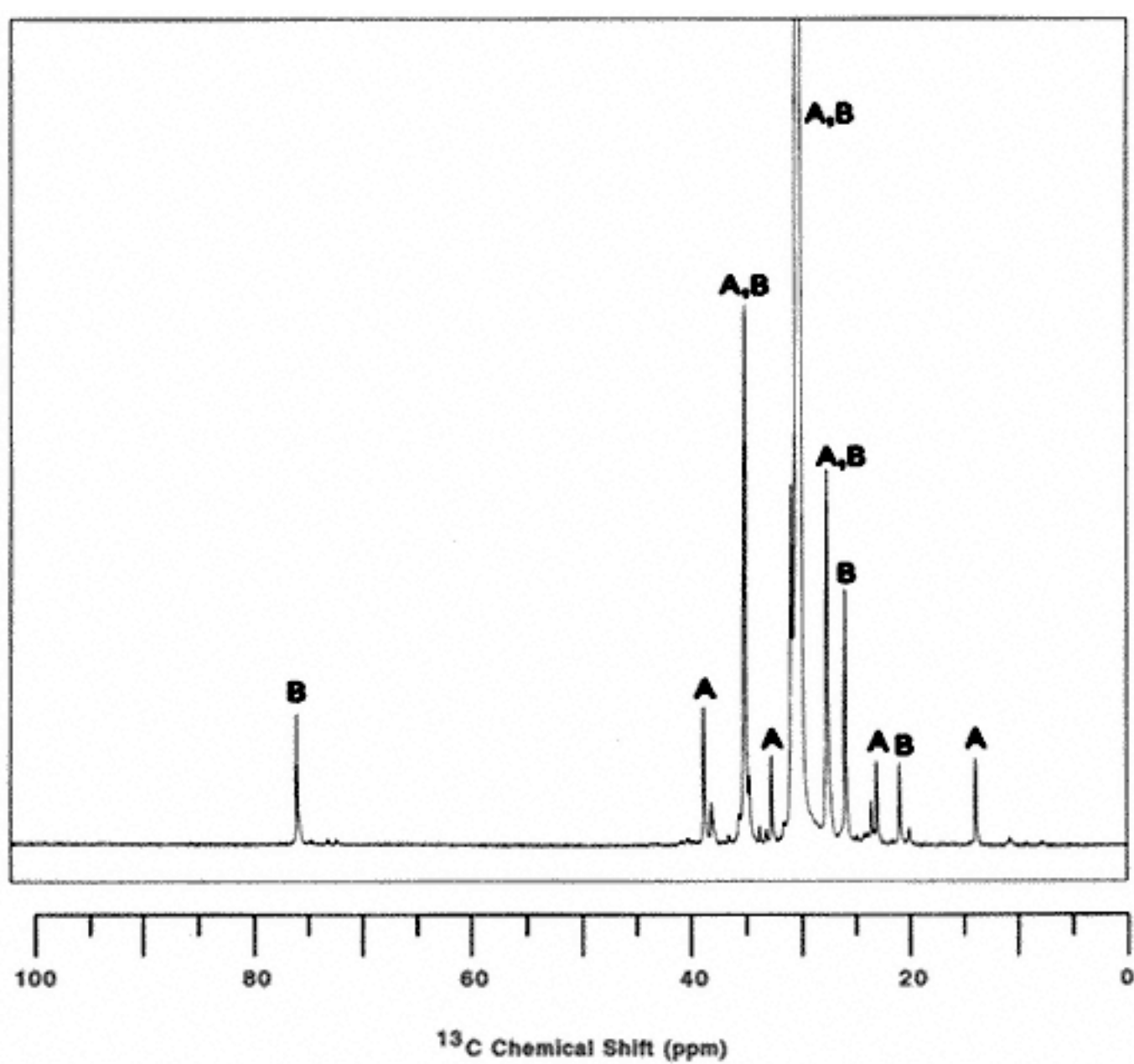
Pulse delay: 2 s

II-A-44—

Poly(Ethylene-Co-1-Octene)/Poly(Ethylene-Co-Vinyl Acetate) (14% VA), 80/20 Blend

Comments

The set of observed resonances is the weighted sum of the component polymers, octene-LLDPE, {II-A-20}, (denoted by **A**), and EVA {II-A-24}, (denoted by **B**); see these entries for detailed assignments. The relative intensities of these peaks will vary according to the exact blend ratio and 1-octene content of the LLDPE component; in some cases, EVA may be the dominant component. These resins are often blended to produce materials of intermediate properties.



Code	Shift (ppm)
B (EVA)	74.6
A (EO)	38.2
A,B	34.6
A,B	30.0
A,B	27.3
B	25.7
A	22.9
B	20.8
A	14.1

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

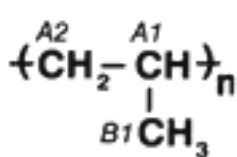
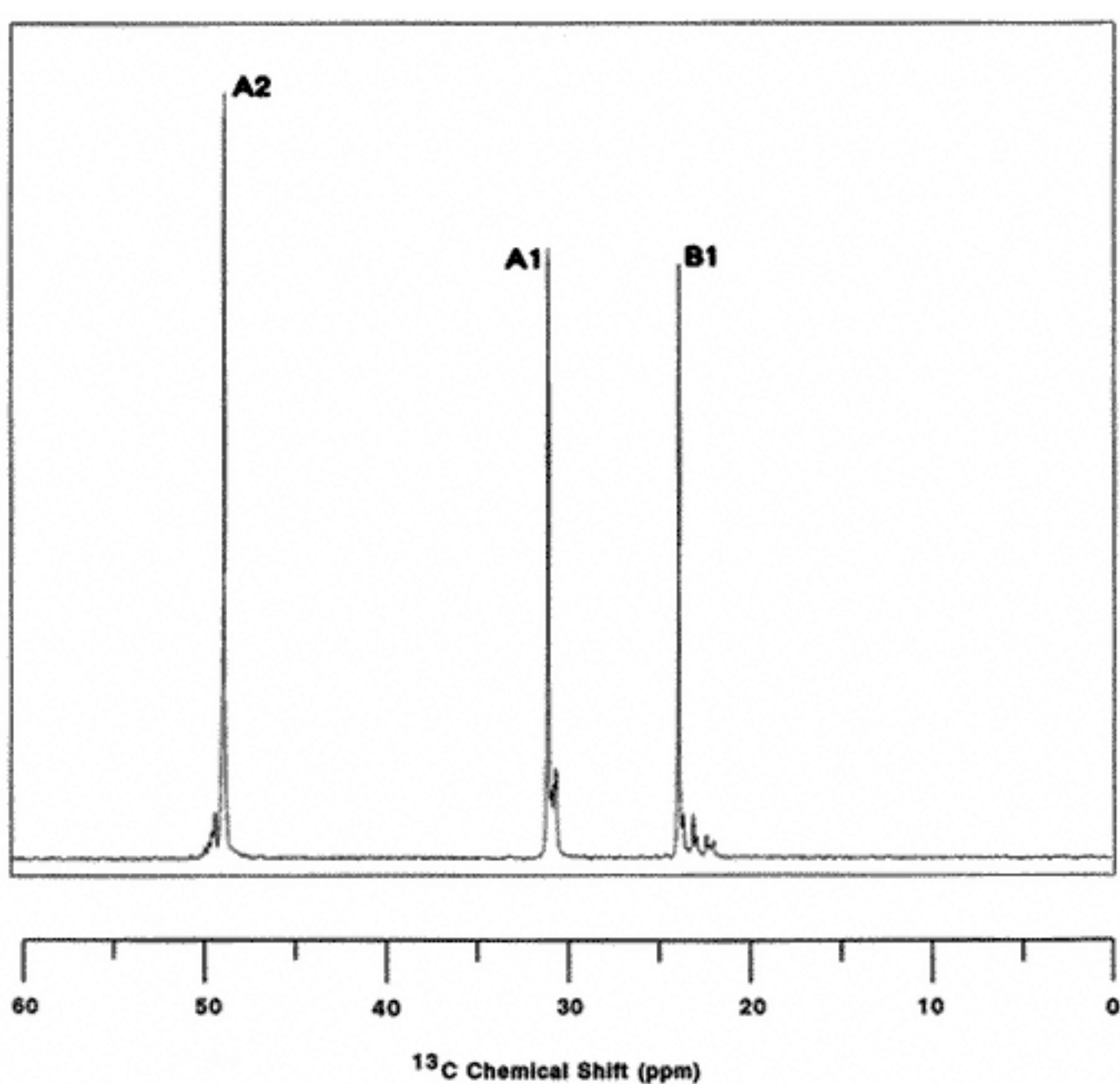
Broadening: 3 Hz

Pulse delay: 2 s

II-B-1— Polypropylene, Isotactic (iPP)

Comments

Splitting of resonances, particularly the methyl carbon at 23 ppm, is due to tacticity of the polymer chain. Isotactic PP has, primarily (85–99%), *mm* sequences, in which methyl groups are situated on the same side of the chain. PP is a thermoplastic commonly used in filaments, fibers, housewares, packaging, and shrink film; it melts at ~160°C.



Code	Shift(ppm)
A1	30.8
A2	48.4
B1	23.6

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 130°C
Solvent: ODCB- d_4 /TCB (3/1 v/v)	Concentration: 30% w/w
Scans: 200	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 3 Hz	Pulse delay: 2 s

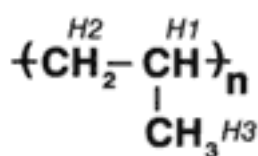
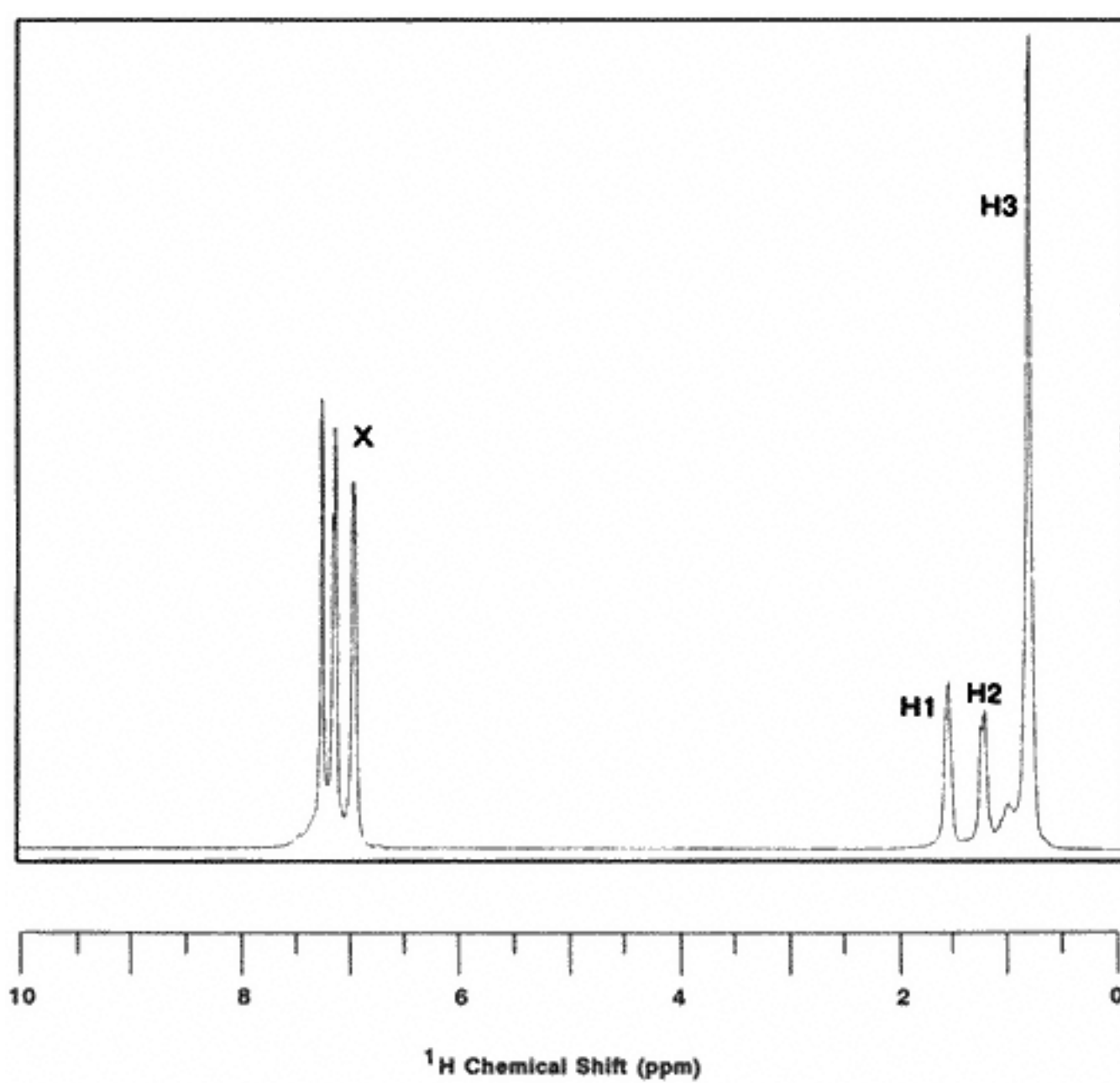
Reference

R. Paukkeri, R. Vaananen, and A. Lehtinen. *Polymer* 34:2488, 1993.

II-B-1H— Polypropylene, Isotactic (iPP)

Comments

Isotactic PP has, primarily (85–99%), *mm* sequences, in which methyl groups are situated on the same side of the chain. PP is a thermoplastic commonly used in filaments, fibers, housewares, packaging, and shrink film; it melts at ~160°C.



Code	Shift (ppm)
H1	1.59
H2	1.27
H3	0.88

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 100

Spectral width: 8 kHz

Data points: 4096

Pulse width: 30°

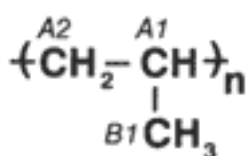
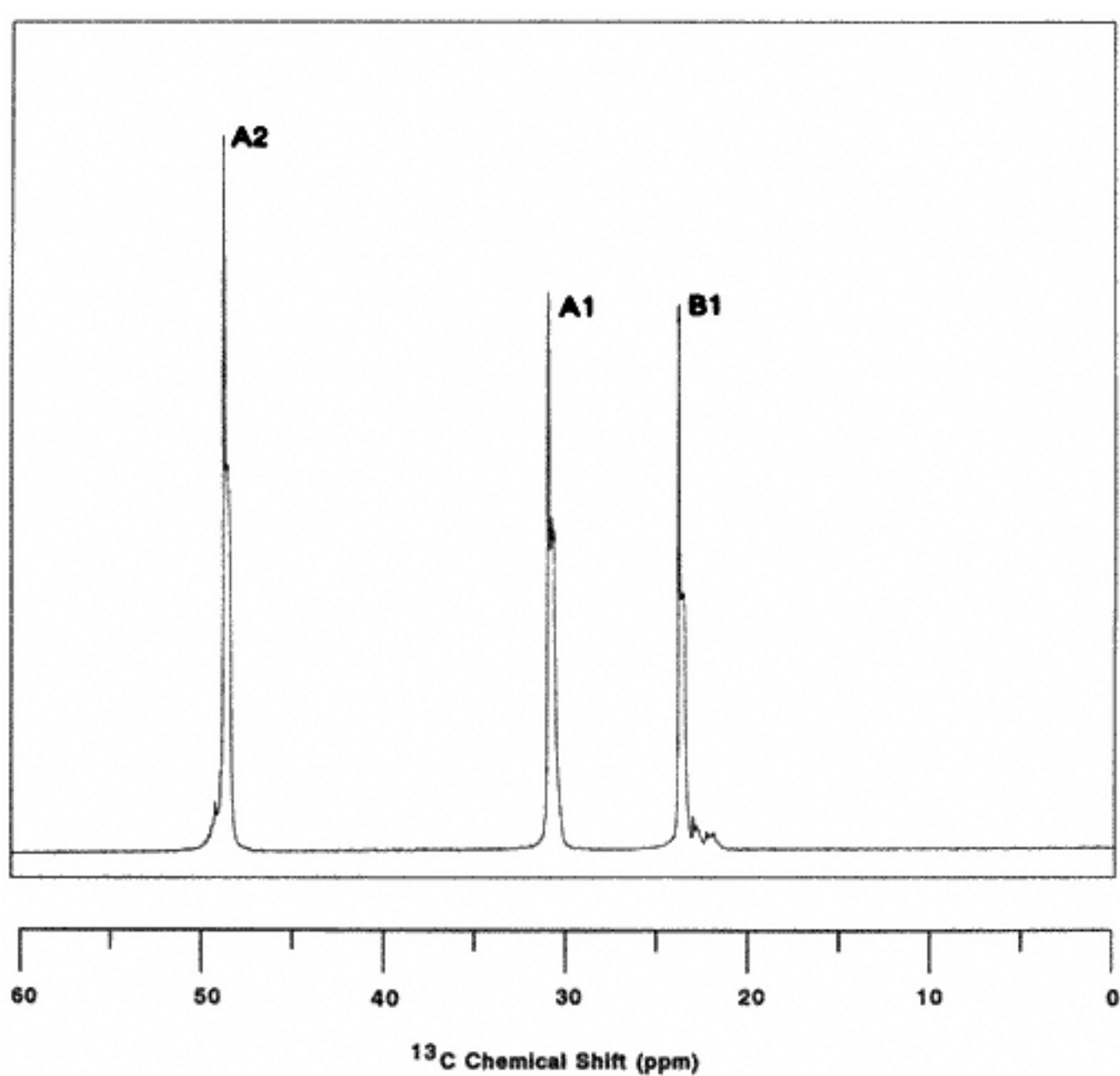
Broadening: 3 Hz

Pulse delay: 5 s

II-B-2— Polypropylene, Stereoblock

Comments

Splitting of resonances, particularly the methyl carbon at 23 ppm, is due to tacticity of the polymer chain. Stereoblock PP is less stereoregular than isotactic PP; it has relatively short *mm* sequences, in which methyl groups are situated on the same side of the chain. PP is a thermoplastic commonly used in filaments, fibers, housewares, packaging, and shrink film.



Code	Shift (ppm)
A1	30.8
A2	48.4
B1	23.7

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

Reference

R. Paukkeri, R. Vaananen, and A. Lehtinen. *Polymer* 34:2488, 1993.

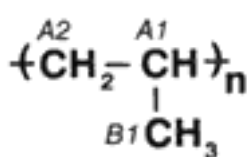
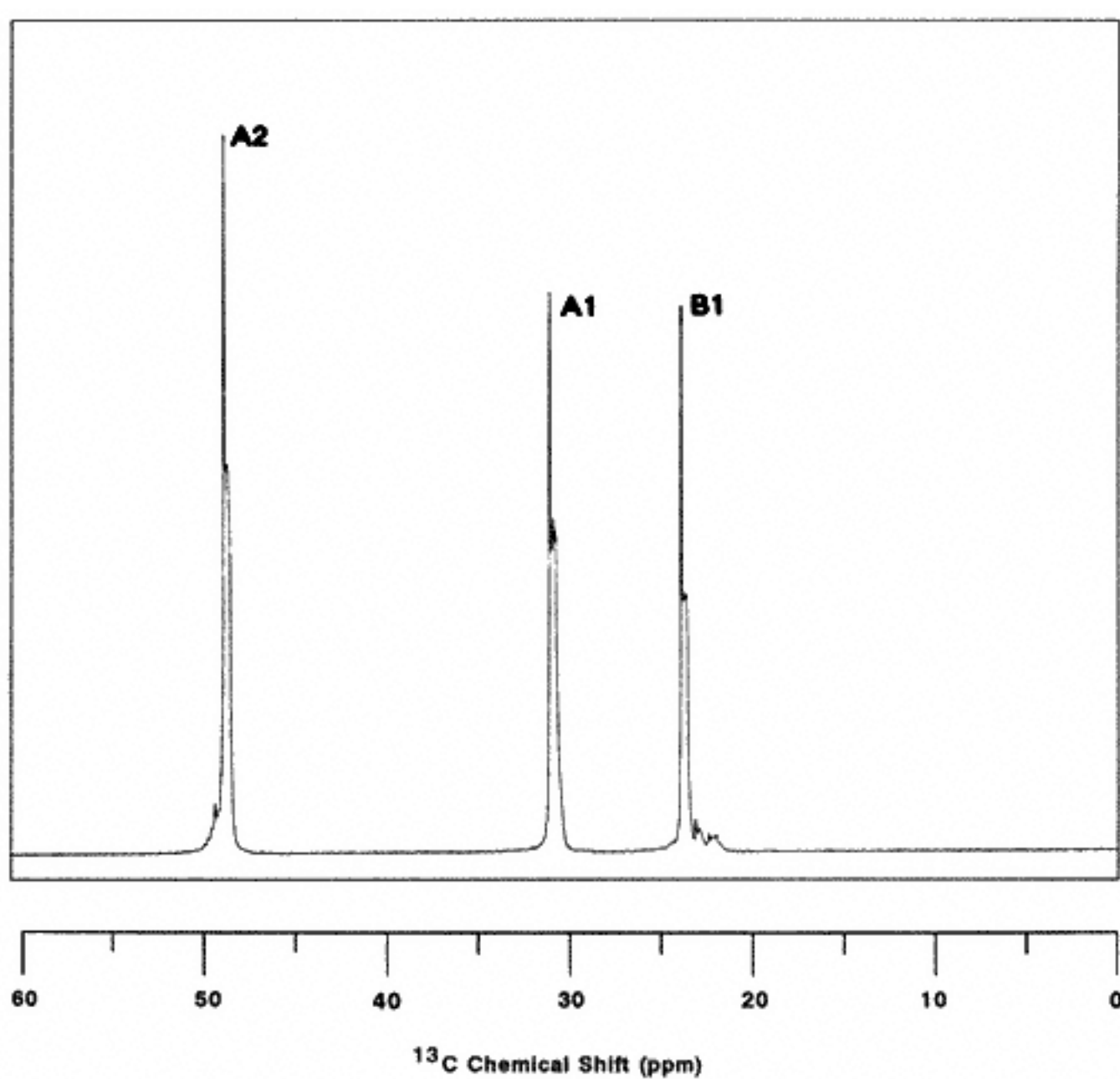
Source

Himont USA, Wilmington, DE.

II-B-3— Polypropylene Syndiotactic (sPP)

Comments

Splitting of resonances, particularly the methyl carbon at 22 ppm, is due to tacticity of the polymer chain. Syndiotactic PP has, primarily (> 90%), *rr* sequences, in which methyl groups are situated on alternating sides of the chain. sPP is a relatively new material; its uses are not yet well established. It melts at ~160°C.



Code	Shift (ppm)
A1	30.6
A2	49.3
B1	22.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 130°C
Solvent: ODCB- d_4 /TCB (3/1 v/v)	Concentration: 30% w/w
Scans: 200	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 3 Hz	Pulse delay: 2 s

Reference

M. Kakugo, T. Miyatake, Y. Naito, and K. Mizumuma. *Makromol. Chem.* 190:505, 1989.

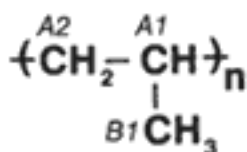
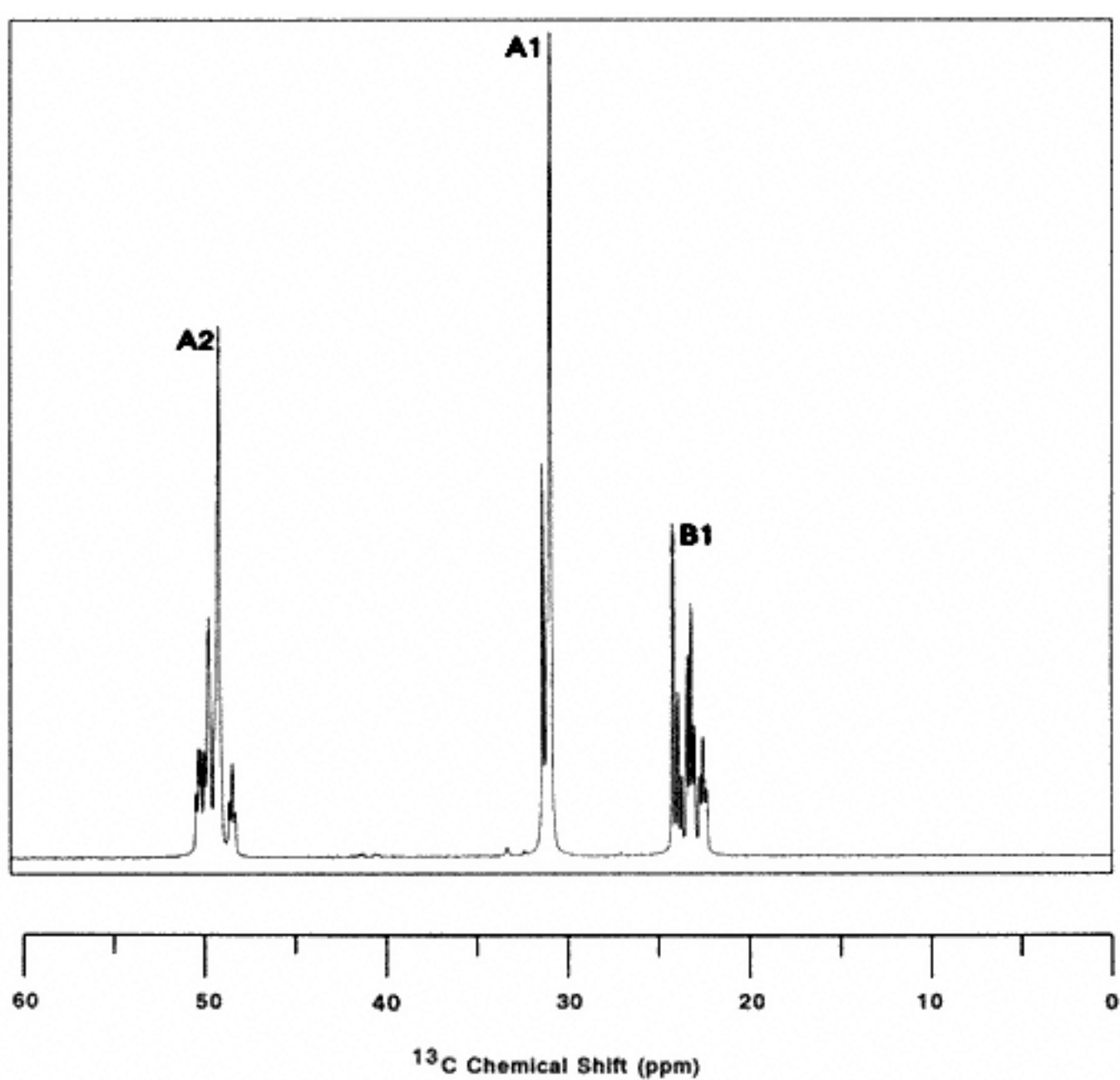
Source

Himont USA, Wilmington, DE.

II-B-4— Polypropylene, Atactic (aPP)

Comments

Splitting of resonances, particularly the methyl carbon at 22 ppm, is due to tacticity of the polymer chain. Atactic PP has comparable levels of *mm*, *mr*, and *rr* groups, because the methyl groups are randomly situated along the chain. aPP is used as an adhesive.



Code	Shift (ppm)
A1	30.5, 31.1
A2	47.7–49.5
B1	22.2–23.9

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

Reference

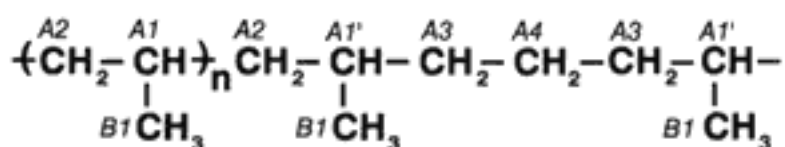
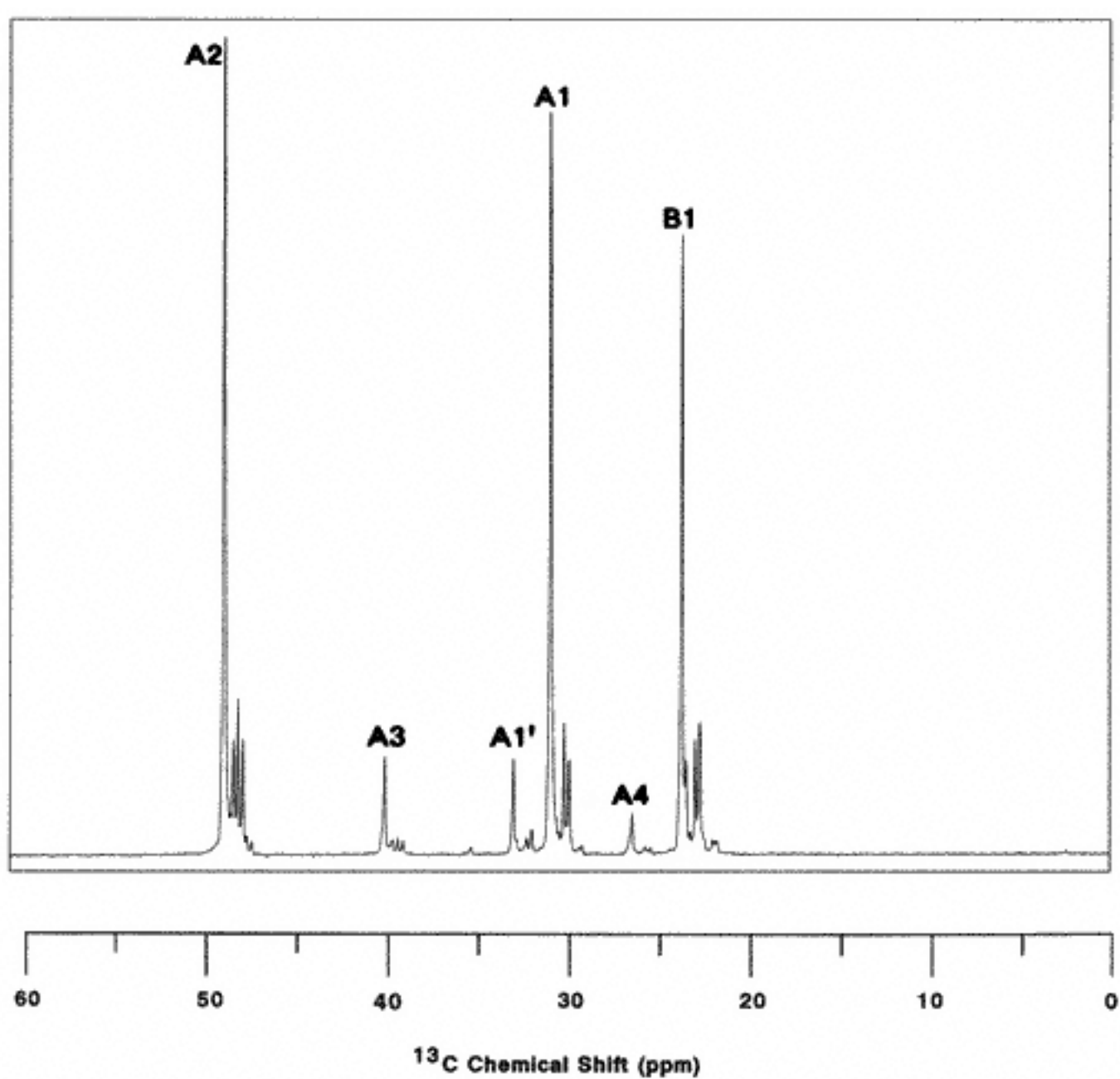
R. Paukkeri, R. Vaananen, and A. Lehtinen. *Polymer* 34:2488, 1993.

II-B-5—

Poly(Propylene-Co-Ethylene) [5%E]

Comments

The propylene segments are mostly isotactic; the ethylene monomers are randomly distributed along the chain. This material has improved clarity and flexibility compared with iPP homopolymer; it is used to produce bottles, films, packaging, and shrink wrap.



Code	Shift (ppm)
A1	30.3
A1'	32.3
A2	47.9
A3	38.9
B1	23.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

Reference

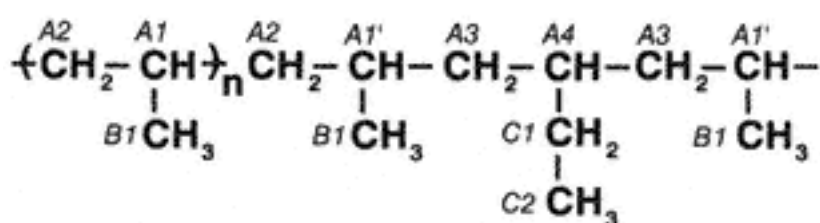
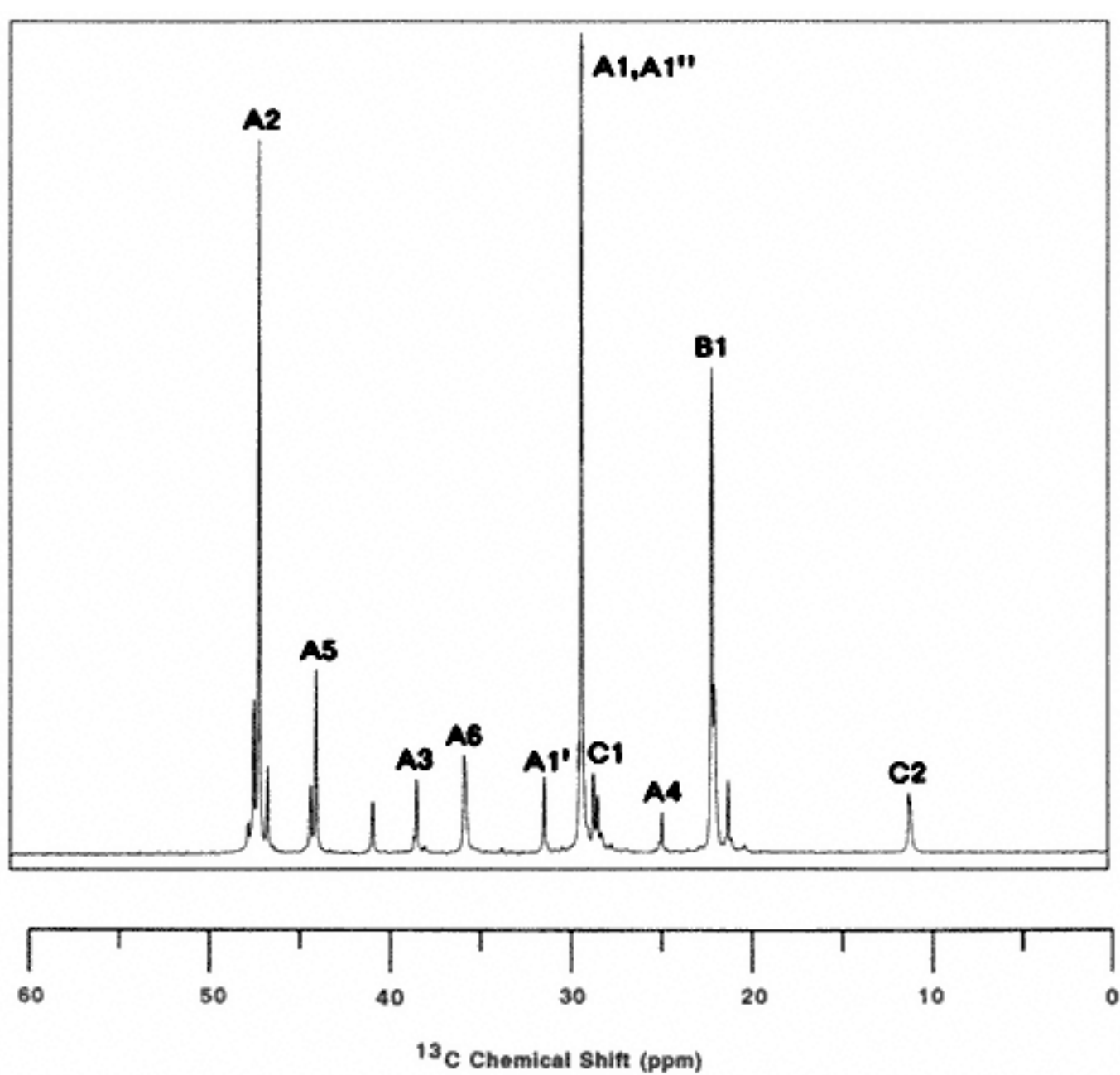
J. R. Paxson and J. C. Randall. *Anal. Chem.* 50:1777, 1978.

II-B-6—

Poly(Propylene-Co-1-Butene)

Comments

The propylene segments are mostly isotactic; the butene monomers are randomly distributed along the chain. This material has improved clarity and flexibility compared with iPP homopolymer; it is used to produce bottles, films, packaging, and shrink wrap.



Code	Shift (ppm)
A1	28.4
A1'	28.4
A2	46.3
A3	43.2
A4	35.7
B1	21.6
C1	28.3
C2	10.6

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

References

A. Aoki, T. Hayashi, T. Asakura. *Macromolecules* 25:155, 1992; H. N. Cheng. *J. Polym. Sci. Polym. Phys. Ed.* 21:573, 1983; J. C. Randall. *Macromolecules* 11:592, 1978.

Source

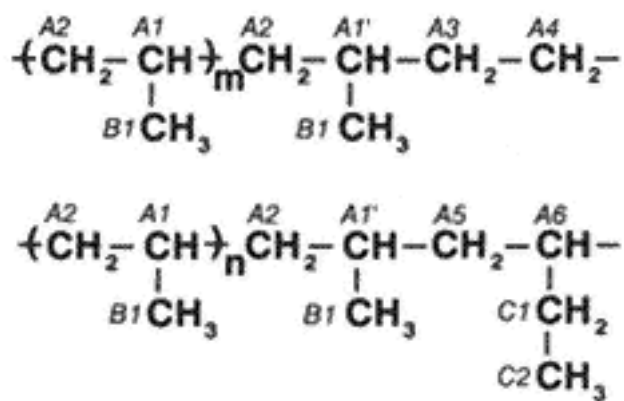
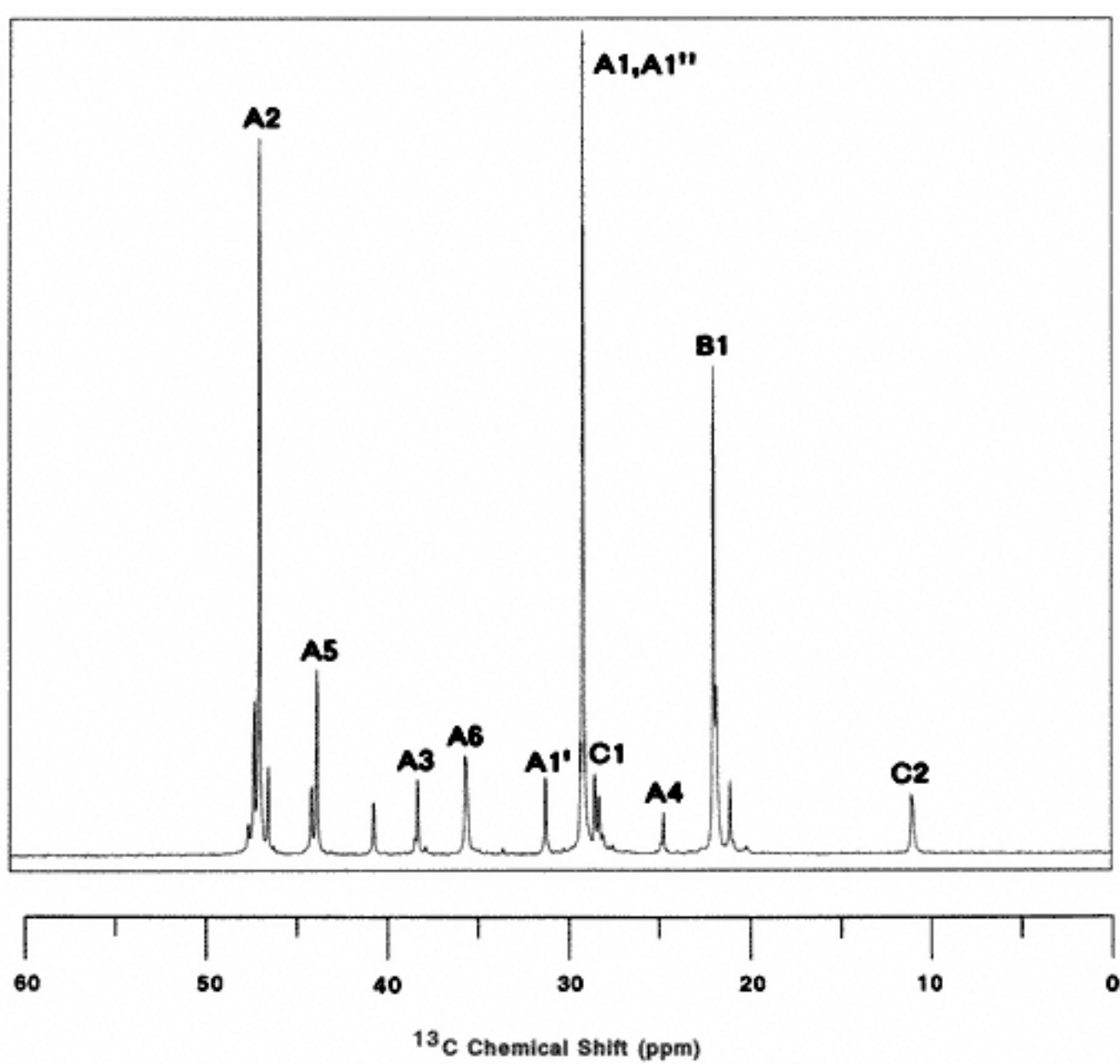
H. N. Cheng, Hercules, Inc., Wilmington, DE.

II-B-7—

Poly(Propylene-Co-1-Butene-Co-Ethylene)

Comments

The propylene segments are mostly isotactic; the ethylene and butene monomers are randomly distributed along the chain. This material has improved clarity and flexibility compared with iPP homopolymer; it is used to produce bottles, films, packaging, and shrink wrap.



Code	Shift (ppm)
A1	28.7
A1'	30.0
A2	46.4
A3	37.7
A4	24.4
A5	43.5
A6	35.2
B1	21.7
C1	27.9
C2	10.9

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

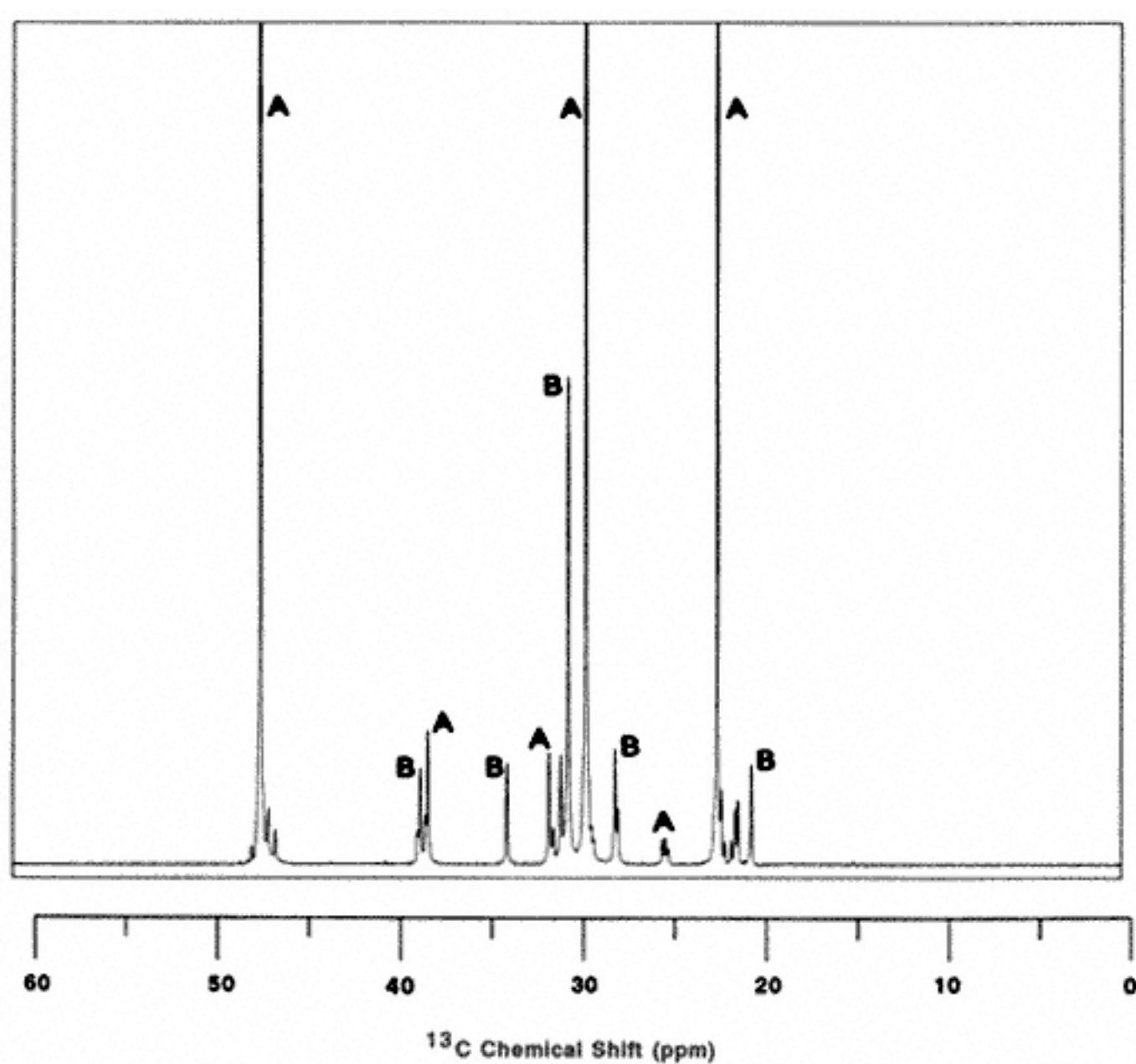
Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

II-B-8—**Poly(Propylene-Co-Ethylene)/Poly(Ethylene-Co-Propylene) (40%P), 80/20 Blend****Comments**

The set of observed resonances is the weighted sum of the component polymers, poly(propylene-co-ethylene) {II-B-6}, denoted by **A** and EPR {II-A-8}, denoted by **B**; see these entries for detailed assignments. The relative intensities of these peaks will vary according to the exact blend ratio. EPR is added to improve the toughness of the base polymer.



Code	Shift (ppm)
A (PrE)	46.6
B (EPR)	38.0
A	37.6
B	33.3
A	31.4
B	30.0
A	29.1
B	27.5
A	24.4
A	21.8, 21.0
B	20.1

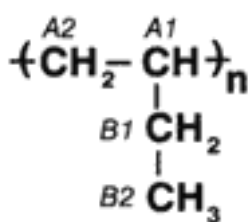
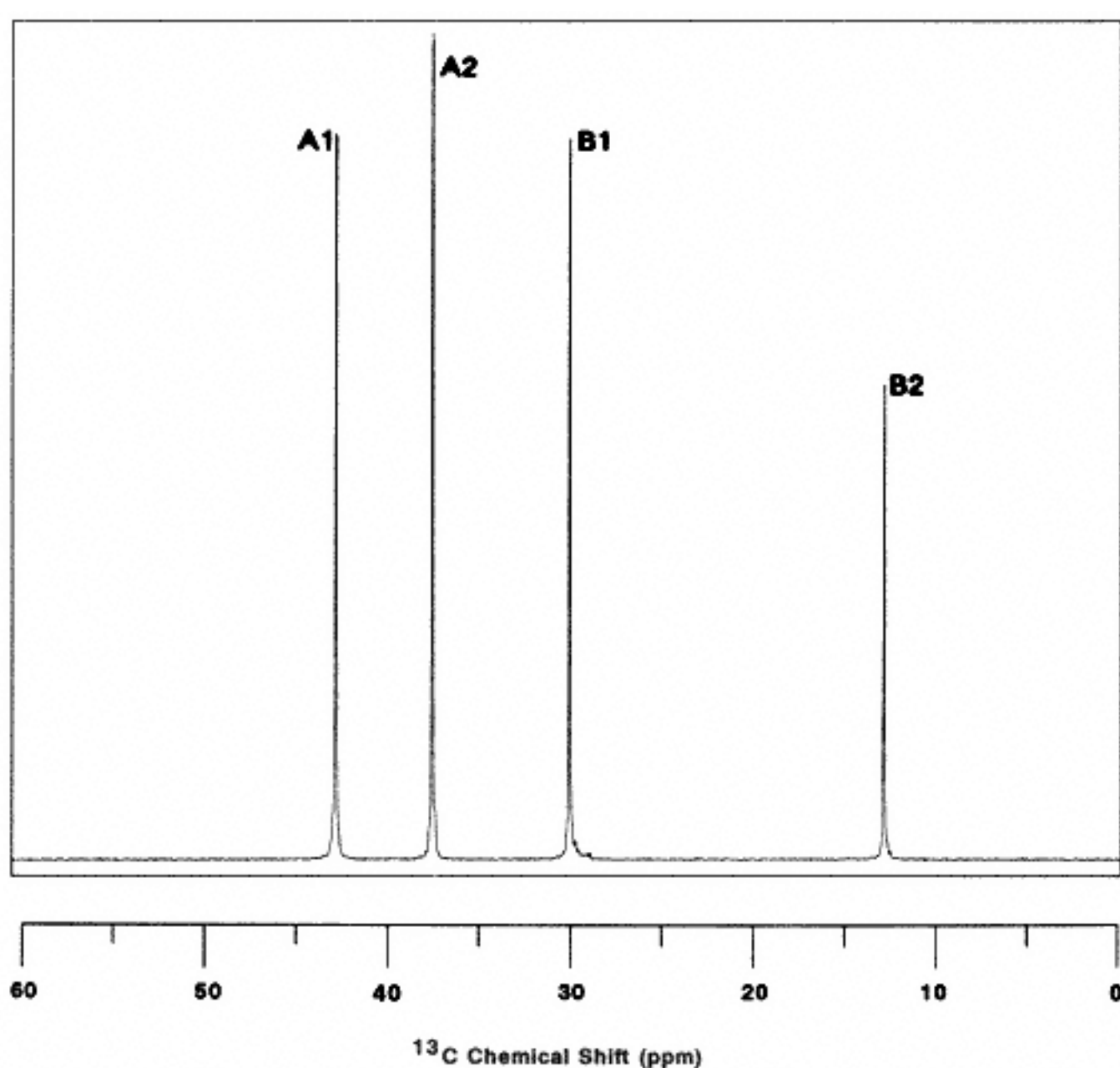
Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 130°C
Solvent: ODCB- d_4 /TCB (3/1 v/v)	Concentration: 30% w/w
Scans: 200	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 3 Hz	Pulse delay: 2 s

**II-C-1—
Poly(1-Butene), Isotactic (PB)**

Comments

Slight tacticity splitting can be observed, particularly for the methyl resonance at 12.9 ppm. The polymer is commonly used for pipe, cable insulation, and food packaging; it melts between 125 and 130°C.



Code	Shift (ppm)
A1	42.4
A2	37.3
B1	29.9
B2	12.9

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

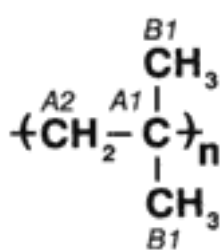
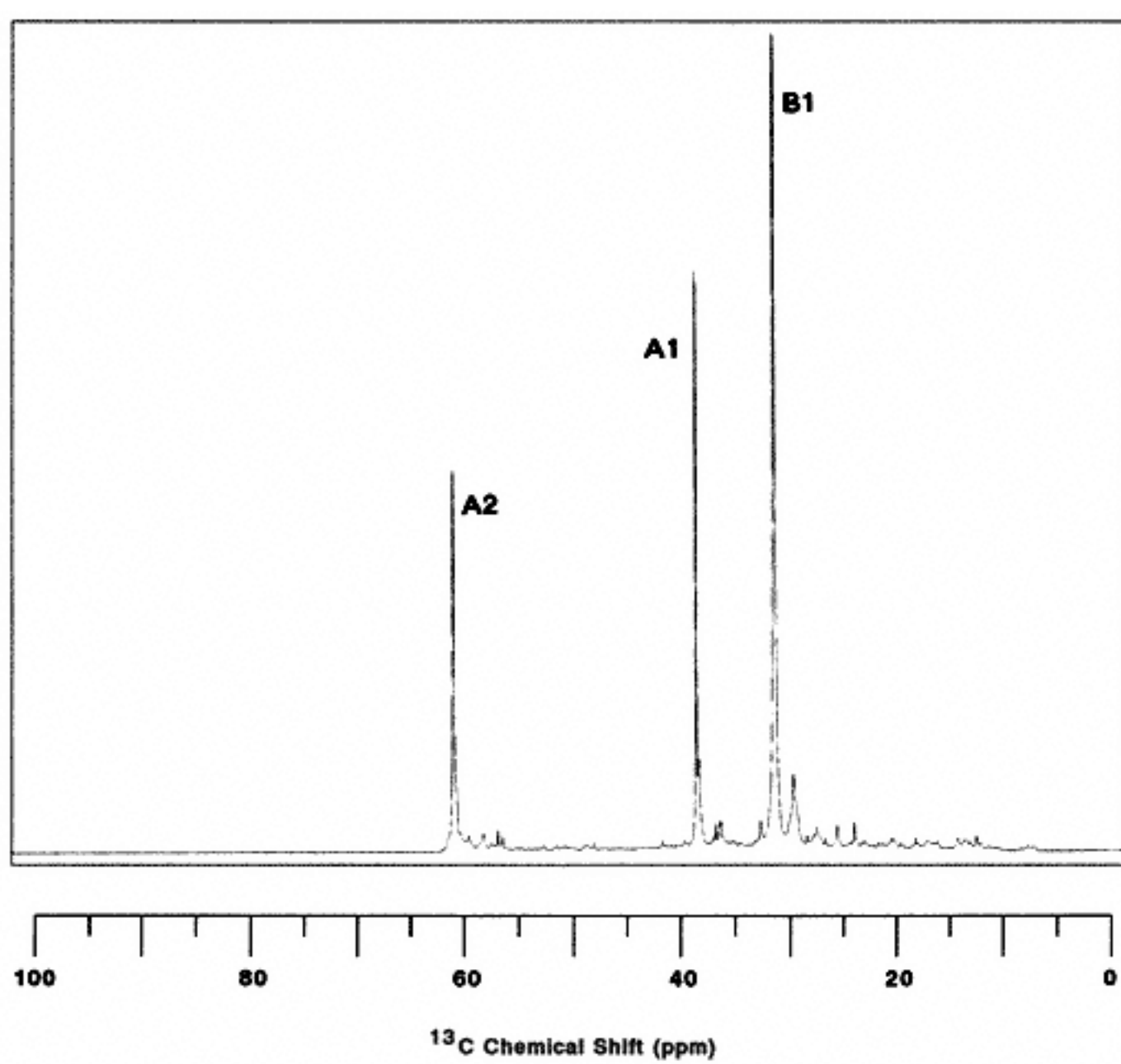
Reference

T. Asakura, K. Omaki, K. Yatamoto, S. Zhu, and R. Chujo. *Rep. Prog. Polym. Phys. Jn.* 27:557, 1984.

**II-C-2—
Polyisobutylene (PIB)**

Comments

The small resonances arise primarily from various chain-end structures in this low-MW sample. Low-MW PIB is sometimes added to polymers, such as polyethylene, to increase film tackiness, or to polystyrene to improve processing ease. Higher-MW forms are elastomeric.



Code	Shift (ppm)
A1	38.6
A2	60.0
B1	31.6

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

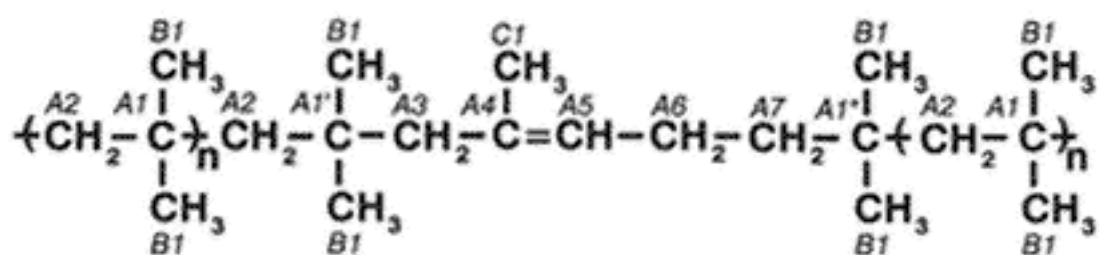
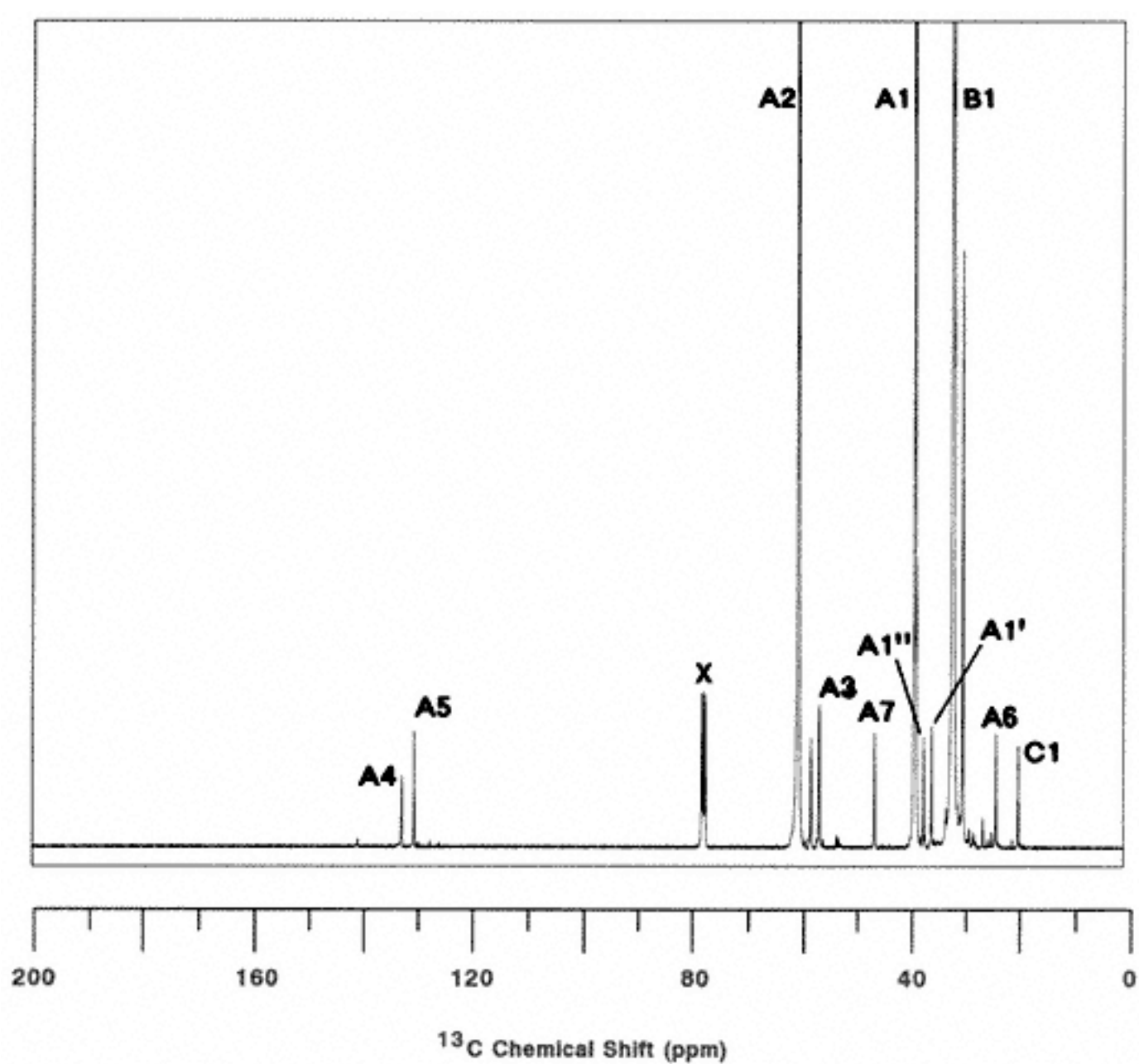
II-C-3

II-C-3—

Poly(Isobutylene-Co-Isoprene) (BR, Butyl Rubber)

Comments

Isoprene is present in the *cis*-form. Solvent resonances are marked by X. Butyl rubber has low permeability to gases, but it tends to be incompatible in blends with other common elastomers. It is commonly used for tires and sporting goods.



Code	Shift (ppm)
A1	38.3
A1'	35.2
A1''	36.6
A2	59.7
A3	55.9
A4	132.3
A5	130.0
A6	23.2
A7	45.5
B1	31.3
C1	18.6

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

ReferenceC. Y. Chu and R. Vukov. *Macromolecules* 18:1423, 1985.**Source**

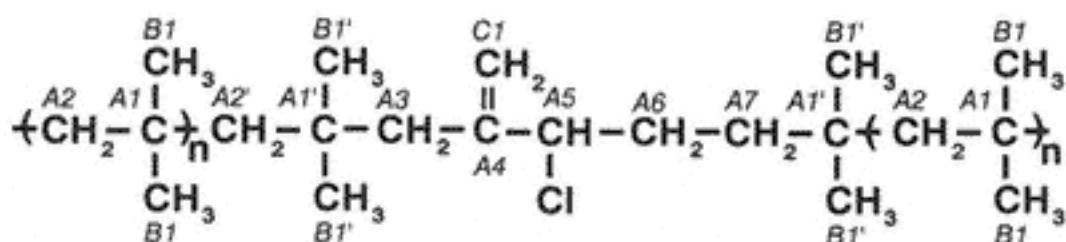
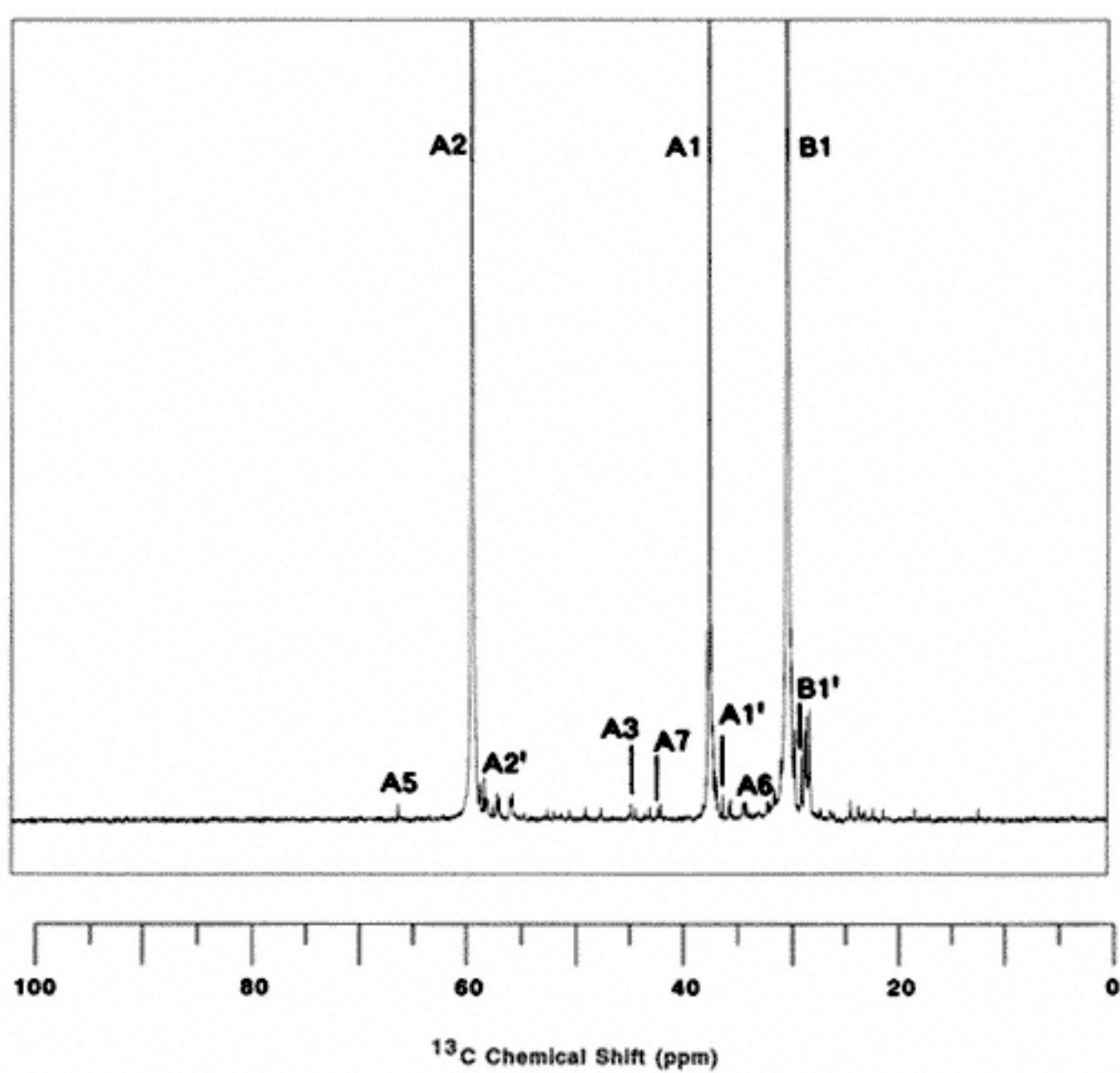
Exxon Chemical Company, Baytown, TX.

II-C-4—

Poly(Isobutylene-Co-Isoprene), Chlorinated (Chlorinated Butyl Rubber)

Comments

The small resonances arise primarily from various chain-end structures. Chlorination of the isoprene portion of the polymer causes rearrangement, which provides potential sites for cross-linking. Butyl rubber has low permeability to gases, but it tends to be incompatible in blends with other common elastomers. It is commonly used for tires and sporting goods.



Code	Shift (ppm)
A1	38.4
A1'	37.2
A2	60.0
A2'	57.6
A3	45.4
A4	147.0
A5	66.6
A6	35.0
A7	43.1
B1	31.3
B1'	29.7
C1	115.9

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

ReferenceC. Y. Chu, K. N. Watson, and R. Vukov. *Rubber Chem. Technol.* 60:636, 1987.**Source**

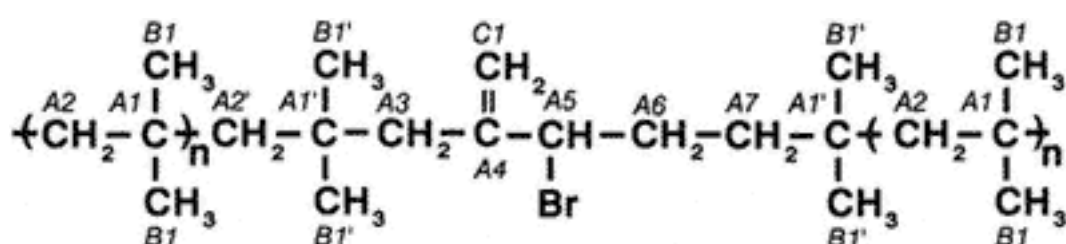
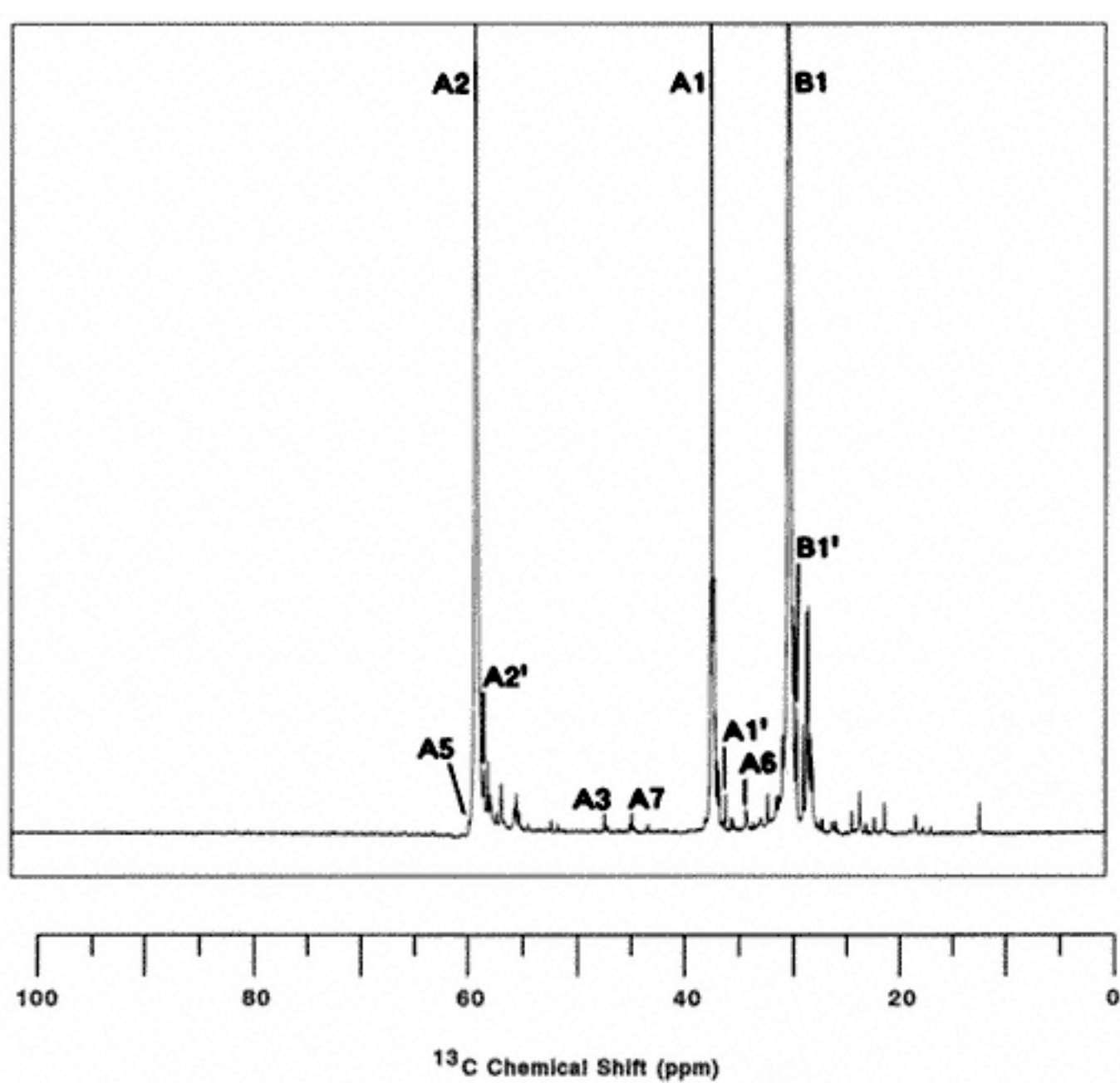
Exxon Chemical Company, Baytown, TX.

II-C-5—

Poly(Isobutylene-Co-Isoprene), Brominated (Brominated Butyl Rubber)

Comments

The small resonances arise primarily from various chain-end structures. Bromination of the isoprene portion of the polymer causes rearrangement, which provides potential sites for cross-linking. Butyl rubber has low permeability to gases, but it tends to be incompatible in blends with other common elastomers. It is commonly used for tires and sporting goods.



Code	Shift (ppm)
A1	38.4
A1'	37.1
A2	60.0
A2'	57.6
A3	47.9
A4	147.7
A5	60.2
A6	35.3
A7	45.9
B1	31.3
B1'	29.7
C1	116.3

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

Pulse delay: 2 s

ReferenceC. Y. Chu, K. N. Watson, and R. Vukov. *Rubber Chem. Technol.* 60:636, 1987.**Source**

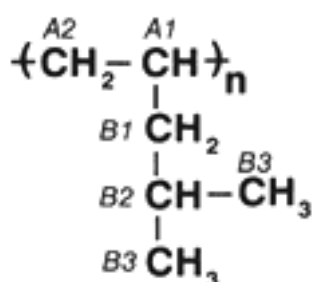
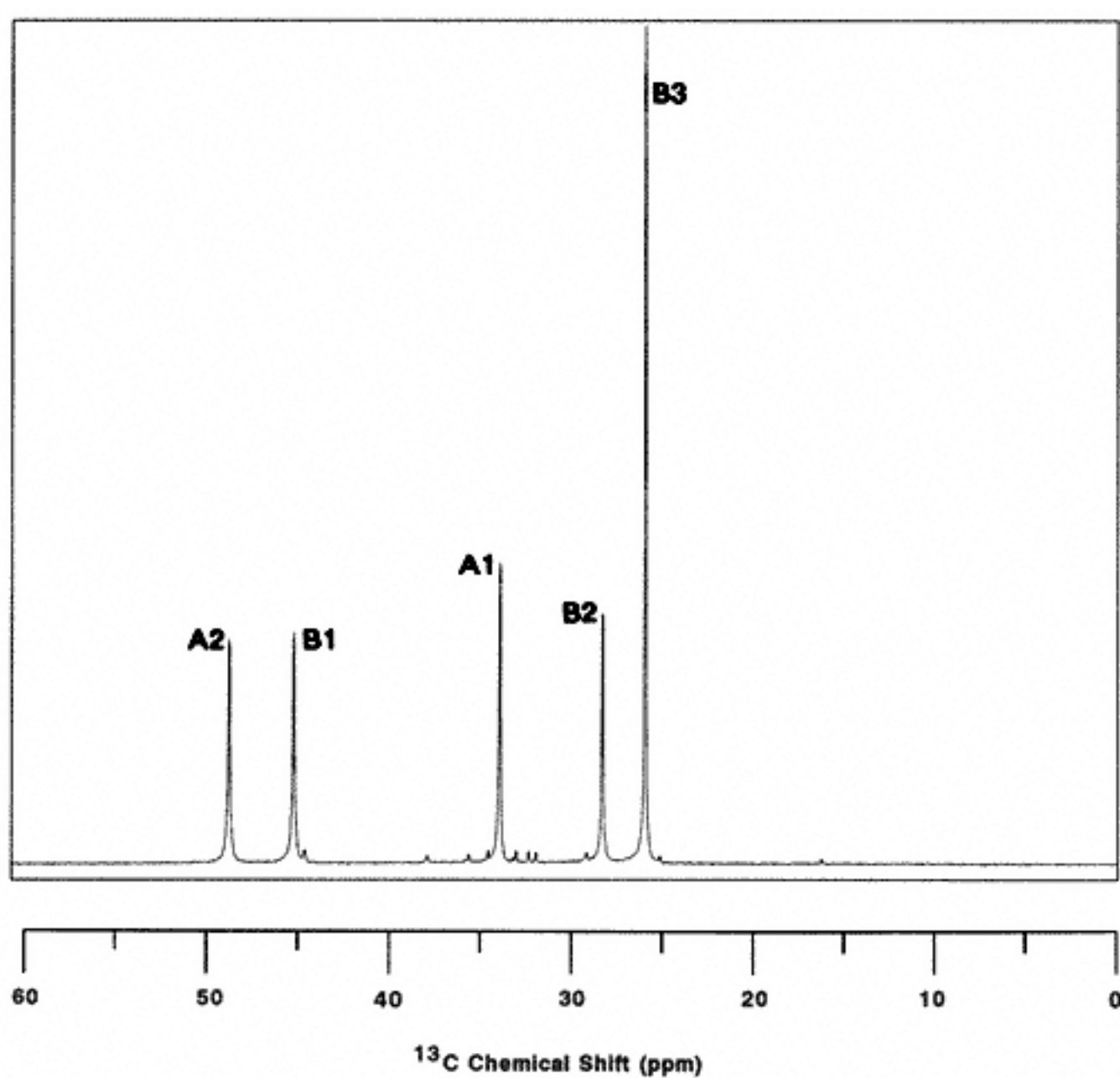
Exxon Chemical Company, Baytown, TX.

II-C-6—

Poly(4-Methyl-1-Pentene), Isotactic (PMP)

Comments

Little tacticity splitting is observed for this highly isotactic polymer. The material is very stiff, and has good electrical properties. It has a high melting point, $\sim 235^{\circ}\text{C}$, and retains its properties over a wide temperature range. Because of this, PMP is commonly used for food and cooking containers, lighting fixtures, and laboratory and medical ware.



Code	Shift (ppm)
A1	33.6
A2	48.1
B1	44.8
B2	27.9
B3	25.7

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 130°C
Solvent: ODCB- d_4 /TCB (3/1 v/v)	Concentration: 30% w/w
Scans: 200	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 3 Hz	Pulse delay: 2 s

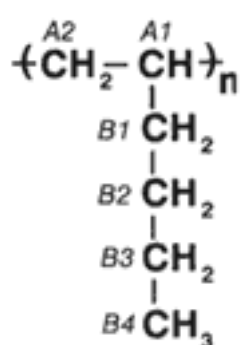
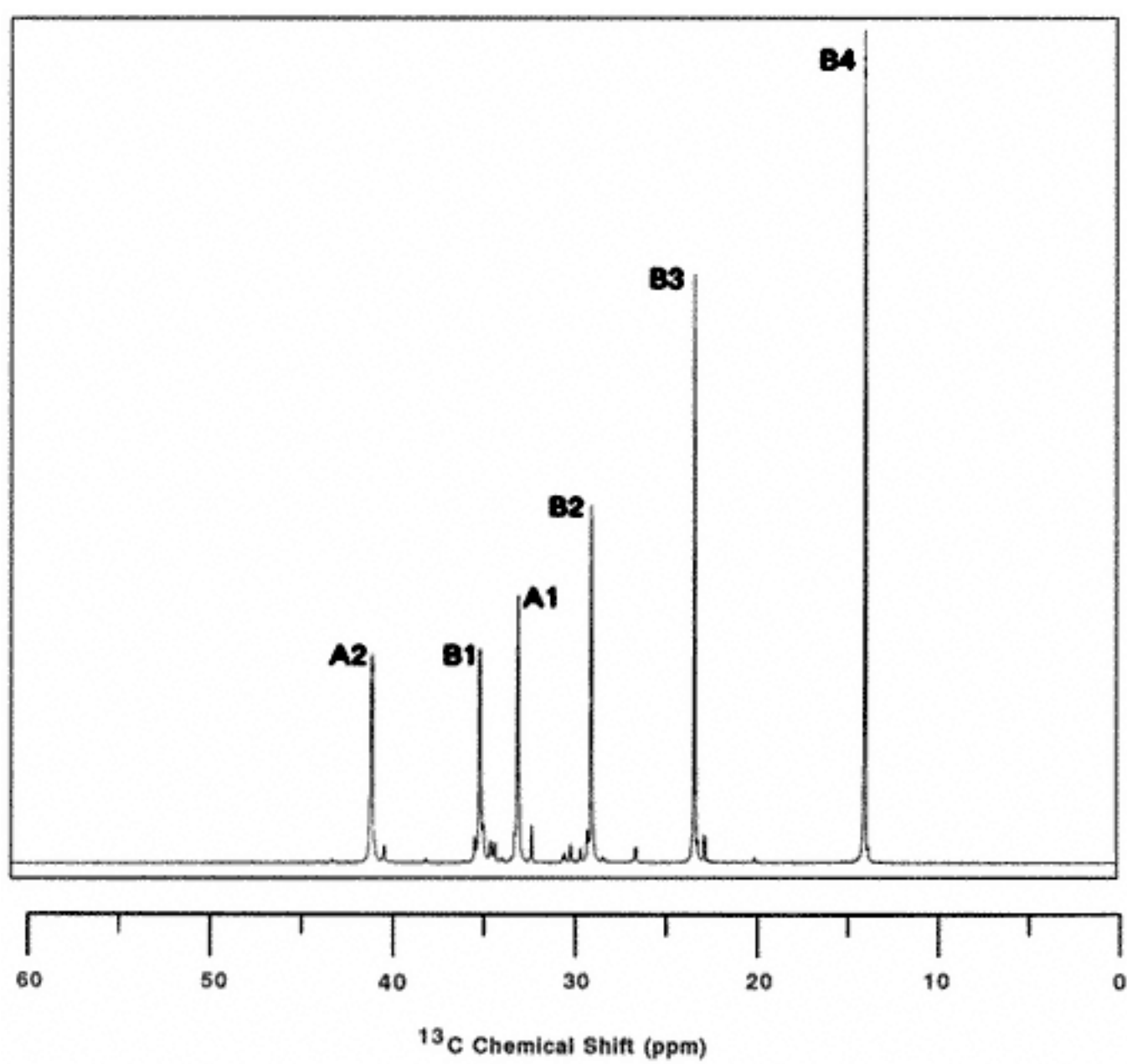
References

A. Mizuno and H. Kawasaki. *Polymer* 33:57, 1992; A. Altomare, R. Solaro, F. Ciardelli, L. Barazzoni, F. Menconi, and F. Masi. *Makromol. Chem. Makromol. Symp.* 59:369, 1992.

**II-C-7—
Poly(1-Hexene), Isotactic**

Comments

Slight tacticity splitting is observed, particularly for the backbone carbons. This polymer is a sticky liquid, and is not currently available commercially.



Code	Shift (ppm)
A1	32.5
A2	40.3
B1	34.5
B2	28.6
B3	23.0
B4	13.8

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 130°C
Solvent: ODCB- d_4 /TCB (3/1 v/v)	Concentration: 30% w/w
Scans: 200	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 3 Hz	Pulse delay: 2 s

References

J. C. W. Chien and B. M. Gong. *J. Polym. Sci. Polym. Chem.* 31:1747, 1993; H. Q. Liu, A. Deffieux, and P. Sigwalt. *Polym. Bull.* 24:355, 1990.

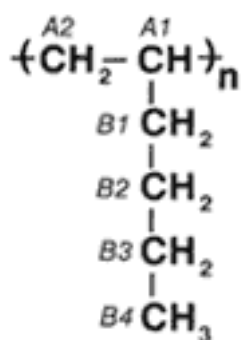
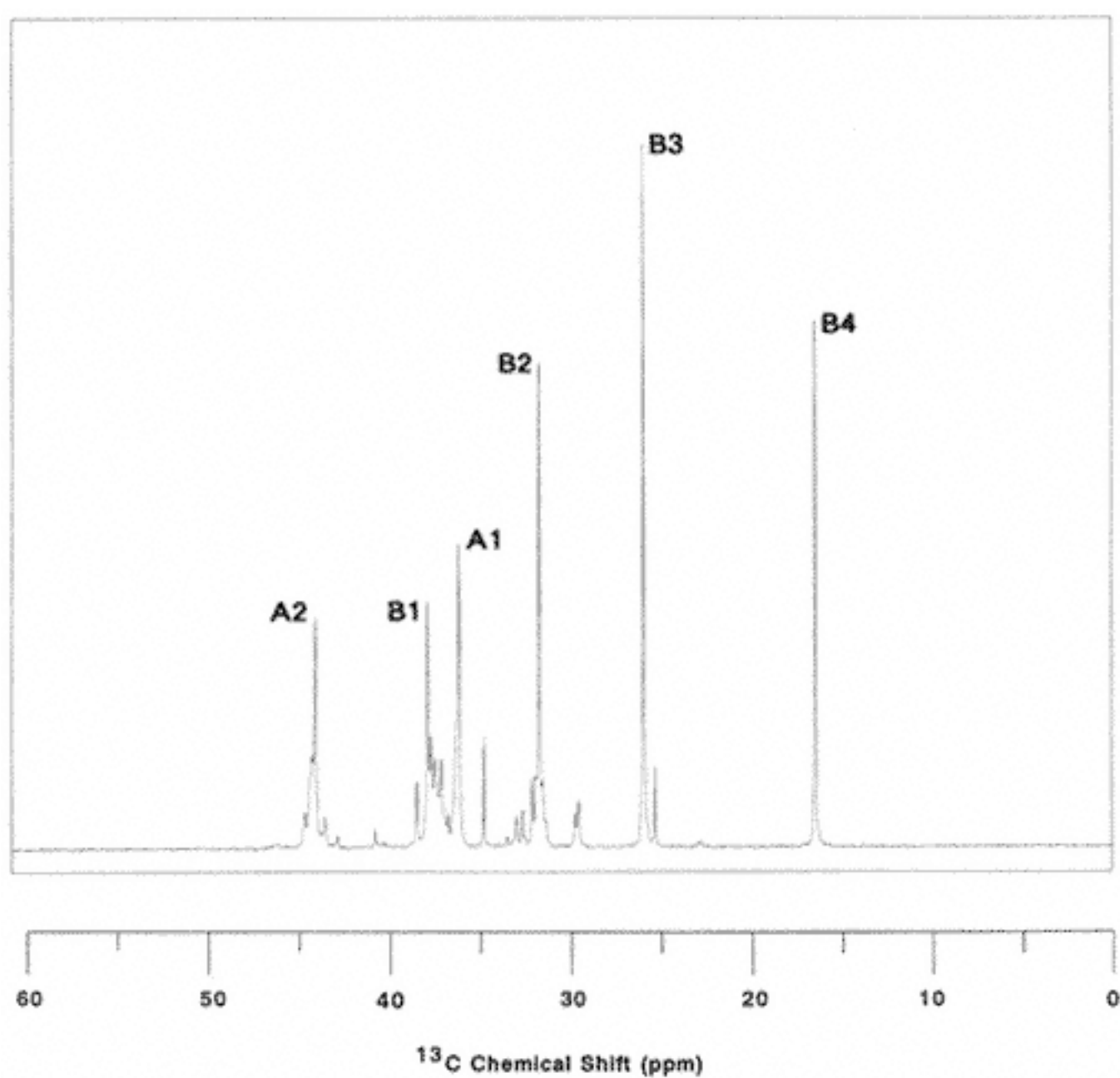
Source

R. P. Duttweiler, Mobil Chemical Company, Edison, NJ.

**II-C-8—
Poly(1-Hexene), Atactic**

Comments

Significant tacticity splitting is observed, particularly for the backbone carbons. This polymer is a sticky liquid, and is not currently available commercially.



Code	Shift (ppm)
A1	35.6
A2	43.4
B1	37.4
B2	31.3
B3	25.6
B4	16.1

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 130°C
Solvent: ODCB- d_4 /TCB (3/1 v/v)	Concentration: 30% w/w
Solvent: ODCB- d_4 /TCB (3/1 v/v)	Concentration: 30% w/w
Scans: 200	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 3 Hz	Pulse delay: 2 s

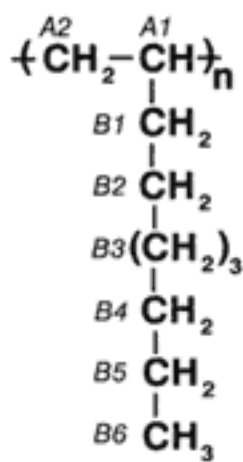
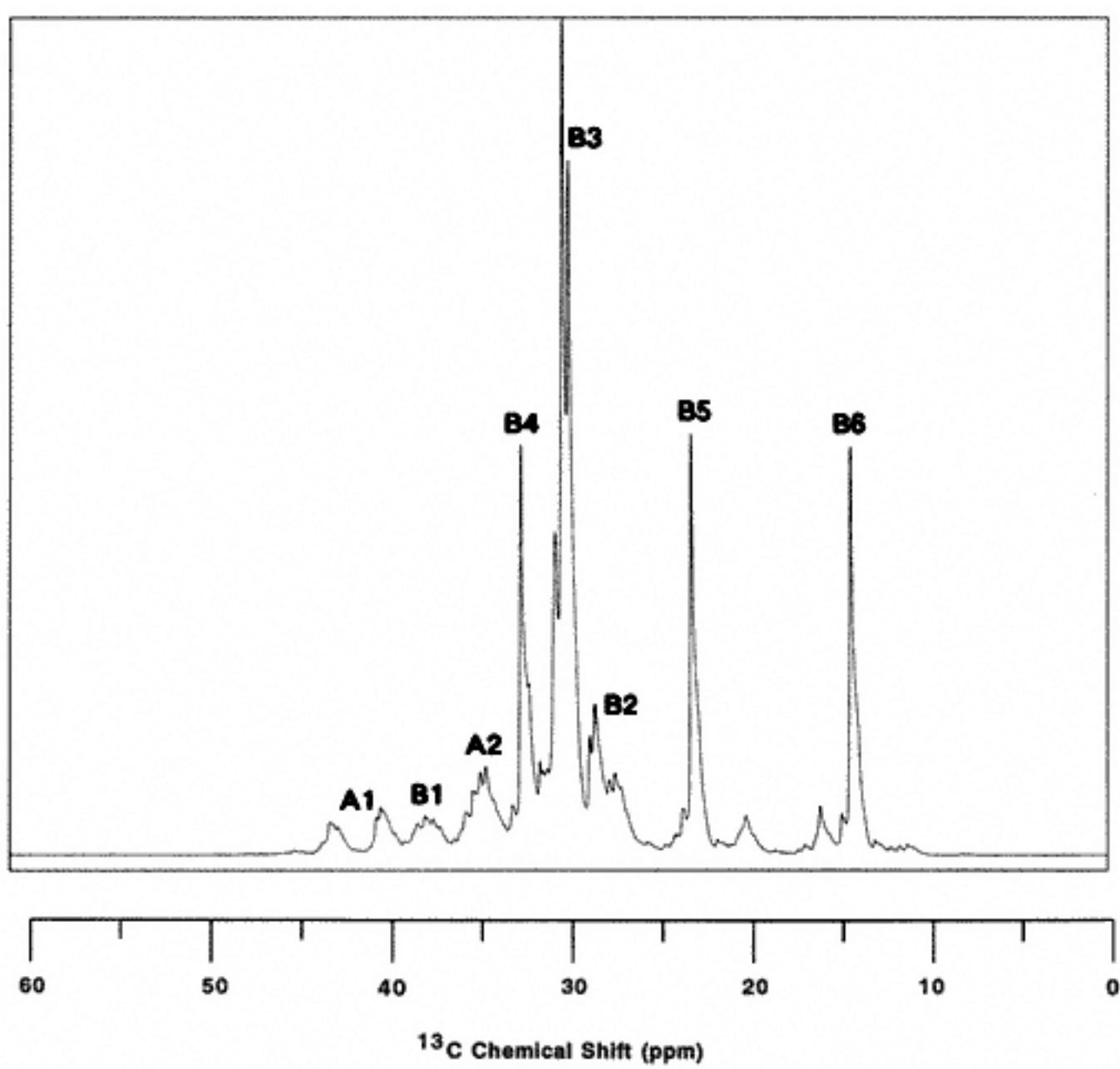
References

J. C. W. Chien and B. M. Gong. *J. Polym. Sci. Polym. Chem.* 31:1747, 1993; H. Q. Liu, A. Deffieux, and P. Sigwalt. *Polym. Bull.* 24:355, 1990.

**II-C-9—
Poly(1-Decene), Atactic**

Comments

Significant tacticity splitting is observed, particularly for the backbone carbons. This polymer is a viscous liquid, and in low-MW form, is used as a lubricant.



Code	Shift (ppm)
A1	34.1
A2	39.8
B1	37.3
B2	26.6
B3	30.0
B4	32.1
B5	22.9
B6	14.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB-d₄/TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 3 Hz

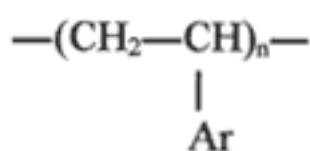
Pulse delay: 2 s

Reference

B. Pena, J. A. Delgado, A. Bello, and E. Perez. *Makro. Chem. Rapid Commun.* 12:353, 1991.

III— Aliphatic Backbones: Aromatic Pendant Groups

Polymers in this group have the general structure:



A

where Ar designates an aromatic group, either a hydrocarbon or a heterocyclic ring. The most important polymer in this group is, by far, polystyrene (PS), where Ar is simply a phenyl ring. About 6 billion lb (2.72 billion kg) of the homopolymer and its major copolymers were produced in 1994 [1]. It is one of the most common plastics found in many household products, such as disposable dishware, toys, and appliance housings. It has several commercially significant copolymers, most notably those with butadiene (Bd) as comonomer. At high Bd levels, these copolymers are elastomers (see Chapter VI). High-impact polystyrene (HIPS), a low-Bd copolymer, is much less brittle than PS homopolymer [2]. Several polymers containing derivatized styrene are also available commercially, and these find uses in specialty applications, as do polymers of heterocyclic monomers.

III.A— Sample Preparation and Spectral Acquisition

At room temperature, aromatic polymers are soluble in a wide variety of organic solvents: methylene chloride- d_2 , chloroform- d , tetrahydrofuran- d_8 , benzene- d_6 , and toluene- d_8 [3].

For ^{13}C spectra, nonaromatic solvents are generally preferred, to avoid overlap with some of the polymer's resonances. Quantitative ^{13}C peak areas for most carbons can be achieved with a 90° pulse, 15-s pulse (relaxation) delay, and gating of the ^1H decoupling to suppress nuclear Overhauser effects (NOEs). Appropriate conditions for quantitative ^1H spectra are a 5-s pulse delay, following a 90° pulse.

III.B— Spectral Features

The common ^{13}C resonances for homopolymers in this group occur in two regions: 40–45 ppm for the aliphatic backbone carbons, and 120–150 ppm for the aromatics. For copolymers, additional resonances arise from the second component. Similarly, the spectra of derivatized styrene polymers will exhibit peaks characteristic of the additional functional groups. Most of the polymers in this group are highly stereoirregular, which gives rise to complex patterns of resonances for carbons in or near the chain backbone. This effect is particularly pronounced for the backbone methine and *ipso*-aromatic carbons. A similar situation pertains to ^1H spectra; peaks occur mainly in the aliphatic (1–3 ppm) and aromatic (6–8 ppm) areas, with

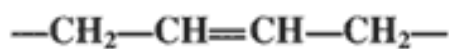
other resonances arising from comonomers or derivitization. Tacticity effects are observed in the ^1H spectrum as well, but they are more difficult to interpret because the spectral features are generally broader than in the ^{13}C spectrum.

III.B.1—

Polymers and Copolymers of Styrene

The ^{13}C spectrum of polystyrene (PS) homopolymer includes backbone resonances closely spaced between 40 and 45 ppm and aromatic resonances between 125 and 145 ppm. Highly syndiotactic PS (*s*PS), produced by metallocene catalysts [4,5], has a simple spectrum because of its high stereoregularity. With ^1H decoupling, single peaks appear for each distinct carbon. By contrast, atactic PS (*a*PS), the more commonly found form of PS, exhibits a complex pattern of resonances for the backbone methine carbon, owing to the irregular stereostructure of this material. Some splitting is also seen for the backbone methylene and the *ipso*-aromatic carbons, but these effects are more subtle. The assignment of specific peaks to particular stereoisomers has been studied in detail [6,7].

Styrene is an important component in many copolymers, particularly when combined with butadiene (Bd). Styrene is often not the predominant component in these copolymers, and spectra of these materials are found in other chapters. Styrene–butadiene copolymers are produced in a wide range of compositions. High-impact PS (HIPS, {III-A-6 and III-A-6H}) has a small amount (5–10 wt%) of incorporated polybutadiene (PBd); {VI-1, VI-1H, VI-2, VI-2H}) rubber, which significantly improves the mechanical properties. The rubber phase is dispersed as microscopic globules throughout a PS matrix. These rubber particles retard crack propagation, thereby greatly reducing the brittleness of PS. Although the Bd content of HIPS (or any other styrene–butadiene copolymer) can be quantified from either the ^{13}C or the ^1H spectrum, ^1H NMR is usually the faster approach. The broad resonance(s) at 5.6 ppm are due to the double bonds (*cis* and *trans*) in the Bd component:



B

and they are readily distinguished from both the aromatic (6.3–7.5 ppm) and aliphatic (0.9–3 ppm) carbons. If the double-bond (A_{DB}) and the aromatic (A_{Arom}) peak areas are measured, then the mol-% Bd can be calculated:

$$\text{Mol\%Bd} = \frac{A_{\text{DB}}/2}{A_{\text{Arom}}/5} \quad (\text{III.2})$$

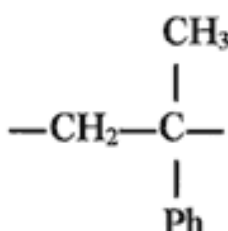
This quantity can be converted to wt% in the usual way. It is generally advisable to avoid using the aliphatic region for this calculation, because mineral oil {X-B-1}, polyisobutylene {II-C-2}, or poly(ethylene glycol) {VII-2, VII-3} may have been added to these copolymers as a processing aid.

Other styrene copolymers are intended for specialty uses; the main features of their spectra are similar to those discussed earlier. In some cases, quantitative analyses, such as that shown in the foregoing are useful for determining the amount of comonomer present.

III.B.2—

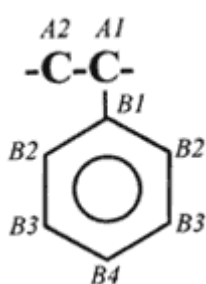
Polymers and Copolymers of Derivatized Styrene

Most polymers in this group are formed by polymerization of ring-substituted styrene. An exception is poly(α -methyl-styrene), in which a methyl group is located on one of the backbone carbons:



C

The spectrum of this polymer is extremely complex {III-B-1}, but its features are still found in two chemical-shift ranges: 20–55 for the aliphatics, and 125–155 for the aromatics. ^{13}C chemical shifts for some substituted styrenic polymers are listed in Table III-1.

TABLE III.1 ^{13}C NMR Chemical Shifts for Some Styrenic Polymers

Polymer	A1	A2	B1	B2	B3	B4	Others
Polystyrene, syndiotactic	40.6	44.0	145.3	127.7	127.7	124.7	—
Polystyrene, atactic	40.5	41–46	145.4	128.0	128.0	125.7	—
Poly(4-methylstyrene), syndiotactic	44.6	40.6	142.6	126–128	126–128	134.6	20.8 (CH ₃)
Poly(4-methylstyrene), atactic	40.5	41–44	142.5	127.5–128.5	127.5–128.5	134.5	21.3 (CH ₃)
Poly(4-hydroxystyrene)	39.8	41–46	135–139	128.3	114.8	154.9	—
Poly(4-methoxystyrene)	39.4	41–45	~140	128.4	113.3	157.5	55.2 (OCH ₃)
Poly(4-acetoxystyrene)	40.0	41–46	143.2	128.7	122.2	149.8	169.5 (OCOCH ₃), 21.3 (OCOCH ₃)
Poly(styrene sulfonic acid), Na ⁺ salt	40–46	40–46	149.2	126.4	128.8	142.6	—

Substitution in the 4-, or *para*, position is the most commonly encountered pattern in ring-substituted polystyrenes. The substituent groups are often reactive, such as hydroxyl {III-B-5}, so that the polymer can be modified for special purposes. In other cases, substitution with unreactive groups, such as methyl {III-B-2 through III-B-4} serves to increase T_g , so that these materials can be used in higher-temperature applications.

At first glance, the ^{13}C and ^1H spectra of derivatized polystyrenes are similar to those of PS; there are, obviously, both aliphatic and aromatic groups of peaks. However, the ^{13}C spectrum of a derivatized PS exhibits **two** resonances at higher chemical shifts (> 130 ppm): one is due to the *ipso* carbon; the other, to the substituted ring carbon. A carbon-containing substituent will contribute its own resonances to the spectrum.

III.B.2—

Polymers and Copolymers of Other Heterocyclic Monomers

Polymers of heterocyclic (usually nitrogen-containing) monomers, such as poly(vinyl pyridine) have no ^{13}C features that immediately distinguish them from hydrocarbon aromatic polymers. Obviously, heterocyclic polymers also exhibit peaks in both the aliphatic and aromatic chemical-shift ranges. The patterns are different from the polystyrenes and derivatized polystyrenes, so they can be identified by comparison to standard spectra, {III-C-1 through III-C-5}.

References

1. *Mod. Plast.* 64 (Jan) 1995.
2. H. Ulrich. *Introduction to Industrial Polymers*. Munich: Hanser Publishers, 1993.
3. J. Brandrup, and E. H. Immergut. *Polymer Handbook*. New York: Wiley, 1975.
4. N. Ishihara, M. Kuramoto, and M. Uoi. *Macromolecules* 21:3356, 1988.
5. A. Zambelli, L. Oliva, and C. Pellicchia. *Macromolecules* 22:2129, 1989.
6. U.-D. Standt and J. Klein. *Die Angewandte Makromol. Chem.* 99:171, 1981.
7. R. Bahulekar, R. S. Ghadage, S. Ponrathnam, and N. R. Ayyangar. *Eur. Polym. J.* 26:721, 1990.

ALIPHATIC BACKBONES: AROMATIC PENDANT GROUPS*A. Polymers and Copolymers of Styrene*

III-A-1	Polystyrene, syndiotactic
III-A-1H	Polystyrene, syndiotactic
III-A-2	Polystyrene, atactic
III-A-2H	Polystyrene, atactic
III-A-3	Poly(styrene-co-4-methylstyrene)
III-A-4	Poly(styrene-co-allyl alcohol)
III-A-5	Poly(styrene-co-acrylonitrile)
III-A-6	Poly(styrene-co-butadiene) [90%S]
III-A-6H	Poly(styrene-co-butadiene) [90%S]

B. Polymers and Copolymers of Substituted Styrene

III-B-1	Poly(α -methylstyrene)
III-B-1H	Poly(α -methylstyrene)
III-B-2	Poly(3-methylstyrene-co-4-methylstyrene)
III-B-3	Poly(4-methylstyrene), syndiotactic
III-B-4	Poly(4-methylstyrene), atactic
III-B-5	Poly(4-hydroxystyrene)
III-B-6	Poly(4-methoxystyrene)
III-B-7	Poly(4-acetoxystyrene)
III-B-8	Poly(styrene sulfonic acid)
III-B-9	Poly(styrene sulfonate), Na ⁺

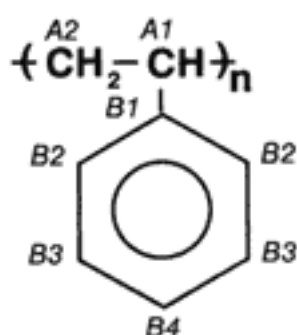
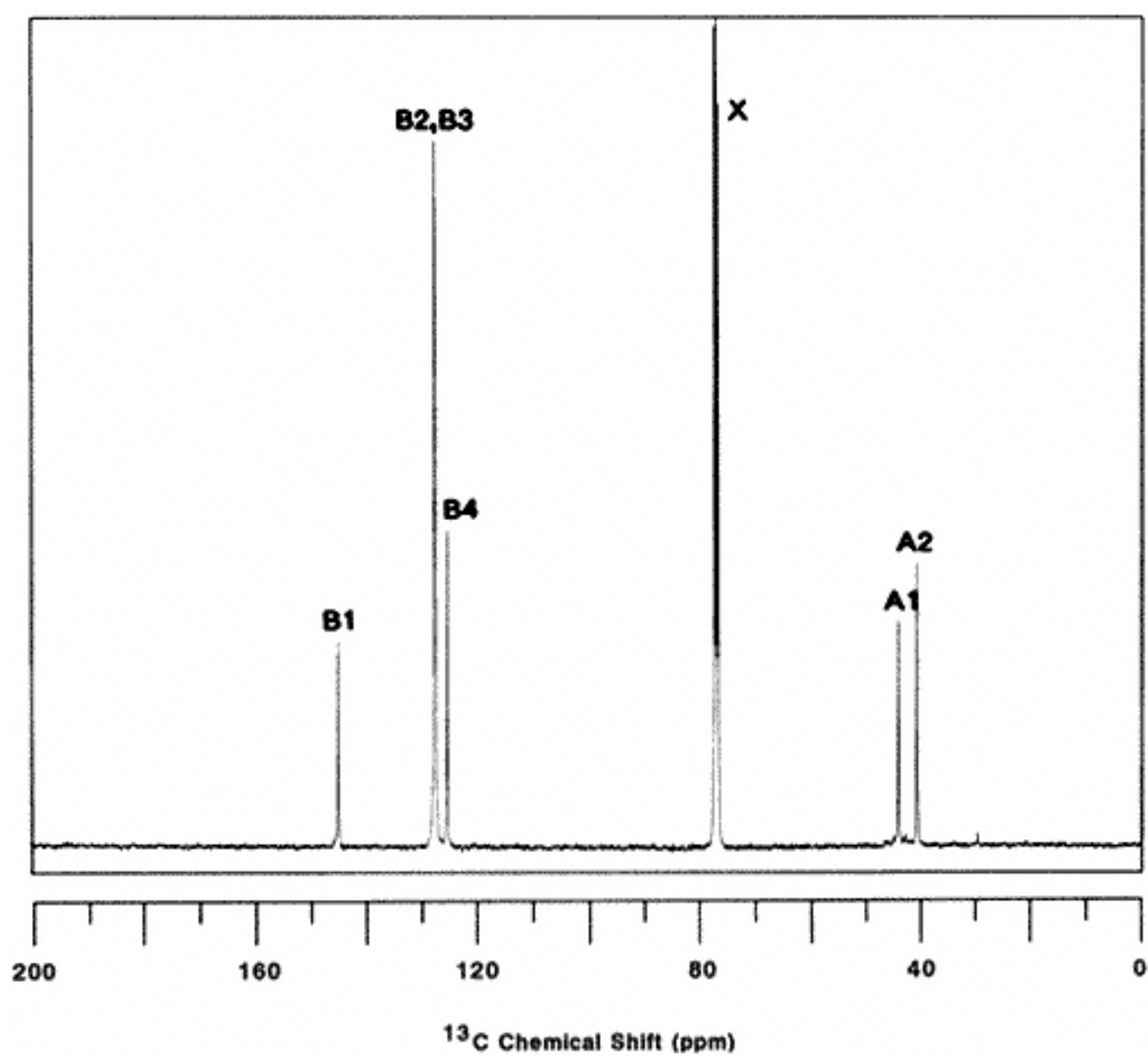
C. Polymers and Copolymers with Heteroaromatic Pendant Groups

III-C-1	Poly(2-vinylpyridine)
III-C-2	Poly(2-vinylpyridine-co-styrene)
III-C-3	Poly(4-vinylpyridine)
III-C-4	Poly(4-vinylpyridine-co-styrene)
III-C-5	Poly(<i>N</i> -vinylcarbazole)

III-A-1— Polystyrene, Syndiotactic (sPS)

Comments

The high degree of stereoregularity causes each distinct carbon to appear as a single peak. Solvent resonances are marked by **X**. This metallocene-catalyzed polymer has been commercialized by Dow.



Code	Shift (ppm)
A1	44.0
A2	40.6
B1	145.3
B2	127.7
B3	127.7
B4	124.7

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 30% w/w
Scans: 200	Spectral width: 25 kHz
Data points: 8192	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 5 s

References

M. A. Gomez, A. E. Tonelli. *Macromolecules* 23:3385, 1990; A. Zambelli, L. Oliva, C. Pellecchia. *Macromolecules* 22:2129, 1989; N. Ishihara, M. Kuramoto, M. Uoi. *Macromolecules* 21:3356, 1988; C. Pellecchia, P. Longo, A. Grassi, P. Ammendola, and A. Zambelli. *Makromol. Chem. Rapid Commun.* 8:277, 1987.

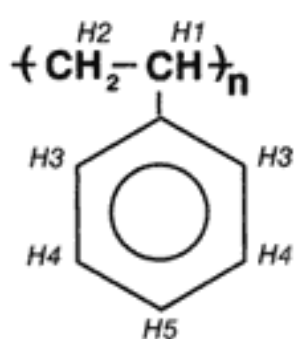
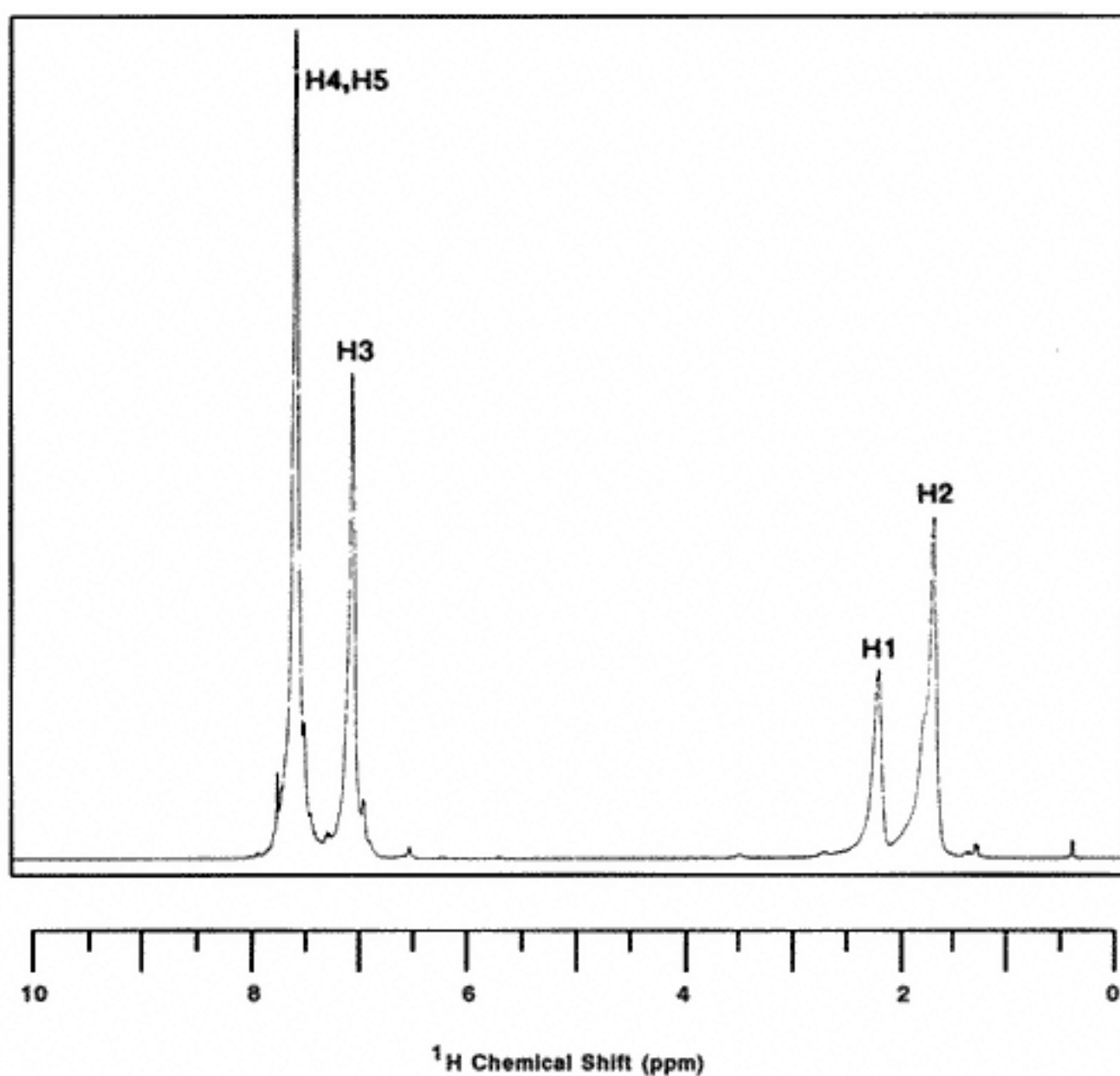
Source

B. Z. Gunesin, Mobil Chemical Company, Edison, NJ.

III-A-1H—
Polystyrene, Syndiotactic (sPS)

Comments

This metallocene-catalyzed polymer has been commercialized by Dow.



Code	Shift (ppm)
H1	2.3
H2	1.7
H3	7.0
H4	7.5
H5	7.5

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

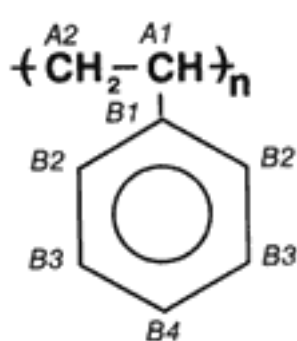
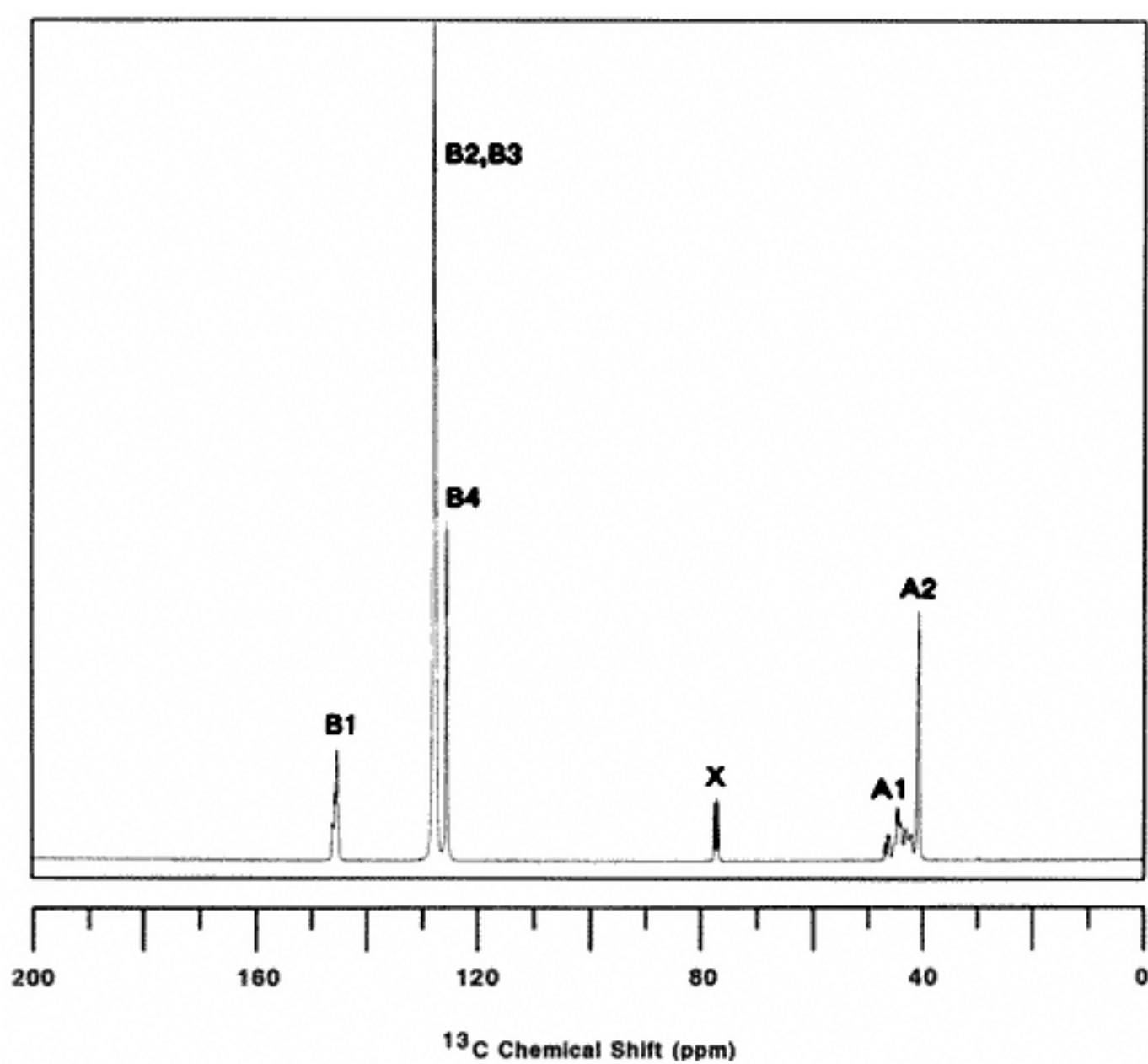
Pulse delay: 5 s

III-A-2—

Polystyrene, Atactic (*a*PS)

Comments

The high degree of stereoirregularity causes splitting, particularly of peaks **A2** and **B1**. Solvent resonances are marked by **X**. *a*PS is one of the most common polymers. It is often called "crystal" polystyrene, because of its high clarity. It also exhibits good stiffness and dimensional stability. It is typically used for injection-molded items such as appliance housings, for biaxially oriented film in blister packs, and for foam.



Code	Shift (ppm)
A1	41–46
A2	40.5
B1	145.4
B2	128.0
B3	128.0
B4	125.7

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

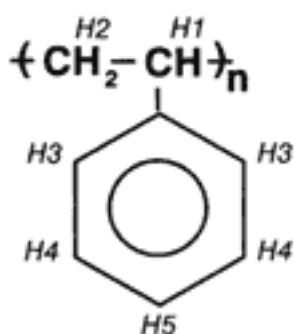
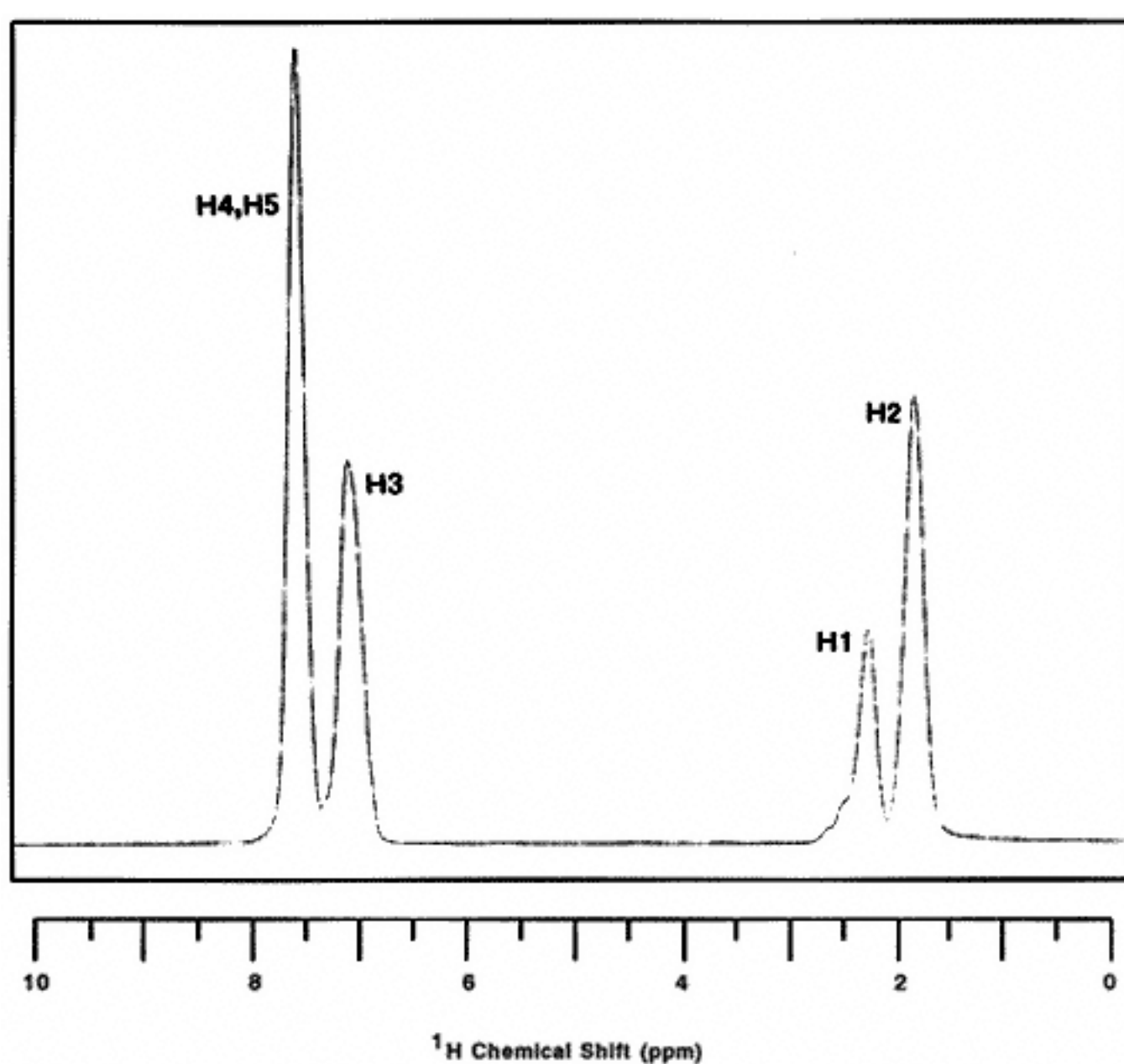
References

R. Bahulekar, R. S. Ghadage, S. Ponrathnam, and N. R. Ayyangar. *Eur. Polym. J.* 26:721, 1990; H. Sato, Y. Tanaka, and K. Hatada. *J. Polym. Sci. Polym. Phys. Ed.* 21:1667, 1983.

III-A-2H—

Polystyrene, Atactic (*a*PS)*Comments*

Tacticity effects are obscured by the broadening caused by sample viscosity. *a*PS is one of the most common polymers. It is often called "crystal" polystyrene, because of its high clarity. It also exhibits good stiffness and dimensional stability. It is typically used for injection-molded items, such as appliance housings, for biaxially oriented film in blister packs, and for foam.



Code	Shift (ppm)
H1	2.3
H2	1.9
H1	7.0
H2	7.5
H5	7.5

*Experimental Parameters*Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

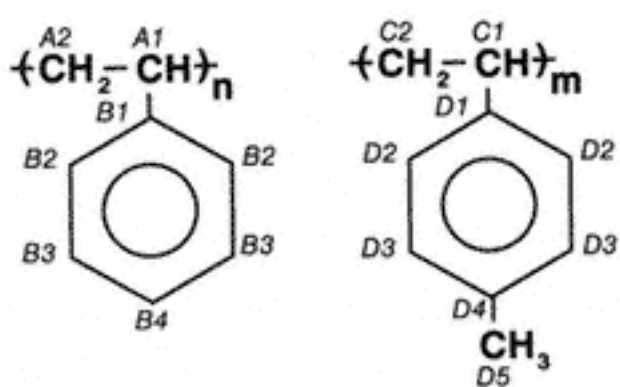
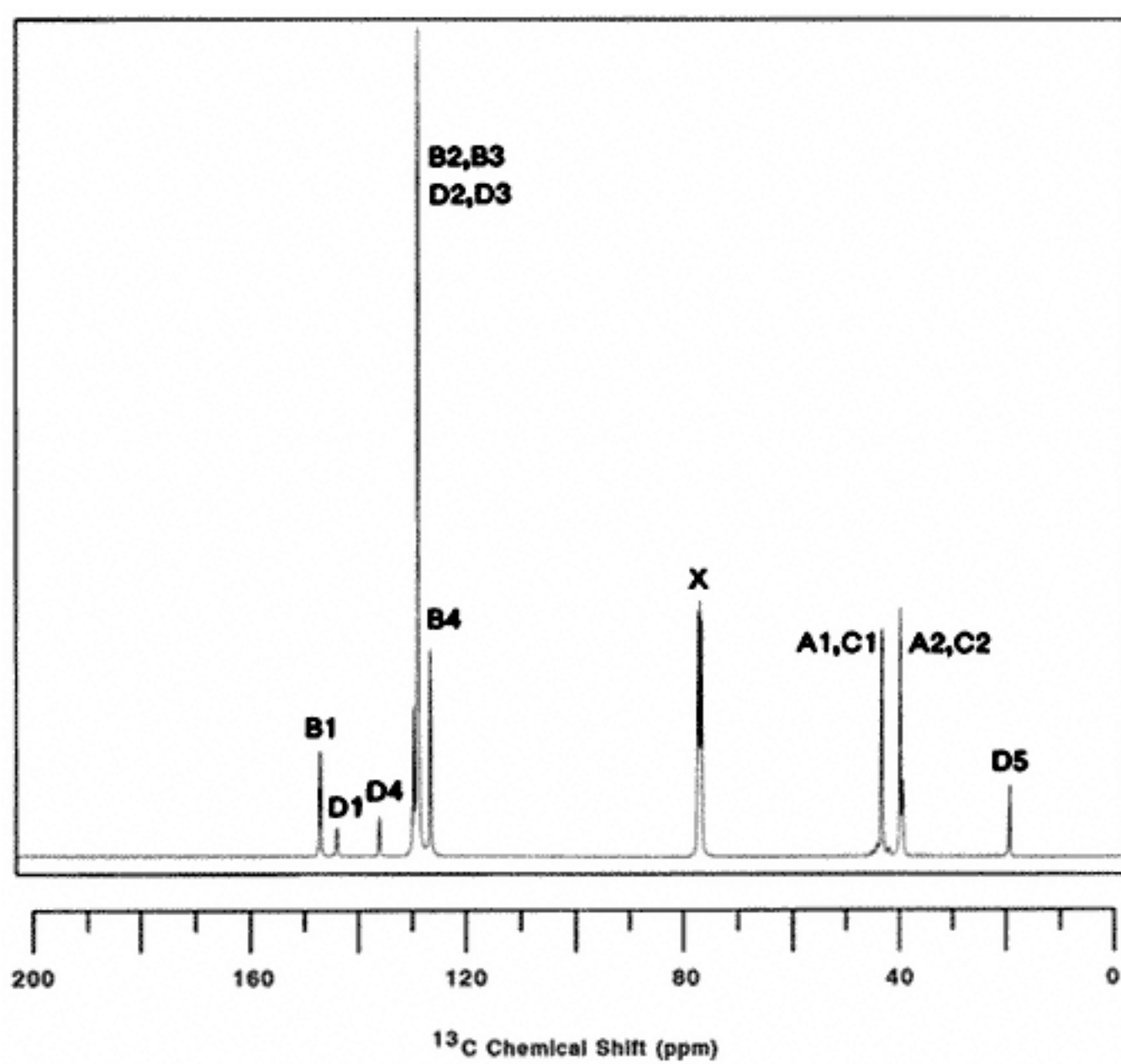
Pulse delay: 5 s

III-A-3

III-A-3—
Poly(Styrene-Co-4-Methylstyrene), Syndiotactic

Comments

The high degree of stereoregularity causes each distinct carbon to appear as a single peak. Solvent resonances are marked by X.



Code	Shift (ppm)
A1	42.0
A2	38.3
B1	143.3
B2	127.0
B3	127.0
B4	123.5
C1	42.0
C2	38.0
D1	140.3
D2	127.1
D3	127.0
D4	133.0
D5	19.9

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

Source

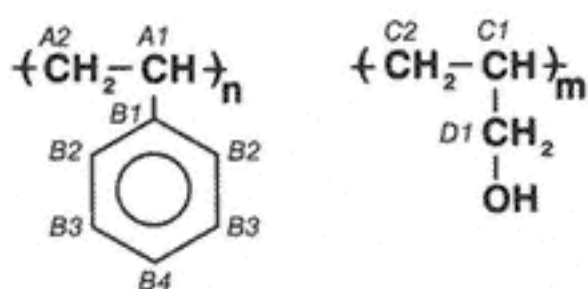
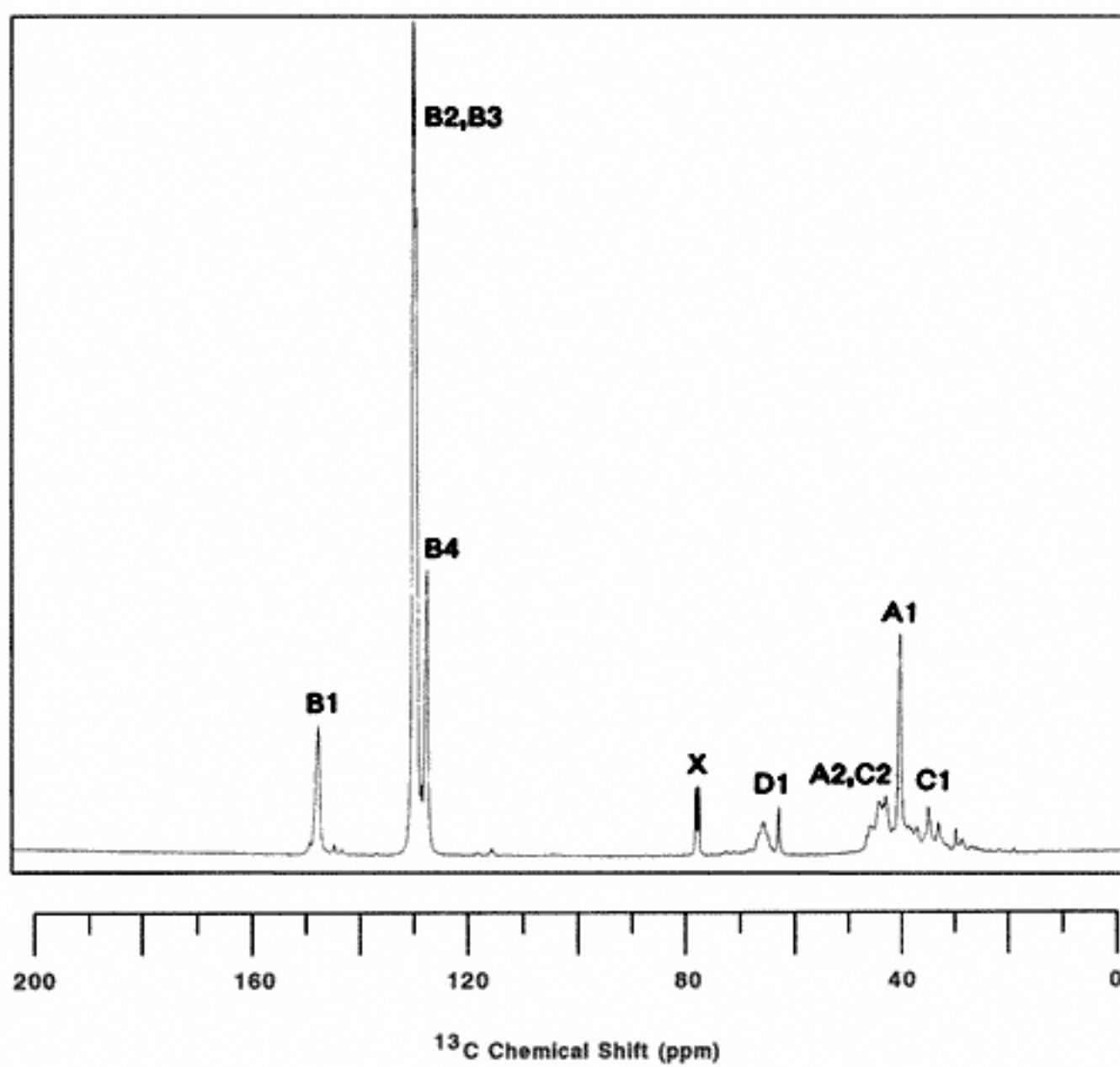
Prof. A. Zambelli, Université di Salerno, Baronissi (SA), Italy.

III-A-4—

Poly(Styrene-Co-Allyl Alcohol)

Comments

The high degree of stereoirregularity causes splitting, particularly of peaks **A1** and **B1**. Solvent resonances are marked by **X**.



Code	Shift (ppm)
A1	41–45
A2	41.1
B1	145.4
B2	128.2
B3	128.2
B4	125.8
C1	~40
C2	35.6
D1	65.3

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

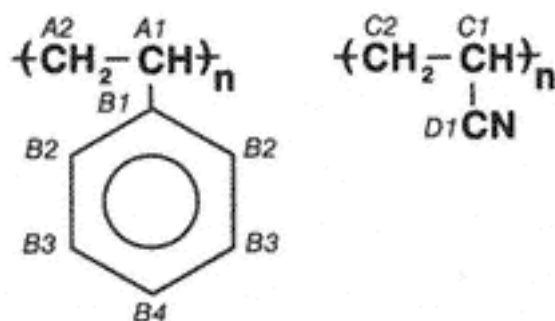
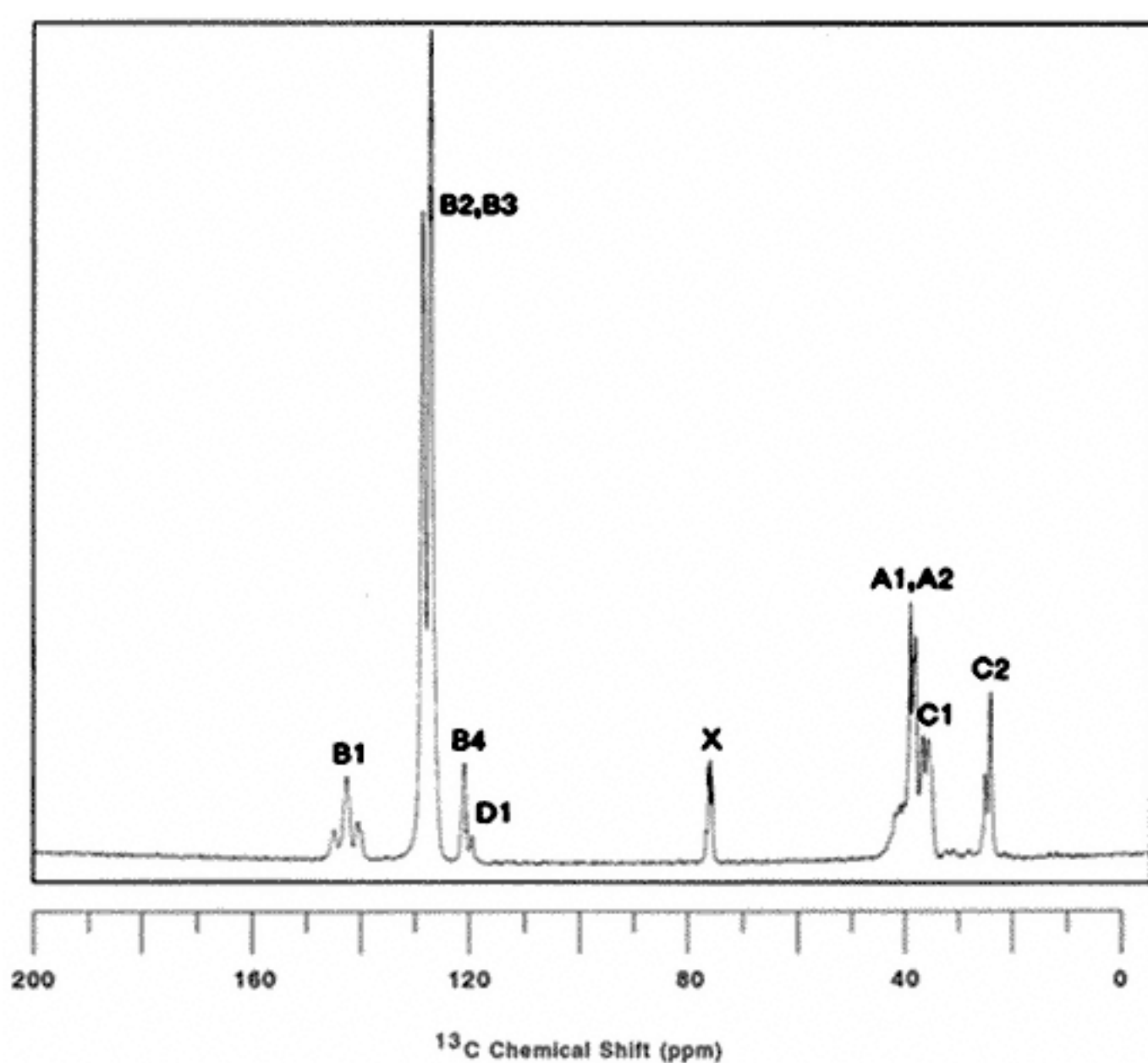
Pulse delay: 2 s

III-A-5—

Poly(Styrene-Co-Acrylonitrile) (SAN)

Comments

The high degree of stereoirregularity causes splitting, particularly of peaks **A1** and **B1**. Solvent resonances are marked by **X**. This material is transparent and glossy, with a high heat-deflection temperature and good chemical resistance. It is used for appliance parts, automobile dashboard components, and battery cases.



Code	Shift (ppm)
A1	42–46
A2	42–46
B1	140–145
B2	127–129
B3	127–129
B4	121.4
C1	37.9
C2	26.6
D1	120.2

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

Reference

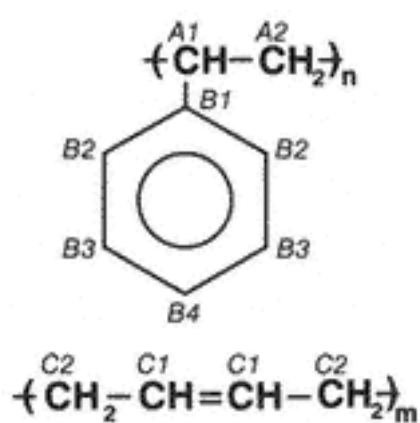
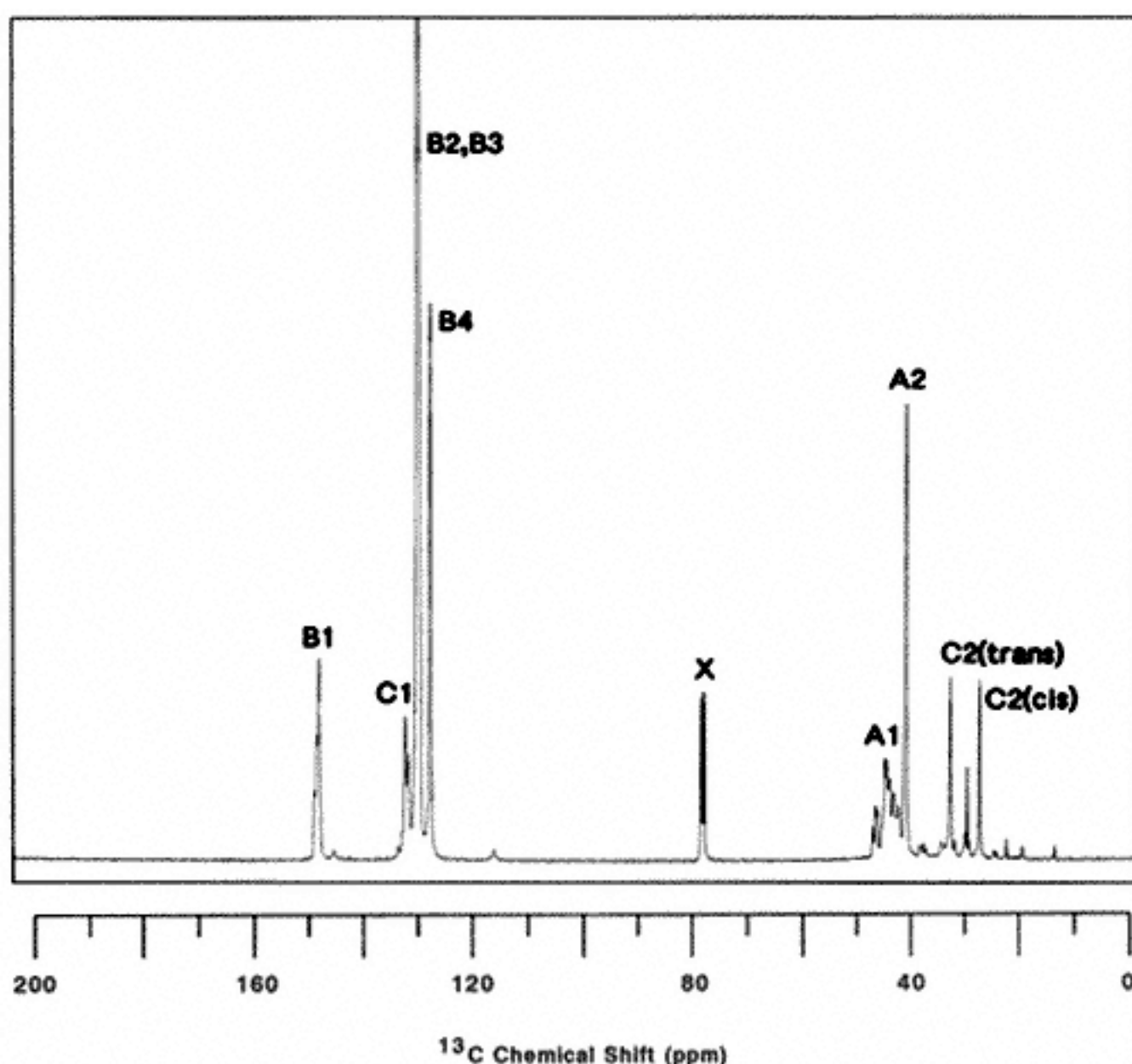
P. F. Barron, D. J. T. Hill, J. H. O'Donnell, and P. W. O'Sullivan. *Macromolecules* 17:1967, 1984.

III-A-6—

Poly(Styrene-Co-Butadiene) [90%St] (HIPS)

Comments

High-impact polystyrene (HIPS) is a microscopic blend of polybutadiene (PBd) dispersed in a polystyrene (PS) matrix. The high degree of stereoirregularity causes splitting of the PS resonances, particularly for peaks **A1** and **B1**. Solvent resonances are marked by **X**. The PBd component may be either *cis*- and *trans*- {VI-A-2}, as shown here, or *cis* only {VI-A-1}. Because of the presence of the rubber (PBd) phase, HIPS exhibits much better mechanical properties than PS alone. HIPS is used in packaging (particularly food containers) and disposable dishware.



Code	Shift (ppm)
A1	41–46
A2	40.8
B1	145.6
B2	128.2
B3	128.2
B4	125.9
C1 (<i>cis</i>)	27.3
C1 (<i>trans</i>)	32.9
C2	130.7

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

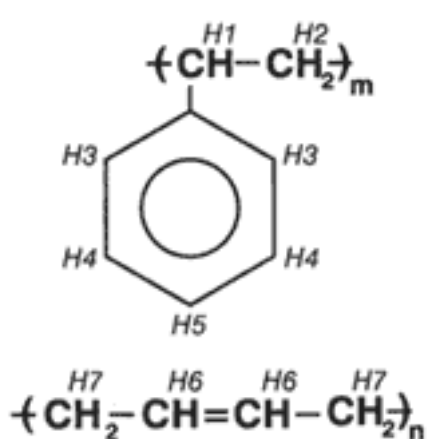
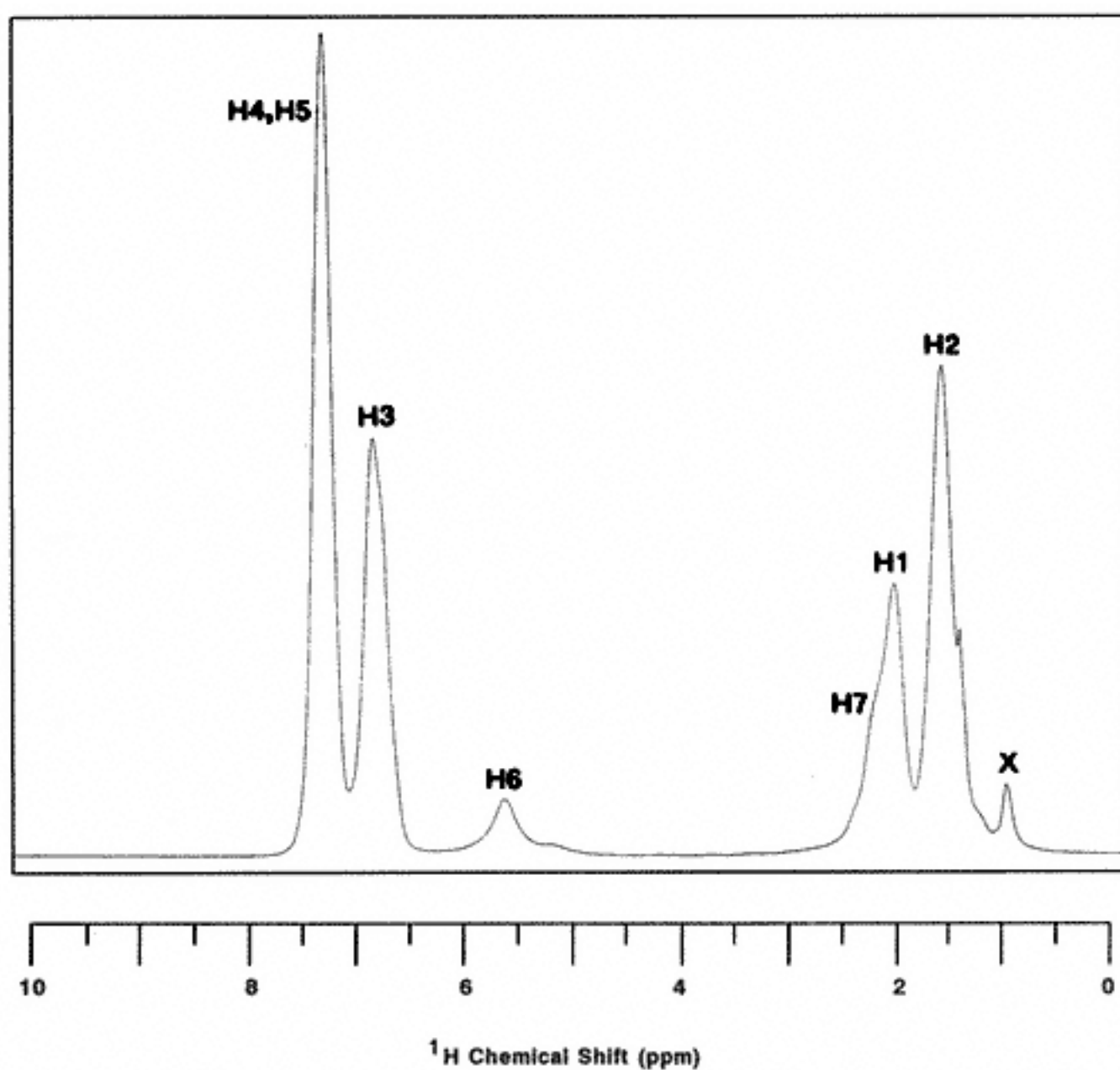
ReferenceE. Kobayashi, J. Furukawa, M. Ochiai, and T. Tsujimoto. *Eur. Polym. J.* 19:871, 1983.

III-A-6H—

Poly(Styrene-Co-Butadiene) [90%St]

Comments

High-impact polystyrene (HIPS) is a microscopic blend of polybutadiene (PBd) dispersed in a polystyrene (PS) matrix. Tacticity effects are obscured by the broadening owing to sample viscosity. The PBd component may be either *cis*- and *trans*- {VI-A-2H}, as shown here, or *cis*- only {VI-A-1H}. The PBd content can be measured, based on the area of peak **H6**, as discussed in the introduction to this chapter. Because of the presence of the rubber (PBd) phase, HIPS exhibits much better mechanical properties than PS alone. HIPS is used in packaging (particularly food containers) and disposable dishware.



Code	Shift (ppm)
H1	2.1
H2	1.7
H3	6.8
H4	7.3
H5	7.3
H6	5.6
H7	2.3

Experimental ParametersNucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

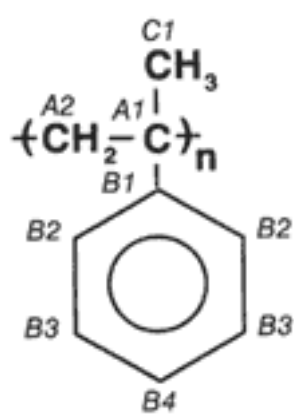
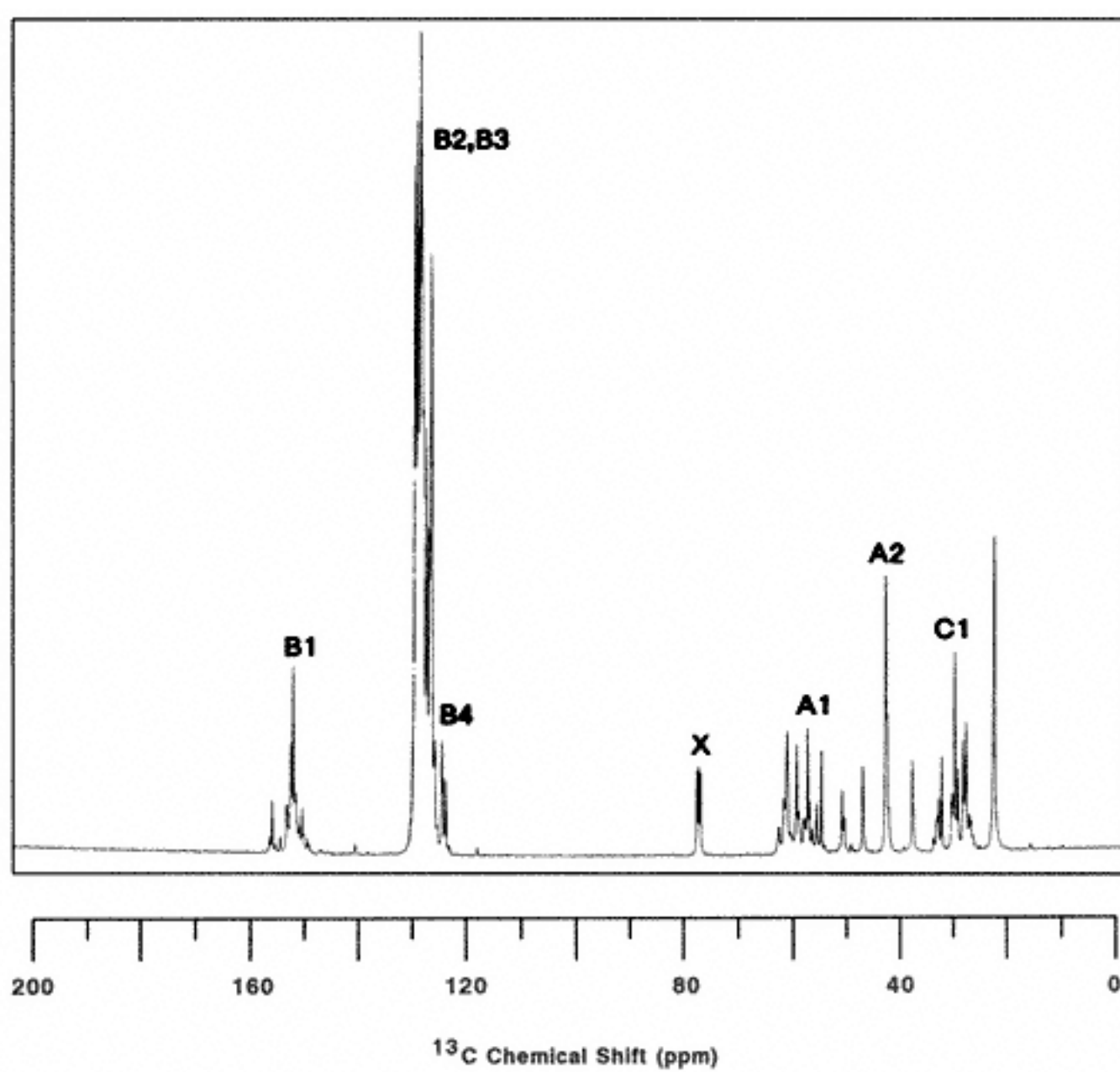
Broadening: 5 Hz

Pulse delay: 5 s

III-B-1—

Poly(α -Methylstyrene) (P α MS)*Comments*

The high degree of stereoirregularity causes splitting of all resonances. Solvent resonances are marked by **X**. This material has a higher T_g than polystyrene, and can be used in higher-temperature applications. Low molecular weight P α MS polymers are used as plasticizers.



Code	Shift (ppm)
A1	54–64
A2	40–45
B1	145–155
B2	~125
B3	~125
B4	~123
C1	24–34

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

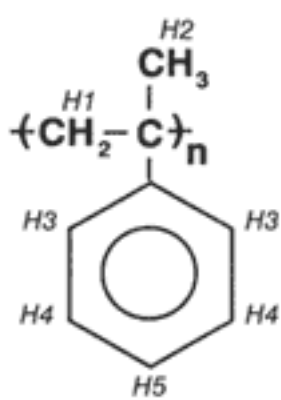
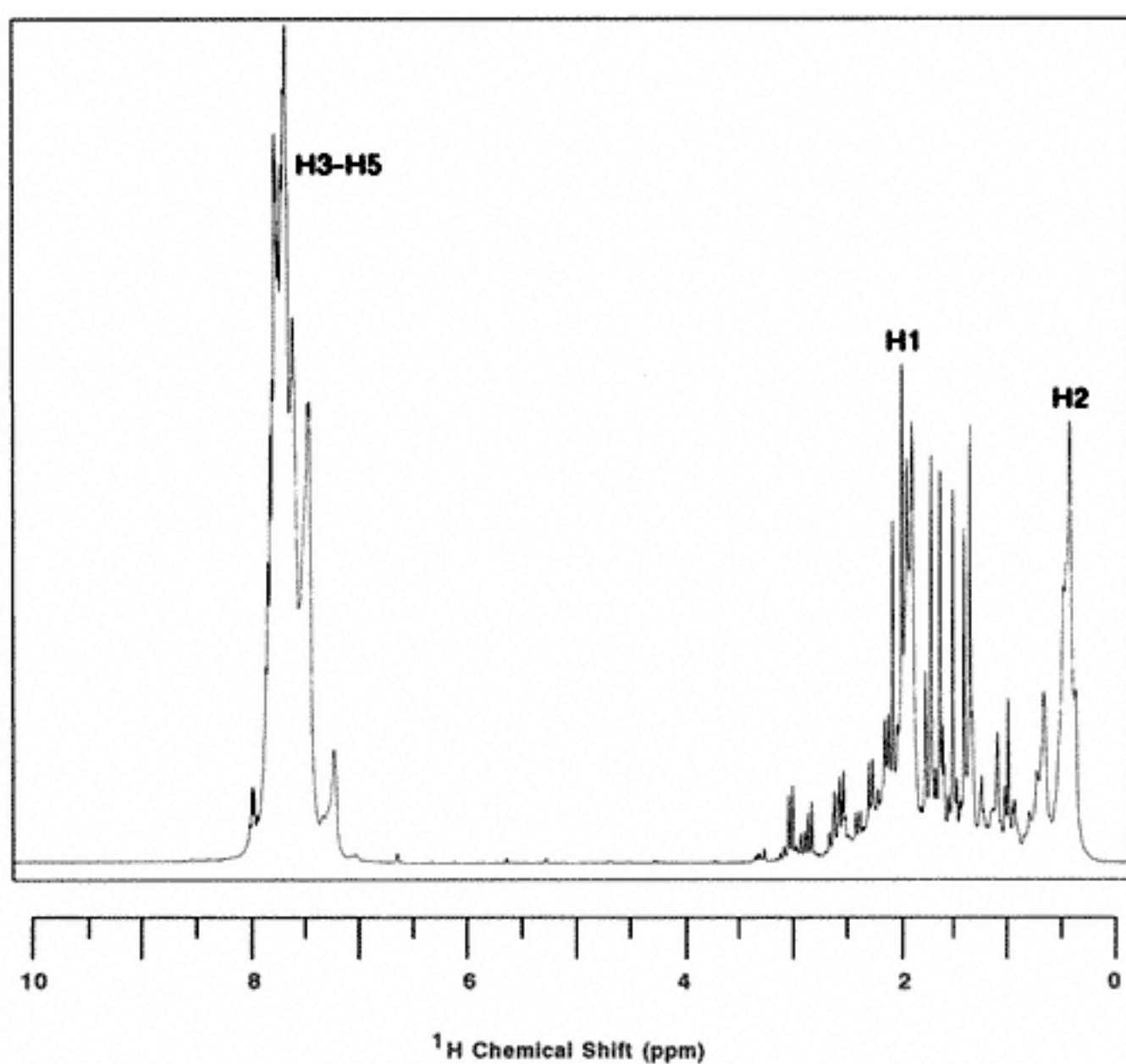
Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

III-B-1H—**Poly(α -Methylstyrene) (P α MS)****Comments**

The high degree of stereoirregularity causes splitting of all resonances, even with line broadening caused by sample viscosity. This material has a higher T_g than polystyrene, and can be used in higher-temperature applications. Low molecular weight P α MS polymers are used as plasticizers.



Code	Shift (ppm)
H1	1.5–3
H2	0.5–1
H3	7–8
H4	7–8
H5	7–8

Experimental ParametersNucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

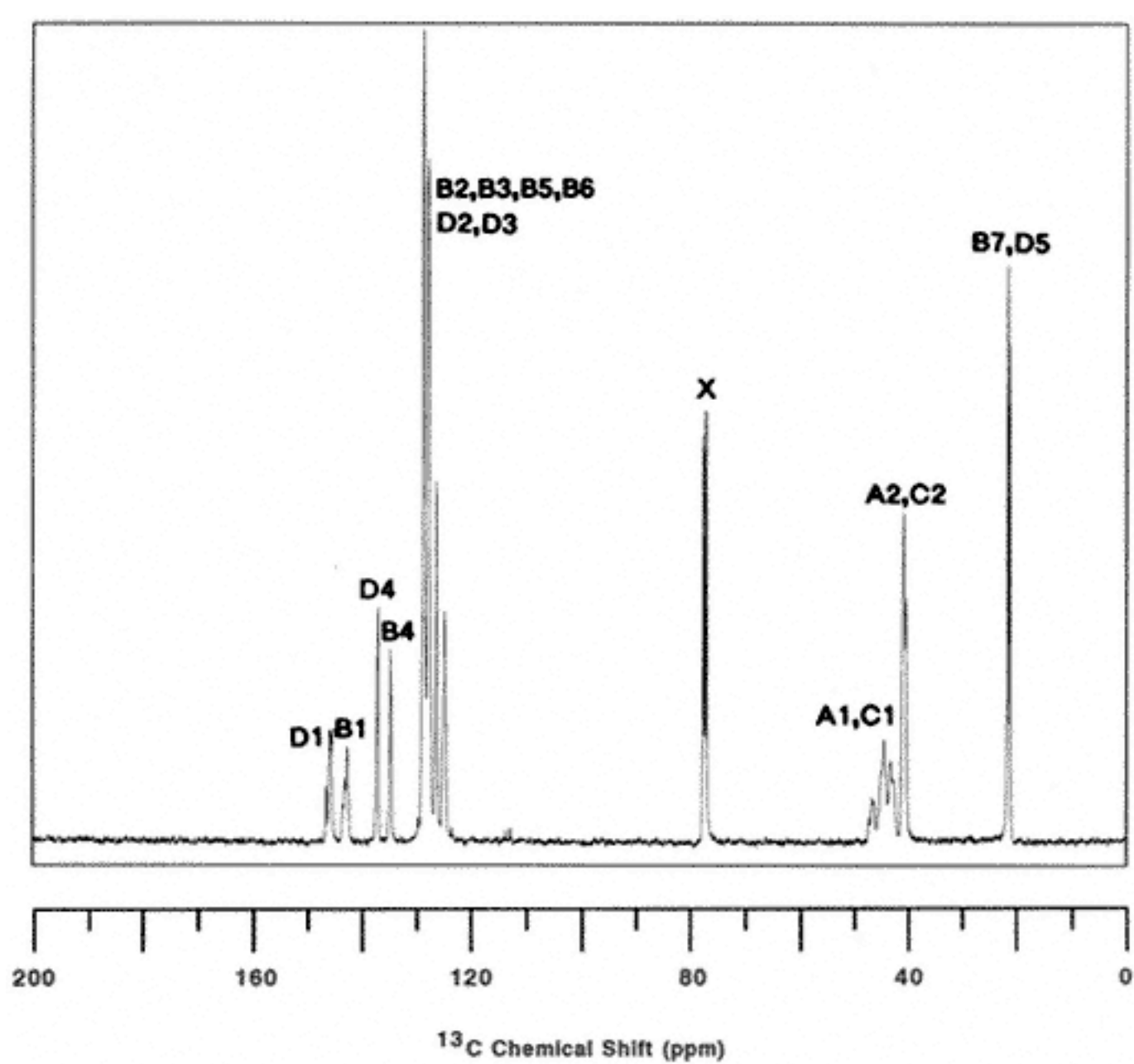
Broadening: 5 Hz

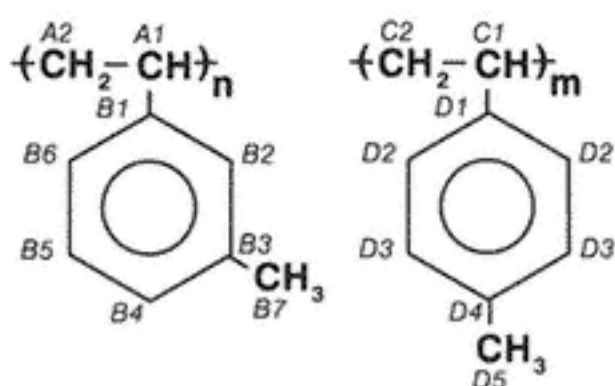
Pulse delay: 5 s

**III-B-2—
Poly(3-Methylstyrene-Co-4-Methylstyrene)**

Comments

Also known as poly(vinyl toluene) (PVT). The high degree of stereoirregularity causes splitting of resonances, particularly for peaks **A1**, **C1**, **B1**, and **D1**. Solvent resonances are marked by **X**. PVT is used to cross-link unsaturated polyesters and in paints and varnishes.





Code	Shift (ppm)
A1	42–48
A2	40.6
B1	142.6
B2	128–130
B3	128–130
B4	134.7
B5	128–130
B6	124.9
B7	21.2
C1	42–48
C2	40.6
D1	145.7
D2	128–130
D3	128–130
D4	137.2
D5	21.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

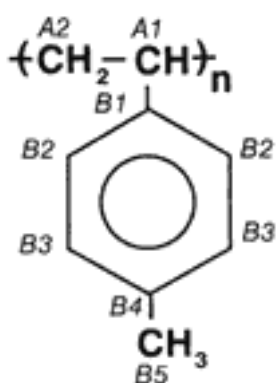
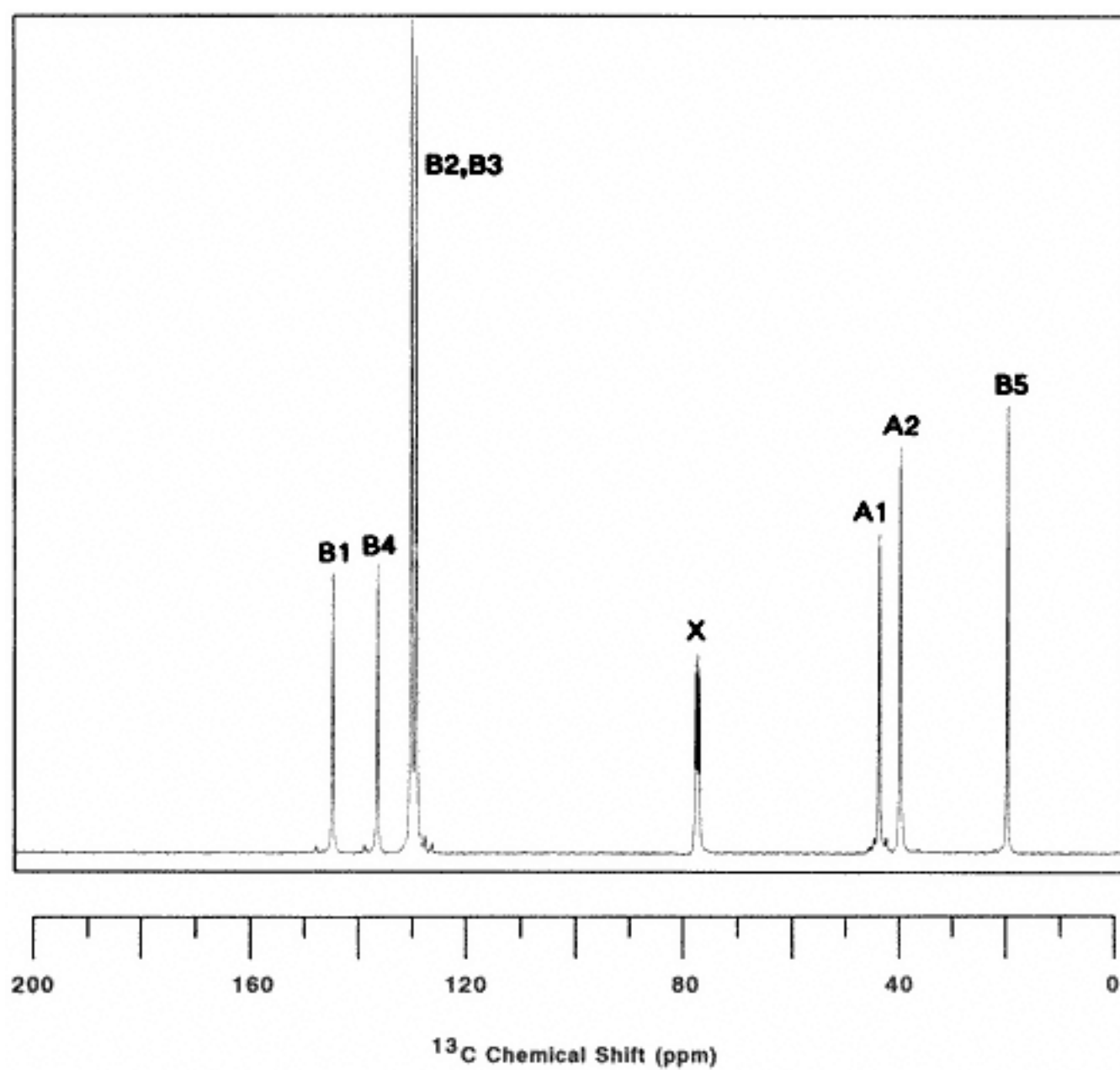
Reference

T. Okada. *Polym. J.* 11:843, 1979.

**III-B-3—
Poly(4-Methylstyrene), Syndiotactic**

Comments

The high degree of stereoregularity causes each distinct carbon to appear as a single peak. Solvent resonances are marked by **X**.



Code	Shift (ppm)
A1	44.6
A2	40.6
B1	142.6
B2	126–128
B3	126–128
B4	134.6
B5	20.8

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

References

A. Grassi, P. Longo, A. Proto, A. Zambelli. *Macromolecules* 22:104, 1989; L. Abis, E. Albizzati, G. Conti, U. Giannini, L. Resconi, S. Spera. *Makromol. Chem. Rapid Commun.* 9:209, 1988; N. Isihara, M. Kuramoto, and M. Uoi. *Macromolecules* 21:3356, 1988.

Source

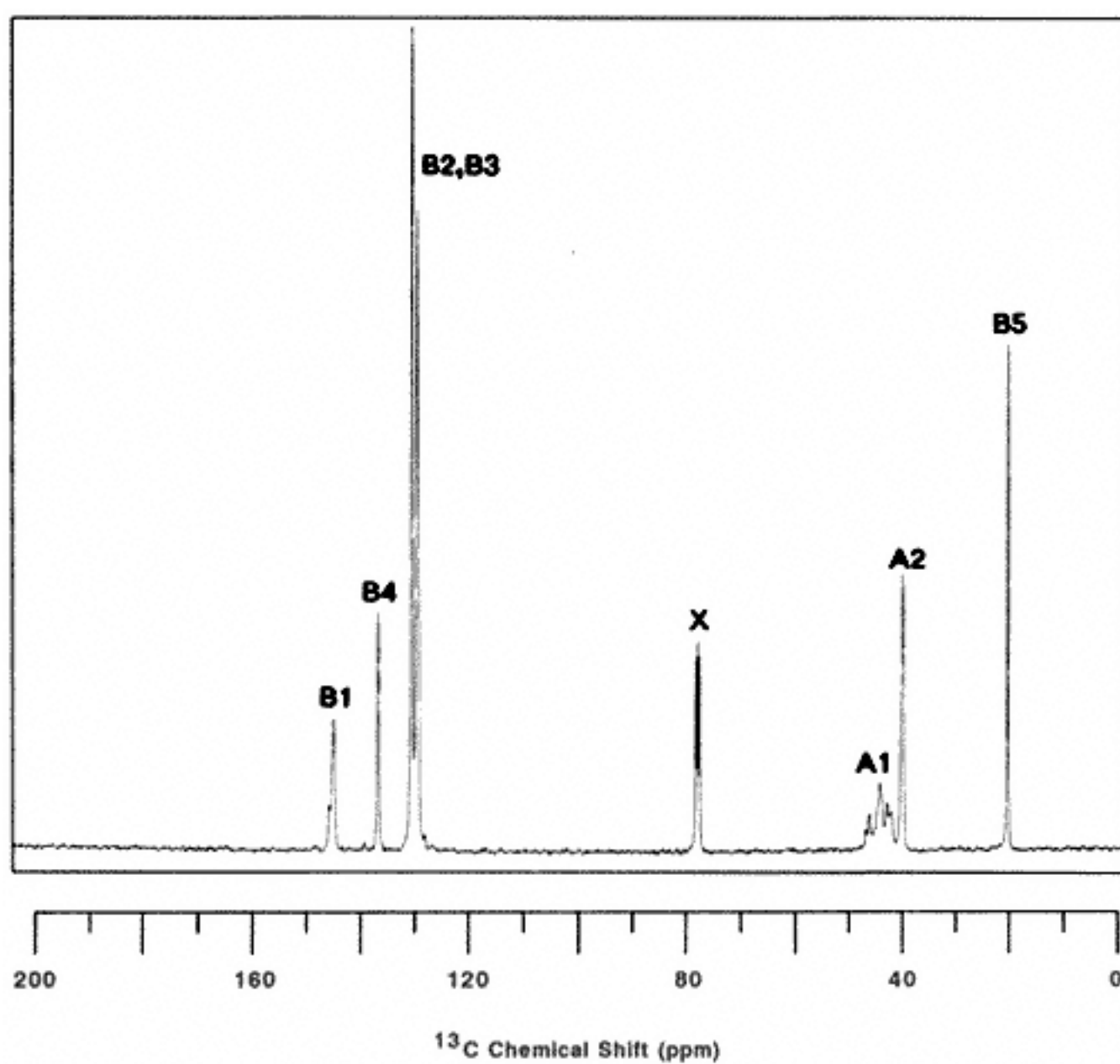
Prof. A. Zambelli, Università di Salerno, Baronissi (SA), Italy.

III-B-4—

Poly(4-Methylstyrene), Atactic

Comments

The high degree of stereoirregularity causes splitting of resonances, particularly peaks **A1** and **B1**. Solvent resonances are marked by **X**.



Code	Shift (ppm)
A1	42–46
A2	40.5
B1	142.5
B2	127.5–128.5
B3	127.5–128.5
B4	134.5
B5	21.3

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

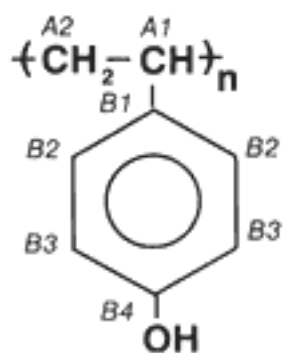
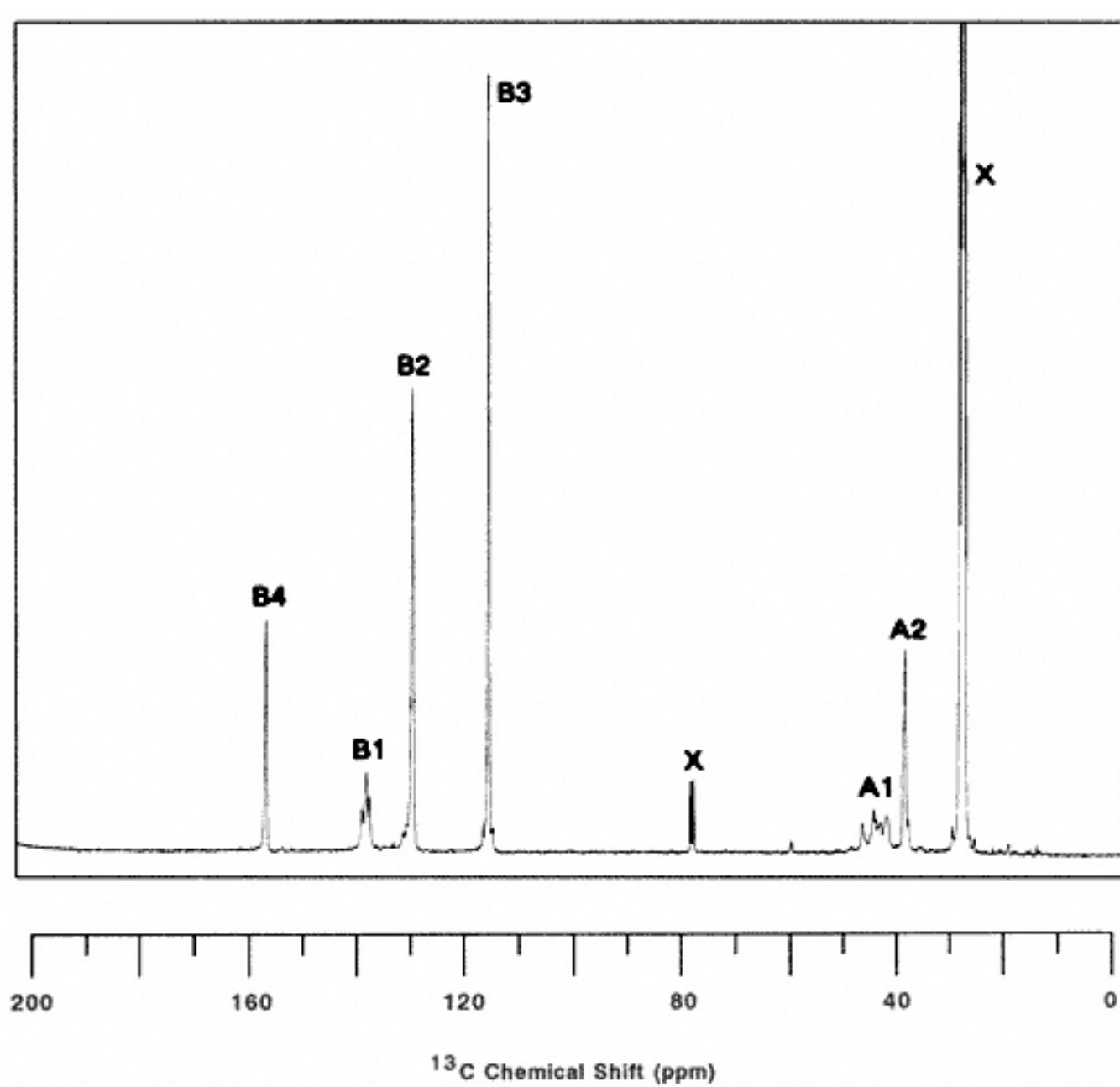
Reference

T. Okada. *Polym. J.* 11:843, 1979.

**III-B-5—
Poly(4-Hydroxystyrene)**

Comments

The high degree of stereoirregularity causes splitting of resonances, particularly peaks **A1** and **B1**. Solvent resonances are marked by **X**. The hydroxyl group offers a site for further derivitization of polystyrene.



Code	Shift (ppm)
A1	42–48
A2	39.8
B1	135–139
B2	128.3
B3	114.8
B4	154.9

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: acetone- d_6 /CDCl $_3$

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

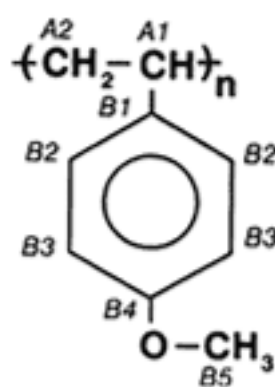
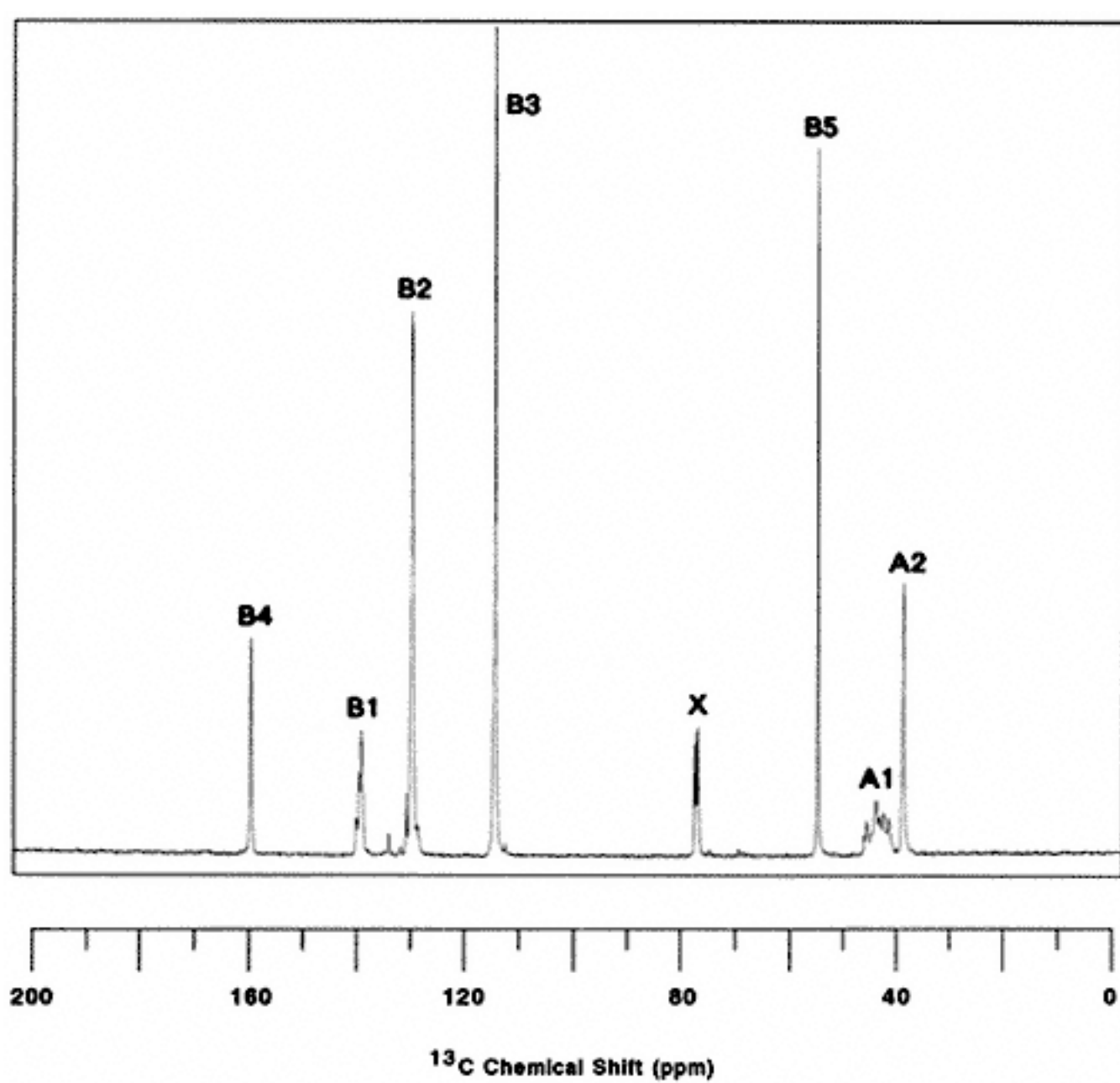
Source

Hoechst-Celanese, Corpus Christi, TX.

**III-B-6—
Poly(4-Methoxystyrene)**

Comments

The high degree of stereoirregularity causes splitting of resonances, particularly peaks **A1** and **B1**. Solvent resonances are marked by **X**. The methoxy group offers a site for further derivitization of polystyrene.



Code	Shift (ppm)
A1	42–48
A2	39.4
B1	~140
B2	128.4
B3	113.3
B4	157.5
B5	55.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

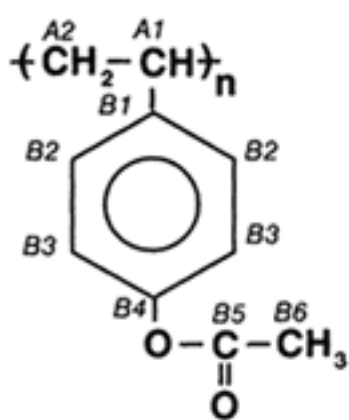
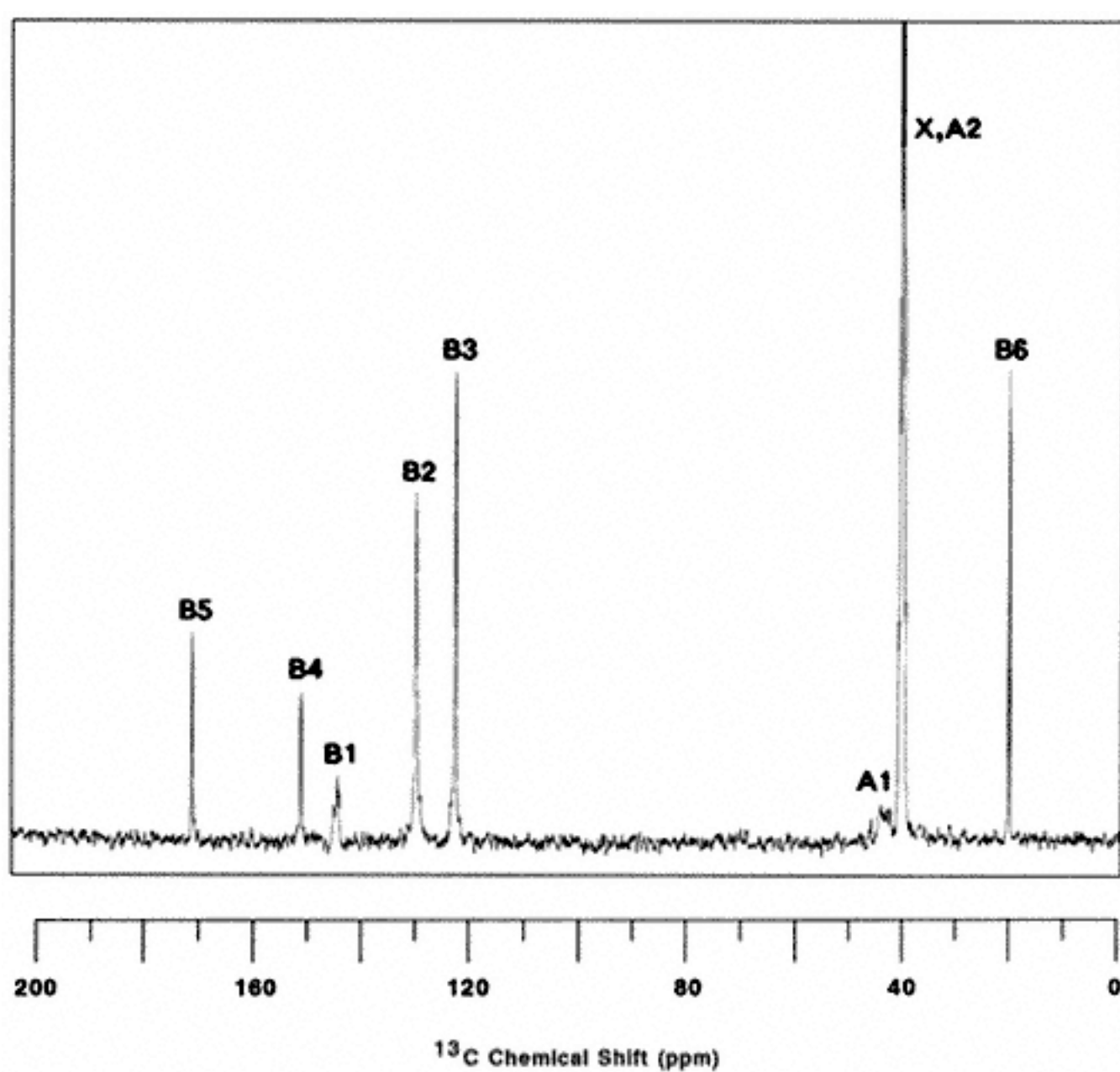
Broadening: 2 Hz

Pulse delay: 2 s

**III-B-7—
Poly(4-Acetoxy styrene)**

Comments

The high degree of stereoirregularity causes splitting of resonances, particularly peaks **A1** and **B1**. Solvent resonances are marked by **X**. The acetoxy group offers a site for further derivitization of polystyrene.



Code	Shift (ppm)
A1	41–46
A2	40.0
B1	143.2
B2	128.7
B3	122.2
B4	149.8
B5	169.5
B6	21.3

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: acetone- d_6

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

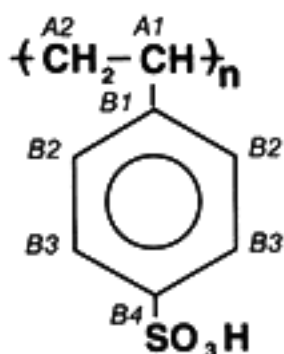
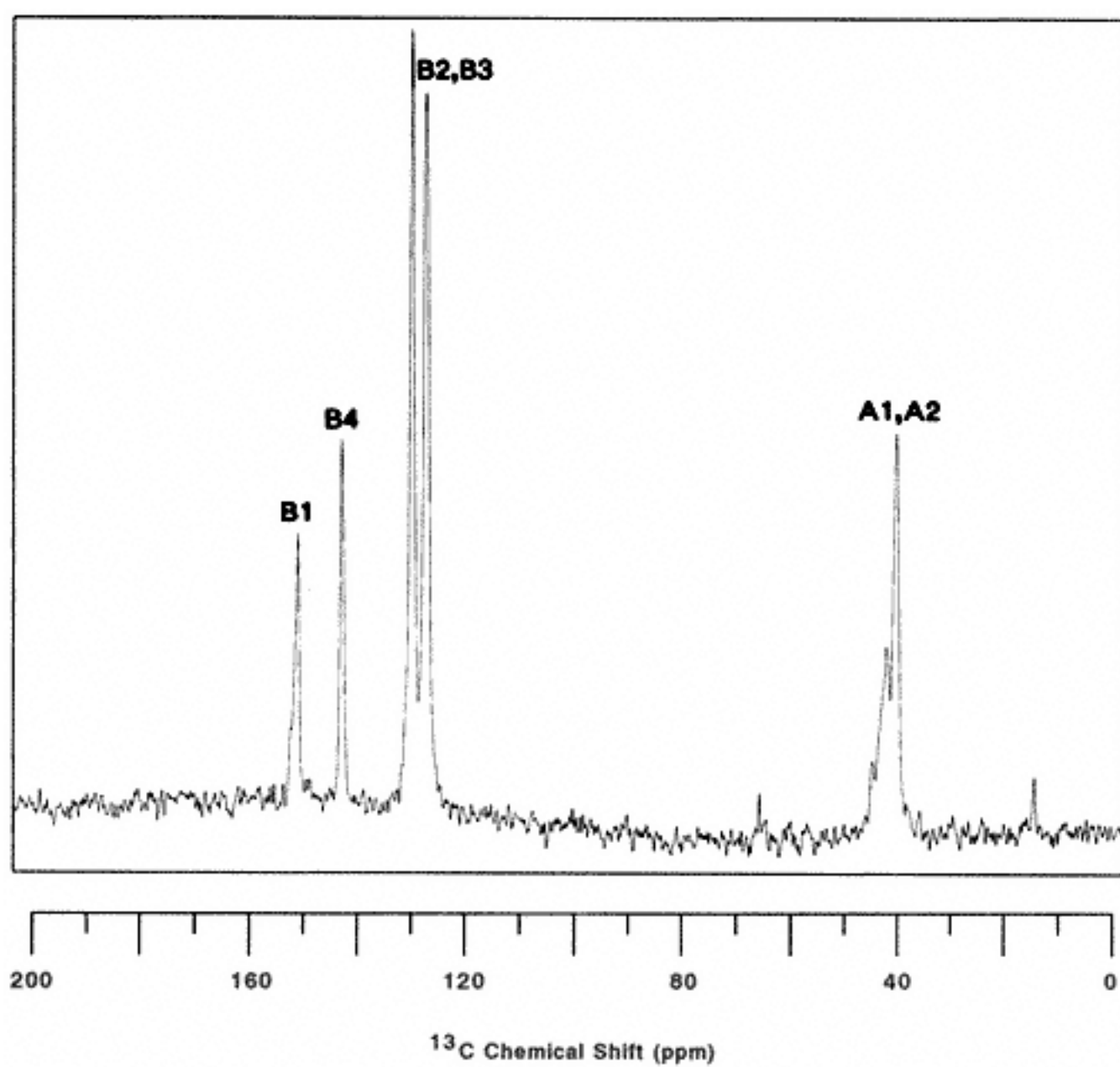
Broadening: 2 Hz

Pulse delay: 2 s

III-B-8— Poly(Styrene Sulfonic Acid)

Comments

The high degree of stereoirregularity causes splitting of resonances, particularly peaks **A1** and **B1**. The sulfonic acid group offers a site for further derivitization of polystyrene.



Code	Shift (ppm)
A1	40–46
A2	40–46
B1	148.8
B2	126.5–129
B3	126.5–129
B4	141.6

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: D_2O

Concentration: 20% w/w

Scans: 9000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

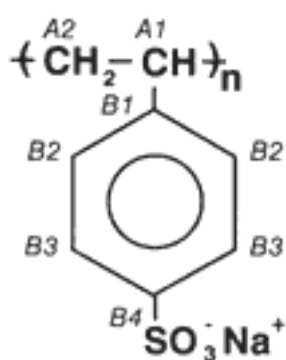
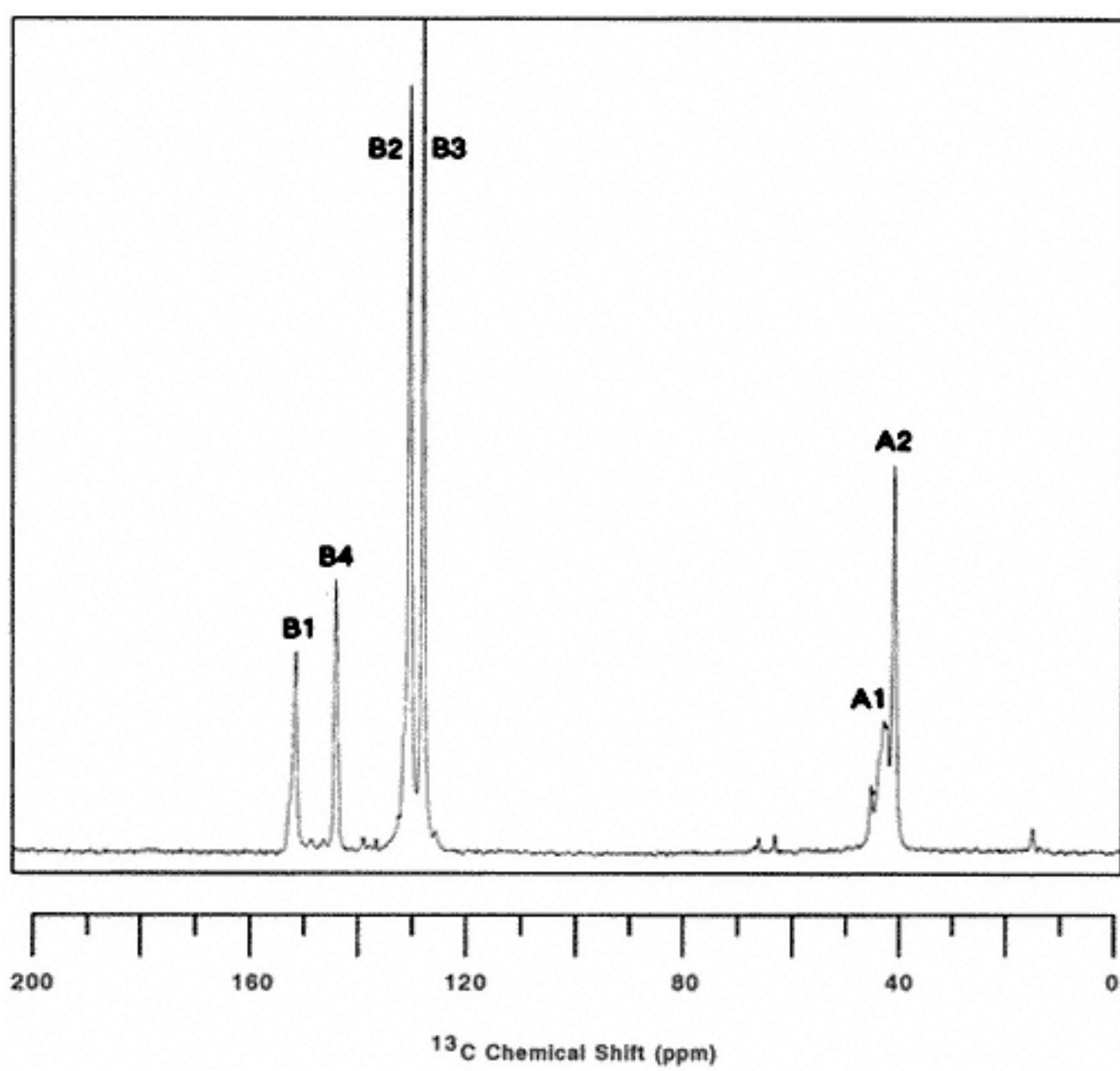
Broadening: 2 Hz

Pulse delay: 2 s

III-B-9—

Poly(Styrene Sulfonate), Na⁺*Comments*

The high degree of stereoirregularity causes splitting of resonances, particularly peaks **A1** and **B1**. The sulfonic acid salt offers a site for further derivatization of polystyrene.



Code	Shift (ppm)
A1	40–46
A2	40–46
B1	149.2
B2	126.4
B3	128.8
B4	142.6

*Experimental Parameters*Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: D₂O

Concentration: 20% w/w

Scans: 32,000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

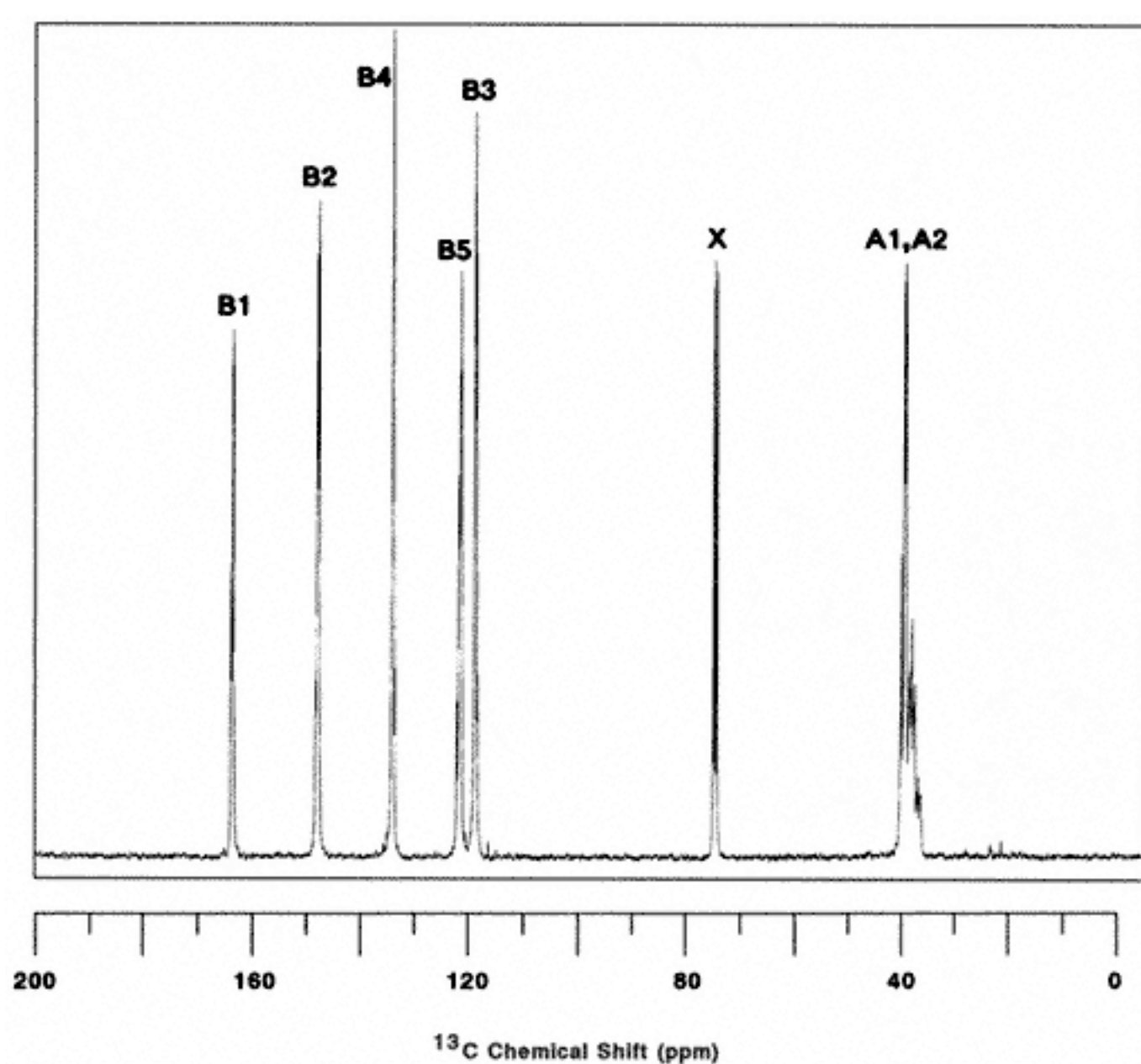
Broadening: 2 Hz

Pulse delay: 2 s

III-C-1— Poly(2-Vinylpyridine) (P2VP)

Comments

The high degree of stereoirregularity causes splitting of resonances, particularly peak **A1**. Solvent resonances are marked by **X**. 2-Vinyl pyridine is often incorporated as a comonomer in elastomer and fiber materials. It serves as a dye-fixation site and adhesive.



Code	Shift (ppm)
A1	42.6
A2	41.5
B1	164.0
B2	149.1
B3	120.8
B4	135.3
B5	122.9

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 30% w/w
Scans: 200	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 2 s

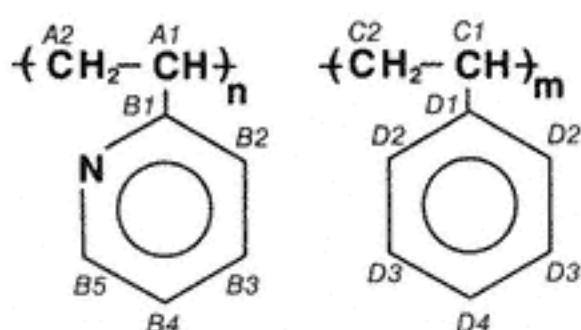
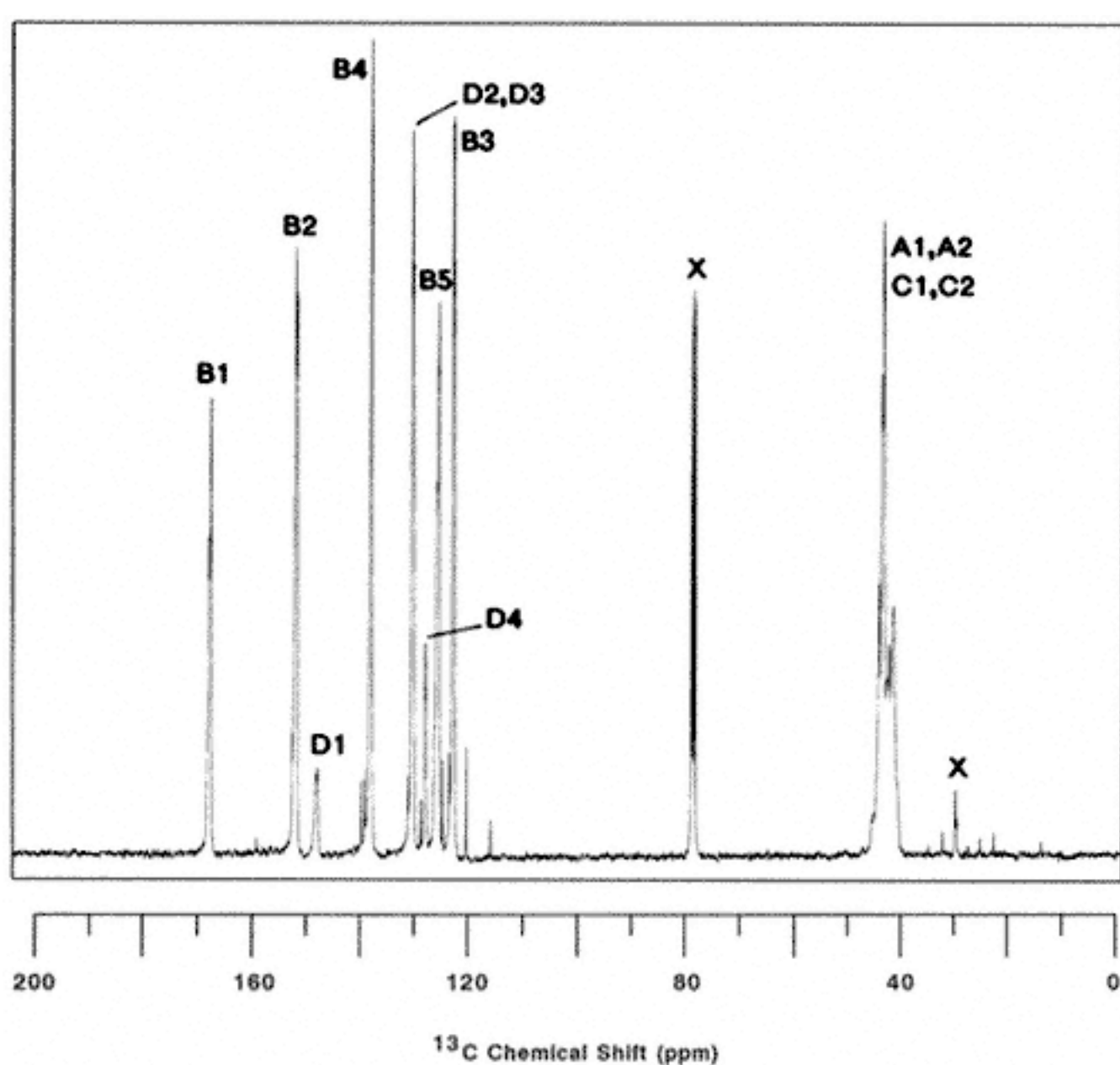
References

A.H. Soum and T. E. Hogen-Esch. *Macromolecules* 18:690, 1985; A. E. Tonelli. *Macromolecules* 18:2579, 1985; A. Dworak, W. J. Freeman, and H. J. Harwood. *Polym. J.* 17:351, 1985.

III-C-2— Poly(2-Vinylpyridine-Co-Styrene)

Comments

The high degree of stereoirregularity causes splitting of resonances, particularly peaks **A1** and **C1**. Solvent resonances are marked by **X**. 2-Vinyl pyridine is often incorporated as a comonomer in elastomer and fiber materials. It serves as a dye-fixation site and adhesive.



Code	Shift (ppm)
A1	42.6
A2	40.7
B1	164.2
B2	148.7
B3	120.3
B4	135.7
B5	123.0
C1	42.6
C2	40.7
D1	144.8
D2	126.5
D3	126.5
D4	125.0

Experimental Parameters

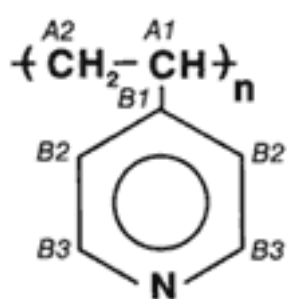
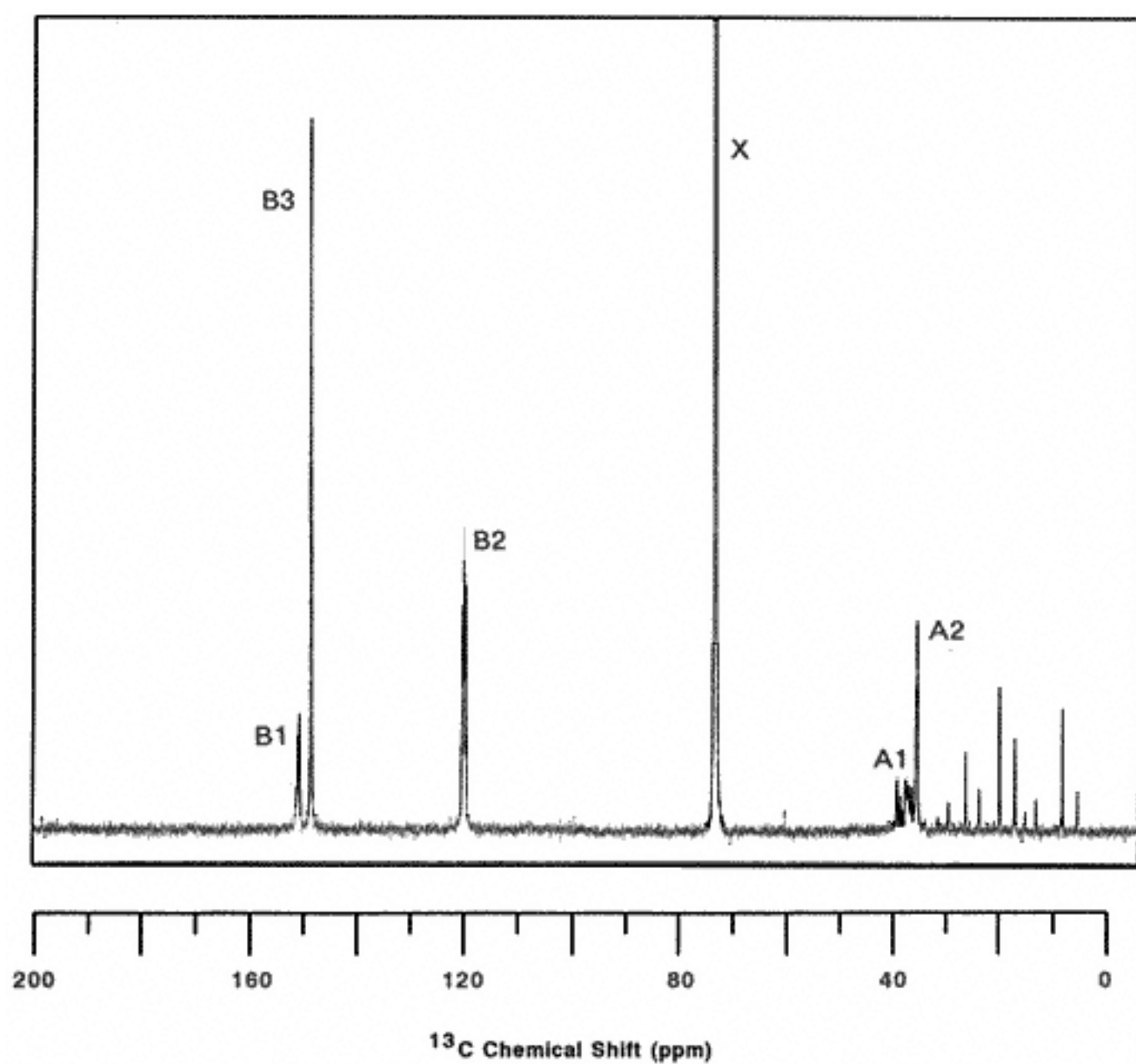
Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 30% w/w
Scans: 200	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 2 s

III-C-3—

Poly(4-Vinylpyridine) (P4VP)

Comments

The high degree of stereoirregularity causes splitting of resonances, particularly peaks **A1** and **B1**. Solvent resonances are marked by **X**. P4VP has been used as a basis for polyelectrolytes.



Code	Shift (ppm)
A1	40.3
A2	37.8
B1	149.8
B2	120.1
B3	147.6

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

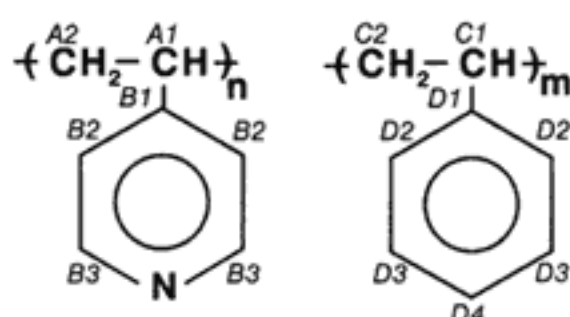
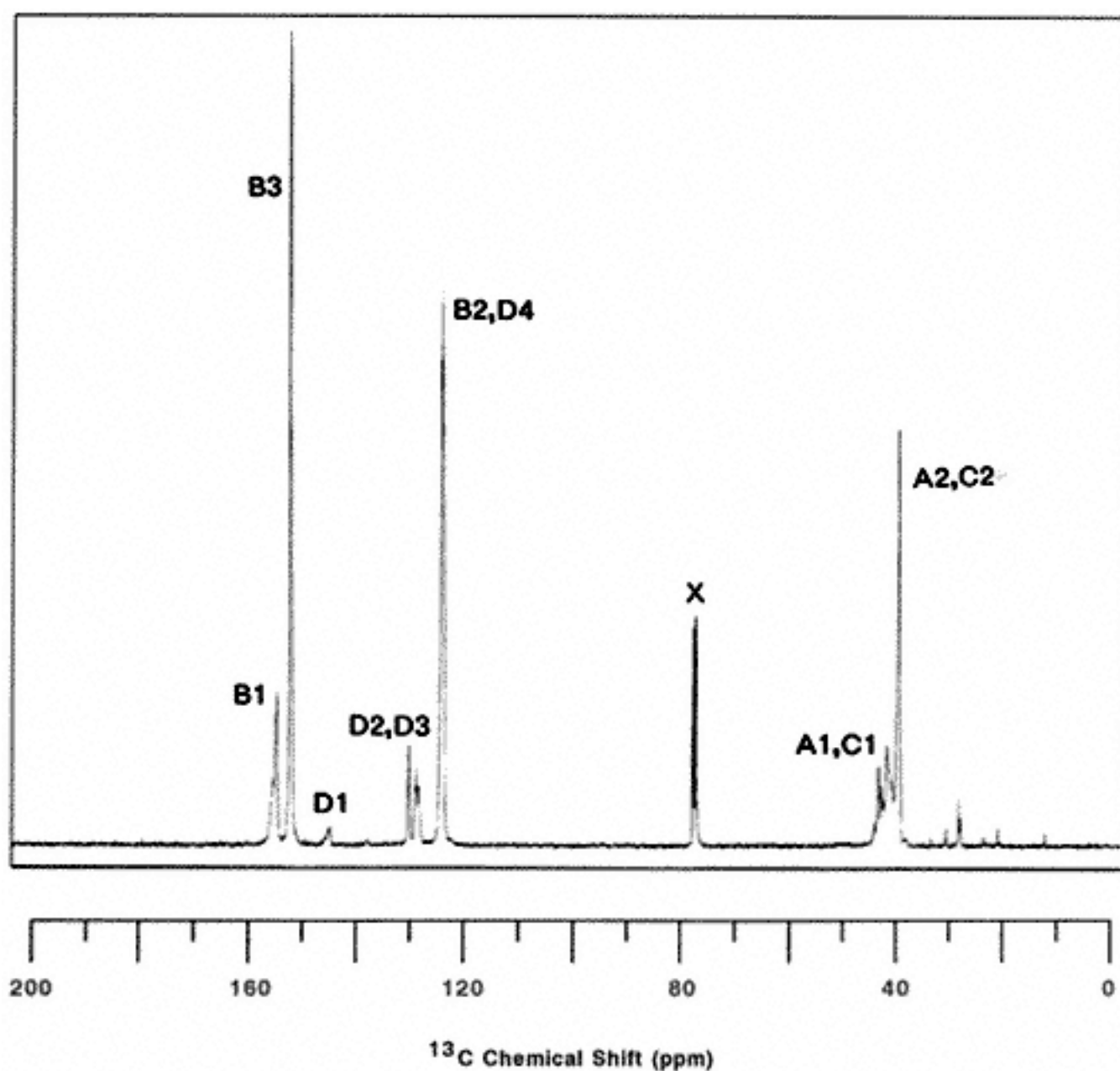
Pulse delay: 2 s

*Reference*A. H. Soum and T. E. Hogen-Esch. *Macromolecules* 18:690, 1985.

III-C-4— Poly(4-Vinylpyridine-Co-Styrene)

Comments

The high degree of stereoirregularity causes splitting of resonances, particularly peaks **A1**, **C1**, **B1**, and **D1**. Solvent resonances are marked by **X**.



Code	Shift (ppm)
A1	40.2
A2	37.7
B1	149.7
B2	120.4
B3	147.7
C1	40.2
C2	37.7
D1	140.3
D2	126.3
D3	124.2
D4	120.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 30% w/w
Scans: 200	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 2 s

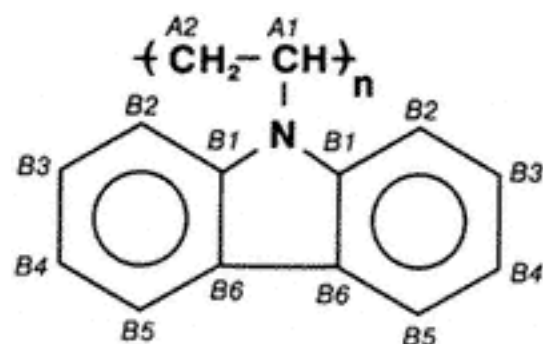
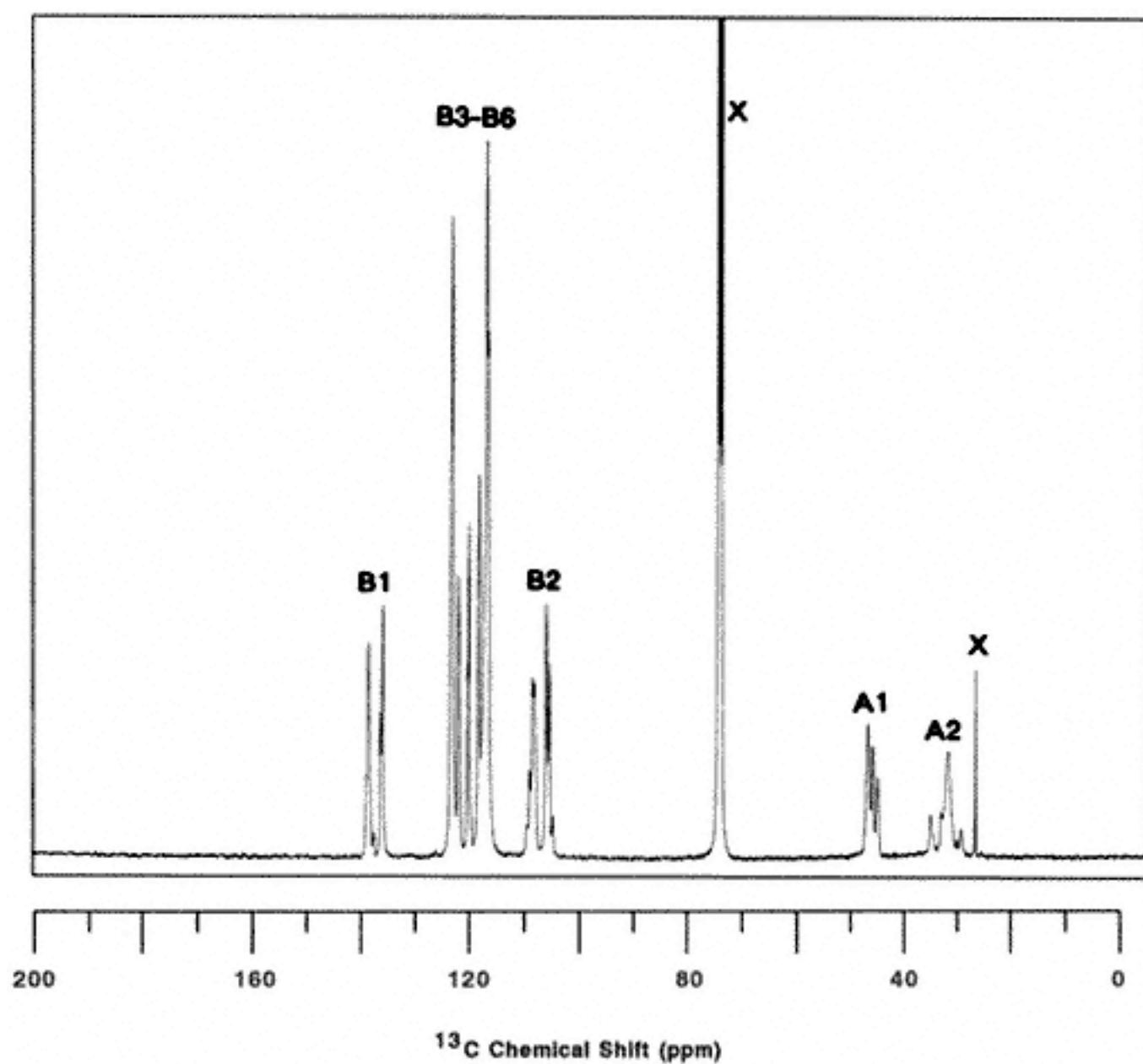
Reference

A. Petit, M. T. Cung, and J. Neel. *Eur. Polym. J.* 23:507, 1987.

III-C-5—

Poly(*N*-Vinylcarbazole) (PNVC)*Comments*

The high degree of stereoirregularity causes splitting of most resonances. Solvent resonances are marked by X. PNVC is a photopolymer and is used as an organic photoconductor for xerography.



Code	Shift (ppm)
A1	48–52
A2	34–40
B1	140.4, 137.5
B2	110.6, 107.5
B3	116–126
B4	116–126
B5	116–126
B6	116–126

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 9000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

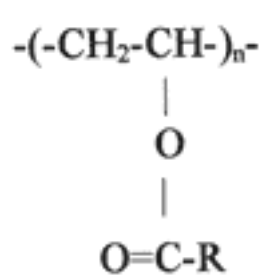
References

A. Natansohn. *J. Polym. Sci. A Polym. Chem. Ed.* 27:4257, 1989; S. J. Mumby and M. S. Beeves. *Polymer* 26:2014, 1985.

IV—

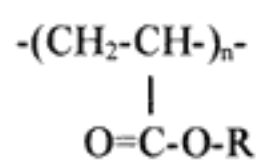
Aliphatic Backbones: Carboxylic Acid, Ester, and Amide Pendant Groups

This group of polymers includes: (a) poly(vinyl esters):



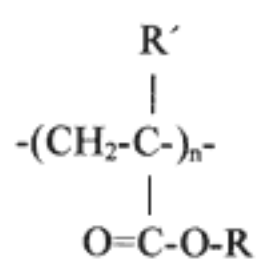
A

(b) polyacrylates:



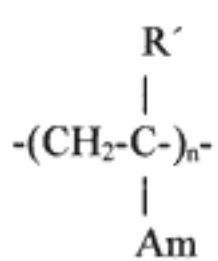
B

(c) α -substituted polyacrylates (where R' is CH₃ for methacrylates, CN for cyanoacrylates):



C

and (d) polymers and copolymers with amide side groups (where R' is usually H or CH₃):

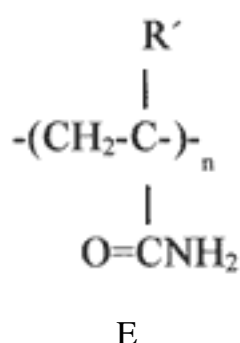


D

where Am denotes a pendant amide, which may be connected to the backbone either through the nitrogen atom or the carbonyl carbon.

Vinyl ester polymers (see Structure **A**) are specialty materials, used primarily in the manufacture of paints and other coatings, or as lubricant additives [1,2]. Poly(vinyl acetate) {IV-A-1} is, by far, the largest-volume material in this category. Polyacrylates (see Structure **B**) and polymethacrylates (see Structure **C** where R' = CH₃) are employed in a wide variety of products, such as coatings, elastomers, and adhesives [1,3,4]. The most common polymer of this type, poly(methyl methacrylate) (PMMA) {IV-C-1} is often generically referred to as "acrylic"; it is also well-known under two trade names: Lucite (DuPont) and Plexiglas (Rohm & Haas). ("Acrylic" fibers, on the other hand, are made from polyacrylonitrile {V-B-9}). Polyacrylates and polymethacrylates with ester groups larger than methyl (i. e., ethyl, butyl, and so on) are used in coatings and textile finishes; polyacrylates are the base for acrylate rubbers. All of these materials are amorphous thermoplastics, and exhibit glass, or softening, transitions, rather than sharp crystalline melting points. Below its glass-transition temperature T_g, a material is glassy and brittle; above T_g, it is rubbery. The T_gs of acrylates and methacrylates cover a wide range, depending on the identity of the ester and any α-substituent. For example, the T_g of poly(methyl acrylate) (PMA) {IV-B-2} is + 6°C; for poly(methyl methacrylate) (PMMA) {IV-C-1}, it is + 105°C [1]. Materials with subambient T_gs, such as PMA, are elastomers at room temperature, whereas those with higher T_gs, such as PMMA, are suitable for applications in which rigidity is required.

Polycyanoacrylates (see Structure C where R' is CN) are very strong adhesives, generically known as "superglues." Water-soluble polyacrylamides:



where R' is either a hydrogen atom or a methyl group, are used as thickeners, flocculating agents, and as binders in adhesive formulations.

IV.A—

Sample Preparation and Spectral Acquisition

Most vinyl ester, acrylate, and methacrylate polymers dissolve in several common solvents: chloroform-d, benzene-d₆, toluene-d₈, tetrahydrofuran-d₈, and acetone-d₆ [5]. Dissolution usually occurs at room temperature, although the process is slow. Water-soluble polymers in this group include poly(acrylic acid) {IV-A-1}, poly(2-hydroxyethyl methacrylate) {IV-C-3}, polyacrylamide {IV-D-1}, and polymethacrylamide {IV-D-2}. As is true for most high polymers, quantitative ¹³C peak areas for most carbons can be achieved by a 90° pulse, 15-s pulse (relaxation) delay, and gated ¹H decoupling to suppress nuclear overhauser effects (NOEs). Under these conditions, relative areas will not be correct for highly mobile nuclei (e.g., methyl groups) or nonprotonated (e.g., carbonyl or quaternary) carbons [6]. Suitable conditions for quantitative ¹H spectra are a 5-s pulse delay following a 90° pulse.

IV.B—

Spectral Features

As expected, the ¹³C and ¹H spectra of polymers in this group resemble those of lower molecular weight esters or amides [6]. The distinguishing features are ¹³C resonances between 170 and 180 ppm (C=O), 50 and 80 ppm (C—O for Structures **A–C**; C—N for some polymers with Structure **D**), and 10 and 50 ppm (backbone carbons and alkyl groups of esters). The ¹H spectrum may be confused with that of an alcohol or ether (CH—O between 3 and 4 ppm) or an amine or amide (NH between 4 and 6 ppm). For this reason, ¹³C NMR is the method of choice for identification of unknown polymers; ¹H may be useful for some quantitative analyses. Table IV-1 lists the chemical shifts for polymers in this group; Table IV-2, the ¹H shifts.

Table IV.1 ^{13}C NMR Chemical Shifts for Vinyl Ester, Acrylate, and Methacrylate Polymers

Polymer	α	$\begin{array}{c} A2 \ A1 \\ -C-C- \\ \ B1 \ B2 \\ O-C-C \\ \\ O \end{array}$		OR		$\begin{array}{c} A2 \ A1 \\ -C-C- \\ \\ O=C-C \\ B1 \ B2 \end{array}$		OR		$\begin{array}{c} \alpha \ C \\ A2 \ \ A1 \\ -C-C- \\ \\ O=C-C \\ B1 \ B2 \end{array}$		B7	B8	B9	B10
		A1	A2	B1	B2	B3	B4	B5	B6						
Poly(vinyl acetate)	—	66.4	38.9	170.0	20.6	—	—	—	—	—	—	—	—	—	—
Poly(vinyl stearate)	—	66.7	38.8	178.3, 172.0	33.9	24.0	30.0	32.3	23.3	14.3	—	—	—	—	—
Poly(acrylic acid)	—	35.6	41.4	177.1	—	—	—	—	—	—	—	—	—	—	—
Poly(methyl acrylate)	—	—	34.8	41.4	174.4	50.6	—	—	—	—	—	—	—	—	—
Poly(ethyl acrylate)	—	34.6	41.4	173.8	60.3	13.1	—	—	—	—	—	—	—	—	—
Poly(isopropyl acrylate)	—	36.1	42.1	174.3	67.3	20.4	—	—	—	—	—	—	—	—	—
Poly(<i>n</i> -butyl acrylate)	—	34.9	40.7	174.9	64.6	30.6	19.1	13.6	—	—	—	—	—	—	—
Poly(isobutyl acrylate)	—	34.9	41.6	174.5	70.2	27.7	19.0	—	—	—	—	—	—	—	—
Poly(hexyl acrylate)	—	35.5	41.4	174.4	62.2	28.7	25.4	31.5	22.6	14.0	—	—	—	—	—
Poly(2-ethylhexyl acrylate)	—	35.7	41.6	174.2	67.2	38.8	30.3	29.0	23.0	13.9	23.7	10.8	—	—	—
Poly(decyl acrylate)	—	35.1	41.5	174.7	64.6	25.9	30.0	30.0	30.0	31.9	22.6	13.9	—	—	—
Poly(dodecyl acrylate)	—	35.1	41.8	174.6	64.9	25.9	30.0	30.0	30.0	30.0	31.9	22.6	13.9	—	—
Poly(octadecyl acrylate)	—	38.0	42.0	174.6	64.7	26.0	30.0	30.0	30.0	30.0	32.0	22.7	13.3	—	—
Poly(methyl methacrylate)	18.1, 16.4 (CH ₃)	54.6	44.5	177.5	51.4	—	—	—	—	—	—	—	—	—	—
Poly(ethyl methacrylate)	18.1, 16.4 (CH ₃)	53.0	44.7	176.1	60.5	13.7	—	—	—	—	—	—	—	—	—
Poly(2-hydroxyethyl methacrylate)	16 (CH ₃)	54	43	178	60	60	—	—	—	—	—	—	—	—	—
Poly(isopropyl methacrylate)	18.1, 16.4 (CH ₃)	53.7	45.4	177.1	68.3	21.5	—	—	—	—	—	—	—	—	—
Poly(<i>n</i> -butyl methacrylate)	18.1, 16.4 (CH ₃)	54.2	44.9	176.7	63.1	30.3	18.4	13.6	—	—	—	—	—	—	—
Poly(isobutyl methacrylate)	18.1, 16.4 (CH ₃)	54.7	44.7	178.4	70.9	27.4	—	—	—	—	—	—	—	—	—
Poly(<i>t</i> -butyl methacrylate)	18.1, 16.4 (CH ₃)	54.7	44.7	176.7	46.0	27.1	—	—	—	—	—	—	—	—	—
Poly(hexyl methacrylate)	18.1, 16.4 (CH ₃)	54.2	44.9	177.6	64.1	28.1	25.4	21.4	21.0	13.9	—	—	—	—	—
Poly(cyclohexyl methacrylate)	18.1, 16.4 (CH ₃)	53.8	45.3	177.7	73.0	31.5	23.9	25.4	—	—	—	—	—	—	—

IV.B.1— Polymers and Copolymers of Vinyl Esters

The C=O resonances of poly(vinyl esters) appear at approximately 170 ppm; the CH—O peaks, between 65 and 75 ppm. Tacticity effects, arising from the stereoirregularity of the ester groups, are readily apparent in these spectra.

Several vinyl acetate (VA) copolymers are commercially significant, although VA is usually not the primary component. Some examples are poly(ethylene-co-vinyl acetate) {II-A-24, 25}, poly(*N*-vinylpyrrolidone-co-vinyl acetate) {IV-D-4}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, and poly(vinyl alcohol-co-vinyl acetate) {V-B-3.}. High-VA copolymers of ethylene and vinyl acetate {IV-A-2} are useful as adhesives. As outlined in Section II.B. 1, quantitative ^1H NMR provides a straightforward method for determination of the VA content in these copolymers; the calculation is done in the same way, regardless of VA content.

IV.B.2— Polymers of Acrylic Acid and Esters

The carbonyl carbon appears at approximately 180 ppm for poly(acrylic acid) (see Structure **B**, where R = H); from 170 to 175 ppm for the polyacrylates. In addition, the ^{13}C spectra of the ester polymers exhibit peaks between 50 and 70 ppm, attributable to the C—O carbon of the R group. The protons attached to this carbon resonate between 4 and 5 ppm; all other ^1H peaks are in the alkyl region, between 0.8 and 3.0. Acrylate polymers tend to be less stereoregular than the vinyl ester polymers, so tacticity effects are even more pronounced, particularly in ^{13}C spectra. As is true for polypropylene (see Sec. II.B.2), details of the stereochemistry can be calculated from the ^{13}C NMR spectrum [7].

Table IV.2 ^1H NMR Chemical Shifts for Vinyl Ester, Acrylate, and Methacrylate Polymers

Polymer	$\begin{array}{c} \text{H2} \quad \text{H1} \\ -\text{CH}_2 - \text{CH}- \\ \\ \text{O} - \text{C} - \text{CH}_2 \cdots \\ \\ \text{O} \end{array}$		OR	$\begin{array}{c} \text{H2} \quad \text{H1} \\ -\text{CH}_2 - \text{CH}- \\ \\ \text{O}=\text{C} - \text{CH}_2 \cdots \\ \\ \text{H3} \cdots \end{array}$		OR	$\begin{array}{c} \text{CH}_3 \text{ H1} \\ \\ \text{H2} - \text{C} - \\ \\ \text{O}=\text{C} - \text{CH}_2 \cdots \\ \\ \text{H3} \cdots \end{array}$	
	H1	H2	H3	H4	H5	H6		
Poly(vinyl acetate)	5.2	2.1	2.3	—	—	—		
Poly(methyl acrylate)	1.8	1.5	3.5	—	—	—		
Poly(ethyl acrylate)	2.3	1.6	4.1	1.2	—	—		
Poly(<i>n</i> -butyl acrylate)	1.9	1.6	4.0	2.2	1.3	0.9		
Poly(isobutyl acrylate)	1.9	1.6	3.8	2.3	0.9	—		
Poly(methyl methacrylate)	1.2–1.4	2.7	4.0	—	—	—		
Poly(ethyl methacrylate)	0.8, 1.0	1.8	4.0	1.2	—	—		
Poly(<i>n</i> -butyl methacrylate)	0.9	1.8	4.0	1.6	1.4	0.9		
Poly(isobutyl methacrylate)	0.9	1.9	3.7	1.8	0.9	—		

IV.B.3—**Polymers and Copolymers of α -Substituted Acrylates**

As expected, the spectra of α -substituted polyacrylates closely resemble those of the vinyl ester polymers and the polyacrylates. There are two distinguishing features in the ^{13}C spectra of these polymers, however. The quaternary carbon in the backbone resonates at approximately 55 ppm, compared with approximately 35 ppm for the analogous carbon in acrylate polymers. More conspicuously, additional resonances appear, owing to the carbon-containing α -group (18 and 16 ppm for CH_3 ; 120 ppm for CN). The protons of the methacrylate α -methyl group are at 2 ppm; the cyanide group, obviously, contributes no peak to the ^1H spectrum. These polymers, usually, are also highly stereoirregular.

IV.B.4—**Polymers and Copolymers with Pendant Amides**

These materials are produced from either acrylic or methacrylic acid amides, in which the amide group is attached to the backbone through the carbonyl, or from compounds such as *N*-vinylpyrrolidone, in which the amide nitrogen is connected directly to the backbone. In either case, the carbonyls resonate between 175 and 185 ppm, and the other carbons appear from 35 to 55 ppm. Noticeable tacticity effects are also observed in spectra of these polymers.

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ALIPHATIC BACKBONES: CARBOXYLIC ACID, ESTER, AND AMIDE PENDANT GROUPS

A. Polymers and Copolymers of Vinyl Esters

IV-A-1	Poly(vinyl acetate)
IV-A-1H	Poly(vinyl acetate)
IV-A-2	Poly(ethylene-co-vinyl acetate) (70% VA)
IV-A-2H	Poly(ethylene-co-vinyl acetate) (70% VA)
IV-A-3	Poly(vinyl stearate)

B. Polymers of Acrylic Acid and Esters

IV-B-1	Poly(acrylic acid)
IV-B-2	Poly(methyl acrylate)
IV-B-2H	Poly(methyl acrylate)
IV-B-3	Poly(ethyl acrylate)
IV-B-3H	Poly(ethyl acrylate)
IV-B-4	Poly(isopropyl acrylate)
IV-B-5	Poly(<i>n</i> -butyl acrylate)
IV-B-5H	Poly(<i>n</i> -butyl acrylate)
IV-B-6	Poly(isobutyl acrylate)
IV-B-6H	Poly(isobutyl acrylate)
IV-B-7	Poly(<i>n</i> -hexyl acrylate)
IV-B-8	Poly(2-ethylhexyl acrylate)
IV-B-9	Poly(decyl acrylate)
IV-B-10	Poly(dodecyl acrylate)
IV-B-11	Poly(octadecyl acrylate)

C. Polymers and Copolymers of α -Substituted Acrylates

IV-C-1	Poly(methyl methacrylate)
IV-C-1H	Poly(methyl methacrylate)
IV-C-2	Poly(ethyl methacrylate)
IV-C-2H	Poly(ethyl methacrylate)
IV-C-3	Poly(2-hydroxyethyl methacrylate)
IV-C-4	Poly(isopropyl methacrylate)
IV-C-5	Poly(<i>n</i> -butyl methacrylate)
IV-C-5H	Poly(<i>n</i> -butyl methacrylate)
IV-C-6	Poly(isobutyl methacrylate)
IV-C-6H	Poly(isobutyl methacrylate)
IV-C-7	Poly(<i>n</i> -butyl methacrylate-co-isobutyl methacrylate)
IV-C-7H	Poly(<i>n</i> -butyl methacrylate-co-isobutyl methacrylate)
IV-C-8	Poly(<i>t</i> -butyl methacrylate)
IV-C-9	Poly(<i>n</i> -hexyl methacrylate)
IV-C-10	Poly(cyclohexyl methacrylate)
IV-C-11	Poly(ethyl cyanoacrylate)
IV-C-11H	Poly(ethyl cyanoacrylate)

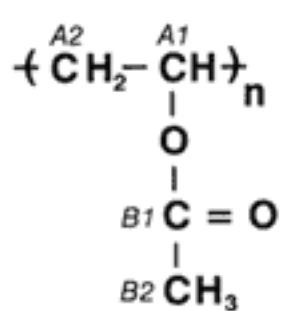
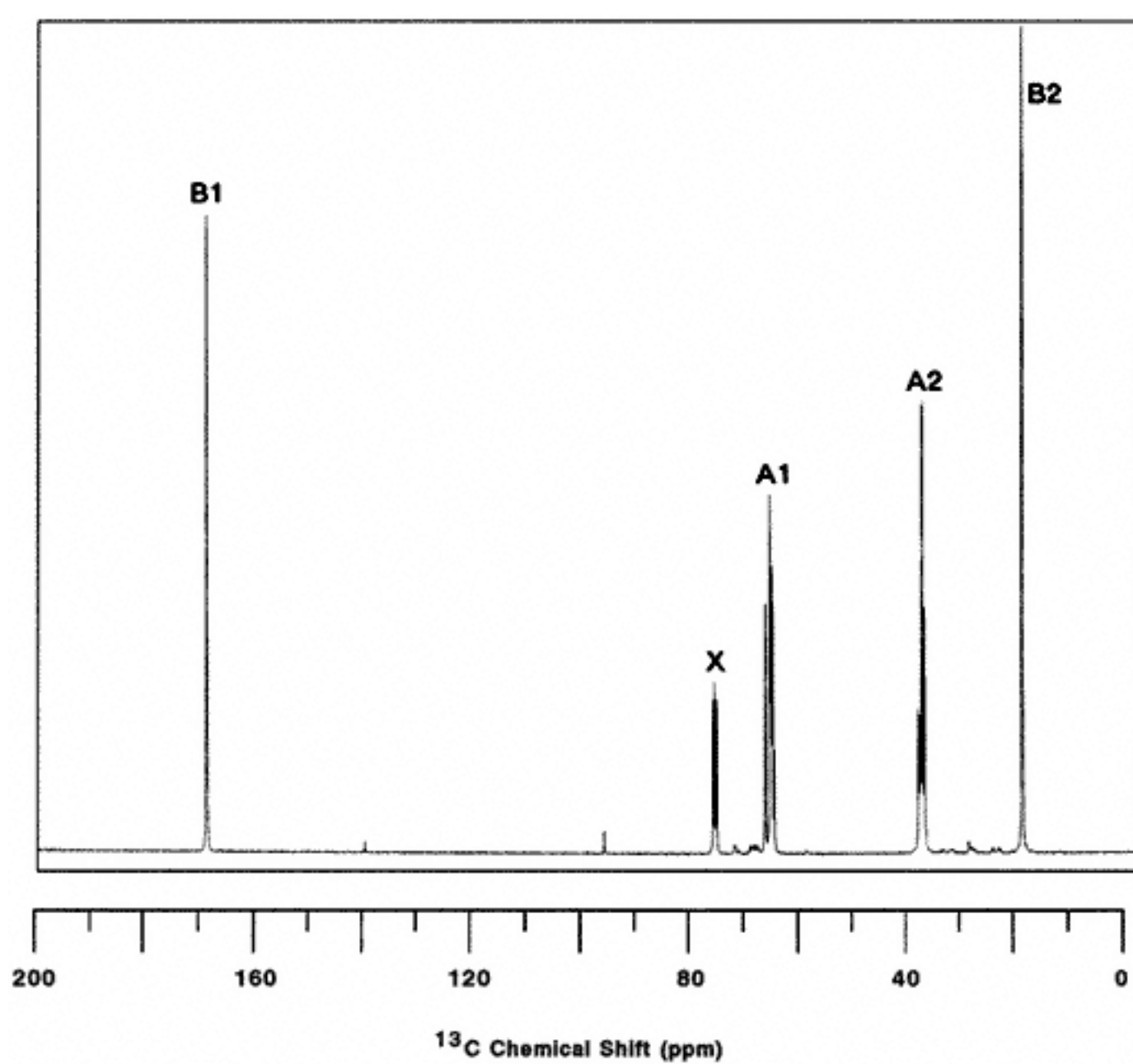
D. Polymers and Copolymers with Pendant Amides

IV-D-1	Polyacrylamide
IV-D-1H	Polyacrylamide
IV-D-2	Polymethacrylamide
IV-D-2H	Polymethacrylamide
IV-D-3	Poly(<i>N</i> -vinyl pyrrolidone)
IV-D-4	Poly(<i>N</i> -vinyl pyrrolidone-co-vinyl acetate)

**IV-A-1—
Poly(Vinyl Acetate) (PVA)**

Comments

Tacticity splitting is observed for the backbone carbons (**A1** and **A2**); solvent resonances are marked by **X**. This polymer, produced by polymerization of vinyl acetate, is the starting material for poly(vinyl alcohol) {IV-B-2}, poly(vinyl formal) {IV-B-5}, and poly(vinyl butyral) {IV-B-6.}. PVA is used as a latex base for interior and exterior paints, as an adhesive, as a binder for paper coatings, and as a textile finish.



Code	Shift (ppm)
A1	66.4
A2	38.9
B1	170.0
B2	20.6

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

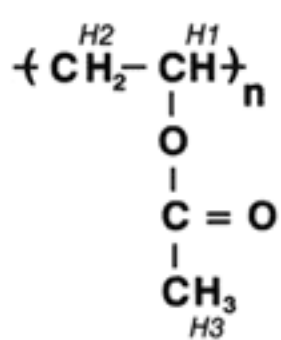
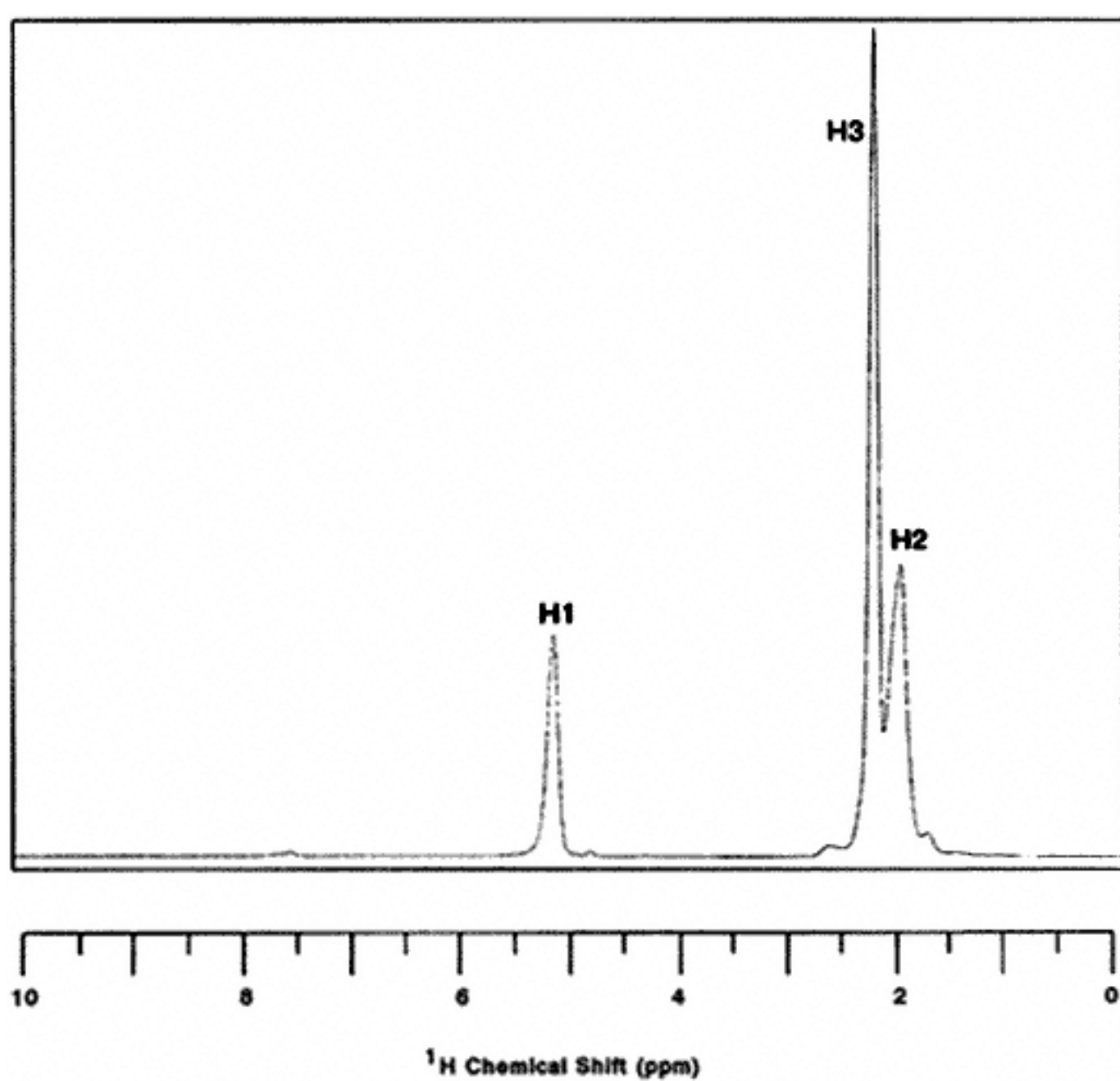
Broadening: 2 Hz

Pulse delay: 2 s

**IV-A-1H—
Poly(Vinyl Acetate) (PVA)**

Comments

Tacticity splittings are not observed because of broadening that is due to sample viscosity. This polymer, produced by polymerization of vinyl acetate, is the starting material for poly(vinyl alcohol) {V-B-2H}, poly(vinyl formal) {V-B-5}, and poly(vinyl butyral) {V-B-6.}. PVA is used as a latex base for interior and exterior paints, as an adhesive, as a binder for paper coatings, and as a textile finish.



Code	Shift (ppm)
H1	5.2
H2	2.1
H3	2.3

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

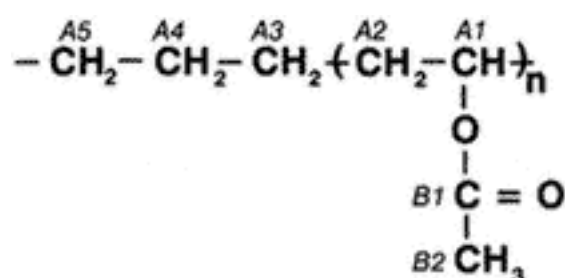
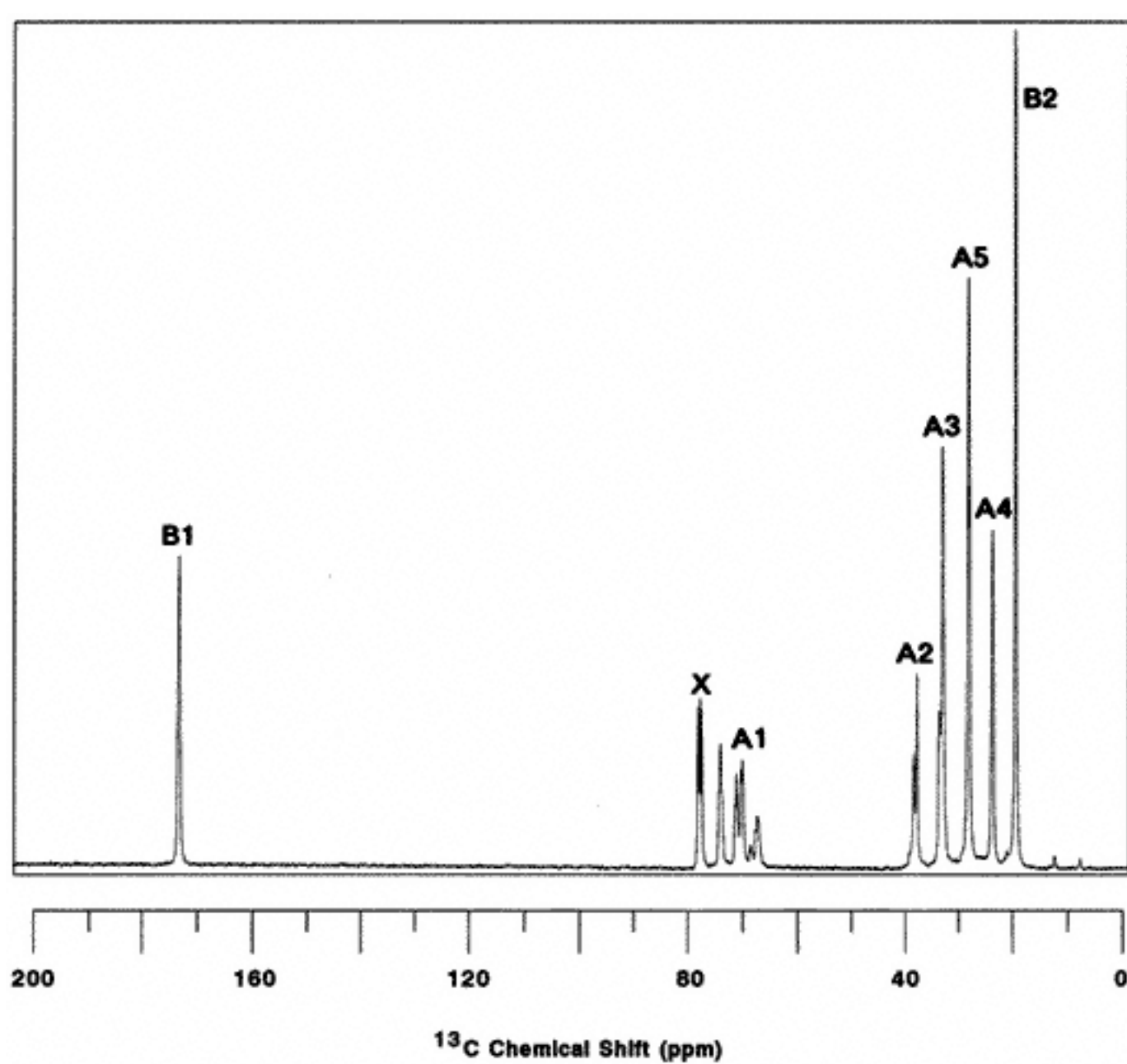
Pulse delay: 5 s

IV-A-2—

Poly(Ethylene-Co-Vinyl Acetate) (EVA) [70% VA]

Comments

At high vinyl acetate concentrations, the VA peaks become predominant in the spectrum (compare with spectra of lower-VA level copolymers {II-A-24, II-A-25}). Solvent resonances are marked by **X**. EVA is a soft thermoplastic material with excellent clarity and heat-seal characteristics. Higher-VA content EVAs are used as elastomers and in adhesives.



Code	Shift (ppm)
A1	66–74
A2	38.0
A3	33.9
A4	24.1
A5	29.3
B1	170.1
B2	20.8

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

References

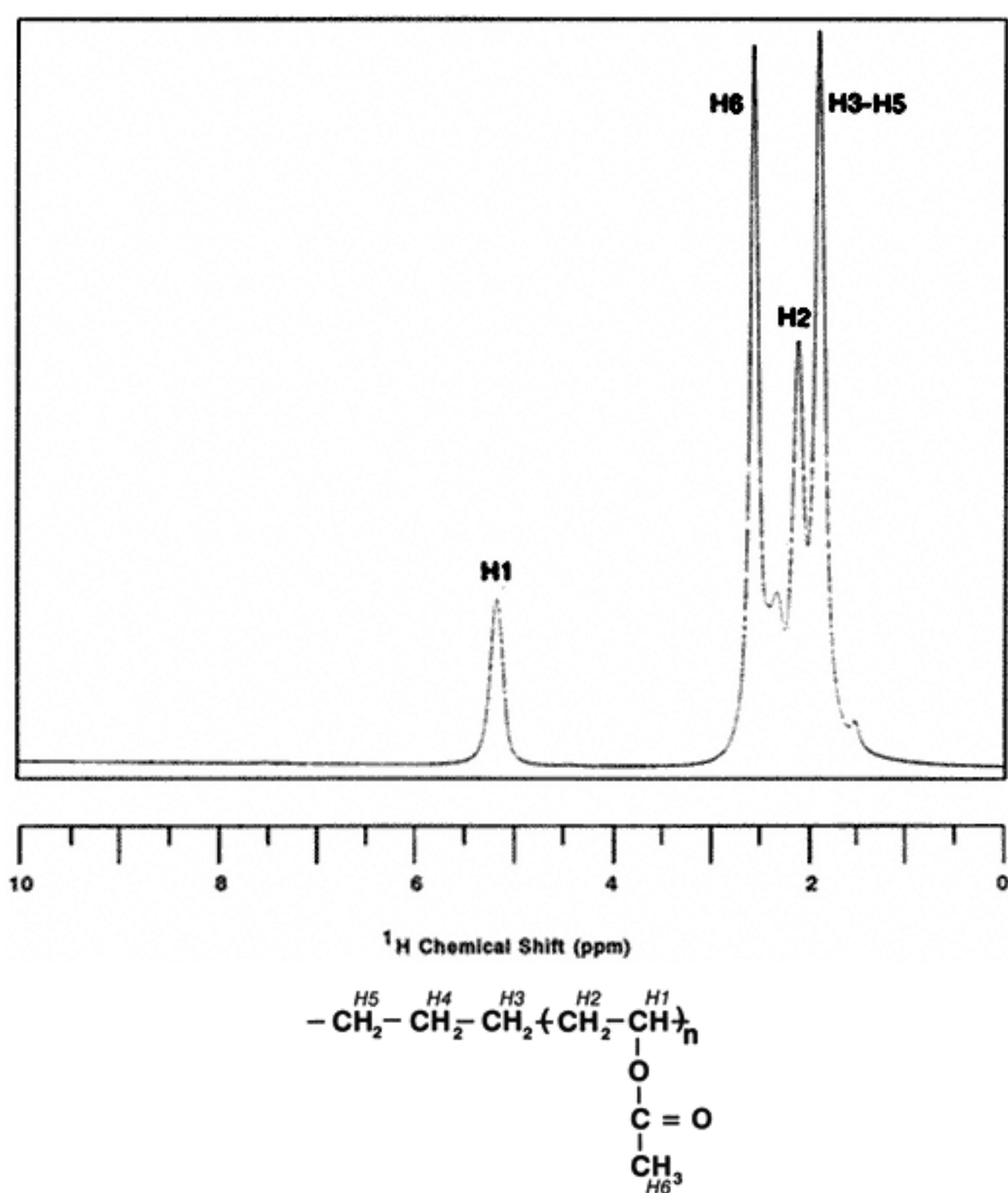
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IV-A-2H—

Poly(Ethylene-Co-Vinyl Acetate) (EVA) [70% VA]

Comments

At high vinyl acetate concentrations, the VA peaks become predominant in the spectrum (compare with spectra of lower-VA level copolymer {II-A-25H}). A distinct resonance arising from incorporation of vinyl acetate appears at 4.7 ppm; this peak can readily be used to quantify the material's VA content. EVA is a soft thermoplastic material with excellent clarity and heat-seal characteristics. Higher-VA content EVAs are used as elastomers and in adhesives.



Code	Shift (ppm)
H1	4.7
H2	1.8
H3	1.1
H4	1.1
H5	1.1
H6	2.2

*Experimental Parameters*Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

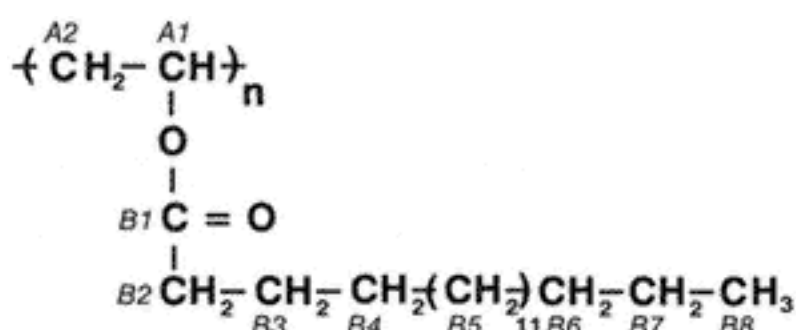
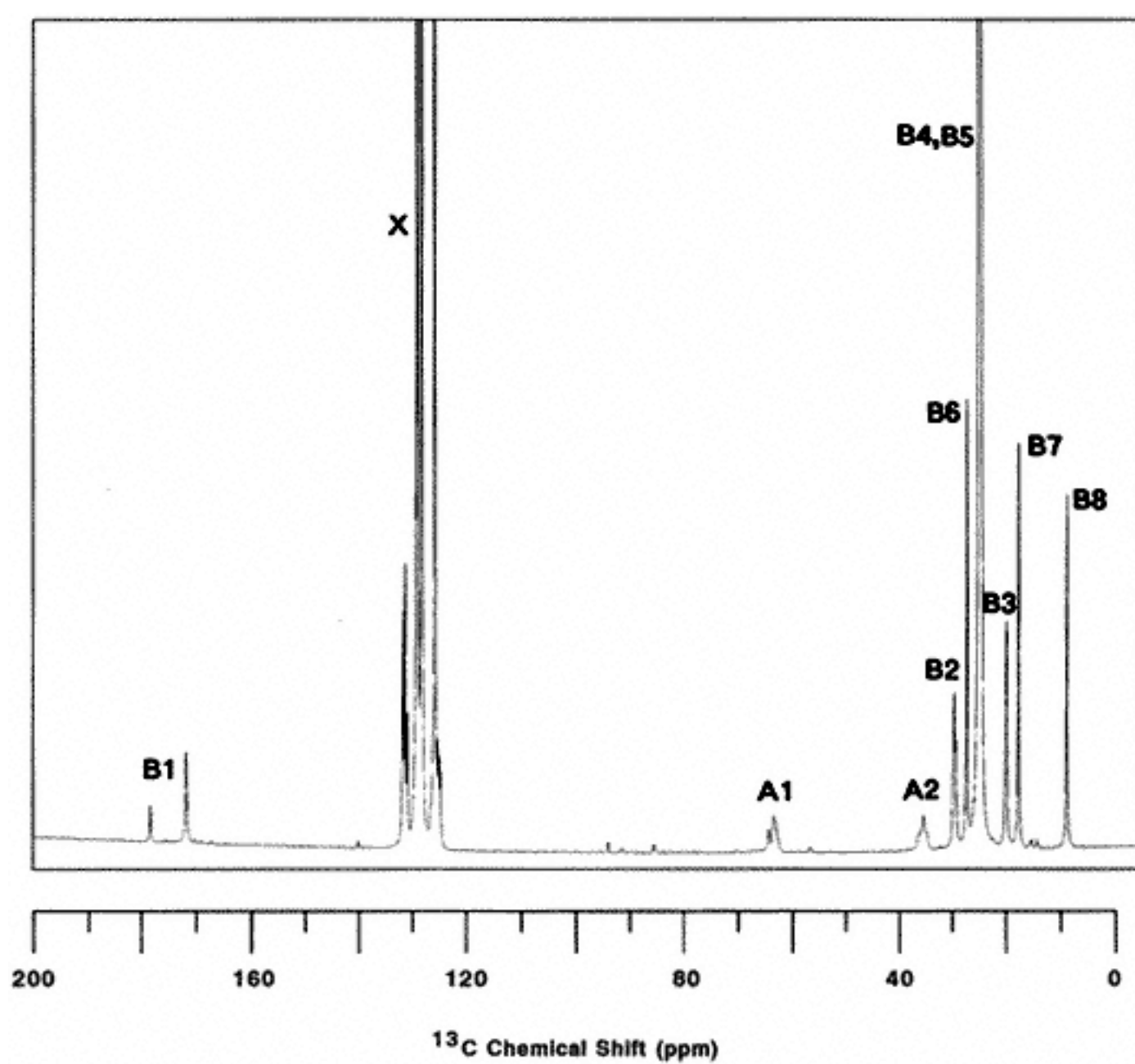
Broadening: 5 Hz

Pulse delay: 5 s

IV-A-3—
Poly(Vinyl Stearate) (PVS)

Comments

Some tacticity splitting is observed for the backbone carbons (A1 and A2); solvent resonances are marked by X. PVS is used primarily as a viscosity modifier for lubricants.



Code	Shift (ppm)
A1	66.7
A2	38.8
B1	178.3, 172.0
B2	33.9
B3	24.0
B4	30.0
B5	30.0
B6	32.3
B7	23.3
B8	14.3

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: ODCB- d_4 /TCB (3/1 v/v)

Concentration: 30% w/w

Scans: 20,000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

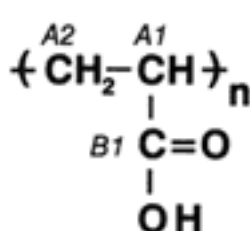
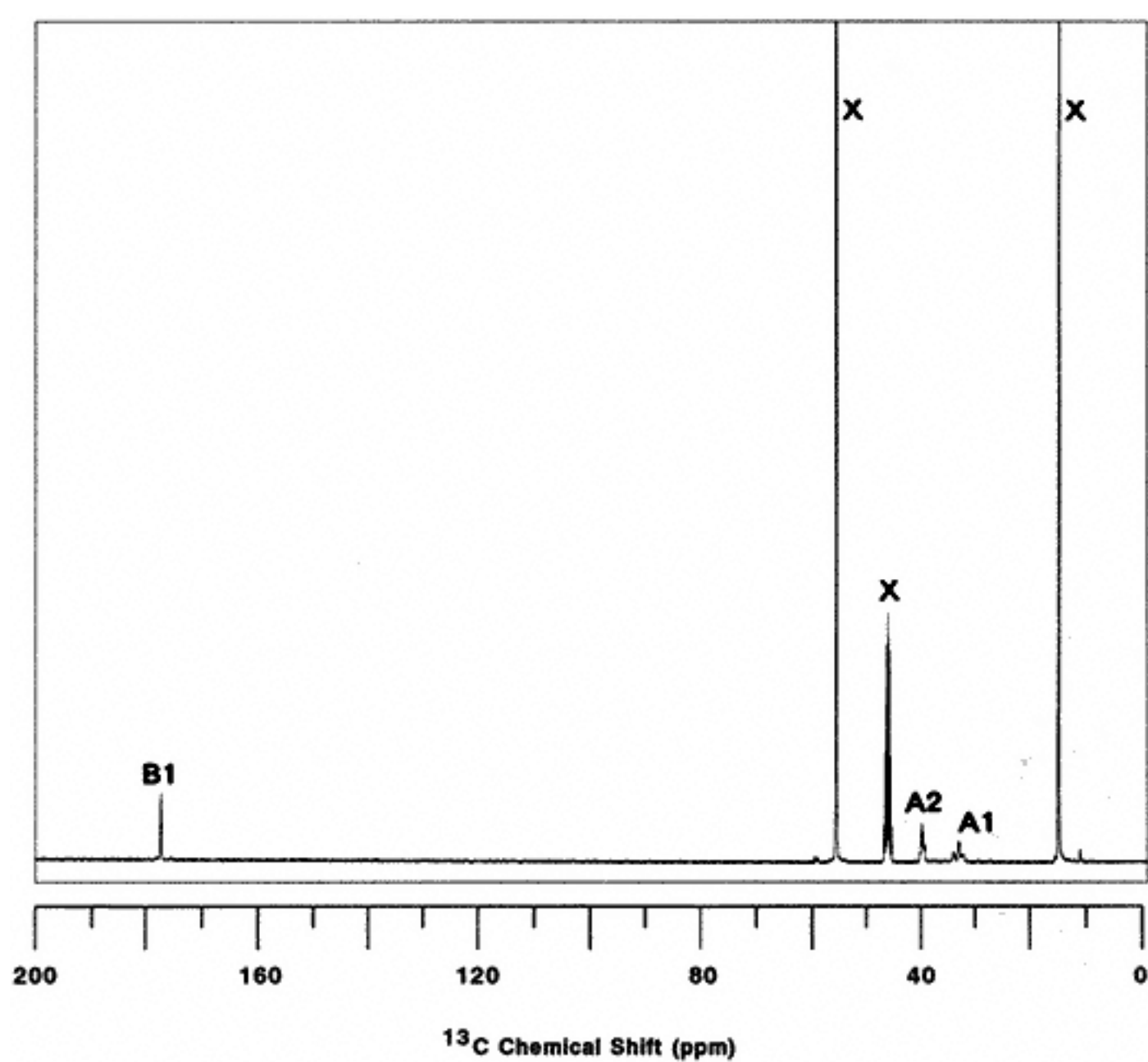
Broadening: 2 Hz

Pulse delay: 5 s

**IV-B-1—
Poly(Acrylic Acid) (PAA)**

Comments

Some tacticity splitting is observed for the backbone carbons (**A1** and **A2**); solvent resonances are marked by **X**. PAA is a water-soluble polyelectrolyte, the salts of which make very highly viscous solutions. It is a superabsorbent material found, for example, in disposable diapers. PAA is also used as a thickener, suspension and as a flocculation agent in emulsions, paints, and textile finishes; a cross-linked form of PAA serves as a cation-exchange resin and dental cement.



Code	Shift (ppm)
A1	35.6
A2	41.4
B1	177.1

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 130°C
Solvent: methanol- d_4 /ethanol	Concentration: 30% w/w
Scans: 1000	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 2 s

References

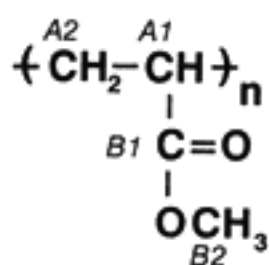
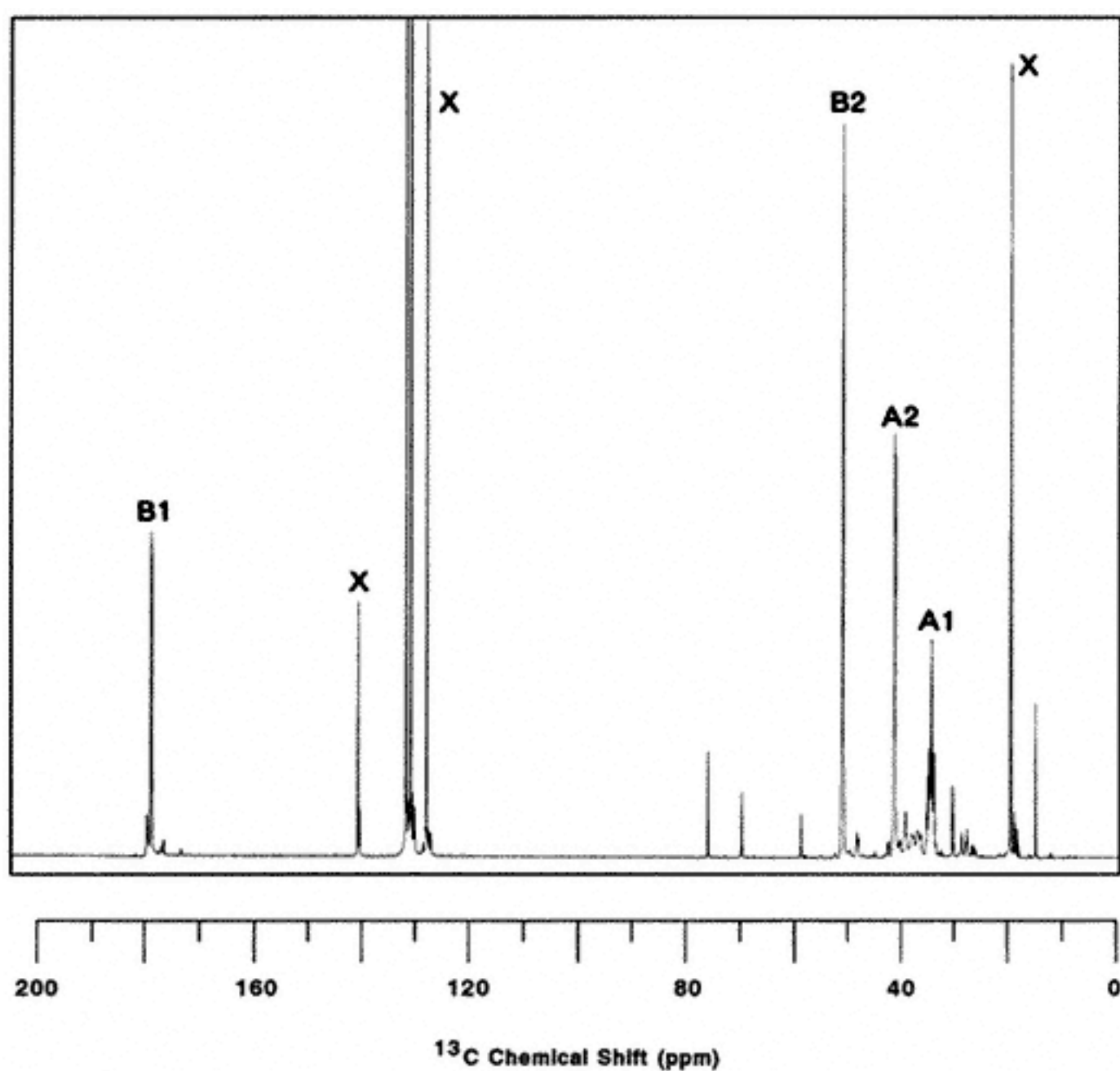
J. Spevacek, M. Suchoparek, and S. Al-Alawi. *Polymer* 36:4125, 1995; K. Beshah. *Makromol. Chem.* 194:3311, 1993; C. Chang, D. D. Muccio, and T. St. Pierre. *Macromolecules* 18:2154, 1985.

IV-B-2—

Poly(Methyl Acrylate) (PMA)

Comments

Some tacticity splitting is observed for methine backbone carbon (A1); solvent resonances are marked by X. PMA is used in, textile modification, as a fiber size and leather finisher.



Code	Shift (ppm)
A1	34.8
A2	41.4
B1	174.4
B2	50.6

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: toluene- d_8 /toluene

Concentration: 30 % w/w

Scans: 4800

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

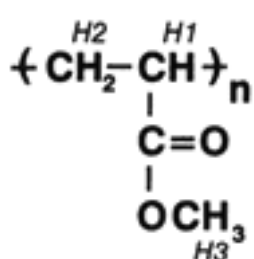
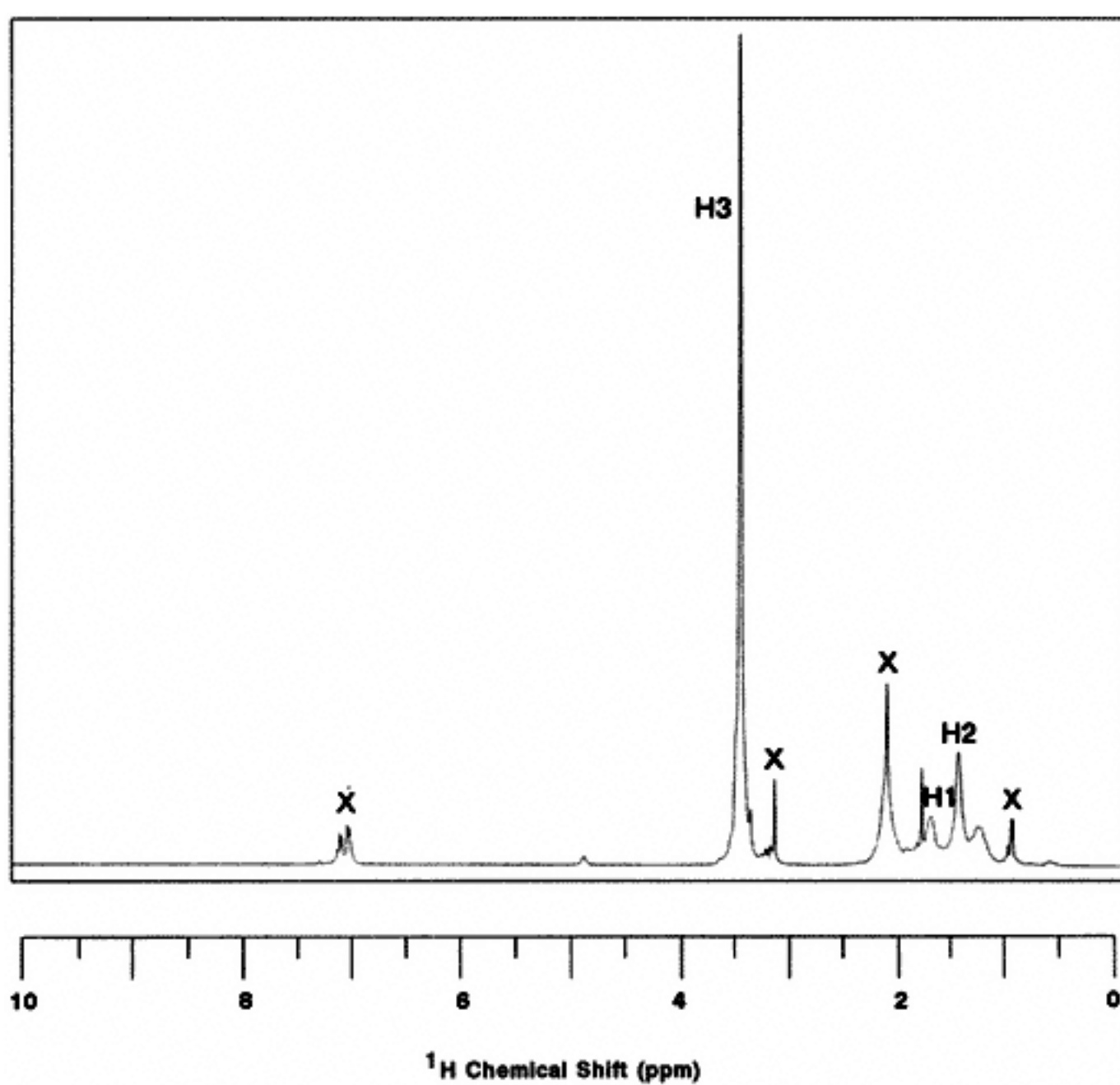
*Reference*T. Kawamura, N. Toshima, and K. Matsuzaki. *Macromol. Chem. Phys.* 196:3415, 1995.*Source*

Scientific Polymer Products, Ontario, NY.

**IV-B-2H—
Poly(Methyl Acrylate) (PMA)**

Comments

Tacticity effects are obscured by broadening from sample viscosity. PMA is used in textile modification, as a fiber size and leather finisher.



Code	Shift (ppm)
H1	1.8
H2	1.5
H3	3.5

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: toluene- d_8 /toluene

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

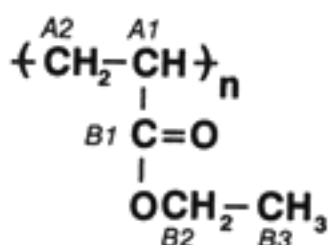
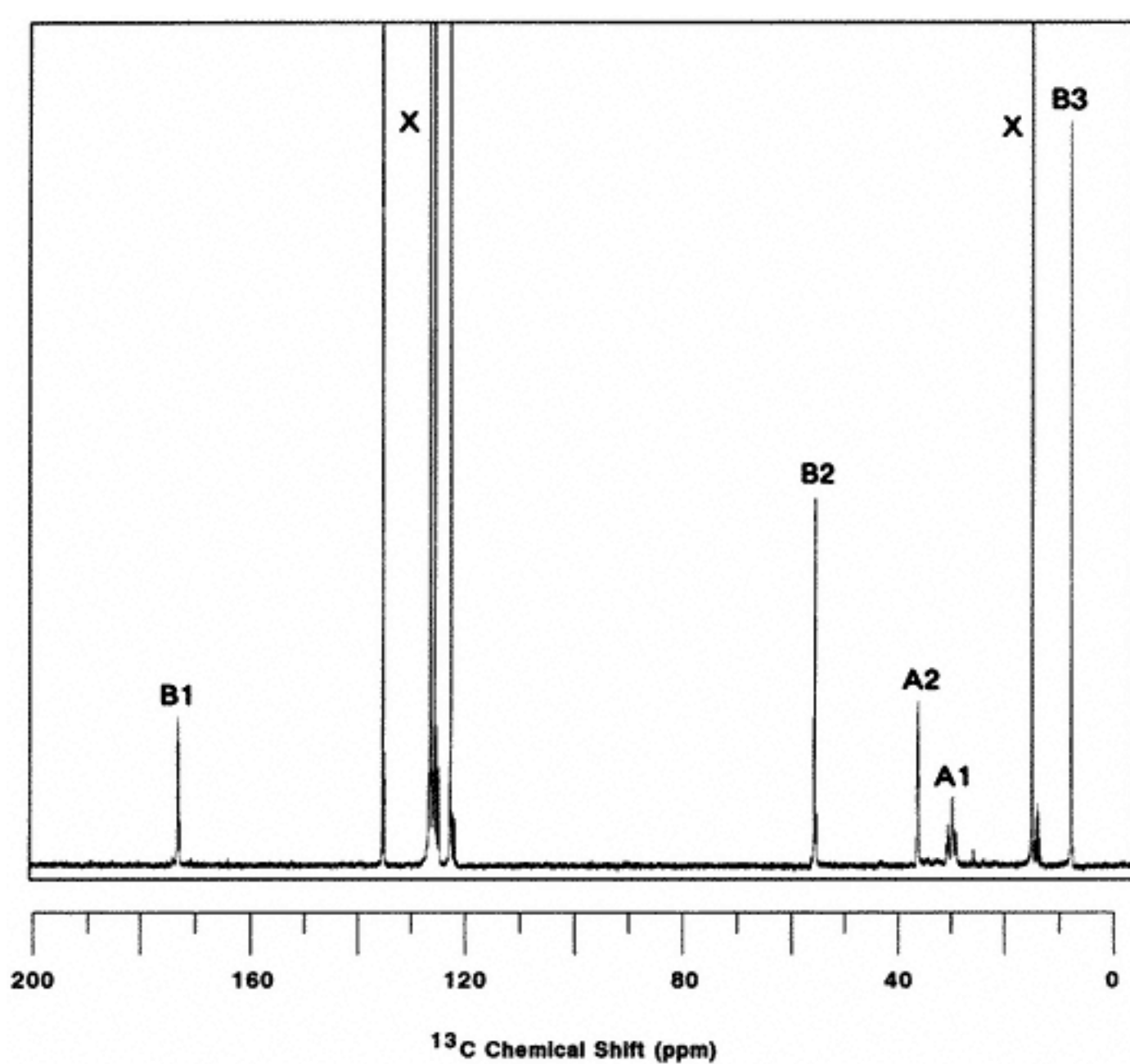
Source

Scientific Polymer Products, Ontario, NY.

**IV-B-3—
Poly(Ethyl Acrylate) (PEA)**

Comments

Some tacticity splitting is observed for the methine backbone carbon (**A1**); solvent resonances are marked by **X**. PEA forms the base for many acrylate rubbers; the polymer is also used for fiber modification and in coating materials.



Code	Shift (ppm)
A1	34.6
A2	41.4
B1	173.8
B2	60.3
B3	13.1

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: toluene- d_8 /toluene	Concentration: 30% w/w
Scans: 32	Spectral width: 25 kHz
Data points: 32768	Pulse width: 90°
Broadening: 1 Hz	Pulse delay: 2

Reference

T. Kawamura, N. Toshima, and K. Matsuzaki, *Macromol. Chem. Phys.* 196:3415, 1995.

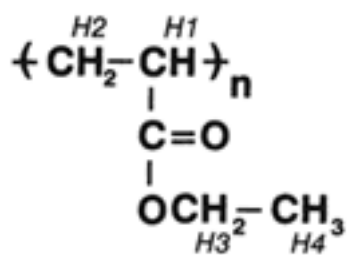
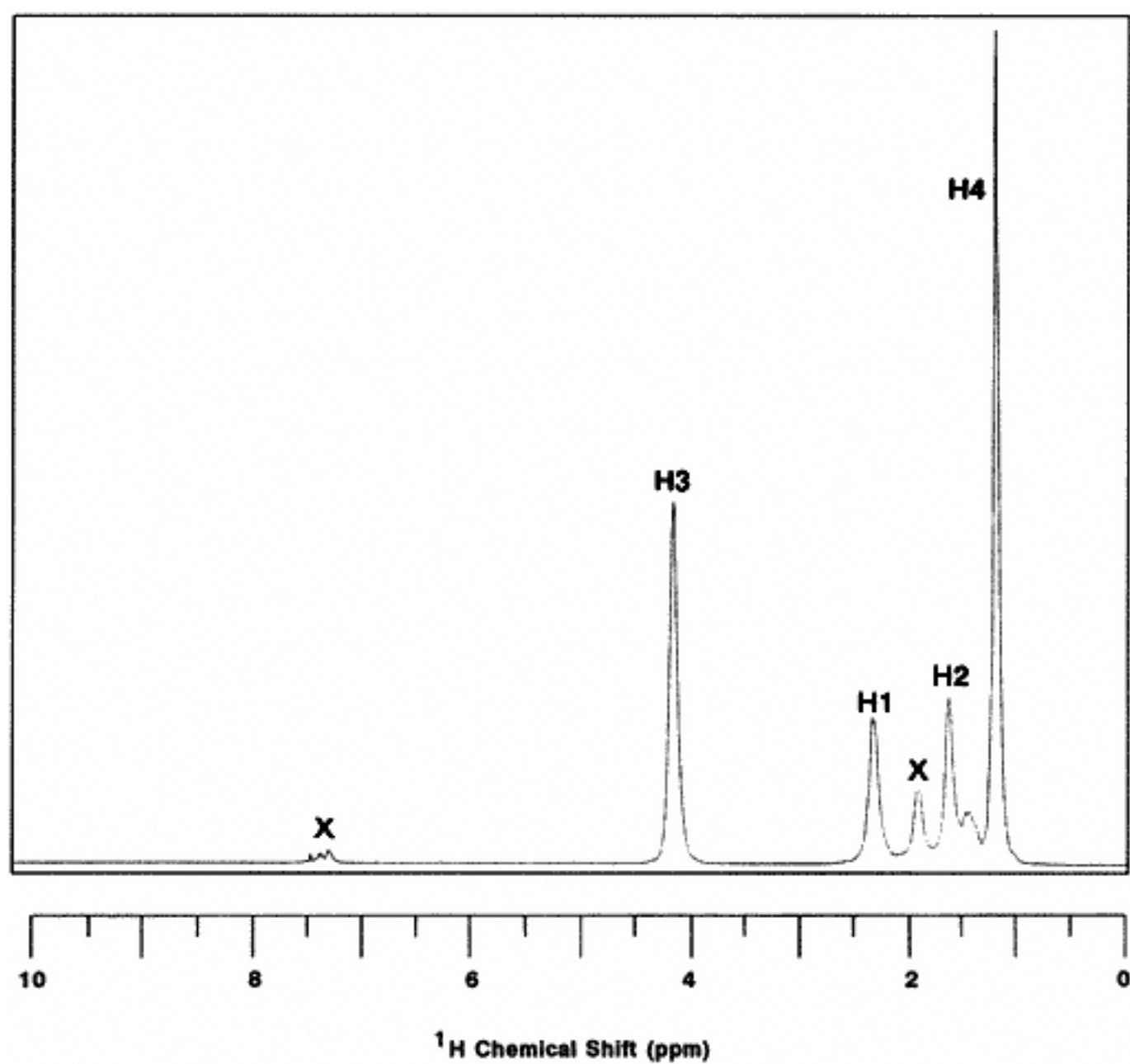
Source

Scientific Polymer Products, Ontario, NY.

**IV-B-3H—
Poly(Ethyl Acrylate) (PEA)**

Comments

Tacticity effects are obscured by broadening caused by sample viscosity. PEA forms the base for many acrylate rubbers; the polymer is also used for fiber modification and in coating materials.



Code	Shift (ppm)
H1	2.3
H2	1.6
H3	4.1
H4	1.2

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: toluene- d_8 /toluene

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data Points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 25 s

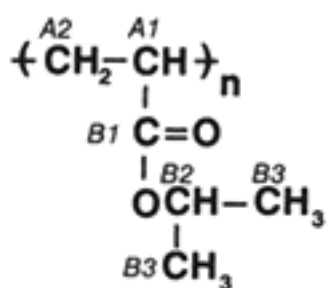
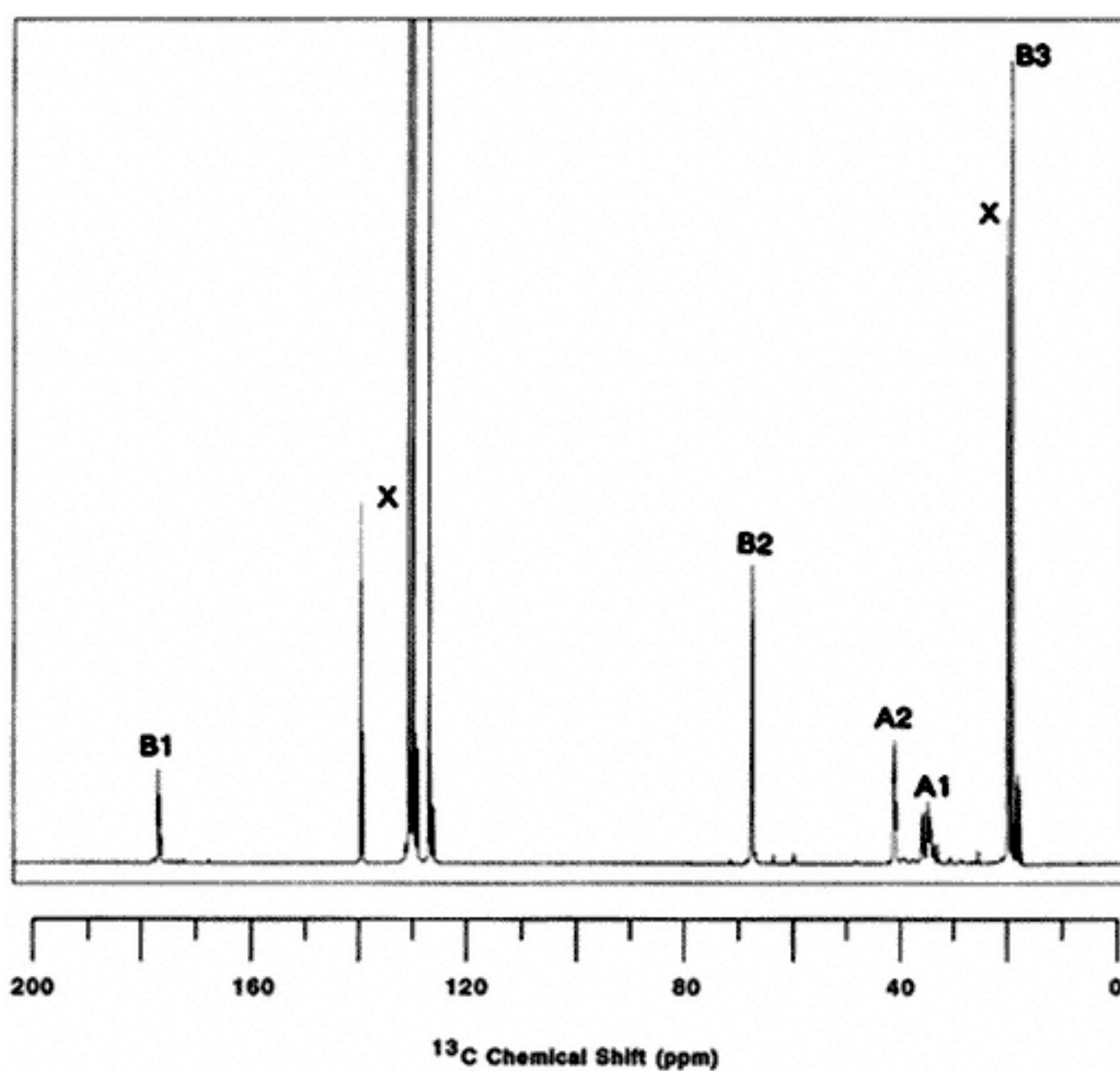
Source

Scientific Polymer Products, Ontario, NY.

**IV-B-4—
Poly(Isopropyl Acrylate) (PiPA)**

Comments

Some tacticity splitting can be observed for the backbone (A1 and A2) and carbonyl carbons (B1); solvent resonances are marked by X.



Code	Shift (ppm)
A1	36.1
A2	42.1
B1	174.3
B2	67.3
B3	20.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: toluene

Concentration: 30% w/w

Scans: 4800

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

Reference

T. Kawamura, N. Toshima, and K. Matsuzaki. *Macromol. Chem. Phys.* 196:3415, 1995.

Source

Scientific Polymer Products, Ontario, NY.

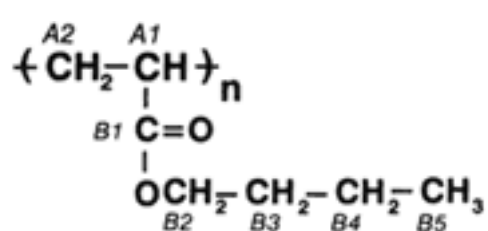
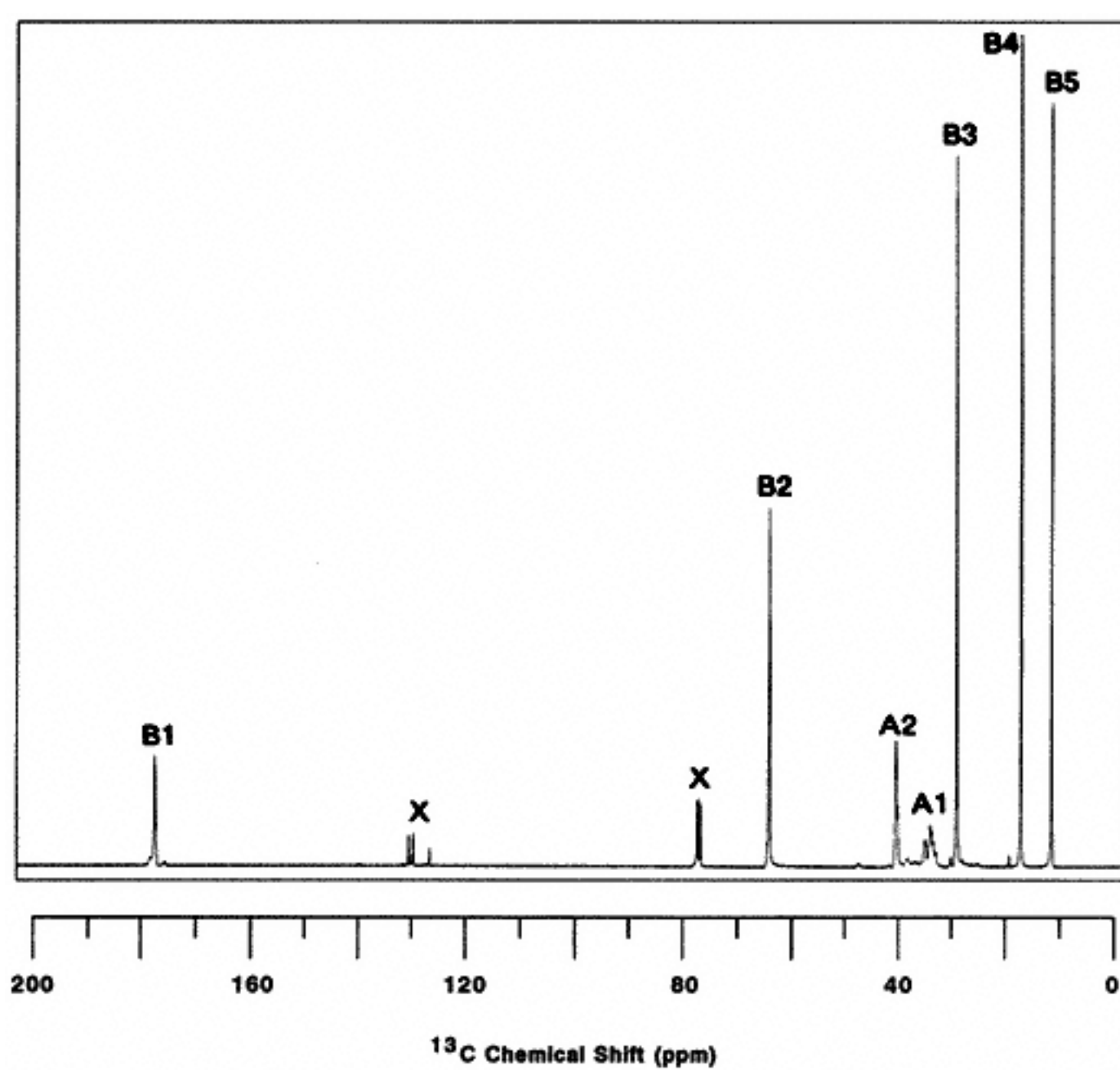
IV-B-5

IV-B-5—

Poly(*n*-Butyl Acrylate) (PBA)

Comments

Some tacticity splitting can be observed for the backbone (A1 and A2) and carbonyl carbons (B1); solvent resonances are marked by X. PBA is used in the formulation of paints and adhesives. It forms a base for acrylic elastomers, particularly when combined with a small amount of acrylonitrile. PBA is sometimes blended with PMMA {IV-C-1} or PVC {V-A-8} as an impact modifier.



Code	Shift (ppm)
A1	34.9
A2	40.7
B1	174.9
B2	64.6
B3	30.6
B4	19.1
B5	13.6

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3 /toluene

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

Reference

T. Kawamura, N. Toshima, and K. Matsuzaki. *Macromol. Chem. Phys.* 196:3415, 1995; G. A. Quinting and R. Cai. *Polym. Sci. Eng.* 69:318, 1993; P. A. Lovell, T. H. Shah, and F. Heatley. *Polymer* 32:98, 1991.

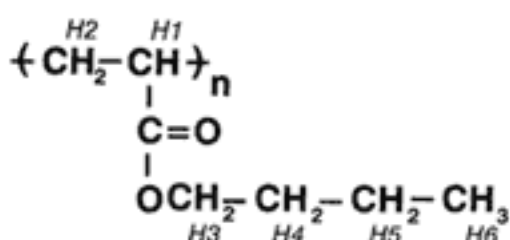
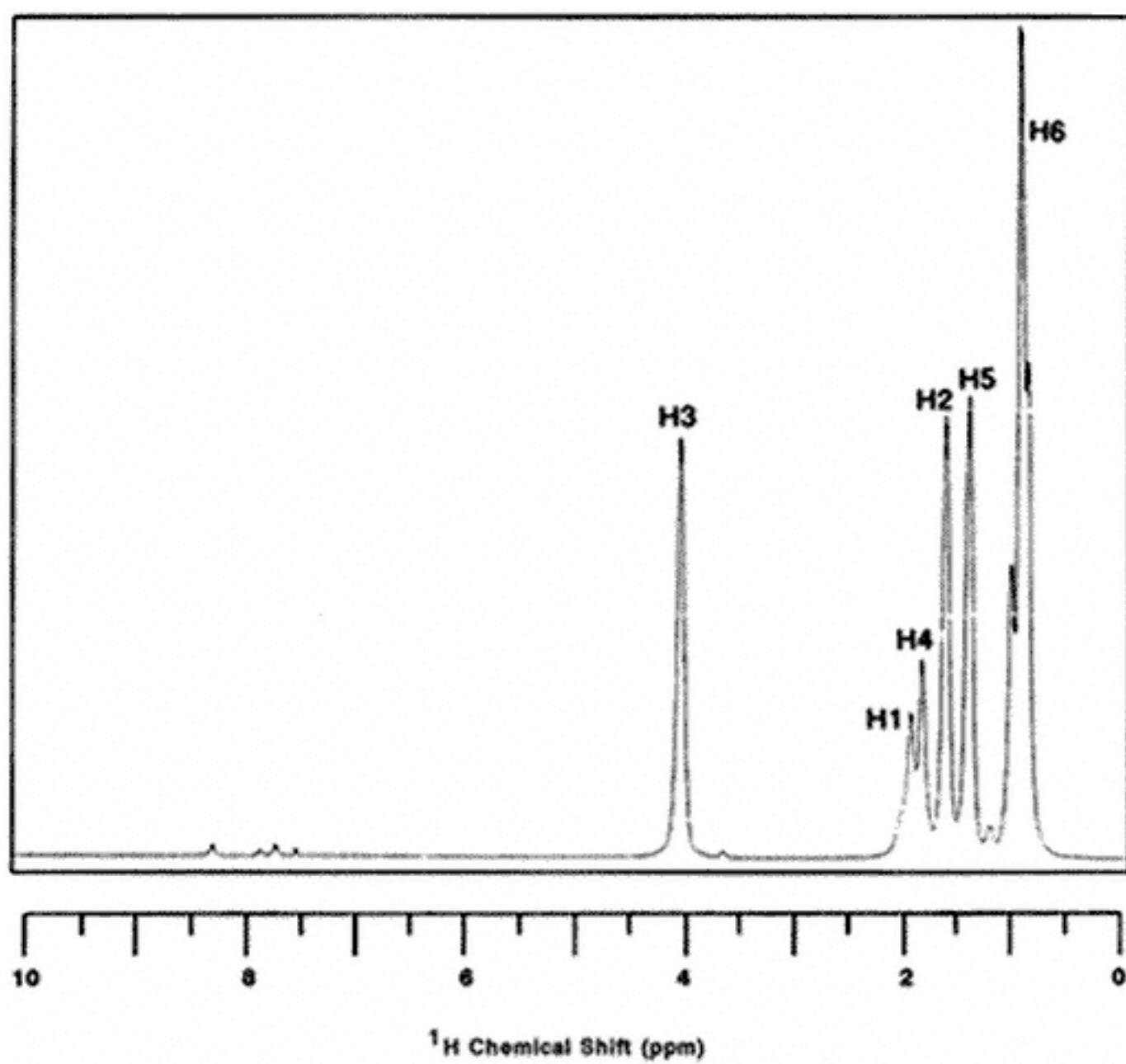
Source

Scientific Polymer Products, Ontario, NY.

**IV-B-5H—
Poly(*n*-Butyl Acrylate) (PBA)**

Comments

Tacticity effects are obscured by broadening from sample viscosity. PnBA is sometimes blended with PMMA {IV-C-1} or PVC {V-A-8} as an impact modifier.



Code	Shift (ppm)
H1	1.9
H2	1.6
H3	4.0
H4	2.2
H5	1.3
H6	0.9

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

Source

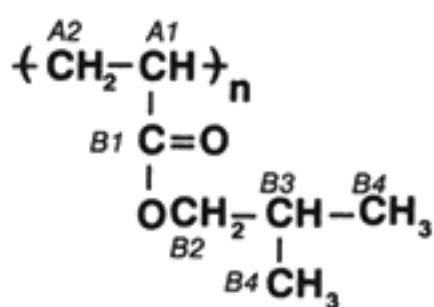
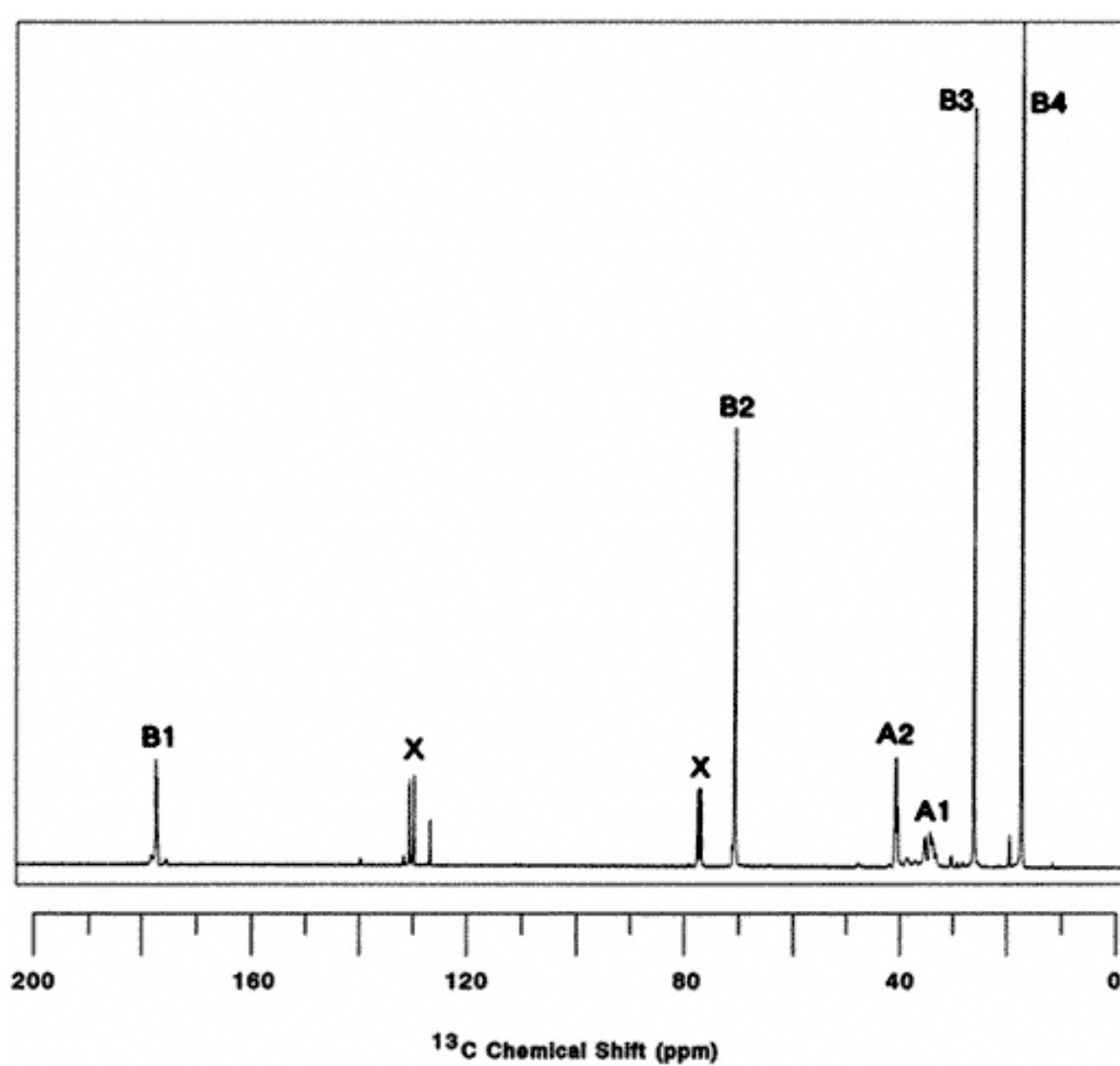
Scientific Polymer Products, Ontario, NY.

IV-B-6—

Poly(Isobutyl Acrylate) (PiBA)

Comments

Tacticity effects are obscured by broadening from sample viscosity. Some tacticity splitting can be observed for the backbone (A1 and A2) and carbonyl (B1) carbons; solvent resonances are marked by X.



Code	Shift (ppm)
A1	34.9
A2	41.6
B1	174.5
B2	70.2
B3	27.7
B4	19.0

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3 /toluene

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

Reference

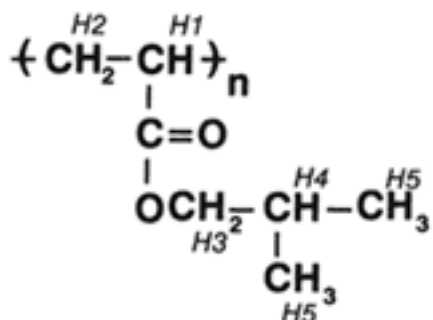
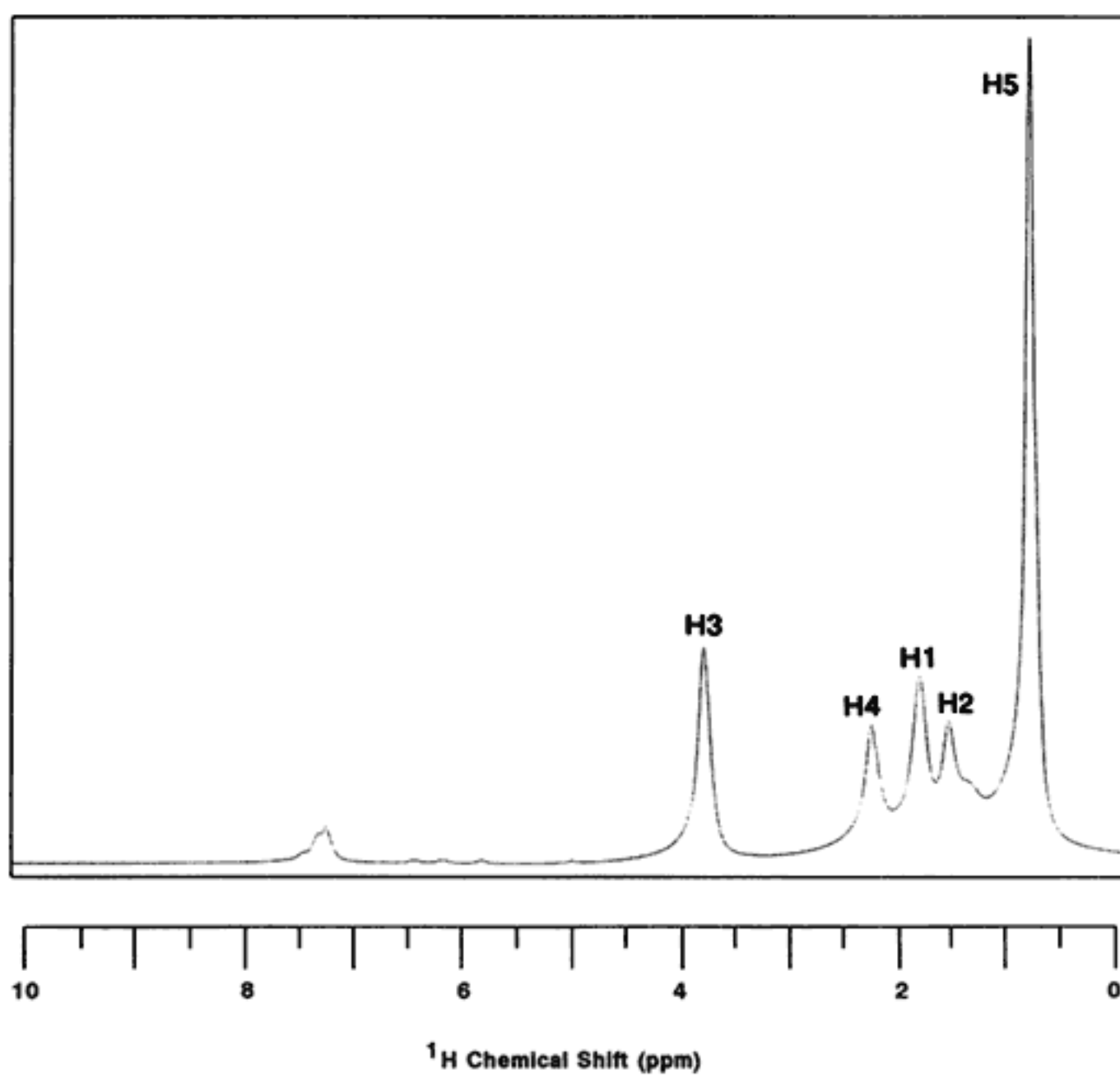
T. Kawamura, N. Toshima, and K. Matsuzaki. *Macromol. Chem. Phys.* 196:3415, 1995.

Source

Scientific Polymer Products, Ontario, NY.

IV-B-6H—**Poly(Isobutyl Acrylate) (PiBA)****Comments**

Tacticity effects are obscured by broadening from sample viscosity. PiBA is used in the formulation of paints and adhesives. It also forms a base for acrylic elastomers.



Code	Shift (ppm)
H1	1.9
H2	1.6
H3	3.8
H4	2.3
H5	0.9

Experimental ParametersNucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3 /toluene

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

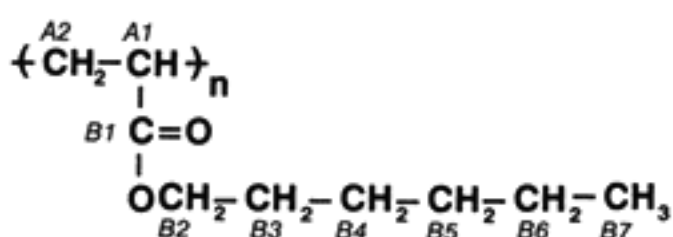
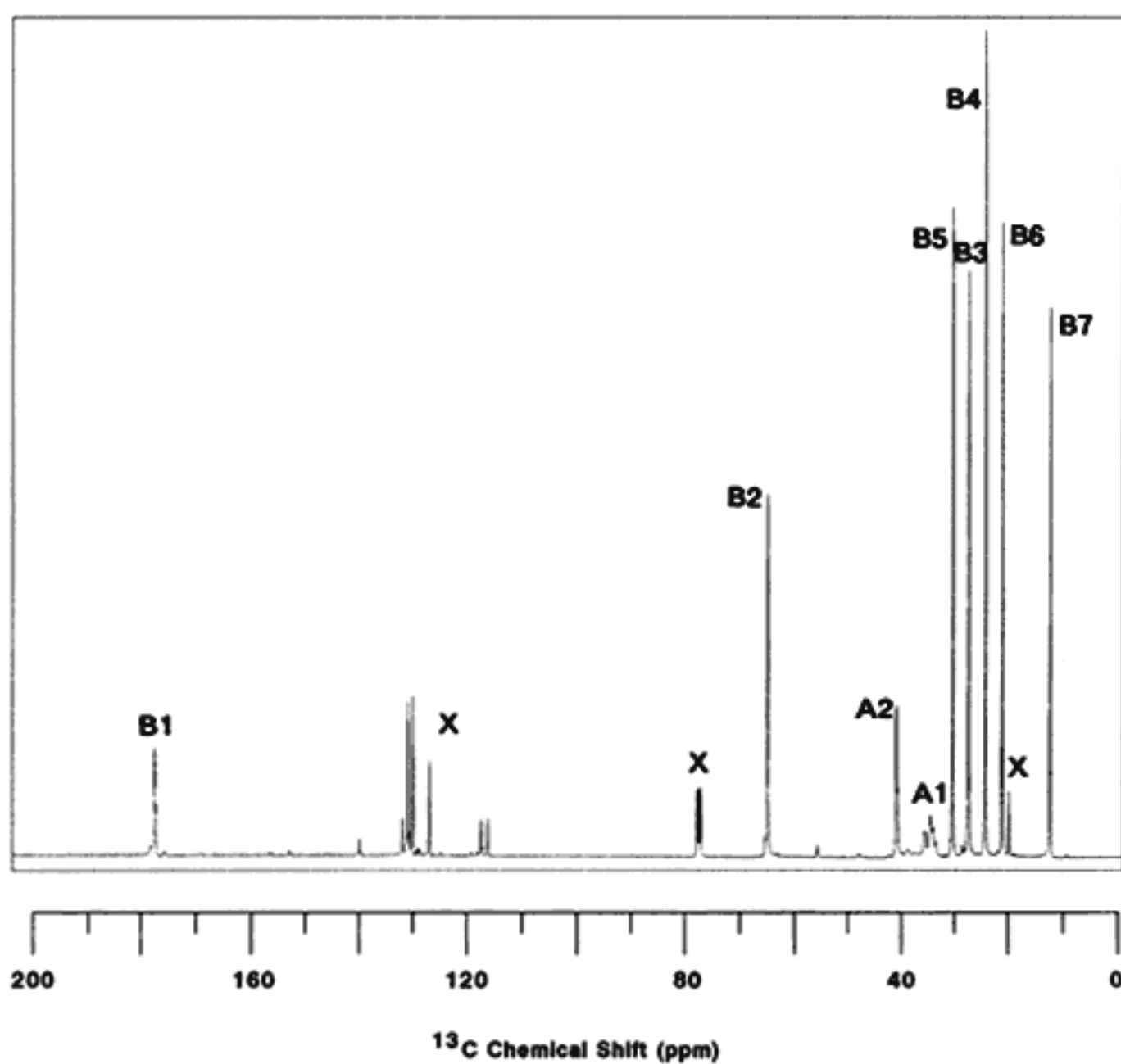
Source

Scientific Polymer Products, Ontario, NY.

**IV-B-7—
Poly(*n*-Hexyl Acrylate)**

Comments

Some tacticity splitting is observed for backbone carbons (**A1** and **A2**); solvent resonances are marked by **X**. This material is used in the formulation of paints and adhesives.



Code	Shift (ppm)
A1	35.5
A2	41.4
B1	174.4
B2	62.2
B3	28.7
B4	25.4
B5	31.5
B6	22.6
B7	14.0

Experimental Parameters

Nucleus: ¹³ C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl ₃ /toluene	Concentration: 30% w/w
Scans: 1000	Spectral width: 25 kHz
Data points: 32768	Pulse width: 90°
Broadening: 1 Hz	Pulse delay: 2 s

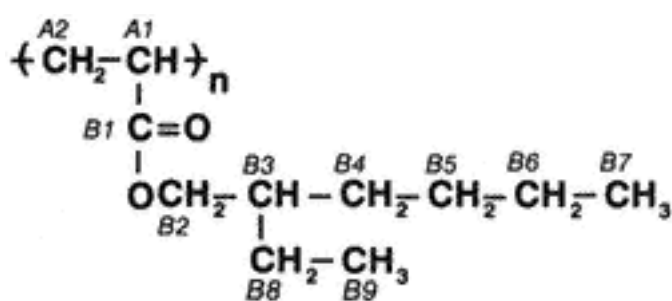
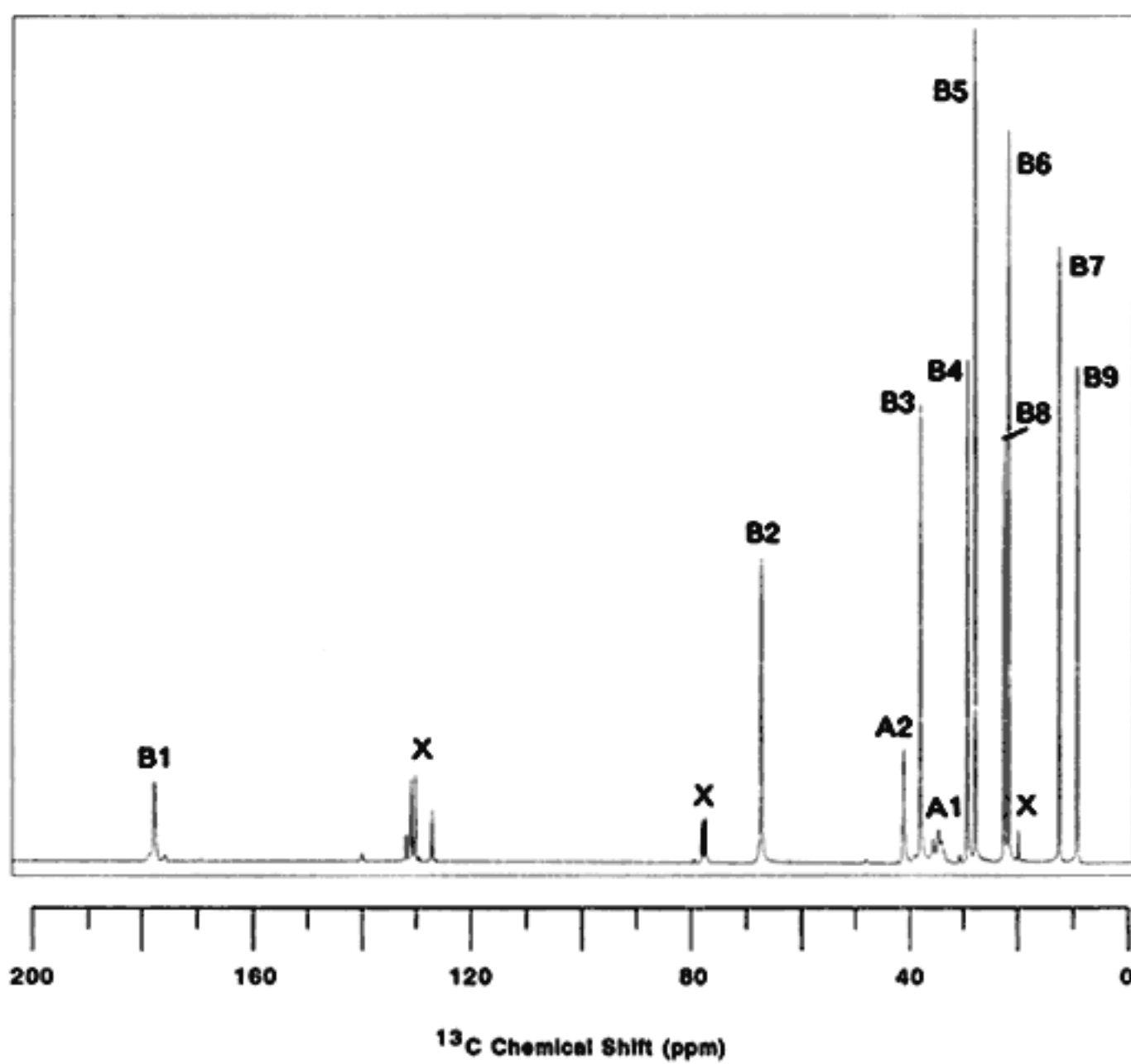
Source

Scientific Polymer Products, Ontario, NY.

**IV-B-8—
Poly(2-Ethylhexyl Acrylate)**

Comments

Some tacticity splitting is observed for backbone carbon **A1**. This material is used in the formulation of paints and adhesives.



Code	Shift (ppm)
A1	35.7
A2	41.6
B1	174.2
B2	67.2
B3	38.8
B4	30.0
B5	29.0
B6	23.0
B7	13.9
B8	23.7
B9	10.8

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃/toluene

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

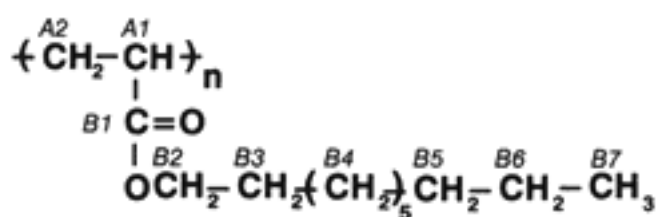
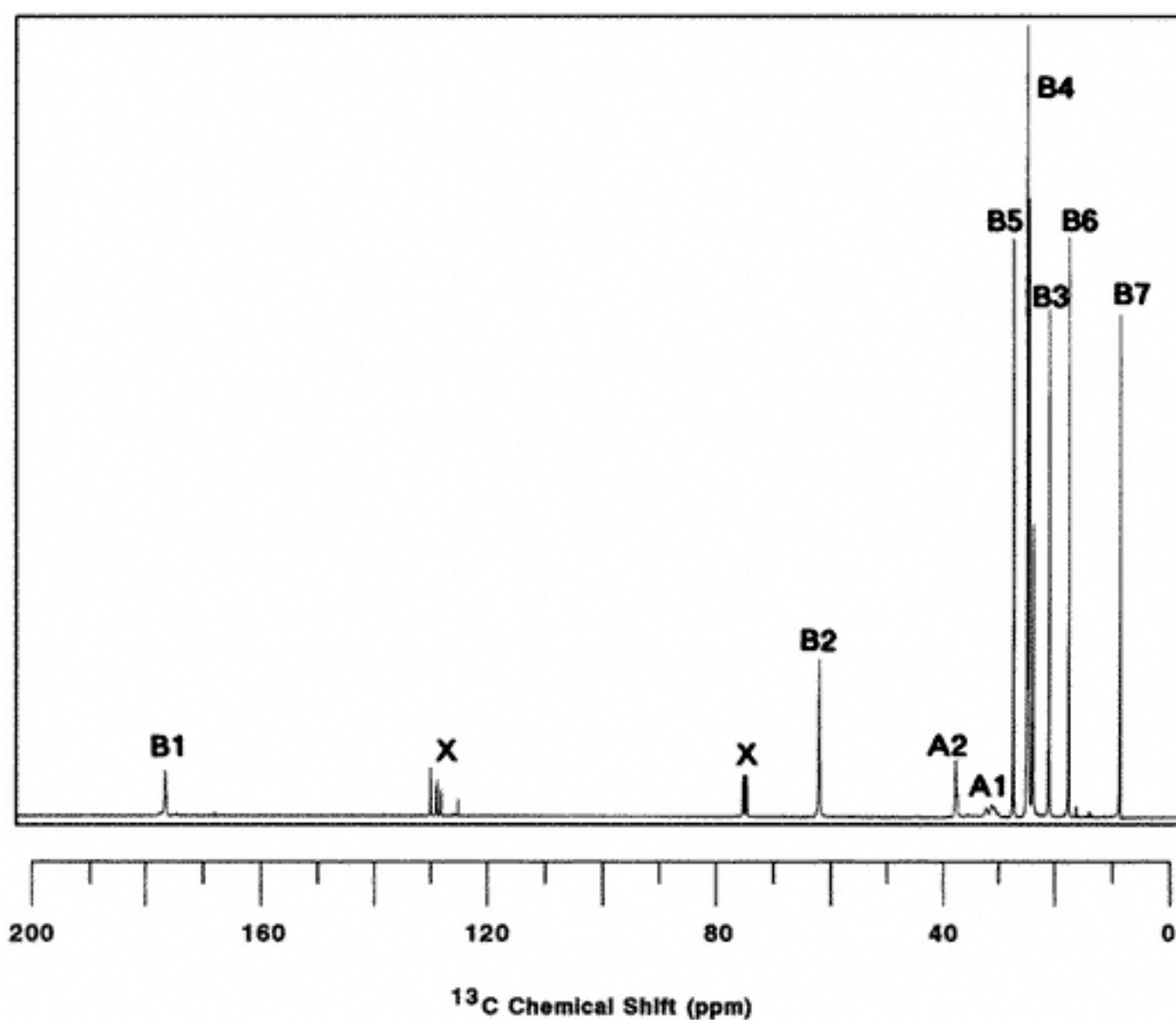
Source

Scientific Polymer Products, Ontario, NY.

**IV-B-9—
Poly(Decyl Acrylate)**

Comments

Some tacticity splitting is observed for backbone carbon **A1**. This material is used in the formulation of paints and adhesives.



Code	Shift (ppm)
A1	35.1
A2	41.5
B1	174.7
B2	64.6
B3	25.9
B4	30.0
B5	31.9
B6	22.6
B7	13.9

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3 /toluene

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

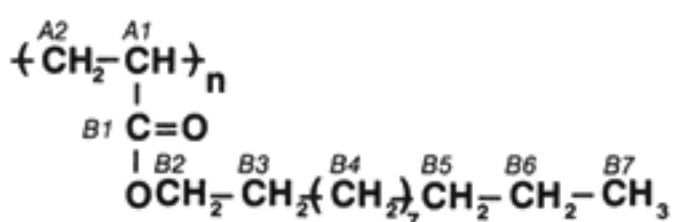
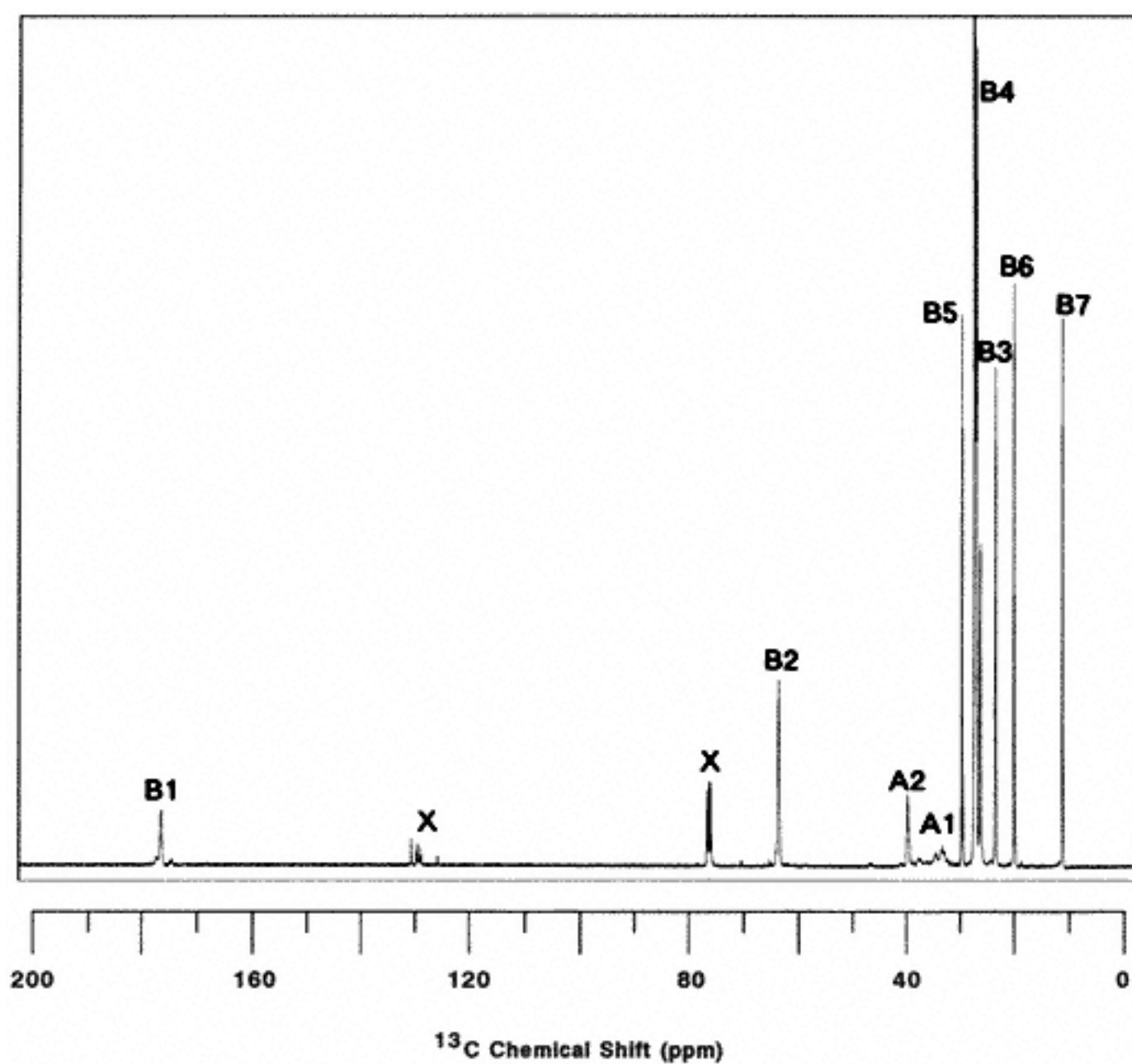
Broadening: 1 Hz

Pulse delay: 2 s

**IV-B-10—
Poly(Dodecyl Acrylate)**

Comments

Some tacticity splitting is observed for backbone carbon **A1**. This material is used in the formulation of paints and adhesives.



Code	Shift (ppm)
A1	35.1
A2	41.8
B1	174.6
B2	64.9
B3	25.9
B4	30.0
B5	32.0
B6	22.6
B7	13.9

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3 /toluene

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

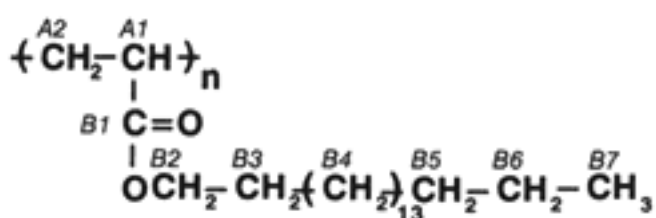
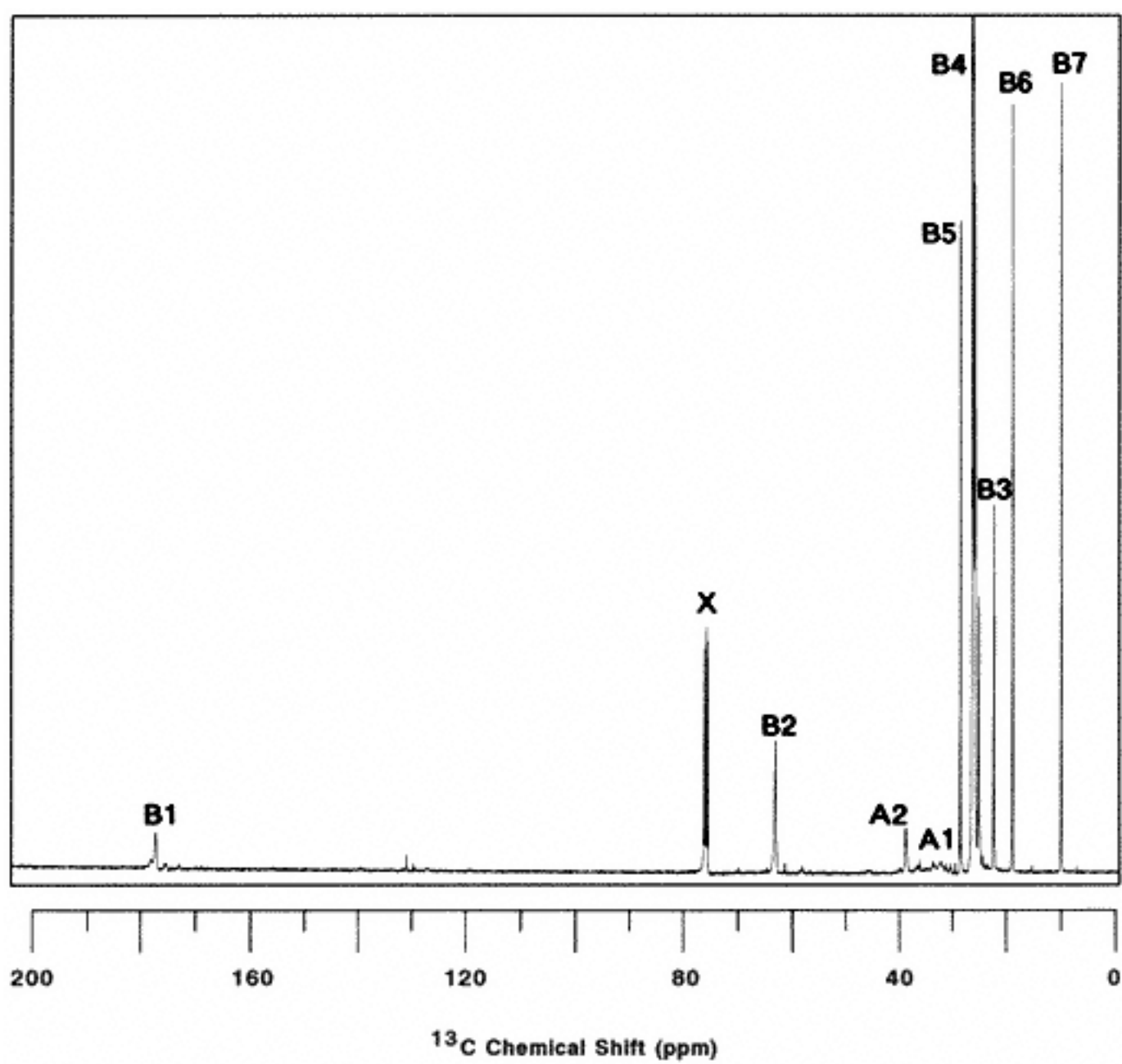
Source

Scientific Polymer Products, Ontario, NY.

**IV-B-11—
Poly(Octadecyl Acrylate)**

Comments

Some tacticity splitting is observed for backbone carbon **A1**. This material is used in the formulation of paints and adhesives.



Code	Shift (ppm)
A1	38.0
A2	42.0
B1	174.6
B2	64.7
B3	26.0
B4	30.0
B5	32.0
B6	22.7
B7	13.3

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

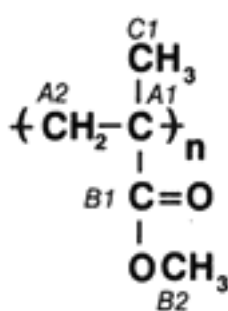
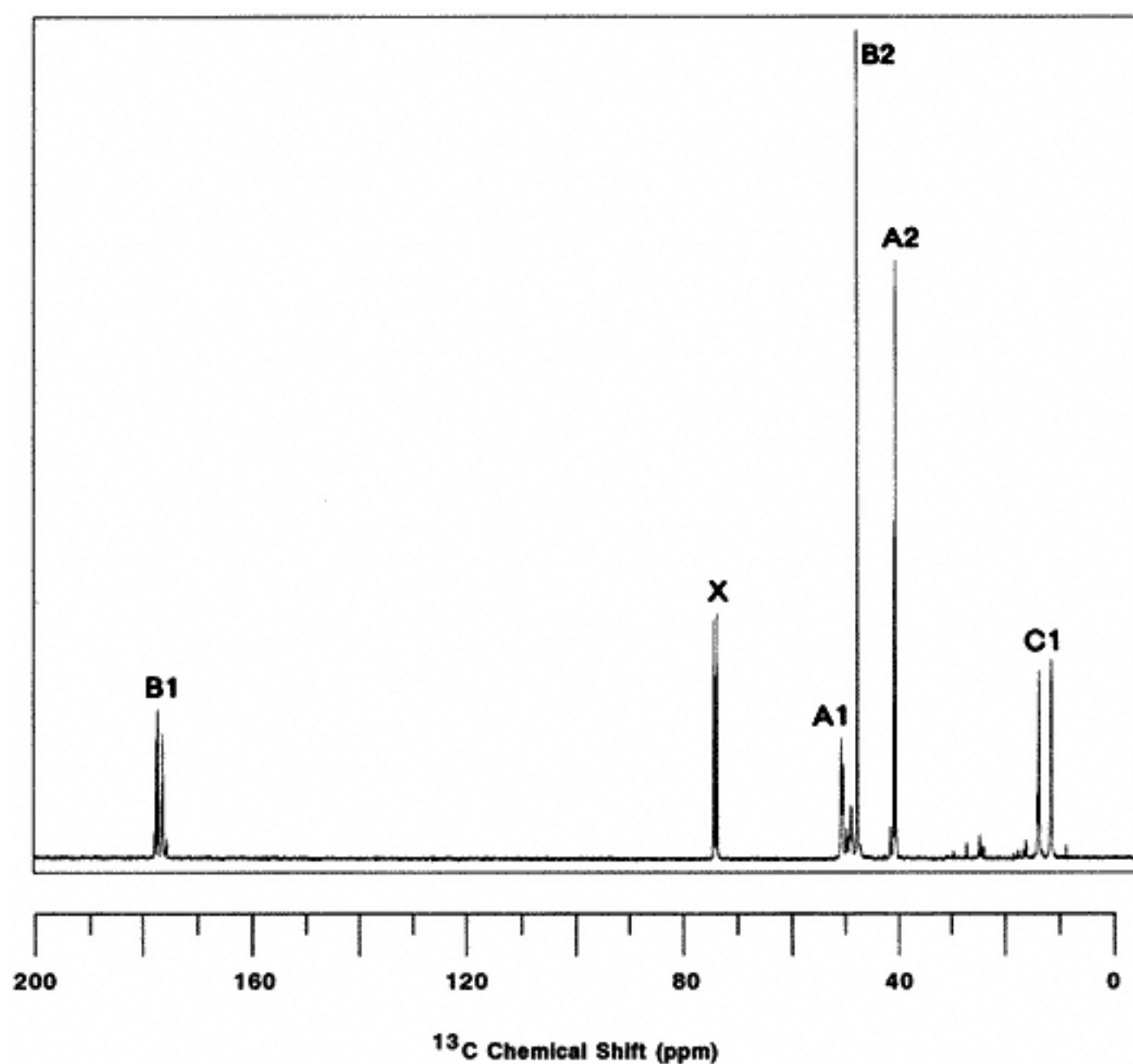
Pulse delay: 2 s

IV-C-1—

Poly(Methyl Methacrylate) (PMMA)

Comments

Also known as Lucite (DuPont) and Plexiglas (Rohm & Haas). Some tacticity splitting can be observed for the backbone (A1 and A2), carbonyl (B1), and α -methyl (C1) carbons; solvent resonances are marked by X. PMMA is a crystal-clear, tough thermoplastic. It weathers well and exhibits good chemical and UV-damage resistance. PMMA is commonly found in applications that exploit its clarity: signs, safety glass, skylights, aircraft windows, lighting fixtures, appliance panels, and taillights. It is often found blended with poly(*n*-butyl acrylate) {IV-B-5}, polyacrylonitrile {V-B-8}, or both.



Code	Shift (ppm)
A1	54.6
A2	44.5
B1	177.5
B2	51.4
C1	18.1, 16.4

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

References

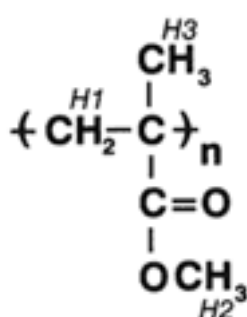
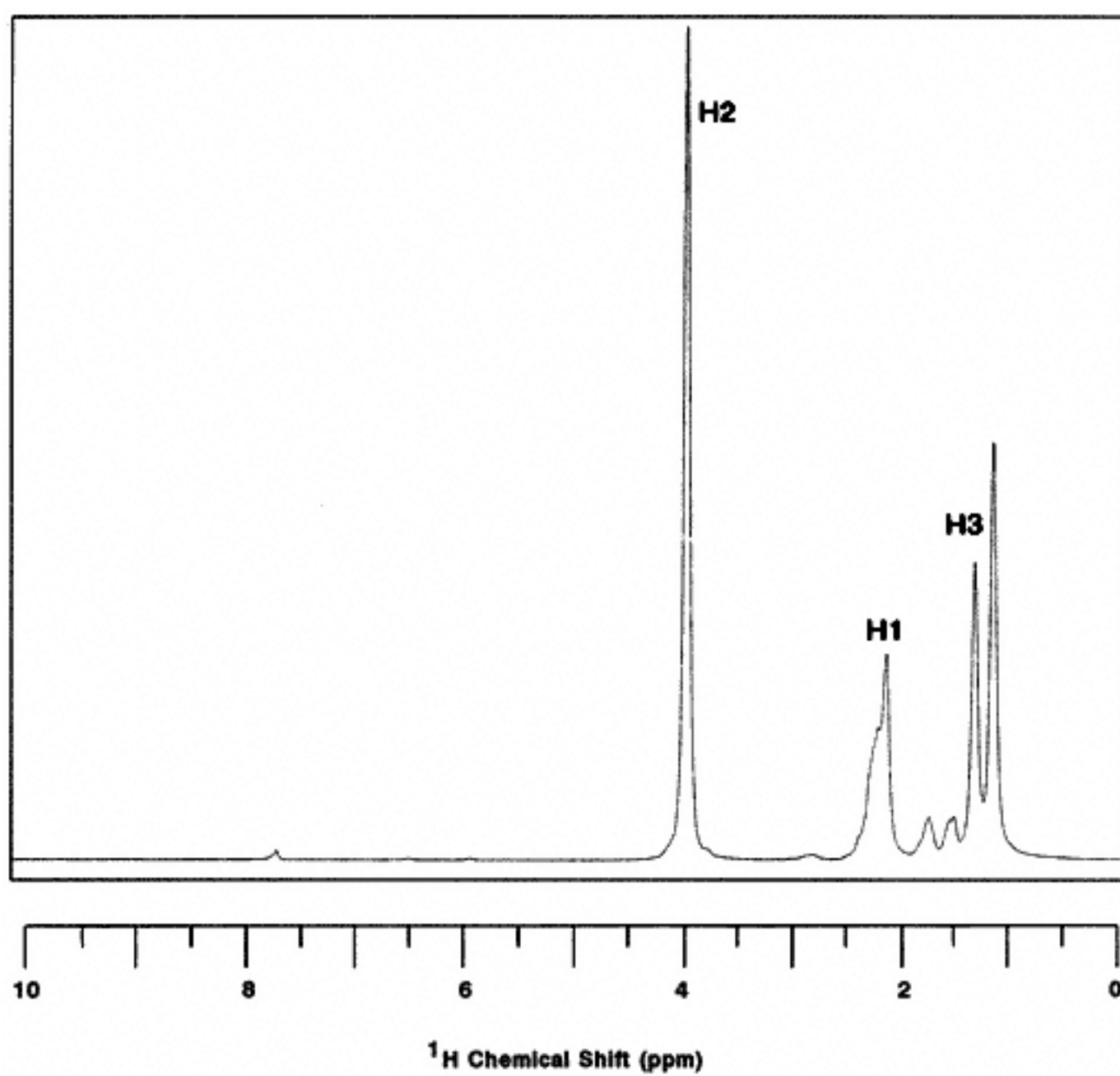
T. Kawamura, N. Toshima, and K. Matsuzaki. *Makromol. Chem. Rapid Commun.* 14:719, 1993; J. J. Kotyk, P. A. Berger, and E. R. Remsen. *Macromolecules* 23:5167, 1990; F. C. Schilling, F. A. Bovey, M. D. Bruch, and S. A. Kozlowski. *Macromolecules* 18:1418, 1985.

IV-C-1H—

Poly(Methyl Methacrylate) (PMMA)

Comments

Also known as Lucite (DuPont) and Plexiglas (Rohm & Haas). Tacticity effects are obscured by broadening that is due to sample viscosity. PMMA is a crystal-clear, tough thermoplastic. It weathers well and exhibits good chemical and UV-damage resistance. PMMA is commonly found in applications that exploit its clarity: signs, safety glass, skylights, aircraft windows, lighting fixtures, appliance panels, and taillights. It is often found blended with poly(*n*-butyl acrylate) {IV-B-5}, polyacrylonitrile {V-B-8}, or both.



Code	Shift (ppm)
H1	2.7
H2	4.0
H3	1.2–1.4

*Experimental Parameters*Nucleus: ¹H (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

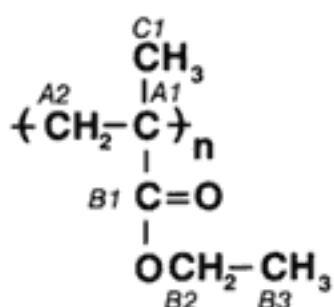
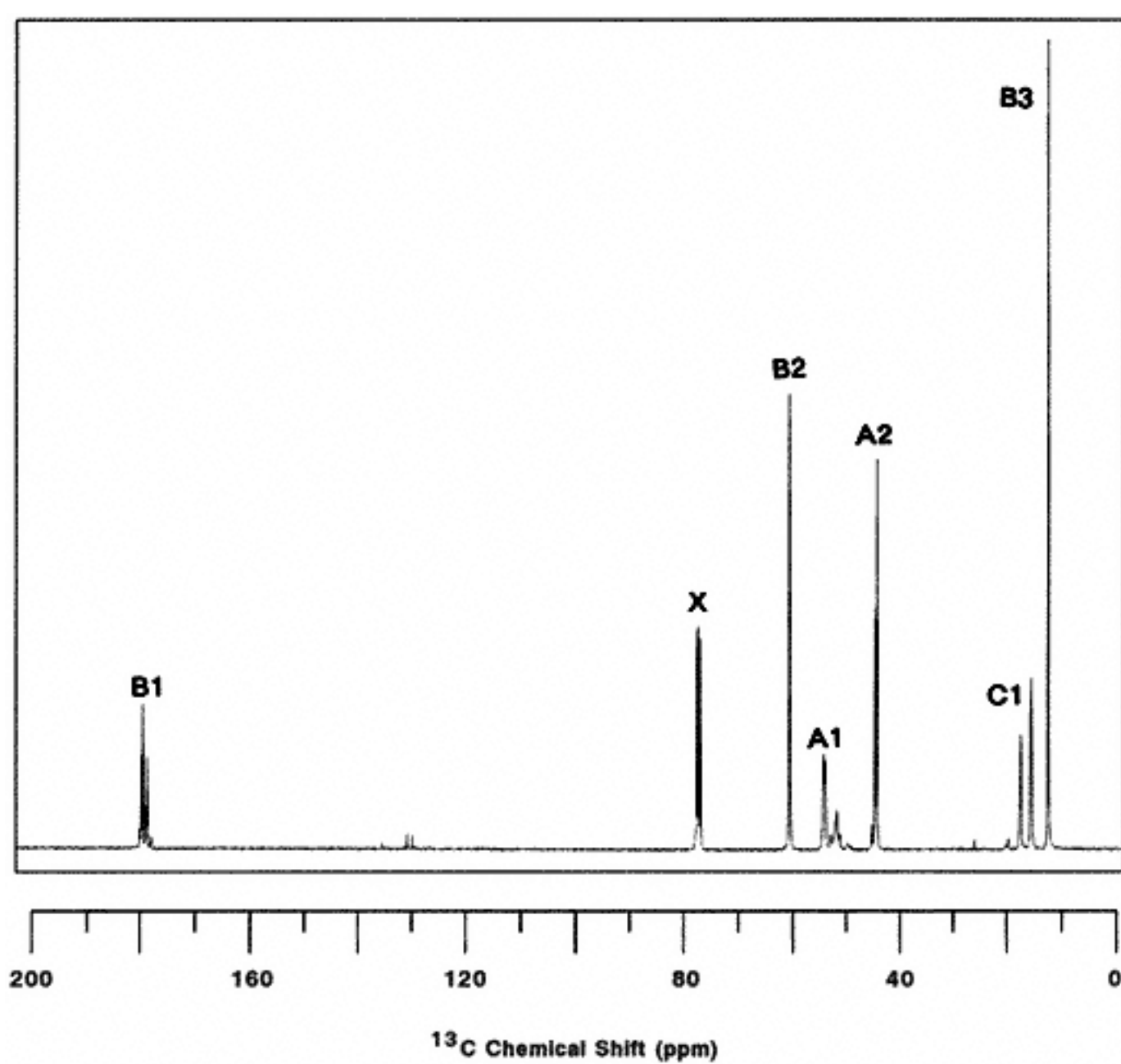
Broadening: 5 Hz

Pulse delay: 5 s

**IV-C-2—
Poly(Ethyl Methacrylate) (PEMA)**

Comments

Some tacticity splitting can be observed for the backbone (A1 and A2), carbonyl (B1), and α -methyl (C1) carbons; solvent resonances are marked by X. PEMA is used as an embedding material and as a textile finish.



Code	Shift (ppm)
A1	53.0
A2	44.7
B1	176.1
B2	60.5
B3	13.7
C1	18.1, 16.4

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

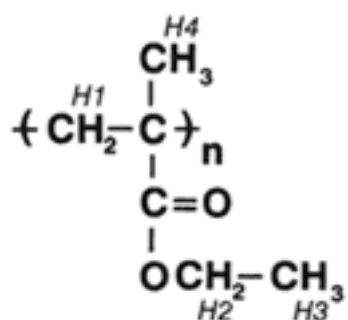
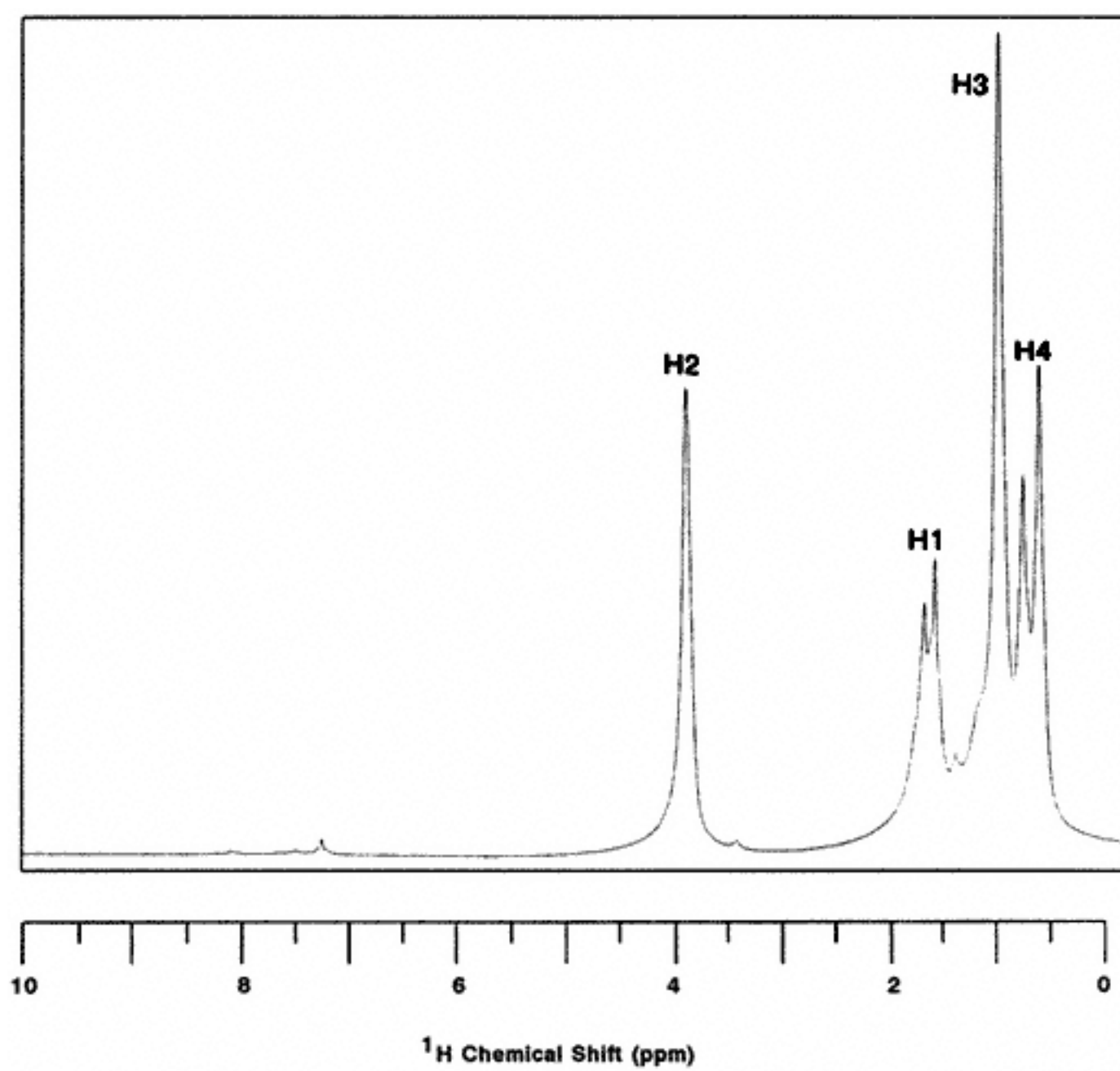
Source

Scientific Polymer Products, Ontario, NY.

IV-C-2H—
Poly(Ethyl Methacrylate) (PEMA)

Comments

Tacticity effects are partially obscured by broadening caused by sample viscosity. PEMA is used as an embedding material and as a textile finish.



Code	Shift (ppm)
H1	1.8
H2	4.0
H3	1.2
H4	0.8, 1.0

Experimental Parameters

Nucleus: ^1H (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

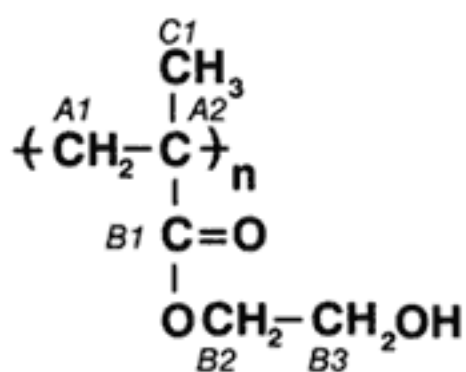
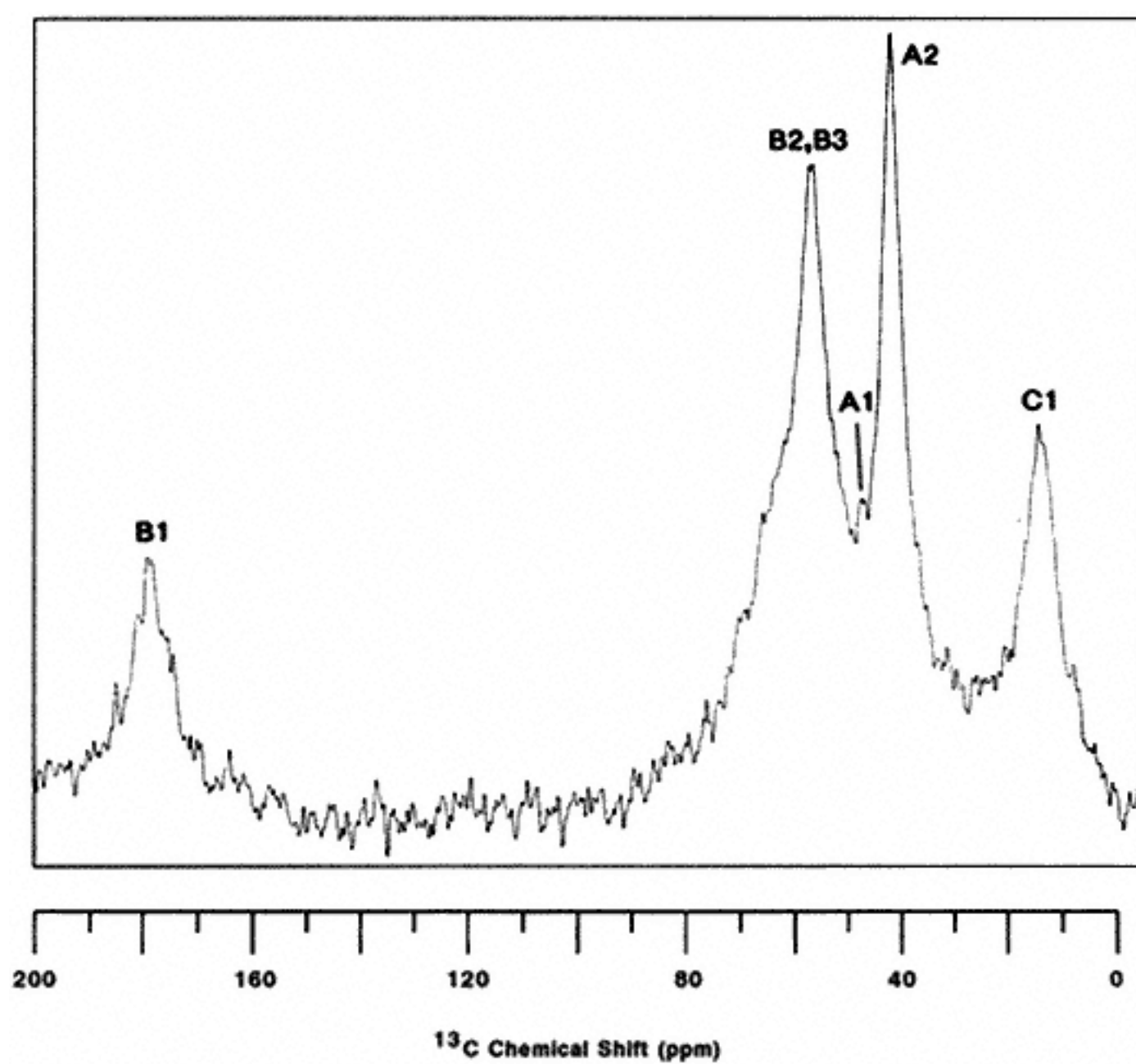
Source

Scientific Polymer Products, Ontario, NY.

**IV-C-3—
Poly(2-Hydroxyethyl Methacrylate)**

Comments

Also known as a *hydrogel*. The polymer swells, rather than dissolves, in water, leading to severely broadened lines that obscure any tacticity splittings. This material is used to manufacture soft contact lenses.



Code	Shift (ppm)
A1	54
A2	43
B1	178
B2	60
B3	60
C1	16

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 80°C

Solvent: D₂O

Concentration: 10% w/w

Scans: 4000

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 10 Hz

Pulse delay: 2 s

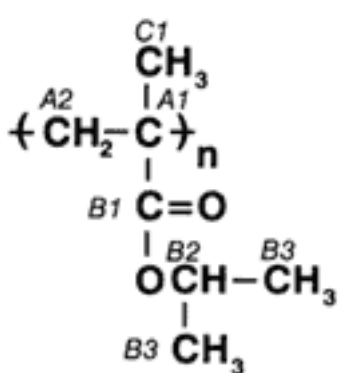
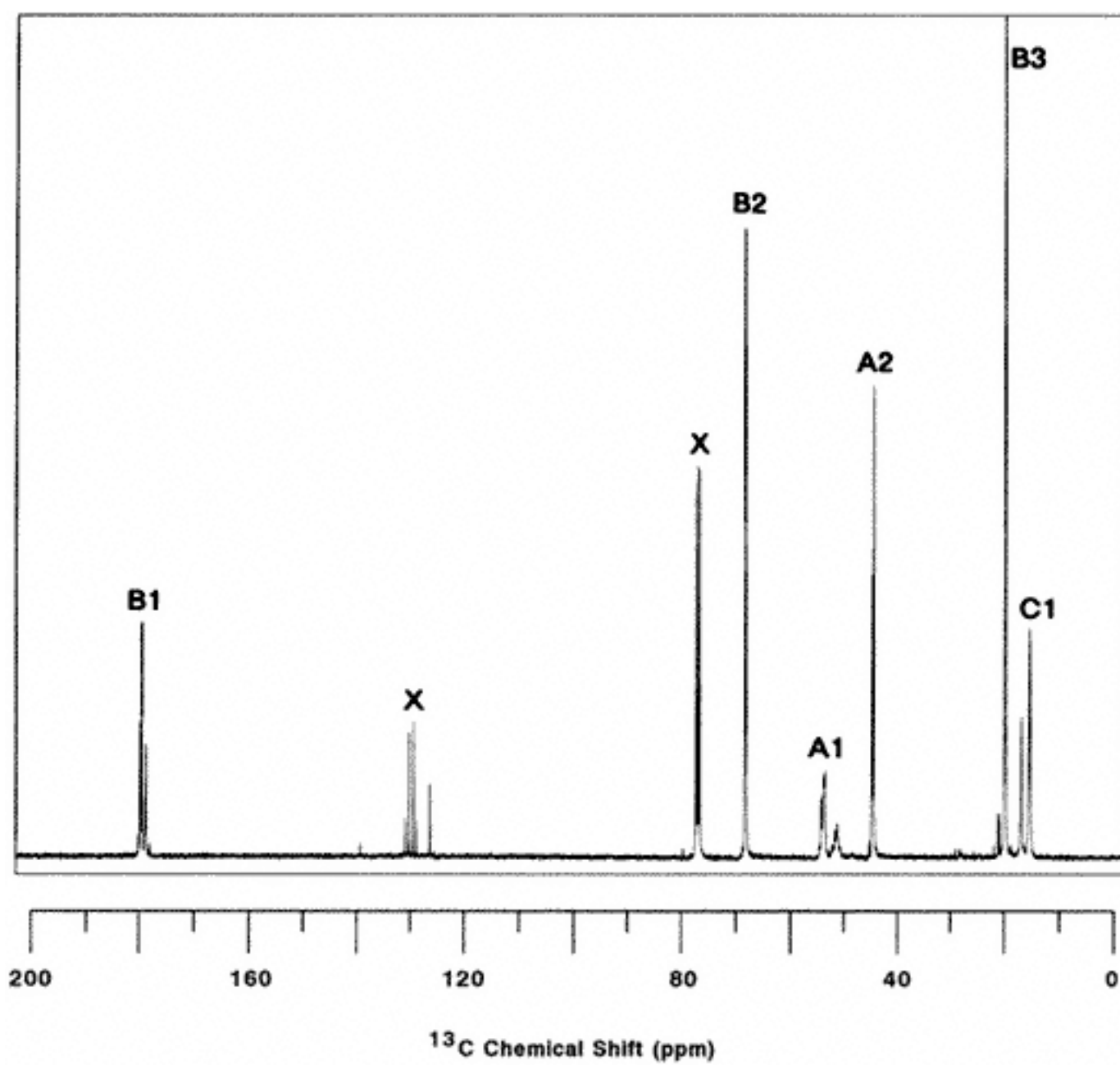
Source

Scientific Polymer Products, Ontario, NY.

**IV-C-4—
Poly(Isopropyl Methacrylate)**

Comments

Some tacticity splitting can be observed for the backbone (A1 and A2), carbonyl (B1), and α -methyl (C1) carbons; solvent resonances are marked by X.



Code	Shift (ppm)
A1	53.7
A2	45.4
B1	177.1
B2	68.3
B3	21.5
C1	18.1, 16.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3 /toluene

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

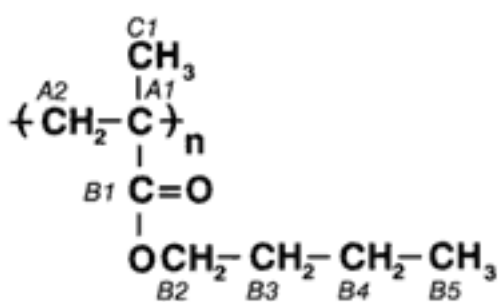
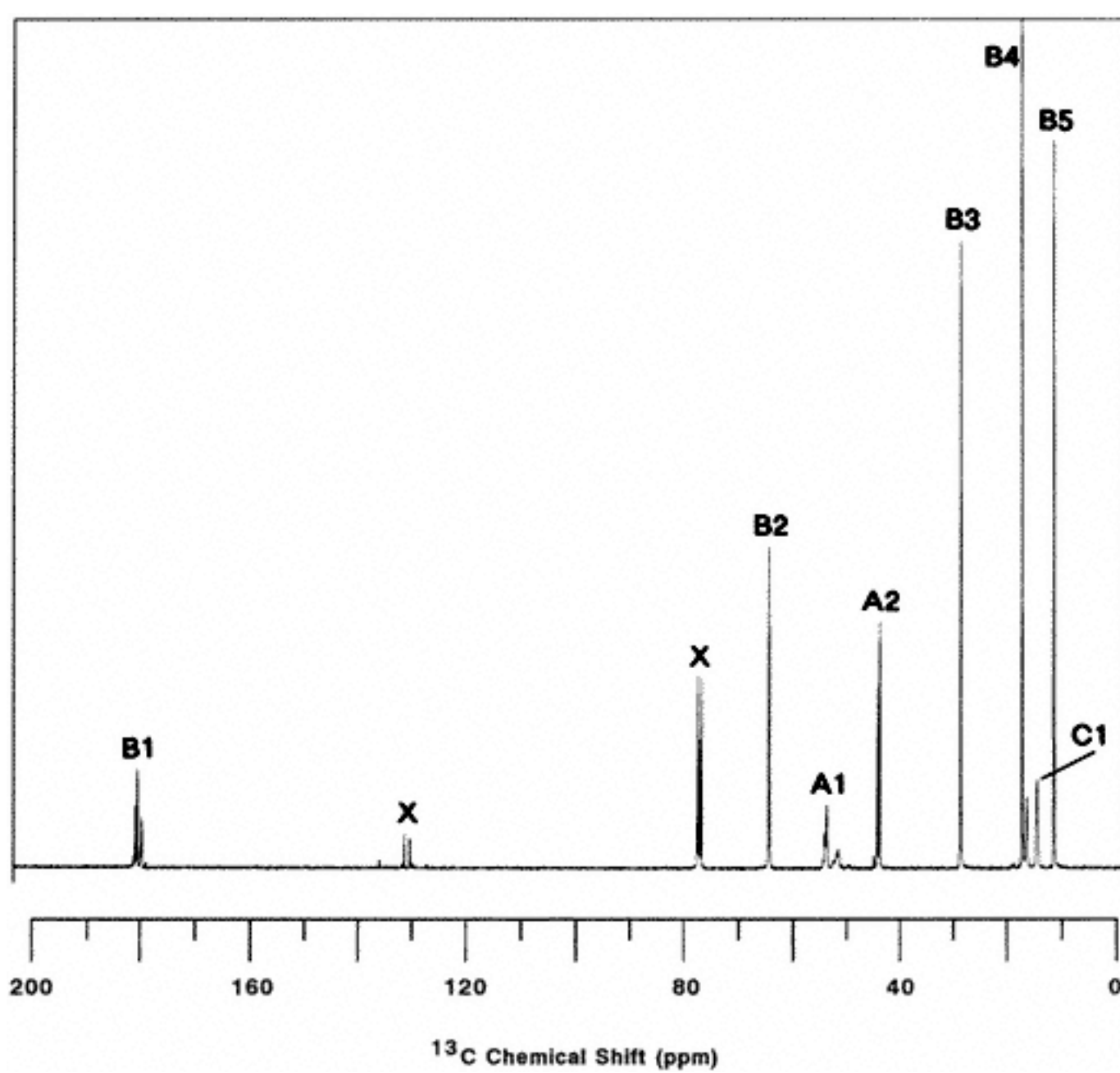
Source

Scientific Polymer Products, Ontario, NY.

IV-C-5—

Poly(*n*-Butyl Methacrylate) (PBMA)*Comments*

Some tacticity splitting can be observed for the backbone (A1 and A2), carbonyl (B1), and α -methyl (C1) carbons; solvent resonances are marked by X. PnBMA is used in adhesives and coatings and as a textile finish.



Code	Shift (ppm)
A1	54.2
A2	44.9
B1	176.7
B2	63.1
B3	30.3
B4	18.4
B5	13.6
C1	18.1, 16.4

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3 /toluene

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

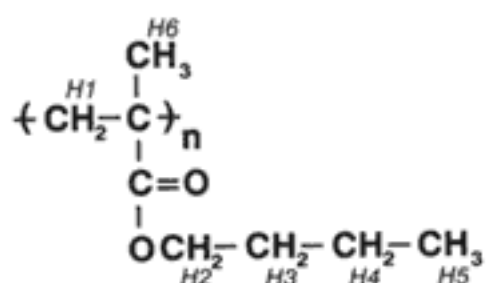
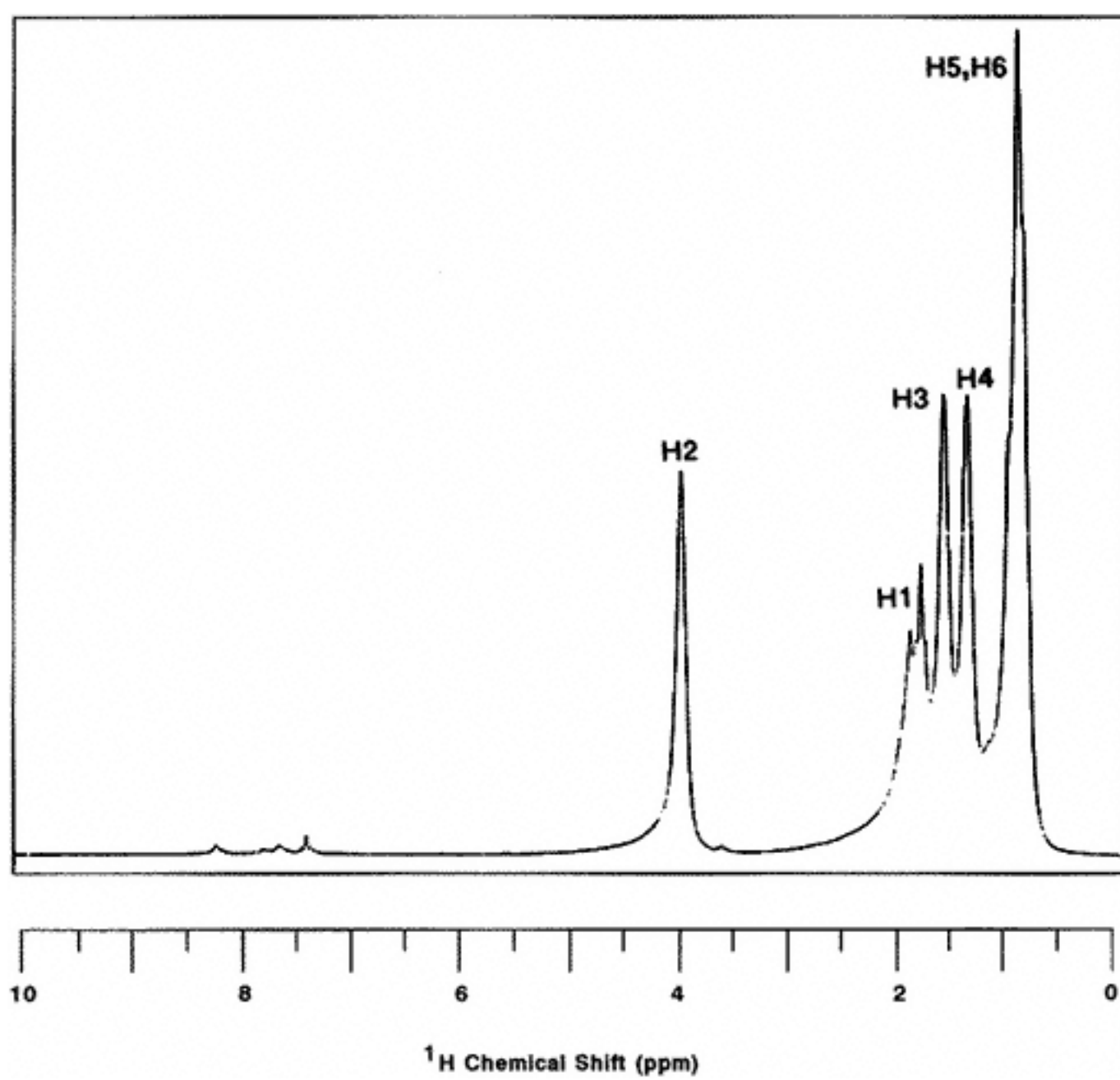
Pulse delay: 2 s

*Reference*G. A. Quinting and R. Cai. *Polym. Sci. Eng.* 69:318, 1993.

IV-C-5H—

Poly(*n*-Butyl Methacrylate) (*Pn* BMA, PBMA)*Comments*

Tacticity effects are obscured by broadening caused by sample viscosity. *Pn*BMA is used in adhesives and coatings and as a textile finish.



Code	Shift (ppm)
H1	1.8
H2	4.0
H3	1.6
H4	1.4
H5	0.9
H6	0.9

*Experimental Parameters*Nucleus: ¹H (400 MHz)

Temperature: 50°C

Solvent: CDCl₃/toluene

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

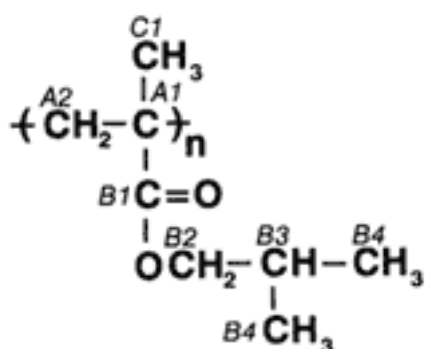
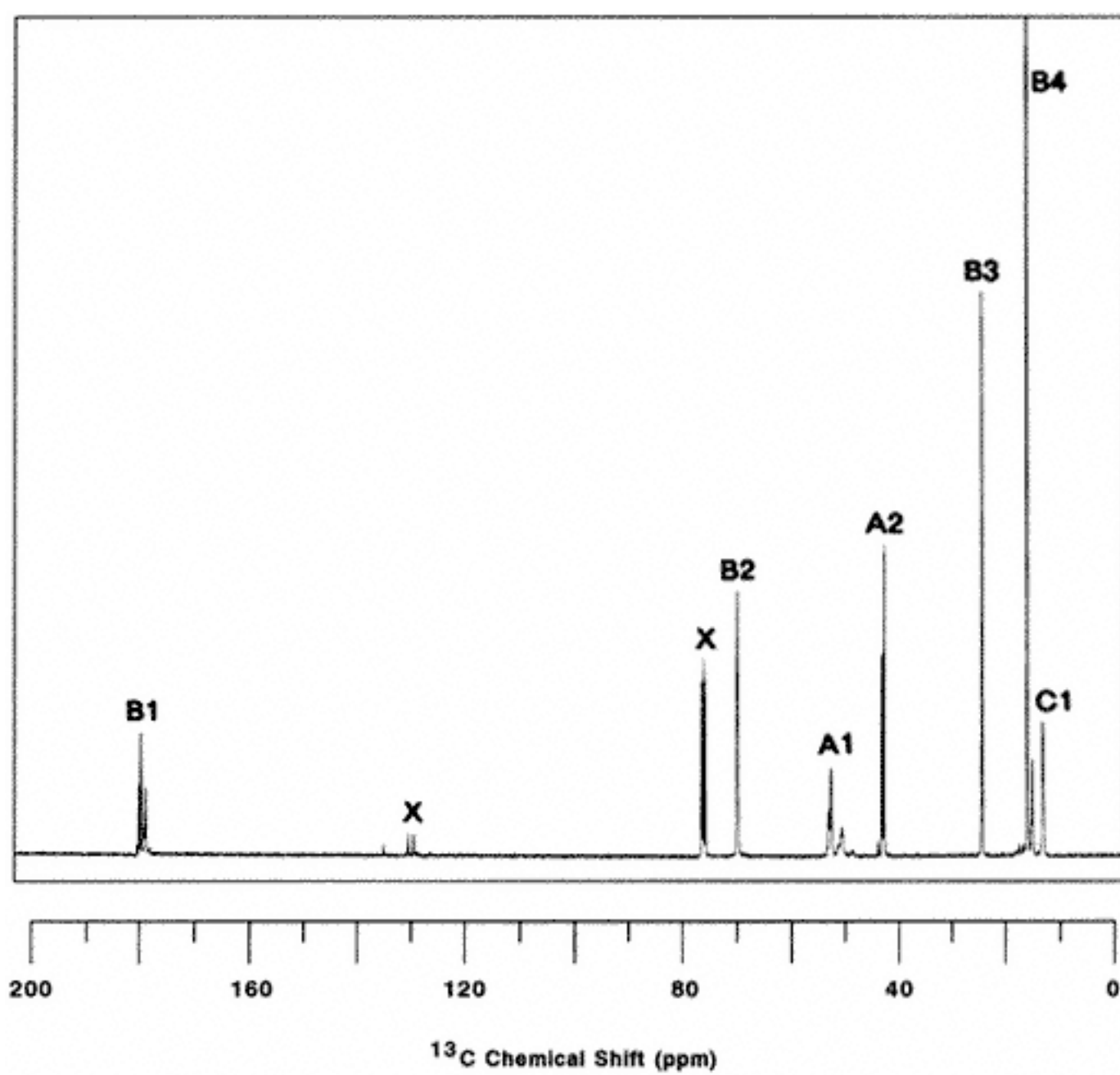
Source

Scientific Polymer Products, Ontario, NY.

**IV-C-6—
Poly(Isobutyl Methacrylate) (PiBMA)**

Comments

Some tacticity splitting can be observed for the backbone (A1 and A2), carbonyl (B1), and α -methyl (C1) carbons; solvent resonances are marked by X. PiBMA is used in coatings and adhesives.



Code	Shift (ppm)
A1	54.7
A2	44.7
B1	178.4
B2	70.9
B3	27.4
B4	19.2
C1	18.1, 16.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3 /toluene

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

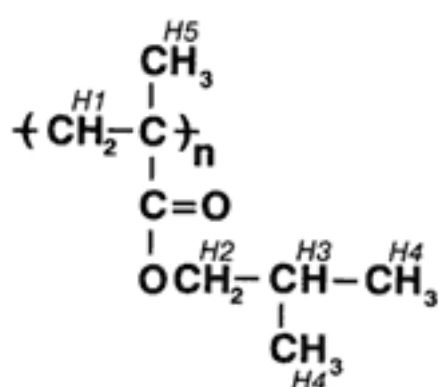
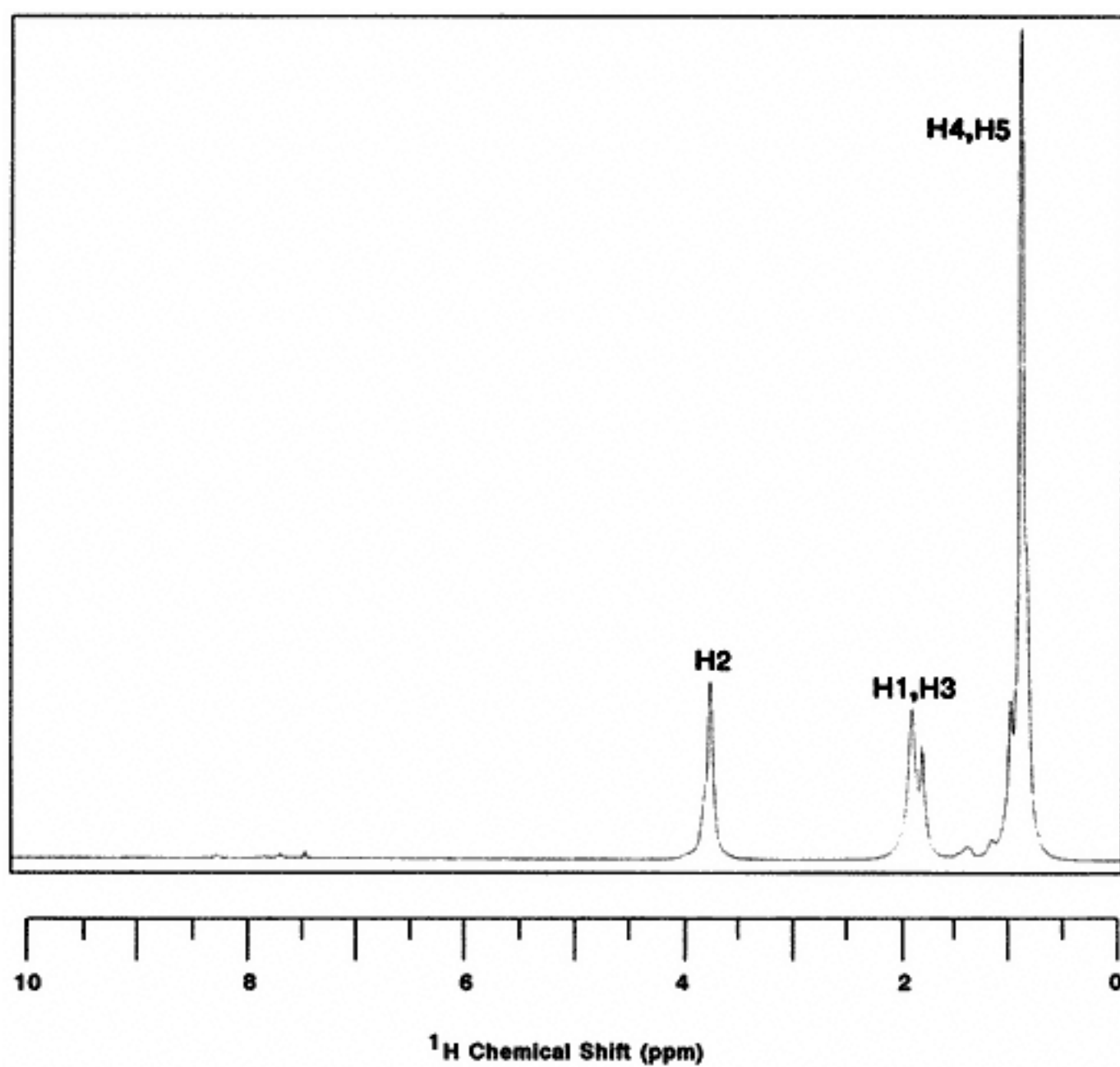
Source

Scientific Polymer Products, Ontario, NY.

IV-C-6H—
Poly(Isobutyl Methacrylate) (PiBMA)

Comments

Tacticity effects are obscured by broadening caused by sample viscosity. PiBMA is used in coatings and adhesives.



Code	Shift (ppm)
H1	1.9
H2	3.7
H3	1.8
H4	0.9
H5	0.9

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3 /toluene

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

Source

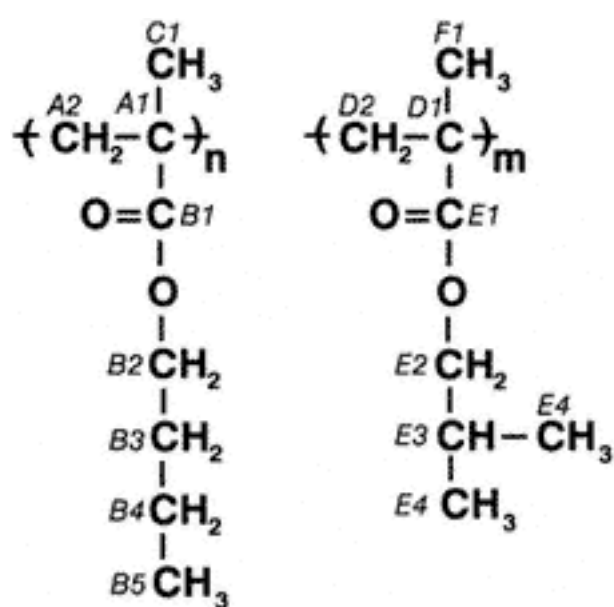
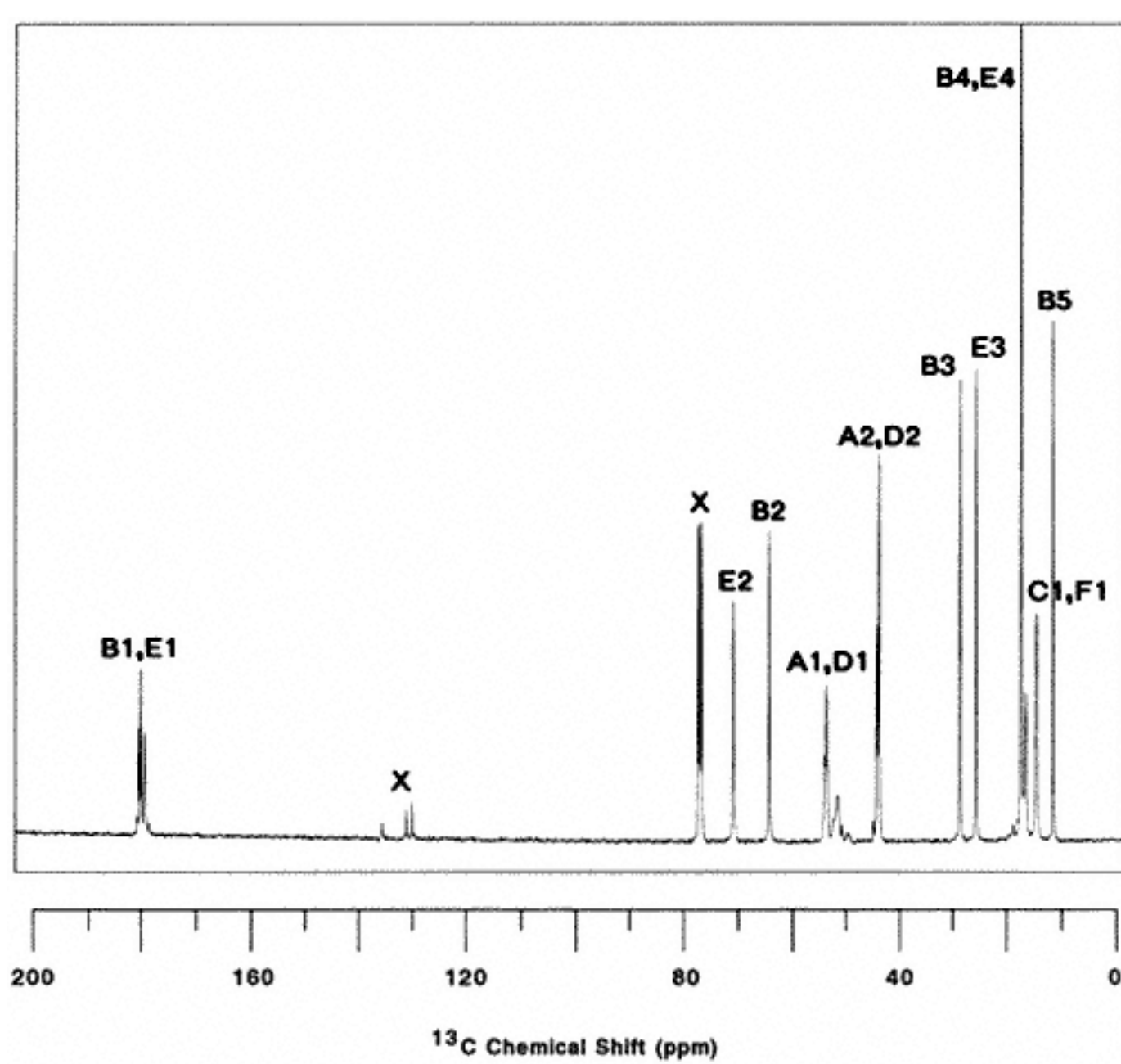
Scientific Polymer Products, Ontario NY.

IV-C-7

IV-C-7—
Poly(*n*-Butyl Methacrylate-Co-Isobutyl Methacrylate)

Comments

Some tacticity splitting can be observed for the backbone (A1, A2, D1, and D2), carbonyl (B1, E1), and α -methyl (C1, F1) carbons; solvent resonances are marked by X. This material is used in adhesive formulations.



Code	Shift (ppm)
A1	54.6
A2	44.5
B1	177.5
B2	64.6
B3	30.2
B4	19.3
B5	13.6
C1	18.1, 16.4
D1	54.6
D2	44.5
E1	177.5
E2	71.0
E3	27.3
E4	19.3
F1	18.1, 16.4

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3 /toluene

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

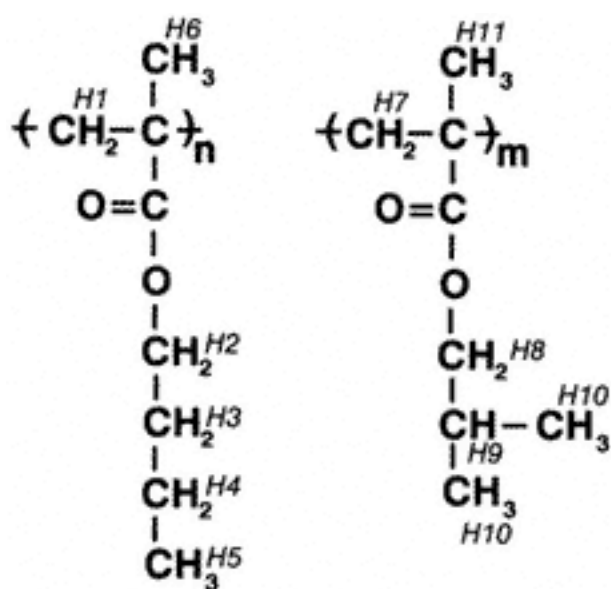
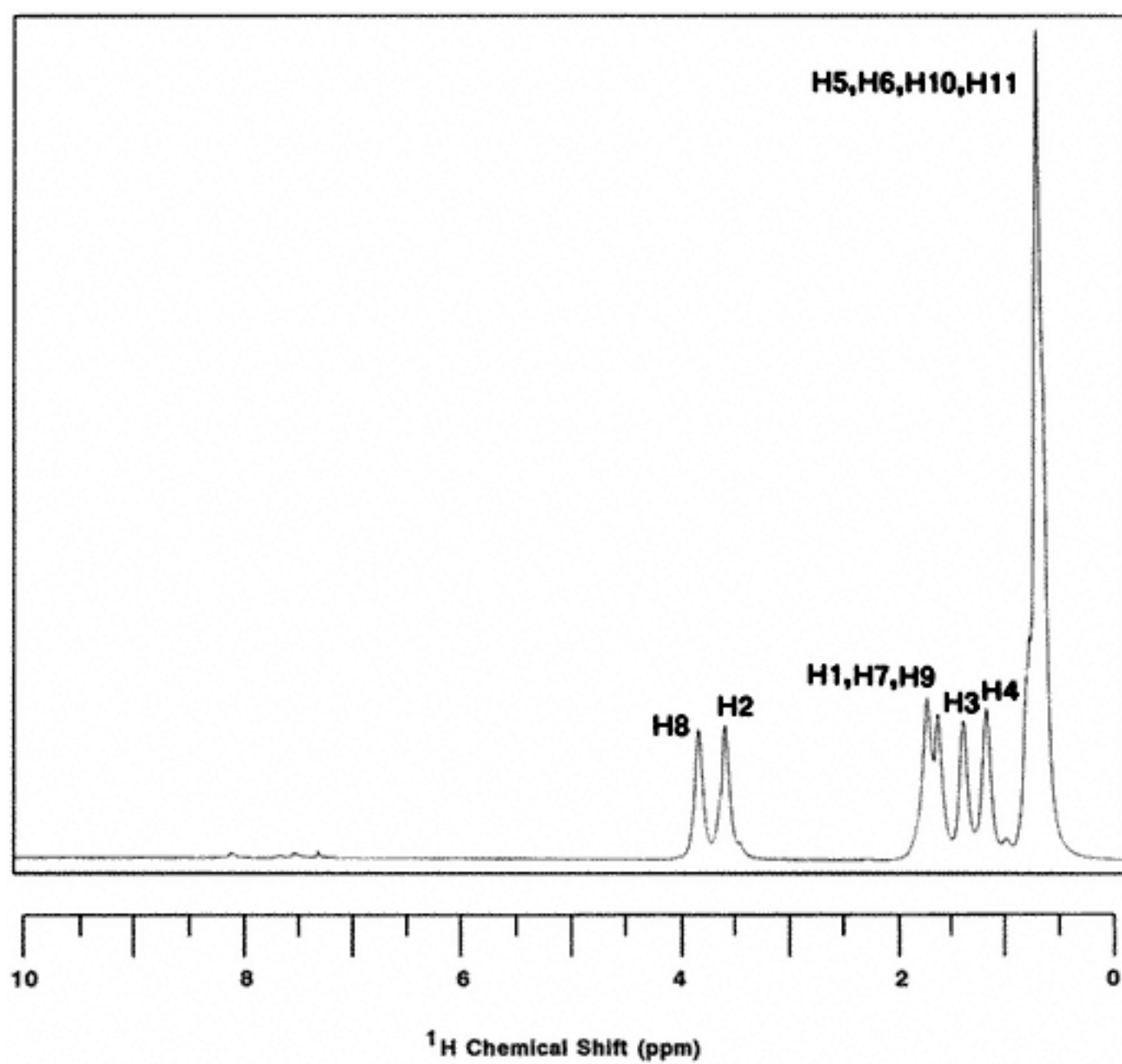
Pulse delay: 2 s

IV-C-7H—

Poly(*n*-Butyl Methacrylate-Co-Isobutyl Methacrylate)

Comments

Tacticity effects are obscured by broadening caused by sample viscosity. This copolymer is used in adhesive formulations.



Code	Shift (ppm)
H1	1.8
H2	3.7
H3	1.6
H4	1.2
H5, H6	0.9
H7	1.8
H8	3.9
H9	1.8
H10, H11	0.9

Experimental ParametersNucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3 /toluene

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

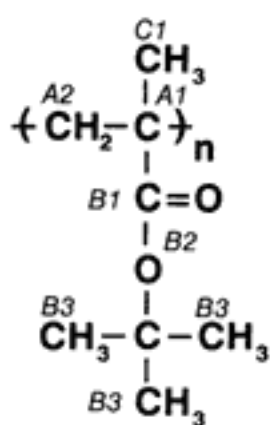
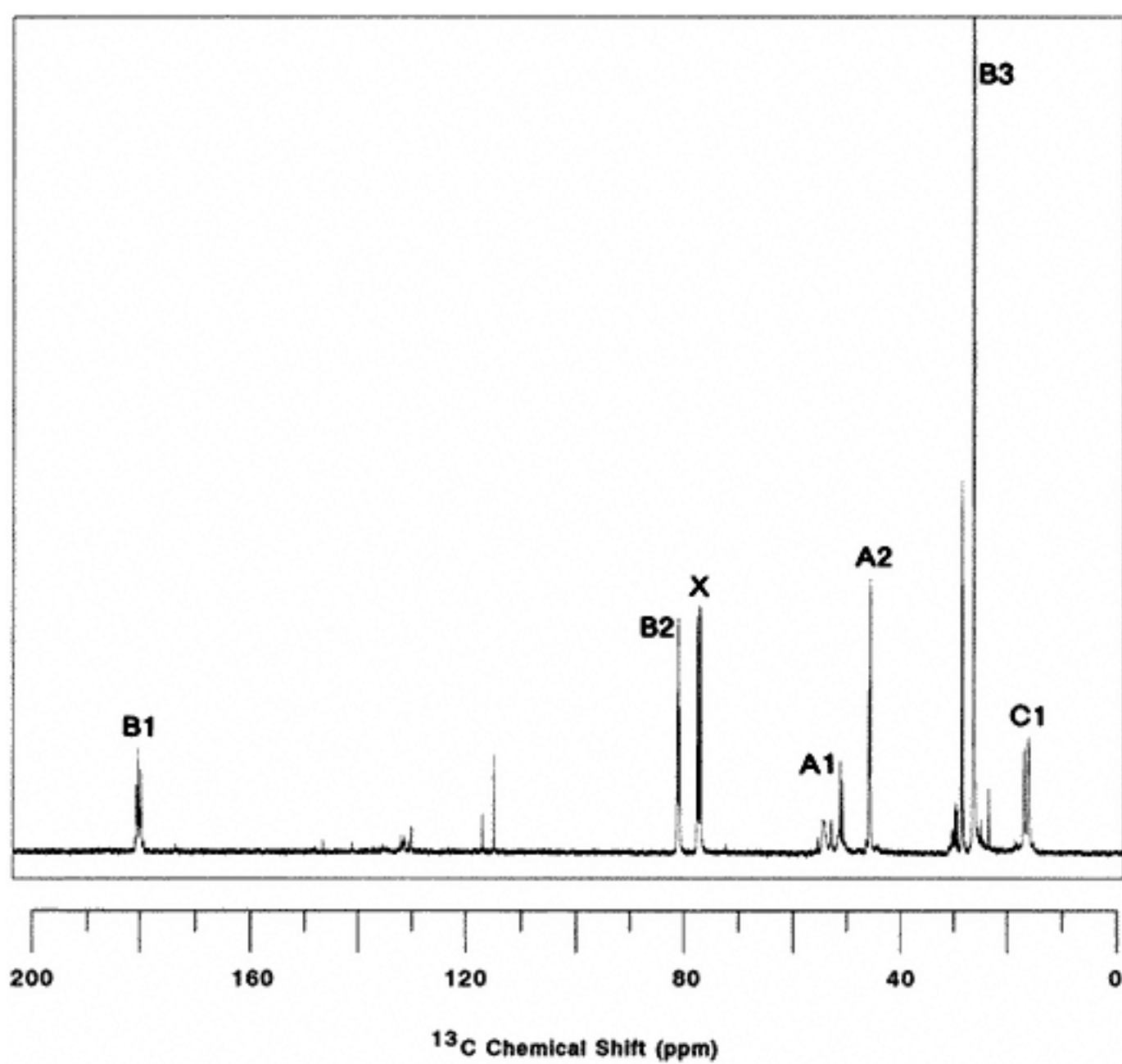
Broadening: 5 Hz

Pulse delay: 5 s

**IV-C-8—
Poly(*t*-Butyl Methacrylate)**

Comments

Some tacticity splitting can be observed for the backbone (**A1** and **A2**), carbonyl (**B1**), and α -methyl (**C1**) carbons; solvent resonances are marked by **X**.



Code	Shift (ppm)
A1	54.7
A2	44.7
B1	178.4
B2	70.9
B3	27.4
C1	18.1, 16.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

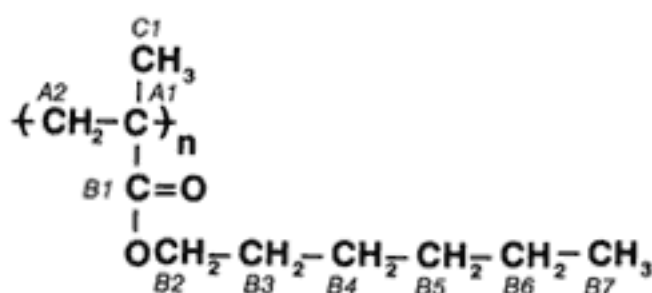
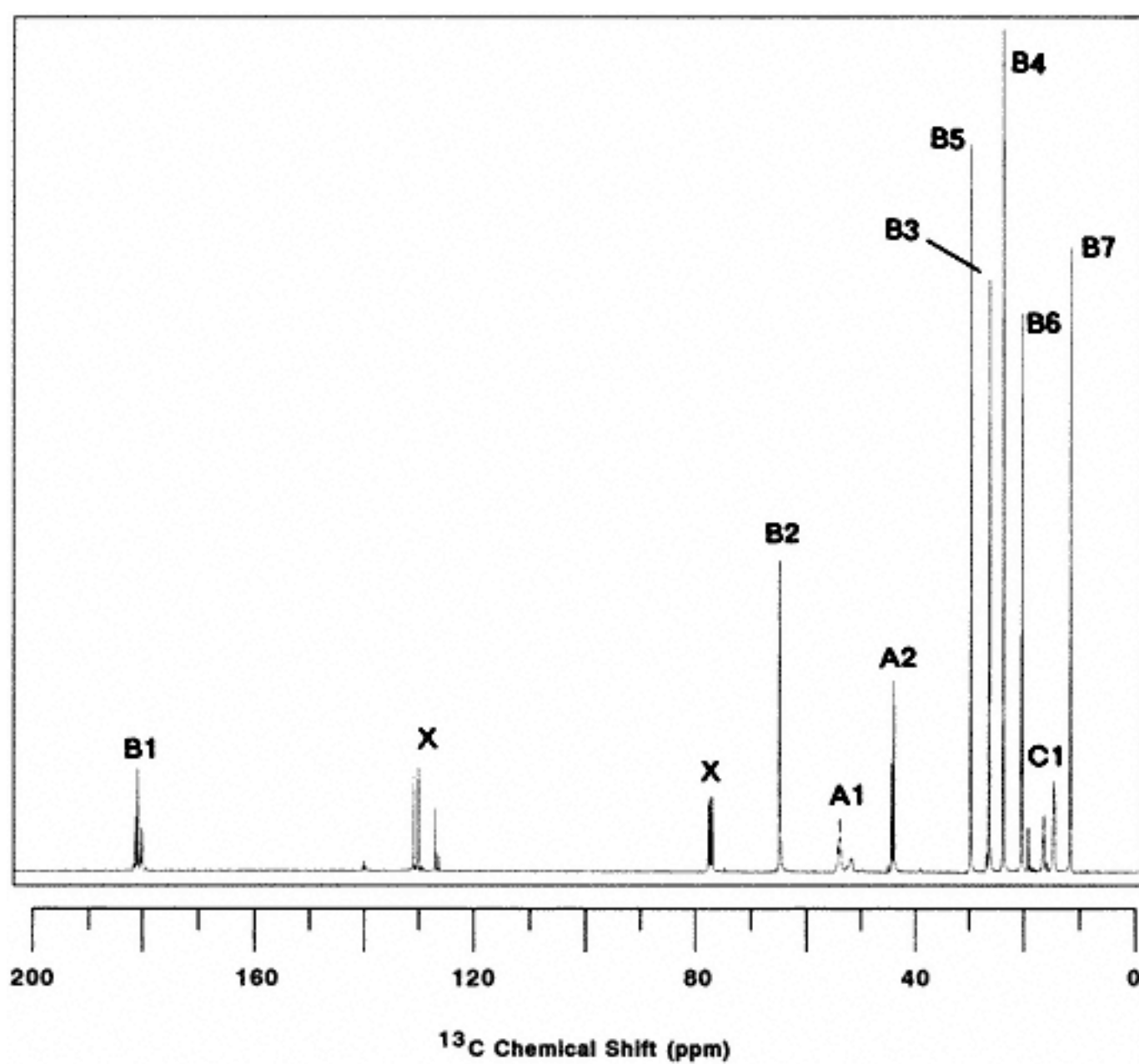
Source

Prof. Cecil Dybowski, University of Delaware, Newark, DE.

**IV-C-9—
Poly(*n*-Hexyl Methacrylate)**

Comments

Some tacticity splitting can be observed for the backbone (A1 and A2), carbonyl (B1), and α -methyl (C1) carbons; solvent resonances are marked by X.



Code	Shift (ppm)
A1	54.2
A2	44.9
B1	177.6
B2	64.1
B3	28.1
B4	25.4
B5	21.4
B6	21.0
B7	13.9
C1	18.1, 16.4

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃/toluene

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

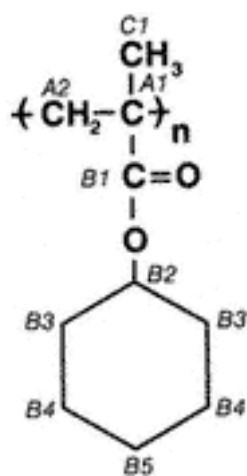
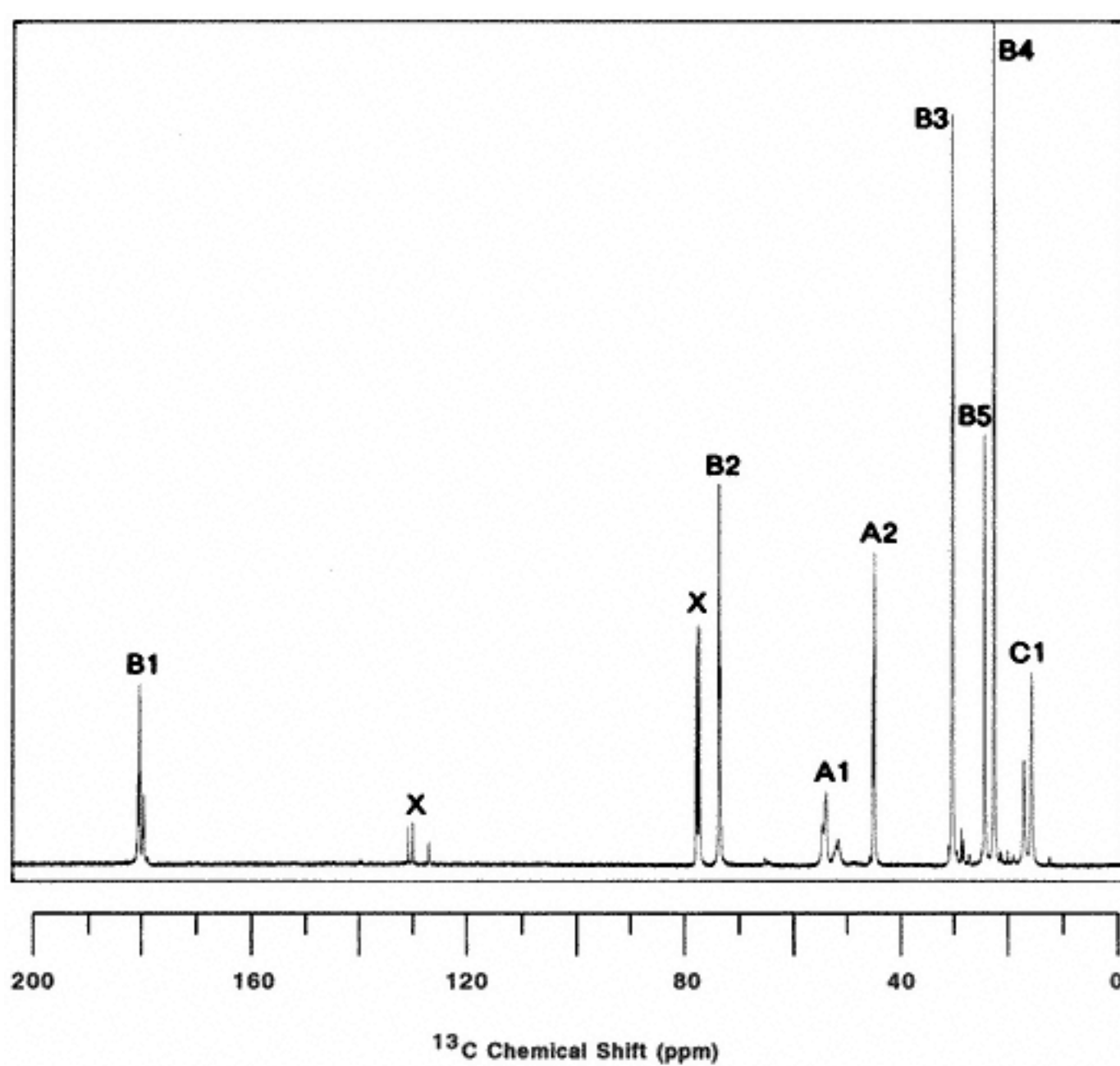
Source

Scientific Polymer Products, Ontario, NY.

**IV-C-10—
Poly(Cyclohexyl Methacrylate)**

Comments

Some tacticity splitting can be observed for the backbone (**A1** and **A2**), carbonyl (**B1**), and α -methyl (**C1**) carbons; solvent resonances are marked by **X**. This material is often used to manufacture optical lenses because it exhibits a low shrink temperature and good casting properties.



Code	Shift (ppm)
A1	53.8
A2	45.3
B1	177.7
B2	73.0
B3	31.5
B4	23.9
B5	25.4
C1	18.1, 16.4

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3 /toluene

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

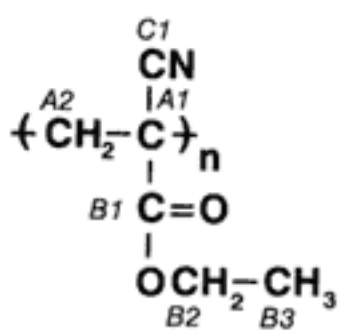
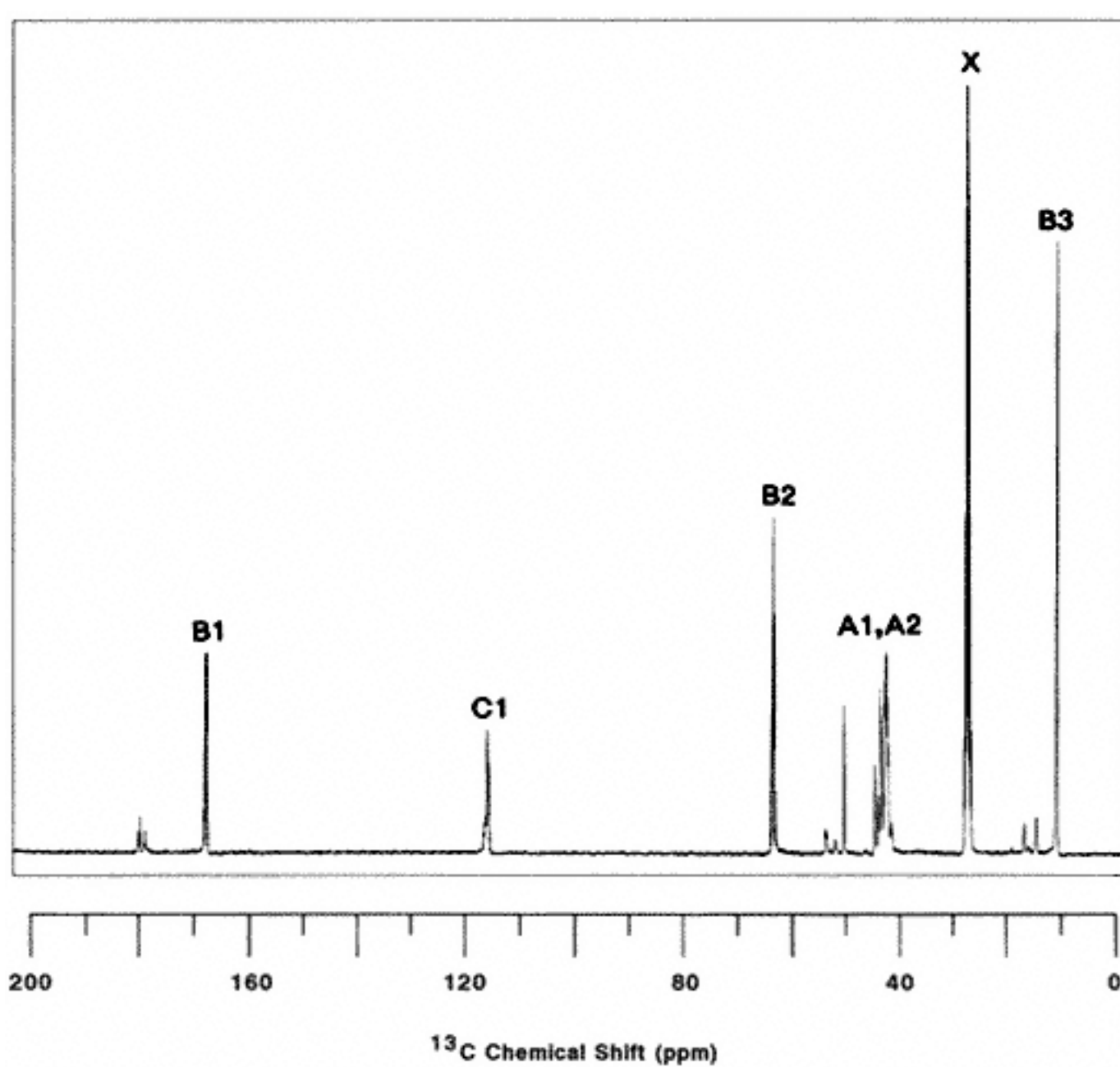
Source

Scientific Polymer Products, Ontario, NY.

**IV-C-11—
Poly(Ethyl Cyanoacrylate)**

Comments

Some tacticity splitting can be observed for the backbone (A1 and A2), carbonyl (B1), and cyanide (C1) carbons; solvent resonances are marked by X. This material is used as an adhesive, commonly referred to as "superglue."



Code	Shift (ppm)
A1	42–46
A2	51.2
B1	165.7
B2	63.9
B3	12.9
C1	115.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: acetone- d_6

Concentration: 10% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

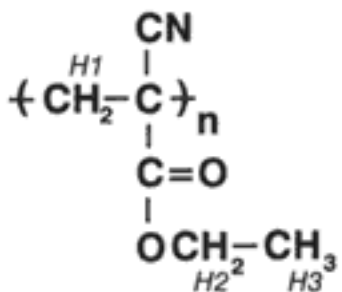
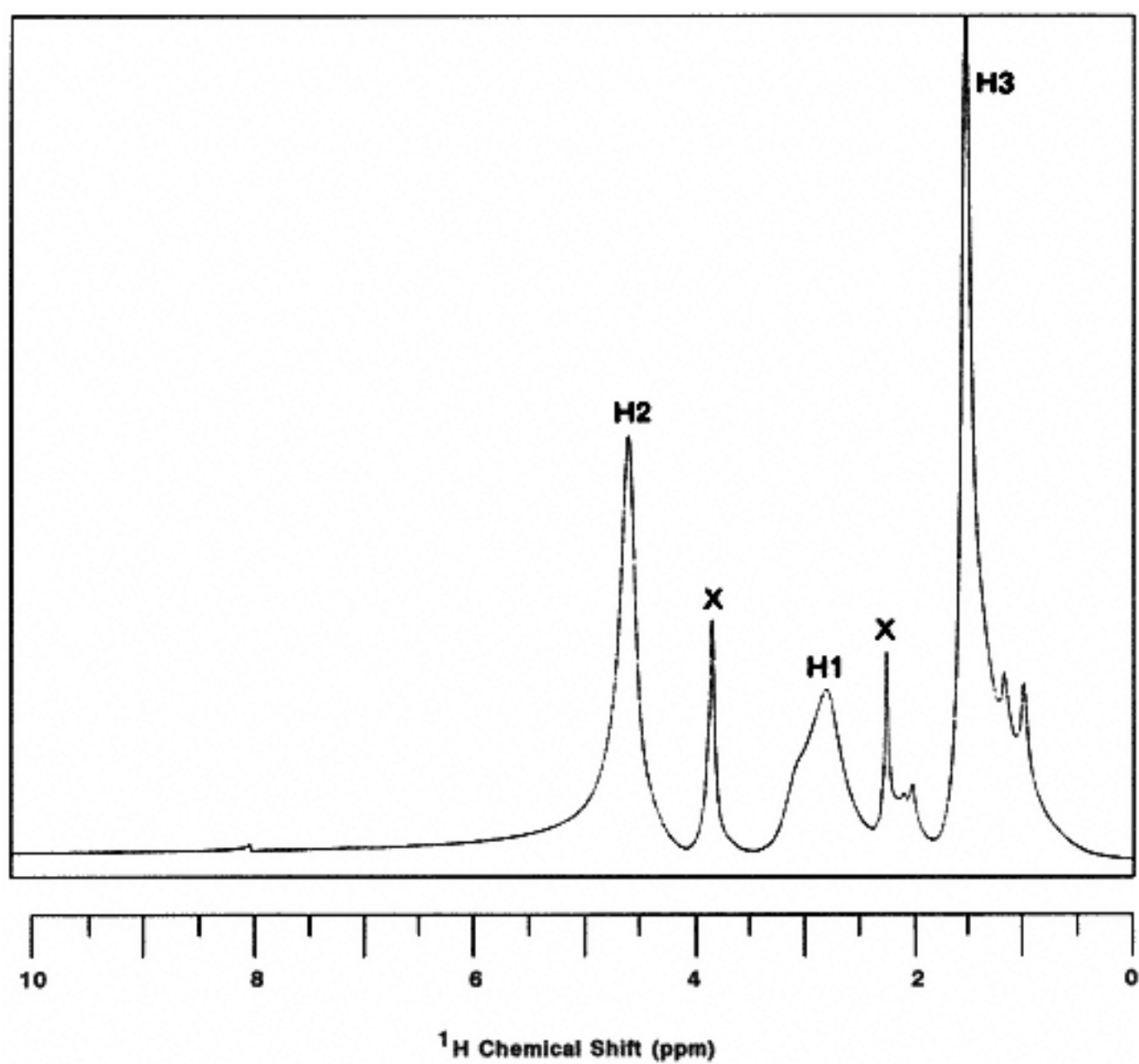
Reference

M. Stein. *J. Appl. Polym. Sci.* 46:2217, 1992.

IV-C-11H—
Poly(Ethyl Cyanoacrylate)

Comments

Tacticity effects are obscured by broadening caused by sample viscosity. This material is used as an adhesive, commonly referred to as "superglue."



Code	Shift (ppm)
H1	2.8
H2	4.5
H3	1.6

Experimental Parameters

Nucleus: ¹H (400 MHz)

Temperature: 50°C

Solvent: acetone-d₆

Concentration: 10% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

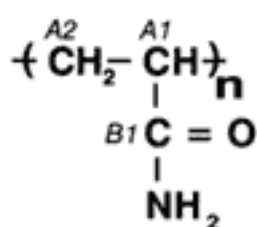
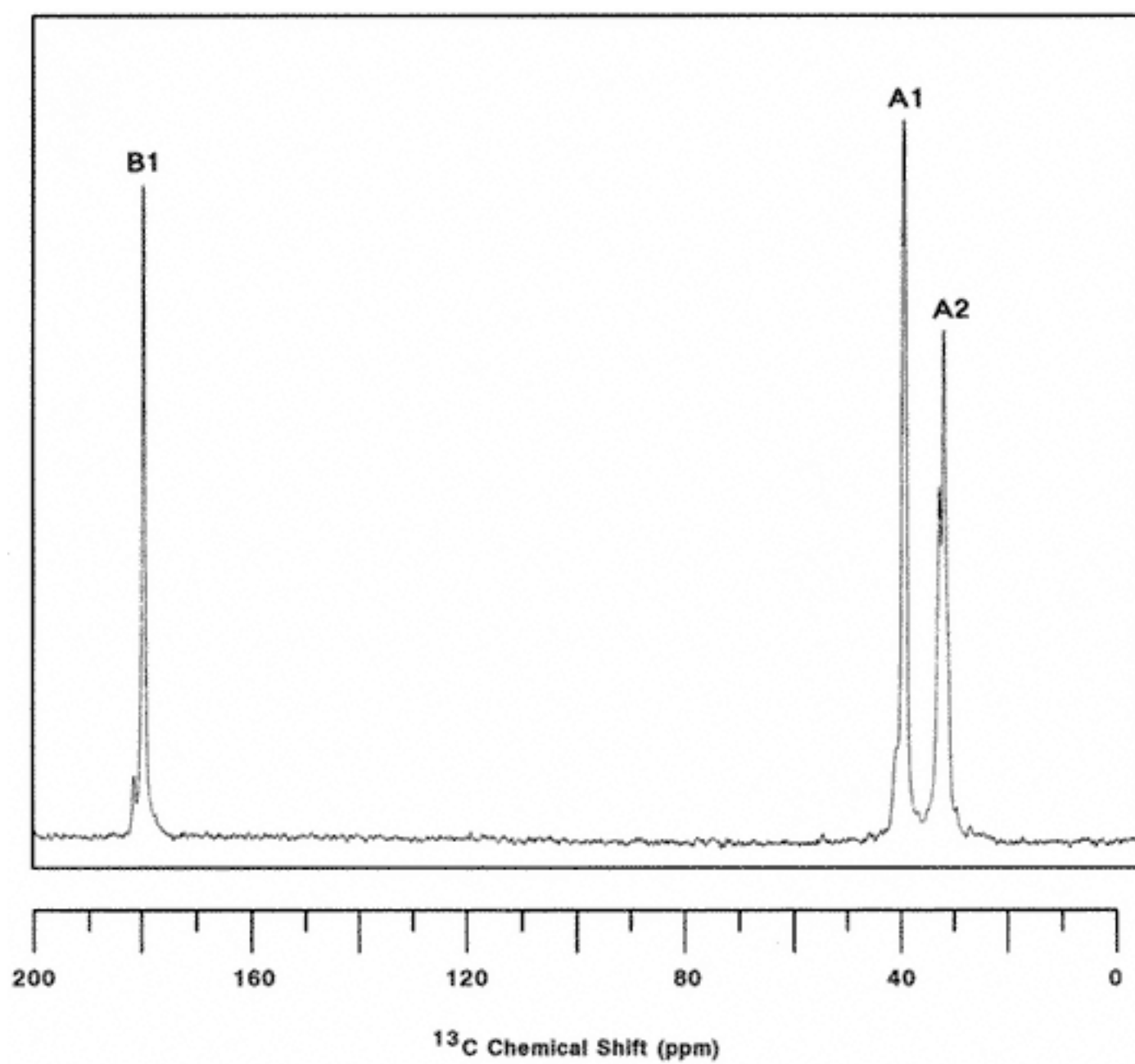
Reference

M. Stein. *J. Appl. Polym. Sci.* 46:2217, 1992.

IV-D-1— Polyacrylamide

Comments

Some tacticity splitting can be observed for all carbons; solvent resonances are marked by X. Polyacrylamide is water-soluble and is used as a flocculating agent and water thickener.



Code	Shift (ppm)
A1	43.3
A2	35.3
B1	180.6

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: D₂O/H₂O

Concentration: 20% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

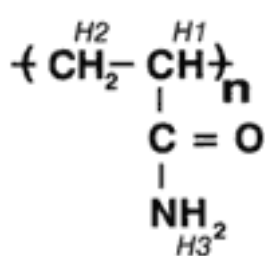
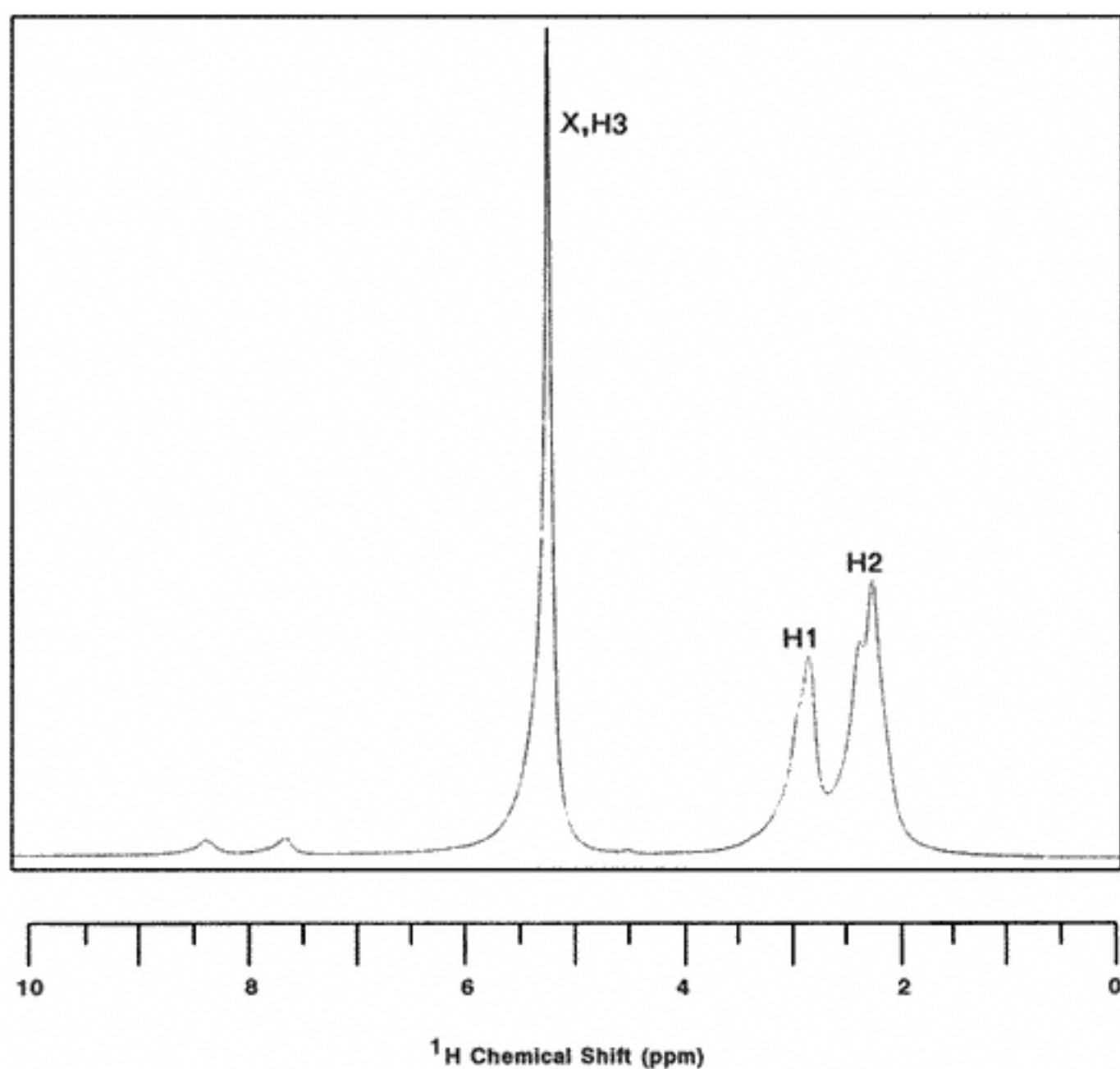
References

K. Hikichi, M. Ikura, and M. Yasuda. *Polym. J.* 20:851, 1988; K. Yasuda, K. Okajima, and K. Kamide. *Polym. J.* 20:1101, 1988.

IV-D-1H— Polyacrylamide

Comments

Tacticity effects are obscured by broadening caused by sample viscosity. Polyacrylamide is water-soluble and is used as a flocculating agent and water thickener.



Code	Shift (ppm)
H1	2.5
H2	2.9
H3	4.8

Experimental Parameters

Nucleus: ¹H (400 MHz)

Temperature: 50°C

Solvent: D₂O/H₂O

Concentration: 30% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

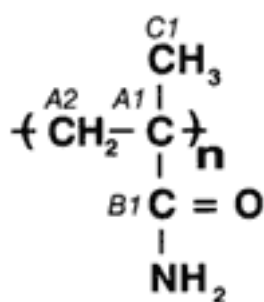
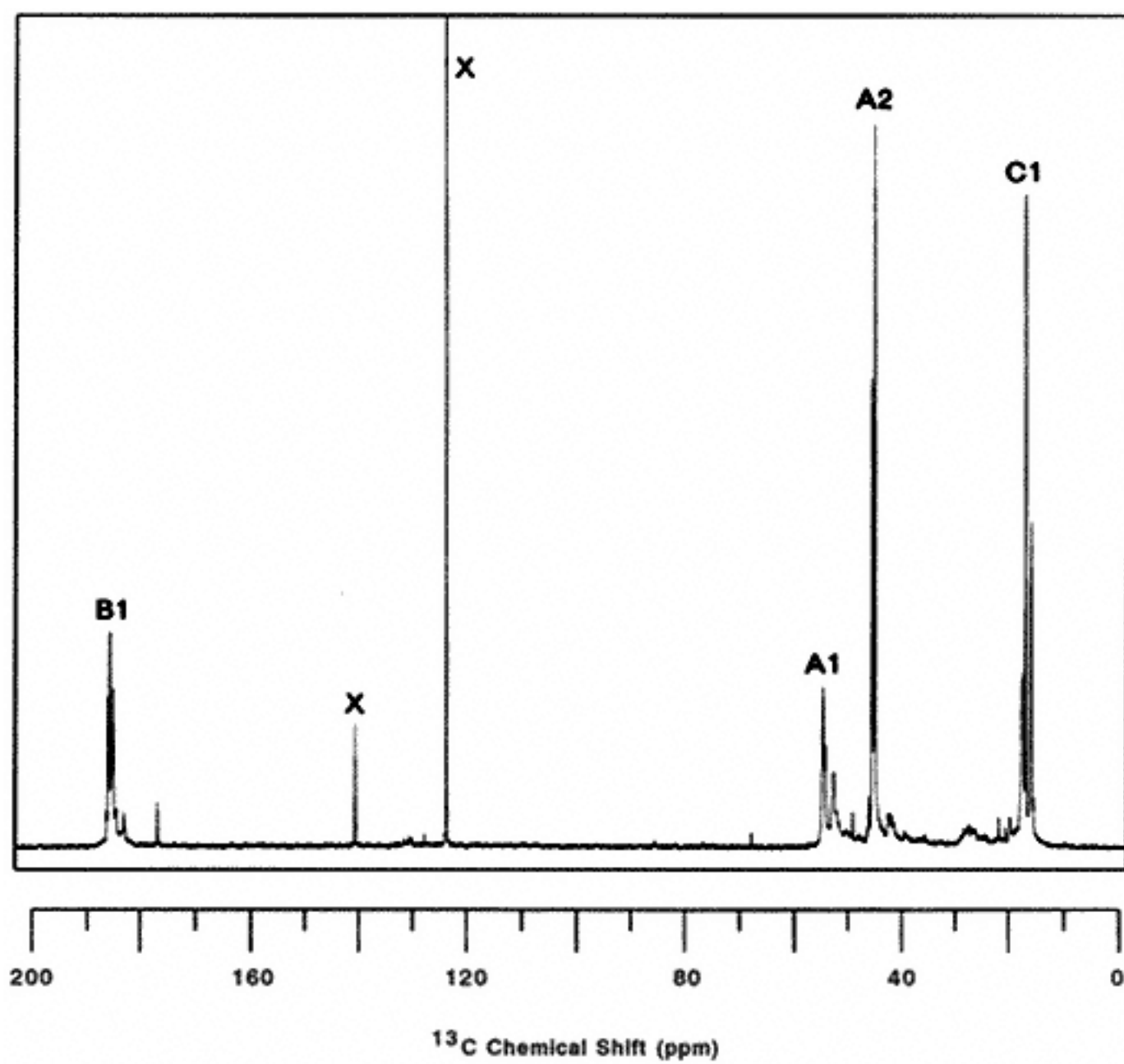
Reference

M. Stein. *J. Appl. Polym. Sci.* 46:2217, 1992.

IV-D-2— Polymethacrylamide

Comments

Some tacticity splitting can be observed for all carbons; resonances marked by **X** are due to residual monomer. Polyacrylamide is water-soluble, and is used as a flocculating agent and water thickener.



Code	Shift (ppm)
A1	54.4
A2	45.1
B1	183.4
C1	18.1

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: D₂O/H₂O

Concentration: 10% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 1 Hz

Pulse delay: 2 s

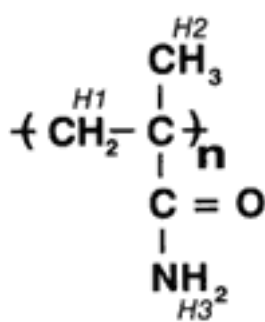
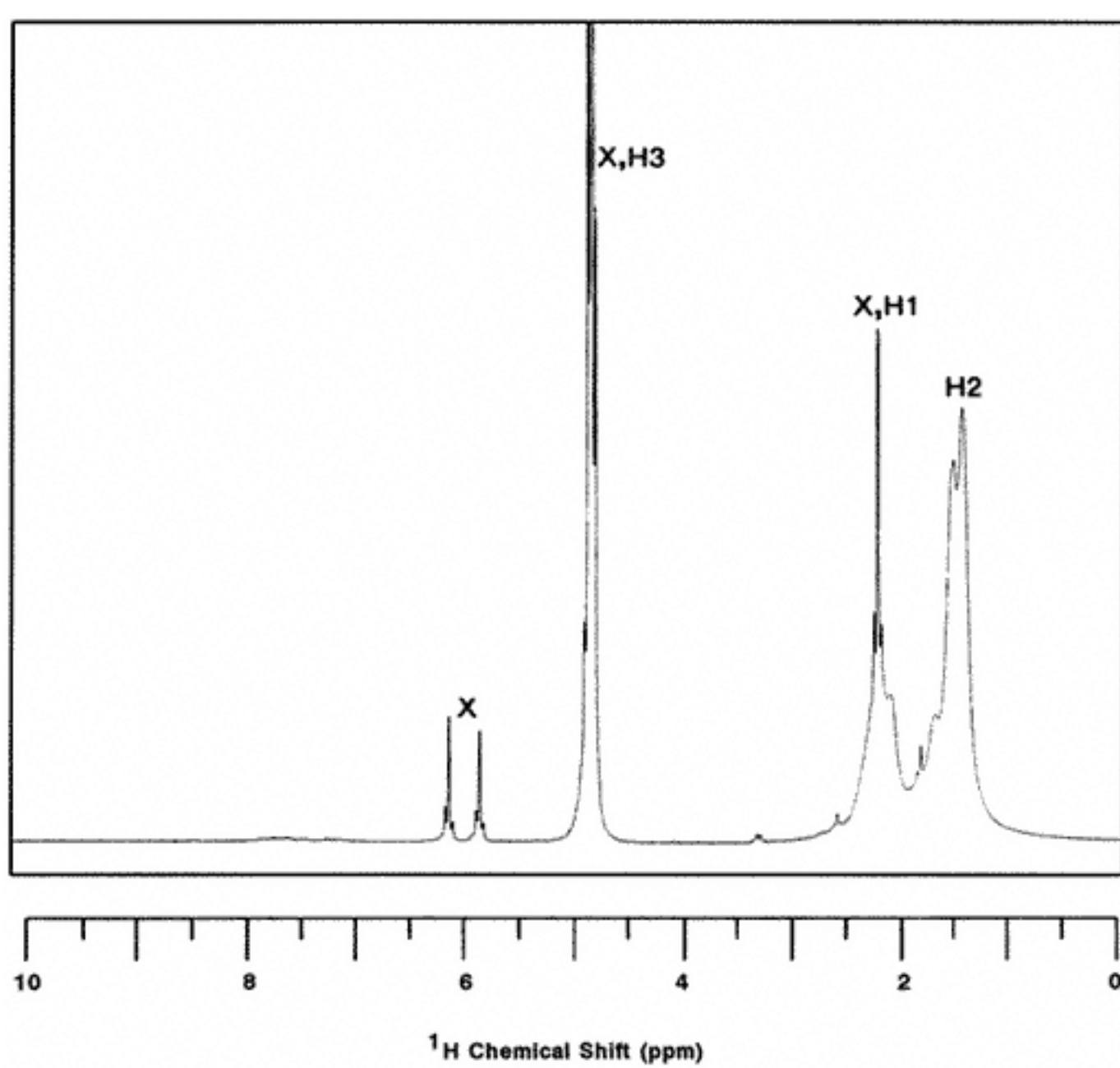
Reference

M. Stein. *J. Appl. Polym. Sci.* 46:2217, 1992.

IV-D-2H— Polymethacrylamide

Comments

Tacticity effects are obscured by broadening caused by sample viscosity. Resonances marked by **X** are due to solvent or residual monomer. Polyacrylamide is water-soluble and is used as a flocculating agent and water thickener.



Code	Shift (ppm)
H1	2.2
H2	1.5
H3	4.8

Experimental Parameters

Nucleus: ^1H (400 MHz)	Temperature: 50°C
Solvent: $\text{D}_2\text{O}/\text{H}_2\text{O}$	Concentration: 30% w/w
Scans: 48	Spectral width: 8 kHz
Data points: 8192	Pulse width: 10°
Broadening: 5 Hz	Pulse delay: 5 s

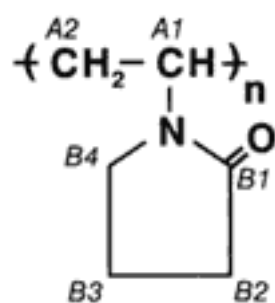
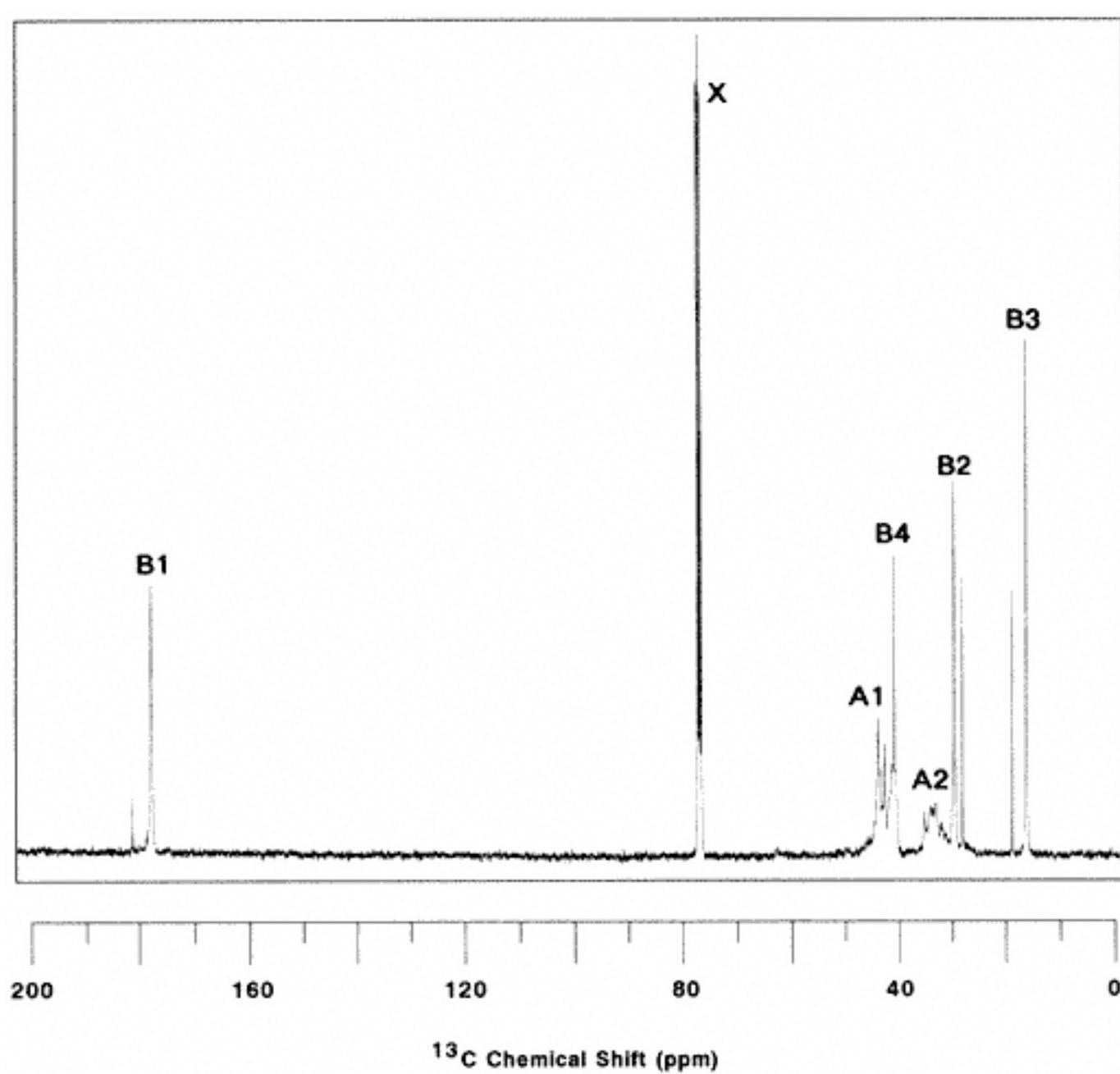
Reference

M. Stein. *J. Appl. Polym. Sci.* 46:2217, 1992.

**IV-D-3—
Poly(*N*-Vinyl Pyrrolidone)**

Comments

Tacticity effects are observed for the backbone carbons (**A1** and **A2**); solvent resonances are marked by **X**. This polymer is water-soluble and is found in hair and skin cosmetics, textiles, and adhesives. It is also used to modify some fibers, such as acrylics, polyesters, and cellulose, for improved dyeability.



Code	Shift (ppm)
A1	45.4
A2	34.8
B1	175.4
B2	31.4, 29.7
B3	20.6, 18.1
B4	41.6

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

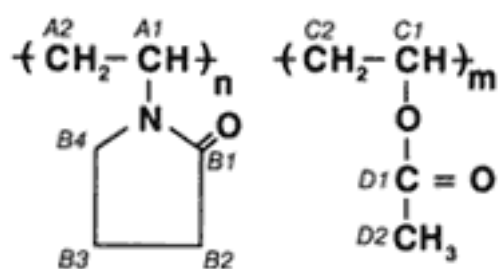
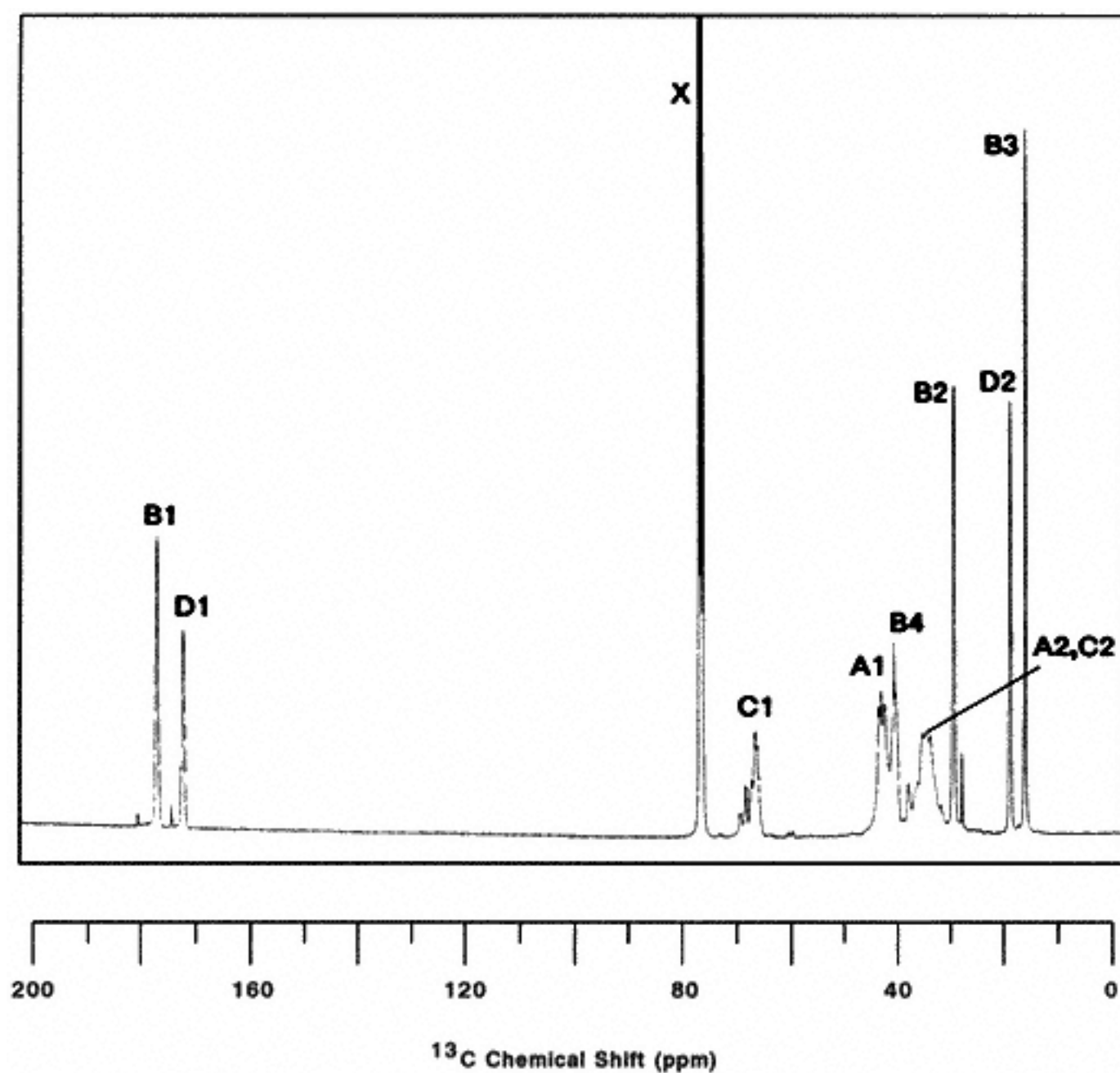
Broadening: 2 Hz

Pulse delay: 2 s

**IV-D-4—
Poly(*N*-Vinyl Pyrrolidone-Co-Vinyl Acetate)**

Comments

Tacticity splitting is observed for the backbone carbons (A1, A2, C1, and C2); solvent resonances are marked by X.



Code	Shift (ppm)
A1	44.2
A2	36.7
B1	175.1
B2	30.9
B3	18.1
B4	41.4
C1	67.0
C2	36.7
D1	170.4
D2	20.6

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

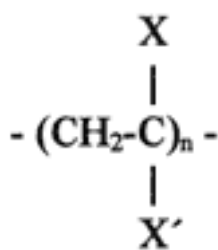
Broadening: 2 Hz

Pulse delay: 2 s

V—

Aliphatic Backbones: Miscellaneous Pendant Groups

Polymers in this group have the general structure:



A

where X and X' are pendant groups not included in Chapters II, III, or IV (i.e., they are not aliphatic groups, aromatic rings, esters, or amides). The polymers included in this chapter have halogens or halogenated alkyls, hydroxyls, olefins, ethers, ketones, or cyanides as the pendant group(s).

The most widespread materials in this category are halogenated polymers, for which X is, usually, either fluorine or chlorine. Fluoropolymers such as Teflon and Viton ({ V-A-3 through V-A-7}; both DuPont products) are greatly valued for their surface properties and chemical inertness [1]. Poly(vinyl chloride) (PVC) {V-A-8}, commonly called "vinyl," is found in in both rigid (pipe and construction materials) and flexible (artificial leather and rainwear) forms [1]. Over 10 billion lb (4.5 billion kg) of PVC were used in various applications in 1995 [2]. Poly(vinylidene chloride) (PVdC, in which X and X' are both Cl) and its copolymers {V-A-11 through V-A-14} compose the group of materials generally known as Saran (Dow). Polyacrylonitrile (PAN) {IV-B-8 and V-B-9} fibers are commonly referred to as "acrylic" [1]. The other polymers in this group have highly specialized uses.

V.A—

Sample Preparation and Spectral Acquisition

Because this group includes so many different types of pendant groups, it is not possible to generalize about appropriate solvents. Some specific recommendations are listed in Table V-1 [3]. One commercially important polymer not listed in Table V-1, or included in this collection, is polytetrafluoroethylene (Teflon), which is soluble only at extremely high temperatures (> 300°C) not achievable with ordinary nuclear magnetic resonance (NMR) instrumentation.

As is true for most high polymers, quantitative ^{13}C spectral accumulation conditions can be readily achieved. A 30-s pulse (relaxation) delay after a 90° pulse will normally ensure correct relative ^{13}C peak areas for most carbons when the ^1H decoupling is gated to suppress the nuclear overhauser effects (NOEs). Conditions for quantitative ^1H spectra are even less stringent: a 5-s pulse delay following a 90° pulse.

Table V.1 Suitable Deuterated Solvents for Selected Vinyl Polymers

Polymer	Solvent(s)
Poly(vinyl fluoride)	Dimethylformamide-d ₇
Poly(vinylidene fluoride)	Acetone-d ₆ , chloroform-d
Vinylidene fluoride copolymers	Acetone-d ₆
Poly(vinyl chloride)	Benzene-d ₆ , dimethylformamide-d ₇ , dimethylsulfoxide-d ₆ , methylene chloride-d _{2a} , tetrahydrofuran-d ₈ , toluene-d ₈
Poly(vinylidene chloride)	Dimethylsulfoxide-d ₆ (hot), tetrahydrofuran-d ₈ (hot)
1,2-Polybutadiene	Chloroform-d
Poly(vinyl alcohol)	Dimethylformamide-d ₇ , dimethylsulfoxide-d ₆ , water-d ₂ (hot)
Poly(vinyl methyl ether)	Acetone-d ₆ , benzene-d ₆ , chloroform-d ^a , carbon tetrachloride, ethanol-d ₆ , methanol-d ₄ , methylene chloride-d _{2a} , toluene-d ₈
Poly(vinyl formal)	Acetone-d ₆ , benzene-d ₆ , chloroform-d, ethanol-d ₆ , methanol-d ₄ , methylene chloride-d ₂ , tetrahydrofuran-d ₈ , toluene-d ₈
Poly(vinyl butyral)	Acetone-d ₆ , benzene-d ₆ , chloroform-d, ethanol-d ₆ , methanol-d ₄ , methylene chloride-d ₂ , tetrahydrofuran-d ₈ , toluene-d ₈
Poly(vinyl methyl ketone)	Acetone-d ₆ , chloroform-d, dimethylformamide-d _{7a} , pyridine-d ₅ , tetrahydrofuran-d ₈
Polyacrylonitrile	Dimethylformamide-d _{7a} , dimethylsulfoxide-d ₆ , dioxane-d ₈
Polymethacrylonitrile	Acetone-d ₆ , dimethylformamide-d ₇ , dimethylsulfoxide-d ₆ , methylene chloride-d ₂ , pyridine-d _{5a}

^a May interfere with polymer resonances.

V.B— Spectral Features

The ¹³C and ¹H spectra of polymers in this group exhibit a wide variety of chemical shifts, because so many different pendant groups are included. ¹³C chemical shifts of the homopolymers in this chapter are summarized in Table V-2. Most of these polymers' spectra exhibit pronounced tacticity effects [4].

V.B.1— *Polymers and Copolymers with Pendant Halogens*

Fluorinated carbons in fluoropolymers typically exhibit ¹³C resonances in the range 70–130 ppm. An immediately striking feature of the ¹H-decoupled ¹³C spectrum of a fluoropolymer is its complexity, owing to the presence of ¹³C–¹⁹F J-couplings. ¹⁹F and ¹³C are both spin-1/2 nuclei [5], so, if ¹⁹F decoupling is not also applied during spectral acquisition, the ¹³C resonances will be split by nearby ¹⁹F nuclei. First-order splitting arising from directly bonded ¹⁹Fs follows the same pattern as ¹³C–¹H couplings: —CF₃ splits into a quartet, —CF₂—into a triplet, and so on. Second- and higher-order splitting are usually not observed, because of the relatively broad linewidths usually observed in polymer spectra. The presence of other effects, such as tacticity, regioselectivity, or sequences (in copolymers) complicate the spectra even further. ¹⁹F NMR may also be employed to study the structure of fluoropolymers. ¹⁹F chemical shifts for these materials range from ~–50 to –250 ppm. Two-dimensional NMR techniques have been effectively used to sort out the assignments [6–8]. In particular, J-resolved spectroscopy elucidated the microstructures of poly(vinyl fluoride) {V-A-1} [6,7] and poly(vinylidene fluoride) {V-A-2} [8].

Chlorinated polymers are very common in everyday products. The resonances of chlorinated carbons appear at somewhat lower shifts than those of the fluorinated carbons; they are observed at 40–90 ppm. The ¹³C spectrum of a chloropolymer is much simpler than that of the analogous fluoropolymer, because the chlorine nucleus does not split ¹³C, although tacticity effects are still present. Poly(vinyl chloride) (PVC) {V-A-8}, often simply called "vinyl," exhibits two ¹³C resonances: CH₂ at about 45 ppm and CHCl at about 55 ppm. *Rigid* PVC has found uses in building siding, flooring, pipe, and bottles, but its stiffness makes it unsuitable for many applications. Addition of a *plasticizer* to PVC makes the material flexible by lowering the glass-transition temperature T_g. *Flexible* PVC can be used for products such as furniture coverings or waterproof clothing [1]. Plasticizers are typically used in fairly high concentrations (5–25%), so their presence can easily be detected by NMR. The most common are phthalate esters, particularly di-2-ethylhexyl phthalate (DEHP) {X-A-5}.

Table V.2 ^{13}C Chemical Shifts for Selected Vinyl Homopolymers
$$\begin{array}{c}
 \text{X} \\
 \text{A2} \mid \text{A1} \\
 -\text{C}-\text{C}- \\
 \mid \\
 \text{X}'
 \end{array}$$

Polymer	X	X'	A1	A2	Others
Poly(vinyl fluoride)	F	H	89.7	41.5	—
Poly(vinylidene fluoride)	F	F	120.8	44.4	—
Poly(vinyl chloride)	Cl	H	54.9	45.7	—
Poly(vinylidene chloride)	Cl	Cl	84.3	61.6	—
1,2-Polybutadiene	$\text{CH}=\text{CH}_2$	H	41.9	39.6	143.4 ($\text{CH}=\text{CH}_2$) 115.1 ($\text{CH}=\text{CH}_2$)
Poly(vinyl alcohol)	OH	H	68.4	45.3	—
Poly(vinyl methyl ether)	OCH_3	H	75.8	38–41	56.4 (OCH_3)
Poly(vinyl methyl ketone)	$\text{O}=\text{C}-\text{CH}_3$	H	48.0	32.5	210.6 ($\text{O}=\text{C}-\text{CH}_3$) 29.5 ($\text{O}=\text{C}-\text{CH}_3$)
Polyacrylonitrile	CN	H	33.9	28.1	121.2 (CN)
Polymethacrylonitrile	CN	CH_3	49.5	33.0	123.3 (CN) 26–27 (CH_3)

V.B.2—***Polymers and Copolymers with Miscellaneous Pendant Groups***

This group includes materials with hydrocarbon backbones and pendant groups that have not been discussed in earlier parts of this compilation. Because these polymers have a variety of different side groups, it is not possible to generalize about the observed chemical shifts. The spectrum can, however, often be interpreted with the aid of simple chemical-shift calculation schemes (see Sec. I.C.2) or tabulations of shifts for low molecular model compounds [5].

References

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6. M. D. Bruch, F. A. Bovey, and R. E. Cais. *Macromolecules* 17:2547, 1984.
7. M. D. Bruch. *Macromolecules* 22:151, 1989.
8. R. E. Cais and J. M. Kometani. *Macromolecules* 18:1354, 1985.

ALIPHATIC BACKBONES: MISCELLANEOUS PENDANT GROUPS*A. Polymers and Copolymers with Pendant Halogens*

V-A-1	Poly(vinyl fluoride)
V-A-1F	Poly(vinyl fluoride)
V-A-2	Poly(vinylidene fluoride)
V-A-2F	Poly(vinylidene fluoride)
V-A-3	Poly(vinylidene fluoride-co-tetrafluoroethylene-co-perfluoro(methyl vinyl ether)-co-bromotetrafluorobutene)
V-A-3F	Poly(vinylidene fluoride-co-tetrafluoroethylene-co-perfluoro(methyl vinyl ether)-co-bromotetrafluorobutene)
V-A-4	Poly(vinylidene fluoride-co-tetrafluoroethylene-co-perfluoro(methyl vinyl ether)-co-bromotetrafluorobutene)
V-A-4F	Poly(vinylidene fluoride-co-tetrafluoroethylene-co-perfluoro(methyl vinyl ether)-co-bromotetrafluorobutene)
V-A-5	Poly(vinylidene fluoride-co-hexafluoropropylene)
V-A-5F	Poly(vinylidene fluoride-co-hexafluoropropylene)
V-A-6	Poly(vinylidene fluoride-co-hexafluoropropylene-co-tetrafluoroethylene)
V-A-6F	Poly(vinylidene fluoride-co-hexafluoropropylene-co-tetrafluoroethylene)
V-A-7	Poly(vinylidene fluoride-co-hexafluoropropylene-co-tetrafluoroethylene-co-bromotetrafluorobutene)
V-A-7F	Poly(vinylidene fluoride-co-hexafluoropropylene-co-tetrafluoroethylene-co-bromotetrafluorobutene)
V-A-8	Poly(vinyl chloride)
V-A-8H	Poly(vinyl chloride)
V-A-9	Poly(vinyl chloride-co-vinyl acetate) [5% VA]
V-A-9H	Poly(vinyl chloride-co-vinyl acetate) [5% VA]
V-A-10	Poly(vinyl chloride-co-vinyl acetate-co-vinyl alcohol)
V-A-11	Poly(vinyl chloride-co-vinylidene chloride) [5% VdC]
V-A-12	Poly(vinyl chloride-co-vinylidene chloride) [20% VdC]
V-A-13	Poly(vinylidene chloride)
V-A-14	Poly(vinylidene chloride-co-acrylonitrile)

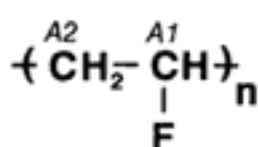
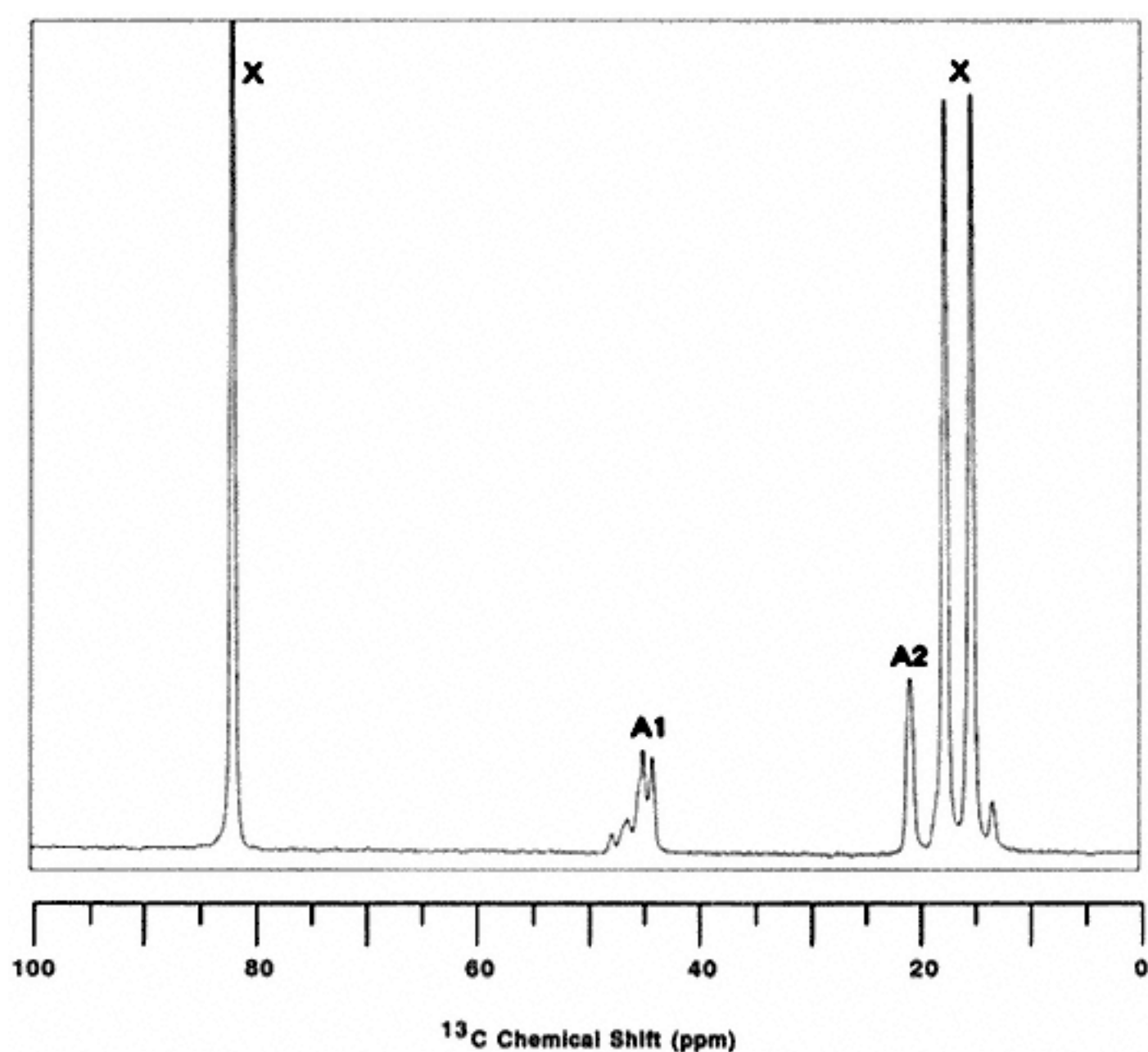
B. Polymers and Copolymers with Miscellaneous Pendant Groups

V-B-1	1,2-Polybutadiene
V-B-1H	1,2-Polybutadiene
V-B-2	Poly(vinyl alcohol)
V-B-2H	Poly(vinyl alcohol)
V-B-3	Poly(vinyl alcohol-co-vinyl acetate) [20% VA]
V-B-4	Poly(vinyl methyl ether)
V-B-5	Poly(vinyl formal)
V-B-6	Poly(vinyl butyral)
V-B-7	Poly(vinyl methyl ketone)
V-B-8	Polyacrylonitrile
V-B-9	Polymethacrylonitrile

V-A-1—
Poly(Vinyl Fluoride) (PVF)

Comments

The halogenated carbon (A1) is split because of J-coupling between ^{13}C and ^{19}F . Further complexity arises from regioirregularities (i.e., head-to-head versus tail-to-tail sequences). Solvent resonances are marked by X. PVF is used as a coating for aluminum and galvanized steel.



Code	Shift (ppm)
A1	89.7
A2	41.5

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 120°C

Solvent: dimethylformamide- d_7

Concentration: 10% w/w

Scans: 20,000

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

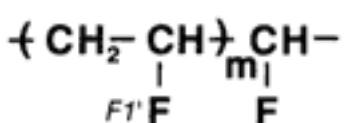
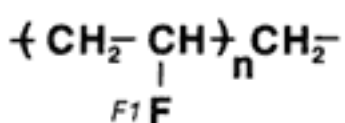
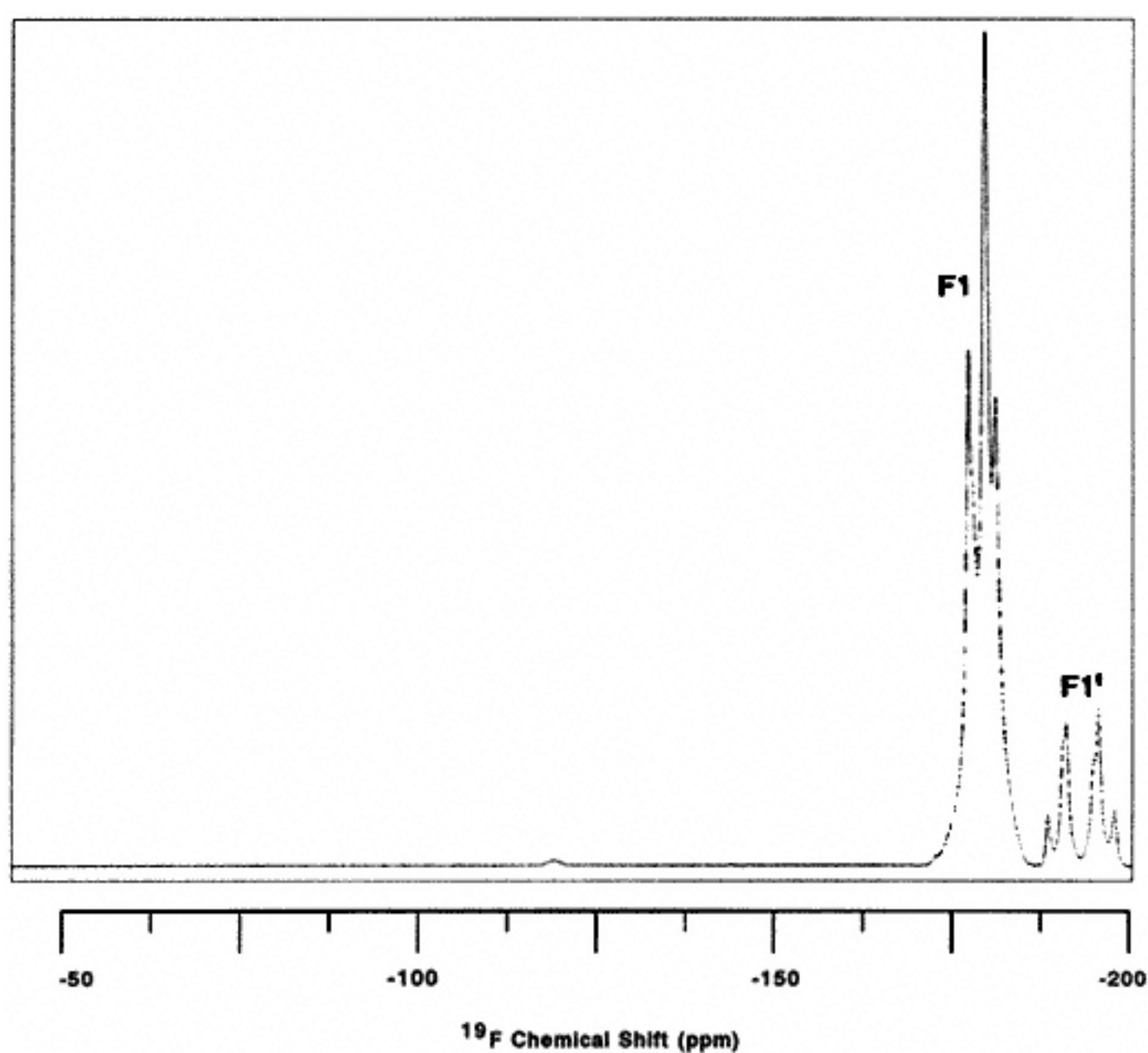
Broadening: 10 Hz

Pulse delay: 5 s

V-A-1F—
Poly(Vinyl Fluoride) (PVF)

Comments

The fluorine is split because of J-coupling between ^{19}F and ^1H . Regioirregularities (i.e., head-to-head versus tail-to-tail additions) give rise to distinct resonances. Further complexity is due to longer regiosequences. PVF is used as a coating for aluminum and galvanized steel. This spectrum was recorded by M. H. Frey, JEOL USA, Peabody, MA.



Code	Shift (ppm)
F1	~-180
F1'	~-195

Experimental Parameters

Nucleus: ^{19}F (376.1 MHz)	Temperature: 100°
Solvent: DMSO- d_6	Concentration: 10% w/w
Scans: 256	Spectral width: 75 kHz
Data points: 8192	Pulse width: 45°
Broadening: 20 Hz	Pulse delay: 1 s

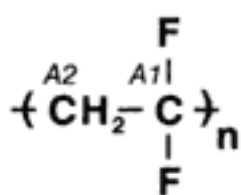
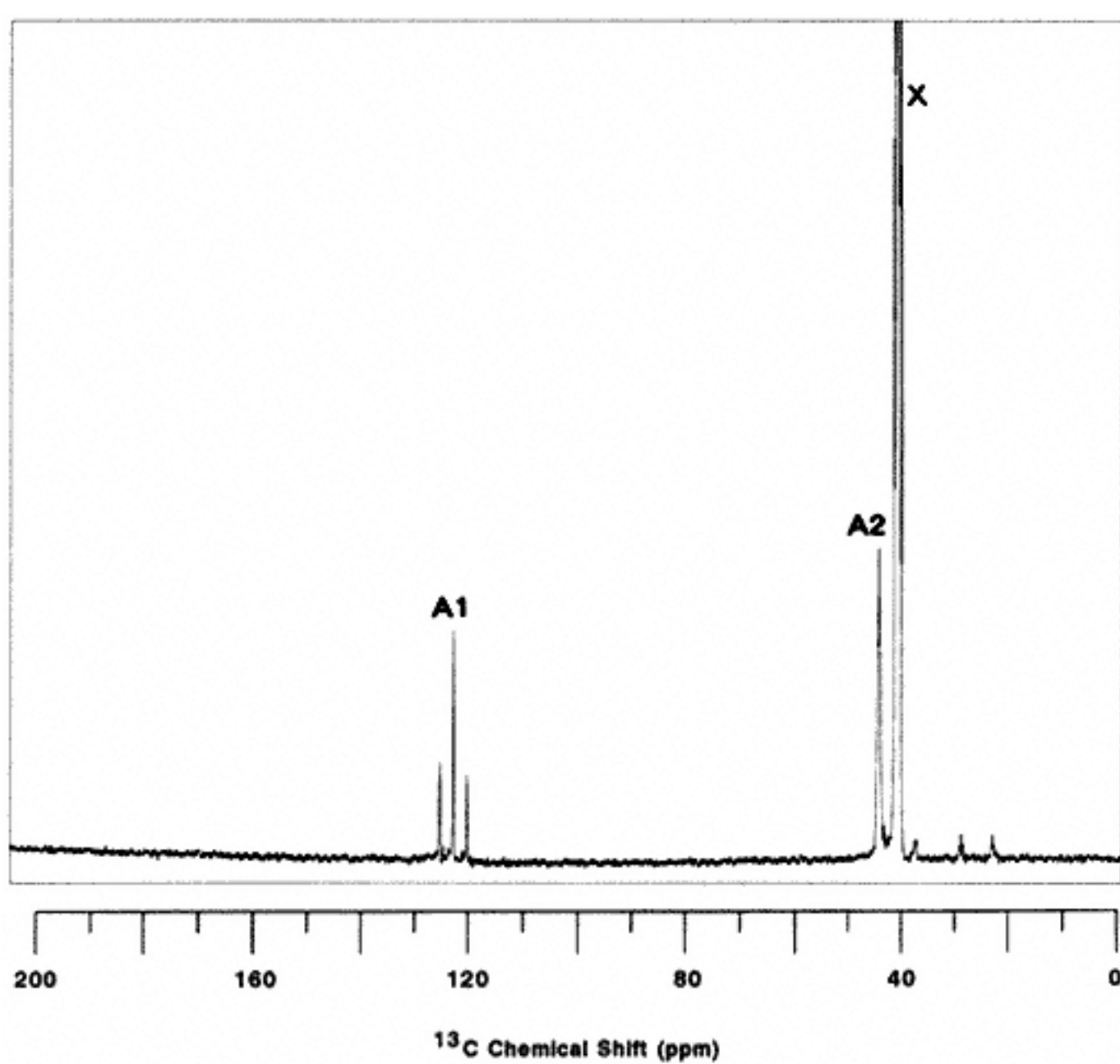
References

D. W. Ovenall and R. E. Uschold. *Macromolecules* 24:3235, 1991; M. D. Bruch. *Macromolecules* 22:151, 1989; M. D. Bruch, F. A. Bovey, and R. E. Cais. *Macromolecules* 17:2547, 1984.

V-A-2—

Poly(Vinylidene Fluoride) (PVdF)**Comments**

The halogenated carbon (**A1**) is split into a triplet because of J-coupling between ^{13}C and ^{19}F . Solvent resonances are marked by **X**. PVdF is used for wire and cable insulation in computers, aircraft, and geophysical applications; it is also found in piping, tank lining, valves, and pumps for corrosive substances.



Code	Shift (ppm)
A1	120.8
A2	44.4

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 120°C

Solvent: DMSO- d_6

Concentration: 10% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

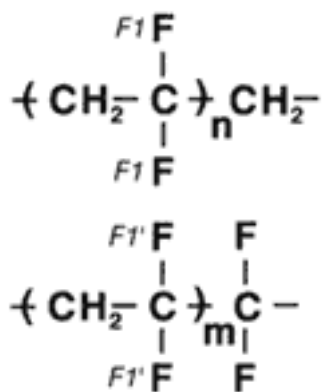
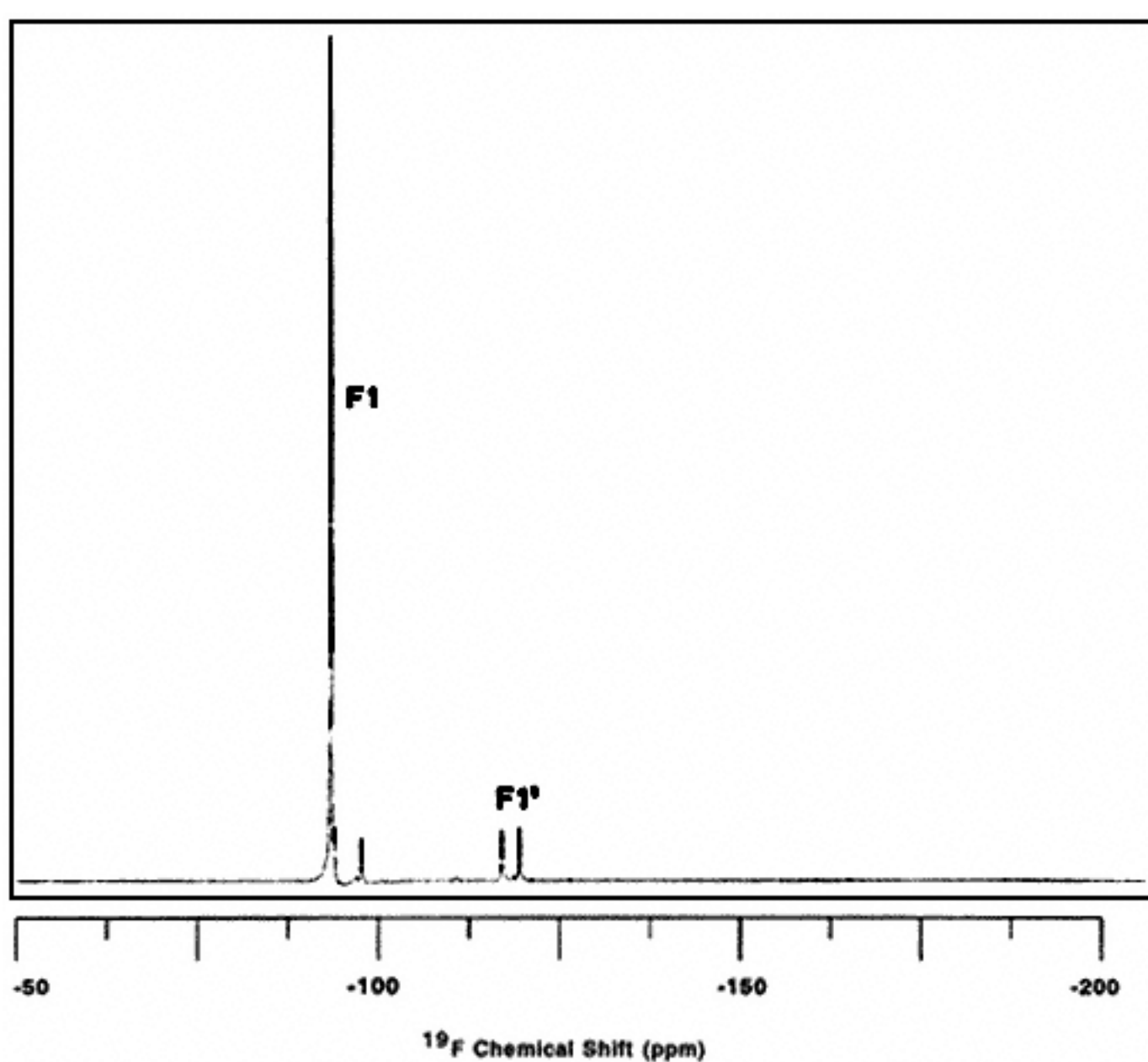
Broadening: 2 Hz

Pulse delay: 2 s

V-A-2F—

Poly(Vinylidene Fluoride) (PVdF)**Comments**

Regioirregularities (i.e., head-to-head versus tail-to-tail additions) give rise to distinct resonances. Further complexity is due to longer regiosequences. PVdF is used for wire and cable insulation in computers, aircraft, and geophysical applications; it is also found in piping, tank lining, valves, and pumps for corrosive substances. This spectrum was recorded by M. H. Frey, JEOL USA, Peabody, MA.



Code	Shift (ppm)
F1	-92.0, -95.9
F1'	-114.2, -116.5

Experimental Parameters

Nucleus: ^{19}F (376.1 MHz)	Temperature: 50°C
Solvent: acetone- d_6	Concentration: 10% w/w
Scans: 256	Spectral width: 75 kHz
Data points: 8192	Pulse width: 45°
Broadening: 10 Hz	Pulse delay: 1 s

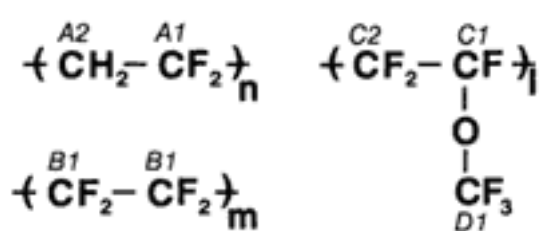
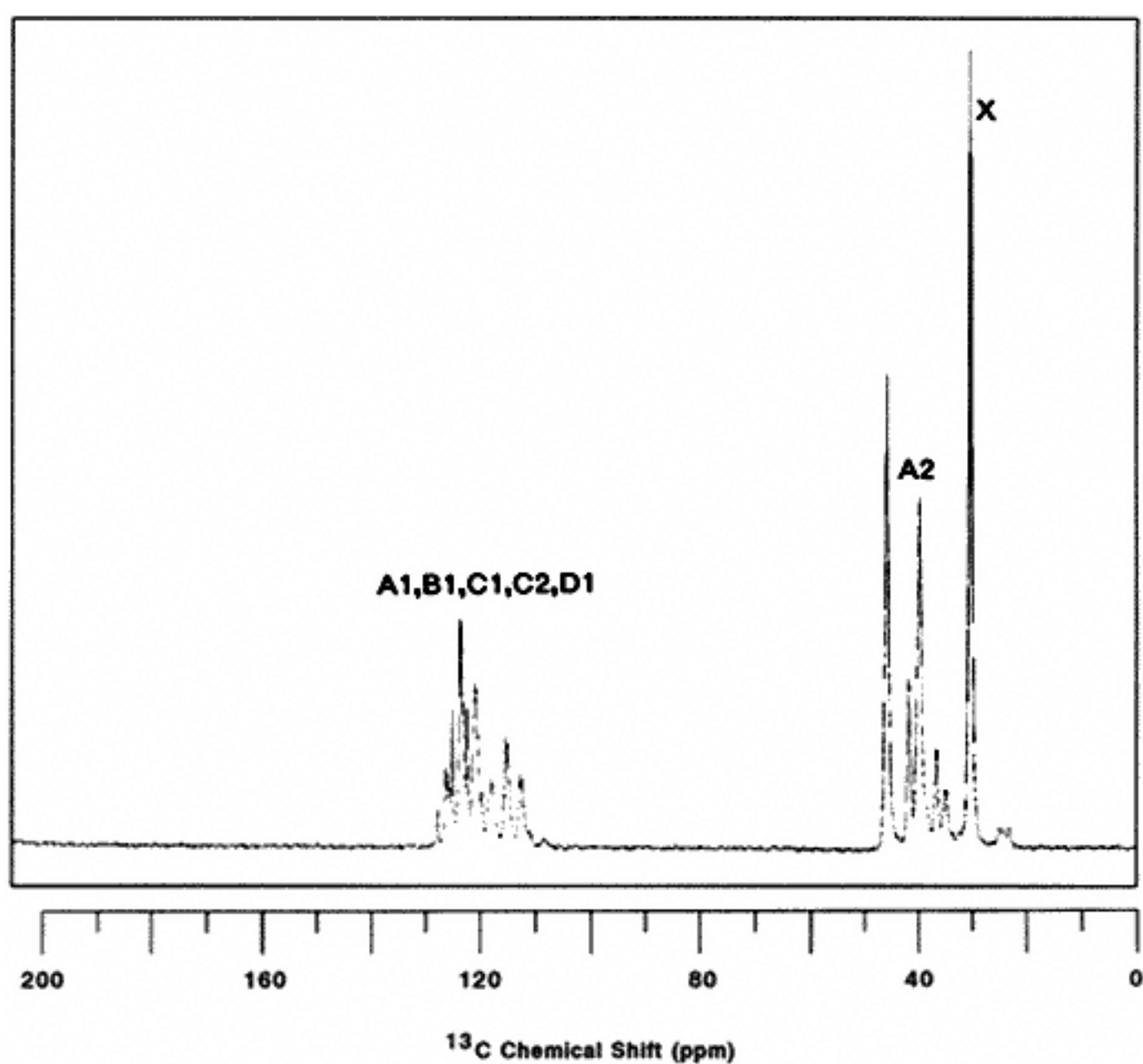
References

R. E. Cais and J. M. Kometani. *Macromolecules* 18:1354, 1985; F.-T. Lin and F.-M. Lin. *J. Macromol. Sci. Chem.* A26:1, 1989.

V-A-3—

Poly(Vinylidene Fluoride-Co-Tetrafluoroethylene-Co-Perfluoro(Methyl Vinyl Ether)-Co-Bromotetrafluorobutene)*Comments*

Also known as Viton GLT (DuPont) elastomer. The spectrum is complex because of overlapping multiplets caused by J-coupling between ^{13}C and ^{19}F , and because of the presence of regiosequences (i. e., head-to-head versus head-to-tail additions). The bromotetrafluorobutene component is too small to be observed in this spectrum. Solvent resonances are marked by **X**. Fluoroelastomers such as this material maintain their properties over a wide temperature range. They are also chemically inert and are used in demanding applications, such as heavy industrial equipment and aircraft.



Code	Shift (ppm)
A1	109–123
A2	38–44
B1	109–123
C1	109–123
C2	109–123
D1	109–123

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: acetone- d_6

Concentration: 10% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

Source

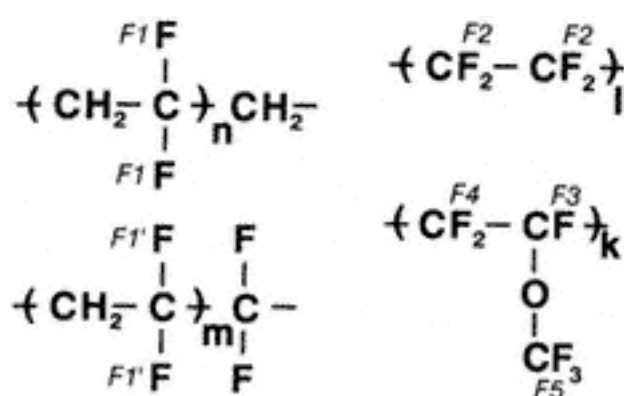
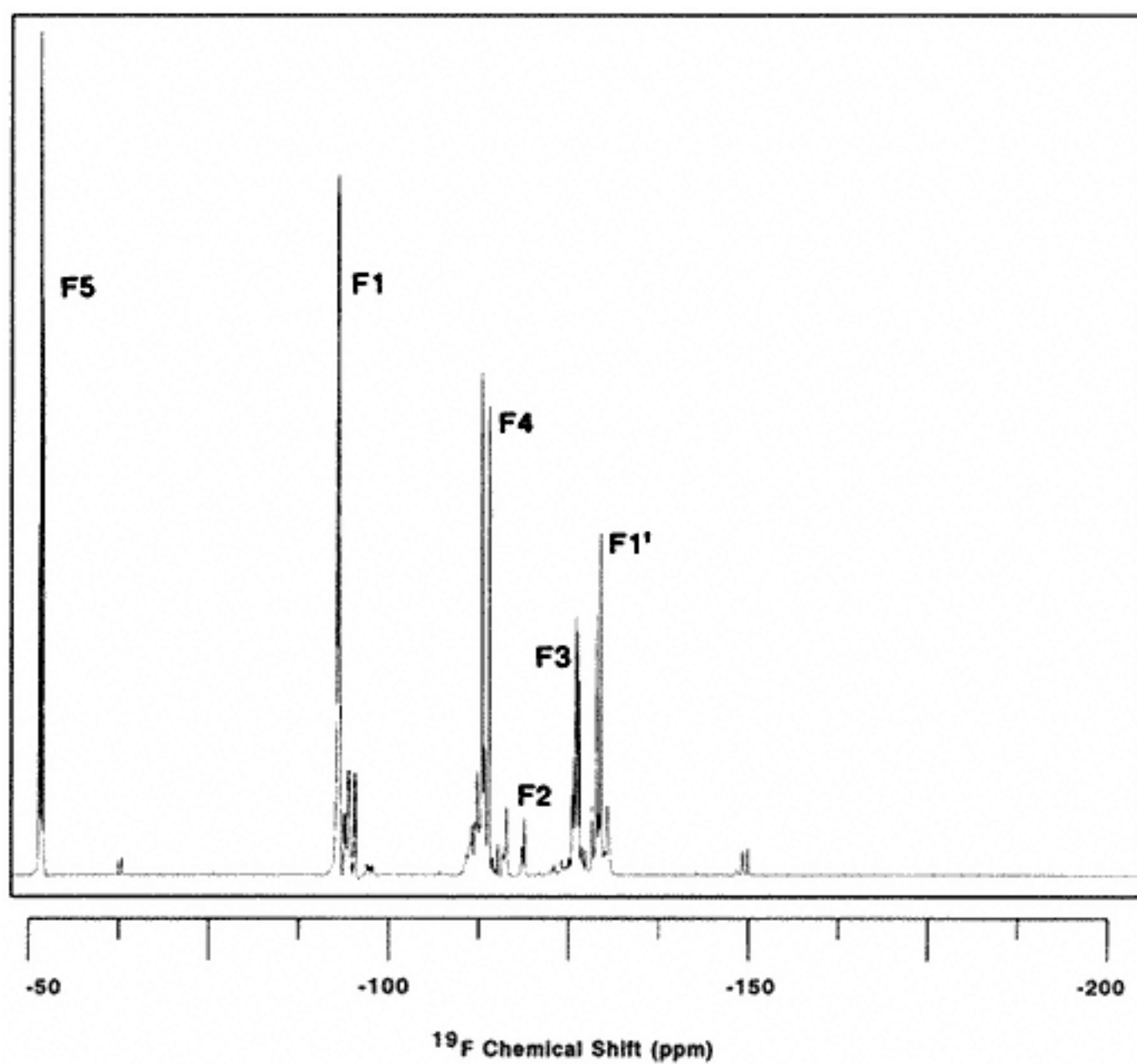
DuPont Elastomers, Wilmington, DE.

V-A-3F—

Poly(Vinylidene Fluoride-Co-Tetrafluoroethylene-Co-Perfluoro(Methyl Vinyl Ether)-Co-Bromotetrafluorobutene)

Comments

Also known as Viton GLT (DuPont) elastomer. The spectrum is complex because of the presence of regiosequences (i.e., head-to-head versus head-to-tail additions). The bromotetrafluorobutene component is too small to be observed in this spectrum. Fluoroelastomers, such as this material, maintain their properties over a wide temperature range. They are also chemically inert, and are used in demanding applications, such as heavy industrial equipment and aircraft. This spectrum was recorded by M. H. Frey, JEOL USA, Peabody, MA.



Code	Shift (ppm)
F1	-92.2
F1'	-126.6
F2	-116.2
F3	-122.9
F4	-110.3
F5	-52.6

Experimental ParametersNucleus: ^{19}F (376.1 MHz)

Temperature: 50°C

Solvent: acetone- d_6

Concentration: 10% w/w

Scans: 256

Spectral width: 75 kHz

Data points: 8192

Pulse width: 45°

Broadening: 10 Hz

Pulse delay: 1 s

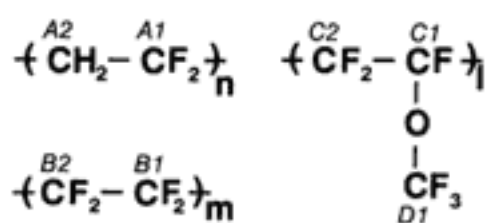
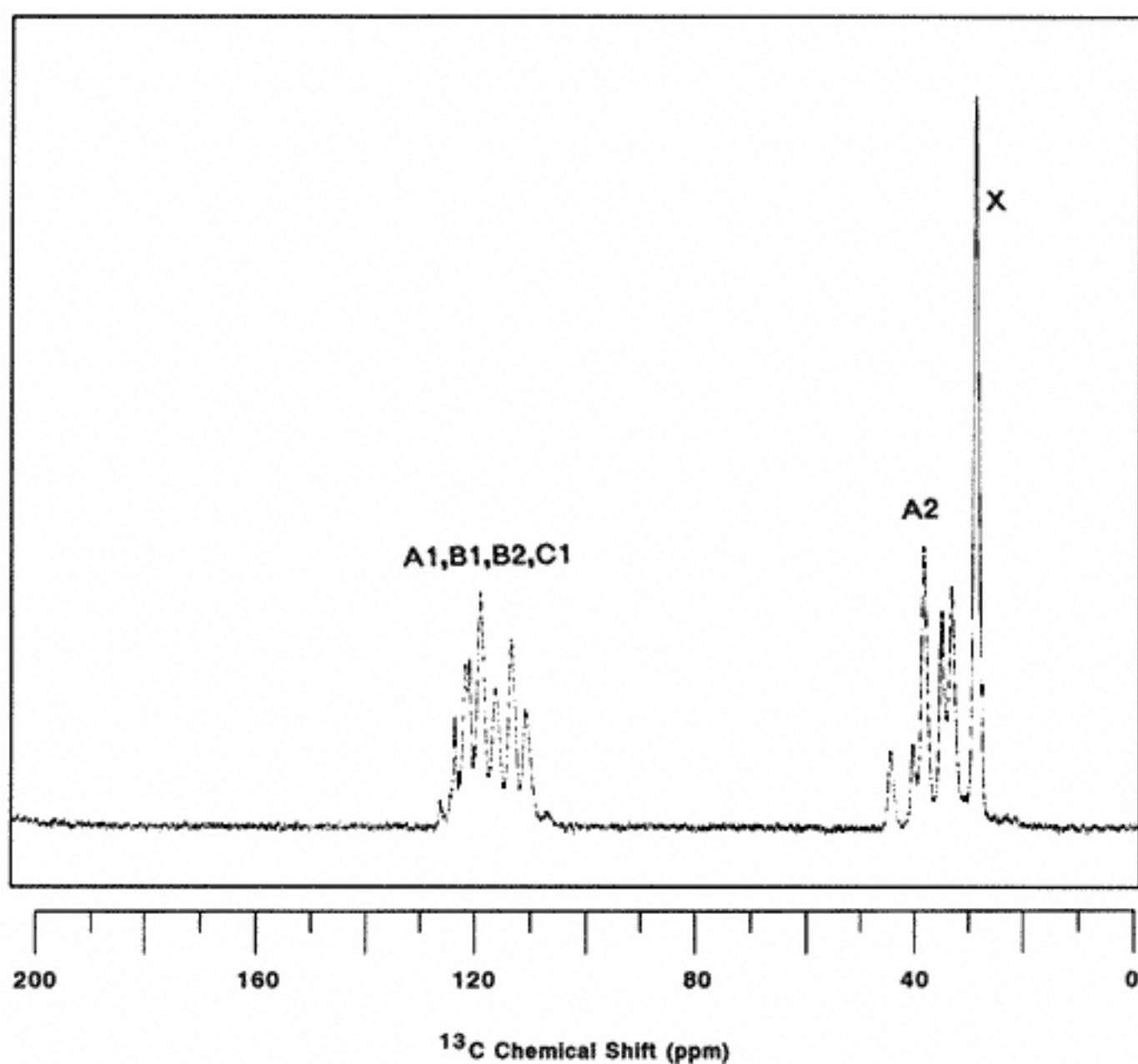
ReferenceM. Pianca, P. Bonardelli, M. Tato, G. Cirillo, and G. Moggi. *Polymer* 28:224, 1987.**Source**

DuPont Elastomers, Wilmington, DE.

V-A-4—

Poly(Vinylidene Fluoride-Co-Tetrafluoroethylene-Co-Perfluoro(Methyl Vinyl Ether)-Co-Bromotetrafluorobutene)*Comments*

Also known as Viton GFLT (DuPont) elastomer. The spectrum is complex because of overlapping multiplets caused by J-coupling between ^{13}C and ^{19}F , and because of the presence of regiosequences (i. e., head-to-head versus head-to-tail additions). The bromotetrafluorobutene component is too small to be observed in this spectrum. Solvent resonances are marked by **X**. Fluoroelastomers such as this material maintain their properties over a wide temperature range. They are also chemically inert, and are used in demanding applications, such as heavy industrial equipment and aircraft.



Code	Shift (ppm)
A1	108–122
A2	40.6
B1	108–122
C1	108–122
C2	108–122
D1	108–122

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: acetone- d_6	Concentration: 10% w/w
Scans: 1000	Spectral width: 25 kHz
Data points: 8192	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 2 s

Source

DuPont Elastomers, Wilmington, DE.

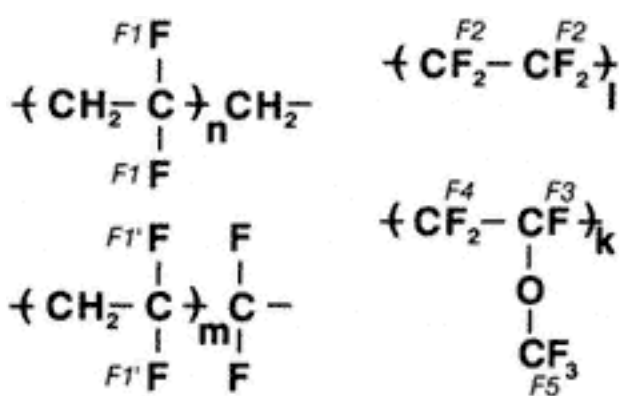
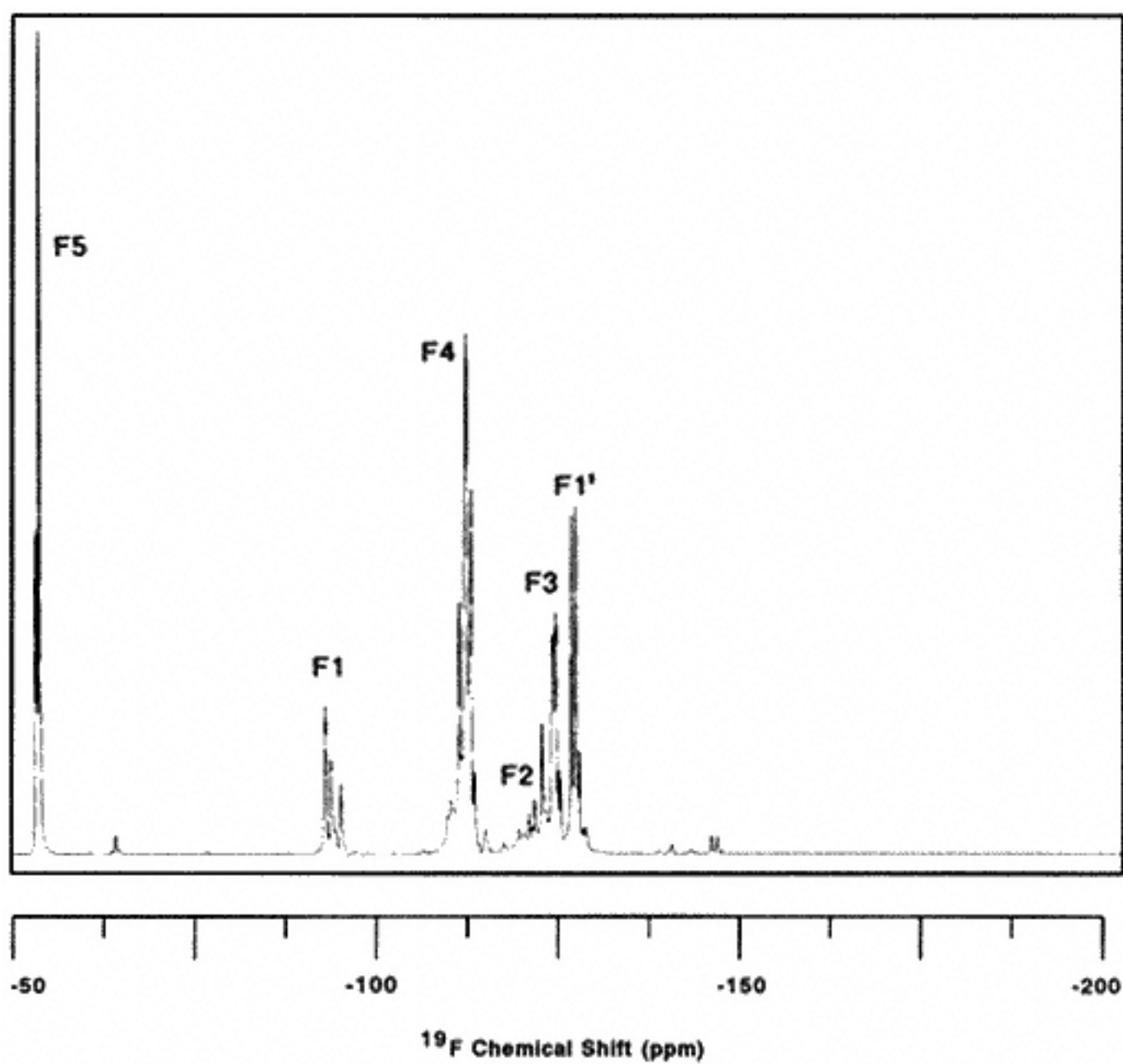
V-A-4F

V-A-4F—

Poly(Vinylidene Fluoride-Co-Tetrafluoroethylene-Co-Perfluoro(Methyl Vinyl Ether)-Co-Bromotetrafluorobutene)

Comments

Also known as Viton GFLT (DuPont) elastomer. The spectrum is complex because of the presence of regiosequences (i.e., head-to-head versus head-to-tail additions). The bromotetrafluorobutene component is too small to be observed in this spectrum. Fluoroelastomers, such as this material, maintain their properties over a wide temperature range. They are also chemically inert, and are used in demanding applications, such as heavy industrial equipment and aircraft. This spectrum was recorded by M. H. Frey, JEOL USA, Peabody, MA.



Code	Shift (ppm)
F1	~-93
F1'	-126.1
F2	-120.5
F3	-123.1
F4	-111.2
F5	-53.2

Experimental ParametersNucleus: ^{19}F (376.1 MHz)

Temperature: 50°C

Solvent: acetone- d_6

Concentration: 10% w/w

Scans: 256

Spectral width: 75 kHz

Data points: 8192

Pulse width: 45°

Broadening: 10 Hz

Pulse delay: 1 s

Source

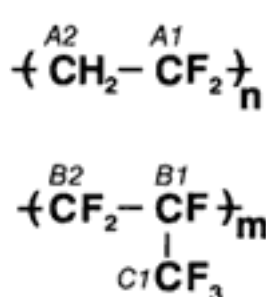
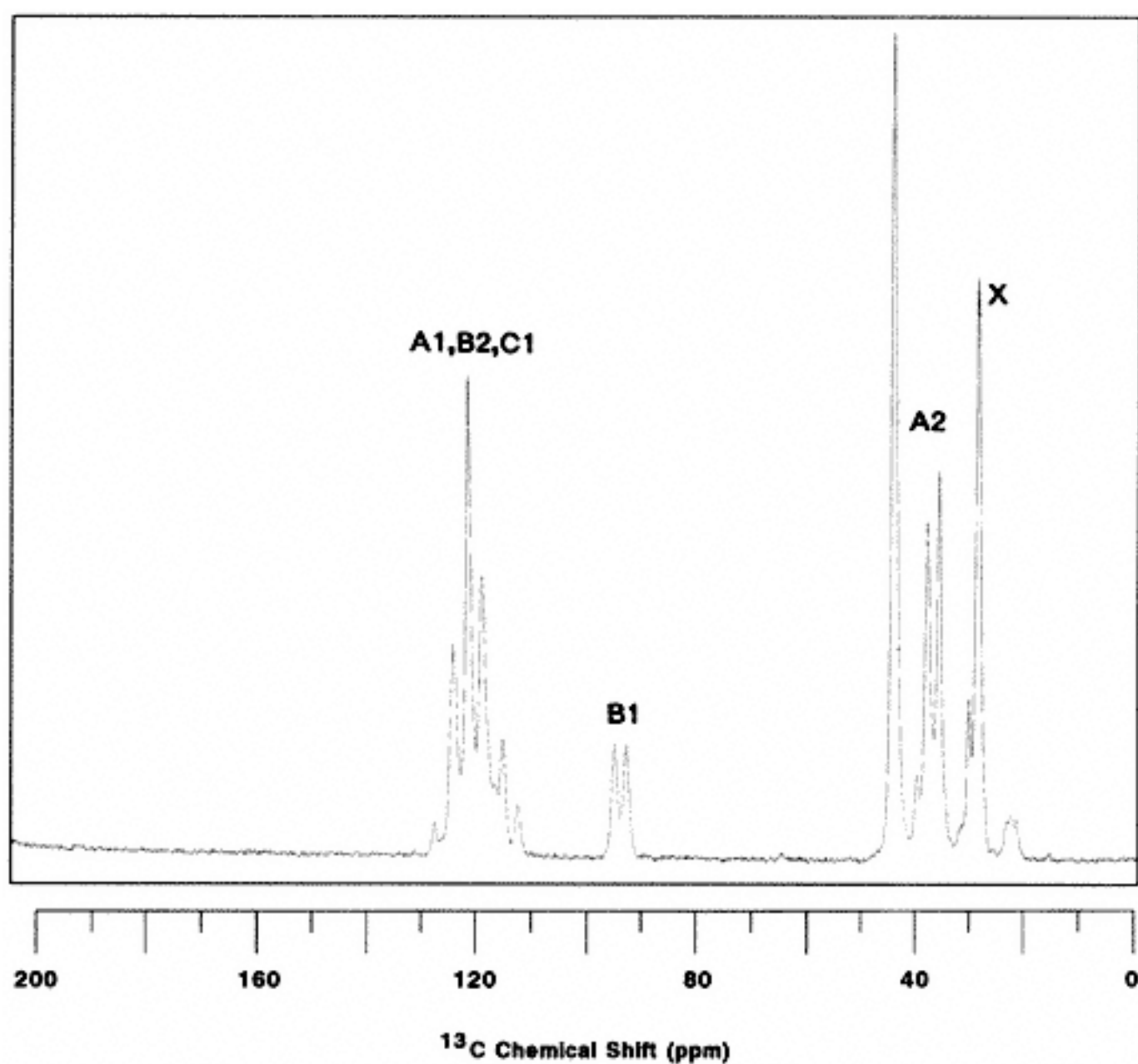
DuPont Elastomers, Wilmington, DE.

V-A-5—

Poly(Vinylidene Fluoride-Co-Hexafluoropropylene)

Comments

Also known as Viton A (DuPont) elastomer. The spectrum is complex because of overlapping multiplets caused by J-coupling between ^{13}C and ^{19}F , and because of the presence of regiosequences (i. e., head-to-head versus head-to-tail additions). Solvent resonances are marked by X. Fluoroelastomers such as this material maintain their properties over a wide temperature range. They are also chemically inert, and are used in demanding applications, such as heavy industrial equipment and aircraft.



Code	Shift (ppm)
A1	110–126
A2	35–44
B1	~92
B2	110–126
C1	110–126

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 100°C

Solvent: acetone- d_6

Concentration: 10% w/w

Scans: 1000

Spectral width: 75 kHz

Data points: 8192

Pulse width: 45°

Broadening: 2 Hz

Pulse delay: 1 s

Source

DuPont Elastomers, Wilmington, DE.

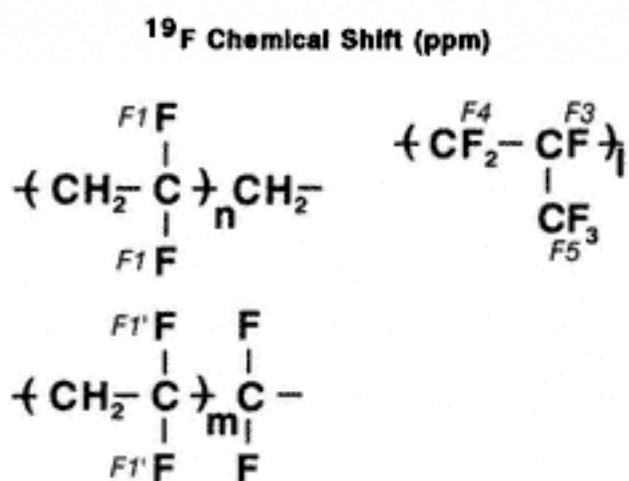
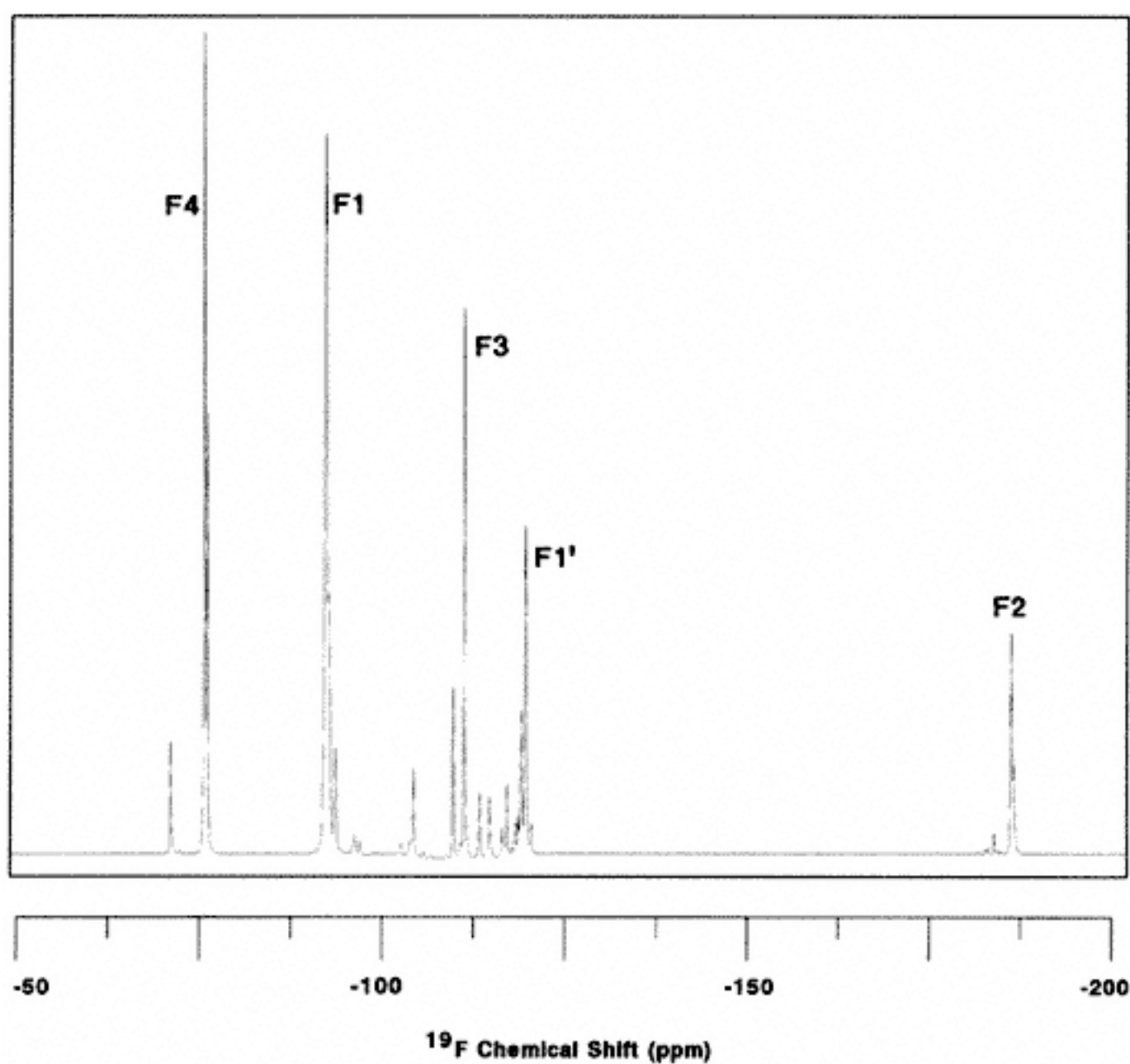
I-A-5F

V-A-5F—

Poly(Vinylidene Fluoride-Co-Hexafluoropropylene)

Comments

Also known as Viton A (DuPont) elastomer. The spectrum is complex because of the presence of regiosequences (i.e., head-to-head versus head-to-tail additions). Fluoroelastomers, such as this material, maintain their properties over a wide temperature range. They are also chemically inert, and are used in demanding applications, such as heavy industrial equipment and aircraft. This spectrum was recorded by M. H. Frey, JEOL USA, Peabody, MA.



Code	Shift (ppm)
F1	-92.2
F1'	-119.0
F2	-184.9
F3	-110.8
F4	-75.8

Experimental ParametersNucleus: ^{19}F (376.1 MHz)

Temperature: 50°C

Solvent: acetone- d_6

Concentration: 10% w/w

Scans: 256

Spectral width: 75 kHz

Data points: 8192

Pulse width: 45°

Broadening: 10 Hz

Pulse delay: 1 s

ReferenceG. Lustinger, B. Meurer, and G. Weill. *Polymer* 33:4920, 1992.**Source**

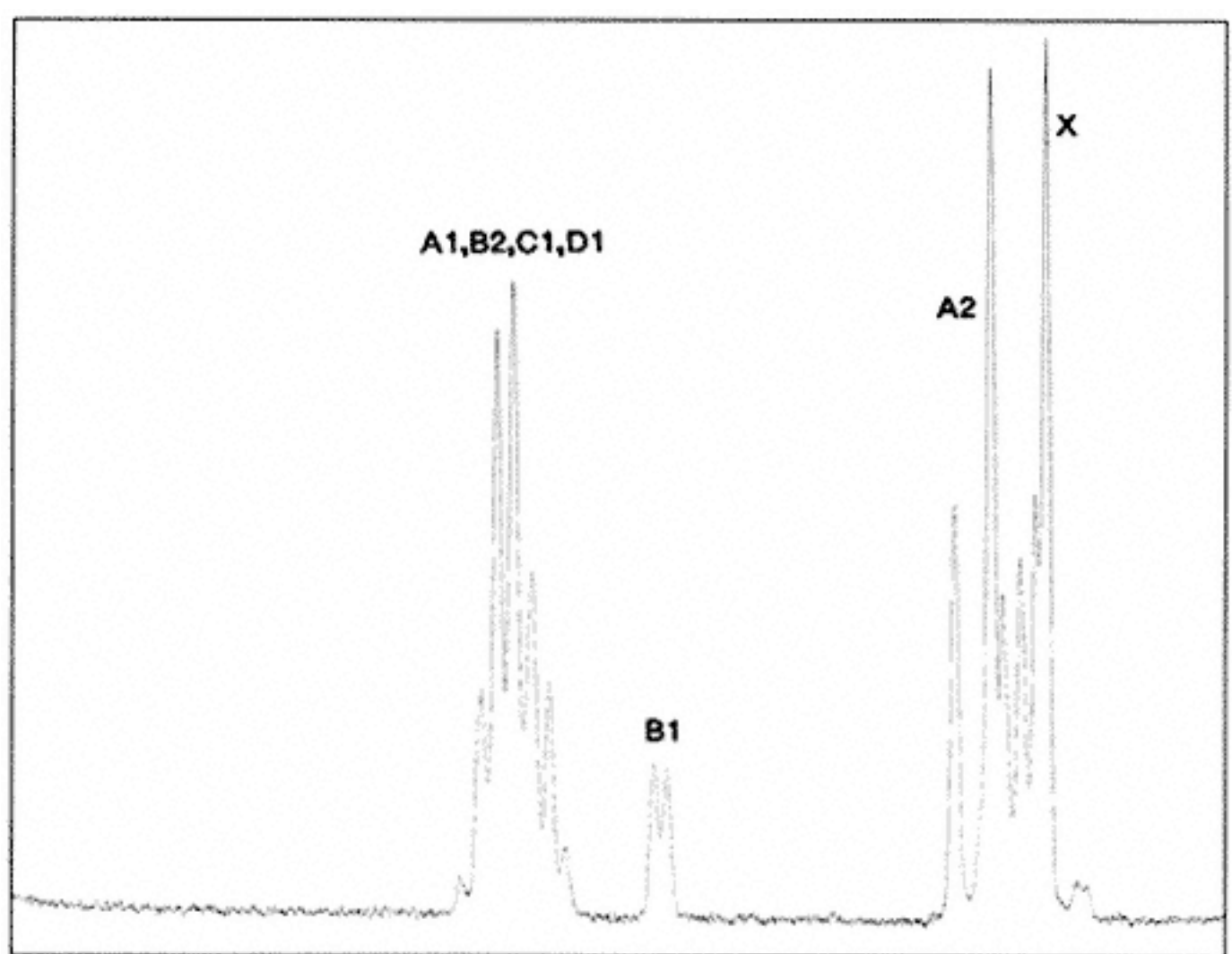
DuPont Elastomers, Wilmington, DE.

V-A-6—

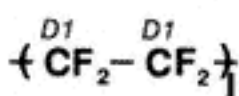
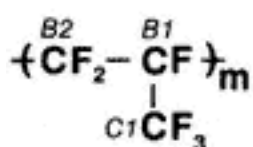
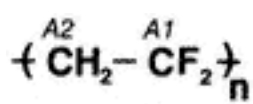
Poly(Vinylidene Fluoride-Co-Hexafluoropropylene-Co-Tetrafluoroethylene)

Comments

Also known as Viton B (DuPont) elastomer. The spectrum is complex because of overlapping multiplets caused by J-coupling between ^{13}C and ^{19}F , and because of the presence of regiosequences (i. e., head-to-head versus head-to-tail additions). Solvent resonances are marked by **X**. Fluoroelastomers, such as this material, maintain their properties over a wide temperature range. They are also chemically inert, and are used in demanding applications, such as heavy industrial equipment and aircraft.



^{13}C Chemical Shift (ppm)



Code	Shift (ppm)
A1	109–123
A2	36–45
B1	93
B2	109–123
C1	109–123
D1	109–123

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: acetone- d_6

Concentration: 10% w/w

Scans: 1000

Spectral width: 25 kHz

Data Points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

Source

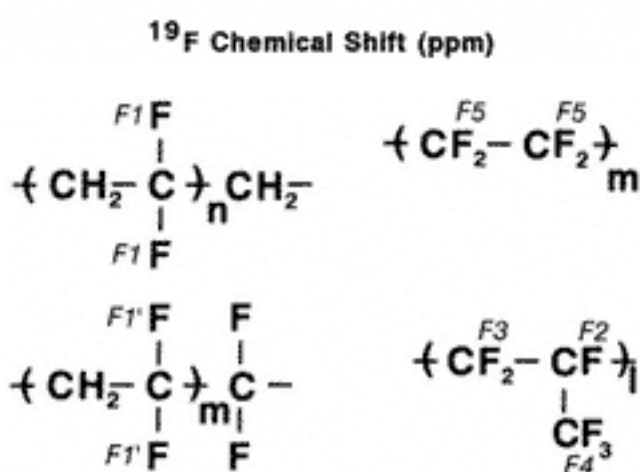
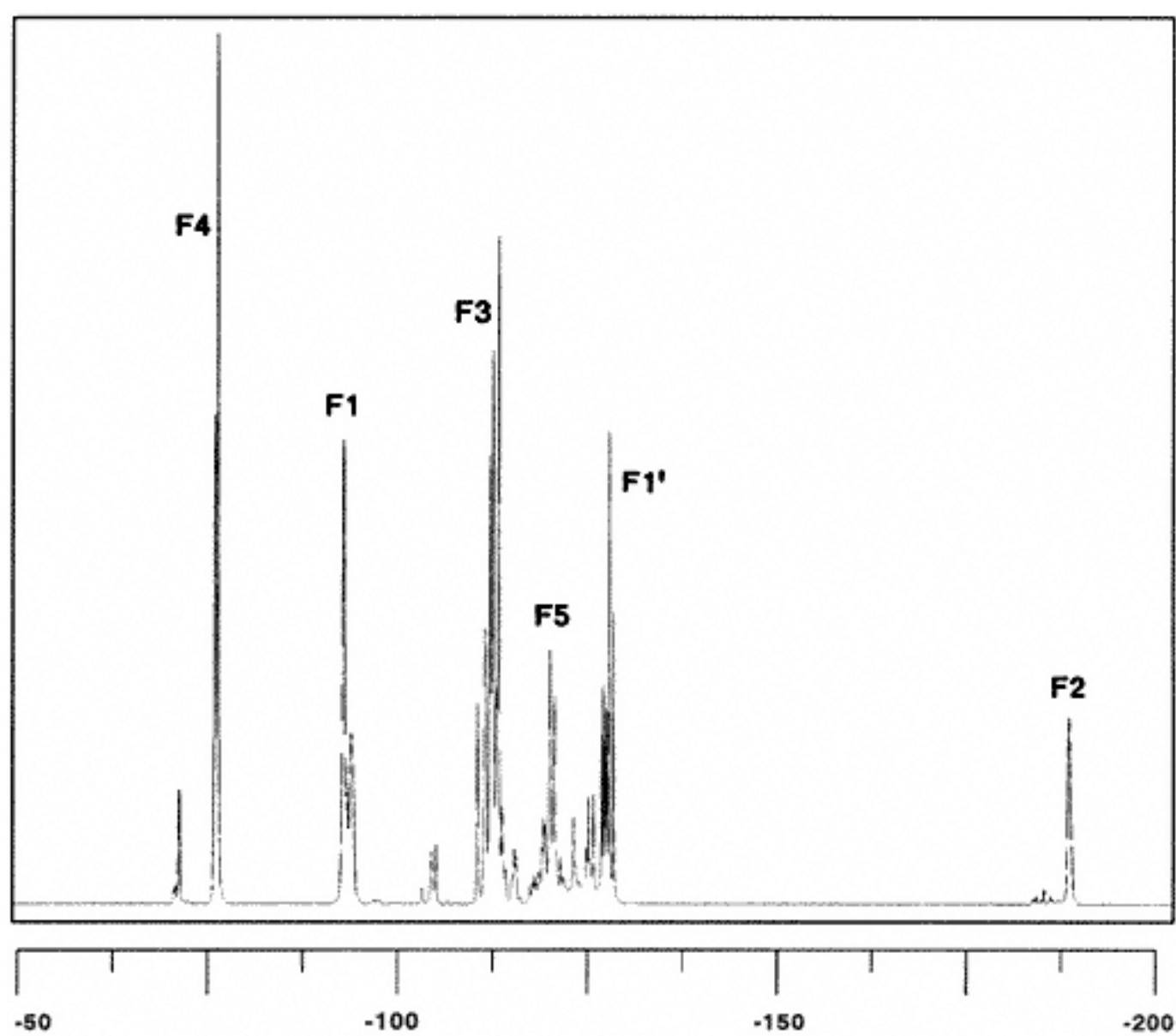
DuPont Elastomers, Wilmington, DE.

V-A-6F—

Poly(Vinylidene Fluoride-Co-Hexafluoropropylene-Co-Tetrafluoroethylene)

Comments

Also known as Viton B (DuPont) elastomer. The spectrum is complex because of overlapping multiplets caused by J-coupling between ^{13}C and ^{19}F , and because of the presence of regiosequences (i. e., head-to-head versus head-to-tail additions). Fluoroelastomers such as this material maintain their properties over a wide temperature range. They are also chemically inert and are used in demanding applications, such as heavy industrial equipment and aircraft. This spectrum was recorded by M. H. Frey, JEOL USA, Peabody, MA.



Code	Shift (ppm)
F1	-92.3
F1'	-125.7
F2	-184.7
F3	-111.7
F4	-75.9
F5	-118.0

Experimental ParametersNucleus: ^{19}F (376.1 MHz)

Temperature: 50°C

Solvent: acetone- d_6

Concentration: 10% w/w

Scans: 256

Spectral width: 75 kHz

Data points: 8192

Pulse width: 45°

Broadening: 10 Hz

Pulse delay: 1 s

Source

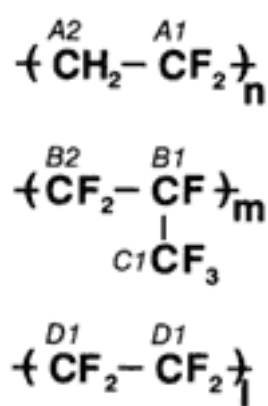
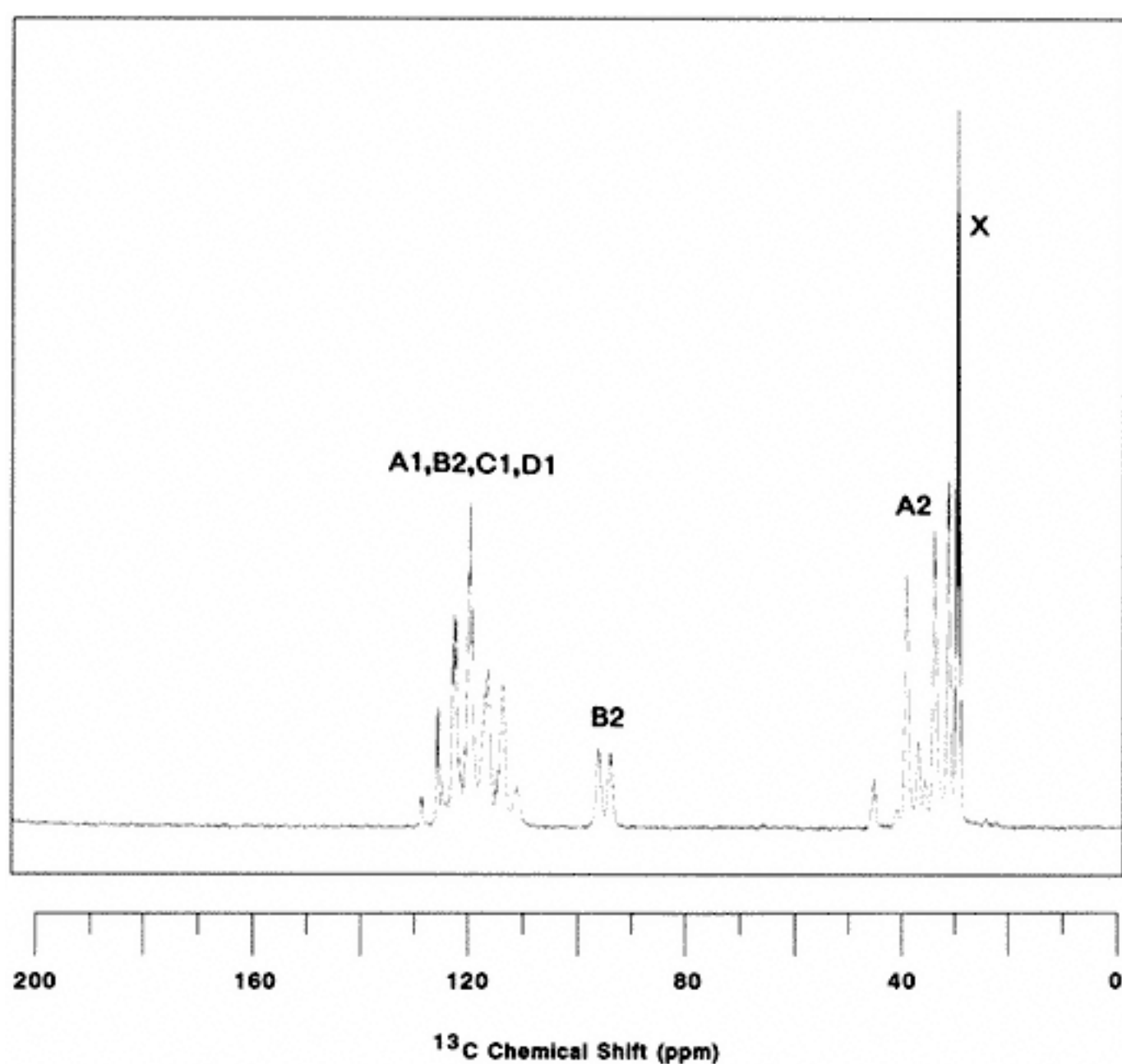
DuPont Elastomers, Wilmington, DE.

V-A-7—

Poly(Vinylidene Fluoride-Co-Hexafluoropropylene-Co-Tetrafluoroethylene-Co-Bromotetrafluorobutene)

Comments

Also known as Viton GF (DuPont) elastomer. The spectrum is complex because of overlapping multiplets caused by J-coupling between ^{13}C and ^{19}F , and because of the presence of regiosequences (i. e., head-to-head versus head-to-tail additions). The bromotetrafluorobutene component is too small to be observed in this spectrum. Solvent resonances are marked by **X**. Fluoroelastomers, such as this material, maintain their properties over a wide temperature range. They are also chemically inert and are used in demanding applications, such as heavy industrial equipment and aircraft.



Code	Shift (ppm)
A1	109–123
A2	32–44
B1	93
B2	109–123
C1	109–123
D1	109–123

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: acetone- d_6

Concentration: 10% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

Source

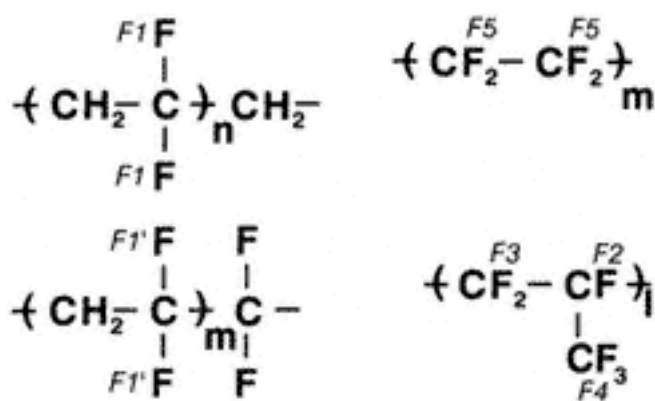
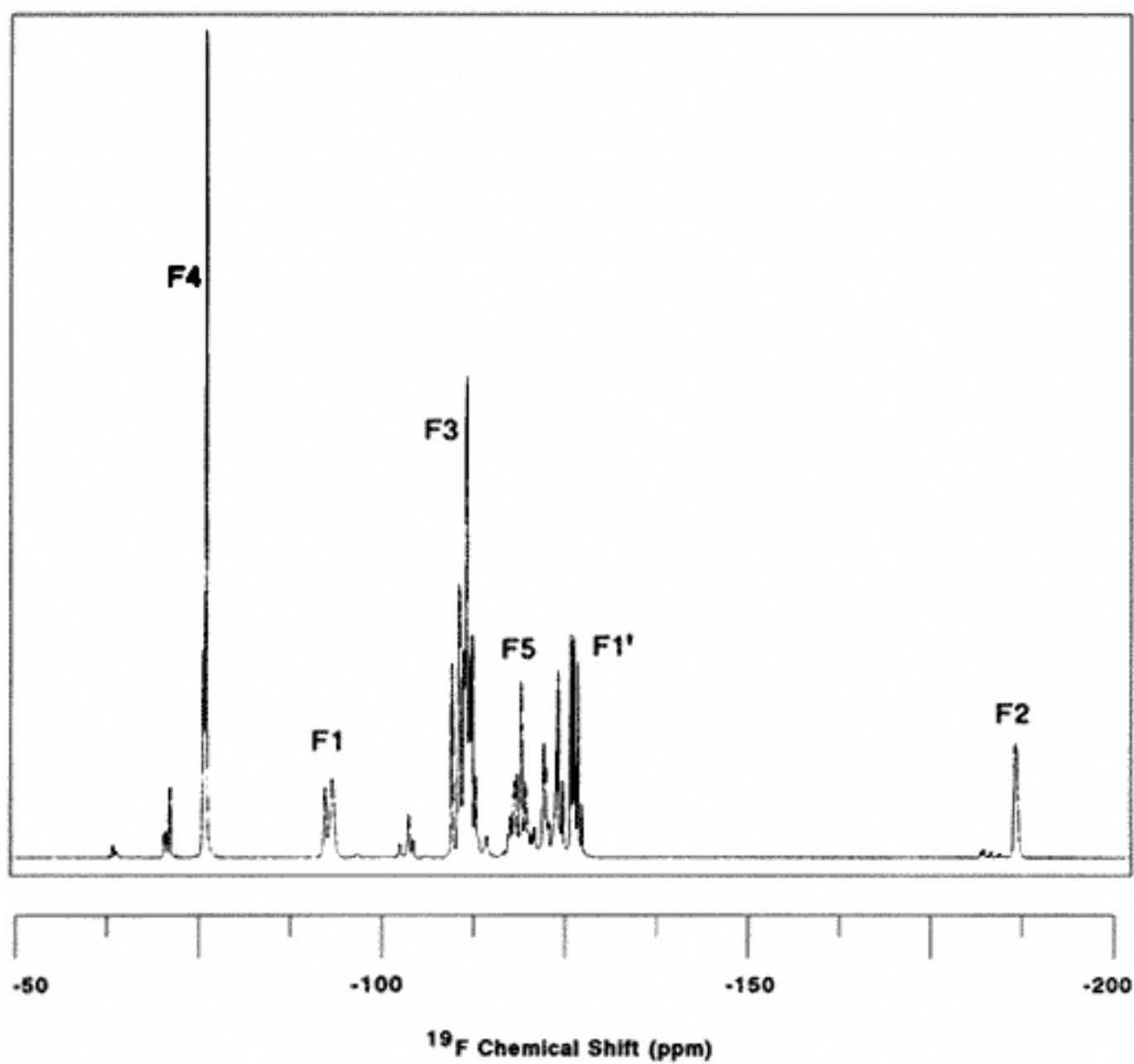
DuPont Elastomers, Wilmington, DE.

V-A-7F—

Poly(Vinylidene Fluoride-Co-Hexafluoropropylene-Co-Tetrafluoroethylene-Co-Bromotetrafluorobutene)

Comments

Also known as Viton GF (DuPont) elastomer. The spectrum is complex because of the presence of regiosequences (i.e., head-to-head versus head-to-tail additions). The bromotetrafluorobutene component is too small to be observed in this spectrum. Fluoroelastomers, such as this material, maintain their properties over a wide temperature range. They are also chemically inert and are used in demanding applications, such as heavy industrial equipment and aircraft. This spectrum was recorded by M. H. Frey, JEOL USA, Peabody, MA.



Code	Shift (ppm)
F1	-92.7
F1'	-126.8
F2	-184.9
F3	-109.2
F4	-76.3
F5	-118.1

Experimental ParametersNucleus: ^{19}F (376.1 MHz)

Temperature: 50°C

Solvent: acetone- d_6

Concentration: 10% w/w

Scans: 25

Spectral width: 75 kHz

Data points: 8192

Pulse width: 45°

Broadening: 10 Hz

Pulse delay: 1 s

Source

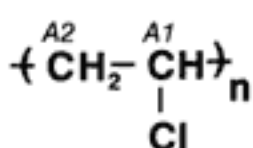
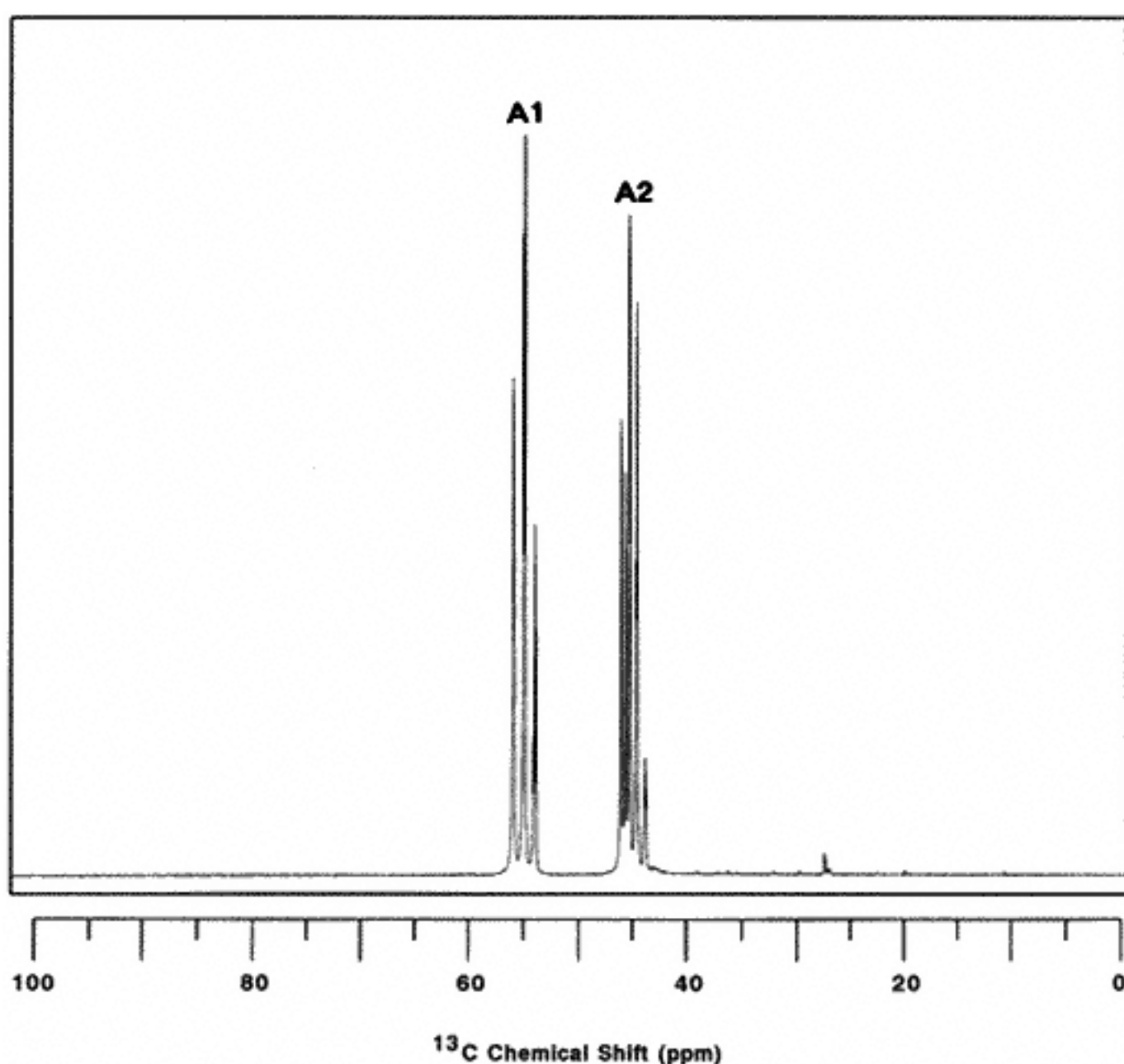
DuPont Elastomers, Wilmington, DE.

V-A-8—

Poly(Vinyl Chloride) (PVC)

Comments

Commonly called "vinyl." Tacticity effects are observed as splitting of both resonances. PVC products often contain a plasticizer (see Chapter X) at a level of several percent; this additive will contribute its own peaks to the spectrum. PVC is often found in blends with other materials, such as chlorinated polyethylene {II-A-5} or polybutadiene {VI-A-1, VI-A-2.}. *Rigid* (unplasticized) PVC is used in building and construction products, such as pipes, flooring, and siding. *Flexible* (plasticized) PVC is commonly found in wire and cable insulation, packaging, pool liners, and vinyl-coated objects. *Plastisol* dispersions are employed to produce artificial leather and wall coverings.



Code	Shift (ppm)
A1	54.9
A2	45.7

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: C_6D_6

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

References

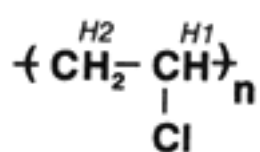
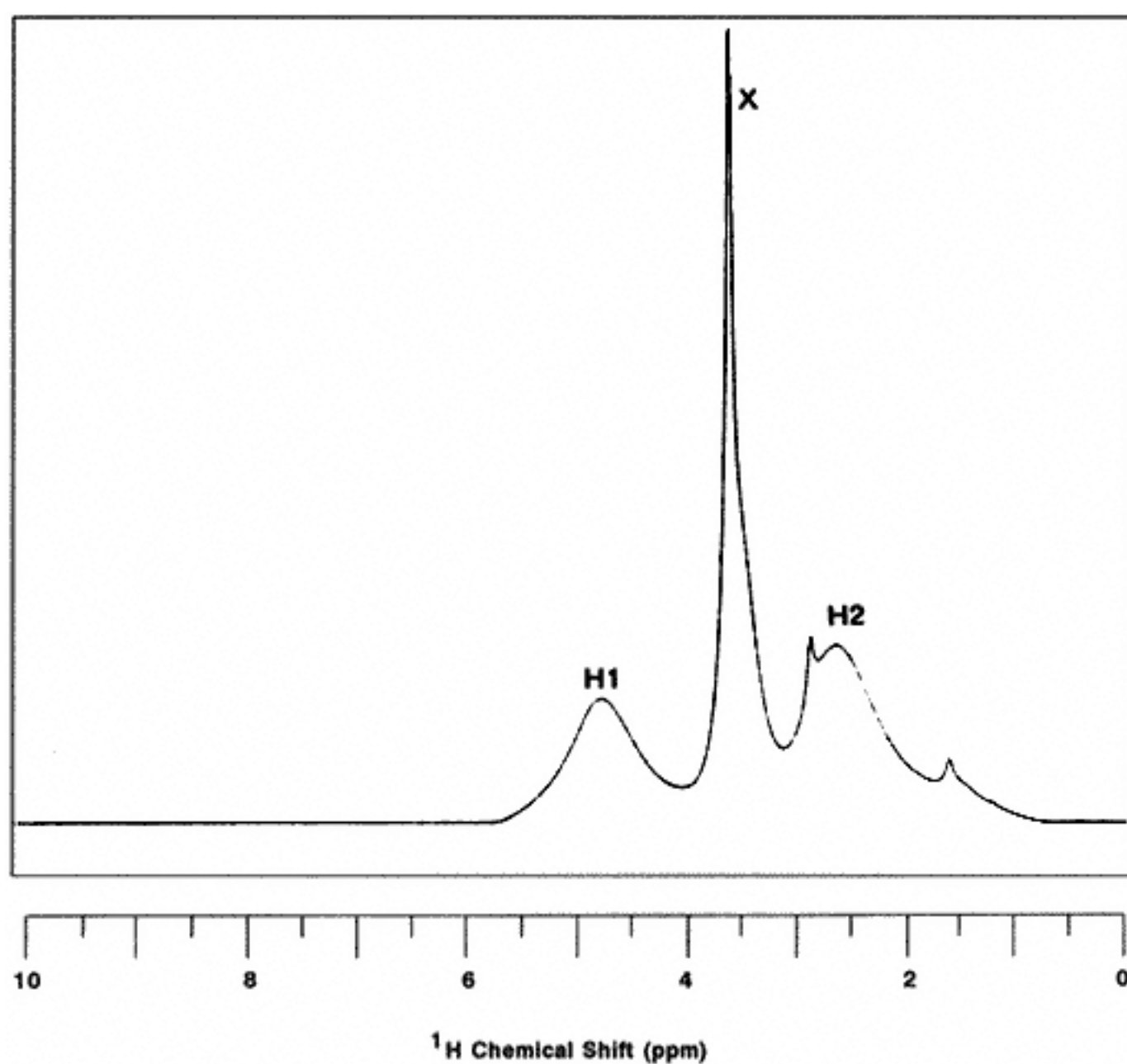
J. Milken, G. Martinez, M. L. Jimeno. *Eur. Polym. J.* 27:483, 1991; G. Martinez, C. Mijangas, J. L. Milken, and A. Alemany. *Makromol. Chem.* 187:2649, 1986; M. W. Crowther, N. M. Szeverenyi, and G. C. Levy. *Macromolecules* 19:1333, 1986; P. A. Mirau and F. A. Bovey. *Macromolecules* 19:210, 1986.

V-A-8H—

Poly(Vinyl Chloride) (PVC)

Comments

Commonly called "vinyl." Tacticity effects are obscured by broadening caused by sample viscosity. PVC products often contain a plasticizer (see Chapter X) at a level of several percent; this additive will contribute its own peaks to the spectrum. PVC is often found in blends with other materials, such as chlorinated polyethylene {II-A-5} or polybutadiene {VI-A-1H, VI-A-2H}. *Rigid* (unplasticized) PVC is used in building and construction products, such as pipes, flooring, and siding. *Flexible* (plasticized) PVC is commonly found in wire and cable insulation, packaging, pool liners, and vinyl-coated objects. *Plastisol* dispersions are employed to produce artificial leather and wall coverings.



Code	Shift (ppm)
H1	4.7
H2	2.6

*Experimental Parameters*Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: DMSO- d_6

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 30°

Broadening: 5 Hz

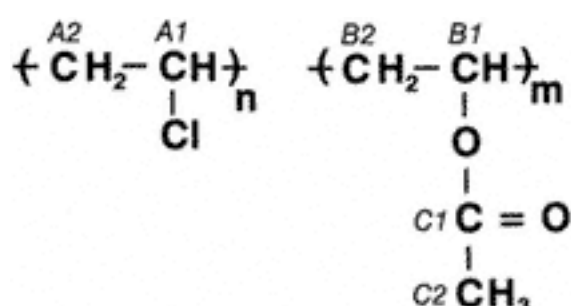
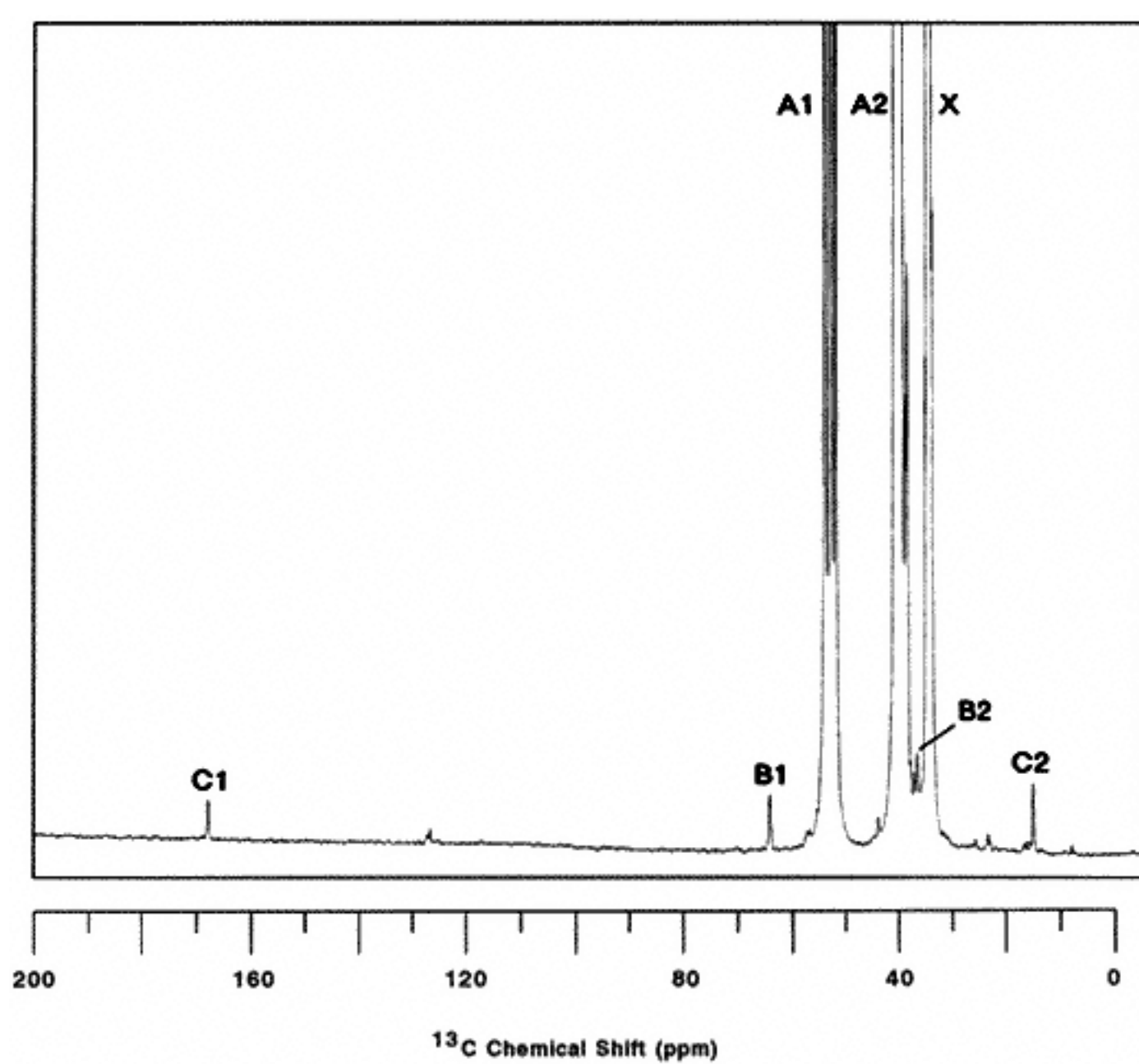
Pulse delay: 2 s

V-A-9—

Poly(Vinyl Chloride-Co-Vinyl Acetate) [2% VA]

Comments

Tacticity splitting is observed for the vinyl chloride carbons (A1 and A2); solvent resonances are marked by X. Incorporation of a small amount of vinyl acetate improves the toughness of PVC {V-A-8}, making it more suitable for applications such as floor tile.



Code	Shift (ppm)
A1	56.6
A2	44.5
B1	68.0
B2	40.3
C1	168.9
C2	20.0

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: DMSO- d_6

Concentration: 10% w/w

Scans: 23,000

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

References

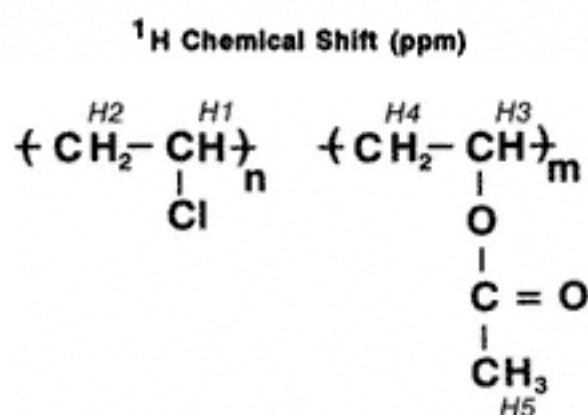
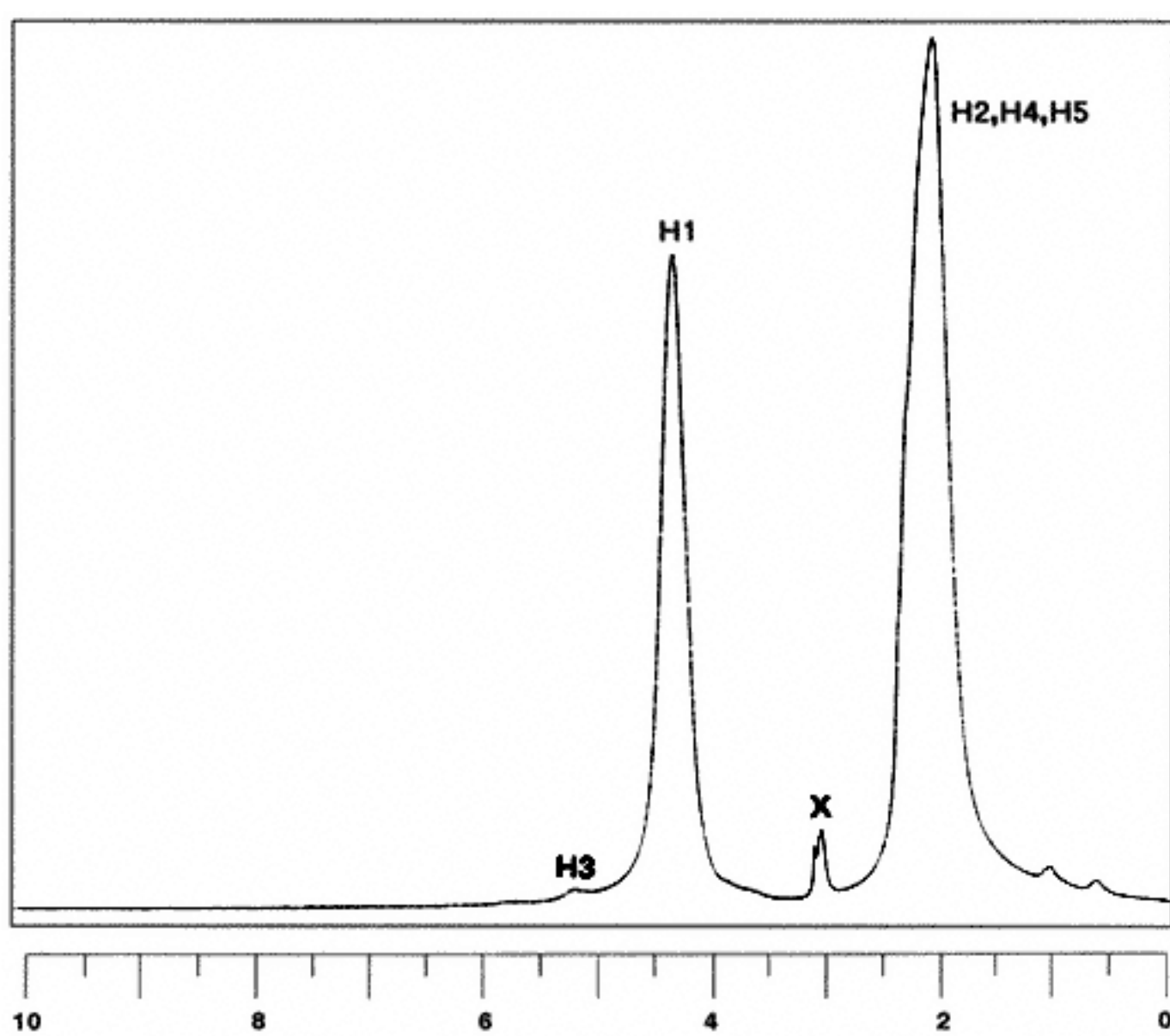
R.J. Schadt, R. D. Gilbert, and R. E. Fornes. *J. Applied Polym. Sci.* 43:484, 1991; K. Schlothauer and S. Horing. *Plaste Kautsch.* 31:183, 1984.

V-A-9H—

Poly(Vinyl Chloride-Co-Vinyl Acetate) [5% VA]

Comments

Tacticity effects are obscured by broadening caused by sample viscosity. Incorporation of a small amount of vinyl acetate improves the toughness of PVC {V-A-8H}, making it more suitable for applications such as floor tile.



Code	Shift (ppm)
H1	4.4
H2	2.2
H3	5.3
H4	2.2
H5	2.2

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: DMSO- d_6

Concentration: 10% w/w

Scans: 12

Spectral width: 8 kHz

Data points: 8192

Pulse width: 30°

Broadening: 5 Hz

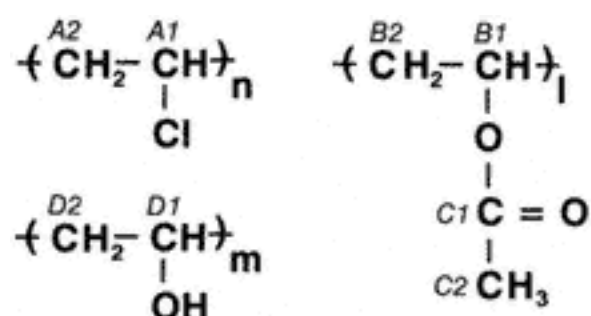
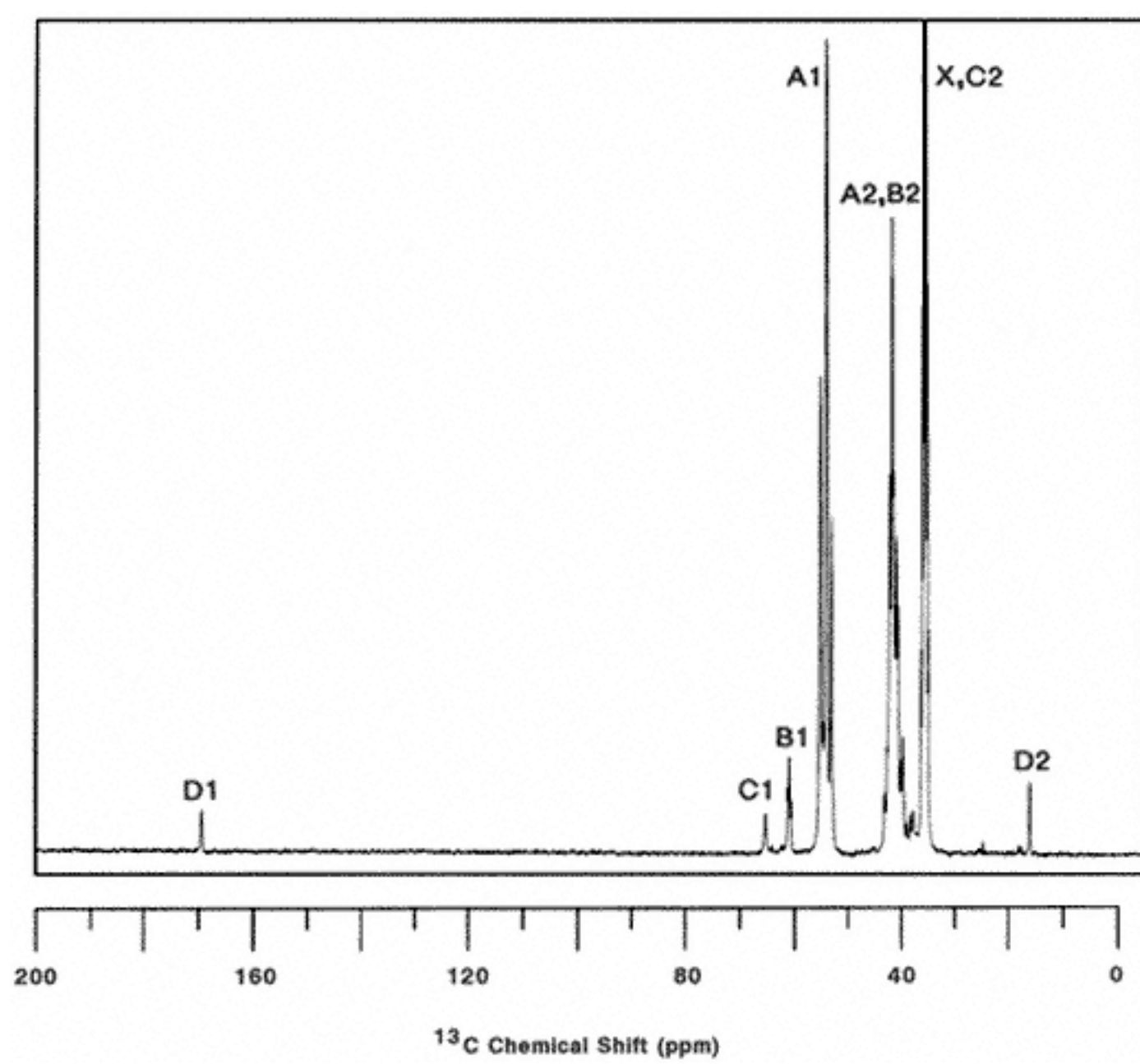
Pulse delay: 2 s

V-A-10—

Poly(Vinyl Chloride-Co-Vinyl Acetate-Co-Vinyl Alcohol) [6% VOH; 3% VA]

Comments

Tacticity effects are observed for the vinyl chloride carbons (A1 and A2), and for the vinyl alcohol methine (B1). Solvent resonances are marked by X. This material is produced by partial hydrolysis of a vinyl chloride-vinyl acetate copolymer {V-A-9}.



Code	Shift (ppm)
A1	58.2
A2	45.4
B1	64.5
B2	45.4
C1	69.5
C2	41.1
D1	170.5
D2	21.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: DMSO- d_6

Concentration: 10% w/w

Scans: 800

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

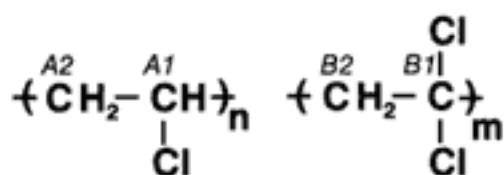
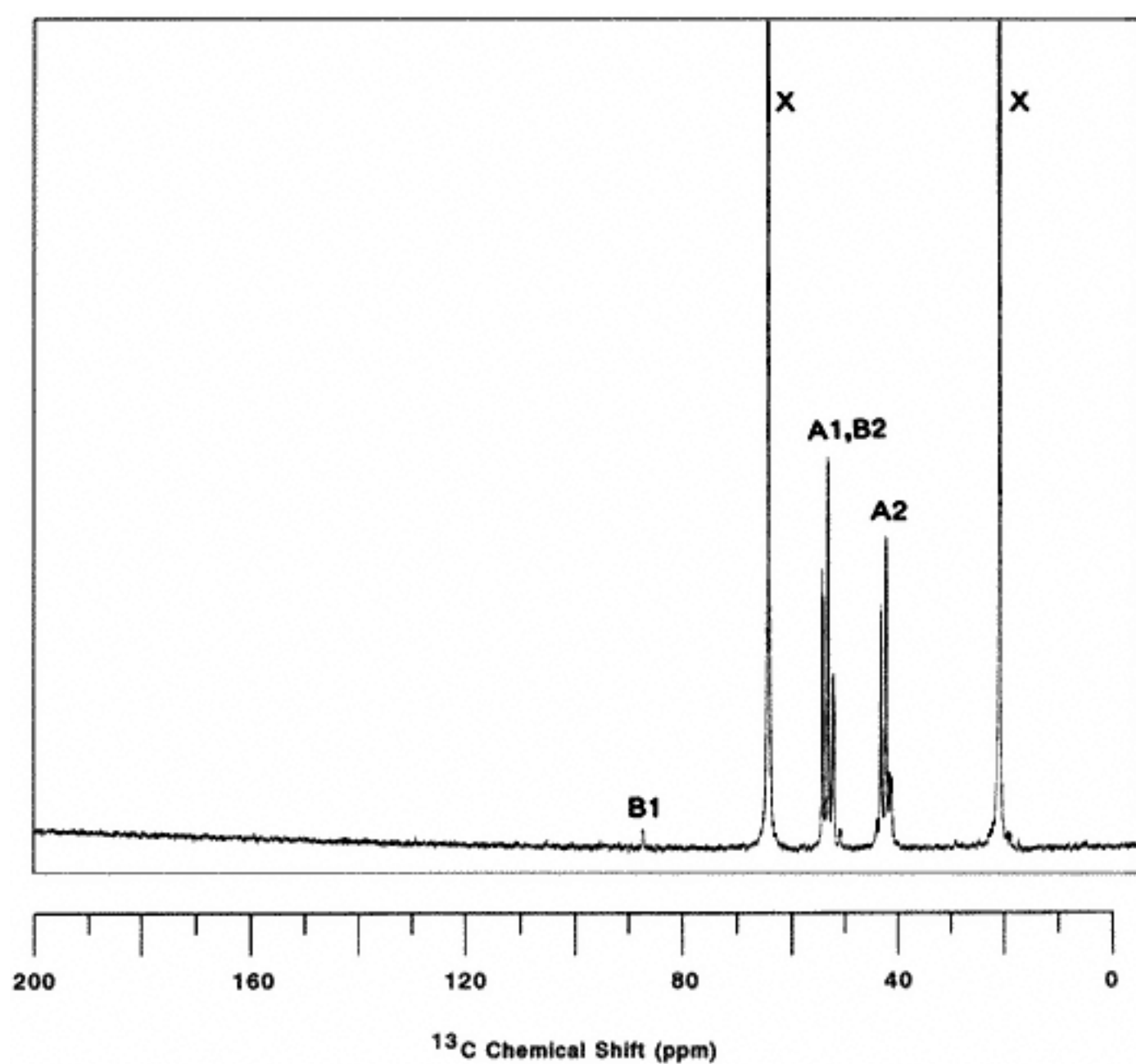
Broadening: 2 Hz

Pulse delay: 2 s

**V-A-11—
Poly(Vinyl Chloride-Co-Vinylidene Chloride) [5% VdC]**

Comments

Tacticity effects are observed for the vinyl chloride carbons (**A1** and **A2**). Solvent resonances are marked by **X**. Incorporation of vinylidene chloride increases the thermal stability and solubility of PVC. This material is used in coatings.



Code	Shift (ppm)
A1	56.3
A2	45.7
B1	90.3
B2	45.1

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: THF- d_8	Concentration: 10% w/w
Scans: 200	Spectral width: 25 kHz
Data points: 8192	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 2 s

References

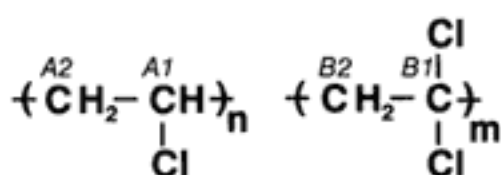
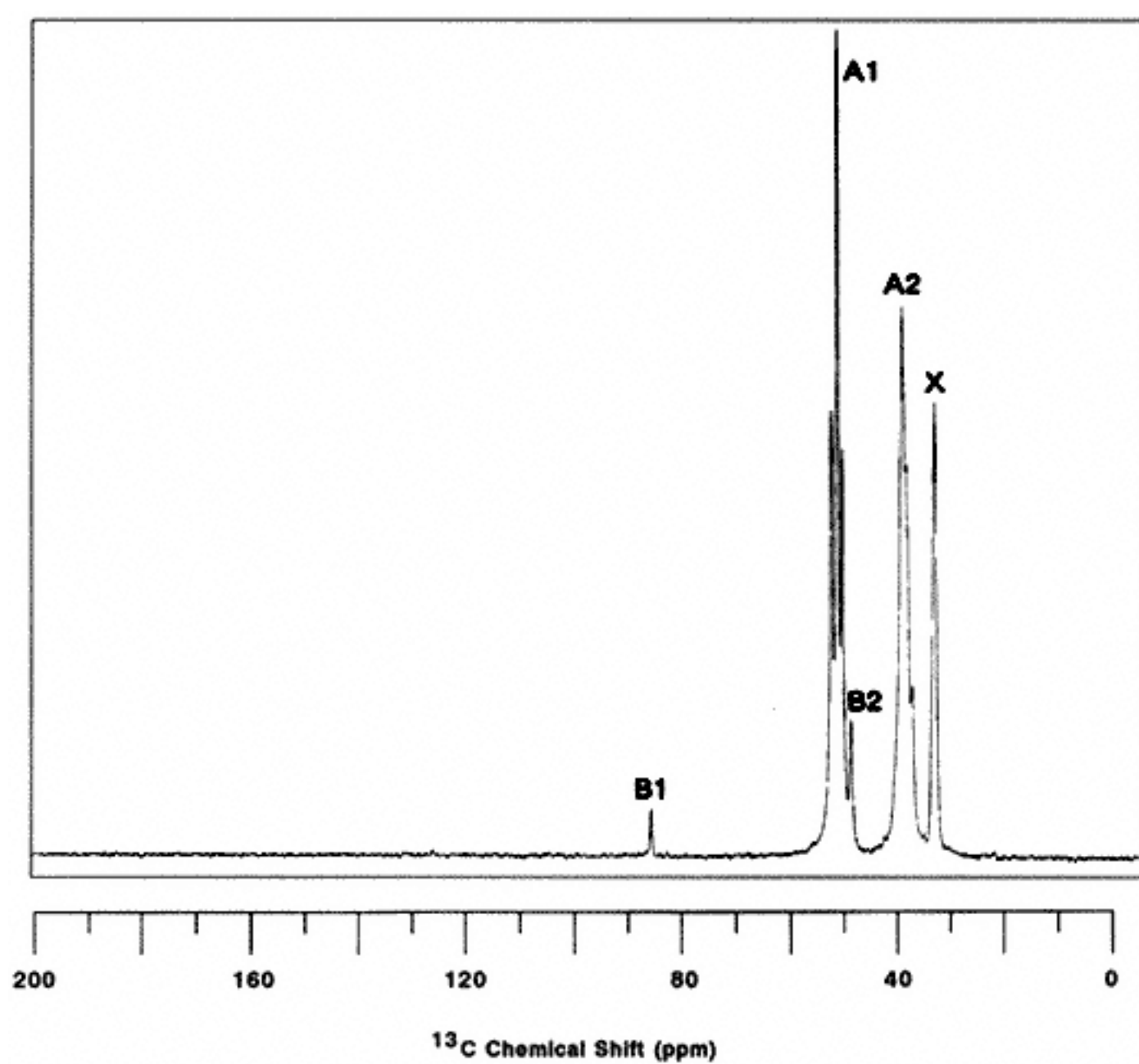
K. Schlothauer, F. Keller, H. Schneider, and B. Wendelt. *Polym. Bull.* 24:473, 1985; R. A. Komoroski and J. P. Shockor. *Macromolecules* 16:1539, 1983.

V-A-12—

Poly(Vinyl Chloride-Co-Vinylidene Chloride) [20% VdC]

Comments

Tacticity effects are observed for the vinyl chloride carbons (A1 and A2). Solvent resonances are marked by X. Incorporation of vinylidene chloride increases the thermal stability and solubility of PVC. This material is used in coatings.



Code	Shift (ppm)
A1	56.3
A2	45.7
B1	90.3
B2	45.1

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: DMSO- d_6

Concentration: 10% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

References

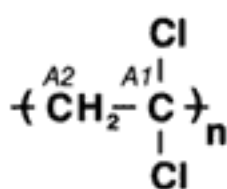
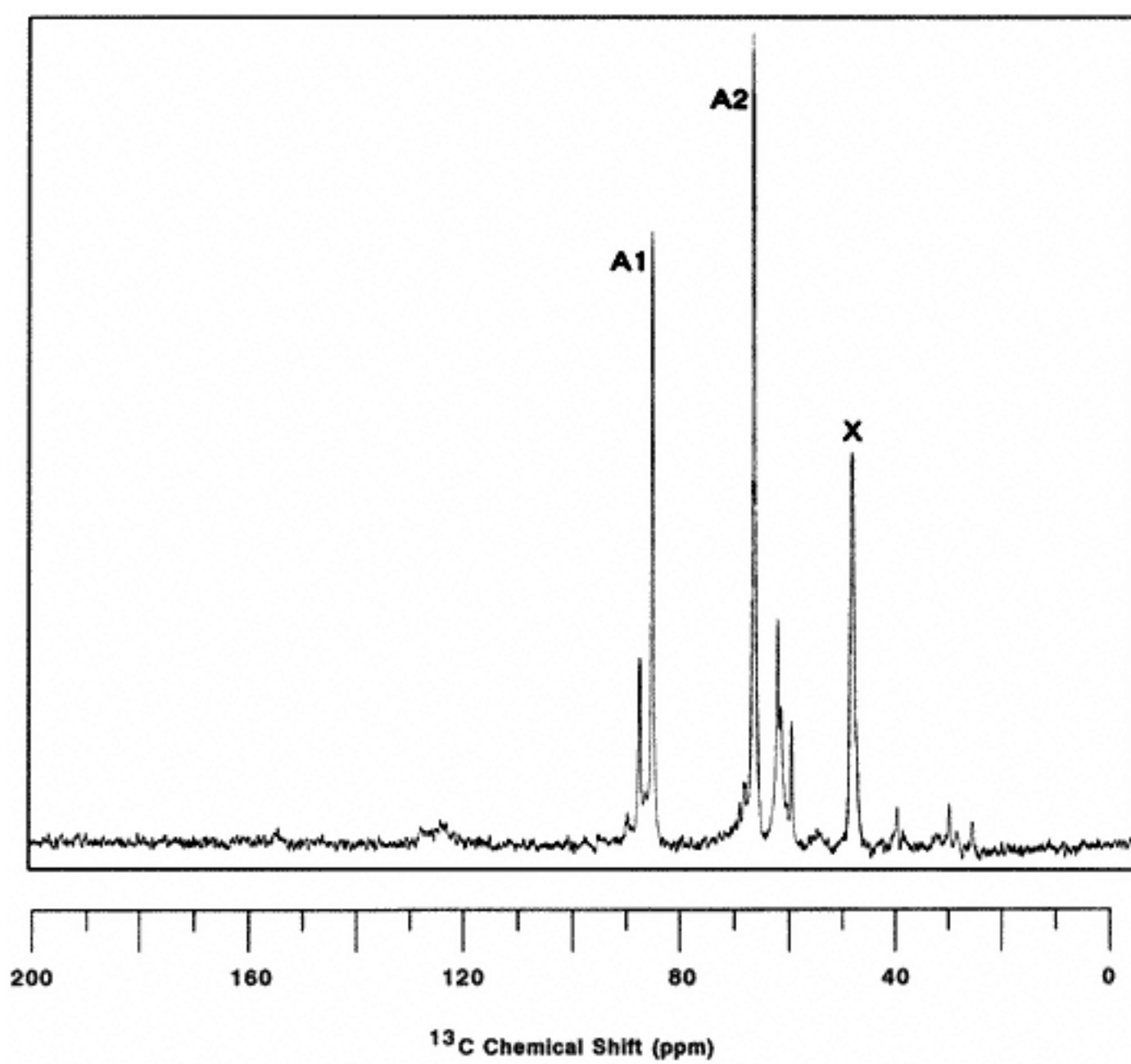
K. Schlothauer, F. Keller, H. Schneider, and B. Wendelt. *Polym. Bull.* 24:473, 1985; R. A. Komoroski and J. P. Shockor. *Macromolecules* 16:1539, 1983.

V-A-13—

Poly(Vinylidene Chloride) (PVdC)

Comments

Also known as Saran (Dow). Solvent resonances are marked by **X**. Commercial grades are often copolymers with vinyl chloride {V-A-11, V-A-12}, acrylates, or acrylonitrile {V-A-14} because these decrease the melting temperature of the polymer, thereby making processing easier. PVdC-containing materials are relatively impermeable to gases and liquids, making them suitable for applications such as food wrap, barrier layers in food, pharmaceutical, and cosmetic packaging, and in coatings for paper and fabric.



Code	Shift (ppm)
A1	84.3
A2	61.6

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 100°C

Solvent: DMSO- d_6

Concentration: 5% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

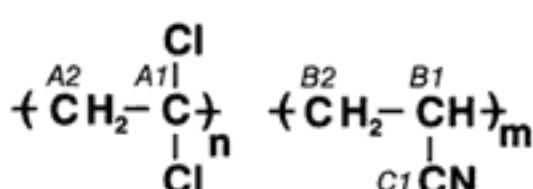
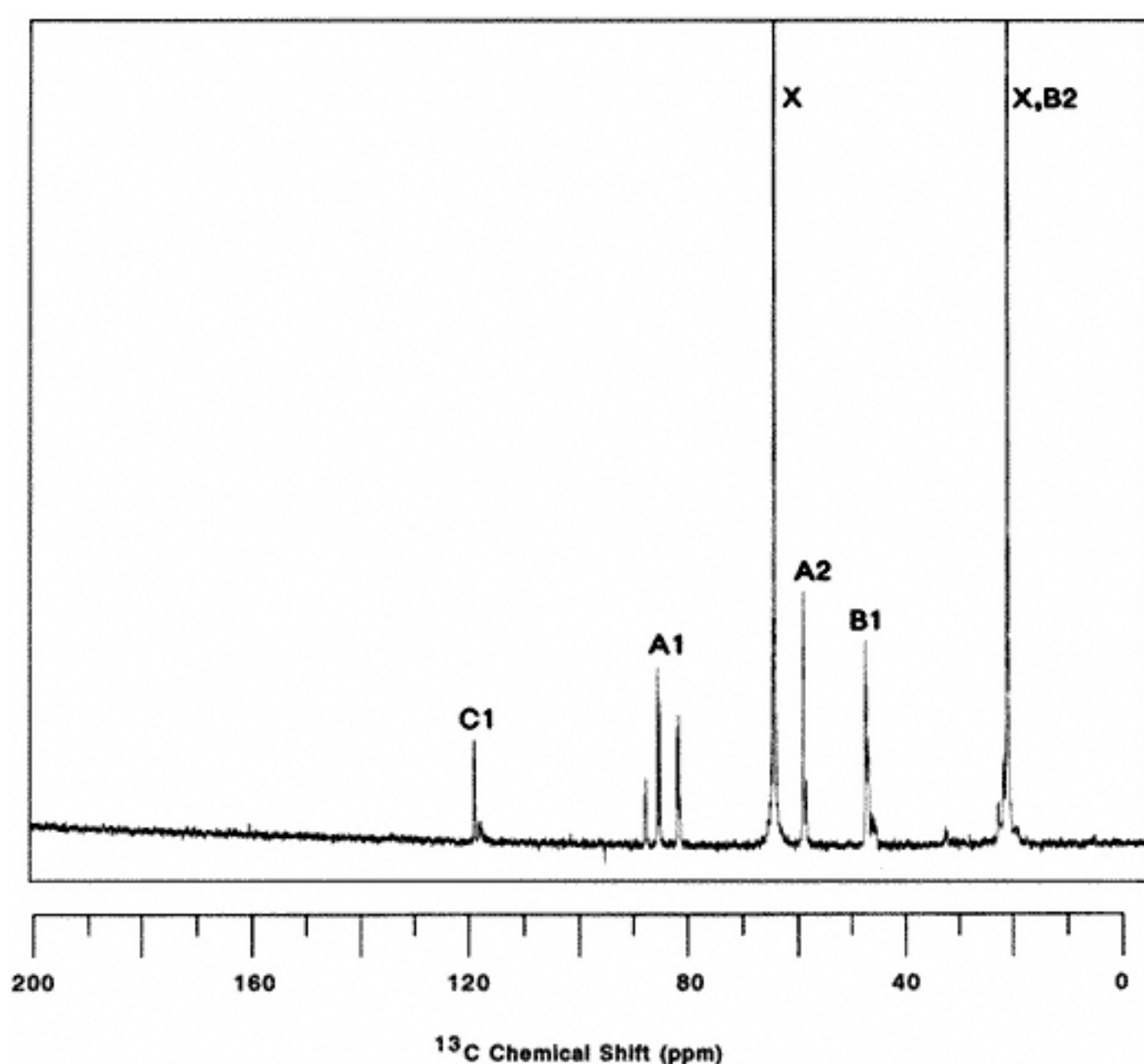
Broadening: 2 Hz

Pulse delay: 2 s

**V-A-14—
Poly(Vinylidene Chloride-Co-Acrylonitrile)**

Comments

Also known as Saran (Dow). Solvent resonances are marked by **X**. Commercial grades may also be poly (vinylidene chloride) homopolymer {V-A-13} or copolymers of vinylidene chloride with vinyl chloride {V-A-11, V-A-12} or acrylates. Copolymers are often preferred because they decrease the melting temperature of the polymer, thereby making processing easier. PVdC-containing materials are relatively impermeable to gases and liquids, making them suitable for applications such as food wrap, barrier layers in food, pharmaceutical, and cosmetic packaging, and in coatings for paper and fabric.



Code	Shift (ppm)
A1	84–90
A2	61.8
B1	51.0
B2	28.1
C1	120.7

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: THF- d_8	Concentration: 5% w/w
Scans: 800	Spectral width: 25 kHz
Data points: 8192	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 2 s

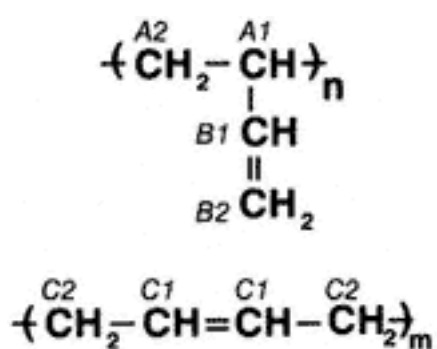
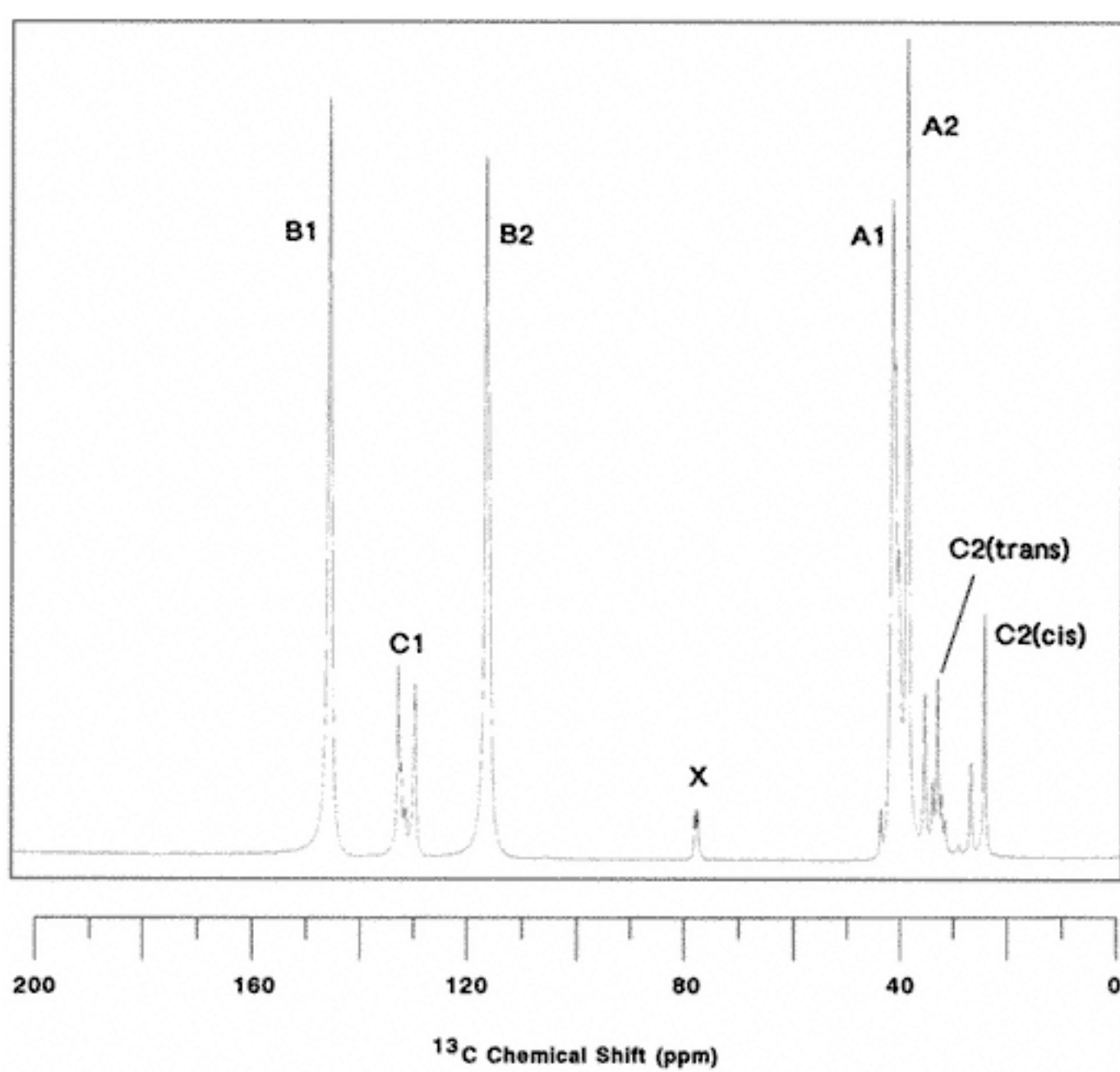
Reference

H. Yamazaki, K. Okajima, and K. Kamide. *Polym. J.* 20:1143, 1988.

V-B-1—
1,2-Polybutadiene (1,2-PBd)

Comments

Some tacticity effects are evident for peak **A1**. The polymer also contains significant amounts of both *cis*-1,4-{VI-A-1, VI-A-2} and *trans*-1,4-{VI-A-2} butadiene units. Solvent resonances are marked by **X**. This material is used in electrical transformers and motors.



Code	Shift (ppm)
A1	41.9
A2	39.6
B1	143.4
B2	115.1
C1 (<i>cis</i>)	128–131
C1 (<i>trans</i>)	128–131
C2 (<i>cis</i>)	28.1
C2 (<i>trans</i>)	33.1

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

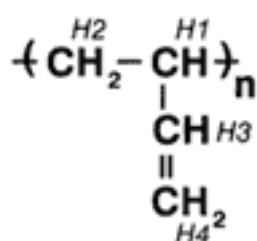
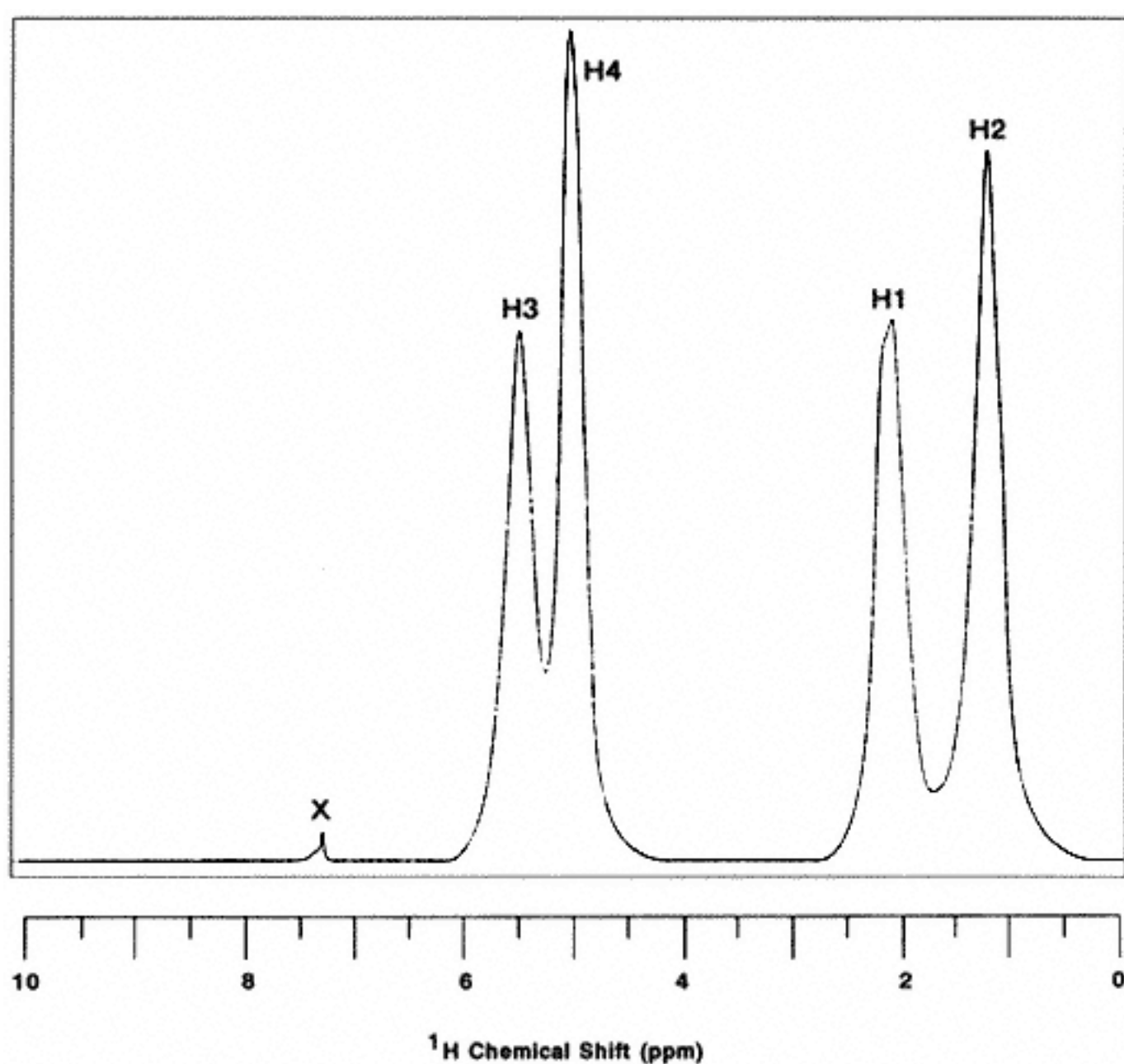
Broadening: 2 Hz

Pulse delay: 2 s

V-B-1H—
1,2-Polybutadiene (1,2-PBd)

Comments

Tacticity effects are obscured by broadening caused by sample viscosity. The polymer also contains significant amounts of both *cis*-1,4-{VI-A-1H, VI-A-2H} and *trans*-1,4-{VI-A-2H} butadiene units, but these resonances are obscured by 1,2-PBd. Solvent resonances are marked by **X**. This material is used in electrical transformers and motors.



Code	Shift (ppm)
H1	2.3
H2	1.3
H3	5.5
H4	5.1

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 12

Spectral width: 8 kHz

Data points: 8192

Pulse width: 30°

Broadening: 5 Hz

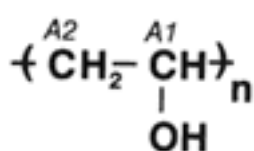
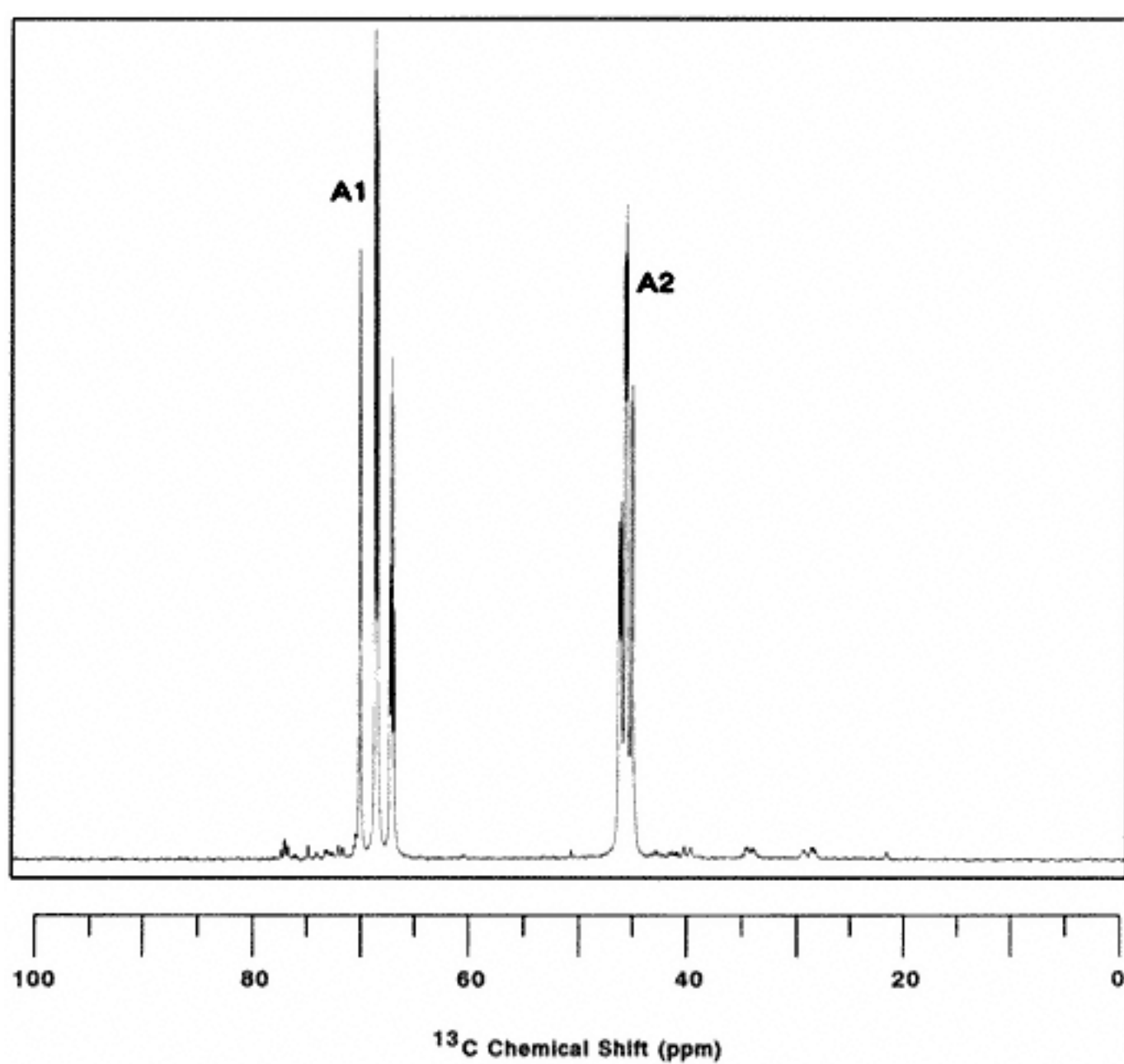
Pulse delay: 2 s

V-B-2—

Poly(Vinyl Alcohol) (PVOH) [99% Hydrolyzed]

Comments

Tacticity splitting is observed for both carbons (A1 and A2). This polymer results from the nearly complete (99%) hydrolysis of poly(vinyl acetate) {IV-A-1}. Water-soluble PVOH is used in adhesives, cements, coatings, and fabric treatments.



Code	Shift (ppm)
A1	68.4
A2	45.3

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: D₂O

Concentration: 10% w/w

Scans: 10,000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

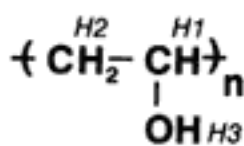
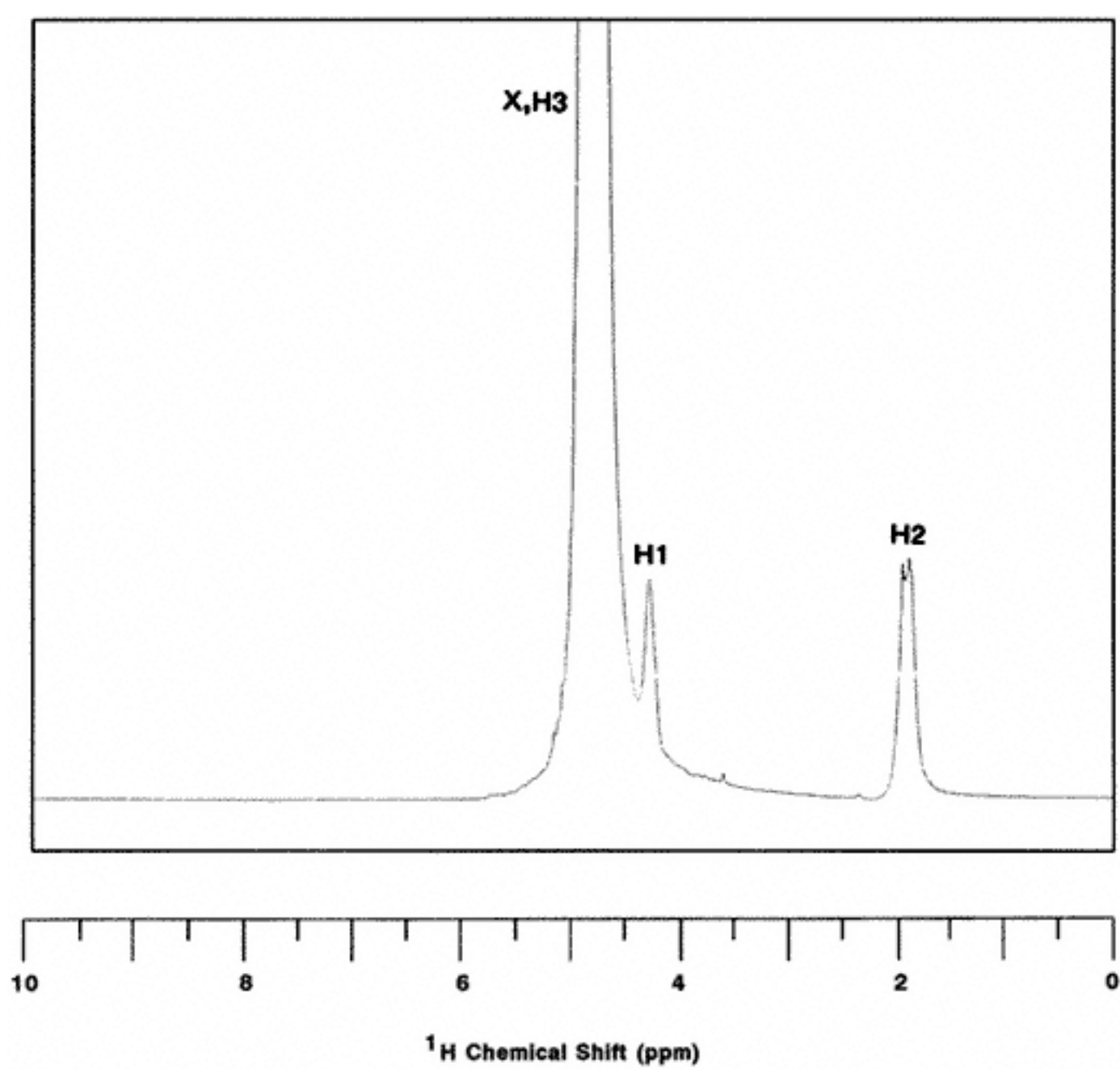
Pulse delay: 5 s

References

F. Imashiro and S. Obara. *Macromolecules* 28:2840, 1995; S. Egboh, H. Tenhu, K. Soljarmo, and F. Sundholm. *Makromol. Chem.* 192:1099, 1991; R. Lebek, K. Schlothauer, A. Krause, and H. Maschner. *Acta Polym.* 40:92, 1989; K. Hikichi and M. Yasuda. *Polym. J.* 19:1003, 1987; F. F. Vercautern and W. A. B. Donners. *Polymer* 27:993, 1986; A. E. Tonelli. *Macromolecules* 18:1086, 1985.

V-B-2H—**Poly(Vinyl Alcohol) (PVOH) [99% Hydrolyzed]****Comments**

Tacticity splitting is largely obscured by broadening caused by sample viscosity. This polymer results from the nearly complete (99%) hydrolysis of poly(vinyl acetate) {IV-A-1H.}. Water-soluble PVOH is used in adhesives, cements, coatings, and fabric treatments.



Code	Shift (ppm)
H1	4.3
H2	1.9
H3	4.8

Experimental ParametersNucleus: ¹H (400 MHz)

Temperature: 50°C

Solvent: D₂O

Concentration: 10% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 30°

Broadening: 5 Hz

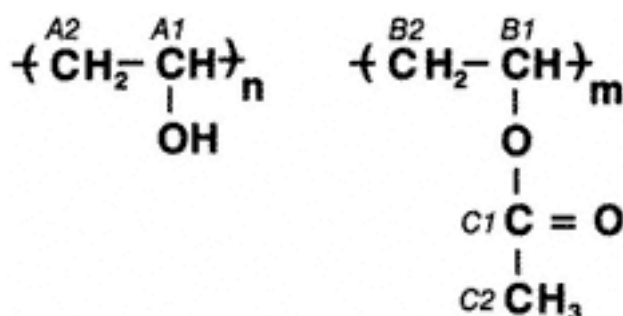
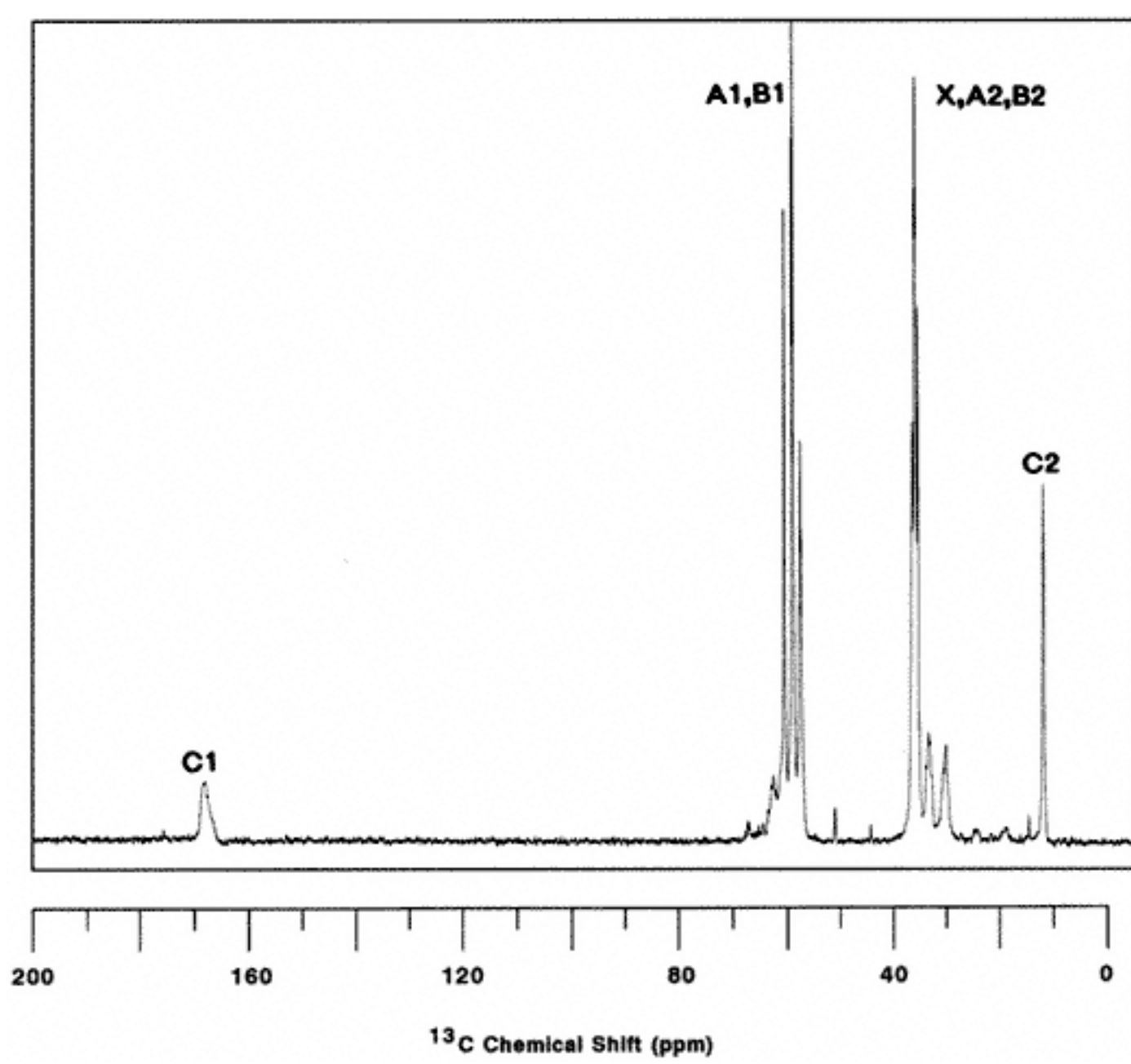
Pulse delay: 2 s

ReferenceG. P. Gippert and L. R. Brown. *Polym. Bull.* 27:585, 1984.

**V-B-3—
Poly(Vinyl Alcohol-Co-Vinyl Acetate)**

Comments

Tacticity splitting is observed for the major resonances (A1 and A2). This polymer results from the partial (80%) hydrolysis of poly(vinyl acetate) {IV-A-1}. This water-soluble polymer is used in adhesives, cements, coatings, and fabric treatments.



Code	Shift (ppm)
A1	62.1
A2	39.4
B1	63.7
B2	33.5
C1	169.4
C2	16.0

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: DMSO- d_6

Concentration: 10% w/w

Scans: 4000

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

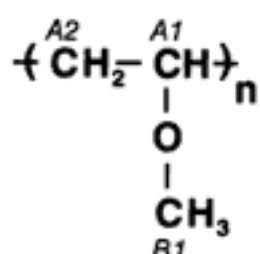
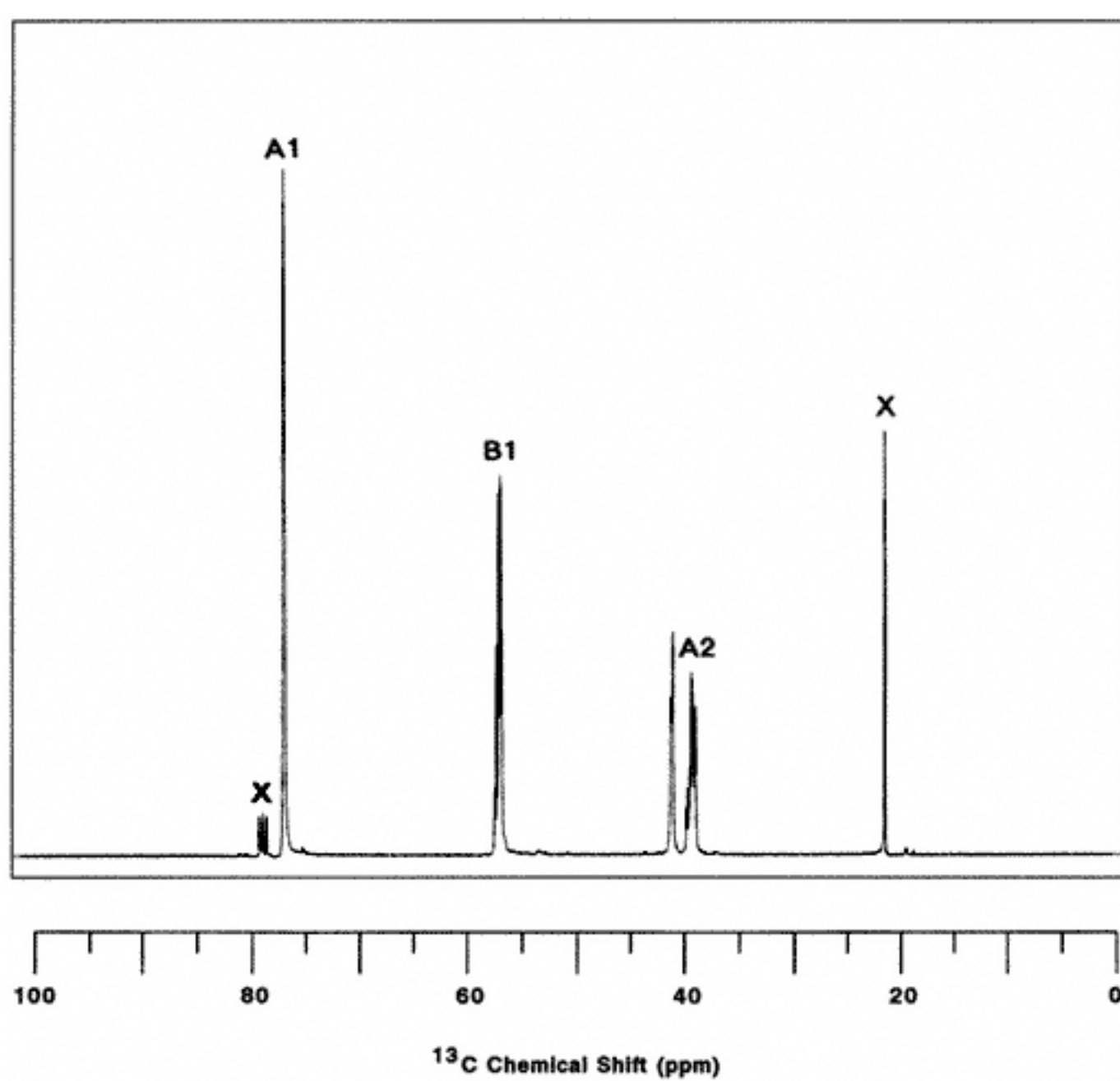
Reference

D. C. Bugada and A. Rudin. *Polymer* 25:1759, 1984.

**V-B-4—
Poly(Vinyl Methyl Ether) (PVME)**

Comments

Tacticity splitting is observed for some carbons; solvent resonances are marked by **X**. Water-soluble PVME is a common ingredient in latex paints, cosmetics, lubricants, greases, coatings, and adhesives. It is also found as a component of some polymer blends.



Code	Shift (ppm)
A1	75.8
A2	40.6, 38.8
B1	56.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 10% w/w
Scans: 160	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 2 s

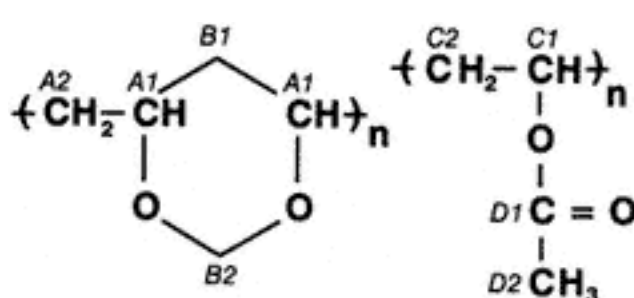
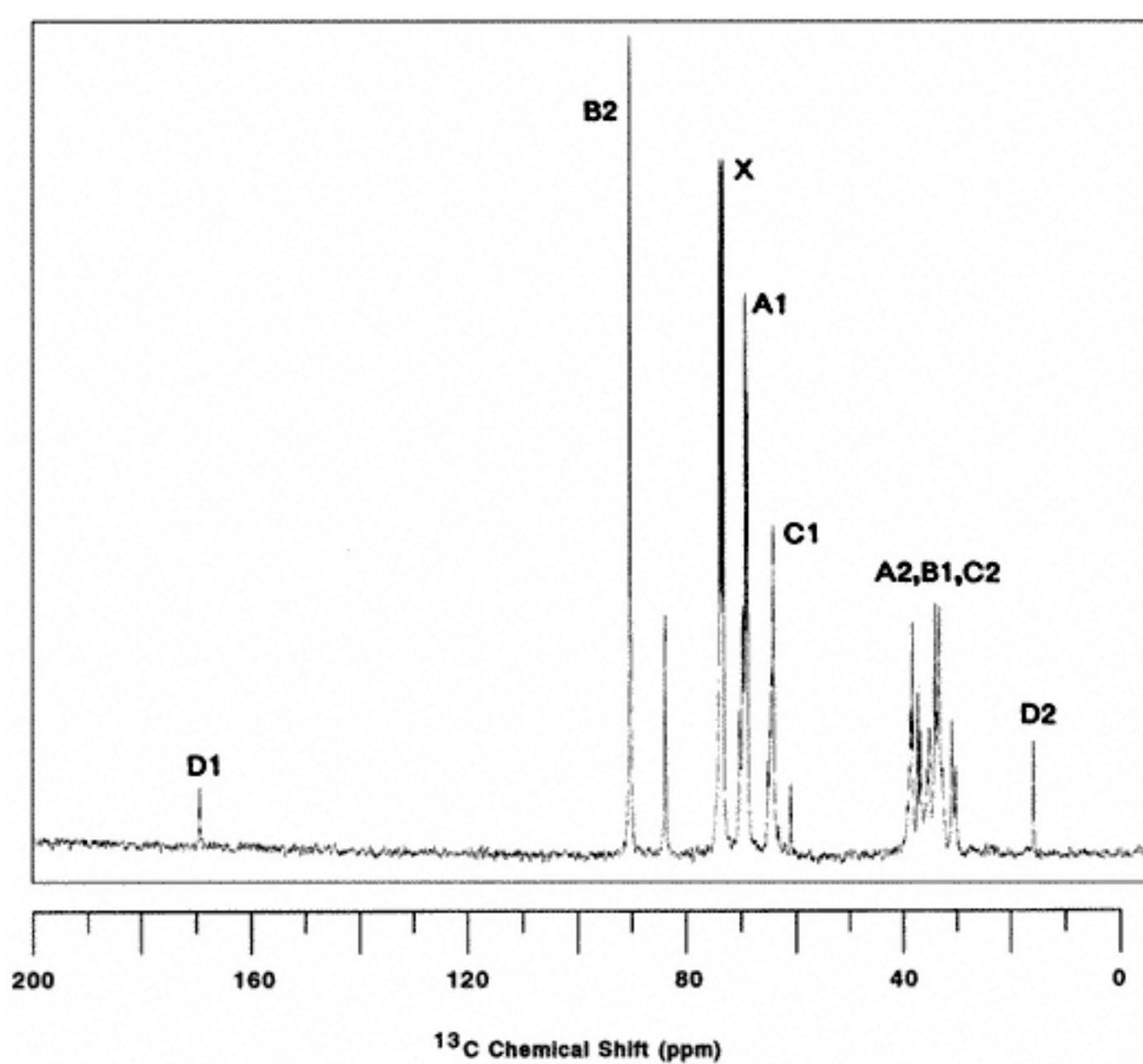
Reference

T. Kawamura, N. Toshima, and K. Matsuzaki. *Macromol. Rapid Commun.* 15:757, 1994.

**V-B-5—
Poly(Vinyl Formal)**

Comments

The spectrum exhibits resonances from both poly(vinyl formal) and one of its precursors poly(vinyl acetate) {IV-A-1}. Solvent resonances are marked by **X**. Poly(vinyl formal) is primarily used to manufacture cotton-like synthetic fibers used in canvas, awnings, and other heavy-duty fabrics. Fibers are first spun from a PVOH solution. Subsequent heat treatment with formaldehyde produces the final polymer.



Code	Shift (ppm)
A1	72.4
A2	34–44
B1	93.4
B2	34–44
C1	67.8
C2	34–44
D1	170.4
D2	20.7

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

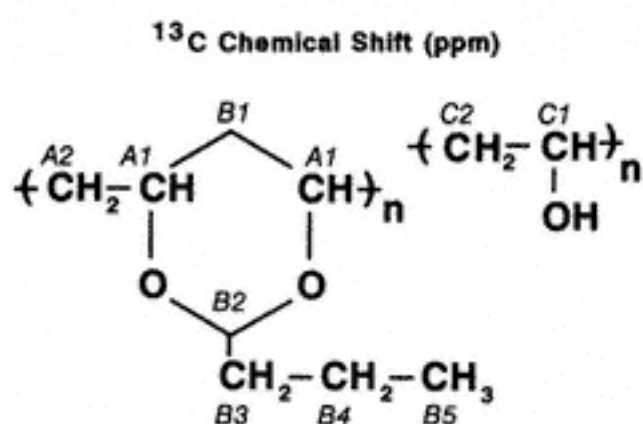
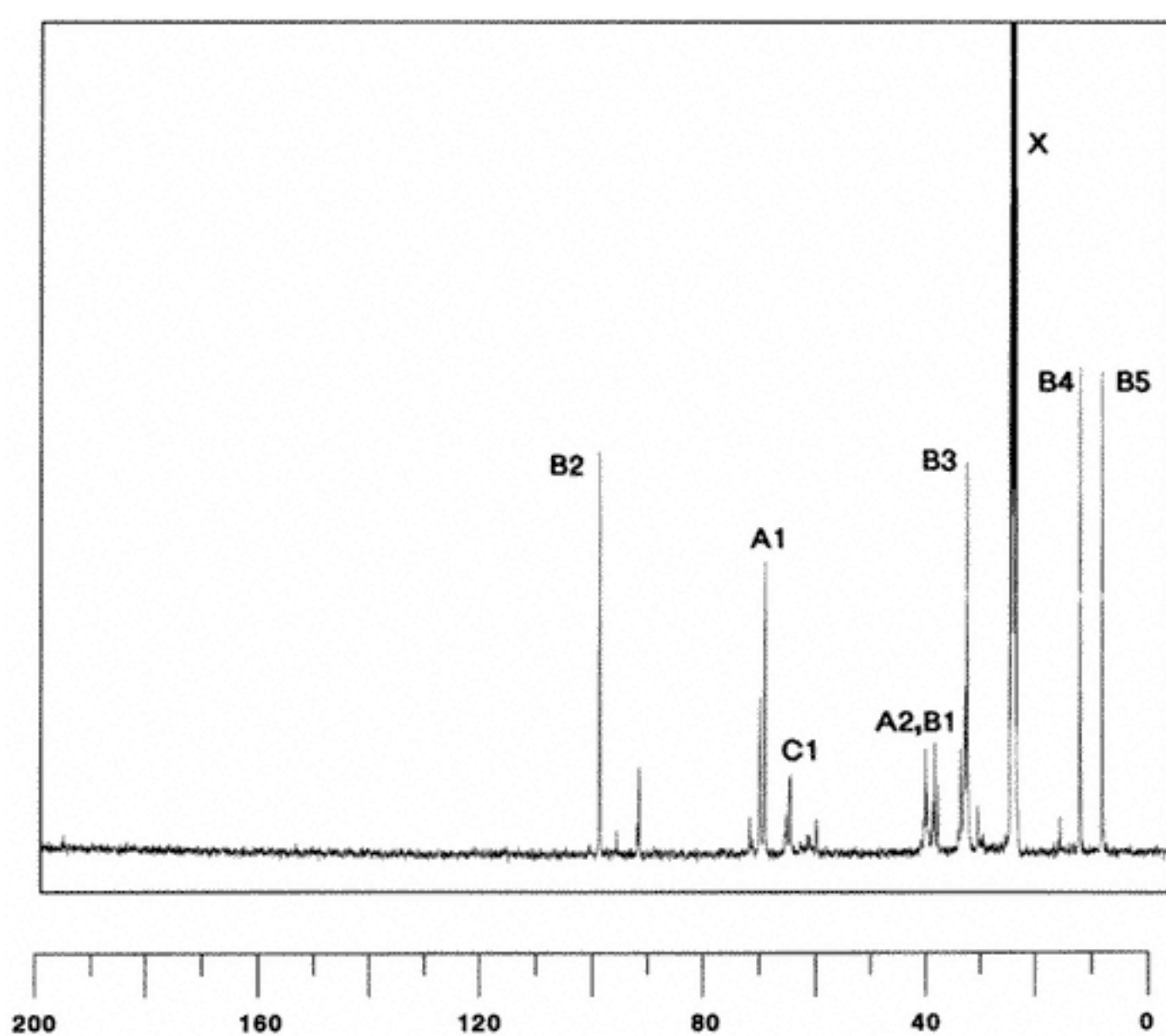
Reference

P.A. Berger, E. R. Remsen, G. C. Leo, and D. J. David. *Macromolecules* 24:2189, 1991.

**V-B-6—
Poly(Vinyl Butyral)**

Comments

The spectrum exhibits resonances from both poly(vinyl butyral) and one of its precursors, poly(vinyl alcohol) (PVOH) {V-B-2, V-B-3}. Solvent resonances are marked by **X**. Poly(vinyl butyral) is primarily used as the adhesive in laminated safety glass; it also improves fiber properties. Poly(vinyl butyral) is prepared by the reaction of PVOH with butyraldehyde in the presence of strong mineral acids.



Code	Shift (ppm)
A1	73.4
A2	42.5
B1	42.5
B2	101.4
B3	37.0
B4	17.2
B5	13.6
C1	64–70
C2	42.5

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: acetone- d_6

Concentration: 10% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

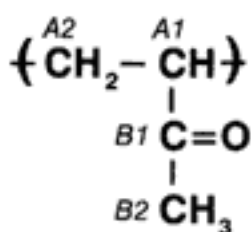
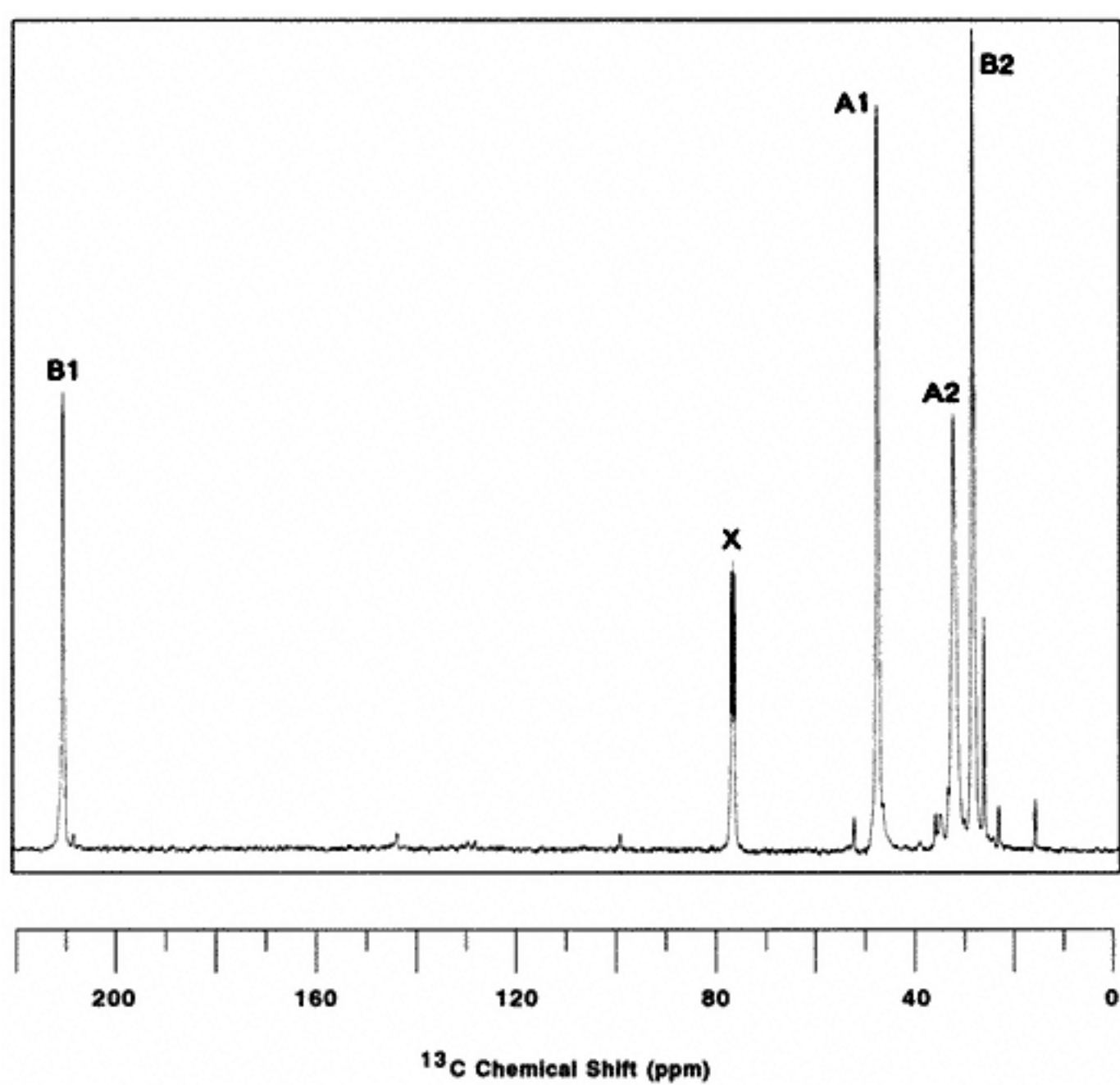
References

P. A. Berger, E. R. Remsen, G. C. Leo, and D. J. David. *Macromolecules* 24:2189, 1991; R. Lebek, K. Schlothauer, A. Krause, and H. Maschner. *Acta Polym.* 40:92, 1989; M. D. Bruch and J. K. Bonesteel. *Macromolecules* 19:1622, 1986.

V-B-7—

Poly(Vinyl Methyl Ketone) (PVK)*Comments*

Solvent resonances are marked by **X**. This material has little commercial use because of its poor thermal and photostability. Vinyl methyl ketone monomer may be incorporated into other polymers to promote photodegradation in environmentally sensitive applications.



Code	Shift (ppm)
A1	48.0
A2	32.5
B1	210.6
B2	29.5

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

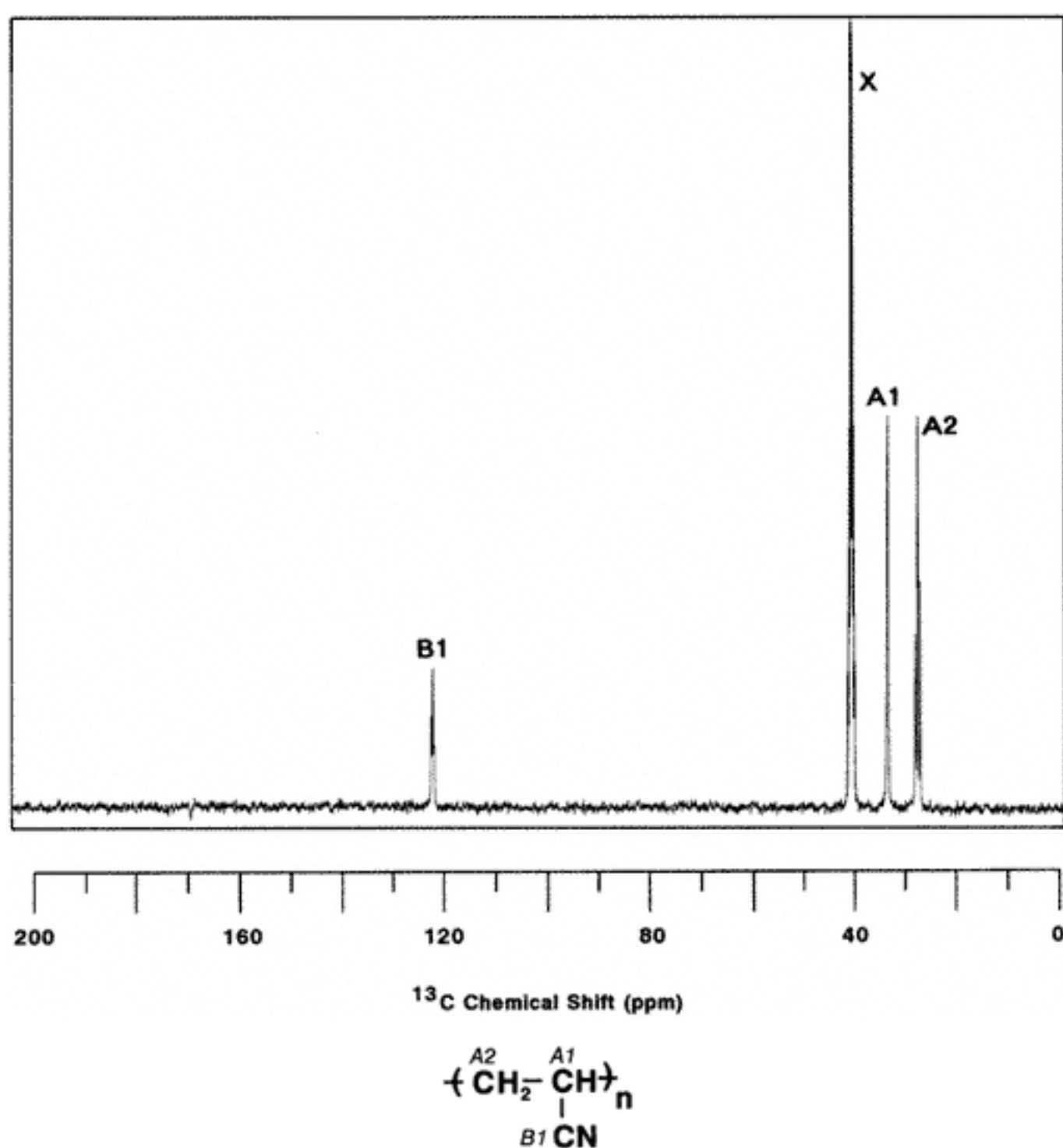
Broadening: 2 Hz

Pulse delay: 2 s

**V-B-8—
Polyacrylonitrile (PAN)**

Comments

Also commonly known as Orlon (DuPont) and Acrylan (Monsanto), or generally, as "acrylic." Tacticity effects are observed for some carbons (**A2** and **B1**); solvent resonances are marked by **X**. PAN forms the basis for acrylic fibers; it may be copolymerized with vinyl acetate, acrylates, methacrylates, sodium styrene sulfonate (to enhance dyeability), or vinyl chloride (to increase fire retardancy). Acrylic fibers are commonly used as an alternative to wool in knitwear, hosiery, jersey fabric, carpets, and blankets. PAN is also the precursor to the strong carbon fibers used in composite materials.



Code	Shift (ppm)
A1	33.9
A2	28.1
B1	121.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: DMSO- d_6	Concentration: 5% w/w
Scans: 400	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 2 s

References

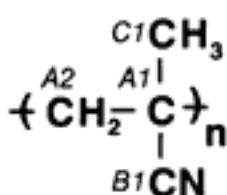
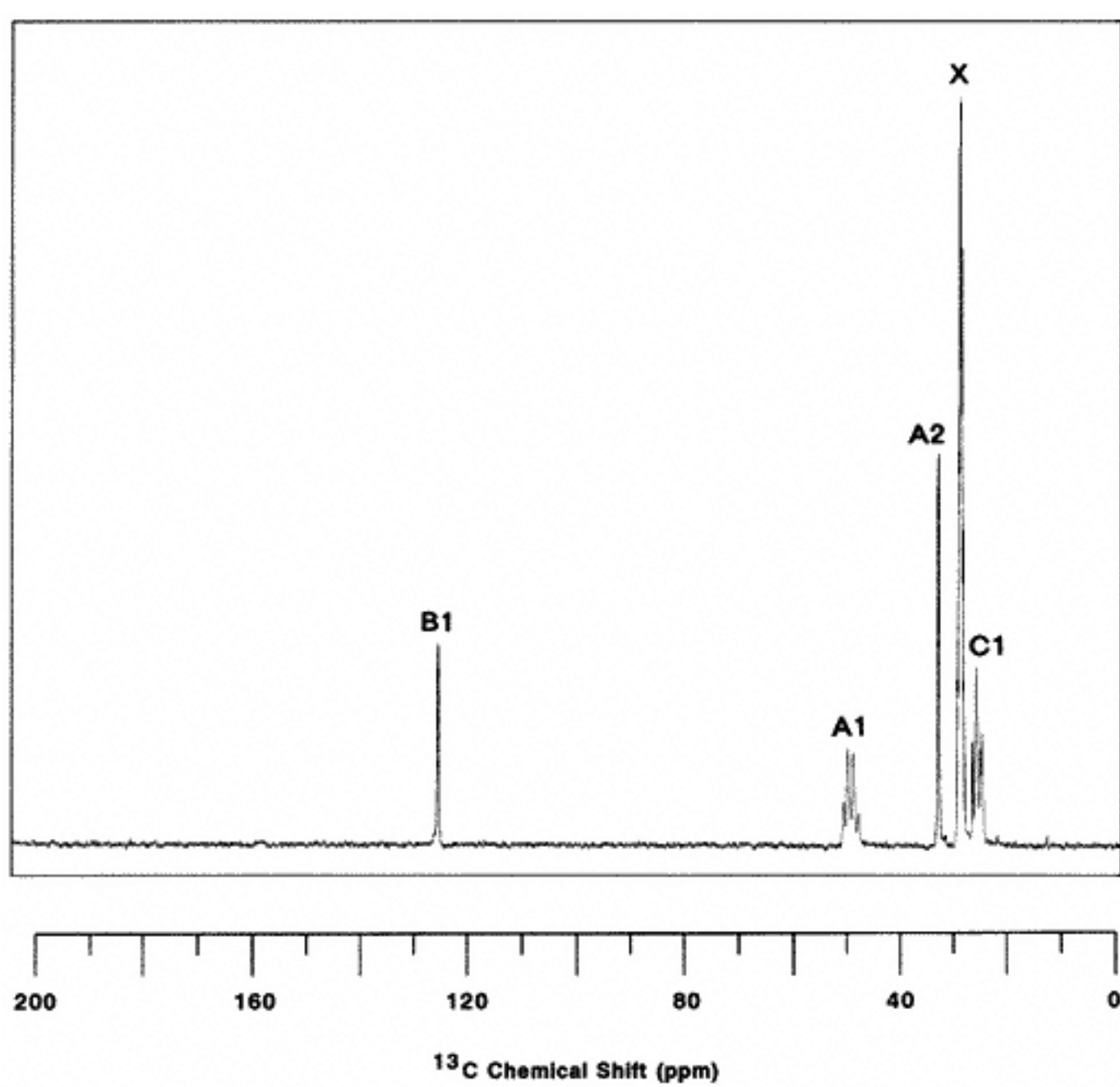
M. Minagawa, T. Takasu, S. Shinozaki, F. Yoshii, and N. Morishita. *Polymer* 36:2343, 1995; K. Kamide, H. Yamazaki, K. Okajima, and K. Hikichi. *Polym. J.* 17:1233, 1985.

V-B-9—

Polymethacrylonitrile (PMAN)

Comments

Tacticity effects are observed for some carbons (**A2** and **B1**); solvent resonances are marked by **X**. PMAN is used in applications similar to polyacrylonitrile {V-B-9}, but it has a lower softening temperature. Acrylic fibers are commonly used as an alternative to wool in knitwear, hosiery, jersey fabric, carpets, and blankets.



Code	Shift (ppm)
A1	49.5
A2	33.0
B1	123.3
C1	26–27

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: DMSO- d_6

Concentration: 5% w/w

Scans: 200

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

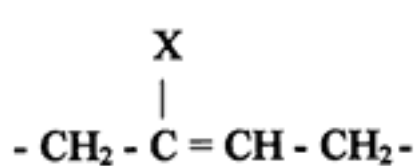
Pulse delay: 2 s

Reference

T. Kawamura, N. Toshima, and K. Matsuzaki. *Macromol. Chem. Phys.* 135:3343, 1994.

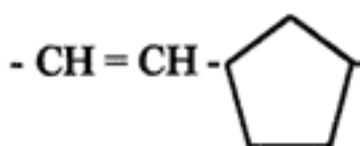
VI— Unsaturated Backbones

Polymers and copolymers in this group have unsaturated the chain backbones; most result from polymerization of a 1,4-diene [1], such as 1,4-butadiene or isoprene (2-methyl-1,4-butadiene). This produces a polymer with a double bond between the second and third carbons of the repeat unit:



A

where X may be a hydrogen atom, a methyl group, or a chlorine atom. Polynorbomene {VI-B-6}:



B

is formed by a ring-opening metathesis polymerization (ROMP) [2]. The monomer units in these elastomeric polymers can occur in either *cis*- or *trans*-configurations; the polymers may be predominantly *cis*-, predominantly *trans*-, or a mixture. Polybutadiene (PBd) (see Structure A with X = H) {VI-A-1, VI-A-1H, VI-A-2, VI-A-2H} is often blended with synthetic or natural rubber to improve wear resistance. *cis*-Polyisoprene (see Structure A with X = CH₃) {VI-B-1, VI-B-1H} is chemically identical to the most prevalent type (*hevea*) of natural rubber; *trans*-polyisoprene {VI-B-2, VI-B-2H} is similar to less common natural forms (*balata* or *gutta percha*). Polychloroprene (see Structure A with X = Cl) {VI-B-5, VI-B-5H}, a synthetic material, is employed when improved chemical resistance is needed [1]. The ¹³C chemical shifts for some common polydienes are summarized in Table VI-1.

Polydienes are often used to modify the properties of other materials. Styrene–diene polymer systems are particularly significant materials. High-impact polystyrene (HIPS) {III-A-6, III-A-6H} includes a small amount (~5%) of polybutadiene (PBd) to enhance the toughness and fracture resistance of the polystyrene base material. This chapter includes the high-Bd styrene–butadiene copolymers, elastomers that are commonly found in applications such as tires, footwear, and adhesives. Acrylonitrile–butadiene–styrenes (ABS) are engineering resins found in appliance and business-machine housings and structural foams [1].

Table VI.1 ^{13}C Chemical Shifts of Some Polydiene Isomers

Polymer	X	Isomer	$ \begin{array}{c} \text{X BI} \\ \\ \text{-CH}_2\text{-C=CH-CH}_2\text{-} \\ \text{A2 A1 A1' A2'} \end{array} $				A2	A2'	B1
			A1	A1'					
Polybutadiene	H	<i>cis</i>	130.0	130.0	28.1	28.1	—		
Polybutadiene	H	<i>trans</i>	130.2	130.2	33.1	33.1	—		
Polyisoprene	CH_3	<i>cis</i>	135.0	125.6	32.2	26.4	22.9(CH_3)		
Polyisoprene	CH_3	<i>trans</i>	134.9	124.5	39.9	26.9	16.0 (CH_3)		
Polychloroprene	Cl	<i>trans</i>	135.4	124.5	38.7	27.0	—		

VI.A—**Sample Preparation and Spectral Acquisition**

At room temperature, polydienes will swell or dissolve in a variety of solvents, such as chloroform- d , benzene- d_6 , and toluene- d_8 [3]. Samples are most easily prepared by allowing a mixture of polymer and solvent to stand for several hours, until the sample becomes homogeneous. Occasionally, air bubbles will form in this gel, but these will usually be removed by normal sample spinning during the NMR experiment. Quantitative ^{13}C conditions are not difficult to achieve: a 5-s pulse delay following a 90° pulse with continuous ^1H decoupling will produce correct relative peak areas. For ^1H spectra, the same parameters (without decoupling) are sufficient.

VI.B—**Spectral Features**

The ^{13}C resonances for the polydienes are found in two chemical-shift ranges: 115–150 ppm for the olefinic carbons, and 20–40 ppm for the aliphatic [4]. The *cis*- or *trans*-configurations in the polymer backbone give rise to different chemical shifts. The spectrum of *cis*-PBd is very simple; its principal peaks (130.0 and 28.1 ppm) correspond to the one olefinic and one aliphatic carbon. The olefinic carbons in *trans*-configurations resonate at nearly the same chemical shift (130.2 ppm), but the aliphatic carbons appear at 33.1 ppm. Several other resonances (143.9, 114.6, 43.8, and 38.5 ppm) appear in the spectra of PBds; they are attributable to the presence of the *I,2*-form {V-B-1}, in which vinyl groups are attached to a saturated backbone. Because the *I,2*-units are potential sites for cross-linking, it is often necessary to determine the relative amounts of *cis*-, *trans*-, and *I,2*- in a polybutadiene sample. This analysis can be readily accomplished from a quantitative ^{13}C spectrum. The average of the peak areas at 114.6 and 143.9 ppm yields $A_{I,2}$, the per-carbon area for a *I,2*-unit. A_{cis} and A_{trans} are given by the resonances at 28.1 and 33.1 ppm, respectively. One may then simply calculate the percentage *cis*-configurations:

$$\% \text{ cis} = \frac{A_{cis}}{A_{cis} + A_{trans} + A_{I,2}} \quad (\text{VI-1})$$

and, likewise, the percentages for *trans* and *I,2*. Similar analyses can be performed for the substituted polydienes (polyisoprene {VI-B-1, VI-B-2} and polychloroprene {VI-B-5}) and their copolymers {VI-A-4, VI-A-6, VI-B-4}.

The ^1H spectra of polydienes include olefinic proton resonances at 4–5 ppm and aliphatics at 1–3 ppm. As in most polymer spectra, the ^1H signals are considerably broader than the ^{13}C , and detailed interpretations are more difficult. ^1H spectra are however useful for rapid measurement of copolymer composition, such as that discussed in Section III.B.1 for the analysis of Bd in styrene-Bd copolymers.

References

1. H. Ulrich. *Introduction to Industrial Polymers*. Munich: Hanser Publishers, 1993.
2. J. A. Johnston, M. Tokles, G. S. Havatny, P. L. Rinaldi, and M. F. Faron. *Macromolecules* 24:5532, 1991.
3. J. Brandrup and E. H. Immergut. *Polymer Handbook*. New York: Wiley, 1975.
4. Y. Tanaka. *Rubber Chem. Technol.* 64:325, 1991.

UNSATURATED BACKBONES*A. Polymers and Copolymers of Butadiene*

VI-A-1	Polybutadiene (<i>cis</i>)
VI-A-1H	Polybutadiene (<i>cis</i>)
VI-A-2	Polybutadiene (<i>cis/trans</i>)
VI-A-2H	Polybutadiene (<i>cis/trans</i>)
VI-A-3	Polybutadiene diol
VI-A-3H	Polybutadiene diol
VI-A-4	Poly(styrene-co-butadiene), ABA block
VI-A-4H	Poly(styrene-co-butadiene), ABA block
VI-A-5	Poly(styrene-co-butadiene), random
VI-A-5H	Poly(styrene-co-butadiene), random
VI-A-6	Poly(acrylonitrile-co-butadiene-co-styrene)

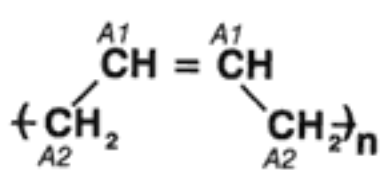
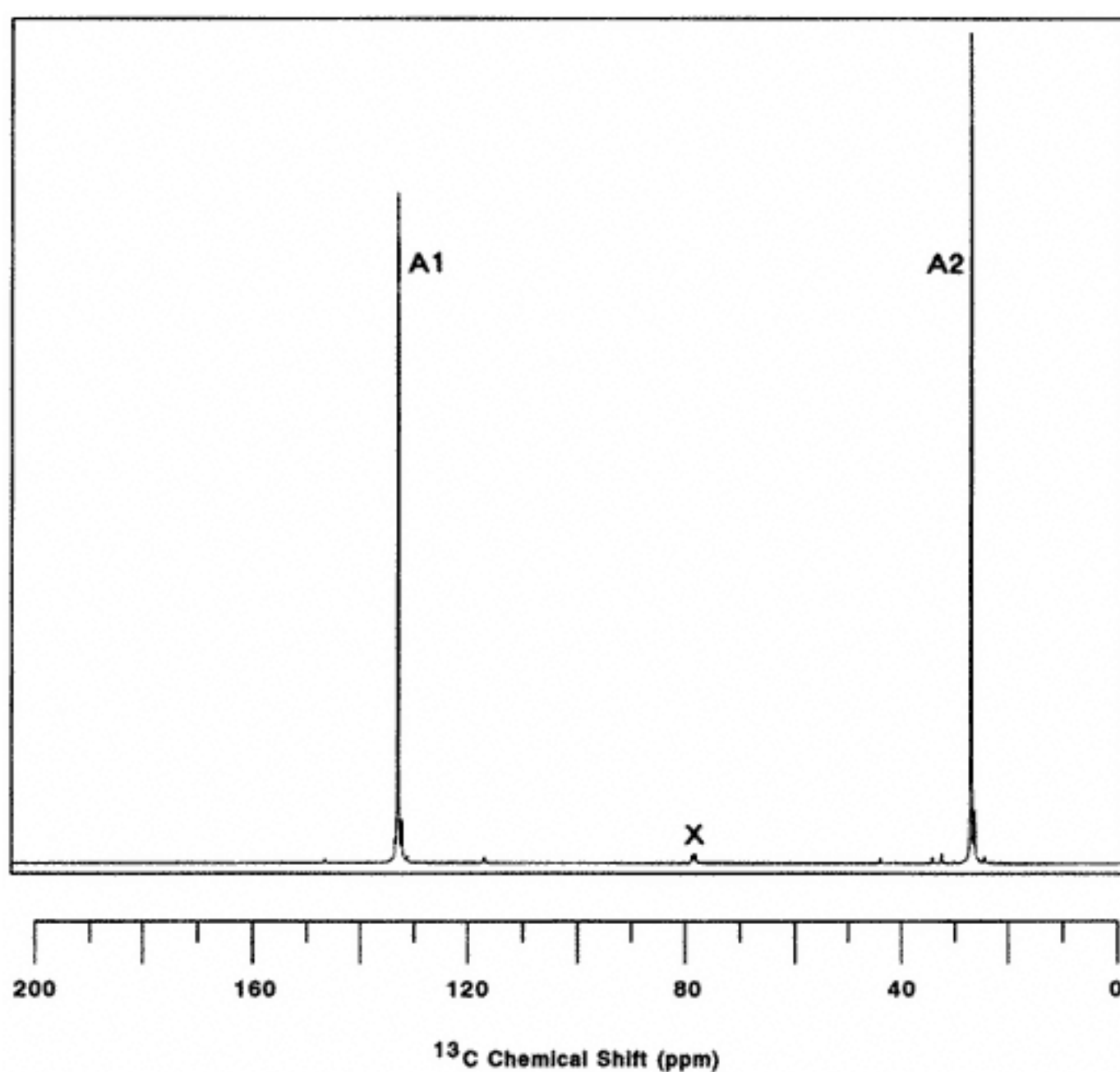
B. Polymers and Copolymers of Other Dienes

VI-B-1	Polyisoprene (<i>cis</i>)
VI-B-1H	Polyisoprene (<i>cis</i>)
VI-B-2	Polyisoprene (<i>trans</i>)
VI-B-2H	Polyisoprene (<i>trans</i>)
VI-B-3	Polyisoprene, chlorinated
VI-B-4	Poly(styrene-co-isoprene)
VI-B-4H	Poly(styrene-co-isoprene)
VI-B-5	Polychloroprene (<i>trans</i>)
VI-B-5H	Polychloroprene (<i>trans</i>)
VI-B-6	Polynorbornene

**VI-A-1—
Polybutadiene (*Cis*) (*c*-PBd)**

Comments

cis-Polybutadiene is the predominant isomer, but small (~1%) amounts of *trans*- and *1,2*-configurations are also observed {compare with VI-A-2}. The *1,2*-units provide sites for grafting or cross-linking. Solvent resonances are marked by **X**. This material is also called *butadiene rubber*, not to be confused with *butyl rubber* {II-C-2 through II-C-5}. PBd is a component of styrene–elastomer systems, such as high-impact polystyrene (HIPS) {III-A-6}, styrene–butadiene copolymers {VI-A-4, VI-A-5}, and acrylonitrile–butadiene–styrene (ABS) resin {VI-A-6}. PBd itself is also used in tires, hoses, and gaskets.



Code	Shift(ppm)
A1 (<i>cis</i>)	130.0
A2 (<i>cis</i>)	28.1

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 30% w/w
Scans: 1000	Spectral width: 25 kHz
Data points: 32768	Pulse width: 90°
Broadening: 5 Hz	Pulse delay: 5 s

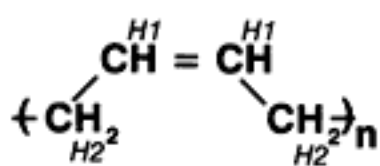
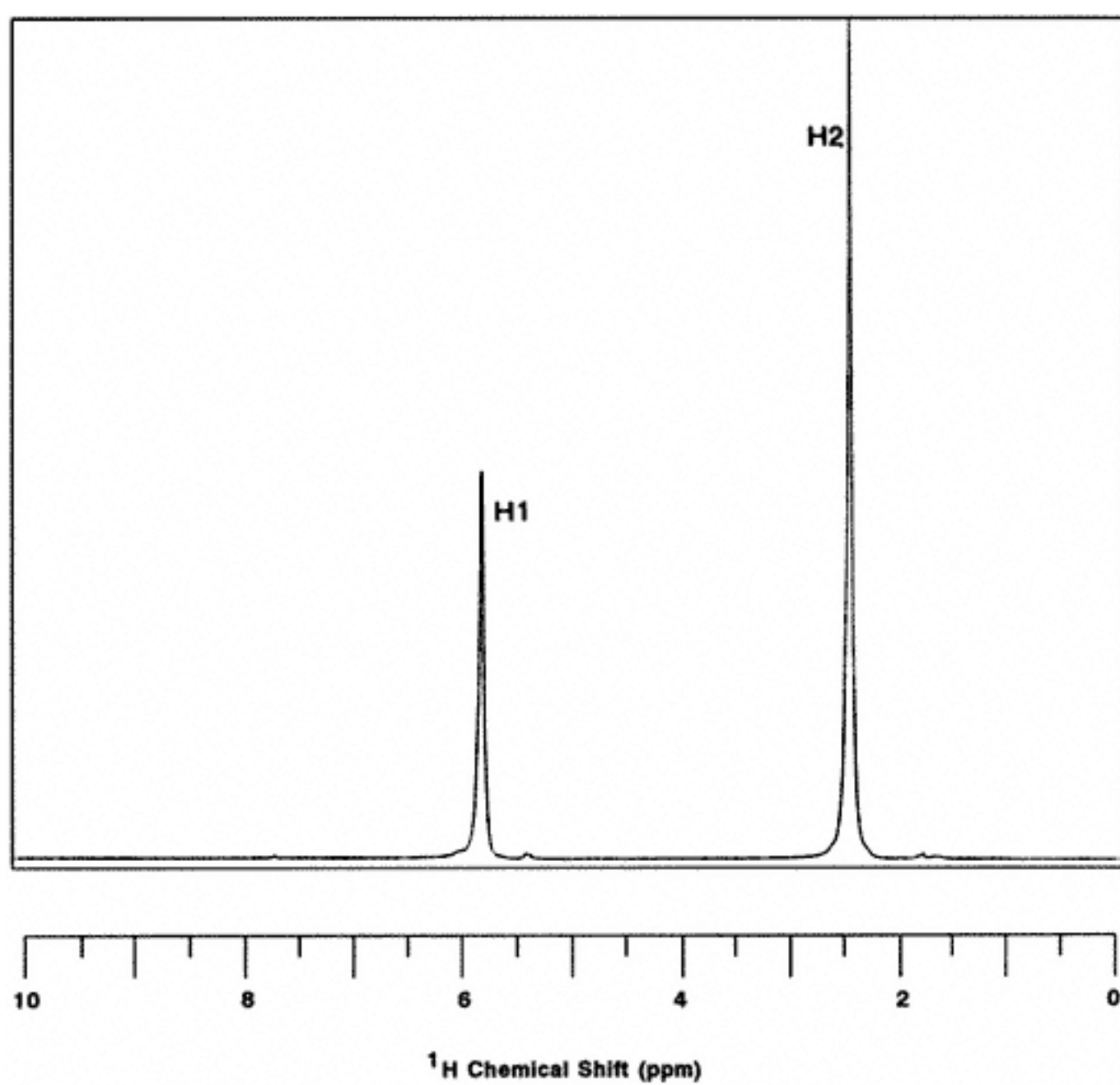
References

H. Sato, K. Takebayashi, and Y. Tanaka. *Macromolecules* 20:2418, 1987; G. van der Velden, C. Didden, T. Veermans, and J. Beuler. *Macromolecules* 20:1252, 1987.

**VI-A-1H—
Polybutadiene (Cis) (c-PBd)**

Comments

cis-Polybutadiene is the predominant isomer, but small (~1%) amounts of *trans*- and *1,2*-configurations are also observed {compare with VI-A-2H}. The *1,2*-units provide sites for grafting or cross-linking. This material is also called *butadiene rubber*, not to be confused with *butyl rubber*. PBd is a component of styrene–elastomer systems, such as high-impact polystyrene (HIPS) {III-A-6H}, styrene–butadiene copolymers {VI-A-4H, VI-A-5H}, and acrylonitrile–butadiene–styrene (ABS) resin. PBd itself is also used in tires, hoses, and gaskets.



Code	Shift (ppm)
H1	5.8
H2	2.4

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

Reference

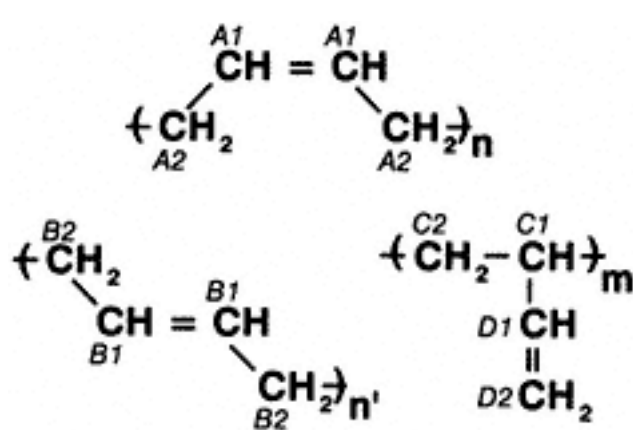
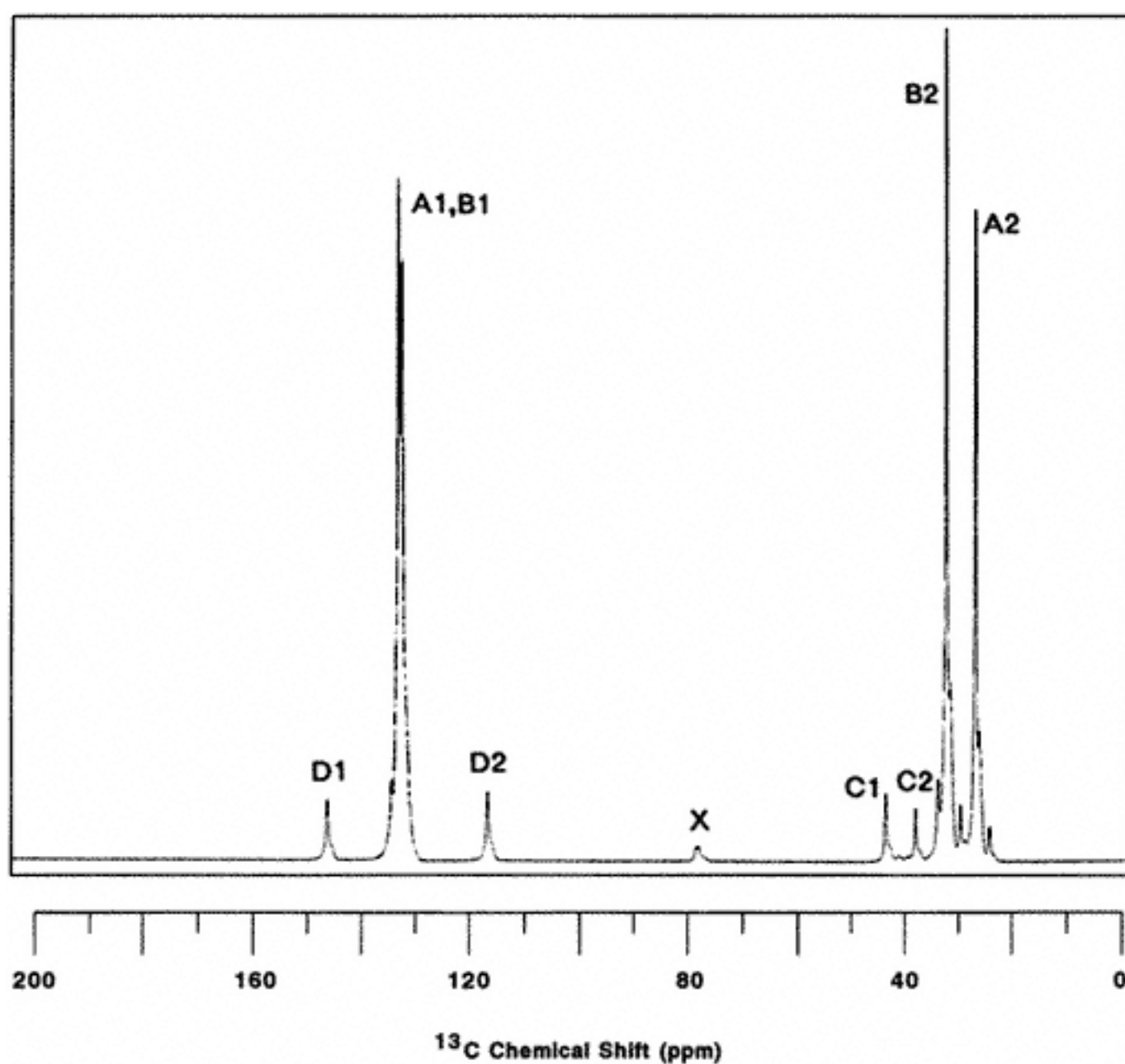
T. Katoh, M. Ikura, and K. Hikichi. *Polym. J.* 20:185, 1988.

VI-A-2—

Polybutadiene (*Cis/Trans*) (*c,t-PBd*)

Comments

Both *cis*- and *trans*- isomers predominate (~50% *t*, ~40% *c*), but small amounts (~10%) of *1,2*-configurations are also observed {compare with VI-A-1}. The *1,2*-units provide sites for grafting or cross-linking. Solvent resonances are marked by X. This material is also called *butadiene rubber*, not to be confused with *butyl rubber* {II-C-2 through II-C-5}. PBd is used in styrene–elastomer systems, such as high-impact polystyrene (HIPS) {III-A-6}, styrene–butadiene copolymers {VI-A-4, VI-A-5}, and acrylonitrile–butadiene–styrene (ABS) resin {VI-A-6}. In addition to these uses, PBd is also found in tires, hoses, and gaskets.



Code	Shift (ppm)
A1	130.0
A2	28.1
B1	130.2
B2	33.1
C1	43.4
C2	38.1
D1	142.6
D2	114.2

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 8192

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

References

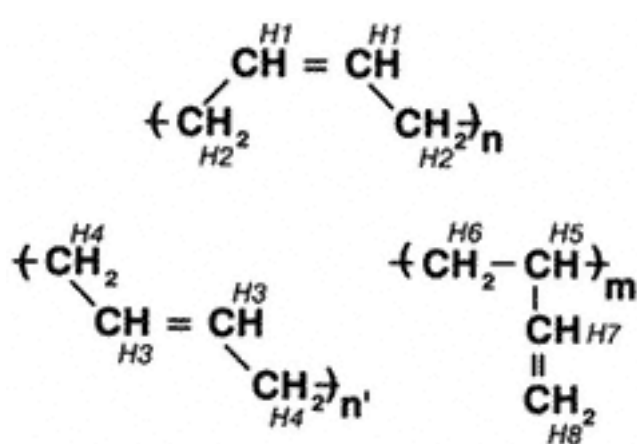
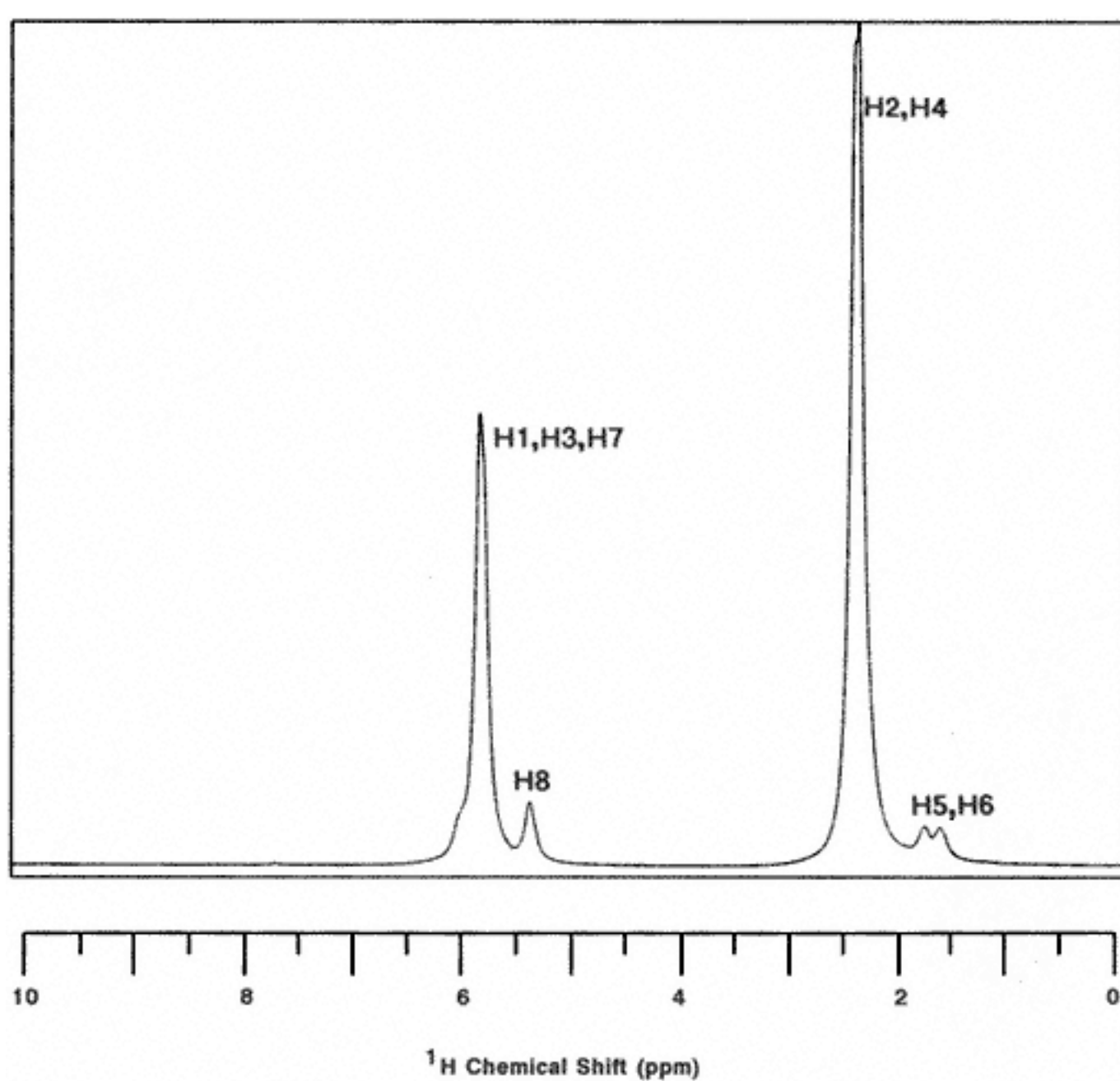
H. Sato, K. Takebayashi, and Y. Tanaka. *Macromolecules* 20:2418, 1987; G. van der Velden, C. Didden, T. Veermans, and J. Beuler. *Macromolecules* 20:1252, 1987.

VI-A-2H—

Polybutadiene (*Cis/Trans*) (*c,t*-PBd)

Comments

Both *cis*- and *trans*-isomers predominate (~50% *t*, ~40% *c*), but small amounts (~10%) of *1,2*-configurations are also observed {compare with VI-A-1}. The *1,2*-units provide sites for grafting or cross-linking. This material is also called *butadiene rubber*, not to be confused with *butyl rubber*. PBd is used in styrene–elastomer systems, such as high-impact polystyrene (HIPS) {III-A-6H}, styrene–butadiene copolymers {VI-A-4H, VI-A-5H}, and acrylonitrile–butadiene–styrene (ABS) resin. In addition to these uses, PBd is also found in tires, hoses, and gaskets.



Code	Shift (ppm)
H1	5.8
H2	2.4
H3	5.8
H4	2.4
H5	1.8, 1.6
H6	1.8, 1.6
H7	5.8
H8	5.4

Experimental ParametersNucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

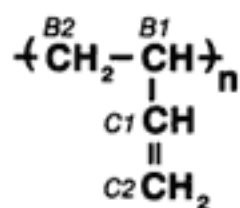
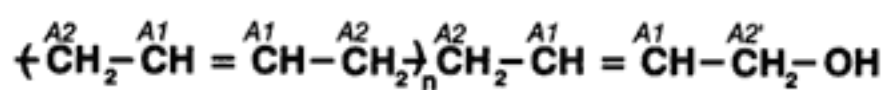
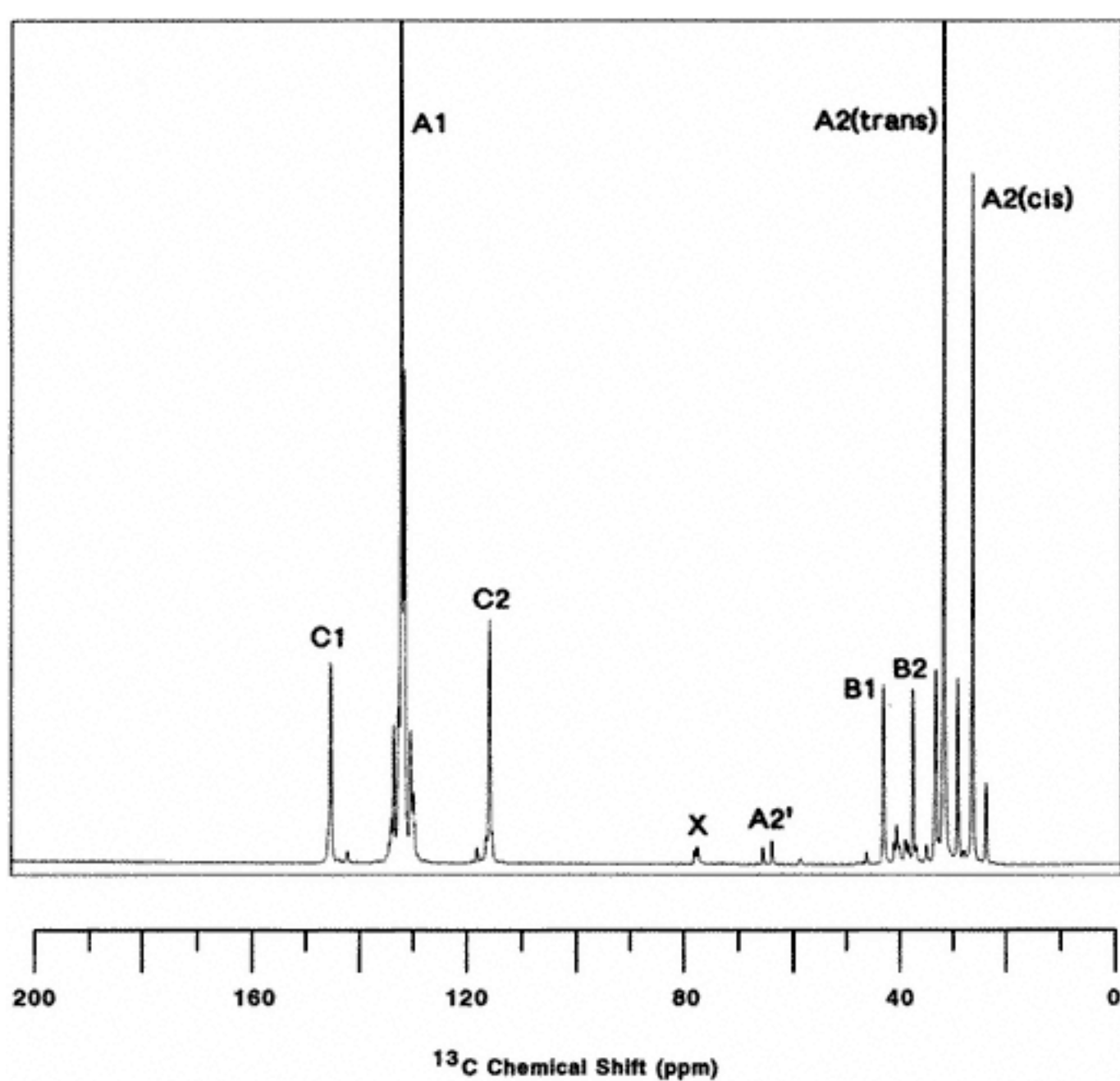
Pulse delay: 5 s

ReferenceT. Katoh, M. Ikura, and K. Hikichi. *Polym. J.* 20:185, 1988.

VI-A-3—
Polybutadiene Diol

Comments

The *cis*- and *trans*-isomers predominate, but small amounts of *1,2*-configurations are also observed {compare with VI-A-1 and VI-A-2}. The *1,2*-units provide sites for grafting or cross-linking; the hydroxyl end groups are also reactive. Solvent resonances are marked by X. This material is used to produce some polyurethane elastomers.



Code	Shift (ppm)
A1 (<i>cis</i>)	130.0
A1 (<i>trans</i>)	130.2
A2 (<i>cis</i>)	28.1
A2 (<i>trans</i>)	33.1
A2'	63–65
B1	43.4
B2	38.1
C1	142.6
C2	114.2

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 2 Hz

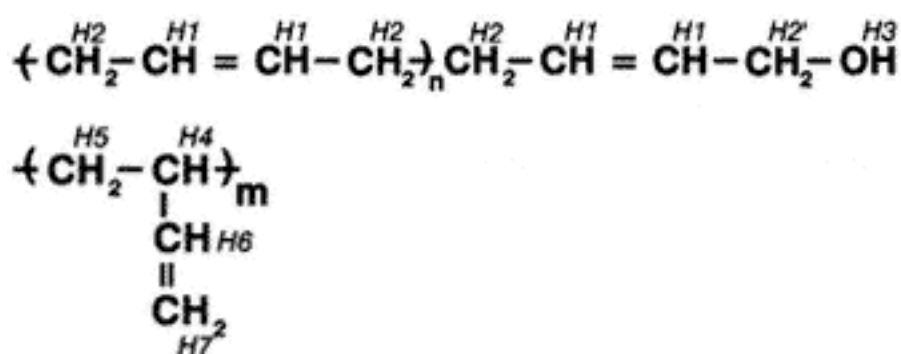
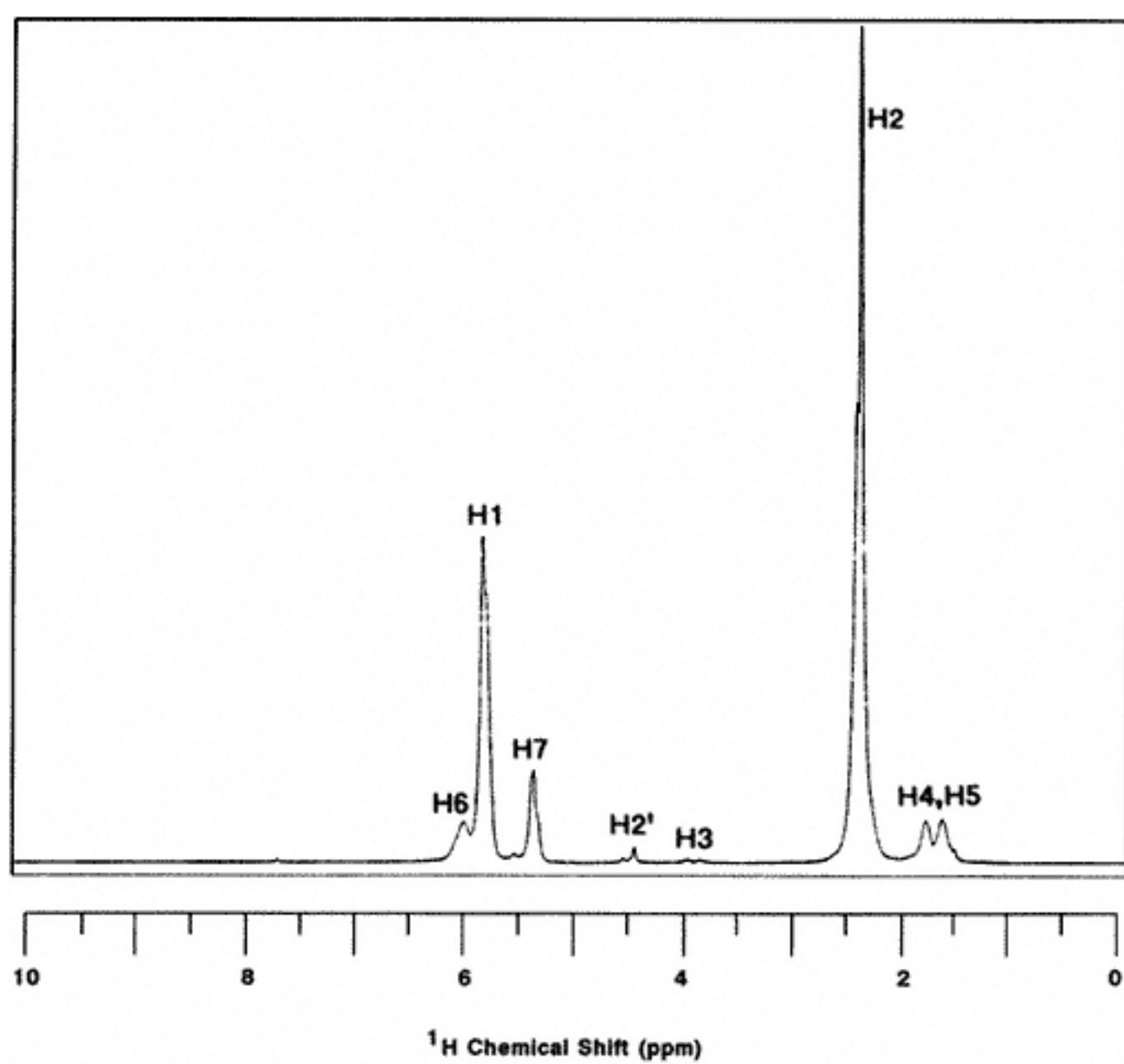
Pulse delay: 2 s

ReferenceW. D. Vilar, S. M. C. Menezes, and L. Akcelrud. *Polym. Bull.* 33:557, 1994.

VI-A-3H— Polybutadiene Diol

Comments

The *cis*- and *trans*-isomers predominate, but small amounts of *1,2*-configurations are also observed {compare with VI-1H and VI-2H}. The *1,2*-units provide sites for grafting or cross-linking; the hydroxyl end groups are also reactive. This material is used to produce some polyurethane elastomers.



Code	Shift (ppm)
H1	5.8
H2	2.4
H2'	4.4
H3	3.8–4.0
H4	1.8, 1.6
H5	1.8, 1.6
H6	6.0
H7	5.3

Experimental Parameters

Nucleus: ¹ H (400 MHz)	Temperature: 50°C
Solvent: CDCl ₃	Concentration: 30% w/w
Scans: 24	Spectral width: 8 kHz
Data points: 8192	Pulse width: 10°
Broadening: 5 Hz	Pulse delay: 5 s

Reference

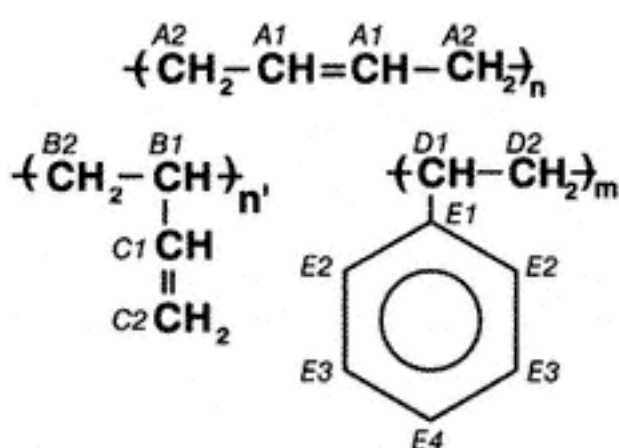
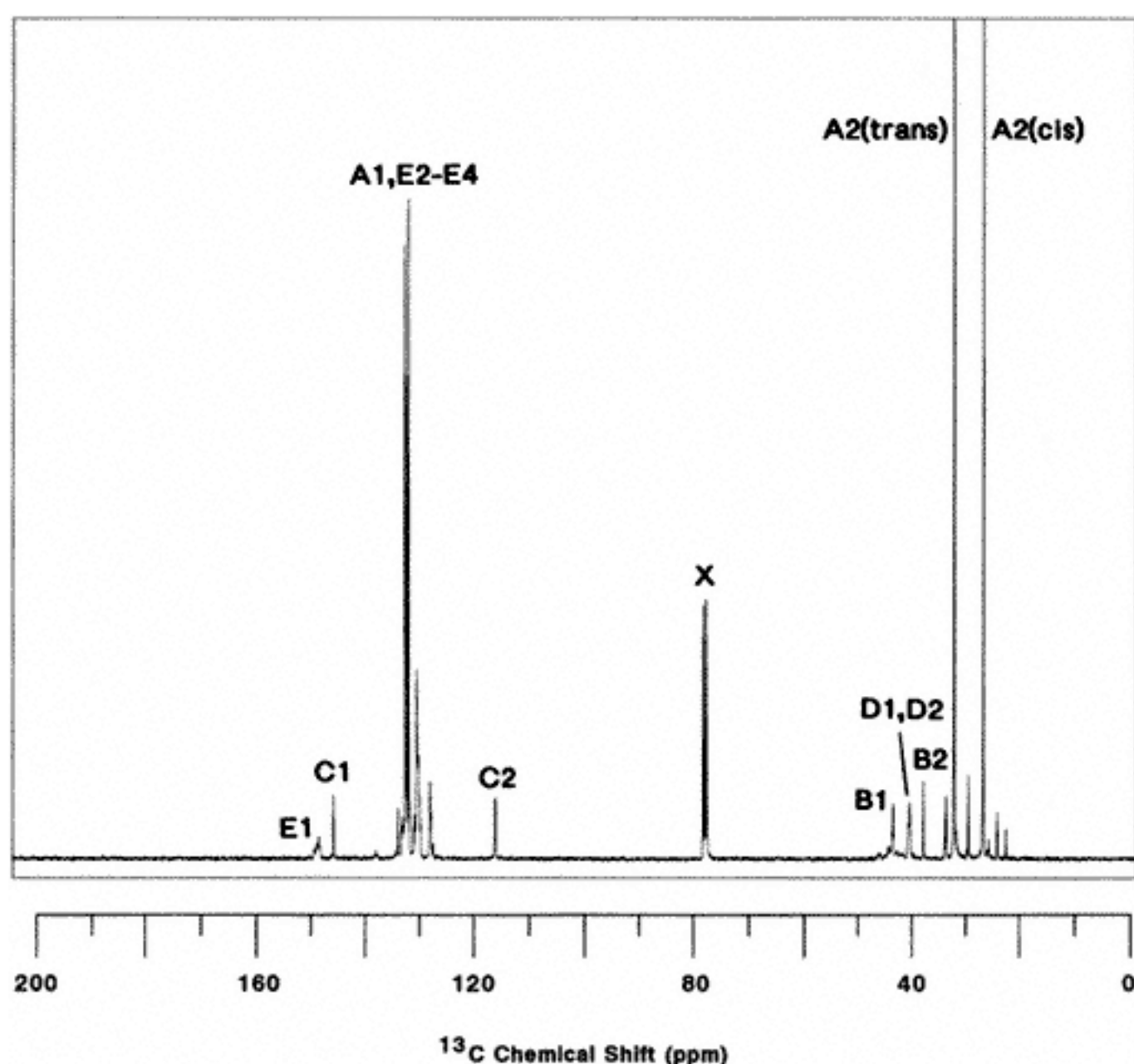
W. D. Vilar, S. M. C. Menezes, L. Akcelrud. *Polym. Bull.* 33:557, 1994.

VI-A-4

VI-A-4— Poly(Styrene-Co-Butadiene), ABA Block

Comments

Also known as Kraton (Shell), Styrolux (BASF), and K-Resin (Phillips). Both *cis*- and *trans*-butadiene isomers predominate, but small amounts of *1,2*-configurations are also observed. Solvent resonances are marked by **X**. These styrene—butadiene block copolymers have a polybutadiene core flanked by polystyrene segments (styrene—butadiene rubbers {VI-A-5}, on the other hand, are random copolymers). Because the relative block lengths are quite long, the styrene—butadiene junctions are small, and the spectrum looks similar to the combination of the spectra of polystyrene {III-A-2} and polybutadiene (VI-A-2) homopolymers. Block copolymers are used in footwear, adhesives, and automobile parts, and are often blended with other resins, such as polypropylene {II-B-1, II-B-2}, polystyrene {III-A-1}, poly(styrene-co-acrylonitrile) {III-A-5}, high-impact polystyrene {III-A-6}, or polycarbonate {VIII-C-1}.



Code	Shift (ppm)
A1	125–132
A2 (<i>cis</i>)	28.1
A2 (<i>trans</i>)	33.1
B1	43.4
B2	38.1
C1	142.6
C2	114.2
D1	41.0
D2	41.0
E1	145.7
E2–E4	125–132

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

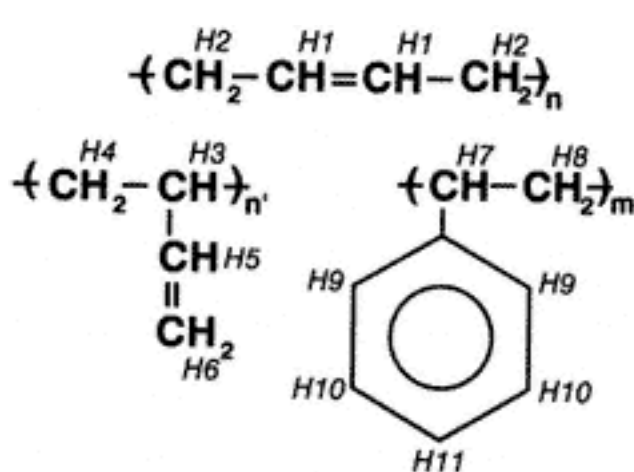
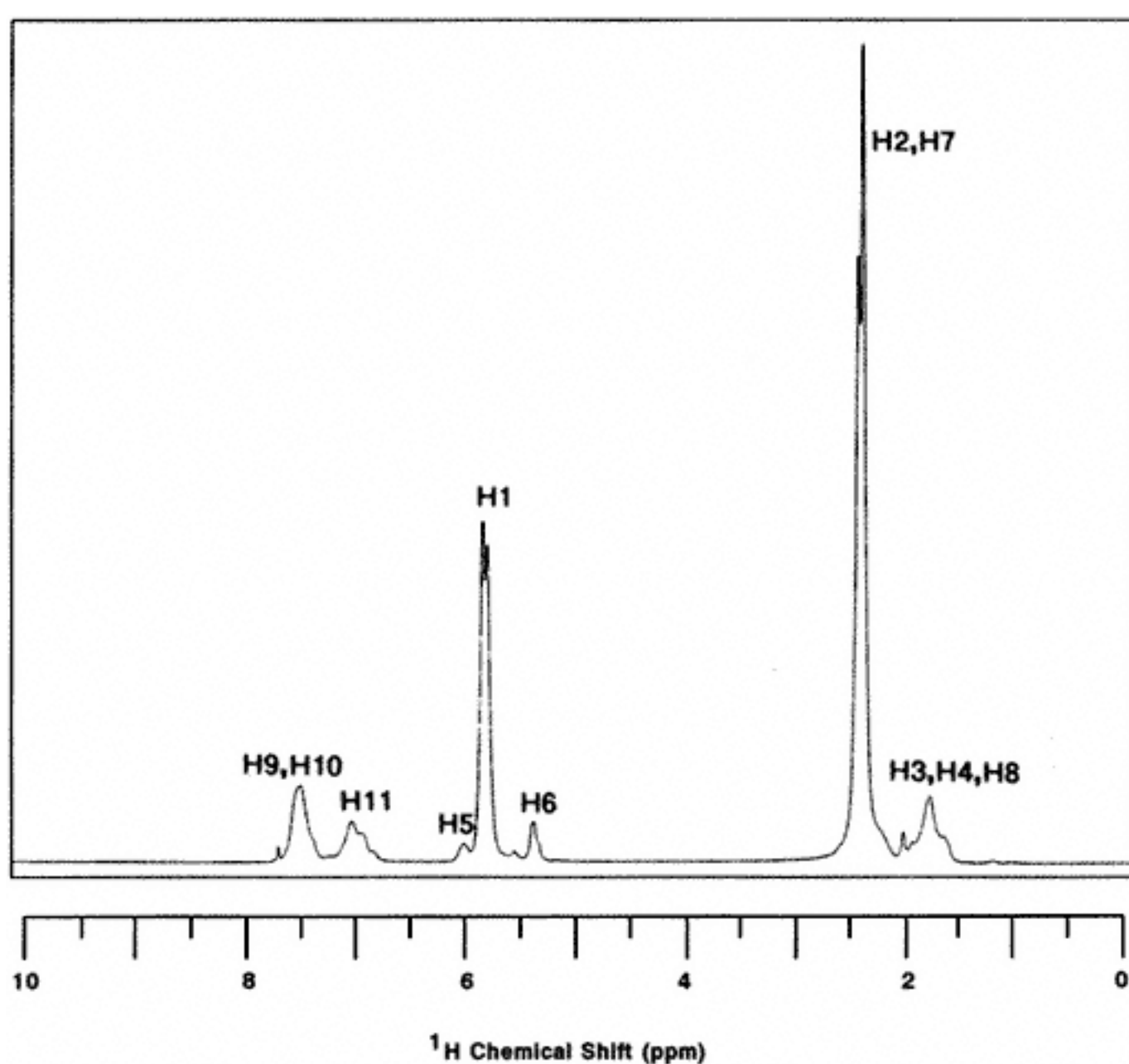
References

H. Sato, T. Ishikawa, K. Takebayashi, and Y. Tanaki. *Macromolecules* 22:1748 (1989); J. Visintainer. *Polym. Bull.* 11:63, 1984; E. Kobayishi, J. Furukawa, M. Ochiai, and T. Tsujimoto. *Eur. Polym. J.* 19:871, 1983.

**VI-A-4H—
Poly(Styrene-Co-Butadiene), ABA Block**

Comments

Also known as Kraton (Shell), Styrolux (BASF), and K-Resin (Phillips). Both *cis*- and *trans*-butadiene isomers predominate, but small amounts of *1,2*-configurations are also observed. These styrene—butadiene block copolymers have a polybutadiene core flanked by polystyrene segments (styrene—butadiene rubbers {VI-A-5H}, on the other hand, are random copolymers). Because the relative block lengths are quite long, the styrene—butadiene junctions are small, and the spectrum looks similar to the combination of the spectra of polystyrene {III-A-2H} and polybutadiene (VI-A-2H) homopolymers. Block copolymers are used in footwear, adhesives, and automobile parts, and they are often blended with other resins, such as polypropylene {II-B-1H}, polystyrene {III-A-1H}, poly(styrene-co-acrylonitrile), high impact-polystyrene {III-A-6H}, or polycarbonate {VIII-C-1H}.



Code	Shift (ppm)
H1	5.8
H2	2.4
H3	1.8
H4	1.8
H5	6.0
H6	5.2
H7	2.4
H8	1.8
H9	7.5
H10	7.5
H11	7.0

Experimental ParametersNucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

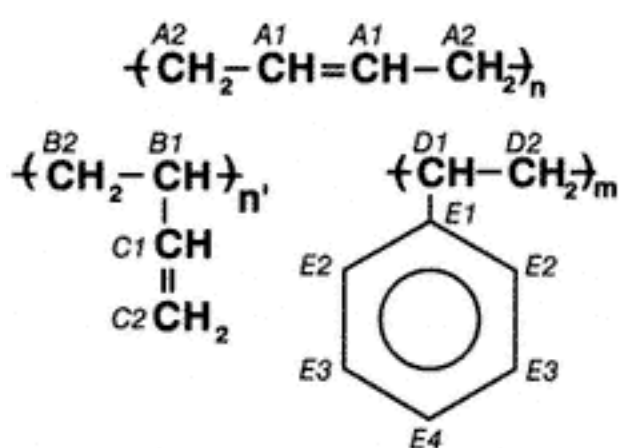
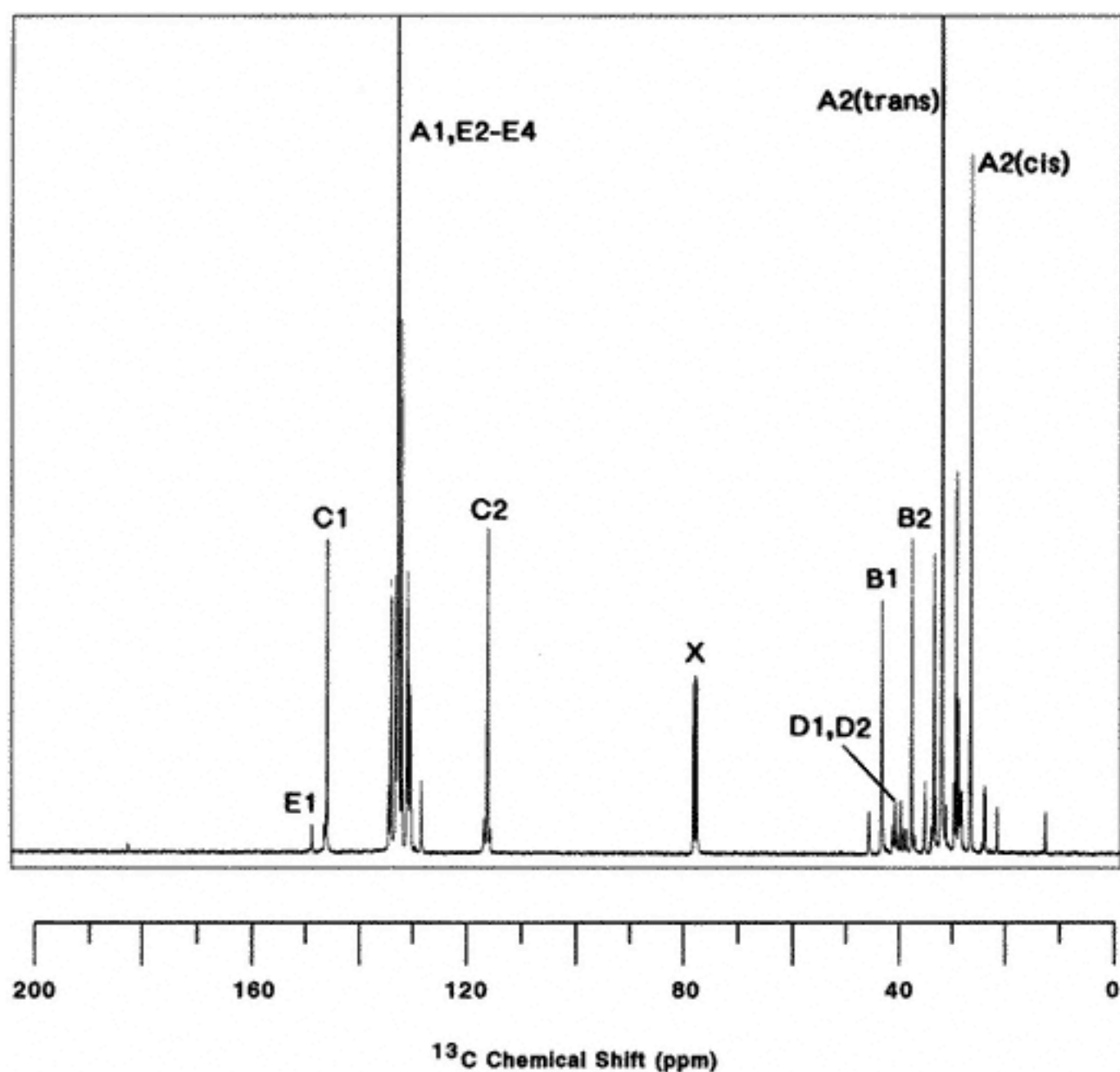
Broadening: 5 Hz

Pulse delay: 5 s

VI-A-5—
Poly(Styrene-Co-Butadiene), Random (SBR)

Comments

Also known as styrene—butadiene rubber (SBR). Both *cis*- and *trans*-butadiene isomers predominate, but small amounts of *1,2*-configurations are also observed. Solvent resonances are marked by **X**. In these random copolymers, monomer sequence effects are quite pronounced because there are no long runs of either styrene or butadiene comonomers. These sequences give rise to the multitude of peaks between 20 and 50 ppm. This is in contrast to styrene—butadiene block copolymers {VI-A-4}. SBR is the most common synthetic elastomer; its most widespread application is in tires. SBR latexes are used for carpet backing, adhesives, and flexible foam.



Code	Shift (ppm)
A1	126–132
A2 (<i>cis</i>)	28.1
A2 (<i>trans</i>)	33.1
B1	43.4
B2	38.1
C1	142.6
C2	114.2
D1	38–42
D2	38–42
E1	146.2
E2–E4	126–132

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

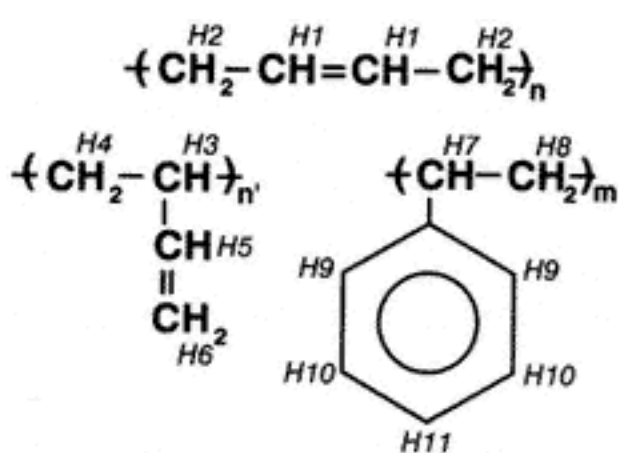
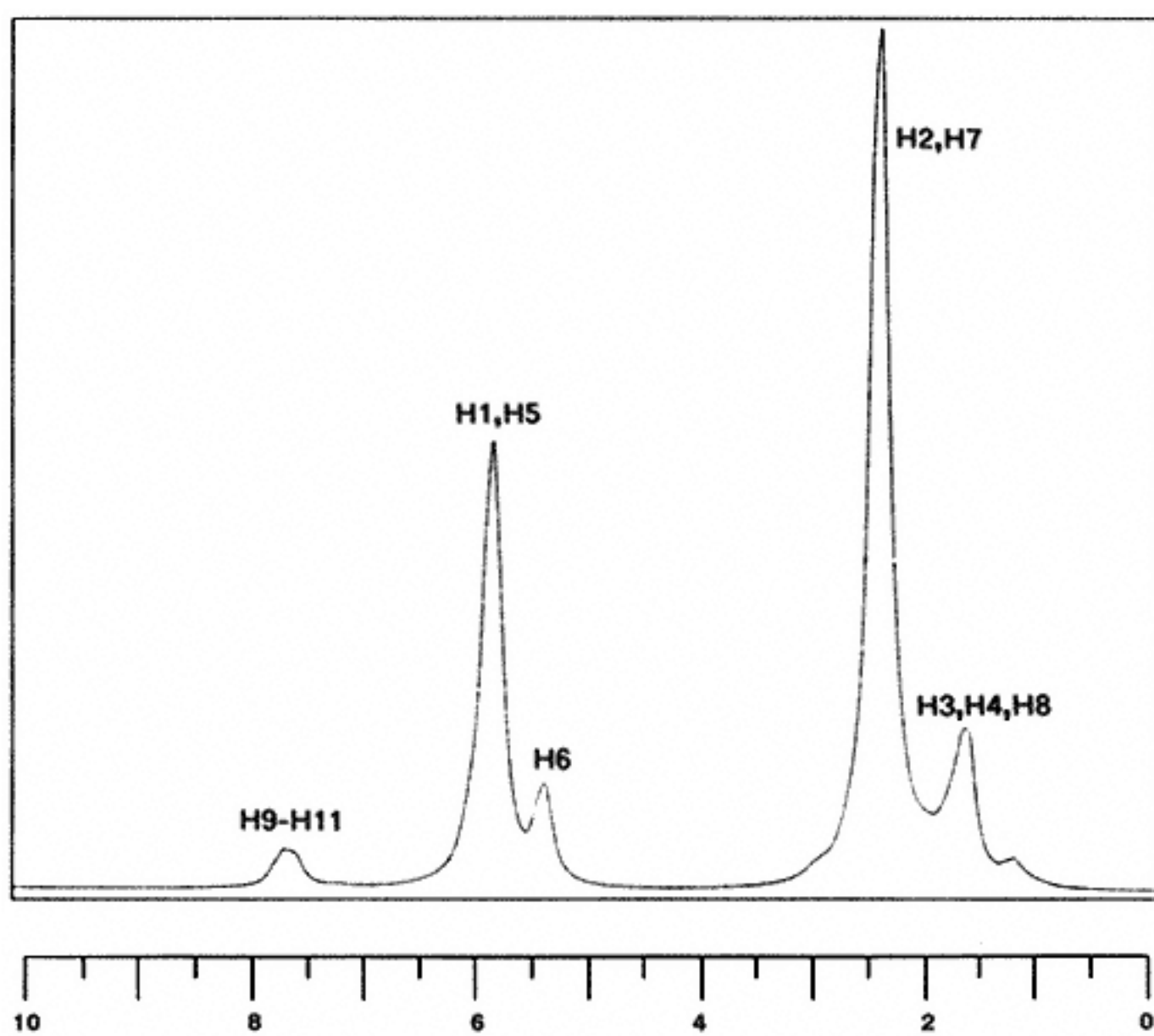
References

H. Sato, T. Ishikawa, K. Takebayashi, and Y. Tanaki. *Macromolecules* 22:1748, 1989; J. Visintainer. *Polym. Bull.* 11:63, 1984; E. Kobayashi, J. Furukawa, M. Ochiai, and T. Tsujimoto. *Eur. Polym. J.* 19:871, 1983.

VI-A-5H—
Poly(Styrene-Co-Butadiene), Random (SBR)

Comments

Also known as styrene—butadiene rubber (SBR). Both *cis*- and *trans*-butadiene isomers predominate, but small amounts of *1,2*-configurations are also observed. In these random copolymers, monomer sequence effects are quite pronounced because there are no long runs of either styrene or butadiene comonomers; this gives rise to peak broadening. This is in contrast to styrene—butadiene block copolymers {VI-A-4H}. SBR is the most common synthetic elastomer; its most widespread application is in tires. SBR latexes are used for carpet backing, adhesives, and flexible foam.



Code	Shift (ppm)
H1	5.8
H2	2.4
H3	1.8
H4	1.8
H5	5.8
H6	5.4
H7	2.4
H8	1.8
H9-H11	7.7

Experimental ParametersNucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

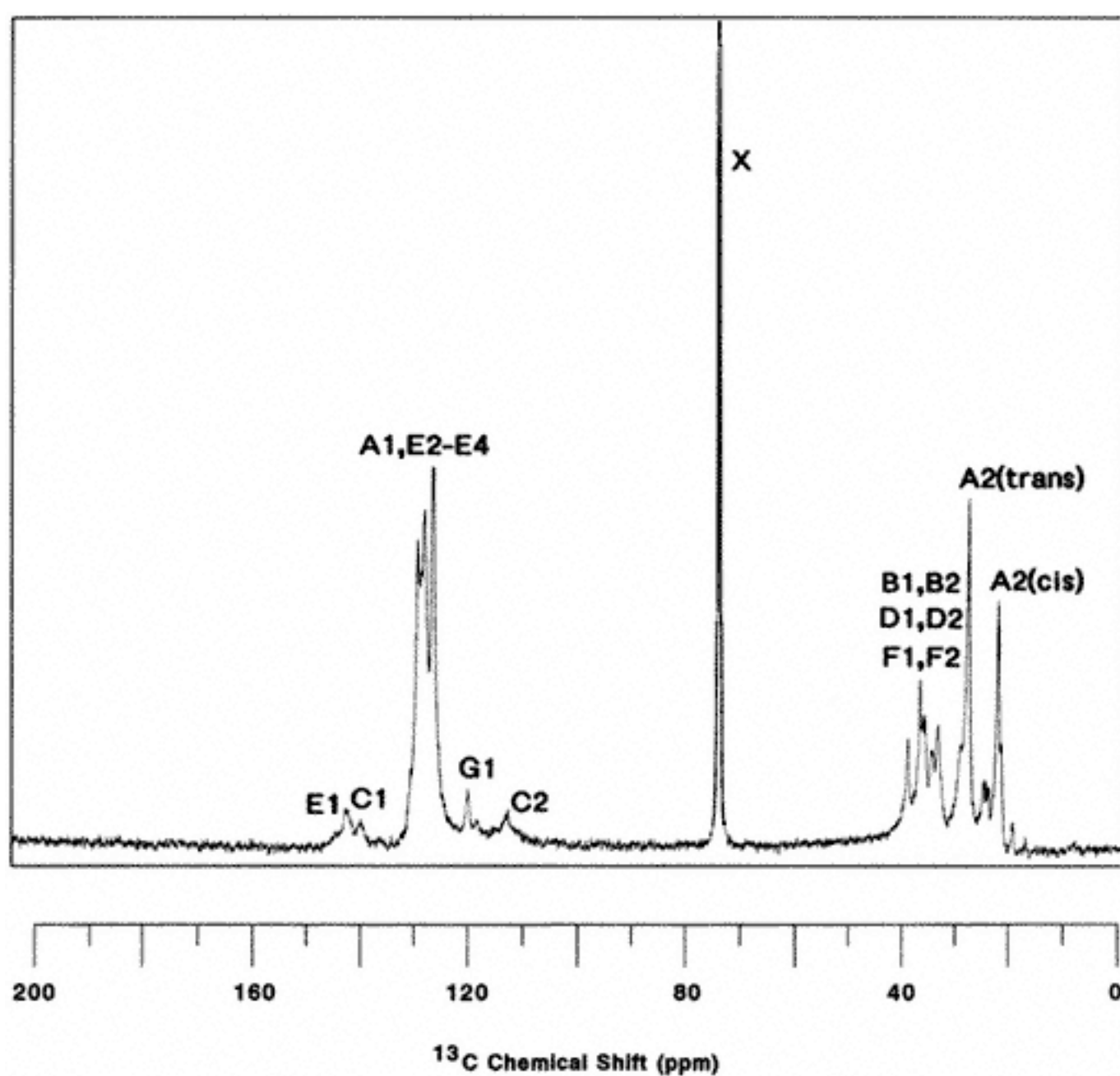
Broadening: 5 Hz

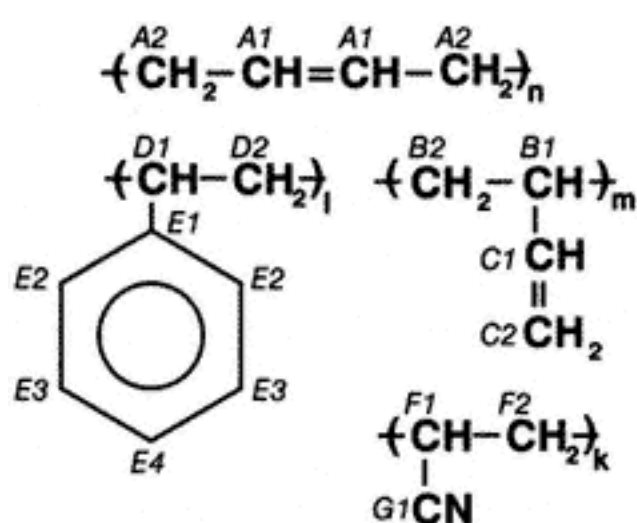
Pulse delay: 5 s

**VI-A-6—
Poly(Acrylonitrile-Co-butadiene-Co-Styrene) (ABS)**

Comments

Both *cis*- and *trans*-butadiene isomers predominate, but small amounts of *1,2*-configurations are also observed. Solvent resonances are marked by **X**. These block copolymers have a polybutadiene or styrene—butadiene rubber {VI-A-5} core flanked by grafted styrene and acrylonitrile segments. Comonomer levels and molecular weights can vary in these materials. A fourth component, such as α -methylstyrene, methyl methacrylate, or maleic anhydride, is sometimes included in the copolymer. Poly(vinyl chloride) {VI-A-8} or chlorinated polyethylene {I-A-5} may be blended with ABS to improve its flame retardancy. ABS is classified as an "engineering resin," and it is used for appliance housings and interiors, pipes and fittings, doors, seating, and luggage.





Code	Shift (ppm)
A1	126–131
A2 (<i>cis</i>)	28.1
A2 (<i>trans</i>)	33.1
B1	38–46
B2	38–46
C1	142.6
C2	114.2
D1	38–46
D2	38–46
E1	142.9
E2	126–131
E3	126–131
E4	126–131
F1	38–46
F2	38–46
G1	120.7

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

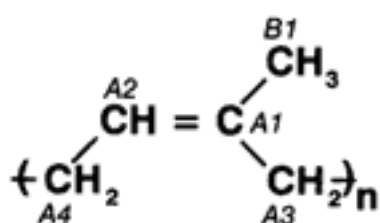
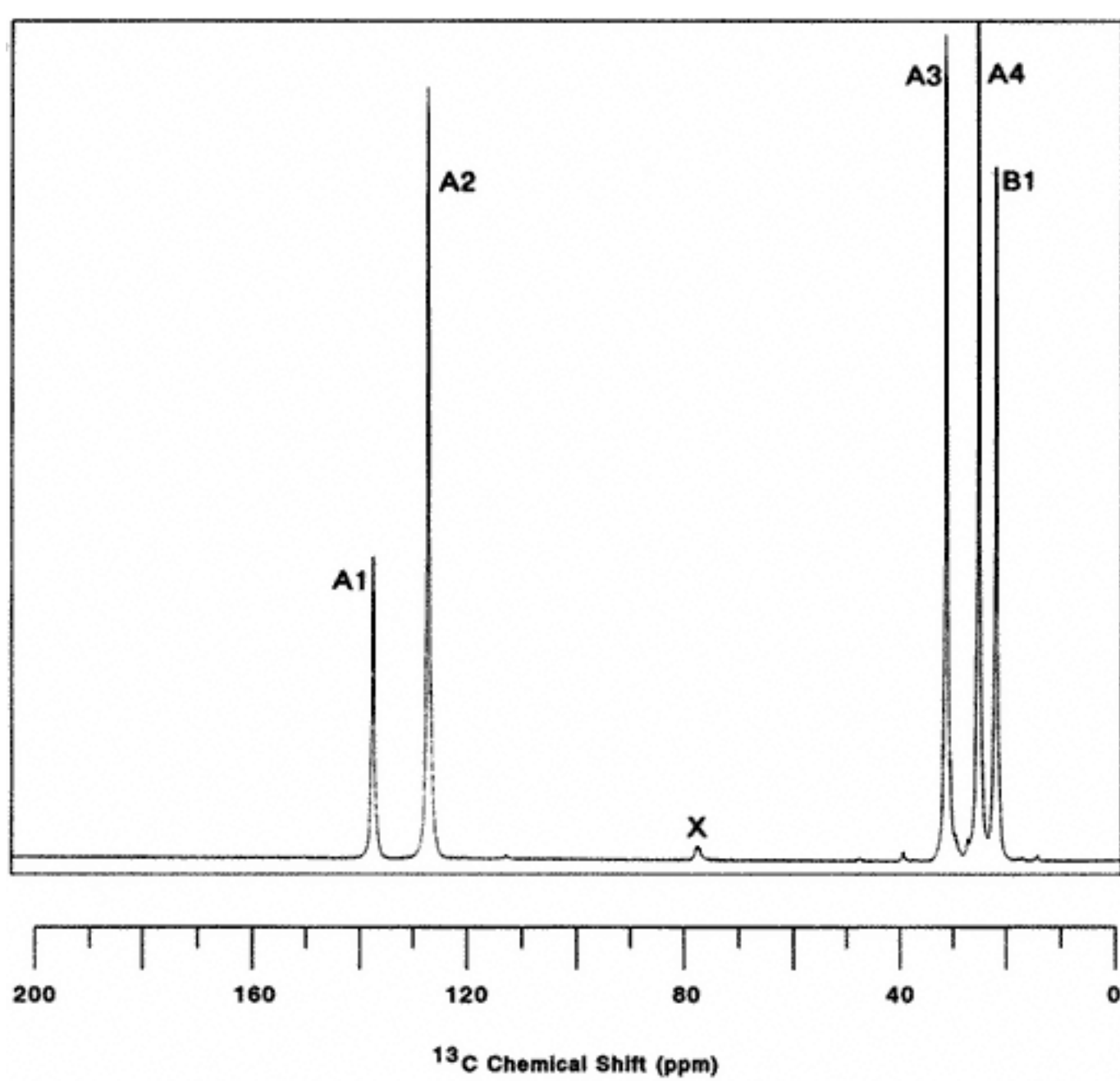
Broadening: 2 Hz

Pulse delay: 2 s

VI-B-1— Polyisoprene (Cis) (c-PI)

Comments

cis-Polyisoprene is the predominant isomer {compare with VI-B-2}. Solvent resonances are marked by **X**. *cis*-Polyisoprene is a synthetic elastomer that is identical with the most common form of natural rubber (*hevea*). Similar to most rubbers, polyisoprene is primarily used to manufacture tires and footwear; it is also found in sporting goods and sealants, such as caulk.



Code	Shift (ppm)
A1	135.0
A2	125.6
A3	32.2
A4	26.4
B1	22.9

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

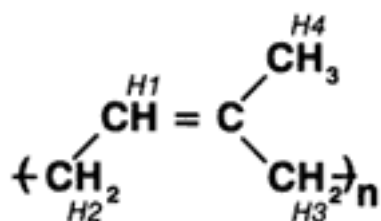
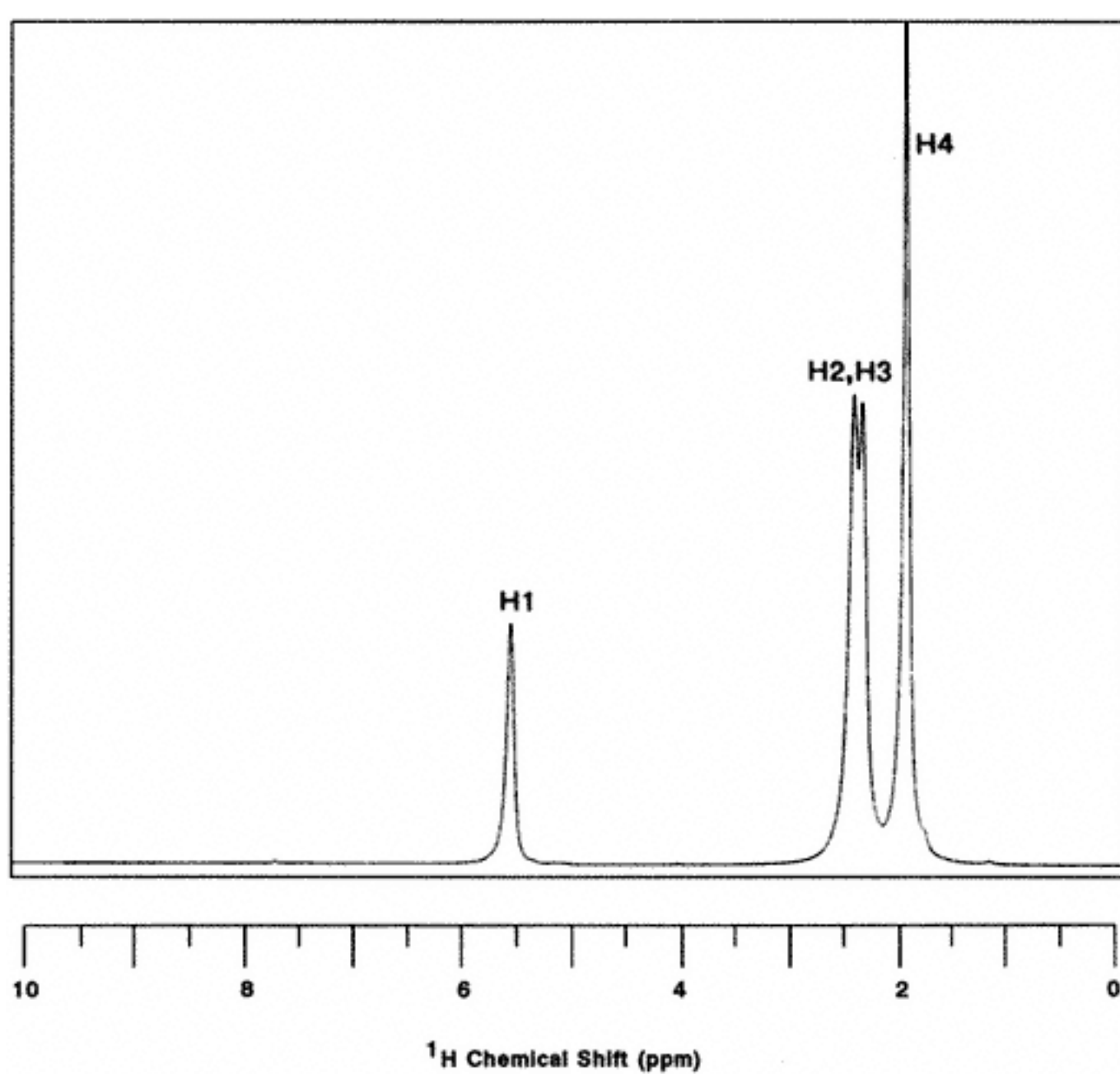
Reference

Y. Tanaka. *J. Appl. Polym. Sci. Appl. Polym. Symp.* 44:1, 1989.

**VI-B-1H—
Polyisoprene (Cis) (c-PI)**

Comments

cis-Polyisoprene is the predominant isomer {compare with VI-B-2H}. *cis*-Polyisoprene is a synthetic elastomer that is identical with the most common form of natural rubber (*hevea*). Similar to most rubbers, polyisoprene is primarily used to manufacture tires and footwear; it is also found in sporting goods and sealants, such as caulk.



CODE	Shift (ppm)
H1	5.5
H2	2.5
H3	2.5
H4	2.0

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

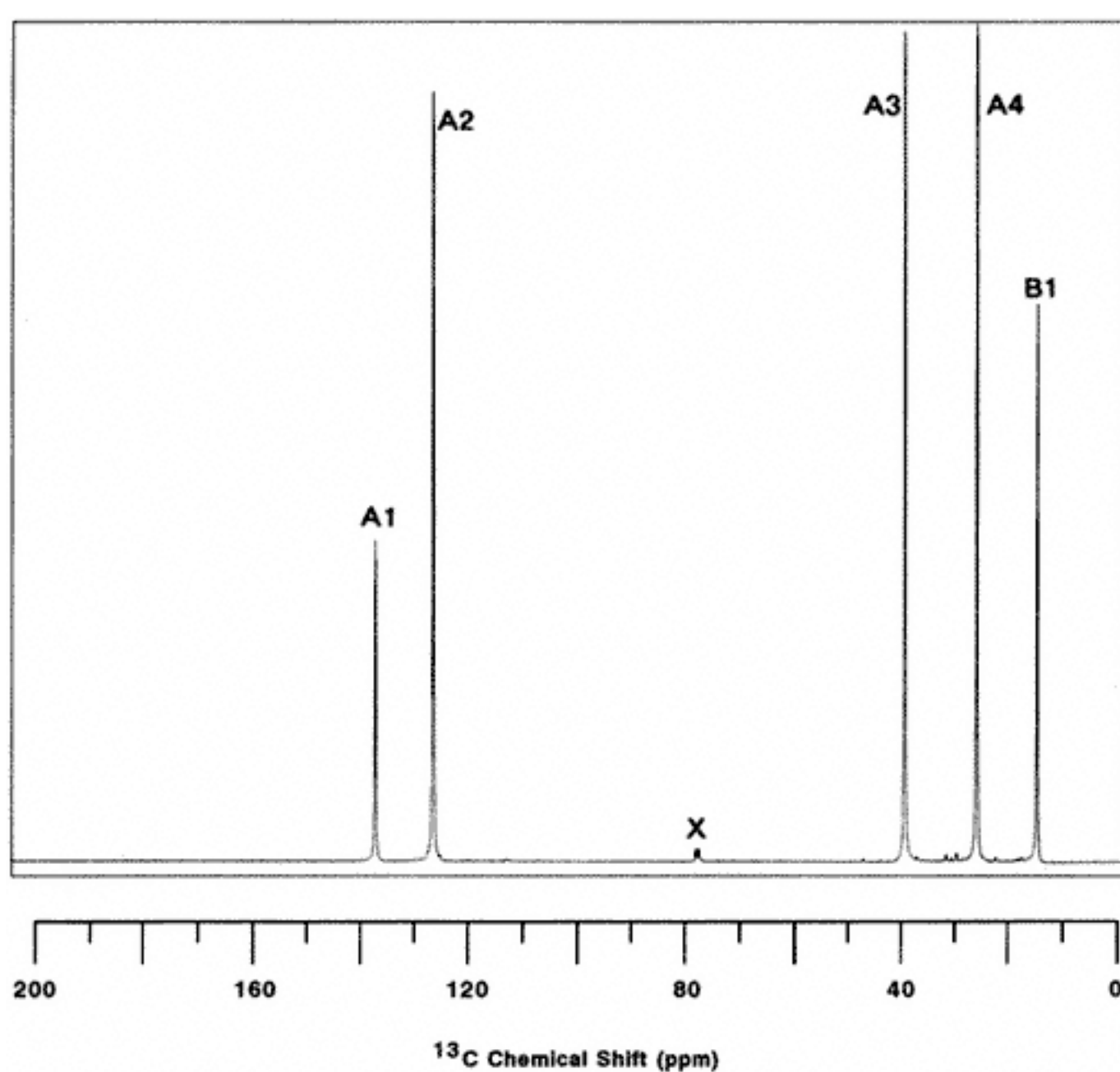
Pulse delay: 5 s

VI-B-2—

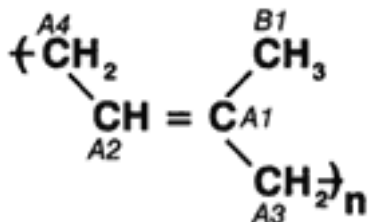
Polyisoprene (Trans) (t-PI)

Comments

trans-Polyisoprene is the predominant isomer {compare with VI-B-I}. Solvent resonances are marked by **X**. *trans*-Polyisoprene is a synthetic elastomer that is nearly identical with the natural rubber *balata* or *gutta percha*. Similar to most rubbers, polyisoprene is primarily used to manufacture tires and footwear; it is also found in sporting goods and sealants, such as caulk.



^{13}C Chemical Shift (ppm)



Code	Shift (ppm)
A1	134.9
A2	124.5
A3	39.9
A4	26.9
B1	16.0

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Datapoints: 32768

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

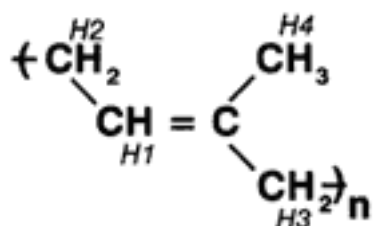
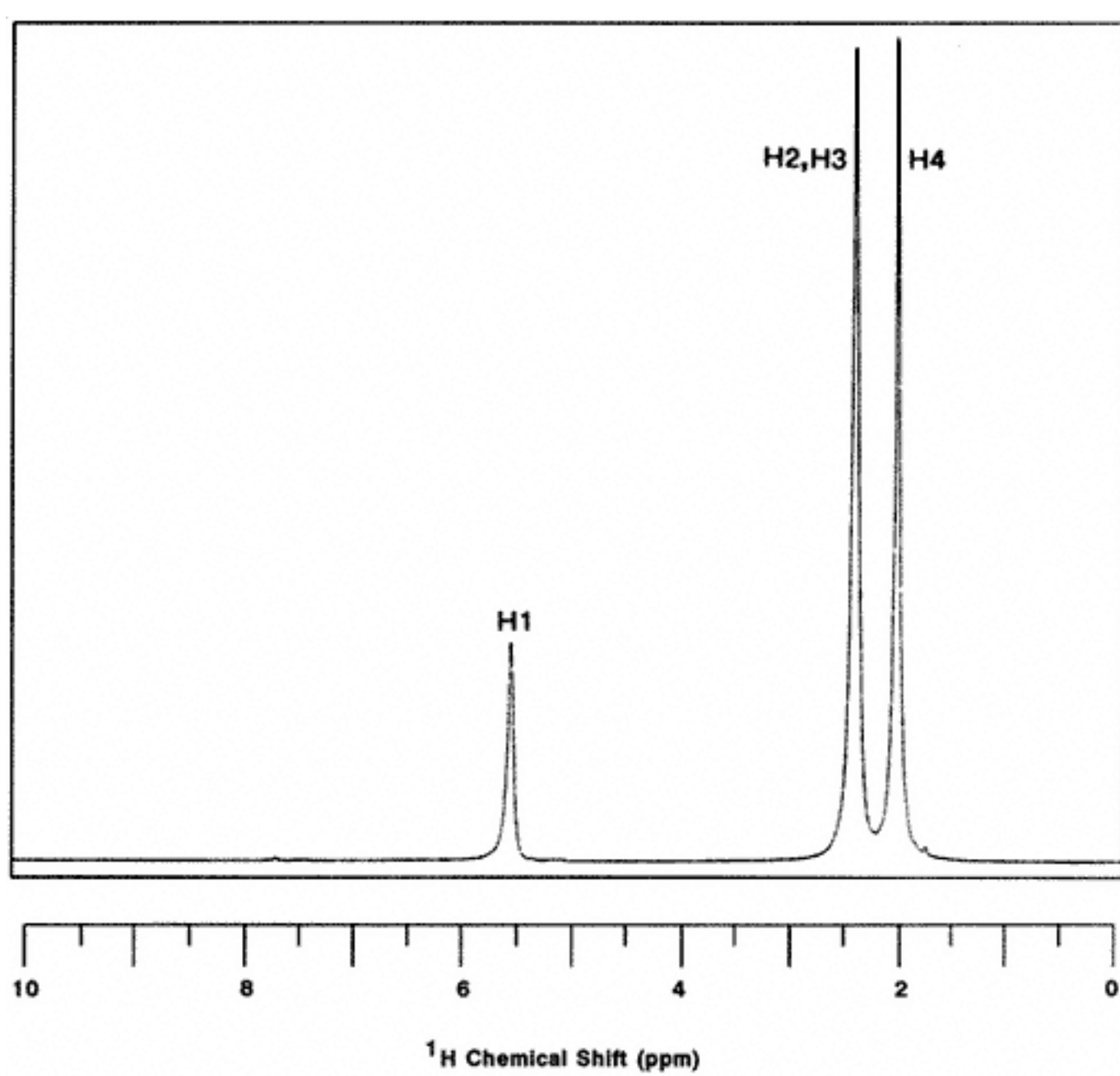
Reference

Y. Tanaka. *J. Appl. Polym. Sci. Appl. Polym. Symp.* 44:1, 1989.

VI-B-2H—
Polyisoprene (Trans) (t-PI)

Comments

trans-Polyisoprene is the predominant isomer {compare with VI-B-1H}. *trans*-Polyisoprene is a synthetic elastomer that is nearly identical with the natural rubber *balata* or *gutta percha*. Like most rubbers, polyisoprene is primarily used to manufacture tires and footwear; it is also found in sporting goods and sealants, such as caulk.



Code	Shift (ppm)
H1	5.5
H2	2.4–2.5
H3	2.4–2.5
H4	1.9

Experimental Parameters

Nucleus: ¹H (400 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

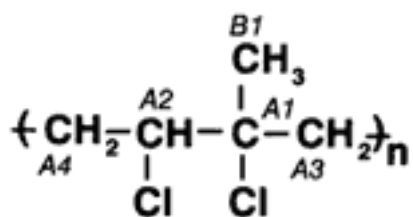
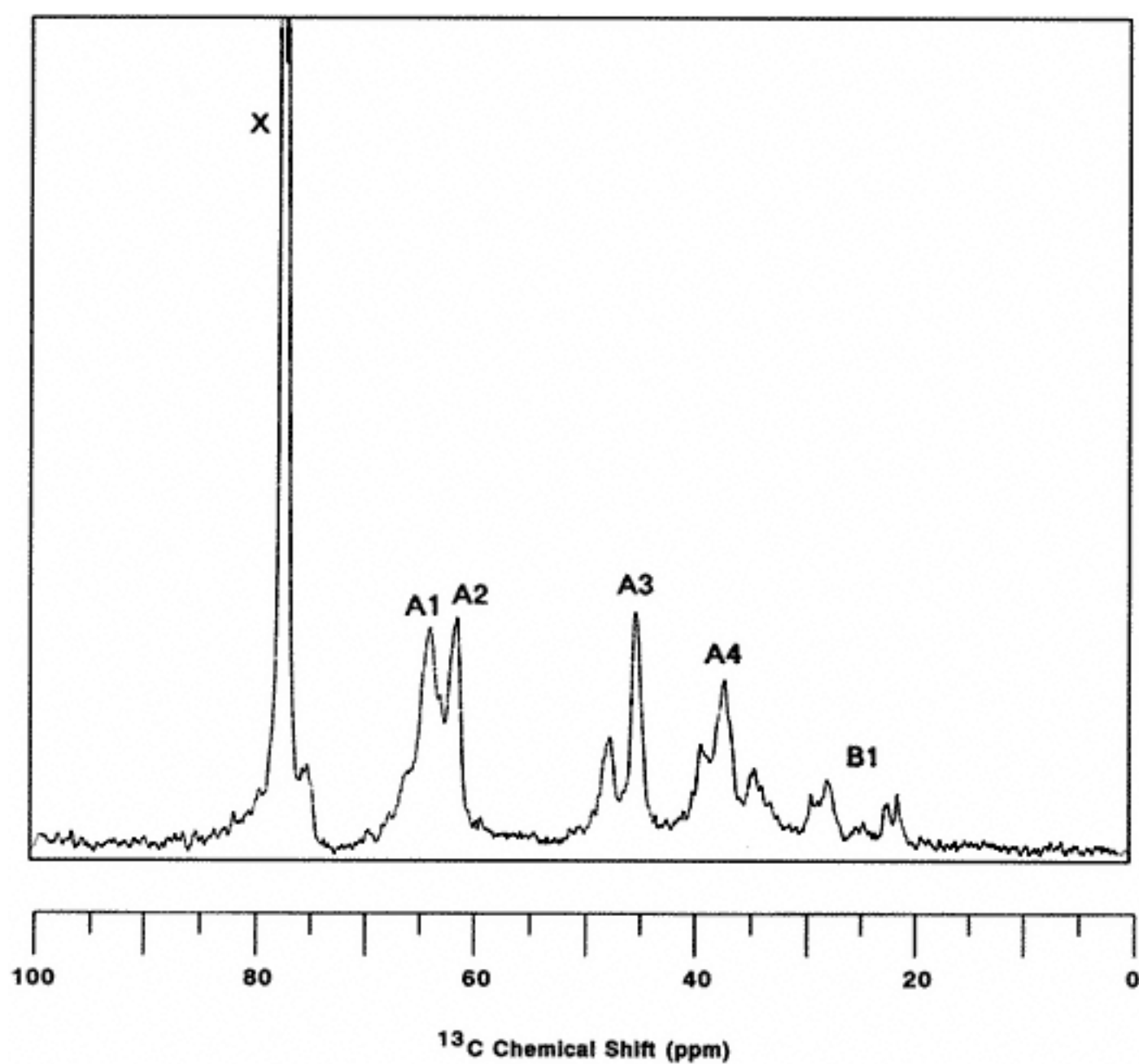
Broadening: 5 Hz

Pulse delay: 5 s

**VI-B-3—
Polyisoprene, Chlorinated**

Comments

Chlorination of polyisoprene {VI-B-1, VI-B-2} removes virtually all unsaturation. Solvent resonances are marked by **X**. Chlorinated rubber is used in heat- and chemical-resistant coatings.



Code	Shift (ppm)
A1	63.6
A2	61.3
A3	45–48
A4	34–39
B1	21–28

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 5% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

Reference

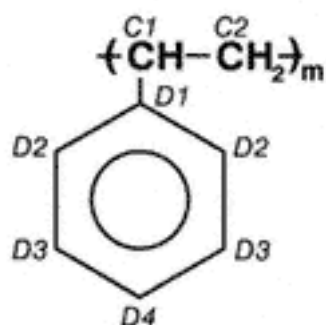
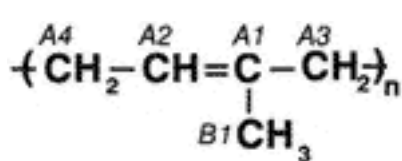
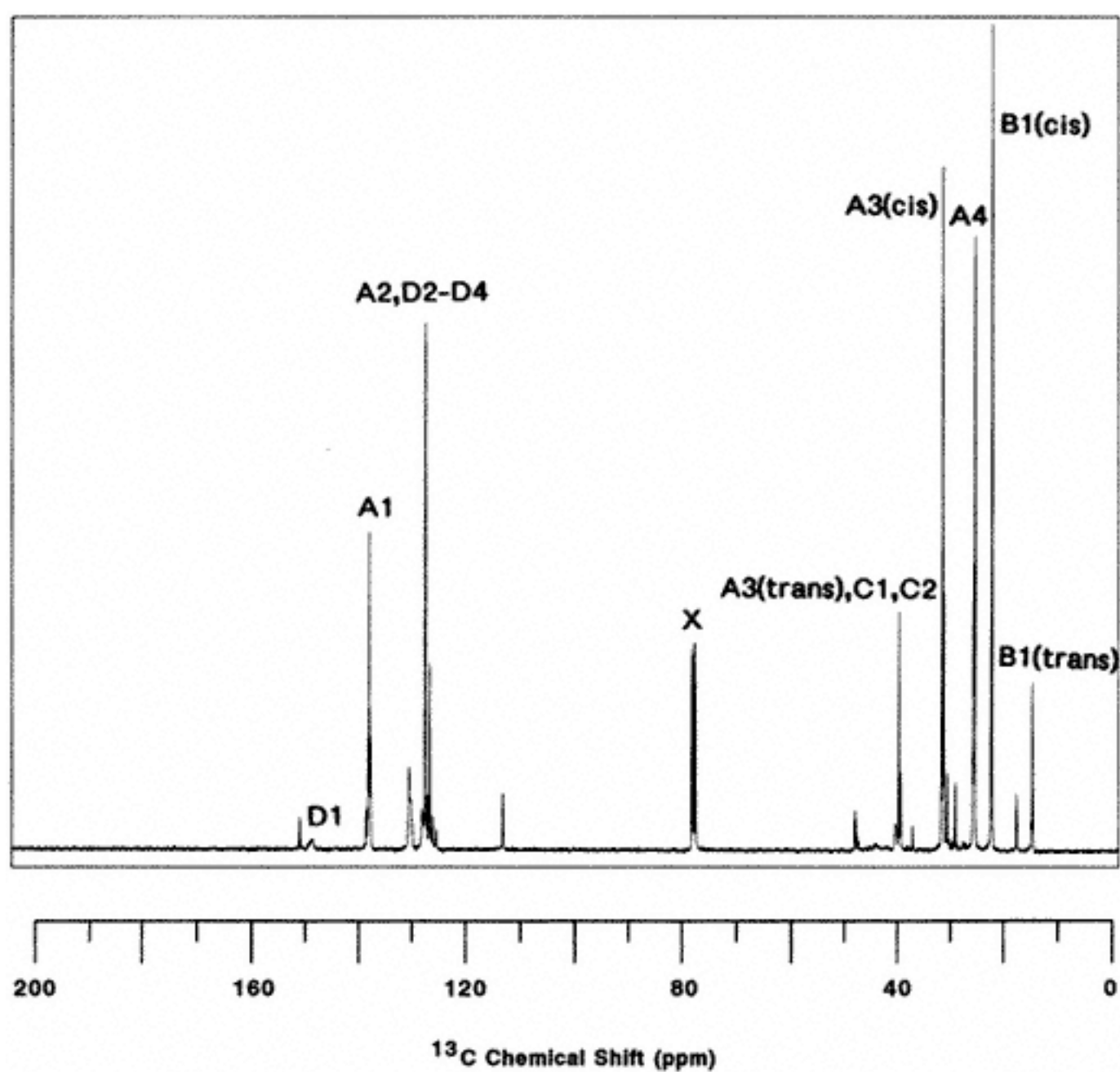
M. V. Eskina, A. S. Khachaturov, L. B. Krentsel, and A. D. Litmanovich. *Eur. Polym. J.* 26:181, 1990.

VI-B-4

**VI-B-4—
Poly(Styrene-Co-Isoprene), Block**

Comments

Both *cis*- and *trans*-isomers predominate. Solvent resonances are marked by **X**. These block copolymers have a polyisoprene core flanked by polystyrene segments. Because the relative block lengths are quite long, the styrene-isoprene junctions are rare, and the spectrum looks similar to the combination of the spectra of polystyrene {III-A-2} and polyisoprene {VI-B-1, VI-B-2} homopolymers. These materials are used in footwear, adhesives, and automobile parts, and are often blended with other resins, such as polypropylene {II-B-1, II-B-2}, polystyrene {III-A-1}, poly(styrene-co-acrylonitrile) {III-A-5}, high-impact polystyrene {III-A-6}, or polycarbonate {VIII-C-1}.



Code	Shift (ppm)
A1	135.7
A2	122–128
A3 (<i>cis</i>)	32.8
A3 (<i>trans</i>)	40.1
A4	27.0
B1 (<i>cis</i>)	23.7
B1 (<i>trans</i>)	15.7
C1	40.1
C2	40.1
D1	147.9
D2–D4	122–128

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

Broadening: 2 Hz

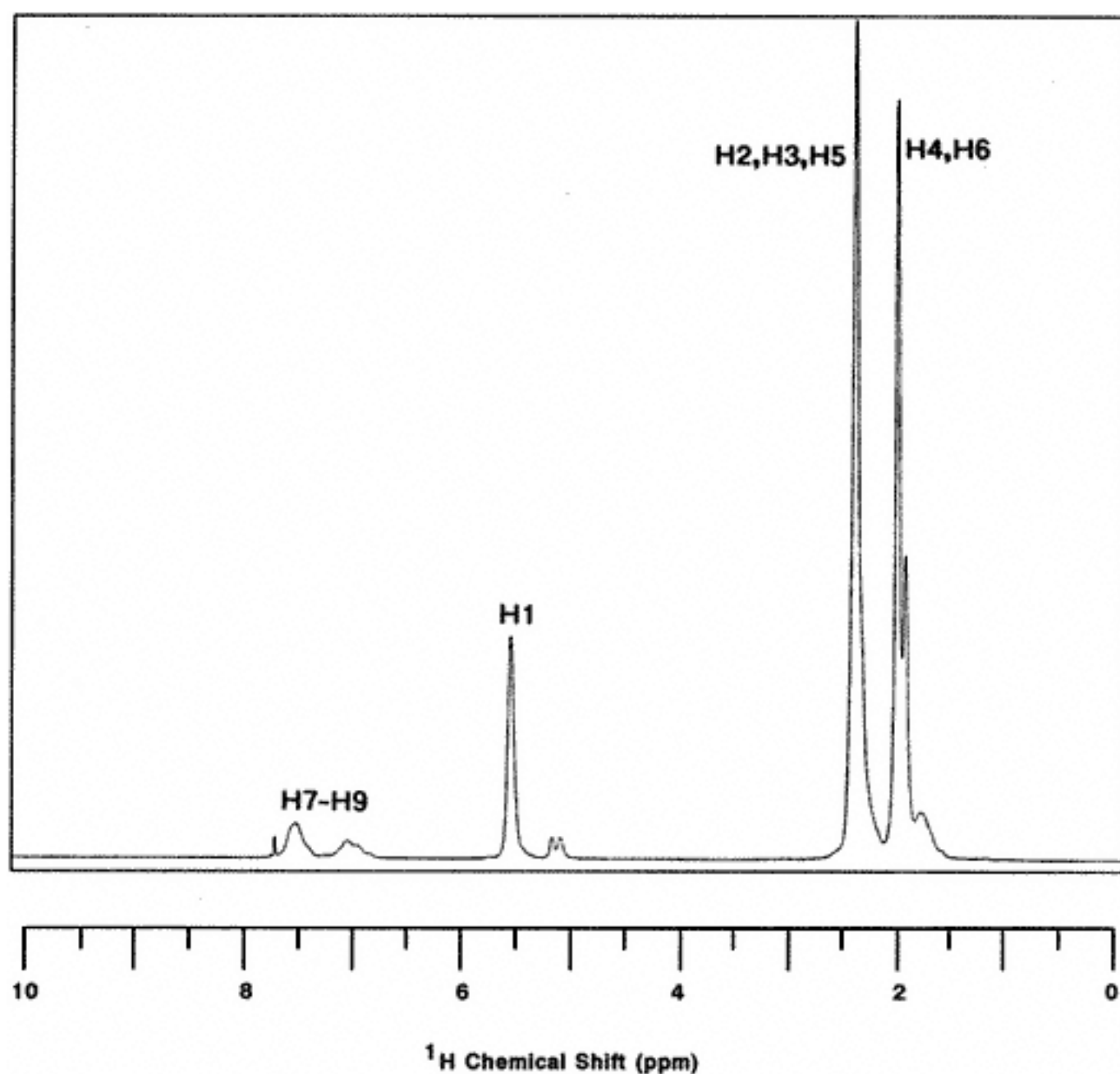
Pulse delay: 2 s

ReferenceC. Pellecchia, A. Proto, and A. Zambelli. *Macromolecules* 25:4450, 1992.

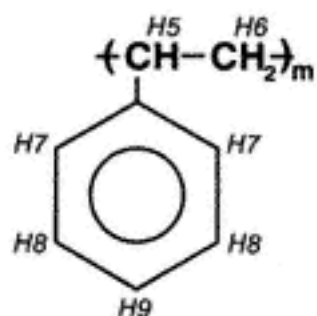
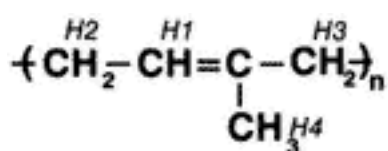
**VI-B-4H—
Poly(Styrene-Co-Isoprene), Block**

Comments

Both *cis*- and *trans*-isomers predominate. These block copolymers have a polyisoprene core flanked by polystyrene segments. Because the relative block lengths are quite long, the styrene-isoprene junctions are rare, and the spectrum looks similar to the combination of the spectra of polystyrene {III-A-2H} and polyisoprene {VI-B-1H, VI-B-2H} homopolymers. These materials are used in footwear, adhesives, and automobile parts, and are often blended with other resins, such as polypropylene {II-B-1H}, polystyrene {III-A-1H}, poly(styrene-co-acrylonitrile), high-impact polystyrene {III-A-6H}, or polycarbonate.



¹H Chemical Shift (ppm)



Code	Shift (ppm)
H1	5.5
H2	2.5
H3	2.5
H4	2.1
H5	2.5
H6	2.1
H7-H9	7.0-7.5

Experimental ParametersNucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

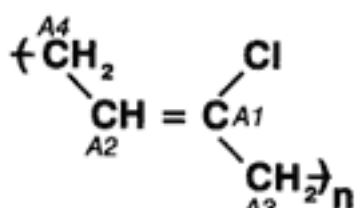
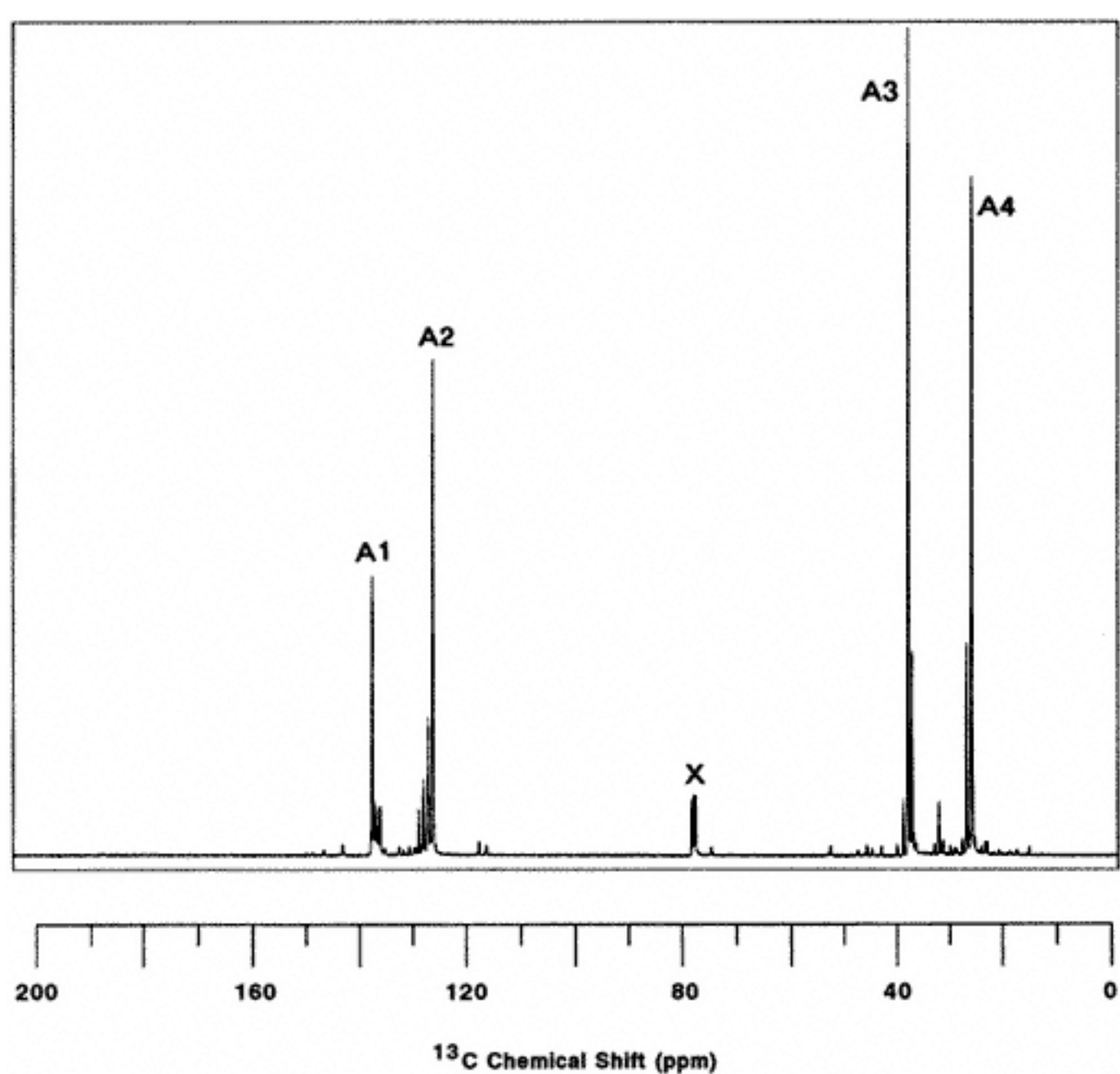
Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

**VI-B-5—
Polychloroprene (Trans)****Comments**

Also known as Neoprene (DuPont), *trans*-polychloroprene is the predominant isomer. Solvent resonances are marked by X. Polychloroprene is a synthetic material that has elastomeric properties similar to those of natural rubber. Its resistance to chemical attack, however, is much greater. The main uses of polychloroprene are in foam, industrial, automotive, and construction applications.



Code	Shift (ppm)
A1	135.4
A2	124.5
A3	38.7
A4	27.0

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 32768

Pulse width: 90°

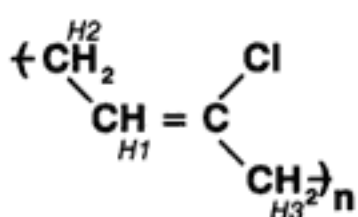
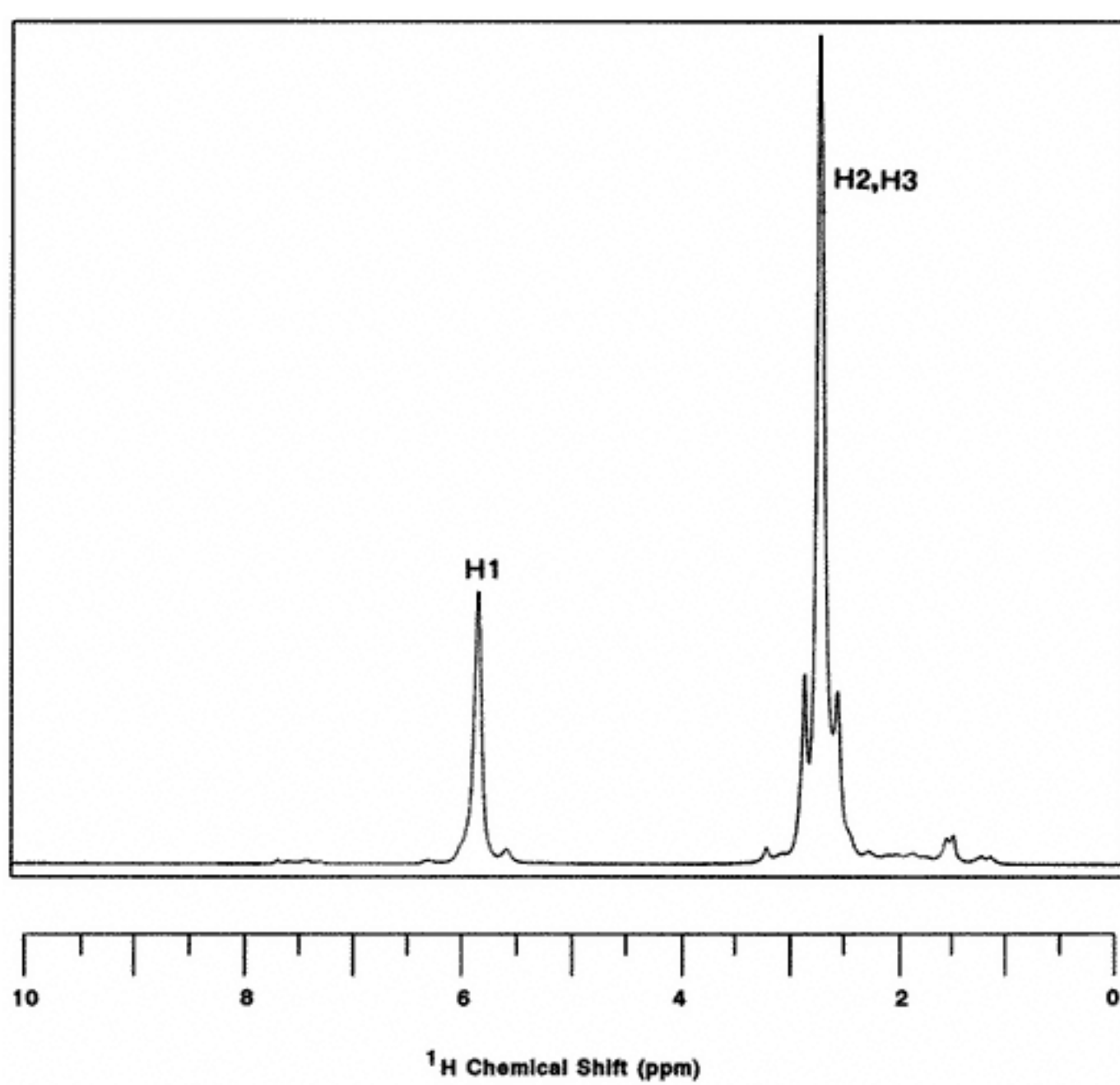
Broadening: 2 Hz

Pulse delay: 2 s

**VI-B-5H—
Polychloroprene (Trans)**

Comments

Also known as Neoprene (DuPont), *trans*-polychloroprene is the predominant isomer. Polychloroprene is a synthetic material that has elastomeric properties similar to those of natural rubber. Its resistance to chemical attack, however, is much greater. The main uses of polychloroprene are in foam, industrial, automotive, and construction applications.



Code	Shift (ppm)
H1	5.8
H2	2.8
H3	2.8

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 30% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

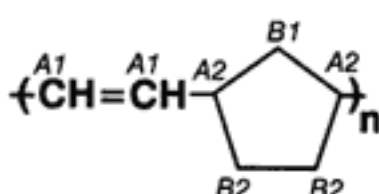
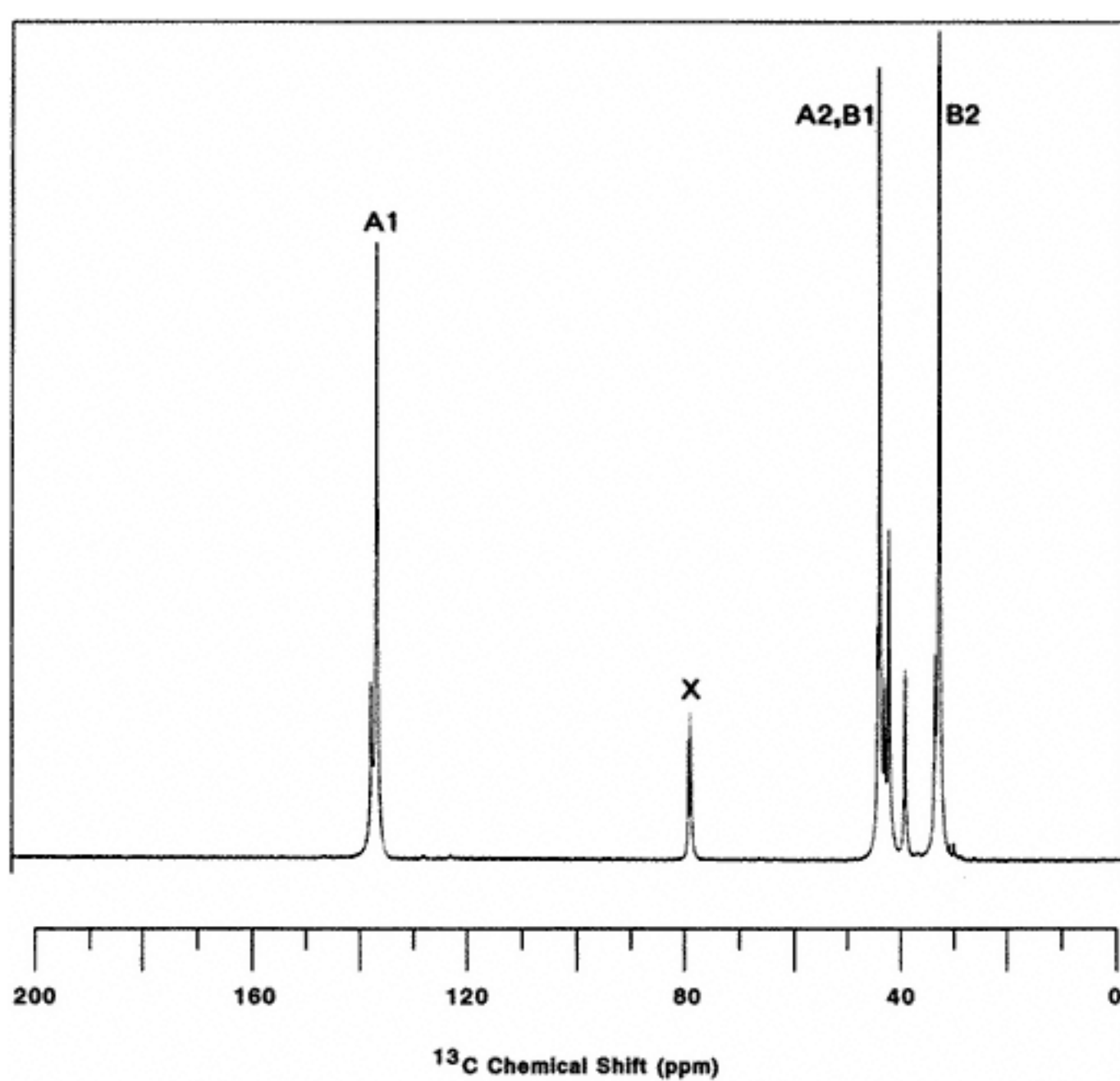
Broadening: 5 Hz

Pulse delay: 5 s

VI-B-6— Polynorbornene (PNB)

Comments

The spectrum is complicated by the existence of *cis*- and *trans*-configurations about the double bond and through the cyclopentyl ring. The predominant forms are *cis-cis*. Solvent resonances are marked by **X**. PNB is a relatively new material formed by ring-opening metathesis polymerization (ROMP). It is an elastomer used in automotive applications.



Code	Shift (ppm)
A1	133.5
A2	44.1
B1	41.8
B2	33.4

Experimental Parameters

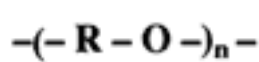
Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 30% w/w
Scans: 800	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 2 s

References

J. A. Johnston, M. Tokles, G. S. Havatny, P. L. Rinaldi, and M. F. Farona. *Macromolecules* 24:5532, 1991; C. Mehler and W. Risse. *Makromol. Chem. Rapid Commun.* 12:255, 1991.

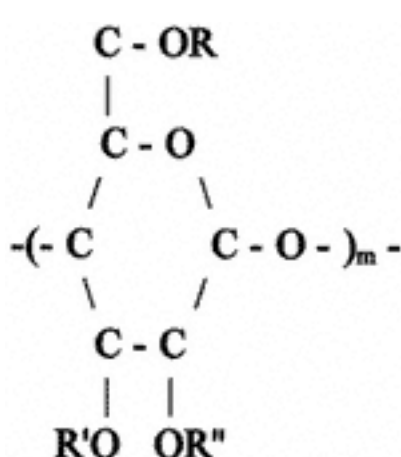
VII— Ether Backbones

Polymers in this group have ether linkages in the chain backbone:



A

They may be linear *polyethers*, in which R is either aliphatic or aromatic; or *polysaccharides*, in which the R group is a six-membered, oxygen-containing ring with pendant groups:



B

Linear polyethers are synthetic polymers. Polysaccharides, such as cellulose and its derivatives, are produced from natural materials.

The simplest alkyl polyether is polyoxymethylene (POM) {VII-A-1}, generically known as polyacetal, in which the R (in Structure A) is a methylene group. POM is an engineering resin used in appliance housings and electronics, building, and transportation system components; over 345 million lb (156.5 million kg) were produced in the United States in 1996 [1]. Other common alkyl polyethers include poly(ethylene glycol) (PEG) {VII-A-3 through VII-A-5} and poly(propylene glycol) (PPG) {VII-A-6 and VII-A-7}, for which R = CH₂—CH₂ and CH(CH₃)—CH₂, respectively. These water-soluble polymers are both hydroxyl-terminated. They are used as water thickeners, plasticizers, surfactants, lubricants, or polymer additives, and are often incorporated into more complex materials, such as polyurethanes {IX-B-1 through IX-B-4} [2].

One frequently encountered aromatic polyether is poly(2,6-dimethyl phenylene oxide) (PPO) {VII-A-10}, which forms one component of General Electric's Noryl class of materials. Noryls are blends of PPO with nylon {VIII-C-1 through VIII-C-8}, polystyrene {III-A-2}, or high-impact polystyrene {III-A-6}. Their excellent impact properties make them useful for appliance housings and automobile parts; 240 million lb (108.9 million kg) of PPO were produced in 1996 [1]. Epoxy resins are also polyethers, usually aromatic [2]. Their applications include adhesives, coatings, and composite materials.

Some of the oldest synthetic materials are derived from cellulose. Celluloid (a mixture of camphor and cellulose nitrate {VII-B-8}) was patented in 1870; it was originally developed as a replacement for ivory, particularly for the production of billiard balls [3]. However, its unfortunate tendency to explode on impact limited its usefulness for this application, and it was replaced by more suitable materials as they became available. Cellulose triacetate {VII-B-6}, also called acetate rayon, was touted as an artificial silk at the Paris Exposition in 1891 [3]. Today, cellulosic polymers are found in electrical components, appliance housings, films, and tapes. Common materials in this group are: (1) cellulose ethers, such as methyl cellulose {VII-B-1}; (2) organic esters of cellulose, such as cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose triacetate {VII-B-6}; and (3) inorganic esters of cellulose, such as cellulose nitrate {VII-B-8} and cellulose sulfate {VII-B-9}. Cornstarch is another polysaccharide; it is often added to synthetic polymers to enhance their biodegradability.

VII.A— Sample Preparation and Spectral Acquisition

Most of the linear polyethers are soluble in common organic solvents, such as chloroform [4]. One exception is polyoxymethylene, which dissolves in dimethylformamide (DMF). Hydroxyl-terminated polyethers, such as PEG and PPG, are water-soluble. Solutions of polystyrene-containing PPO blends (one type of Noryl) may be prepared with chloroform. For nylon-containing Noryl alloys, a solvent that dissolves both components, such as cresol, must be used. The solubility of cellulose derivatives varies; many will dissolve or swell in water, chloroform, or acetone.

Quantitative ^{13}C peak areas for most carbons in polyethers and polysaccharides can be achieved with a 90° pulse, 15-s pulse (relaxation) delay, and gating of the ^1H decoupling to suppress nuclear Overhauser effects (NOEs). Appropriate conditions for quantitative ^1H spectra are a 5-s pulse delay following a 90° pulse.

VII.B— Spectral Features

Resonances of ether carbons (C—C—O) appear at chemical shifts between 50 and 90 ppm [5.]; protons on such carbons, between 3 and 5 ppm. Table VII-1 summarizes the ^{13}C chemical shifts for several common polyethers. Polysaccharides contain a O—C—O linkage, which gives rise to a peak close to 100 ppm. Modified cellulosic materials exhibit additional resonances attributable to the specific functional group that has been introduced [5].

VII.B.1— Linear Polyethers

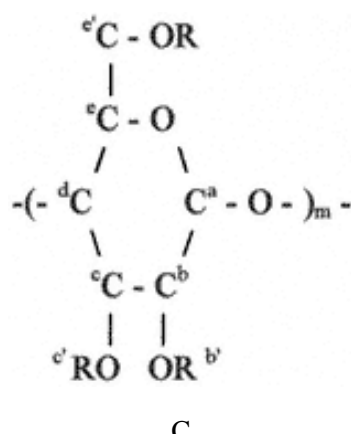
The high molecular weight (MW) forms of linear, nonaromatic polyethers {VII-A-1 through VII-A-9} exhibit very simple ^{13}C and ^1H spectra. The chemical shifts in these spectra are similar to those observed for poly(vinyl ethers), such as poly(vinyl methyl ether) {V-B-4}. Polyether spectra do not exhibit tacticity effects, however. When the molecular weight of a polyether is relatively low, the end-group resonances become visible, as in the MW 1000 grades of PEG {VII-A-4H} and PPG {VII-A-7H}. Either a ^{13}C or ^1H NMR spectrum, recorded under the appropriate quantitative conditions, can be used to determine the average MW of such materials. Take, for example, the ^1H spectrum of low-MW poly(ethylene glycol) {VII-A-4H}. If $A(\text{CH}_2)$, the area of the large methylene resonance at 3.6 ppm, is set to 100, then the area of the terminal hydroxyl resonance $A(\text{OH})$ at 2.6 ppm is 1.1. The molecular weight can be readily calculated:

$$\text{MW(PEG)} = 44 \frac{A(\text{CH}_2)/4}{A(\text{OH})} \quad (\text{VII-1})$$

where 44 is the monomer weight (—CH₂—CH₂—O—). These low-MW polyethers (particularly PEG) may be employed as additives in materials such as polyethylene {II-A-1 through II-A-20}. ^1H NMR has been used to measure the polyether level [6] in such systems.

VII.B.2— Polysaccharides

Many natural materials, most notably cellulose, are composed of long chains of sugar-like monomers; hence, the name *polysaccharides*. There are several distinct types of ether structures in these polymers:



In fact, every carbon is adjacent to at least one oxygen. Of the five ring carbons, one carbon (a) is connected to two oxygens; the others (b-e), to one. In cellulose, all three R (b', c', and e') groups in Structure C are hydrogens. In derivatized cellulosic materials, each Rs may be either hydrogen or a functional group. Because of the large number of ether carbons, the ^{13}C spectra of polysaccharides exhibit many peaks within a relatively small chemical-shift range, between 70 and 85 ppm. The limited solubility of most of these materials causes broadening of these resonances, so that specific assignment can be difficult. Various isomeric arrangements of the pendant ether groups at carbons b, c, and e, and of the ether linkages between carbons a and d, are possible. In cellulosic materials {VII-B-1 through VII-B-9}, the stereochemistry of the inter-ring ether linkages alternates from ring to ring; in the amylose component of cornstarch {VII-B-10}, it does not change. These O—C—O carbons resonate close to 100 ppm in either case.

Most of the commonly encountered cellulosic materials are actually modified forms of cellulose. The substituent introduces resonances at chemical shifts typical of that group, (i.e., ~50 ppm for methoxy, or ~170 and ~20 ppm for acetoxy) [5]. Cellulose ethers, such as methyl cellulose {VII-B-1} or ethyl cellulose {VII-B-3}, are produced by the reaction of an alkalicellulose with an alkyl chloride, with an alkyl sulfate, or with an alcohol and dehydrating agent. This process replaces approximately 30% of the hydroxyl groups with alkoxy functionality. Organic cellulose esters, such as cellulose acetate

Table VII.1 ^{13}C Chemical Shifts of Linear Polyethers

Polymer	<i>A1 A2 ...</i>				Others
	- O - C - C - ...				
	A1	A2	A3	A4	
Polyoxymethylene	91.4	—	—	—	—
Poly(ethylene glycol)	70.6	—	—	—	—
Poly(propylene glycol)	75.8	73.7	—	—	17.1 (CH ₃)
Polyepichlorohydrin	79.5	44.1	—	—	69.9 (CH ₂ Cl)
Polytetrahydrofuran	70.6	26.4	—	—	—
Poly(2,6-dimethylphenylene oxide)	155.3	115.0	133.0	146.0	17.1 (CH ₃)

{VII-B-4} or cellulose propionate {VII-B-7}, result from the treatment of cellulose with the appropriate acid or acid anhydride and a sulfuric acid catalyst. Inorganic cellulose esters, such as cellulose nitrate {VII-A-8} or cellulose sulfate {VII-A-9}, are formed by reaction of cellulose with nitric or sulfuric acids. Most of these processes do not result in complete replacement of the original hydroxyl groups. Determination of the degree of substitution (DS) in some of these materials can be accomplished by ^{13}C NMR [7,8].

References

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2. H. Ulrich. *Introduction to Industrial Polymers*. Munich: Hanser Publishers, 1993.
3. R. M. Roberts. *Serendipity*. New York: Wiley, 1989.
4. J. Brandrup and E. H. Immergut. *Polymer Handbook*. New York: Wiley, 1975.
5. E. Breitmaier and W. Voelter. *Carbon-13 NMR Spectroscopy*. New York: VCH Publishers, 1987.
6. T. A. Kestner, R. A. Newmark, and C. Bardeau. *Polym. Preprints* 37:232, 1996.
7. M. Tezuka, K. Imai, M. Oshima, and T. Chiba. *Makromol. Chem. Phys.* 191:861, 1990.
8. C. M. Buchanan, J. A. Hyatt, and D. W. Lowman, *Macromolecules* 20:2750, 1987.

ETHER BACKBONES

A. Linear Polyethers

VII-A-1	Polyoxymethylene
VII-A-2	Polyoxyethylene
VII-A-3	Poly(ethylene glycol) MW 5000
VII-A-3H	Poly(ethylene glycol) MW 5000
VII-A-4	Poly(ethylene glycol) MW 1000
VII-A-4H	Poly(ethylene glycol) MW 1000
VII-A-5	Poly(ethylene glycol) dibenzoate
VII-A-6	Poly(propylene glycol) MW 5000
VII-A-6H	Poly(propylene glycol) MW 5000
VII-A-7	Poly(propylene glycol) MW 1000
VII-A-7H	Poly(propylene glycol) MW 1000
VII-A-8	Polyepichlorohydrin
VII-A-9	Polytetrahydrofuran
VII-A-10	Poly(2,6-dimethyl- <i>p</i> -phenylene oxide)
VII-A-10H	Poly(2,6-dimethyl- <i>p</i> -phenylene oxide)
VII-A-11	Poly(Bisphenol A-co-epichlorohydrin)

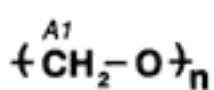
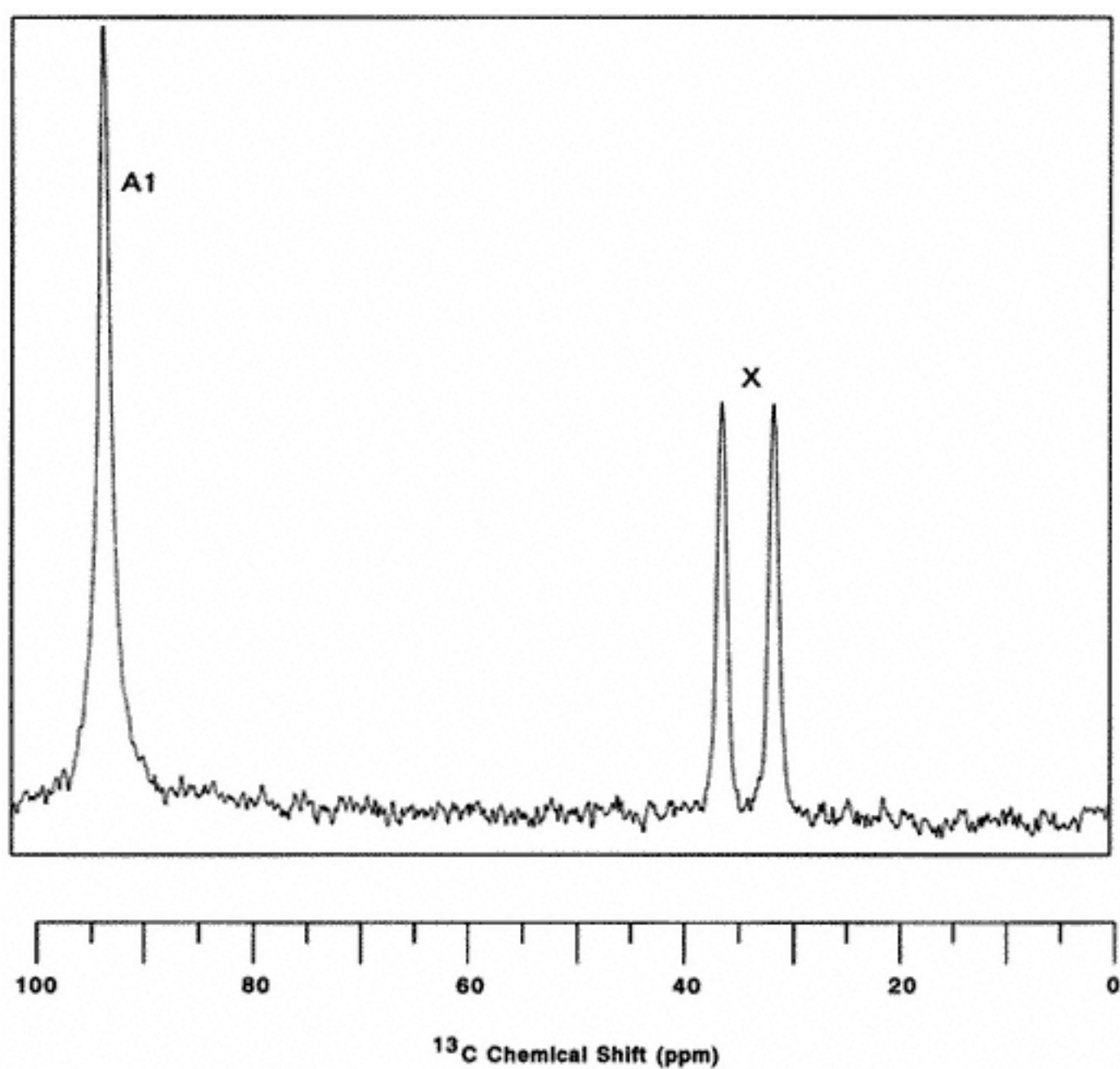
B. Polysaccharides

VII-B-1	Methyl cellulose
VII-B-2	Hydroxypropyl methyl cellulose
VII-B-3	Ethyl cellulose
VII-B-4	Cellulose acetate
VII-B-5	Cellulose acetate butyrate
VII-B-6	Cellulose triacetate
VII-B-7	Cellulose propionate
VII-B-8	Cellulose nitrate
VII-B-9	Cellulose sulfate, Na^+
VII-B-10	Cornstarch

**VII-A-1—
Polyoxymethylene (POM)**

Comments

Also known as poly(methylene oxide), polyacetal, or polyformaldehyde; a common trade name is Delrin (DuPont). A copolymer with ethylene oxide {VII-A-2} is known as Celcon (Ticona). The resonances are broadened because of the material's limited solubility; solvent resonances are marked by **X**. This engineering resin has good mechanical and electrical properties. POM is often blended with polyurethanes {IX-B-1 through IX-B-4} to improve their impact strength, and is used for telephone, appliance, fuel system, pump, and hose parts.



Code	Shift (ppm)
A1	91.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: dimethylformamide- d_7

Concentration: 10% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

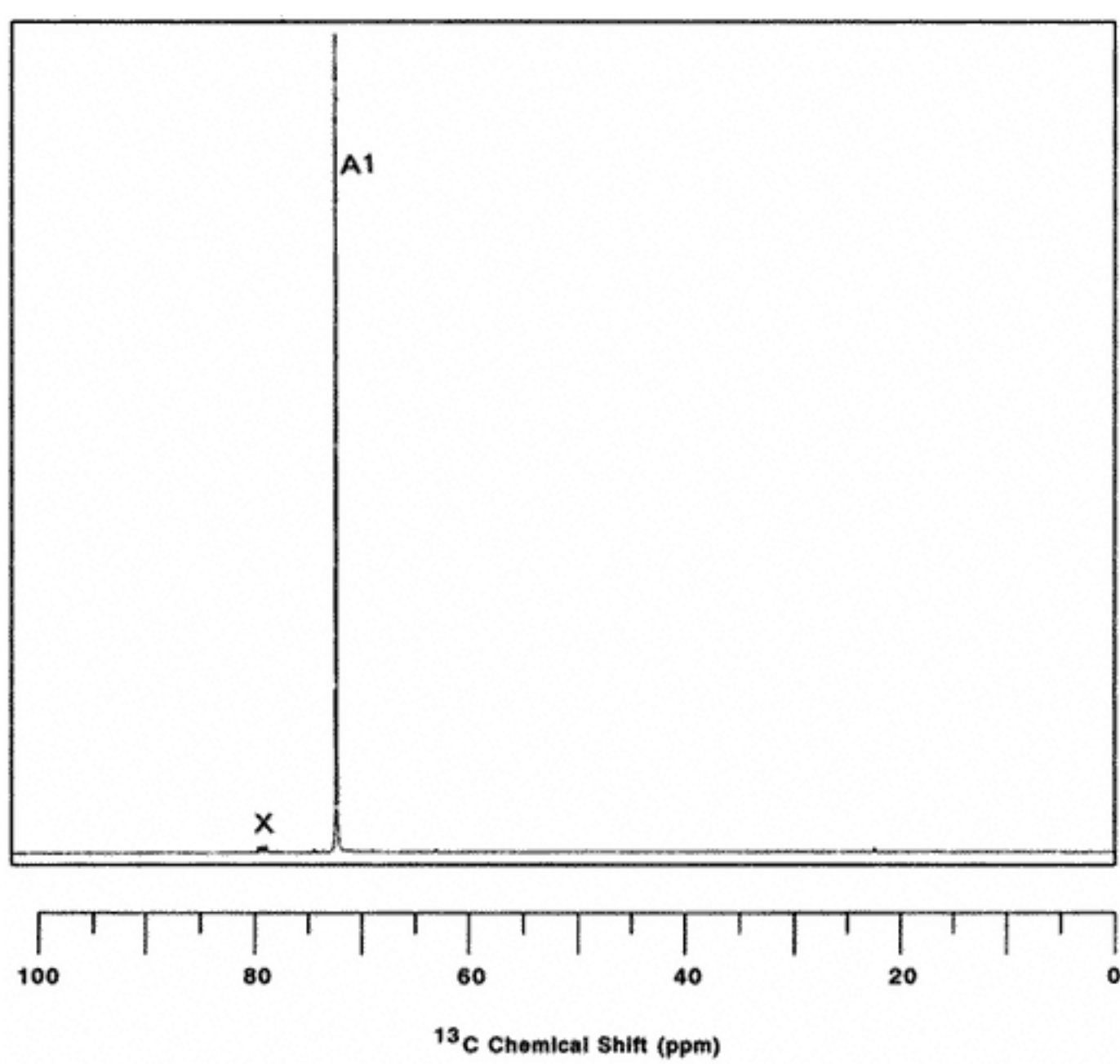
Broadening: 10 Hz

Pulse delay: 5 s

**VII-A-2—
Poly(Oxyethylene) (POE)**

Comments

Also known as poly(ethylene oxide); a copolymer with methylene oxide {VII.A-1} is known as Celcon (Ticona), Solvent resonances are marked by **X**. POE is used in packaging applications and as a water thickener and size.



Code	Shift (ppm)
A1	70.6

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

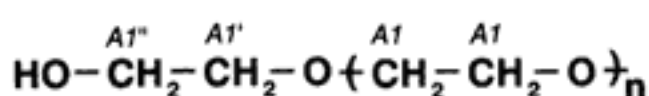
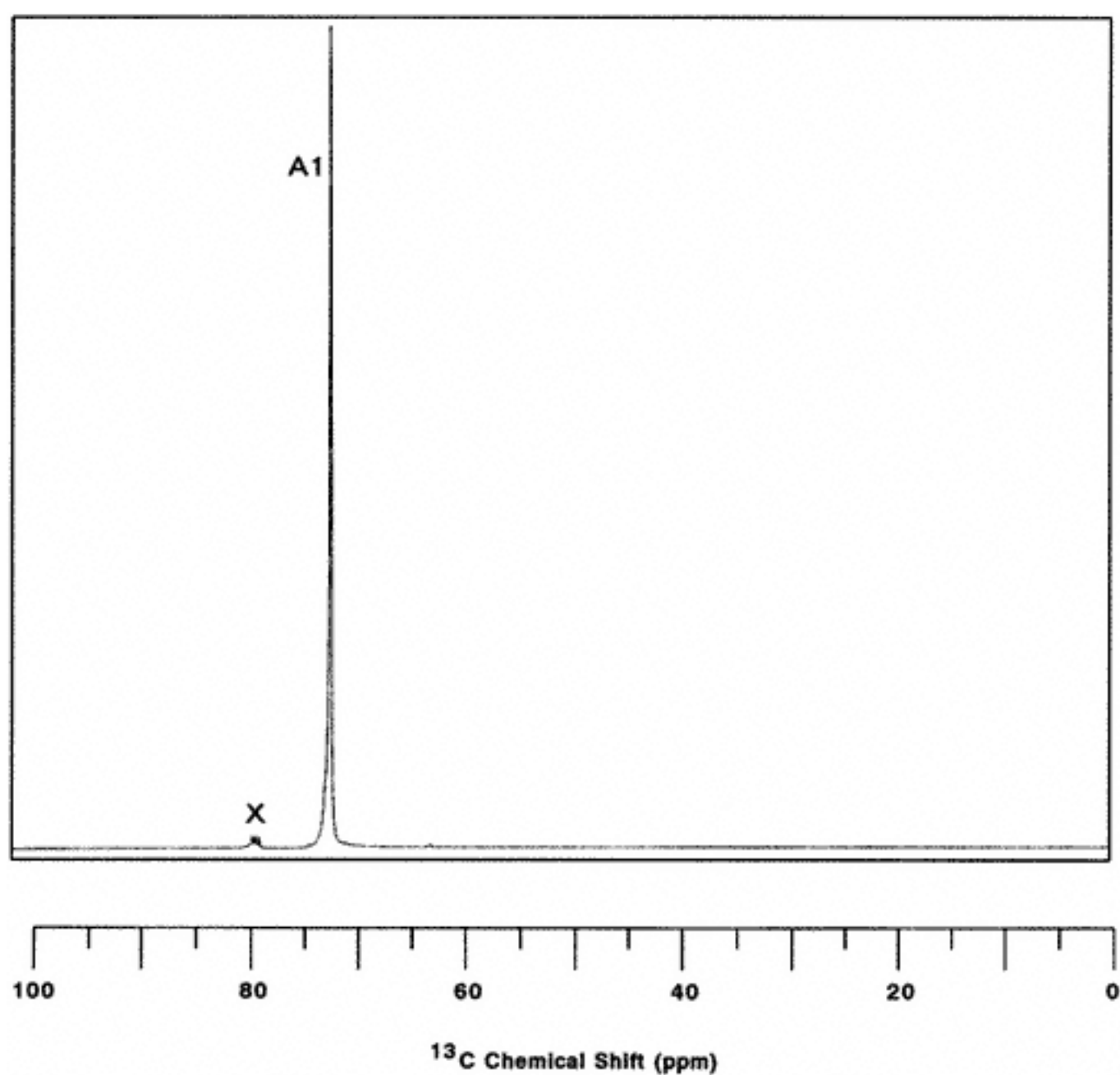
Pulse delay: 5 s

VII-A-3—

Poly(Ethylene Glycol) (PEG) [MW = 5000]

Comments

Also known as Carbowax (Union Carbide), it is available in a wide variety of molecular weights. Resonances associated with the hydroxyl end groups (A1', A1'') are not observed because of the relatively long chain length (~110 units); solvent resonances are marked by X. PEG is a frequent component of polyurethane elastomers and foams {IX-B-1 through IX-B-4}, polyurea polyols, and surfactants. This water-soluble polymer is used as a lubricant, water thickener, plasticizer, and base for cosmetic and pharmaceutical products.



Code	Shift (ppm)
A1	70.6

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

References

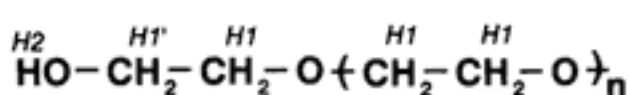
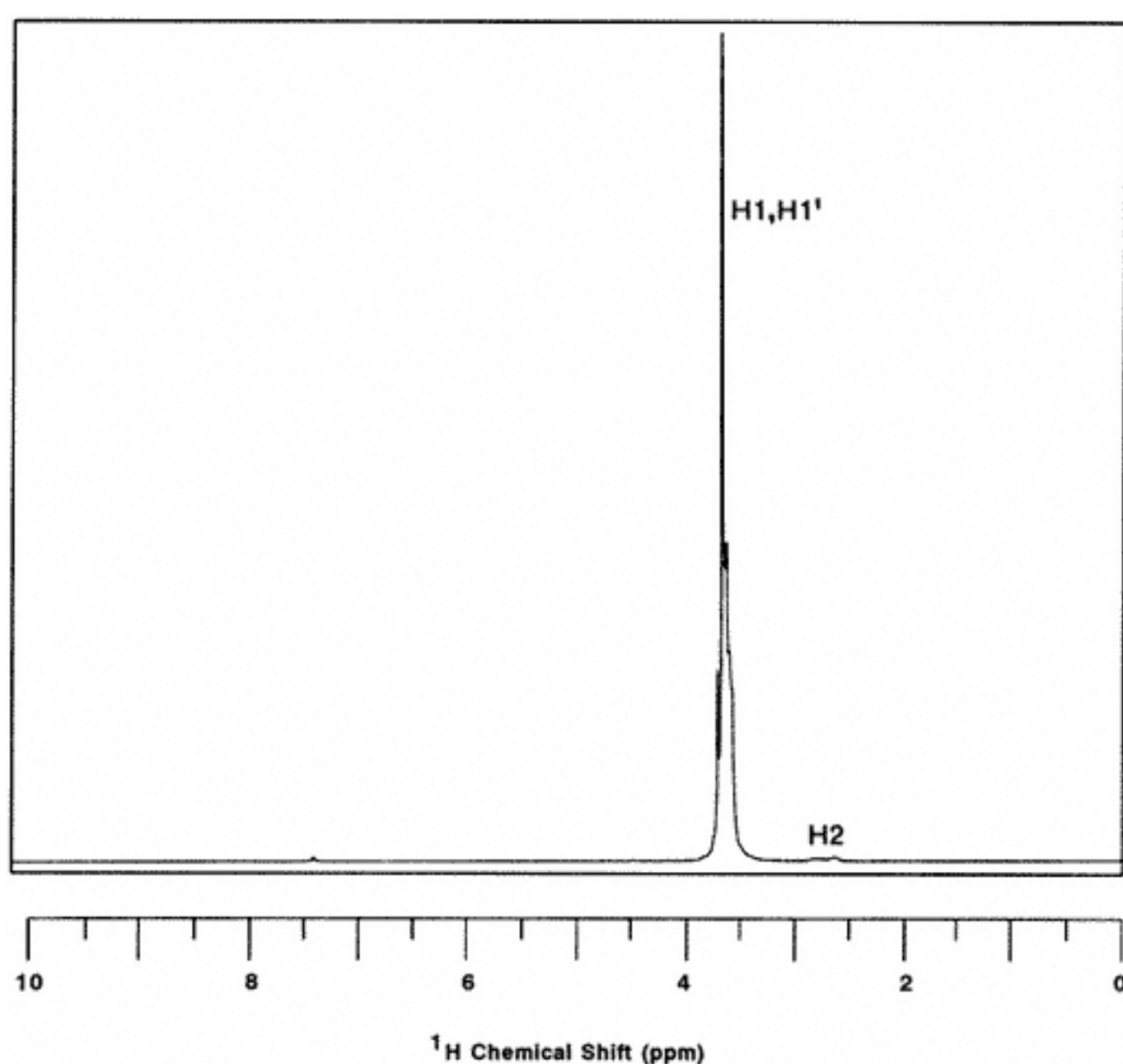
R. H. Carr, J. Hernalsteen, and J. Devos. *J. Appl. Polym. Sci.* 52:1015, 1994; R. de Vos and E. J. Goethals. *Polym. Bull.* 15:547, 1986.

VII-A-3H—

Poly(Ethylene Glycol) (PEG) [MW = 5000]

Comments

Also known as Carbowax (Union Carbide), PEG is available in a wide variety of molecular weights. Resonances associated with the hydroxyl end groups (**H1'**, **H2**) are small because of the relatively long chain length (~110 units). PEG is a frequent component of polyurethane elastomers and foams {X-B-1 through IX-B-4}, polyurea polyols, and surfactants. This water-soluble polymer is used as a lubricant, water thickener, plasticizer, and as a base for cosmetic and pharmaceutical products.



Code	Shift (ppm)
H1	3.6
H1'	3.6
H2	2.6

*Experimental Parameters*Nucleus: ¹H (400 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 20% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

References

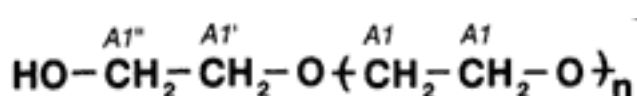
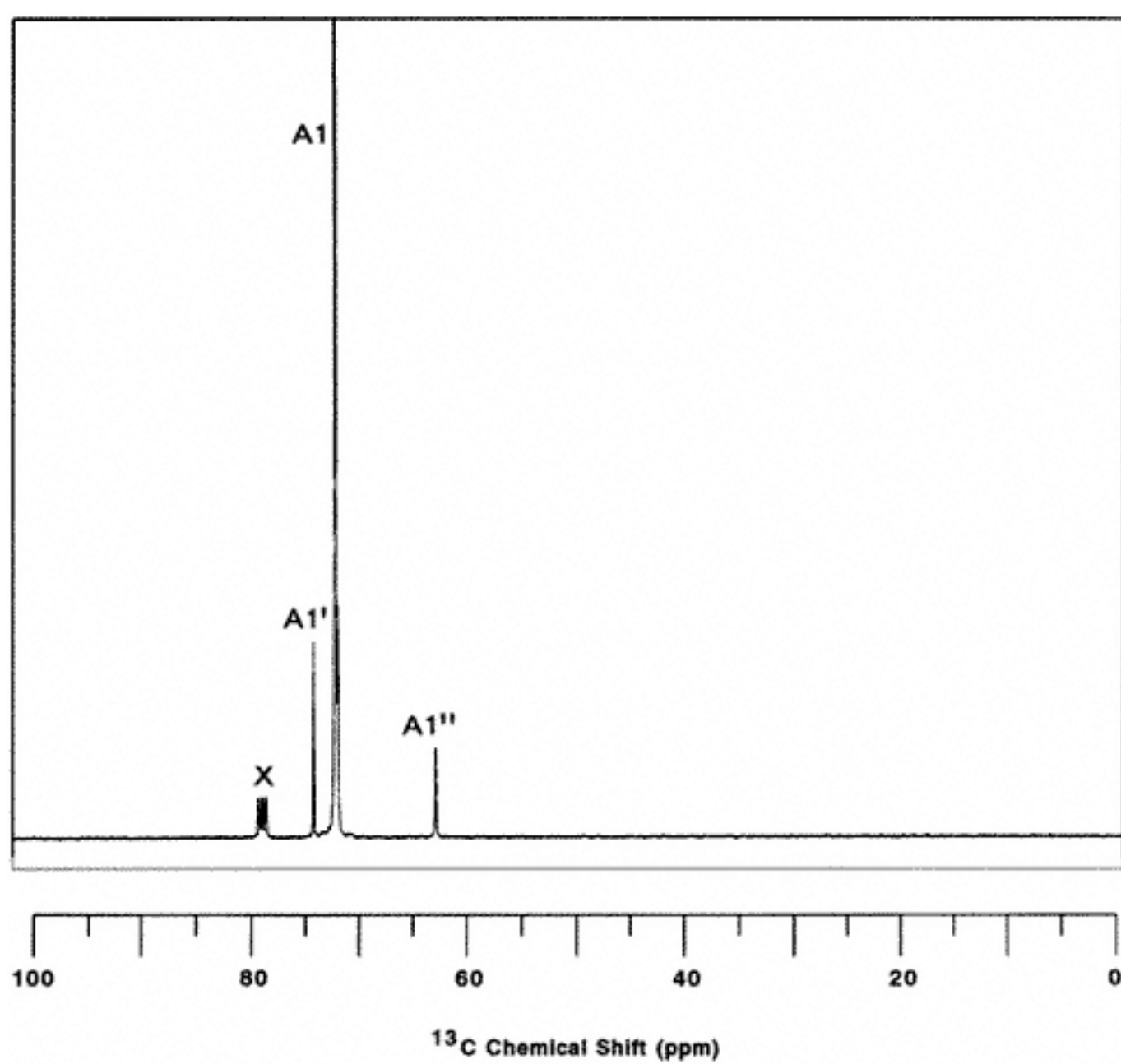
K. Jankova and J. Kops. *J. Appl. Polym. Sci.* 54:1027, 1994; J. M. Dust, Z. Feng, J. M. Harris. *Macromolecules* 23:3742, 1990.

VII-A-4—

Poly(Ethylene Glycol) (PEG) [MW = 1000]

Comments

Also known as Carbowax (Union Carbide), PEG is available in a wide variety of molecular weights. Resonances associated with the hydroxyl end groups (A1', A1'') are larger than in {VII-A-3} because of the relatively shorter chain length (~20 units); solvent resonances are marked by X. PEG is a frequent component of polyurethane elastomers and foams {IX-B-1 through IX-B-4}, polyurea polyols, and surfactants. This water-soluble polymer is used as a lubricant, water thickener, plasticizer, and as a base for cosmetic and pharmaceutical products.



Code	Shift (ppm)
A1	70.6
A1'	72.6
A1''	61.9

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

References

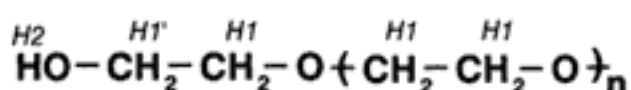
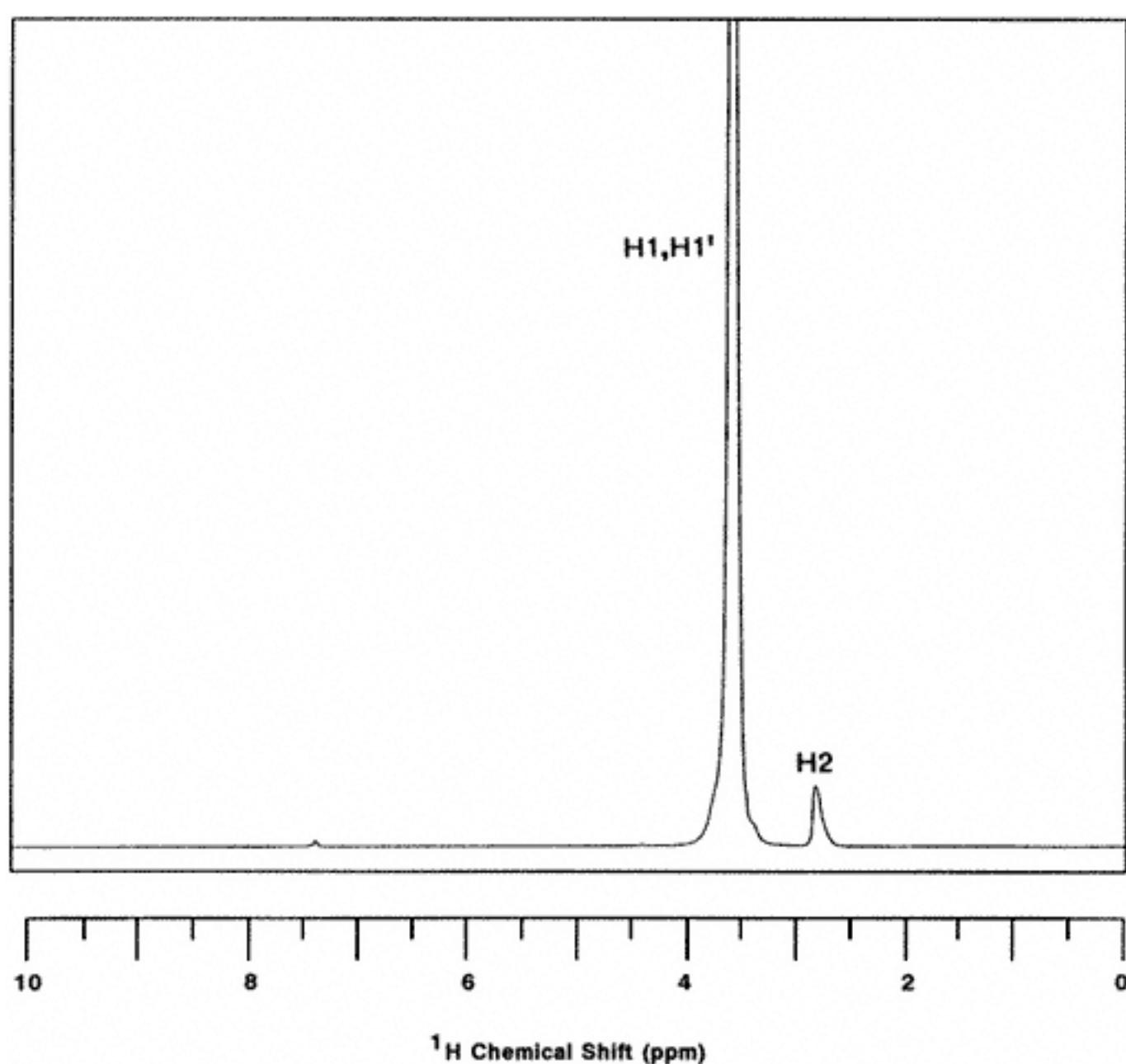
R. H. Carr, J. Hernalsteen, and J. Devos. *J. Appl. Polym. Sci.* 52:1015, 1994; R. de Vos and E. J. Goethals. *Polym. Bull.* 15:547 1986.

VII-A-4H—

Poly(Ethylene Glycol) (PEG) [MW = 1000]

Comments

Also known as Carbowax (Union Carbide) PEG is available in a wide variety of molecular weights. Resonances associated with the hydroxyl end groups (**H1'**, **H2**) are larger than in {VII-A-3H} because of the relatively shorter chain length (~20 units). PEG is a frequent component of polyurethane elastomers and foams {IX-A-1 through IX-A-4}, polyurea polyols, and surfactants. This water-soluble polymer is used as a lubricant, water thickener, plasticizer, and as a base for cosmetic and pharmaceutical products.



Code	Shift (ppm)
H1	3.6
H1'	3.6
H2	2.6

*Experimental Parameters*Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

References

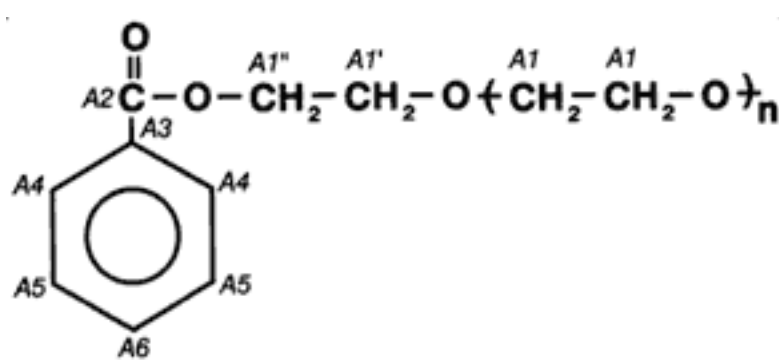
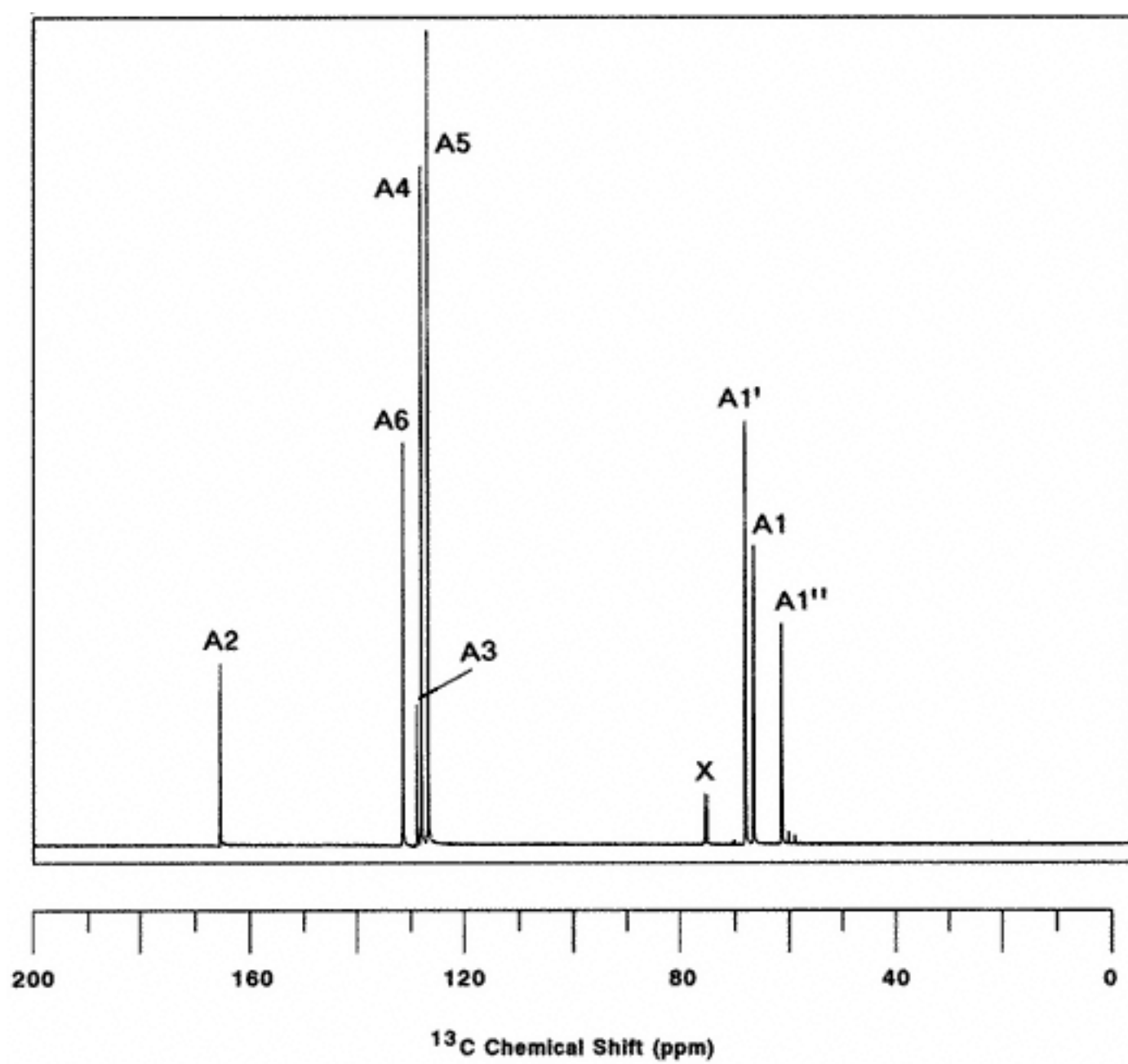
K. Jankova and J. Kops. *J. Appl. Polym. Sci.* 54:1027, 1994; J. M. Dust, Z. Feng, and J. M. Harris. *Macromolecules* 23:3742, 1990.

VII-A-5—

Poly(Ethylene Glycol) Dibenzoate (PEG) [MW = 200]

Comments

End group resonances (A1', A1'') are observed because of the short PEG chain length (~5 units). Solvent resonances are marked by X. This derivatized PEG is used as a plasticizer.



Code	Shift (ppm)
A1	69.0
A1'	70.6
A1''	64.0
A2	166.1
A3	130.1
A4	129.5
A5	128.3
A6	133.1

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

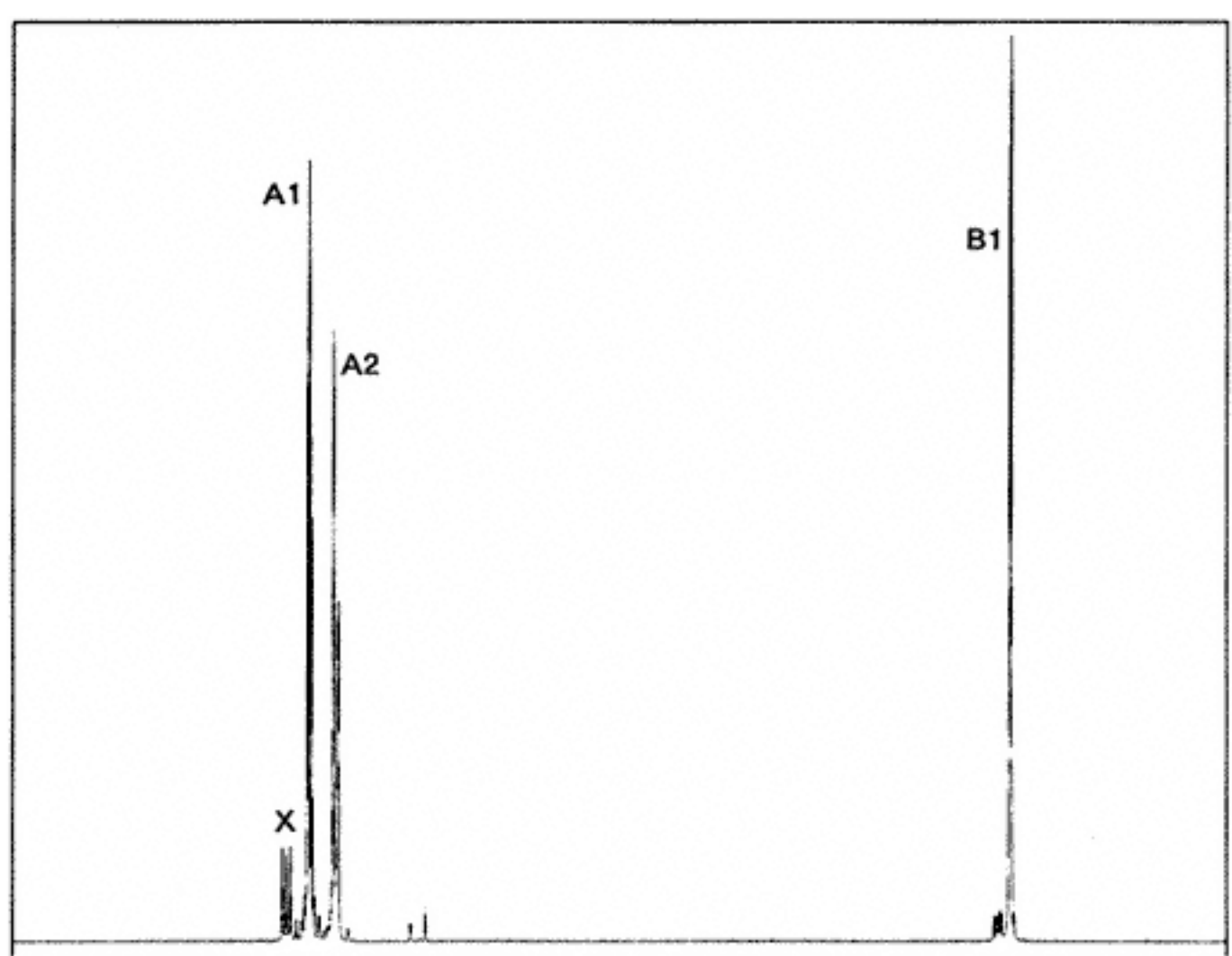
Pulse delay: 5 s

VII-A-6—

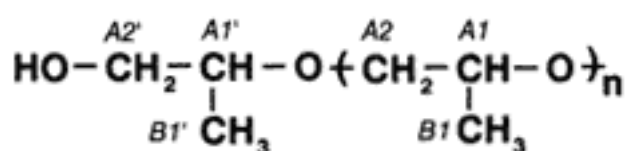
Poly(Propylene Glycol) (PPG) [MW = 5000]

Comments

Resonances associated with end groups (**A1'**, **A2'**, **B1'**) are not observed because of the relatively long chain length (~85 units). Solvent resonances are marked by **X**. PPG, which is available in a wide variety of molecular weights, is a frequent component of polyurethane elastomers and foams {IX-B-1 through IX-B-4}, polyurea polyols, and surfactants. The water-soluble polymer is used as a lubricant, water thickener, plasticizer, and as a base for cosmetic and pharmaceutical products.



^{13}C Chemical Shift (ppm)



Code	Shift (ppm)
A1	75.8
A2	73.7
B1	17.1

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

References

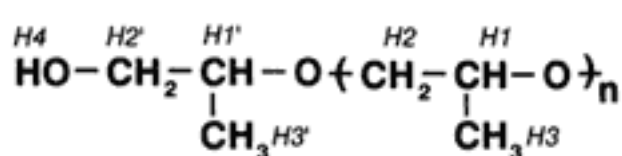
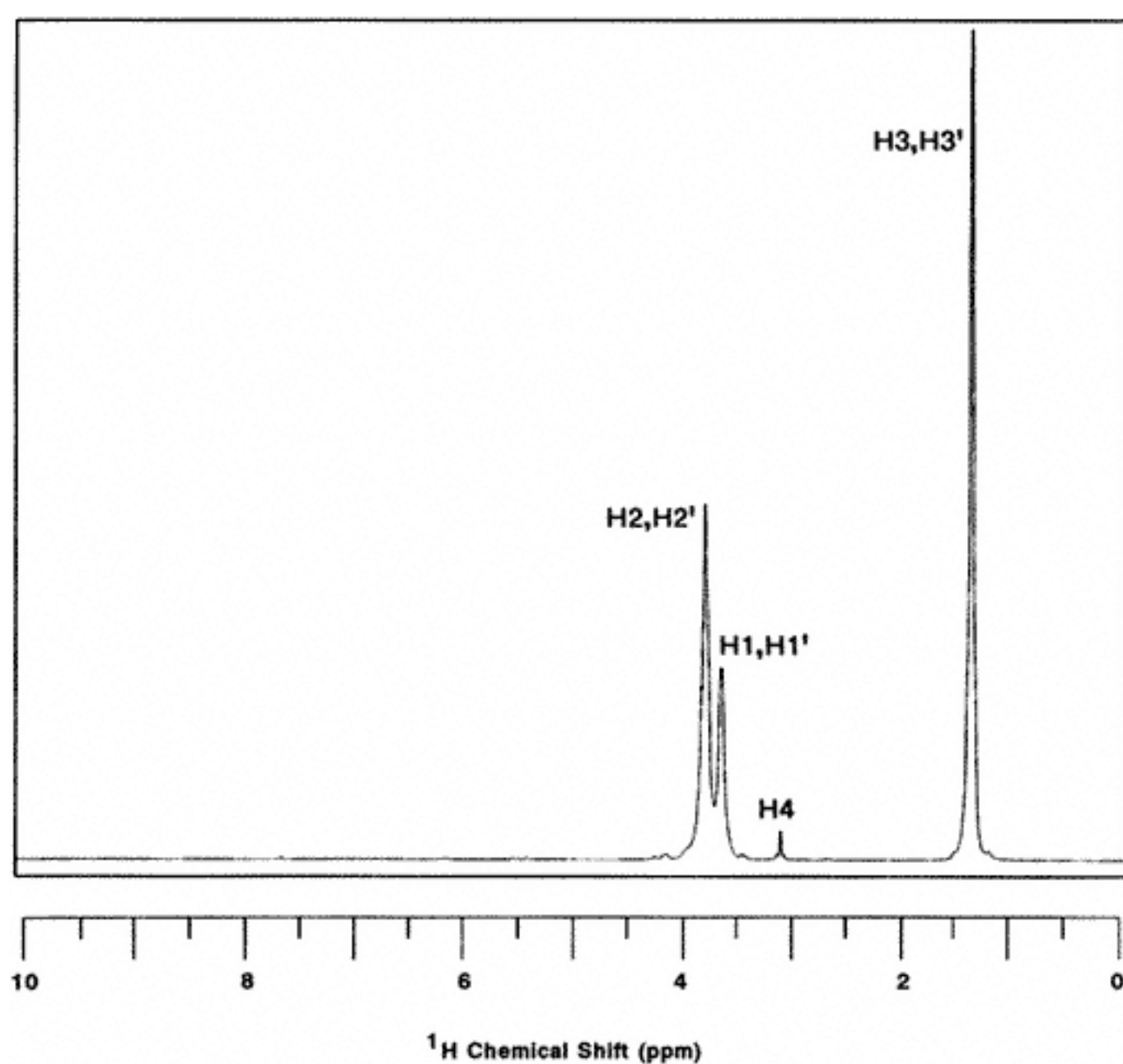
R. H. Carr, J. Hernalsteen, and J. Devos. *J. Appl. Polym. Sci.* 52:1015, 1994; J. Kriz and J. Stehlicek. *Macromol. Chem. Phys.* 195:3877, 1994; F. Heatley, J. G. Tu, and C. Booth. *Makromol. Chem. Rapid Commun.* 15:819, 1993; C. Campbell, F. Heatley, G. Holcroft, and C. Booth. *Polym. J.* 25:831, 1989; F. C. Schilling, and A. E. Tonelli. *Macromolecules* 19:1337, 1986; M. D. Bruch, F. A. Bovey, R. E. Cais, and J. H. Noggle. *Macromolecules* 18:1853, 1985.

VII-A-6H—

Poly(Propylene Glycol) (PPG) [MW = 5000]

Comments

Resonances associated with the hydroxyl end groups (**H1'**, **H2'**, **H3'**, **H4**) are small because of the relatively long chain length (~85 units). PPG, which is available in a wide variety of molecular weights, is a frequent component of polyurethane elastomers and foams {IX-B-1 through IX-B-4}, polyurea polyols, and surfactants. This water-soluble polymer is used as a lubricant, water thickener, plasticizer, and as a base for cosmetic and pharmaceutical products.



Code	Shift (ppm)
H1	3.7
H1'	3.7
H2	3.8
H2'	3.8
H3	1.4
H3'	1.4
H4	3.1

*Experimental Parameters*Nucleus: ¹H (400 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 20% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

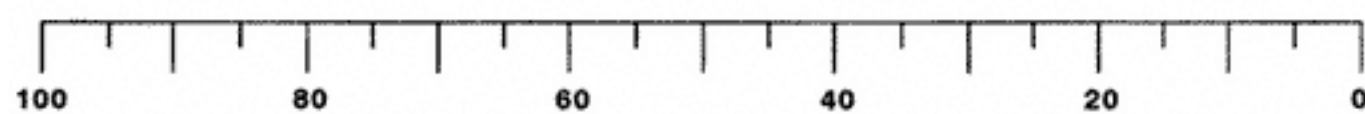
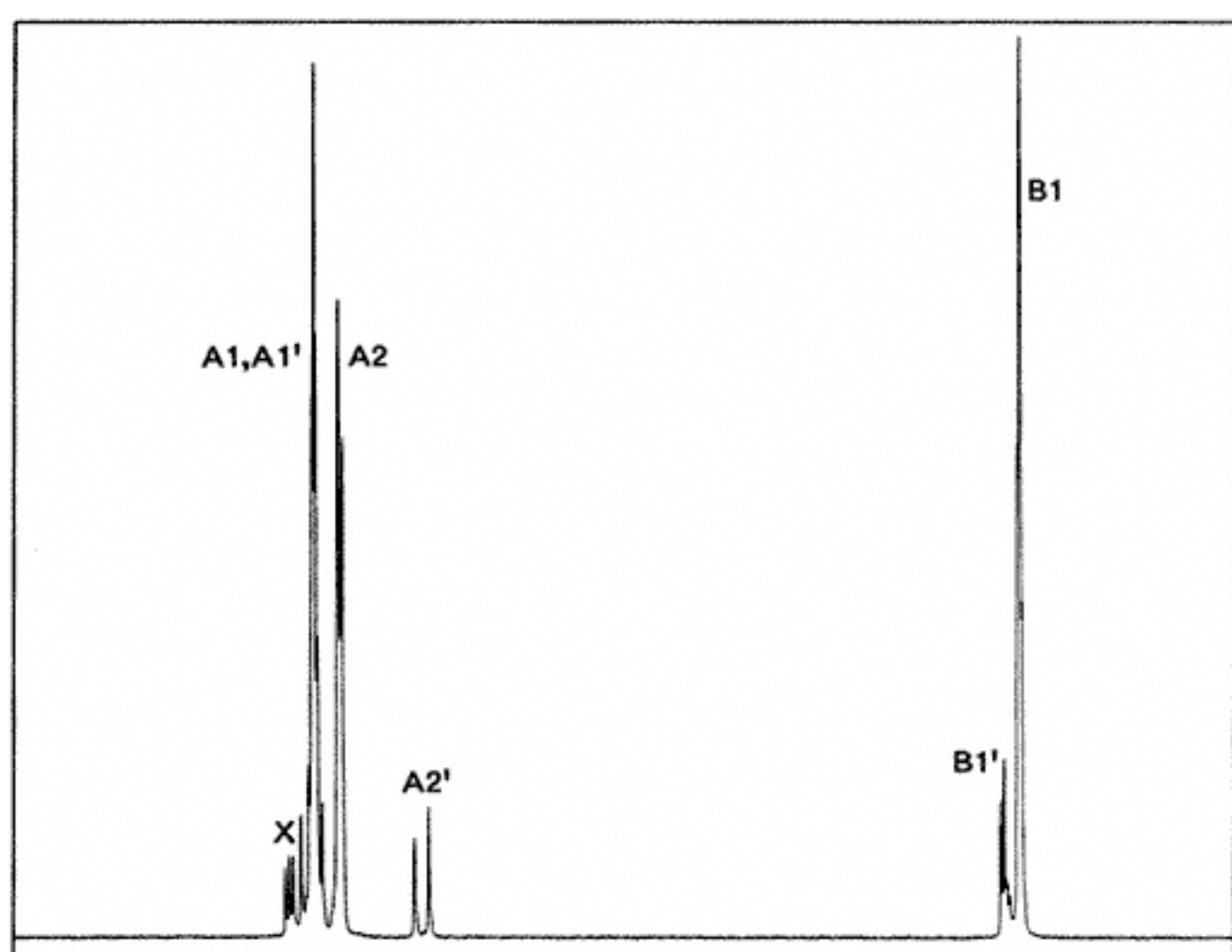
VII-A-7

VII-A-7—

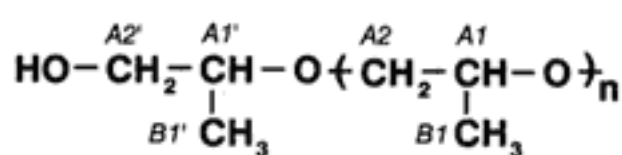
Poly(Propylene Glycol) (PPG) [MW = 1000]

Comments

Resonances associated with end groups (**A1'**, **A2'**, **B1'**) are larger than in {VII-A-6} because of the relatively short chain length (~17 units). Solvent resonances are marked by **X**. PPG, which is available in a wide variety of molecular weights, is a frequent component of polyurethane elastomers and foams {IX-B-1 through IX-B-4}, polyurea polyols, and surfactants. This water-soluble polymer is used as a lubricant, water thickener, plasticizer, and as a base for cosmetic and pharmaceutical products.



¹³C Chemical Shift (ppm)



Code	Shift (ppm)
A1	75.8
A1'	75.8
A2	73.7
A2'	66.1, 67.8
B1	17.4
B1'	19.0

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

References

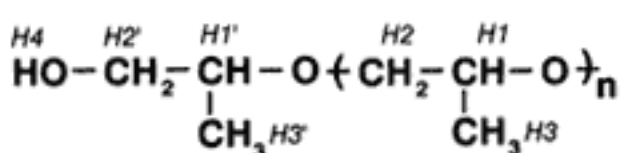
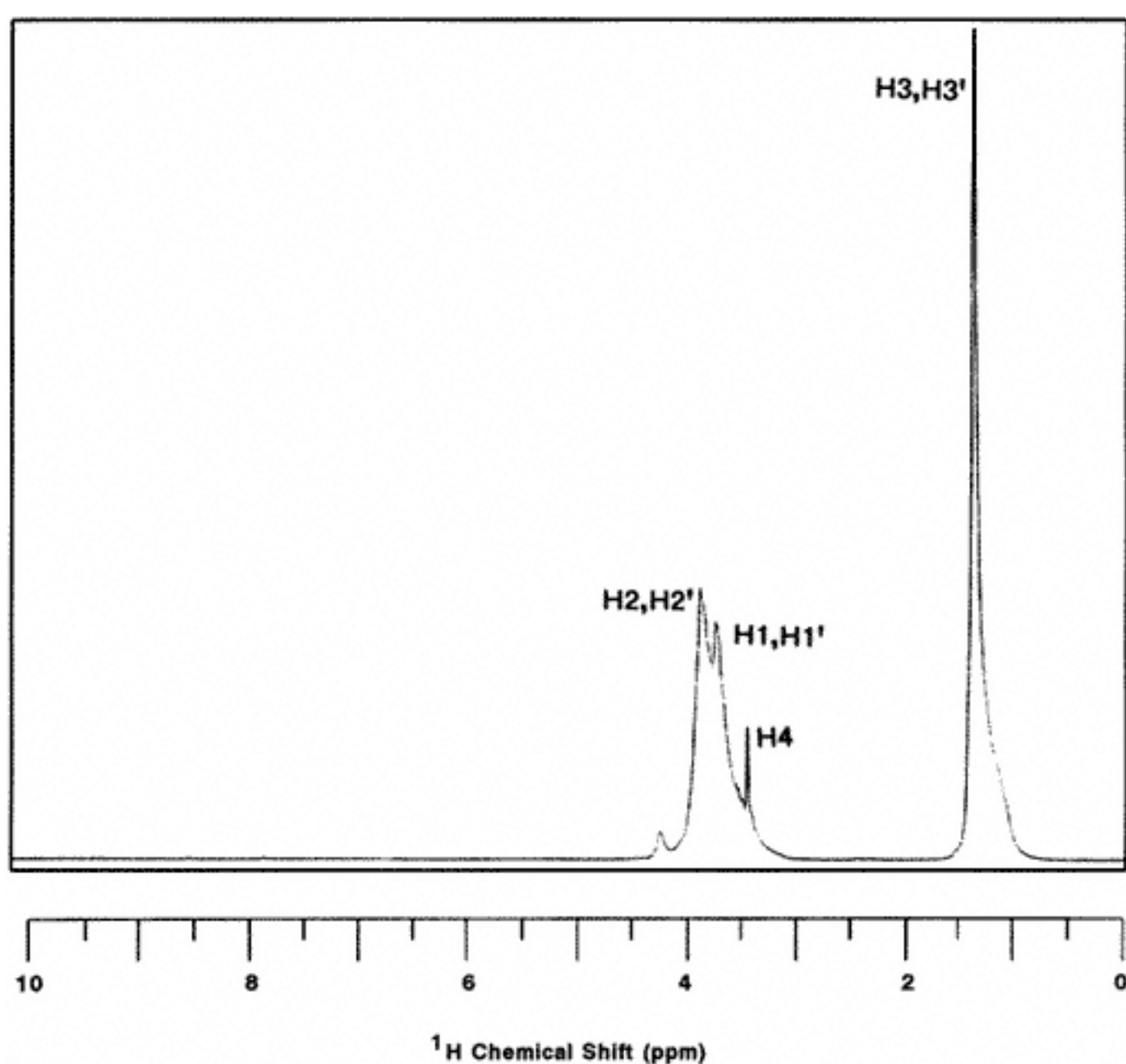
R.H. Carr, J. Hernalsteen, and J. Devos. *J. Appl. Polym. Sci.* 52:1015, 1994; J. Kriz and J. Stehlicek. *Macromol. Chem. Phys.* 195:3877, 1994; F. Heatley, J. G. Tu, C. Booth. *Makromol. Chem. Rapid Commun.* 15:819, 1993; C. Campbell, F. Heatley, G. Holcroft, and C. Booth. *Polym. J.* 25:831, 1989; F. C. Schilling and A. E. Tonelli. *Macromolecules* 19:1337, 1986; M. D. Bruch, F. A. Bovey, R. E. Cais, and J. H. Noggle. *Macromolecules* 18:1853, 1985.

VII-A-7H—

Poly(Propylene Glycol) (PPG) [MW = 1000]

Comments

Resonances associated with end groups (**H1'**, **H2'**, **H3'**, H4) are larger than in {VII-A-6H} because of the relatively shorter chain length (~17 units). PPG, which is available in a wide variety of molecular weights, is a frequent component of polyurethane elastomers and foams {IX-B-1 through IX-B-4}, polyurea polyols, and surfactants. The water-soluble polymer is used as a lubricant, water thickener, plasticizer, and as a base for cosmetic and pharmaceutical products.



Code	Shift (ppm)
H1	3.7
H1'	3.7
H2	3.8
H2'	3.8
H3	1.4
H3'	1.4
H4	3.1

*Experimental Parameters*Nucleus: ¹H (400 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 20% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

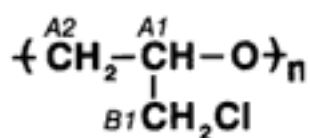
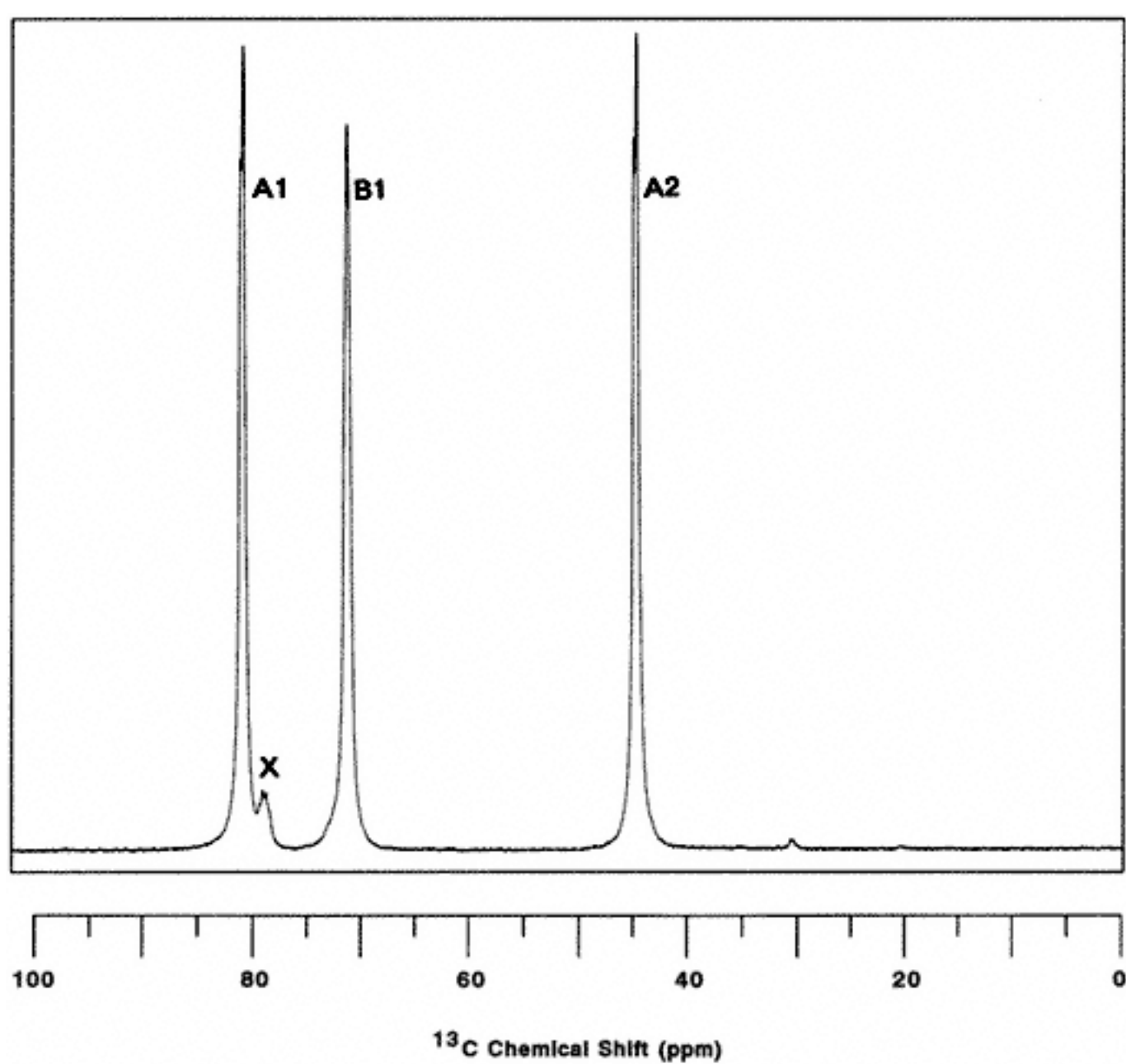
Broadening: 5 Hz

Pulse delay: 5 s

VII-A-8— Polyepichlorohydrin

Comments

Some splitting of the backbone resonances (**A1**, **A2**) is observed because of tacticity effects. Solvent resonances are marked by **X**. This elastomer is available as either a liquid or a solid. The solid is an elastomer with excellent heat and chemical resistance, and an ability to remain flexible at low temperatures.



Code	Shift (ppm)
A1	79.5
A2	44.1
B1	69.9

Experimental Parameters

Nucleus: ^{13}C (100 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 20% w/w
Scans: 100	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 5 Hz	Pulse delay: 5 s

References

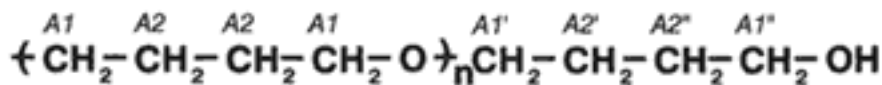
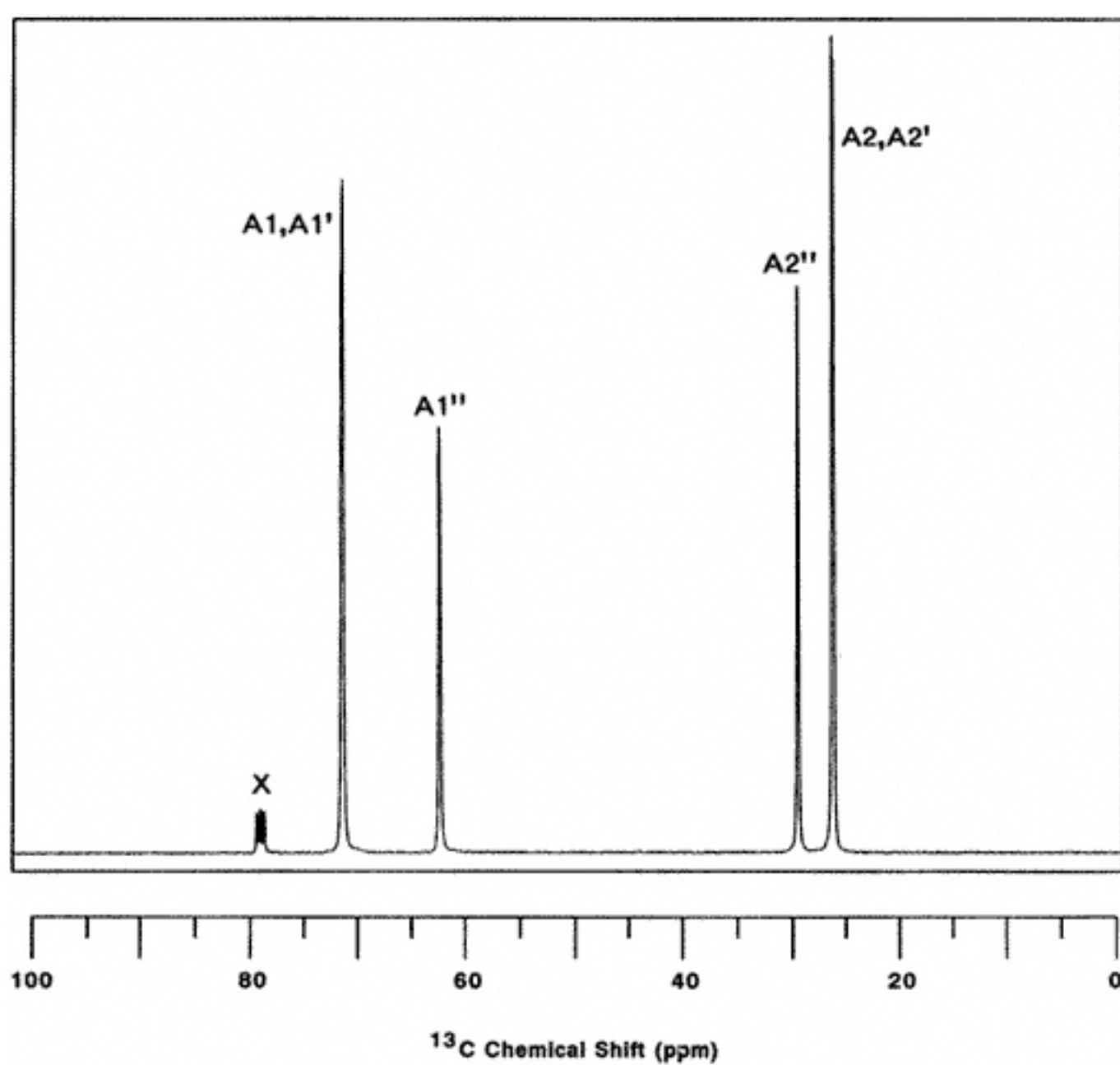
K.R. Lindfors, S. Pan, and P. Dreyfuss. *Macromolecules* 26:2919, 1993; H. N. Cheng and D. A. Smith. *J. Appl. Polym. Sci.* 34:909, 1987.

VII-A-9—

Polytetrahydrofuran (PTHF) [MW = 360]

Comments

Also known as poly(butenediol) or, when hydroxyl-terminated, as poly(tetramethylene glycol) (PTMG). End groups (A1', A1'', A2', A2'') are pronounced because of the short chain length (~6 units). Solvent resonances are marked by X. This polymer is used as a component in thermoplastic elastomers {VIII-B-5} and polyurethanes {IX-B-1 through IX-B-4}.



Code	Shift (ppm)
A1	70.6
A1'	70.6
A1''	61.9
A2	26.4
A2'	26.4
A2''	29.6

*Experimental Parameters*Nucleus: ^{13}C (100 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 24

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

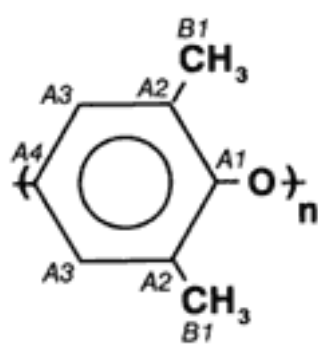
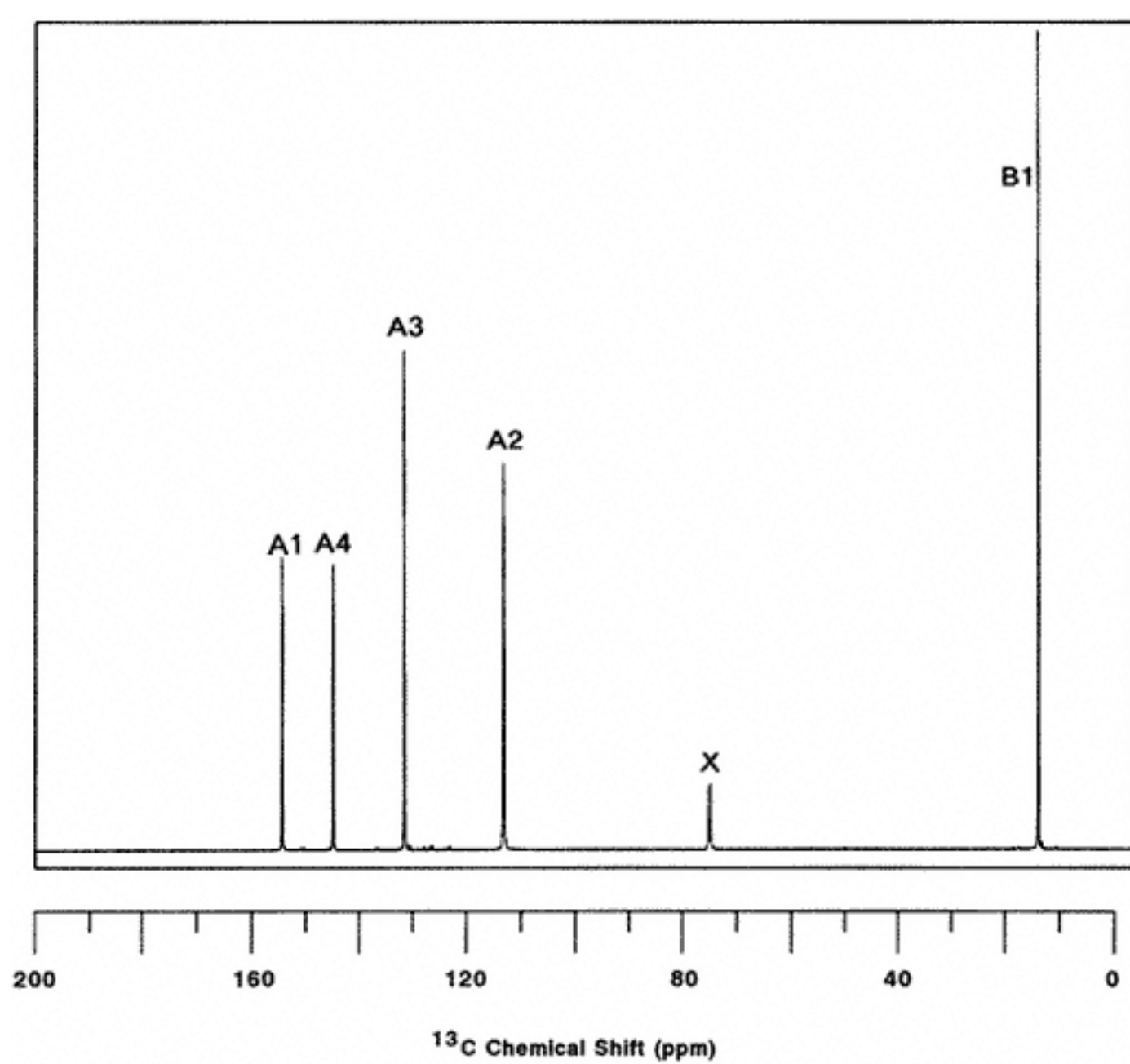
Broadening: 5 Hz

Pulse delay: 5 s

VII-A-10—

Poly(2,6-Dimethyl-*p*-Phenylene Oxide) (PPO)*Comments*

Blends of PPO with polystyrene {III-A-2}, high-impact polystyrene (HIPS) {III-A-6}, or nylon {VIII-C-1 through VIII-C-7}, are known as Noryl (General Electric) alloys. Solvent resonances are marked by X. PPO is used in automotive applications, and for appliance, tool, and business machine housings.



Code	Shift (ppm)
A1	155.3
A2	115.0
A3	133.0
A4	146.0
B1	17.1

Experimental Parameters

Nucleus: ^{13}C (100 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 20% w/w
Scans: 24	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 5 Hz	Pulse delay: 5 s

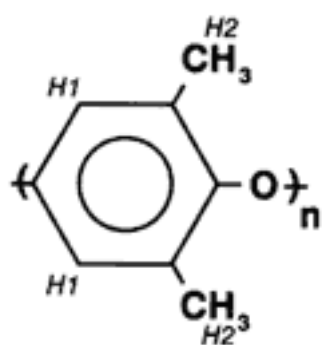
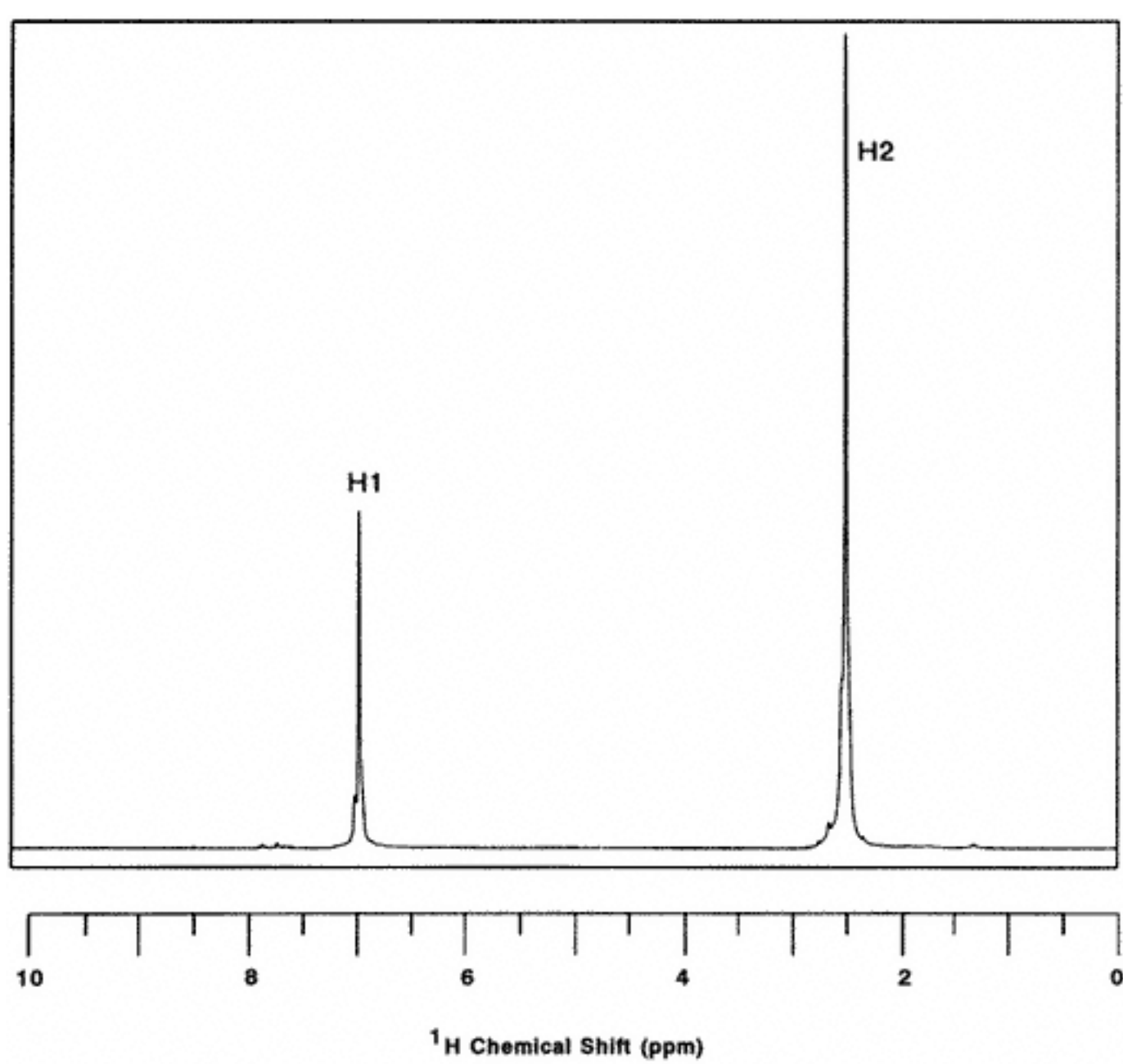
Reference

J. Reuben and A. Biswas. *Macromolecules* 24:648, 1991.

**VII-A-10H—
Poly(2,6-Dimethyl-*p*-Phenylene Oxide)**

Comments

Blends of PPO with polystyrene {III-A-2H}, high-impact polystyrene (HIPS) {III-B-6H}, or nylon {VIII-C-1 through VIII-C-7}, are known as Noryl (General Electric) alloys. PPO is used in automotive applications, and for appliance, tool, and business machine housings.



Code	Shift (ppm)
H1	6.9
H2	2.5

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

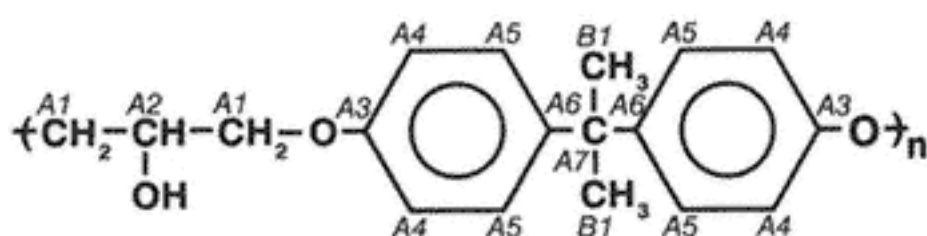
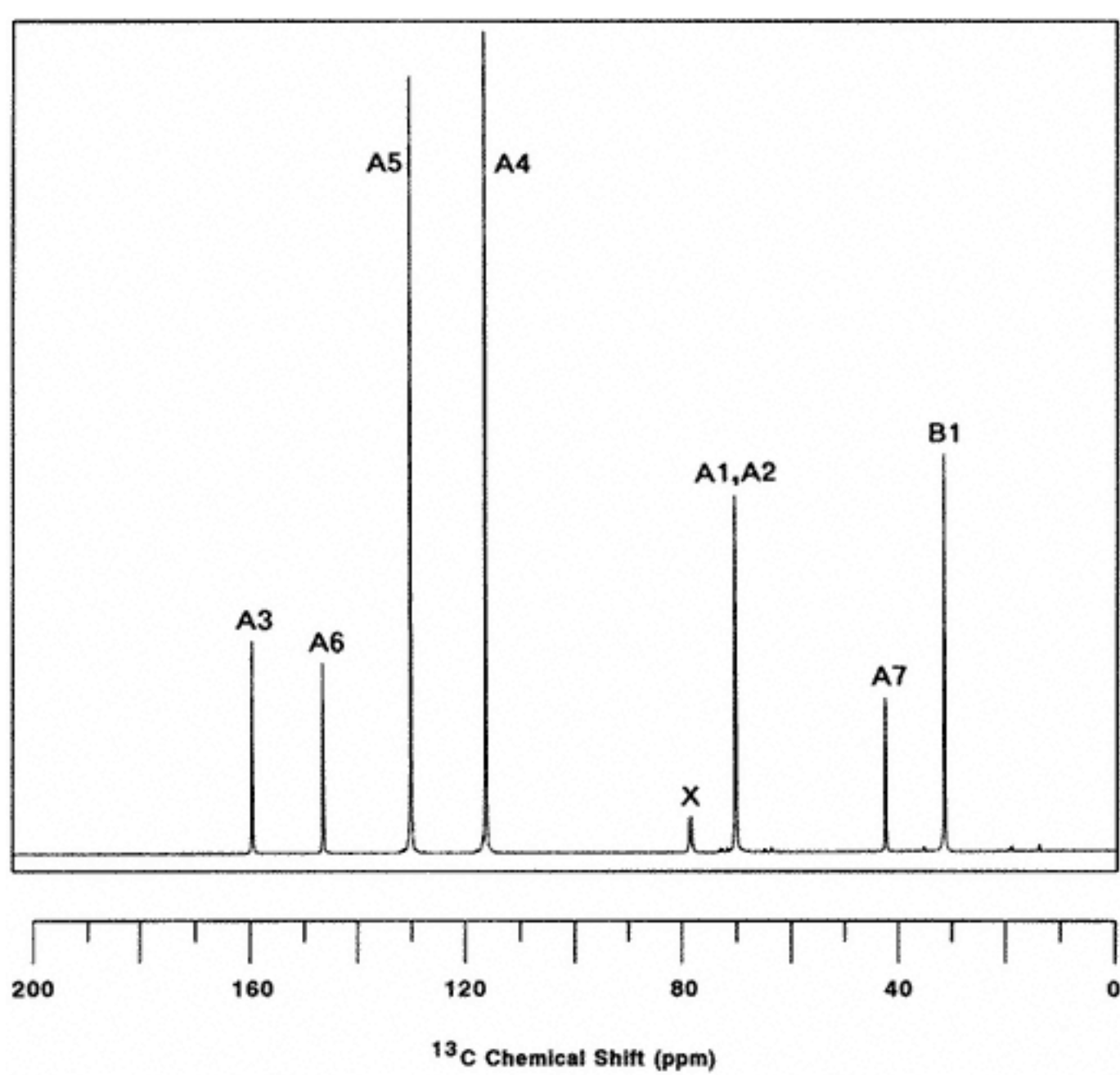
Pulse delay: 5 s

VII-A-11—

Poly(Bisphenol A-Co-Epichlorohydrin)

Comments

Also known as phenoxy resin, this is a type of epoxy polymer. Solvent resonances are marked by X. This transparent material has good temperature stability and chemical resistance. The hydroxyl groups serve as potential cross-linking sites. This material is used in coatings and adhesives, and can be blow-molded into containers and pipe.



Code	Shift (ppm)
A1	69.9
A2	69.9
A3	157.2
A4	114.9
A5	128.5
A6	144.6
A7	42.4
B1	31.6

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 128

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

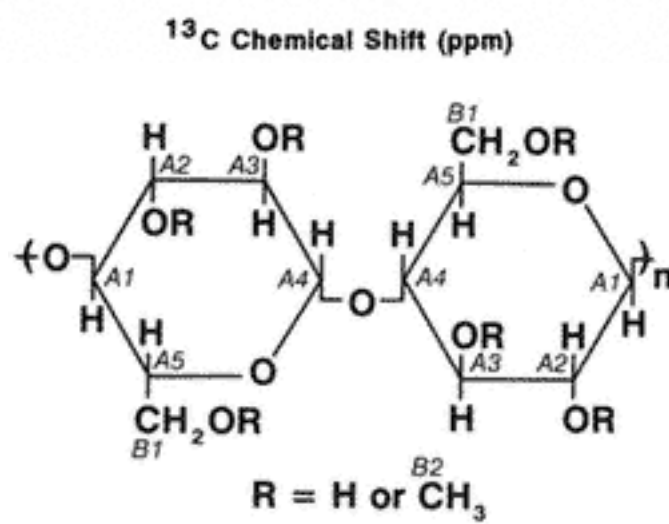
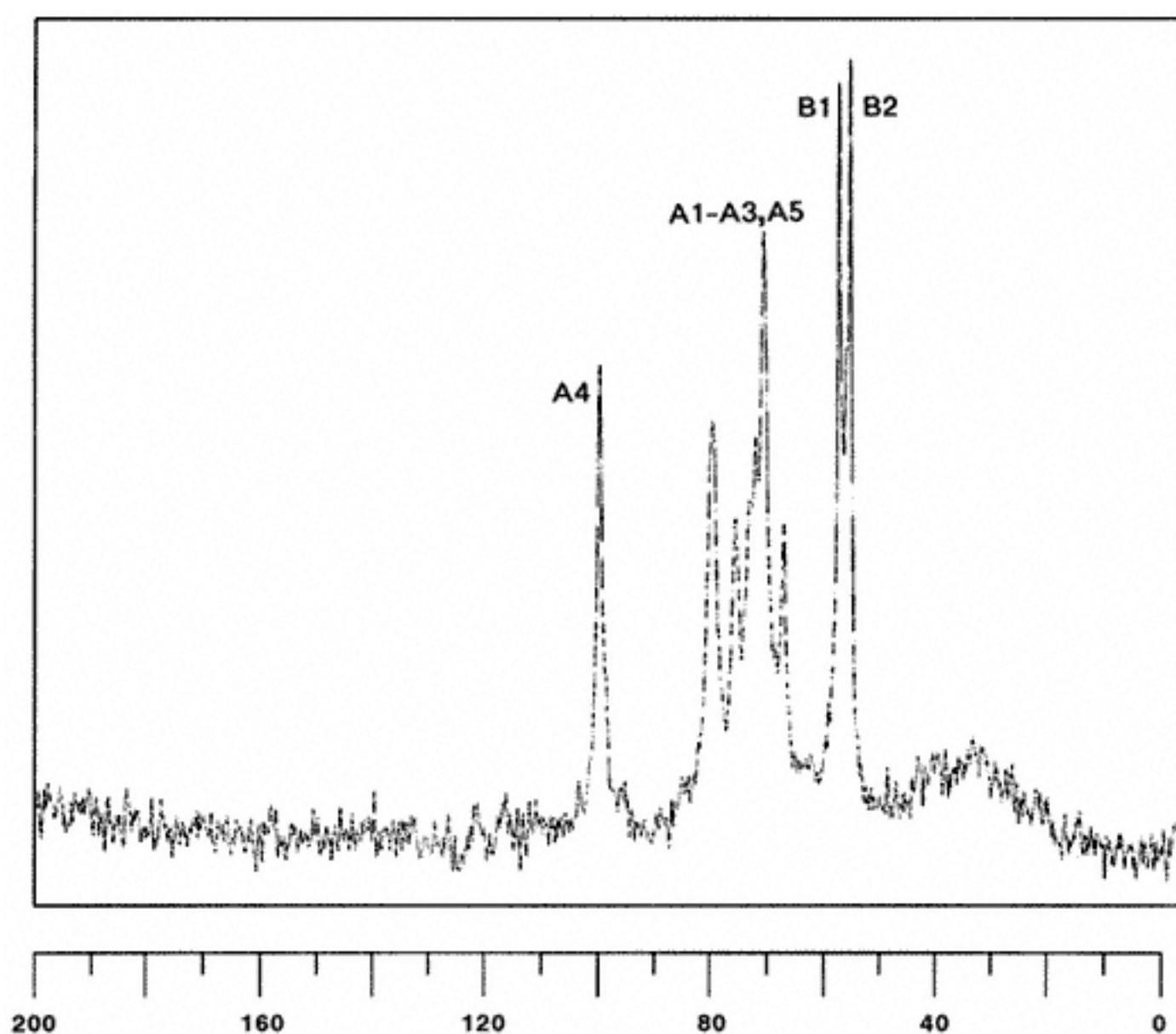
Broadening: 2 Hz

Pulse delay: 5 s

VII-B-1— Methyl Cellulose

Comments

Also known as methocel. The resonances are broadened owing to limited solubility and gel formation. Substitution of H by CH₃ (degree of substitution, DS = 30%) at carbons **A2**, **A3**, and **B1** is incomplete, leading to an envelope of peaks between ~70 and 80 ppm. Shifts because of stereochemistry are also present. Methyl cellulose is used as a thickener and dispersant in paints and foods.



Code	Shift (ppm)
A1	70–83
A2	70–83
A3	70–83
A4	102.6
A5	70–83
B1	61.4
B2	59.0

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 30°C

Solvent: D_2O

Concentration: 5% w/w

Scans: 17,300

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 15 Hz

Pulse delay: 5 s

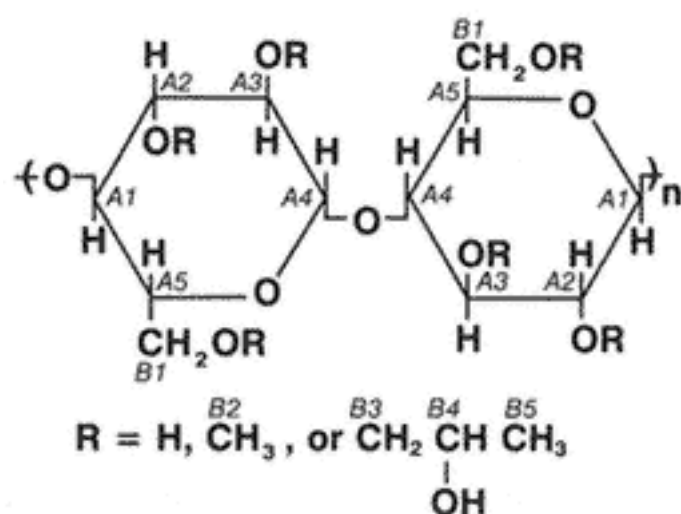
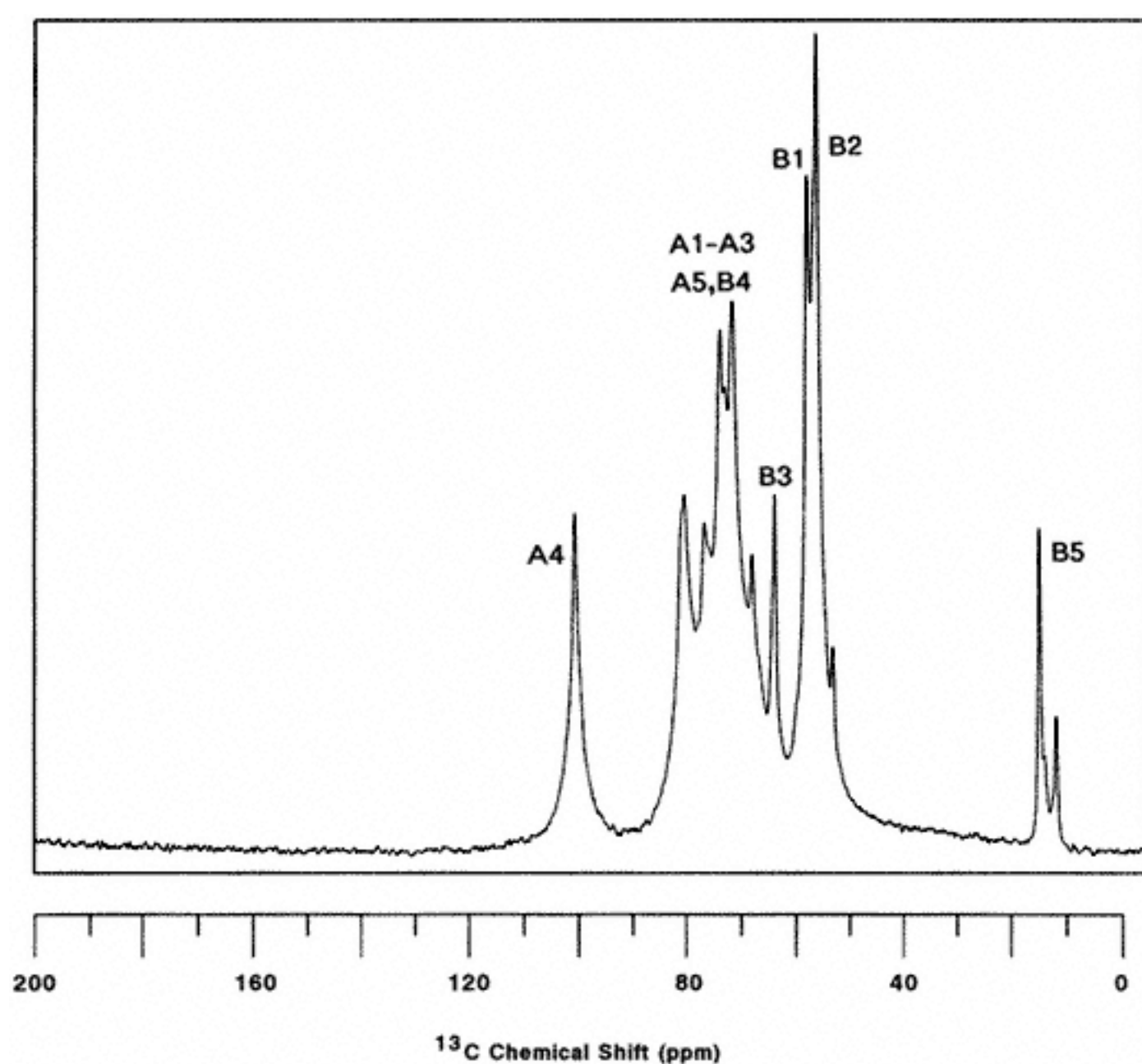
References

Y. Tezuka, K. Imai, M Oshima, and T. Chiba. *Macromolecules* 20:2413, 1989; P. Zadorecki, T. Hjertberg, and M. Arwidsson. *Makromol. Chem.* 188:513, 1987; T. Hjertberg, P. Zadorecki, and M. Arwidsson. *Makromol. Chem.* 187:899, 1986.

VII-B-2—
Hydroxypropyl Methyl Cellulose

Comments

The resonances are broadened owing to limited solubility and gel formation. Substitution of H by CH₃ (degree of substitution, DS = 30%) and CH₂CH(OH)CH₃ (DS = 10%) at carbons **A2**, **A3**, and **B1** is incomplete, leading to an envelope of peaks between ~70 and 80 ppm. Shifts because of stereochemistry are also present. This material is used as a thickener and emulsifier in foods and coatings.



Code	Shift (ppm)
A1	70–85
A2	70–85
A3	70–85
A4	102.8
A5	70–85
B1	60.9
B2	56.3
B3	66.8
B4	70–85
B5	19.0

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: D_2O

Concentration: 20% w/w

Scans: 8400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 15 Hz

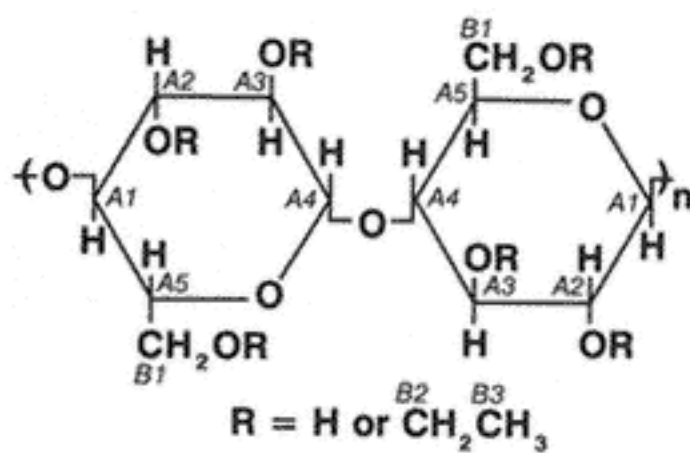
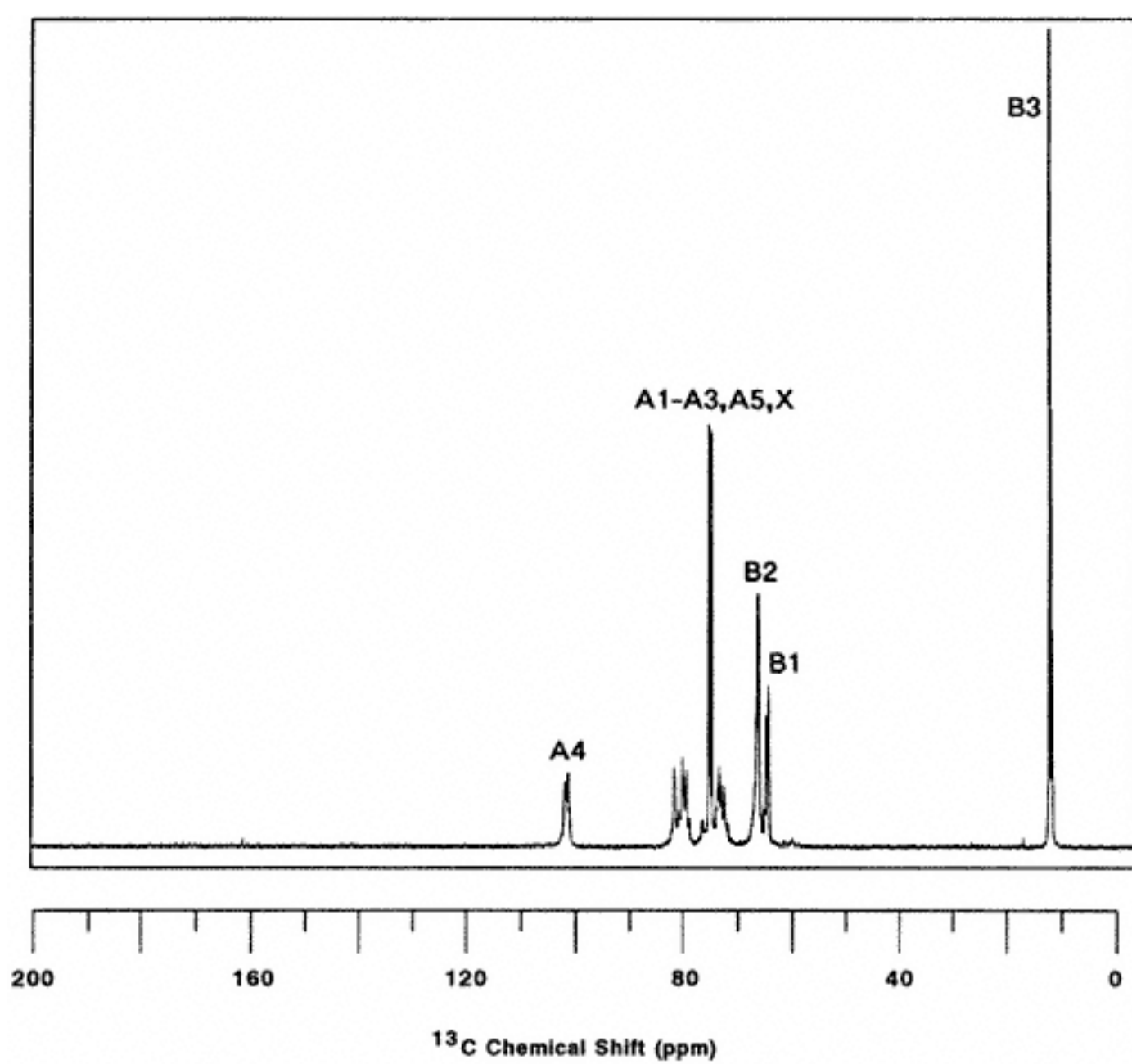
Pulse delay: 5 s

ReferenceY. Tezaka, K. Imai, M. Oshima, and T. Chiba. *Polym. J.* 23:189, 1991.

**VII-B-3—
Ethyl Cellulose (EC)**

Comments

Substitution of H by CH_2CH_3 (degree of substitution, $\text{DS} = 50\%$) at carbons **A2**, **A3**, and **B1** is incomplete, leading to an envelope of peaks between ~ 70 and 80 ppm. Shifts because of stereochemistry are also present. Solvent resonances are marked by **X**. This tough, flexible material is used in electrical applications and for fire extinguisher and electrical component housings.



Code	Shift (ppm)
A1	73–85
A2	73–85
A3	73–85
A4	103.2
A5	73–85
B1	67.0
B2	68.5
B3	15.9

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 15 Hz

Pulse delay: 5 s

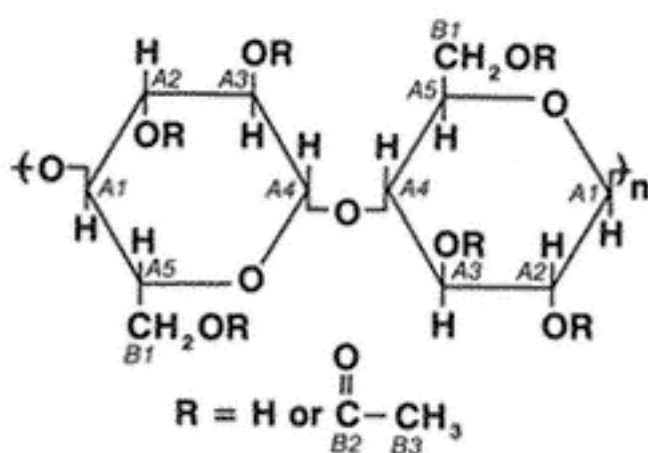
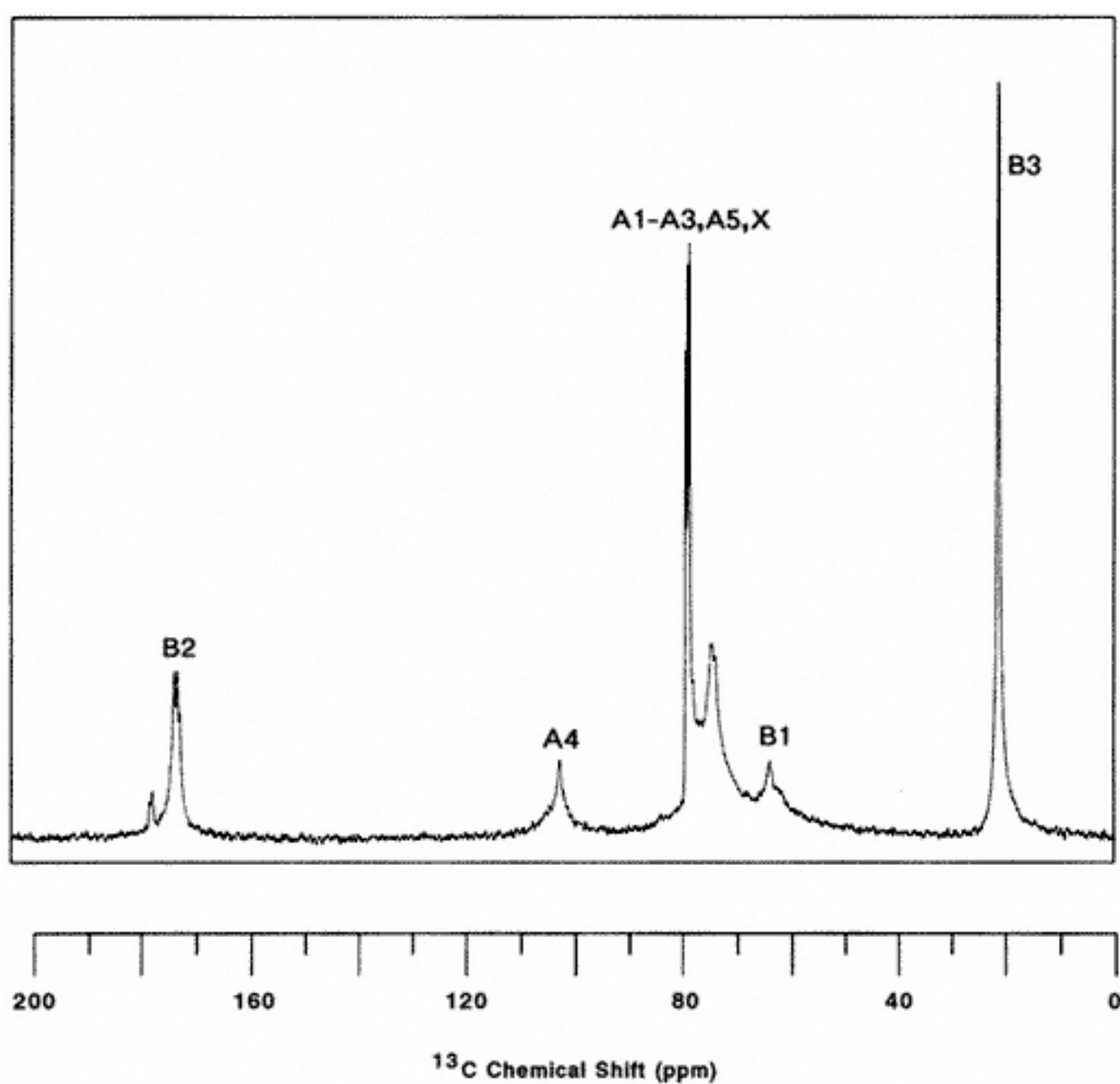
References

P. Zadorecki, T. Hjertberg, and M. Arwidsson. *Makromol. Chem.* 188:513, 1987; T. Hjertberg, P. Zadorecki, and M. Arwidsson. *Makromol. Chem.* 187:899, 1986.

**VII-B-4—
Cellulose Acetate (CA)**

Comments

The resonances are broadened due to limited solubility and gel formation. Substitution of H by C(O)CH₃ (degree of substitution, DS = 40%) at carbons **A2**, **A3**, and **B1** is incomplete, leading to an envelope of peaks between ~70 and 80 ppm. Shifts because of stereochemistry are also present. Solvent resonances are marked by **X**. This material is used for tape backing and for appliance housings.



Code	Shift (ppm)
A1	72.2
A2	72.2
A3	72.2
A4	100.4
A5	72.2
B2	62.4
B2	171.2
B3	20.7

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 15 Hz

Pulse delay: 5 s

References

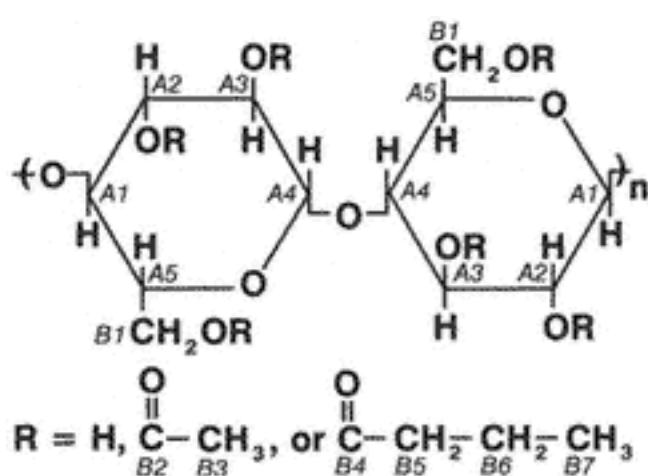
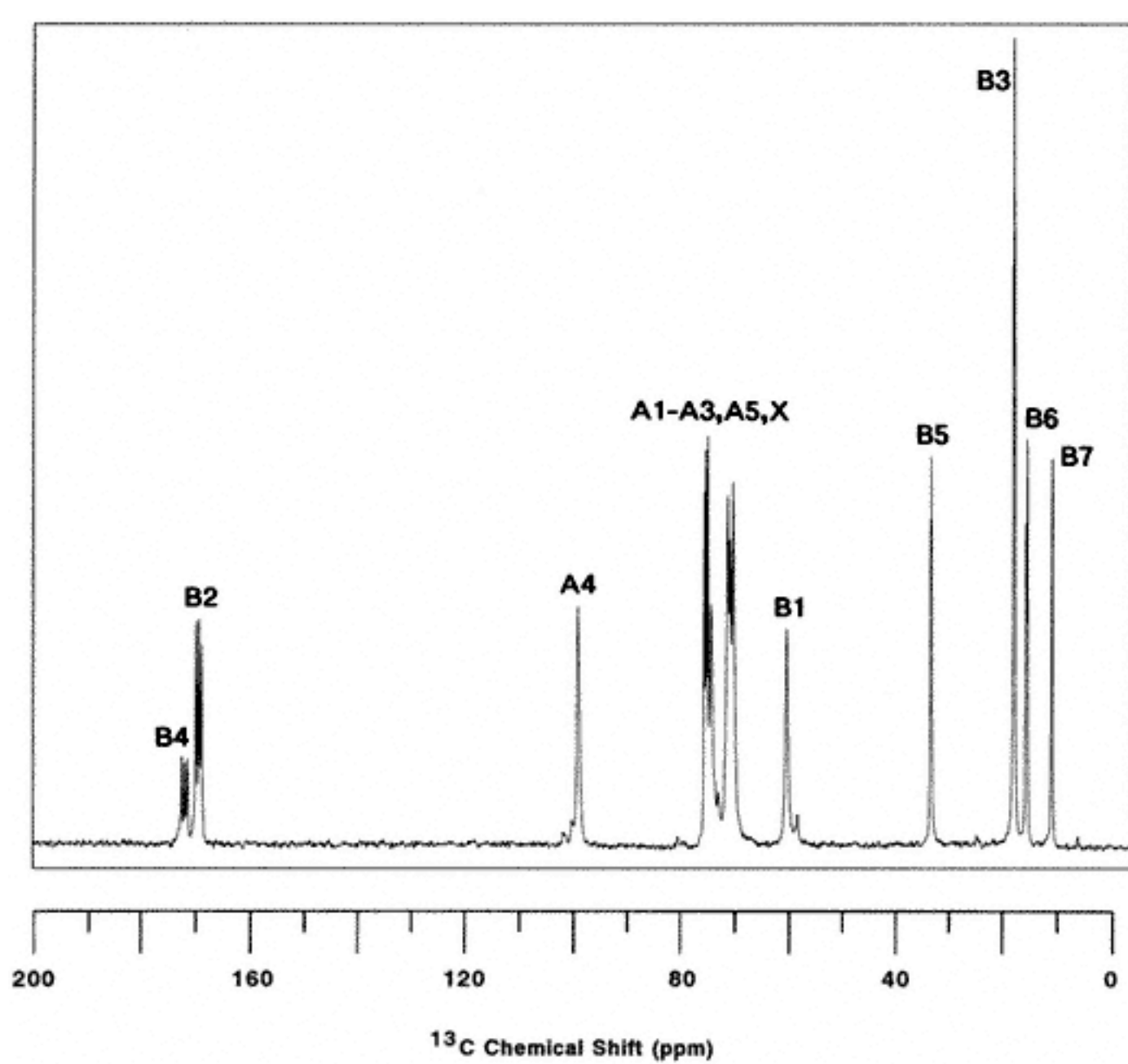
T. Nunes, H. G. Burrows, M. Bastos, G. Feio, and M. H. Gil. *Polymer* 36:479, 1995; C. M. Buchanan, K. J. Edgar, J. A. Hyatt, and A. K. Wilson. *Macromolecules* 24:3050, 1991; K. Kowsaka, K. Okajima, and K. Kamide. *Polym. J.* 20:827, 1986; S. Doyle, R. A. Pethrick, R. K. Harris, J. M. Lane, K. J. Packer, and F. Heatley. *Polymer* 25:19, 1984.

VII-B-5—

Cellulose Acetate Butyrate (CAB)

Comments

Substitution of H by C(O)CH₃ (degree of substitution, DS = 30%) and C(O)CH₂CH₂CH₃ (DS = 20%) at carbons **A2**, **A3**, and **B1** is incomplete, leading to an envelope of peaks between ~70 and 80 ppm. Shifts because of stereochemistry are also present. Solvent resonances are marked by **X**. This material is used for toys, vehicle windows, skylights, and outdoor shelters.



Code	Shift (ppm)
A1	73.3
A2	77.8
A3	73.3
A4	101.0
A5	77.8
B1	62.3
B2	169.4
B3	20.8
B4	173.2
B5	36.1
B6	18.4
B7	13.8

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 800

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

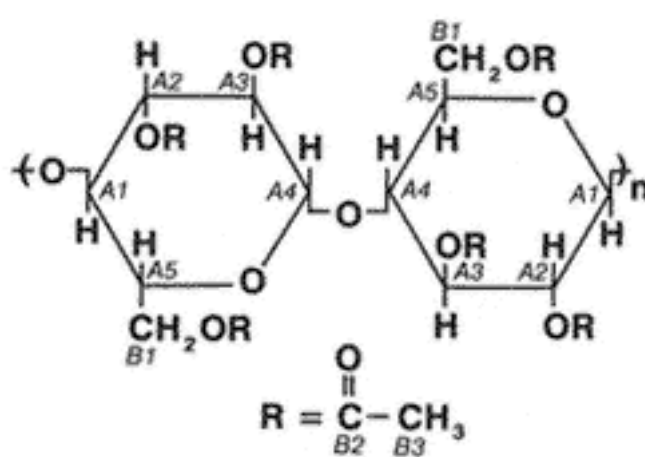
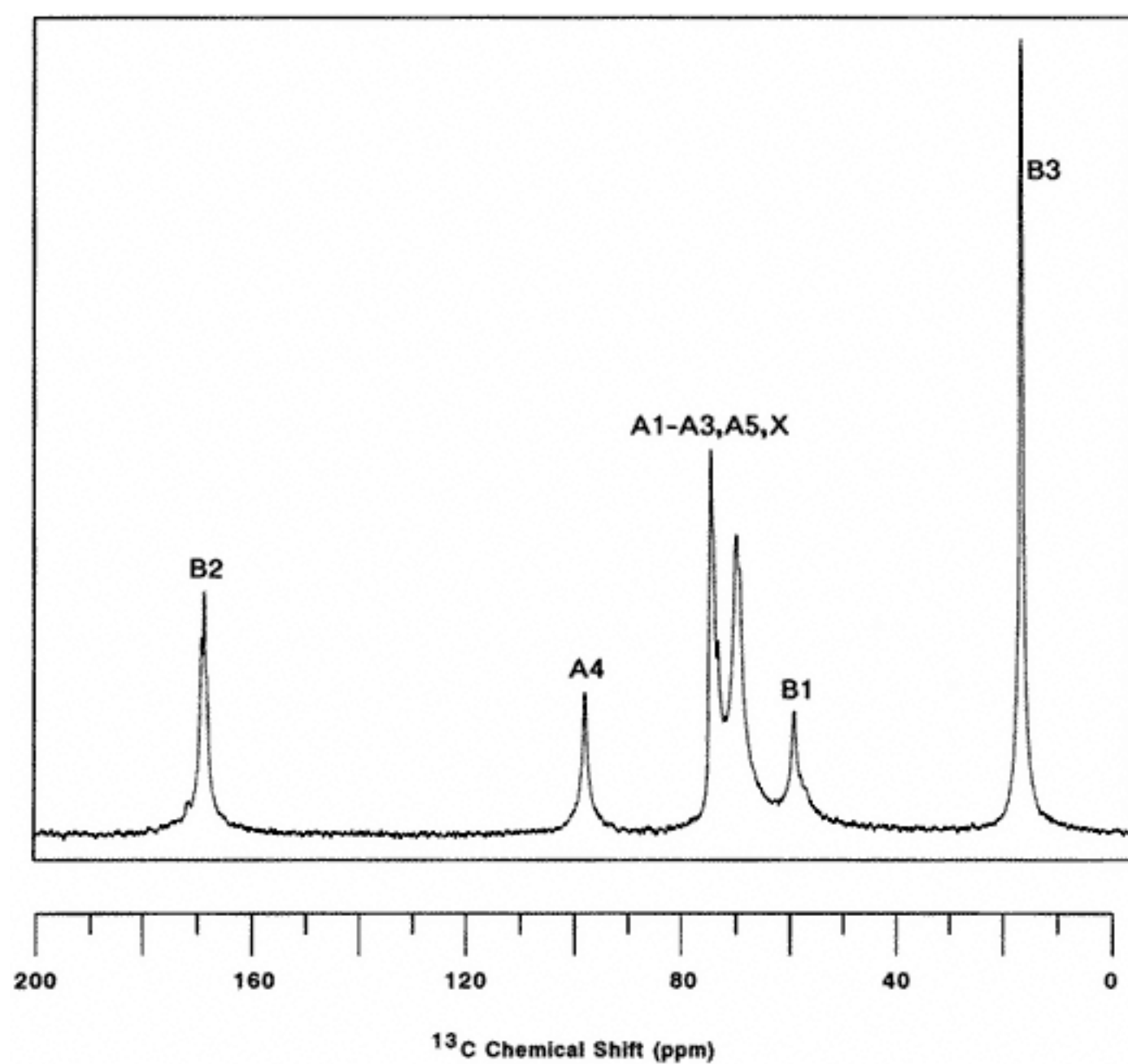
Broadening: 15 Hz

Pulse delay: 5 s

VII-B-6— Cellulose Triacetate

Comments

Also commonly known as acetate rayon (fibers) and acetate (sheet). The resonances are broadened owing to limited solubility and gel formation. Substitution of H by C(O)CH₃ at carbons **A2**, **A3**, and **B1** is nearly complete, so discrete peaks are observed between ~70 and 80 ppm. Shifts because of stereochemistry are also present. Solvent resonances are marked by **X**. The fibers are primarily used for clothing and the sheet in electrical appliances and photographic film backing.



Code	Shift (ppm)
A1	71.8
A2	77.0
A3	71.8
A4	101.1
A5	77.0
B1	62.3
B2	169.4
B3	20.1

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 800

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 15 Hz

Pulse delay: 5 s

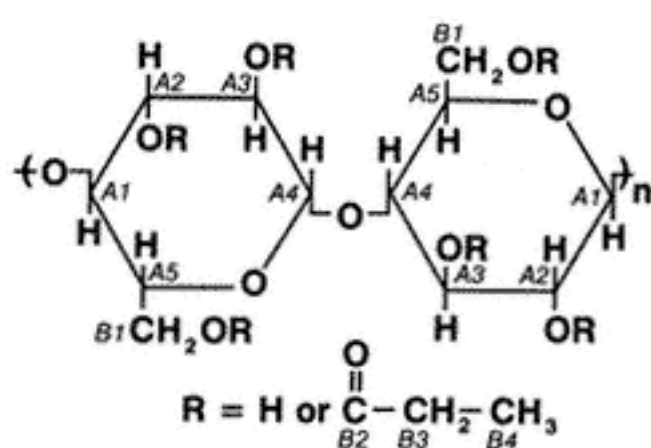
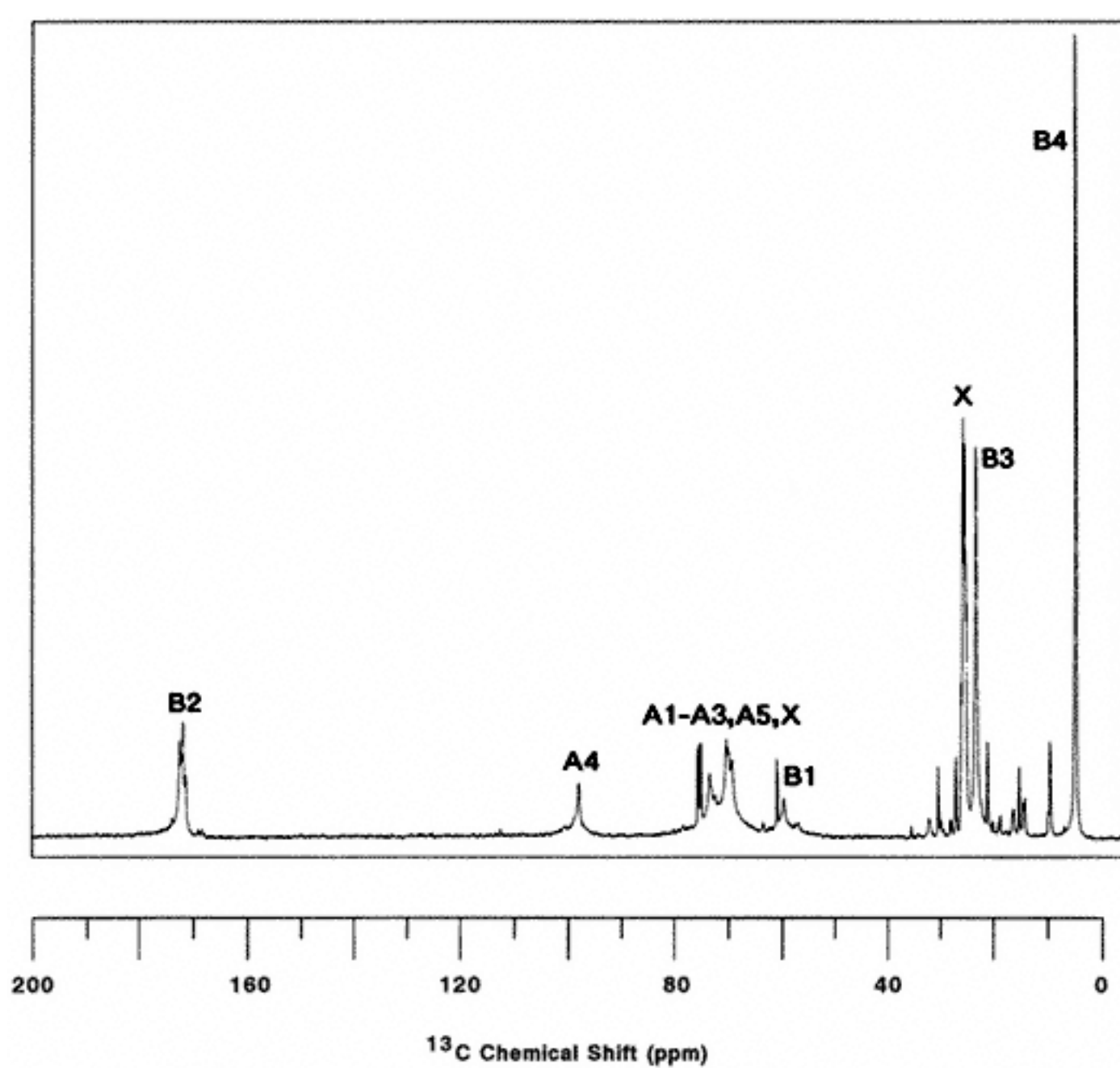
References

K. Kowsaka, K. Okajima, and K. Kamide. *Polym. J.* 20:1091, 1988; C. M. Buchanan, J. A. Hyatt, and D. W. Lowman. *Macromolecules* 20:2750, 1987.

VII-B-7—
Cellulose Propionate

Comments

The resonances are somewhat broadened owing to limited solubility and gel formation. Substitution of H by C(O)CH₂CH₃ at carbons **A2**, **A3**, and **B1** is incomplete, leading to an envelope of peaks between ~70 and 80 ppm. Shifts because of stereochemistry are also present. Solvent resonances are marked by **X**. Cellulose propionate is tougher than cellulose acetate {VII-B-4}, but it is used in similar applications.



Code	Shift (ppm)
A1	70–76
A2	70–76
A3	70–76
A4	100.0
A5	70–76
B1	63.5
B2	172.9
B3	26.9
B4	8.4

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 800

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 15 Hz

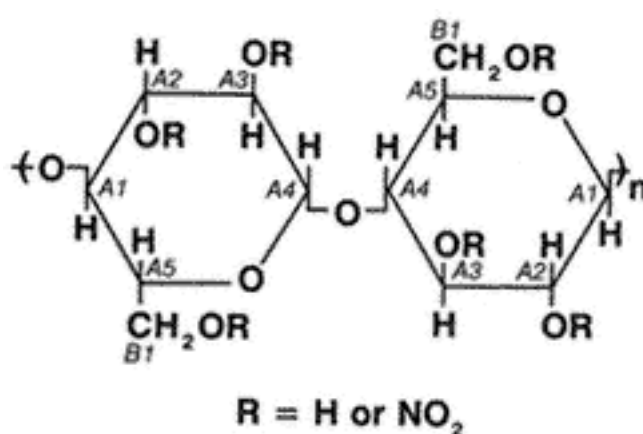
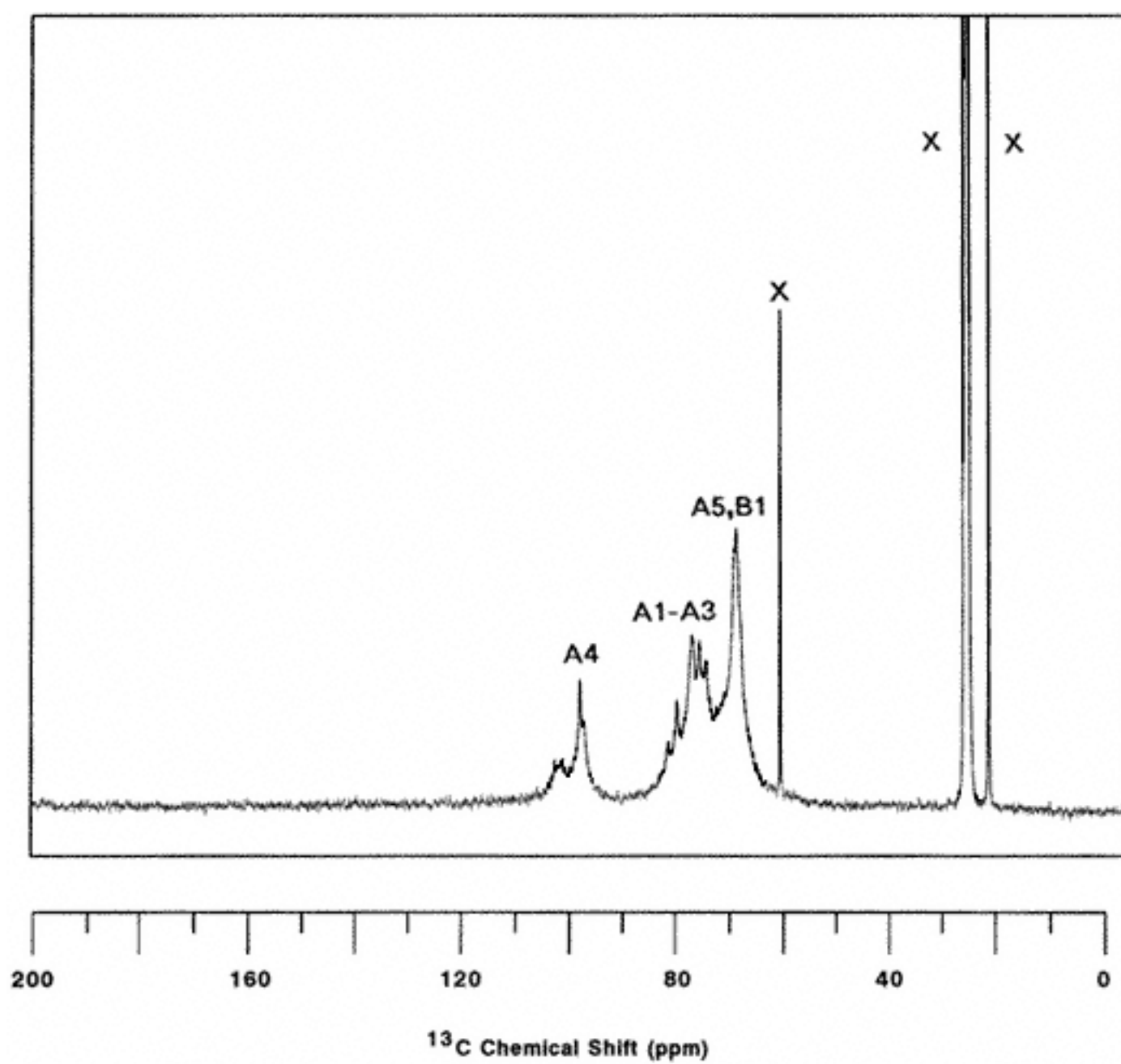
Pulse delay: 5 s

ReferenceT. Nunes, H. G. Burrows, M. Bastos, G. Feio, and M. H. Gil. *Polymer* 36:479, 1995.

VII-B-8— Cellulose Nitrate

Comments

Also commonly known as celluloid or collodion (when mixed with camphor). The resonances are broadened owing to limited solubility and gel formation. Substitution of H by NO_2 at carbons **A2**, **A3**, and **B1** is incomplete, leading to an envelope of peaks between ~ 70 and 80 ppm. Shifts because of stereochemistry are also present. Solvent resonances are marked by **X**. Cellulose nitrate was the first man-made thermoplastic material. Its current uses in coatings and decorative trim are limited by its high flammability. It is a component of some explosives.



Code	Shift (ppm)
A1	70–82
A2	70–82
A3	70–82
A4	100.0
A5	70–82
B1	70–82

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: acetone- d_6 /isopropanol

Concentration: 20% w/w

Scans: 2000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

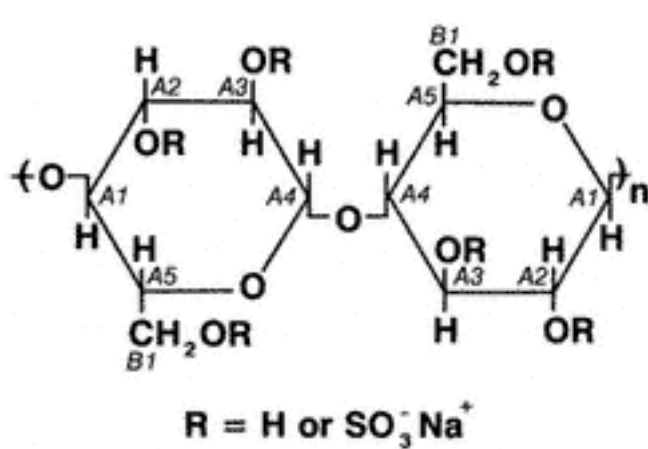
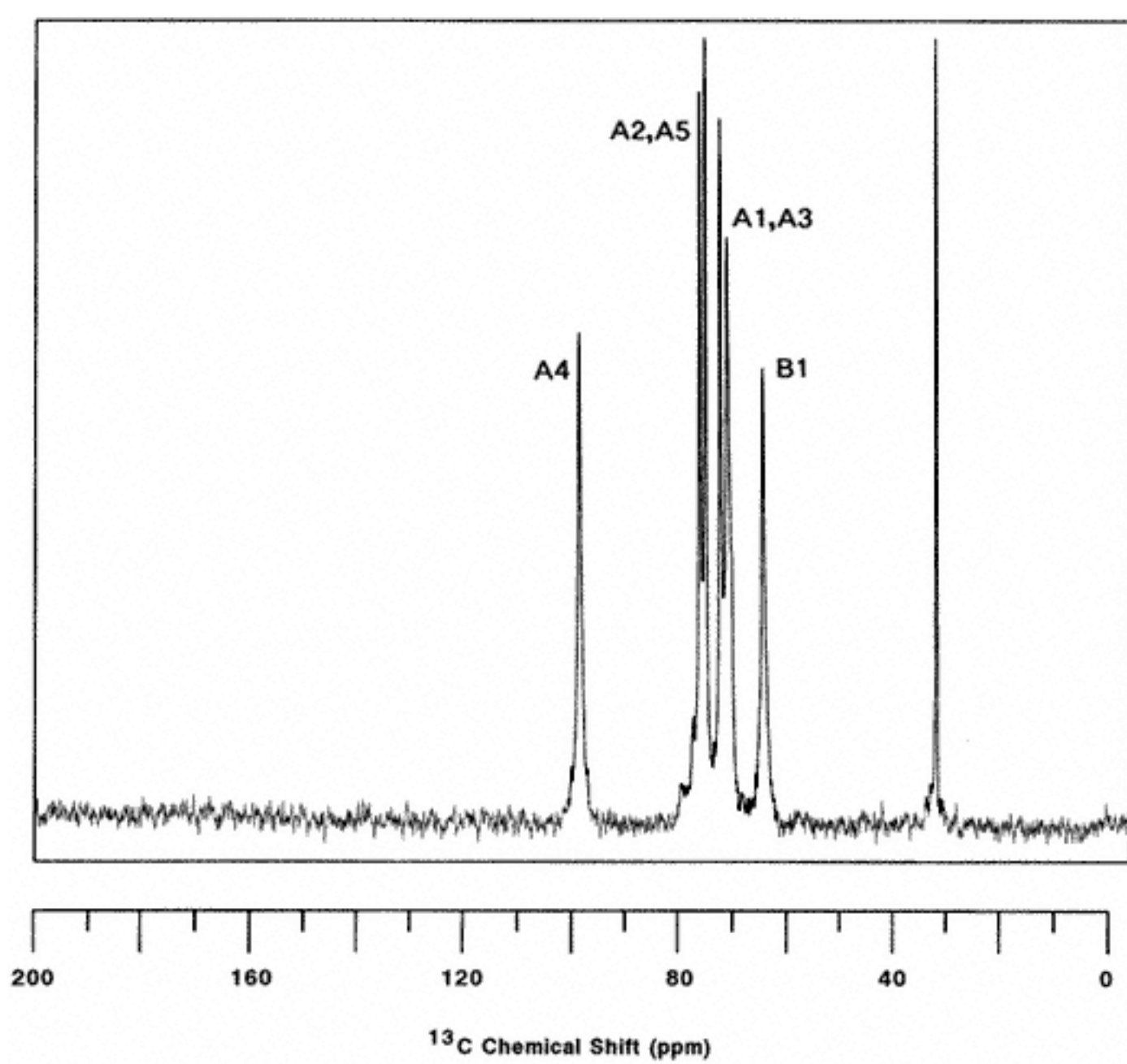
Broadening: 10 Hz

Pulse delay: 5 s

**VII-B-9—
Cellulose Sulfate, Na⁺**

Comments

The resonances are somewhat broadened owing to limited solubility and gel formation. Substitution of H by SO⁻³Na⁺ at carbons **A2**, **A3**, and **B1** is incomplete, leading to an envelope of peaks between ~70 and 80 ppm. Shifts because of stereochemistry are also present. This material is used as a food thickener, sizing agent, viscosity modifier, and pharmaceutical ingredient.



Code	Shift (ppm)
A1	70–82
A2	70–82
A3	70–82
A4	101.5
A5	70–82
B1	68.0

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: D_2O

Concentration: 10% w/w

Scans: 1600

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

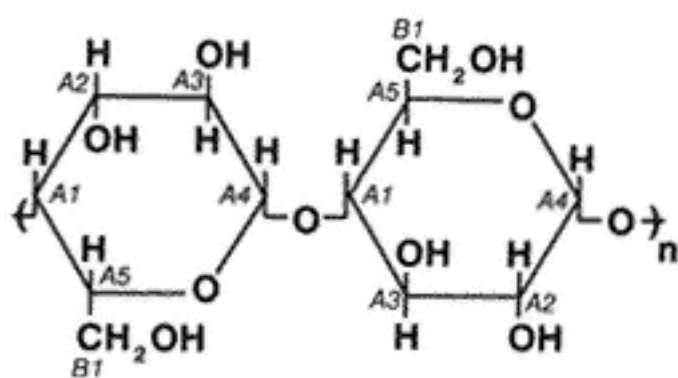
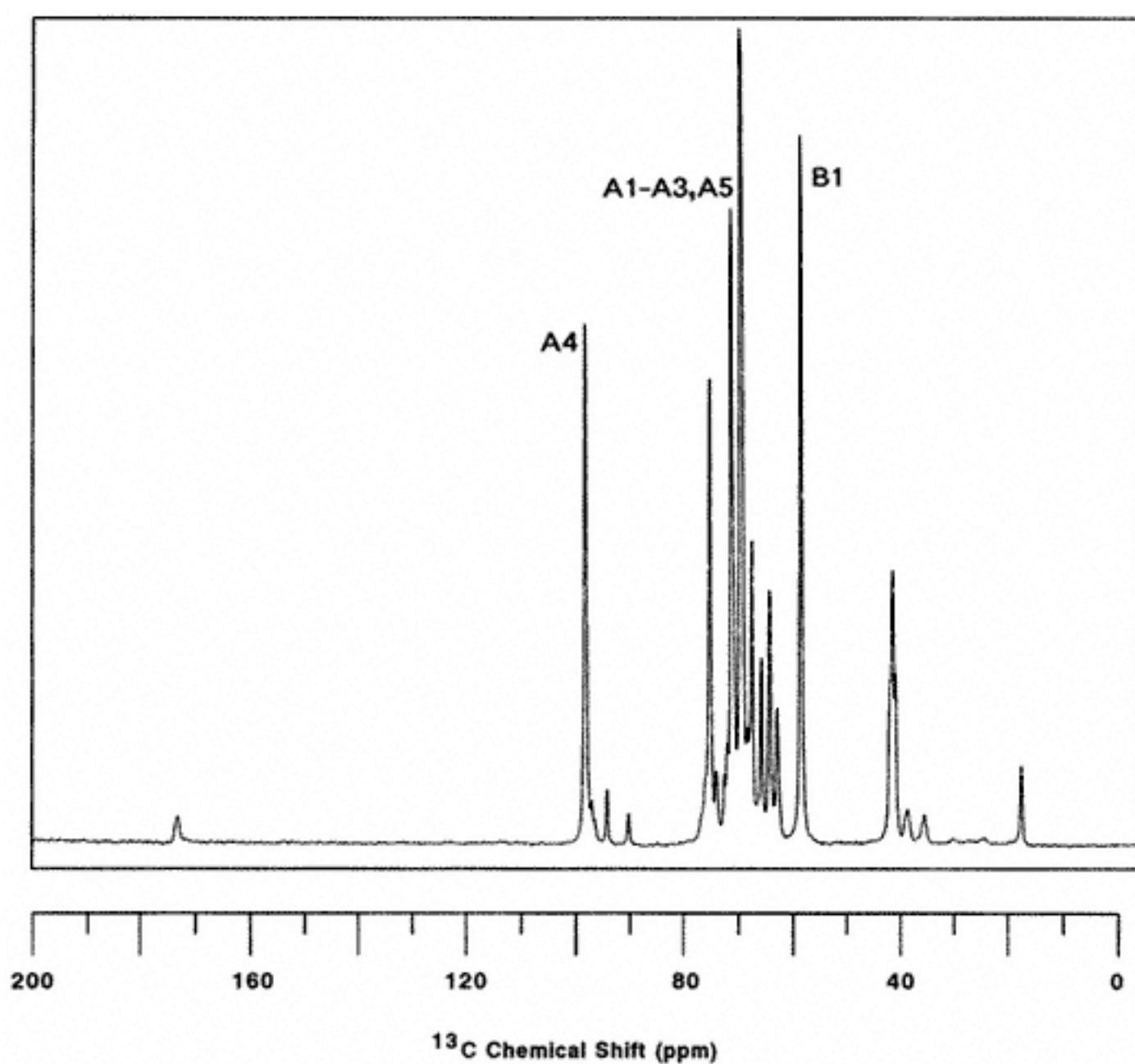
Broadening: 10 Hz

Pulse delay: 5 s

VII-B-10— Cornstarch

Comments

The resonances are somewhat broadened owing to limited solubility and gel formation. The primary component of cornstarch is amylose, which is shown. It also contains amylopectin, a cross-linked form of amylose, but this material is insoluble in water, and does not contribute to this spectrum. Cornstarch is an ingredient in many food preparations; starch foam is a biodegradable packing material. It is often mixed with polyethylene {II-A-1 through II-A-19} to make biodegradable bags and films.



Code	Shift (ppm)
A1	62–82
A2	62–82
A3	62–82
A4	100.0
A5	62–82
B1	61.0

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: D_2O

Concentration: 10% w/w

Scans: 11,100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

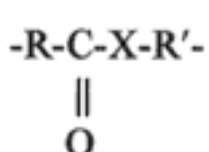
Pulse delay: 5 s

ReferenceM. Gurruchaga, I. Goni, B. Vazquez, M. Valero, and G. M. Guzman. *Macromolecules* 25:3009, 1992.

VIII—

Ester and Amide Backbones

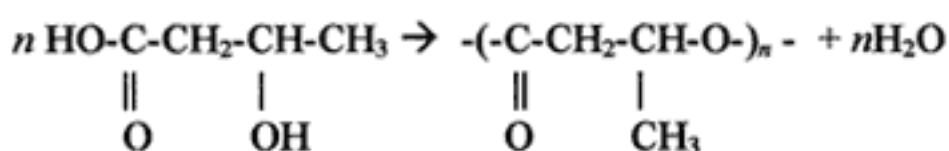
Materials in this group have either ester or amide linkages in the chain backbone:



A

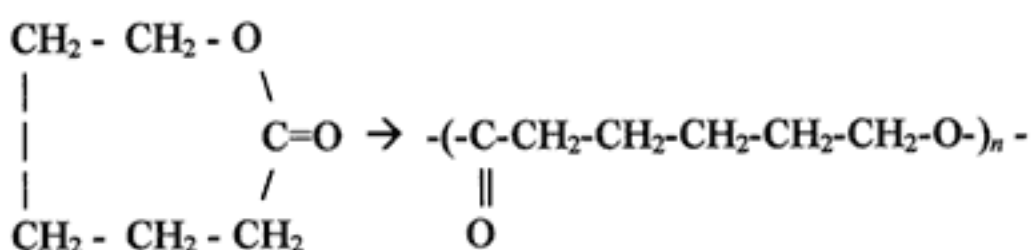
where X is either O or NH. These condensation polymers are commonly referred to as *polyesters* (when X = O) or *polyamides* (when X = NH).

Polyesters can be prepared from (1) hydroxycarboxylic acids, such as 3-hydroxybutyric acid:



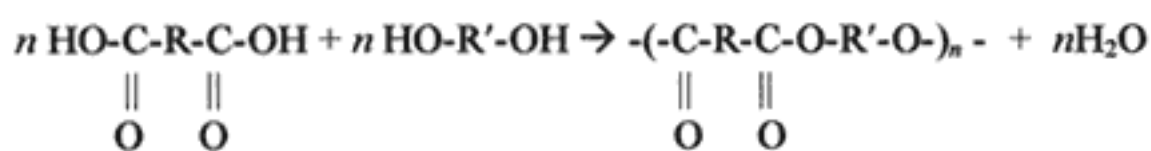
B

(2) by ring-opening of cyclic esters, such as caprolactone:



C

or (3) most commonly, by the reaction of a dicarboxylic acid and a diol:

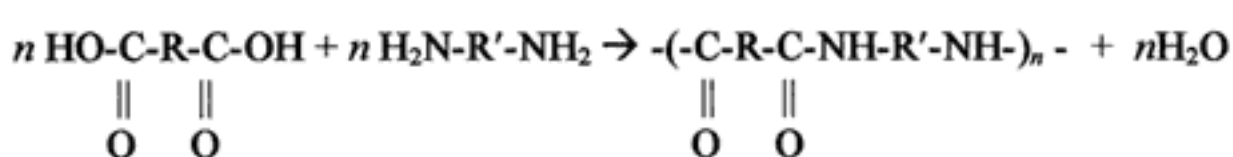


D

The poly(hydroxycarboxylic acids), such as poly(glycolic acid) {VIII-A-1}, poly(lactic acid)s {VIII-A-2 through VIII-A-5}, poly(3-hydroxybutyric acid) {VIII-A-6}, and poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid) {VIII-A-7}, and the polylactones, such as polycaprolactone {VIII-A-8}, are biodegradable. They are often used in medical applica-

tions or as "environmentally friendly" packaging [1]. Aliphatic polyesters may also be incorporated into polyurethanes {IX-B-3, IX-B-4} and other complex polymer systems. Aromatic polyesters, in which the acid component is a benzene dicarboxylic acid (such as phthalic or terephthalic acid) or a naphthene dicarboxylic acid, are familiar materials. The most common is poly(ethylene terephthalate) (PET) {VIII-B-1}, which forms the basis of most "polyester" fibers (such as Dacron), films (such as Mylar), tape backings, and clear plastic beverage bottles. Almost 3 billion lb (1.4 billion kg) of PET were produced in the United States in 1995 [2]. Other aromatic polyesters and copolymers are put to special uses in fiber, tape, and packaging applications [1]; several are commercially significant. In 1995, U. S. manufacturers produced: 1.5 billion lb (0.68 billion kg) of unsaturated polyesters, such as poly(4,4'-dipropoxy-2,2-diphenylpropanefumarate) {VIII-A-11}, poly(diallyl phthalate) {VIII-B-7}, and poly(diallyl isophthalate) {VIII-B-8}; 900 million lb (408 billion kg) of poly(bisphenol A carbonate) {VIII-B-11}, also known as Lexan (General Electric) and its blends; and 270 million lb (122.5 billion kg) of poly(butylene terephthalate) {VIII-B-4} [2].

Many synthetic polyamides are commonly referred to as *nylons*; over 1 billion lb (0.45 billion kg) were consumed in the United States in 1995 [2]. Nylons may be produced by a ring-opening polymerization, as in polyhexaneamide or polycaprolactam {VIII-C-1}, in which the reaction is similar to that shown in Eq. (C), (except that the in-ring oxygen is an NH group), or from the reaction of a dicarboxylic acid and a diamine:



E

Polymers made from difunctional monomers such as caprolactam are referred to as AB nylons; those produced from a diacid and a diamine, as AABB nylons. These polyamides are designated according to the number of carbons in the monomer(s). Lactam-derived nylons are named for the number of carbons in the starting material. Therefore, polyhexaneamide (polycaprolactam) {VIII-C-1} is known as nylon 6, and polydodecaneamide (polylauryllactam) {VIII-C-3}, as nylon 12. Polyamides synthesized from diacid and diamine precursors are designated by the number of carbons in the diacid, followed by the number in the diamine. Thus, poly(hexamethylene hexaneamide) is referred to as nylon 6/6 or nylon 66, because there are six carbons in the diacid (hexanedioic or adipic acid) and six in the diamine. Similarly, poly(hexamethylene dodecaneamide) is called nylon 6/12 or nylon 612. Nylons are best known as fibers for clothing, carpeting, and home furnishings [1], although many molded mechanical components are also made from such materials. Many natural fibers, such as wool and silk, are proteins, which are also polyamides, but they are not included in this compilation because of their limited solubility. Other nonnylon polyamides, such as polyaramid fibers and poly(amide imides), have also been excluded because of their insolubility.

VIII.A—

Sample Preparation and Spectral Acquisition

Polyesters dissolve in a variety of solvents at different temperatures [3]. In general, the aliphatic polyesters are low-melting and soluble in chloroform, although there are exceptions. Poly(glycolic acid), for example, dissolves only in hexafluoroacetone. The aromatic polyesters are sparingly soluble in dimethyl sulfoxide (DMSO) at elevated temperatures (130–150°C). Polyamides are generally soluble in cresol, dimethylformamide (DMF), or DMSO. Conditions for acquiring quantitative spectra are similar to those for other polymers. For ^{13}C , a pulse delay of 30 s following a 90° pulse, combined with gated ^1H decoupling, will yield correct relative areas for most carbons, including some nonprotonated ones. For ^1H , a 5-s delay after a 451° pulse is appropriate.

VIII.B—

Spectral Features

The ^{13}C NMR spectra of aliphatic polyesters bear superficial resemblance to those of the poly(vinyl esters) {IV-A-1 through IV-A-3}, polyacrylates {IV-B-1 through IV-B-11}, and α -substituted polyacrylates {IV-C-1 through IV-C-10}, with carbonyl resonances between 160 and 180 ppm and C—O peaks between 50 and 75 ppm. ^{13}C chemical shifts for a number of common polyesters are summarized in Table VIII-1. ^1H spectra of polyesters exhibit CH—O resonances around 3–4 ppm, and their spectra can, be at first glance, be confused with those of polyethers {VII-A-3H through VII-A-7H}, poly(vinyl esters) {IV-A-1H}, and polyacrylates and related materials {IV-B-2H through IV-B-6H; IV-C-1H through IV-C-7H.}.

Table VIII.1 ^{13}C Chemical Shifts of Some Aliphatic and Aromatic Polyesters

Polymer	$\begin{array}{c} A1\ A2... \\ -\text{O}-\text{C}-\text{C}-\dots-\text{O}- \\ \\ \text{O} \end{array}$			or	$\begin{array}{c} A1\ A2...A2\ A1\ B1\ B2...B2\ B1 \\ -\text{O}-\text{C}-\text{C}-\dots-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\dots-\text{C}-\text{C}- \\ \quad \\ \text{O} \quad \text{O} \end{array}$						Others
	A1	A2	A3		A4	A5	A6	B1	B2	B3	
Poly(glycolic acid)	170.8	63.0	—	—	—	—	—	—	—	—	—
Poly(<i>l</i> -lactic acid)	169.4	69.0	—	—	—	—	—	—	—	—	16.6 (CH ₃)
Poly(<i>d</i> <i>l</i> -lactic acid)	169.4	69.1	—	—	—	—	—	—	—	—	16.6 (CH ₃)
Poly(3-hydroxybutyric acid)	169.5	40.9	67.9	—	—	—	—	—	—	—	19.7 (CH ₃)
Polycaprolactone	173.7	34.5	24.7–28.8	24.7–28.8	24.7–28.8	64.1	—	—	—	—	—
Poly(ethylene succinate)	171.5	28.5	—	—	—	—	61.3	—	—	—	—
Poly(ethylene adipate)	172.8	33.6	23.8	—	—	—	62.0	—	—	—	—
Poly(ethylene terephthalate)	166.0	134.9	130.5	—	—	—	63.9	—	—	—	—
Poly(butylene terephthalate)	166.0	135.0	130.1	—	—	—	65.7	26.0	—	—	—
Poly(1,4-cyclohexanedimethylene terephthalate)	165.7	133.7	129.6	—	—	—	70.1,67.4	37.4,35.3	29.1,25.5	—	—
Poly(diallyl phthalate)	167.7	119.0	129.9–132.6	129.9–132.6	—	—	66.5	67–72	32–38	—	—
Poly(diallyl isophthalate)	165.4	118.3	128–134	128–134	128–132	—	65.8	67.9	27.5	—	—
Poly(ethylene naphthoate)	166.4	135.2	131.0	126.5	131.0	131.0	63.7	—	—	—	—
Poly(butylene naphthoate)	166.7	135.8	130.9	127.0	130.9	130.9	65.8	26.0	—	—	—

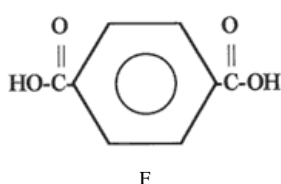
Polyamides can be more easily identified by their ^{13}C spectra than by ^1H ; the former have carbonyl peaks at ~ 175 ppm, but no resonances in the region between 50 and 75 ppm. The ^1H spectra of the polyamides are very similar, and none are included in this chapter.

VIII.B.1— Aliphatic Ester Polymers and Copolymers

The ^{13}C resonances of the aliphatic polyesters appear in the following ranges: 165–175 ppm for $\text{C}=\text{O}$; 50–75 ppm for $\text{C}-\text{O}$; and 10–50 for the other aliphatic resonances. The ^1H spectrum displays a simple pattern as well: 3–6 ppm for CH_n-O and 0.8–2 ppm for the remaining aliphatic protons. Either ^{13}C or ^1H may be used to determine the composition of copolymers and blends in this group, providing that quantitative conditions are applied when recording the spectrum, and that distinct resonances assignable to each component are observed.

VIII.B.2— Aromatic Ester Polymers and Copolymers

The most common aromatic polyesters are those based on terephthalic acid:



although polymers based on naphthenedioic acid have recently become commercially available from BP Amoco. The carbonyl resonances for aromatic polyesters appear at somewhat lower chemical shifts than those for the aliphatic polyesters (i.e., 150–165 ppm versus ~ 175 ppm). As expected, the ring carbons resonate between 115 and 135 ppm. The $\text{C}-\text{O}$ peak in the polyester appears at 50–70 ppm, depending on the exact nature of the diol used, and the other peaks appear where anticipated, based on their chemical identity [4]. Polymers made from hydroxyaromatic acids are commercially available [1], but they are generally insoluble, and so are not included in this collection. ^1H spectra of aromatic polyesters display the expected

Table VIII.2 ^{13}C Peak Ratios and Melting Points for Some Aliphatic Polyamides

Polymer	Nylon designation	C-C/C-N or C-C/ C-C=O	$T_m(^{\circ}\text{C})$ [1]
Polyhexaneamide	6	3	215
Polyundecaneamide	11	8	194
Polydodecaneamide	12	9	179
Poly(hexamethylene hexaneamide)	6/6	3	265
Poly(hexamethylene nonaneamide)	6/9	4.5	205
Poly(hexamethylene decaneamide)	6/10	5	225
Poly(hexamethylene dodecaneamide)	6/12	6	217

resonances: aromatic protons at 6–8 ppm, $\text{CH}_n\text{—O}$ protons between 2.5 and 4 ppm, and other aliphatic protons at less than 2.5 ppm. The composition of copolymers and blends in this group can be measured by either ^{13}C or ^1H , assuming that quantitative conditions have been met, and that resonances specific to each component can be identified.

VIII.B.3— Polyamides

The ^{13}C spectra of polyamides are similar to those of polyesters, except that the C—N group appears at approximately 40 ppm, rather than in the 50–75 ppm range typical of C—O . Polyamides are generally homopolymers; materials with different properties are produced by varying the lengths of the amine and acid segments. From a quantitative ^{13}C NMR spectrum, it is possible to measure the ratio of nitrogen-bonded methylene carbons (C—N) at about 40 ppm relative to those bonded only to a noncarbonyl carbon (C—C) between 24 and 30 ppm, or the ratio of carbonyl-bonded carbons (C—C=O) at approximately 36 ppm relative to C—C . These ratios help to identify the specific nylon, as shown in Table VIII-2. However, it is difficult to distinguish AB- from AABB-type polyamides by NMR (e.g., nylon 6 from nylon 6/6). For example, the ratio C—C/C—N or C—C/C—C=O is 3 for either polyhexaneamide {VIII-C-1} or poly(hexamethylene hexaneamide) {VIII-C-4}. The two materials may be differentiated by melting point, as illustrated in Table VIII-2. The combination of NMR and calorimetry is the best approach for specifically identifying a linear aliphatic polyamide.

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ESTER AND AMIDE BACKBONES*A. Aliphatic Ester Polymers and Copolymers*

VIII-A-1	Poly(glycolic acid)
VIII-A-2	Poly(<i>l</i> -lactic acid)
VIII-A-3	Poly(<i>l</i> -lactic acid-co-glycolic acid)
VIII-A-4	Poly(<i>d,l</i> -lactic acid)
VIII-A-5	Poly(<i>d,l</i> -lactic acid-co-glycolic acid)
VIII-A-6	Poly(3-hydroxybutyric acid)
VIII-A-6H	Poly(3-hydroxybutyric acid)
VIII-A-7	Poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid)
VIII-A-7H	Poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid)
VIII-A-8	Polycaprolactone
VIII-A-8H	Polycaprolactone
VIII-A-9	Poly(ethylene succinate)
VIII-A-10	Poly(ethylene adipate)
VIII-A-11	Poly(4,4'-dipropoxy-2,2-diphenylpropanefumarate)

B. Aromatic Ester Polymers and Copolymers

VIII-B-1	Poly(ethylene terephthalate)
VIII-B-1H	Poly(ethylene terephthalate)
VIII-B-2	Poly(ethylene terephthalate-co-1,4-cyclohexanedimethylene terephthalate)
VIII-B-3	Poly(ethylene terephthalate-co-4-hydroxybenzoic acid)
VIII-B-4	Poly(butylene terephthalate)
VIII-B-4H	Poly(butylene terephthalate)
VIII-B-5	Poly(butylene terephthalate-co-tetramethylene glycol)
VIII-B-5H	Poly(butylene terephthalate-co-tetramethylene glycol)
VIII-B-6	Poly(1,4-cyclohexanedimethylene terephthalate)
VIII-B-7	Poly(diallyl phthalate)
VIII-B-8	Poly(diallyl isophthalate)
VIII-B-9	Poly(ethylene naphthoate)
VIII-B-9H	Poly(ethylene naphthoate)
VIII-B-10	Poly(butylene naphthoate)
VIII-B-10H	Poly(butylene naphthoate)
VIII-B-11	Poly(Bisphenol A carbonate)
VIII-B-11H	Poly(Bisphenol A carbonate)

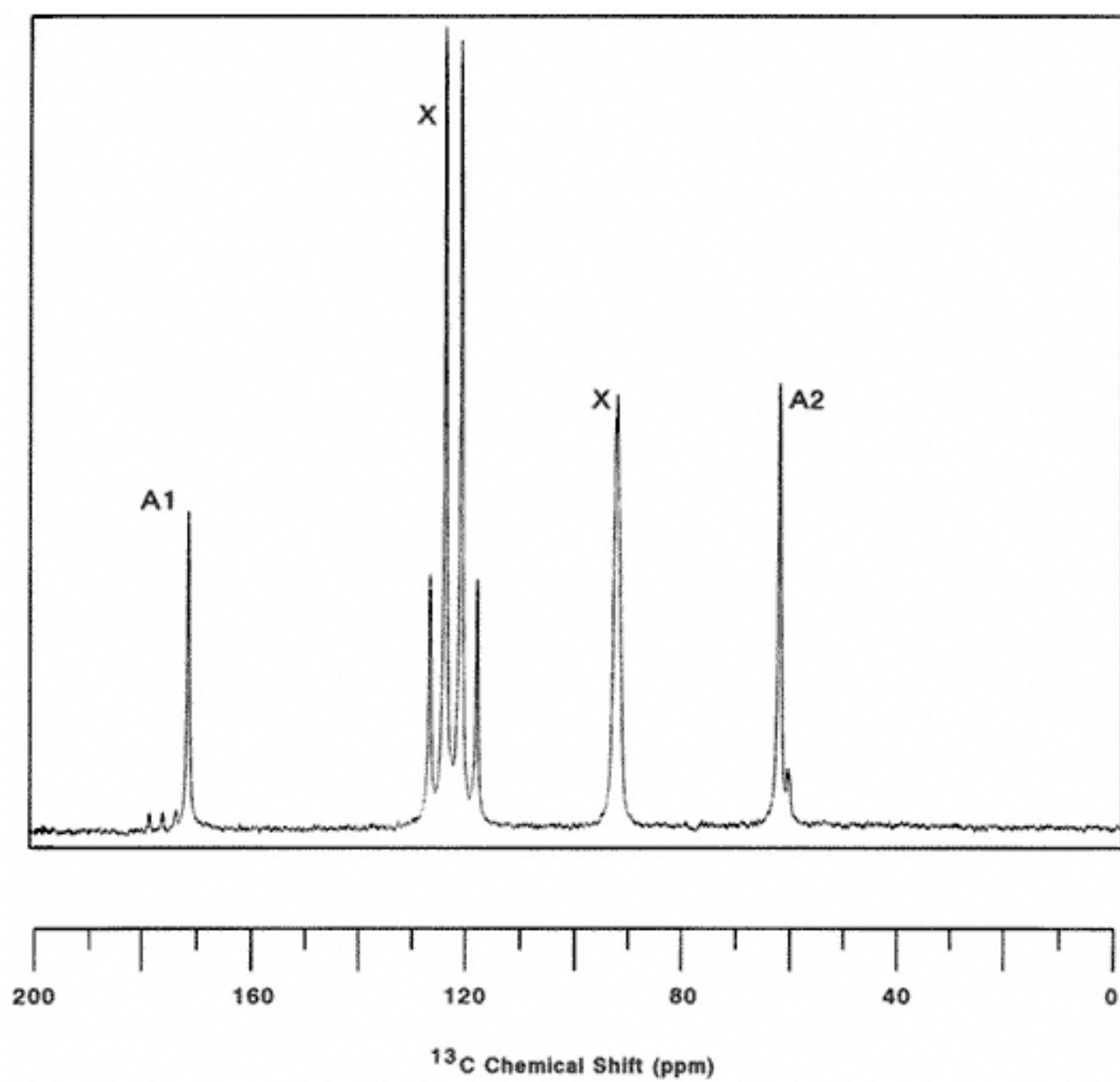
C. Polyamides

VIII-C-1	Polyhexaneamide (nylon 6)
VIII-C-2	Polyundecaneamide (nylon 11)
VIII-C-3	Polydodecaneamide (nylon 12)
VIII-C-4	Poly(hexamethylene hexaneamide) (nylon 6/6)
VIII-C-5	Poly(hexamethylene nonaneamide) (nylon 6/9)
VIII-C-6	Poly(hexamethylene decaneamide) (nylon 6/10)
VIII-C-7	Poly(hexamethylene dodecaneamide) (nylon 6/12)
VIII-C-8	Poly(2,2,4-trimethylhexamethylene terephthalamide-co-2,4,4-trimethylhexamethylene terephthalamide) (nylon 6/T)

**VIII-A-1—
Poly(Glycolic Acid)**

Comments

Also known as polyglycolide. Solvent resonances are marked by **X**. This biodegradable polymer is used in surgical sutures and other medical applications.



Code	Shift (ppm)
A1	170.8
A2	63.0

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: hexafluoroacetone deuterate

Concentration: 10% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

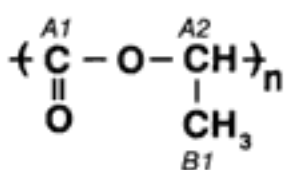
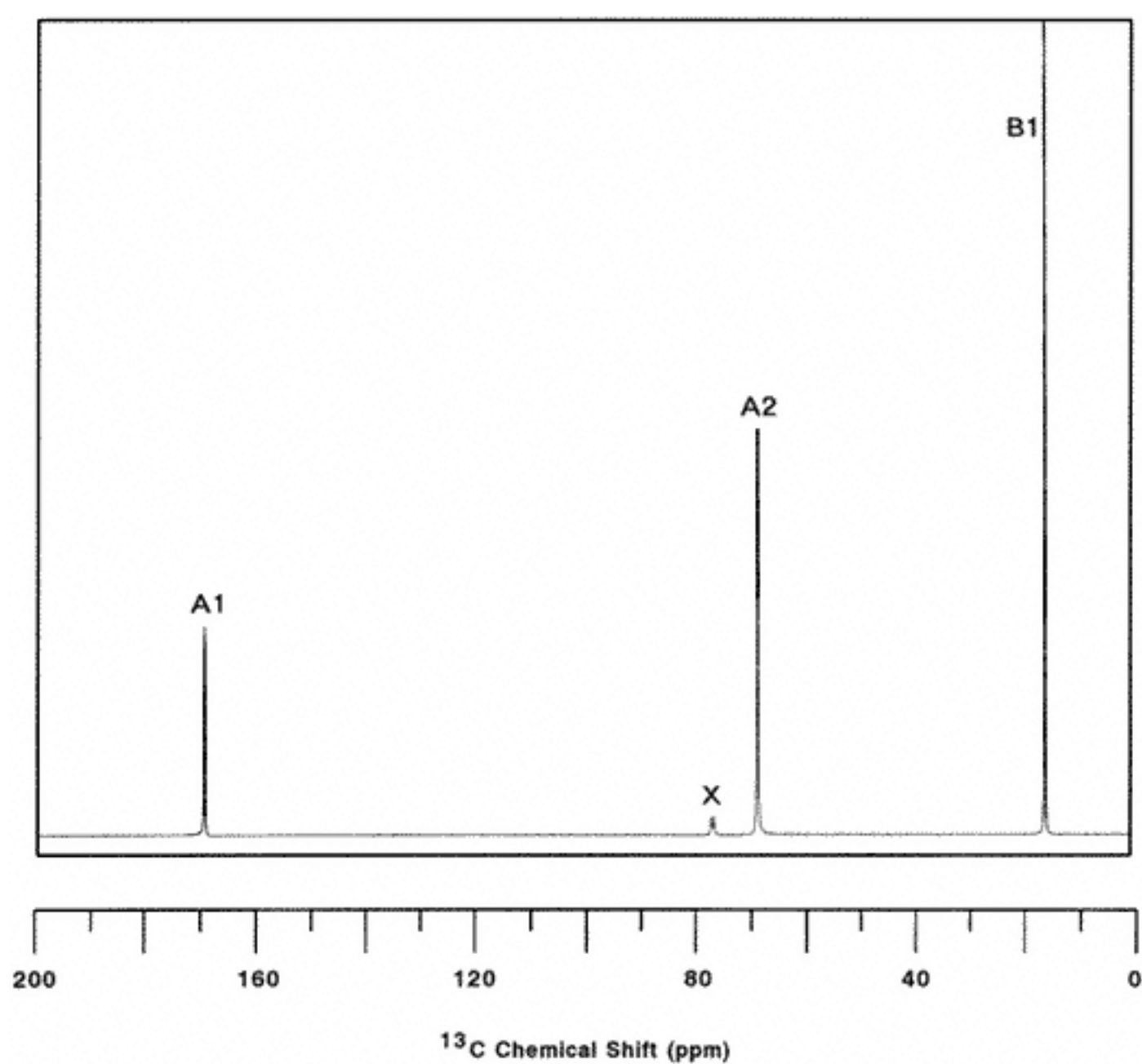
Broadening: 10 Hz

Pulse delay: 5 s

VIII-A-2—
Poly(*l*-Lactic Acid)

Comments

Also known as poly(*l*-lactide). Because of the high stereoregularity of this polymer, the spectrum is extremely simple. Solvent resonances are marked by X. Poly(*l*-lactic acid) is a biodegradable material used in surgical sutures and other medical applications.



Code	Shift (ppm)
A1	169.4
A2	69.0
B1	16.6

Experimental Parameters

Nucleus: ¹³ C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl ₃	Concentration: 20% w/w
Scans: 1000	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 5 s

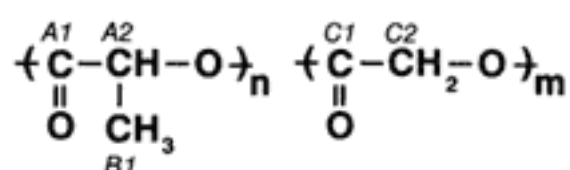
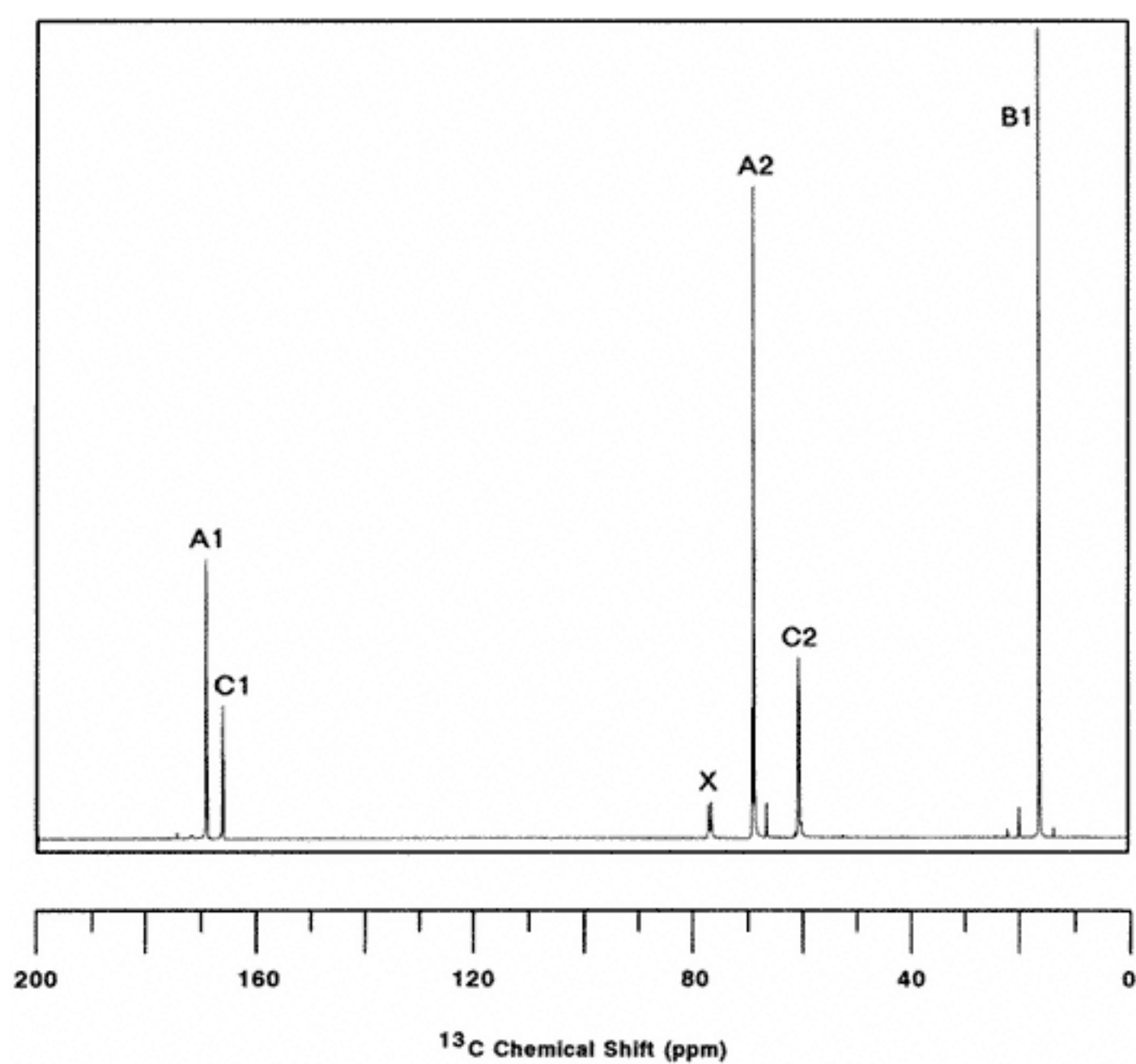
References

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**VIII-A-3—
Poly(*l*-Lactic Acid-Co-Glycolic Acid)**

Comments

Also known as poly(*l*-lactide-co-glycolide). Because of the high stereoregularity of this polymer, the spectrum is relatively simple; some comonomer sequence effects are observed. Solvent resonances are marked by **X**. Poly(*l*-lactic acid-co-glycolic acid) is a biodegradable material used in surgical sutures and other medical applications.



Code	Shift (ppm)
A1	169.6
A2	68.8
B1	16.5
C1	166.5
C2	60.7

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

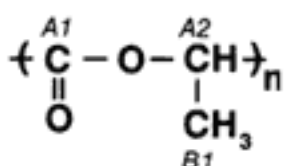
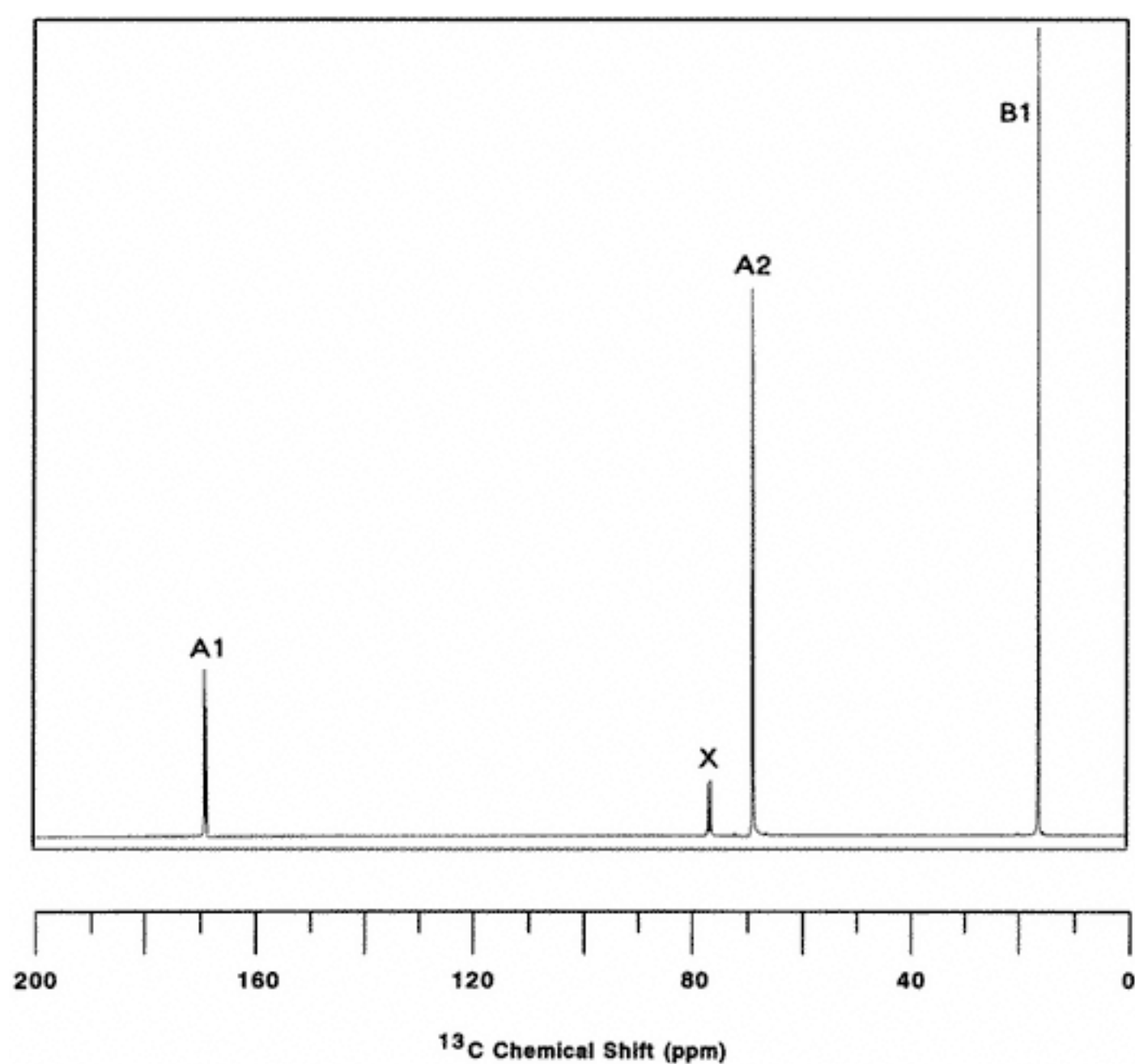
Broadening: 2 Hz

Pulse delay: 5 s

**VIII-A-4—
Poly(*d,l*-Lactic Acid)**

Comments

Also known as poly(*d,l*-lactide). The slight splitting of resonances **A1** and **A2** is due to the stereoirregularity of this polymer. Solvent resonances are marked by **X**. Poly(*d,l*-lactic acid) is a biodegradable material used in surgical sutures and other medical applications.



Code	Shift (ppm)
A1	169.4
A2	69.0
B1	16.6

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 20% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

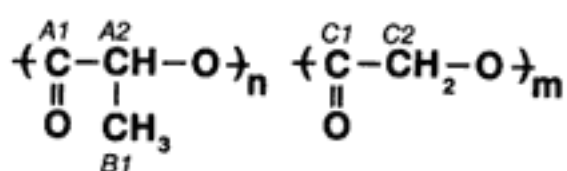
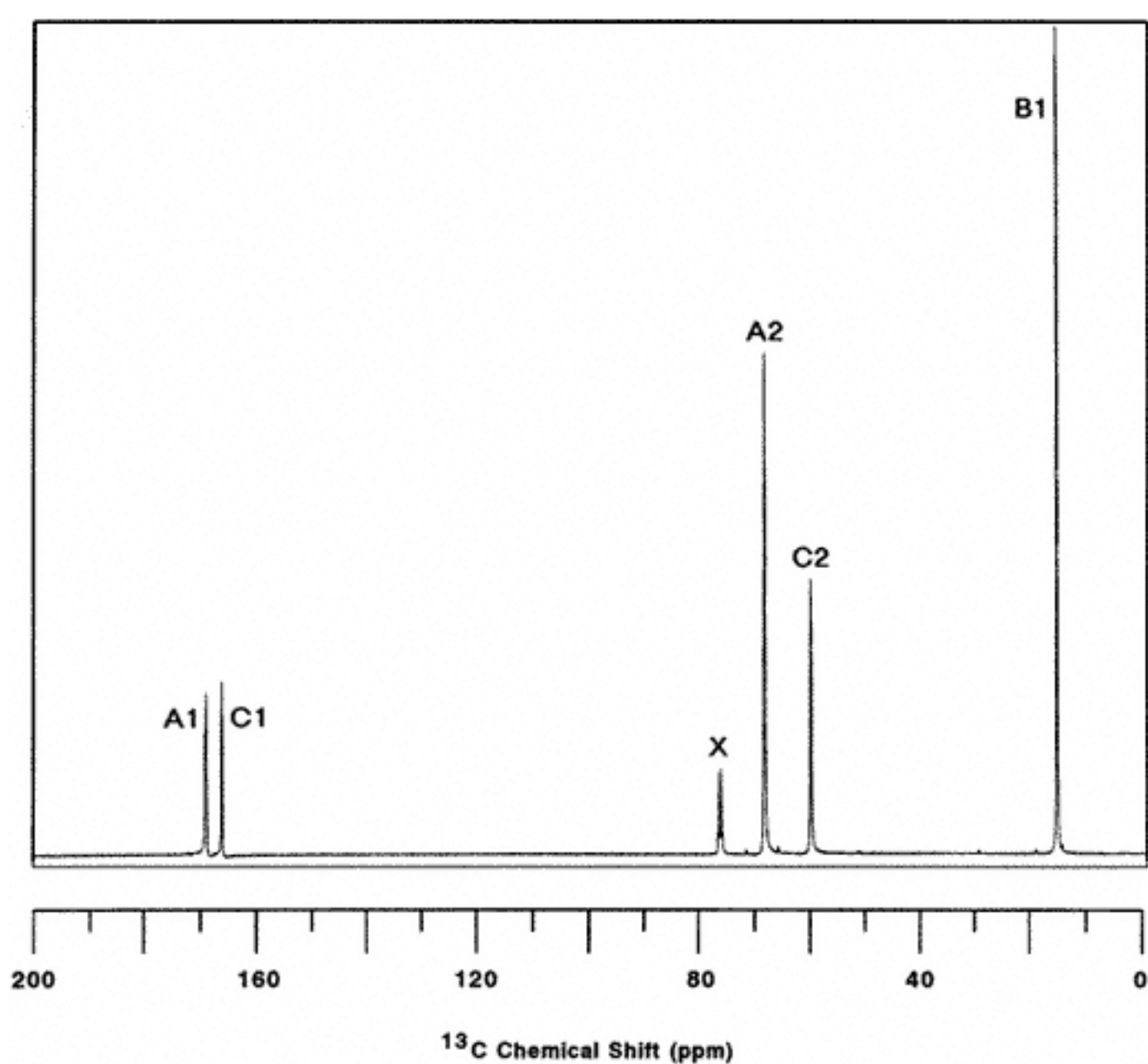
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VIII-A-5—

Poly(*d,l*-Lactic Acid-Co-Glycolic Acid)*Comments*

Also known as poly(*d,l*-lactide-co-glycolide). The slight splitting of resonances **A1** and **A2** is due to the stereoirregularity of this polymer. Solvent resonances are marked by **X**. Poly(*d,l*-lactic acid-co-glycolic acid) is a biodegradable material used in surgical sutures and other medical applications.



Code	Shift (ppm)
A1	169.4
A2	69.1
B1	16.7
C1	166.4
C2	60.9

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

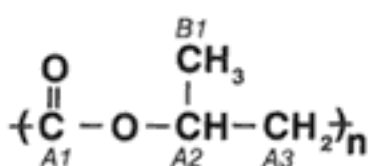
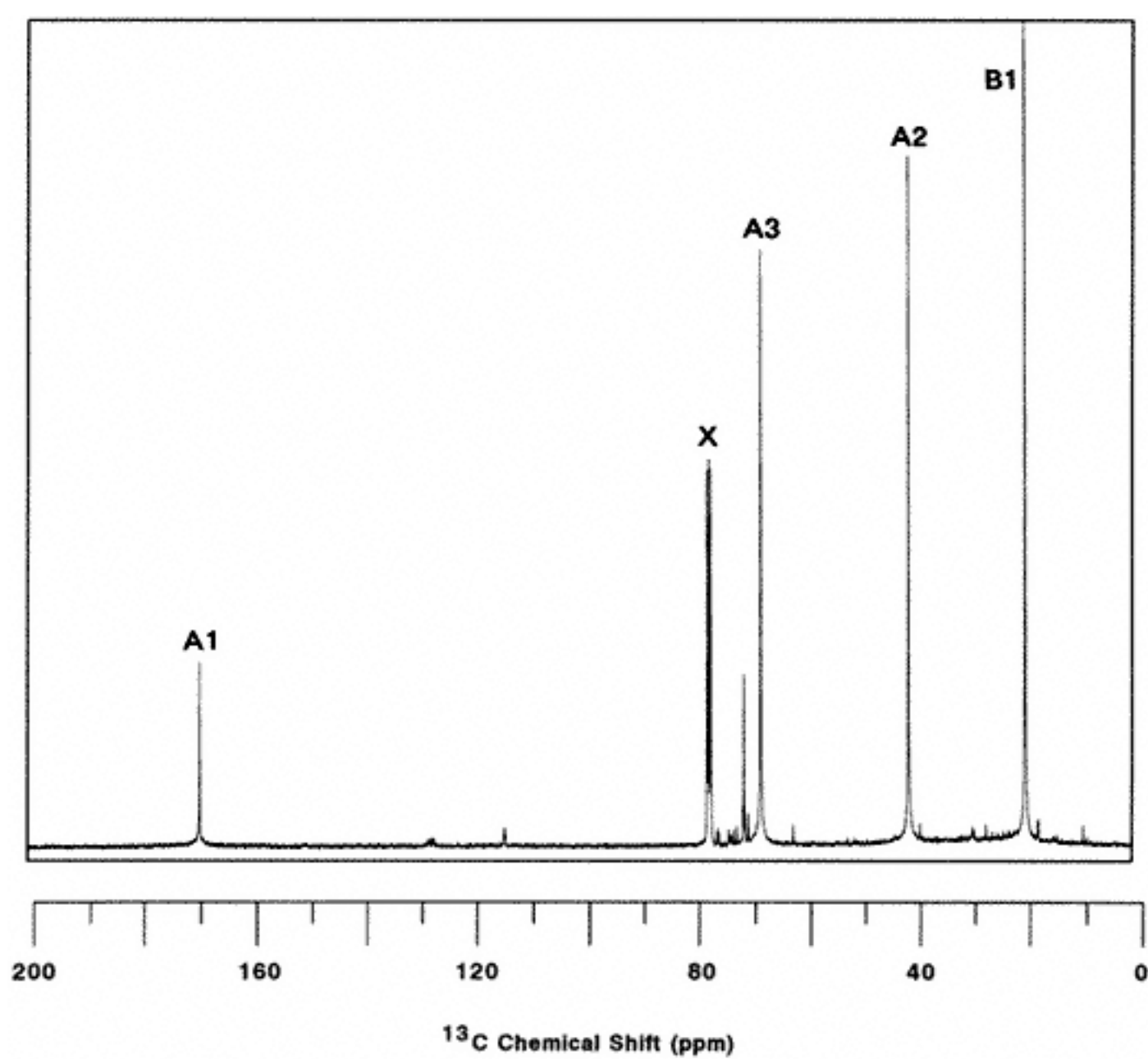
Pulse delay: 5 s

VIII-A-6—

Poly(3-Hydroxybutyric Acid) (PHB)

Comments

Also known as poly(3-hydroxybutyrate) or Biopol (Monsanto). Solvent resonances are marked by **X**. This biodegradable material forms in the cell walls of the bacterium *Alcaligenes eutrophus* when the organism is fed a diet of either glucose or ethanol. With properties similar to polypropylene {II-B-1}, PHB can be processed with conventional molding and extrusion equipment, and it can be used for packaging, medical implants, and pharmaceutical capsules.



Code	Shift (ppm)
A1	169.5
A2	40.9
A3	67.9
B1	19.7

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

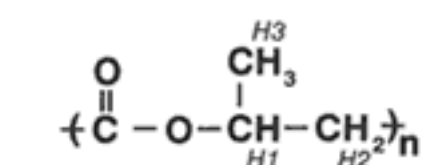
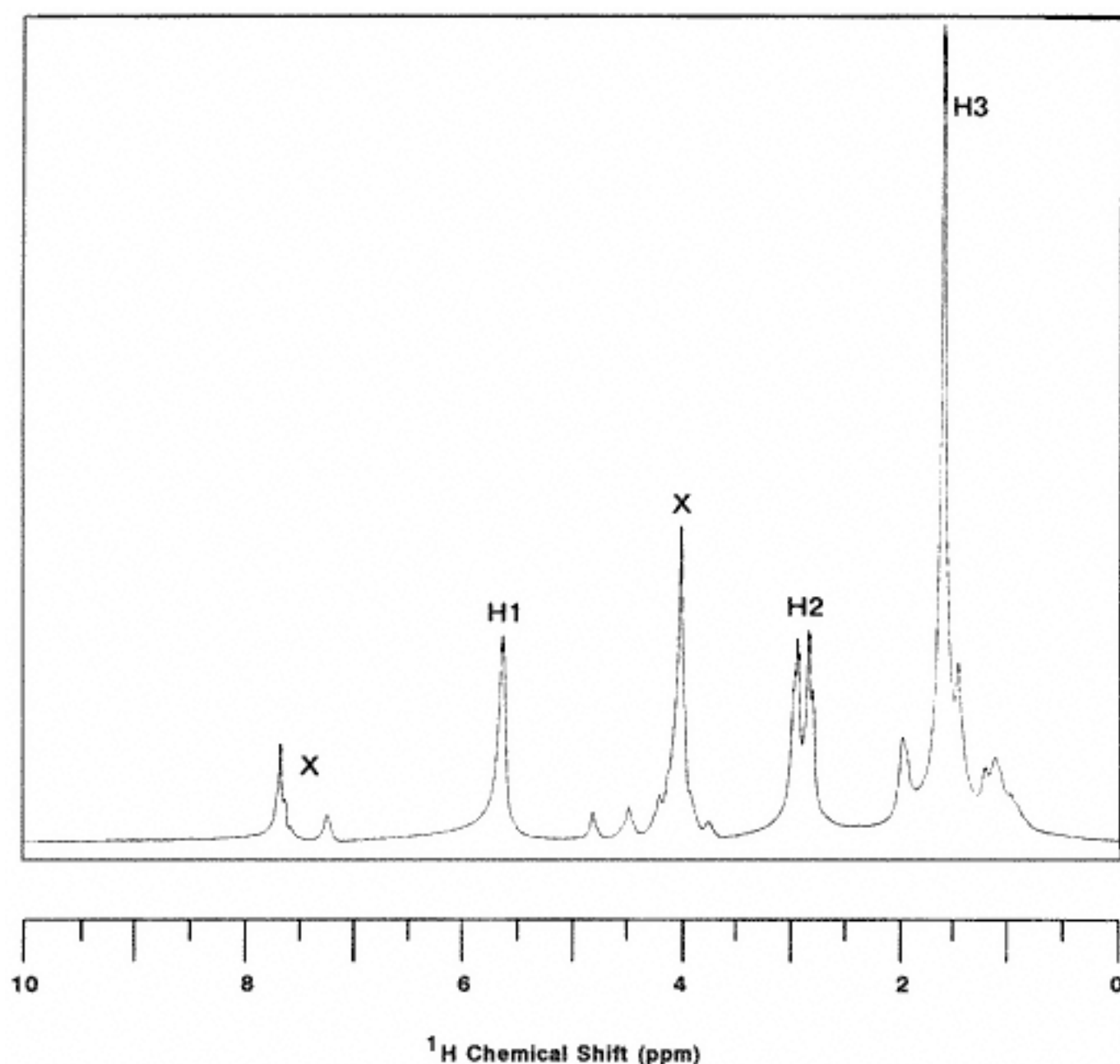
References

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**VIII-A-6H—
Poly(3-Hydroxybutyric Acid)**

Comments

Also known as poly(3-hydroxybutyrate) or Biopol (Monsanto). This biodegradable material forms in the cell walls of the bacterium *Alcaligenes eutrophus* when the organism is fed a diet of either glucose or ethanol. With properties similar to polypropylene {II-B-1H}, PHB can be processed with conventional molding or extrusion equipment, and it can be used for packaging, medical implants, and pharmaceutical capsules.



Code	Shift (ppm)
H1	5.7
H2	2.8, 3.0
H3	1.6

Experimental Parameters

Nucleus: ¹H (400 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 10% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 10 Hz

Pulse delay: 5 s

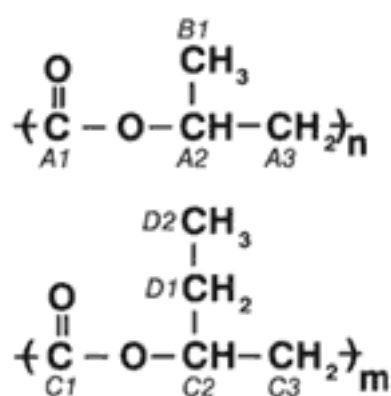
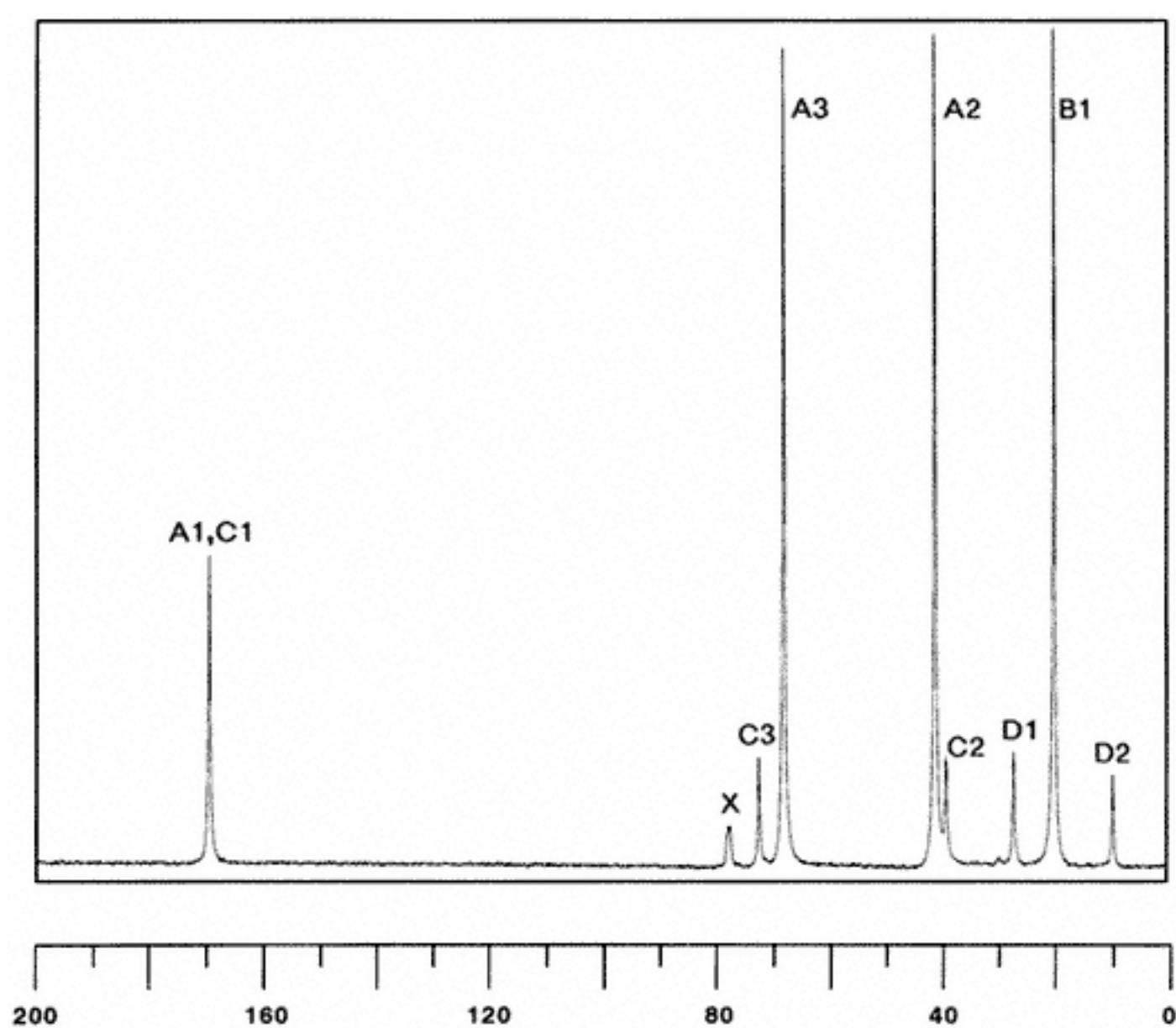
VIII-A-7

VIII-A-7—

Poly(3-Hydroxybutyric Acid-Co-3-Hydroxyvaleric Acid) (PHBV)

Comments

Also known as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) or Biopol (Monsanto). Solvent resonances are marked by **X**. This biodegradable material forms in the cell walls of the bacterium *Alcaligenes eutrophus* when the organism is fed a diet of either glucose or ethanol. With properties similar to polypropylene {II-B-1}, PHBV can be processed with conventional molding or extrusion equipment, and it can be used for packaging, medical implants, and pharmaceutical capsules. PHBV is somewhat more flexible than PHB {VIII-A-6}.



Code	Shift (ppm)
A1	169.4
A2	41.2
A3	67.9
B1	20.1
C1	169.4
C2	39.1
C3	72.7
D1	10.6
D2	27.6

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 2 s

References

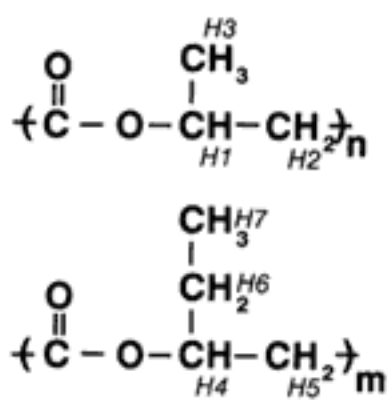
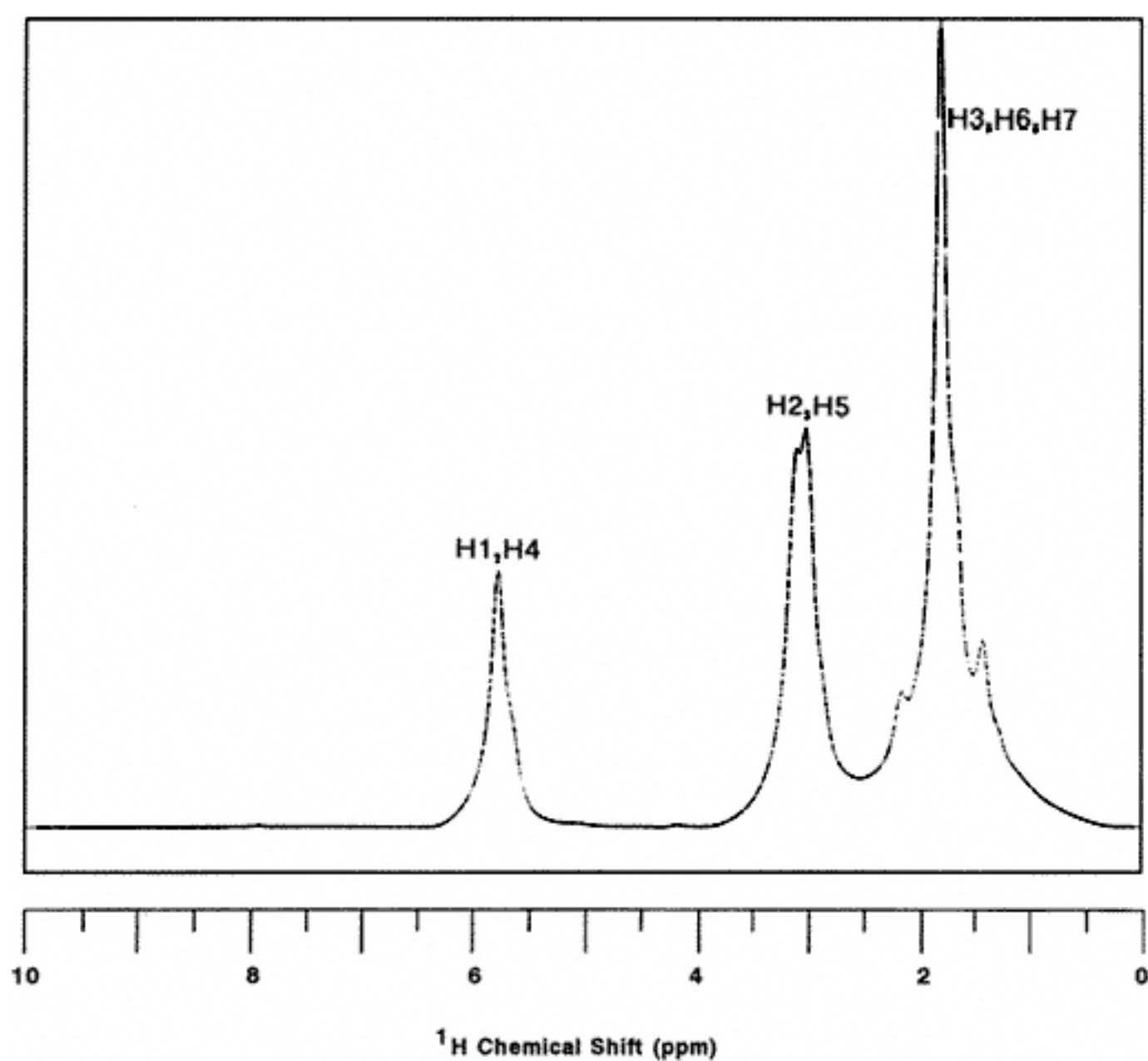
A. Ballistrero, G. Montaudo, G. Impallomeni, R. W. Lenz, Y. B. Kim, and R. C. Fuller. *Macromolecules* 23:5059, 1990; N. Komiya, Y. Inoue, T. Yamamoto, R. Chujo, and Y. Doi. *Macromolecules* 23:1313, 1990; Y. Doi, M. Kunioka, A. Tamaki, Y. Nakamura, and K. Soga. *Makromol. Chem.* 189:1077, 1988; Y. Doi, M. Kunioka, Y. Nakamura, and K. Soga. *Macromolecules* 21:2722, 1988.

VIII-A-7H—

Poly(3-Hydroxybutyric Acid-Co-3-Hydroxyvaleric Acid)

Comments

Also known as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) or Biopol (Monsanto). This biodegradable material forms in the cell walls of the bacterium *Alcaligenes eutrophus* when the organism is fed a diet of either glucose or ethanol. With properties similar to polypropylene {II-B-1H}, PHBV can be processed with conventional molding or extrusion equipment, and it can be used for packaging, medical implants, and pharmaceutical capsules. PHBV is somewhat more flexible than PHB {VIII-A-6H}.



Code	Shift (ppm)
H1	5.8
H2	3.1, 3.0
H3	1.8
H4	5.8
H5	3.1
H6	3.0
H7	1.7

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

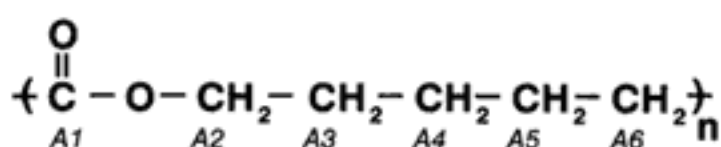
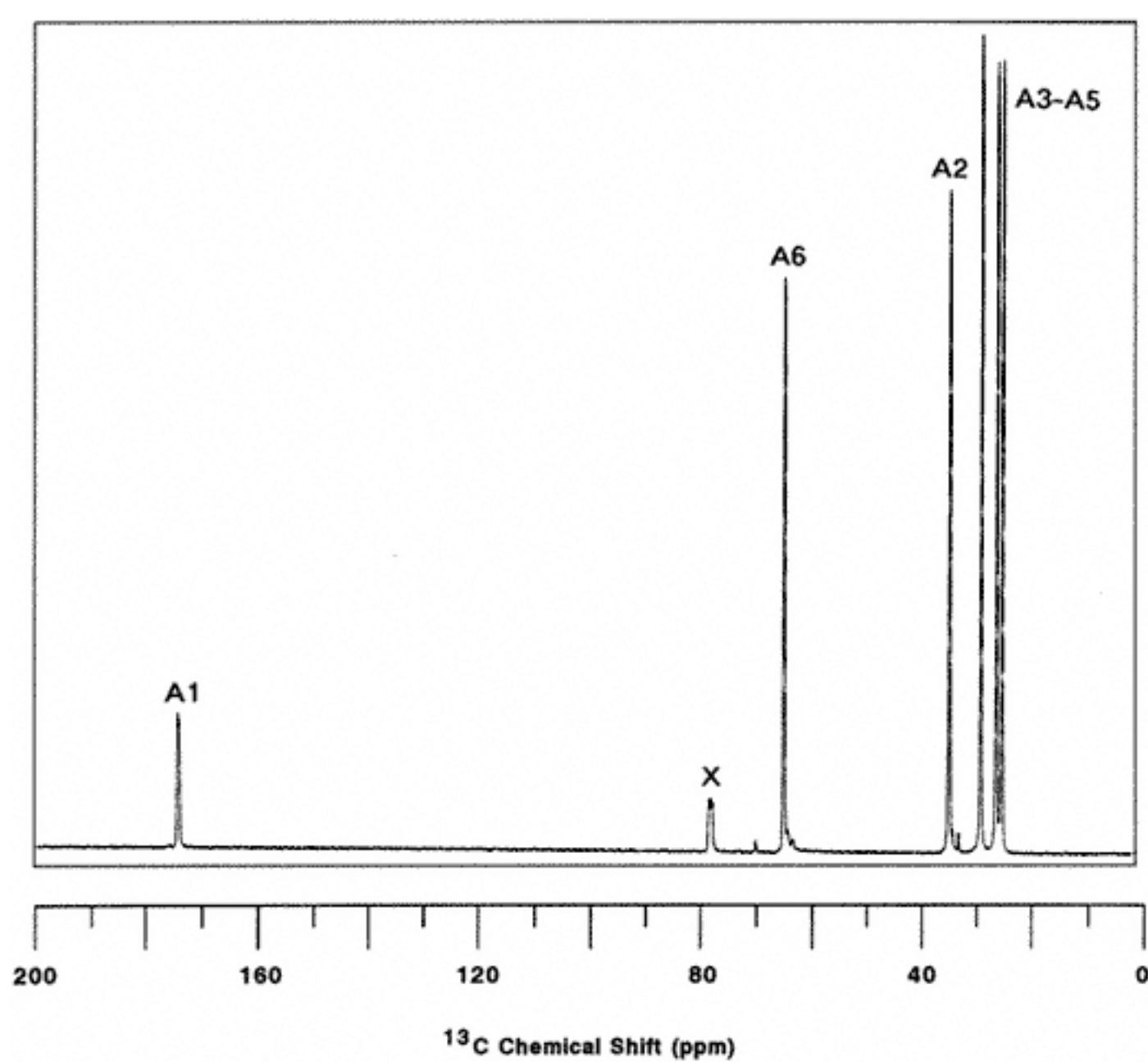
Broadening: 10 Hz

Pulse delay: 5 s

VIII-A-8— Polycaprolactone (PCL)

Comments

The simple linear structure leads to an uncomplicated spectrum; solvent resonances are marked by X. PCL is a low-melting (62°C), biodegradable material. Because it becomes pliable when immersed in hot water, PCL is often used as a modeling or craft medium. It is also incorporated into some polyurethanes {IX-B-4}.



Code	Shift (ppm)
A1	173.7
A2	34.5
A3	24.7–28.8
A4	24.7–28.8
A5	24.7–28.8
A6	64.1

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans 150

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

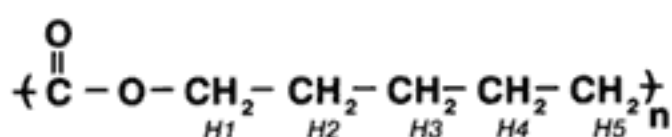
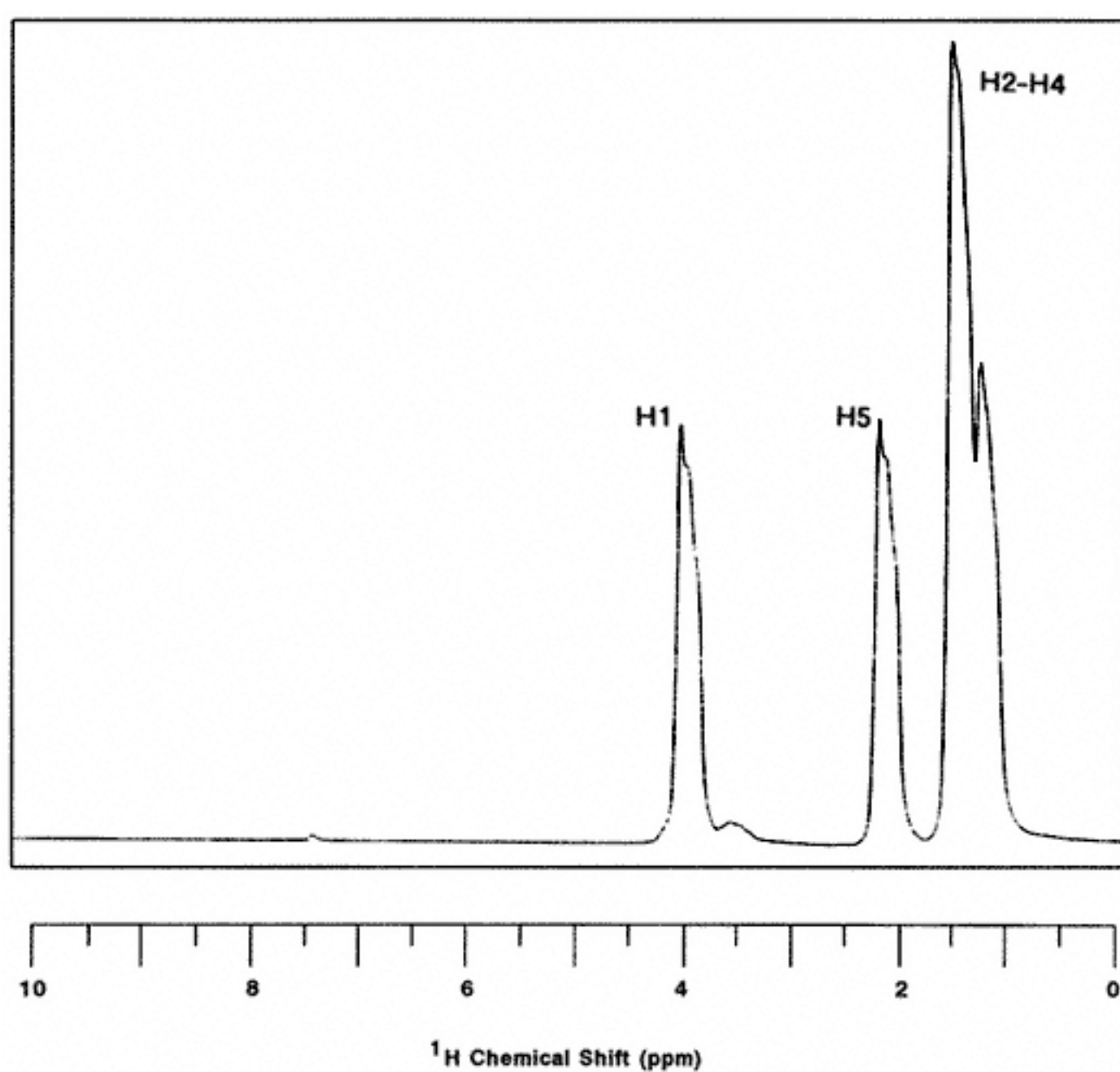
References

P. Dubois, R. Jerome, and P. Teyssie. *Macromolecules* 24:944, 1991; B. Albert, R. Jerome, P. Teyssie, G. Smyth, and V. J. McBrierty. *Macromolecules* 17:2552, 1984.

**VIII-A-8H—
Polycaprolactone (PCL)**

Comments

PCL is a low-melting (62°C), biodegradable material. Because it becomes pliable when immersed in hot water, PCL is often used as a modeling or craft medium. It is also incorporated into some polyurethanes {IX-B-4}.



Code	Shift (ppm)
H1	4.0
H2	1.6
H3	1.6
H4	1.3
H5	2.2

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

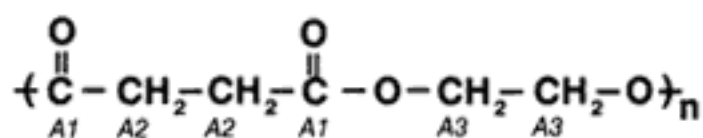
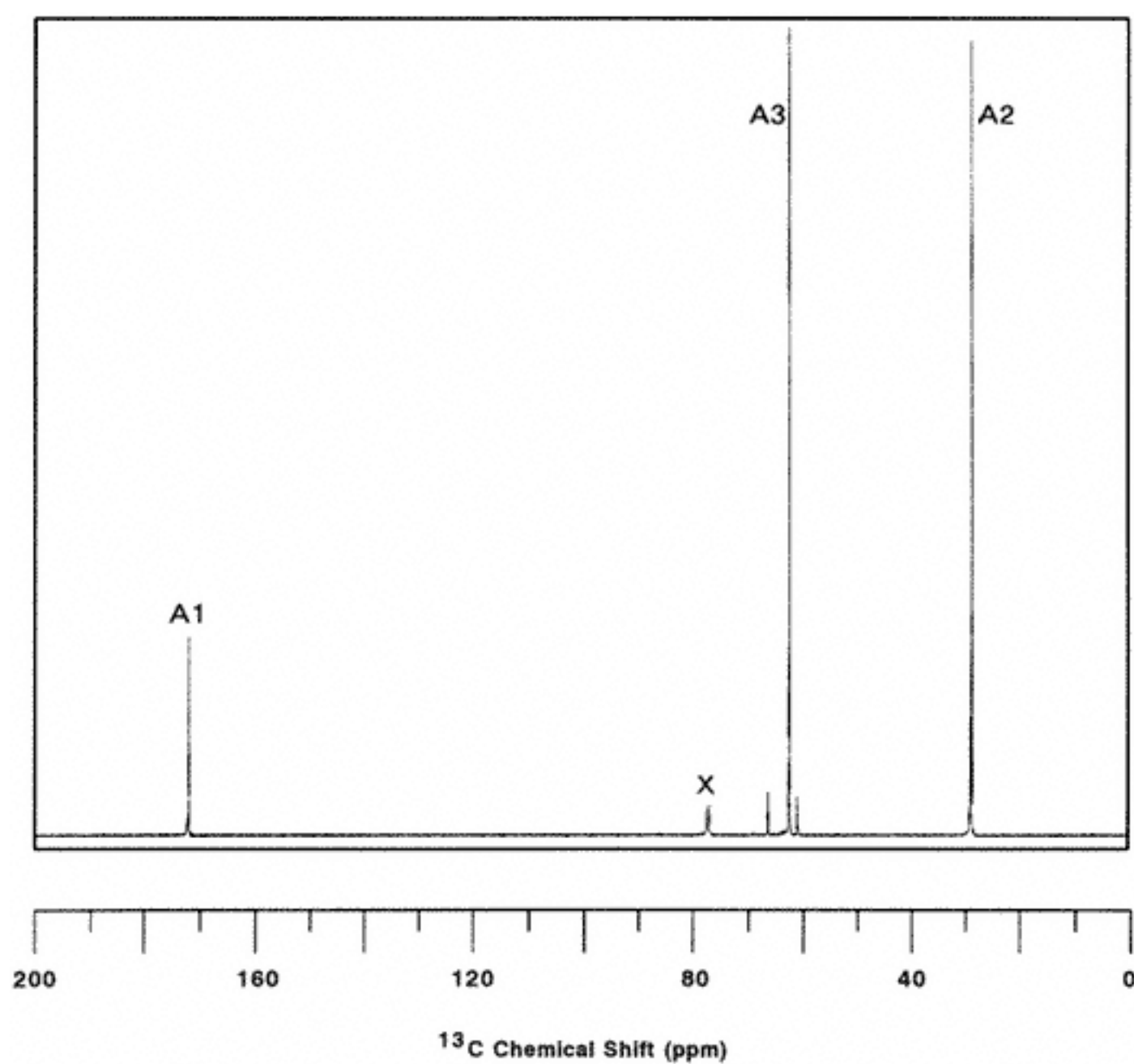
Broadening: 2 Hz

Pulse delay: 5 s

**VIII-A-9—
Poly(Ethylene Succinate)**

Comments

The simple linear structure leads to an uncomplicated spectrum; solvent resonances are marked by X. This polymer is sometimes incorporated into polyurethanes.



Code	Shift (ppm)
A1	171.5
A2	28.5
A3	61.3

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 24

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

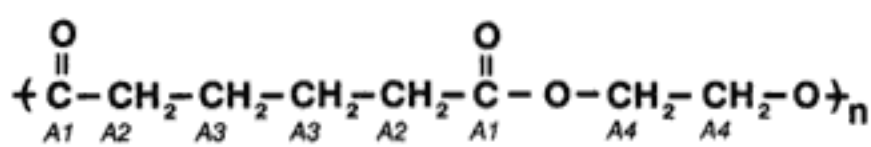
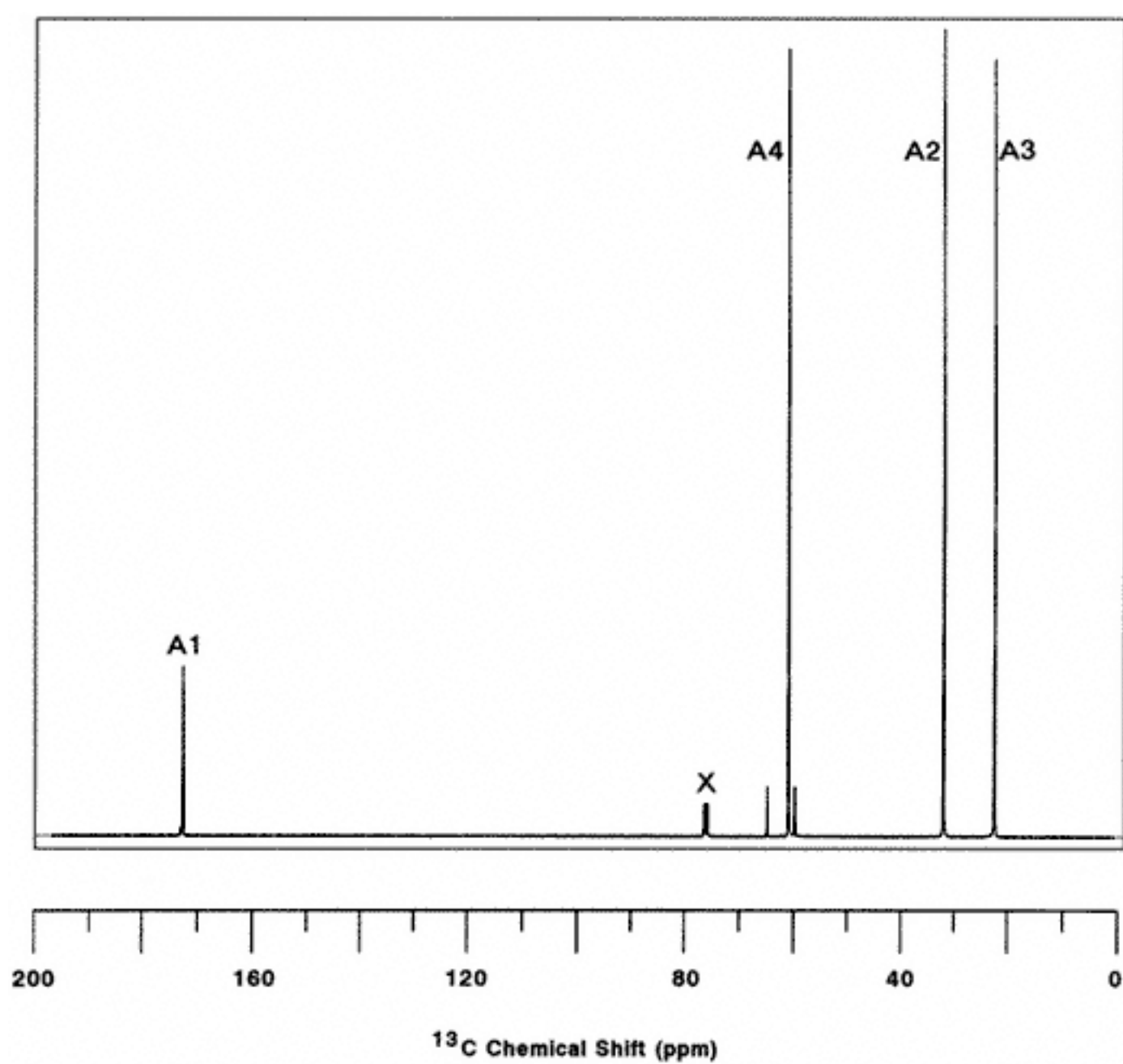
Broadening: 2 Hz

Pulse delay: 5 s

VIII-A-10—
Poly(Ethylene Adipate)

Comments

The simple linear structure leads to an uncomplicated spectrum; solvent resonances are marked by X. This polymer is sometimes incorporated into polyurethanes.



Code	Shift (ppm)
A1	172.8
A2	33.6
A3	23.8
A4	62.0

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 48

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

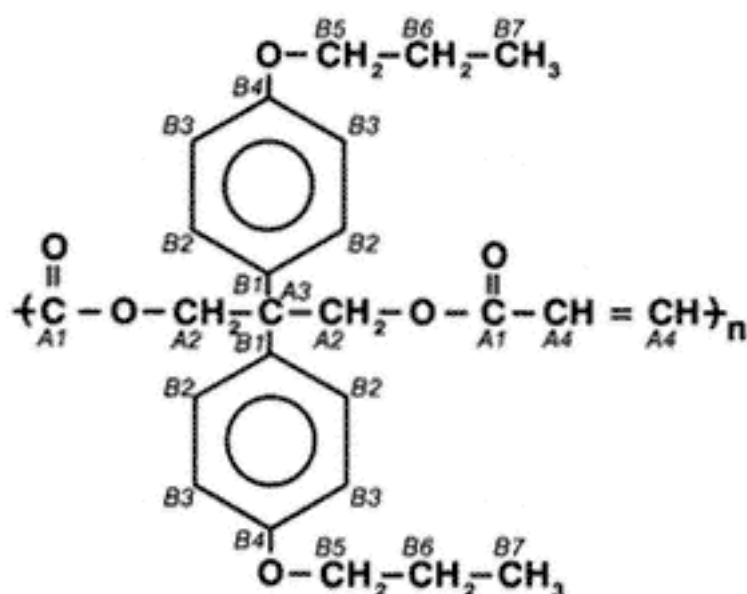
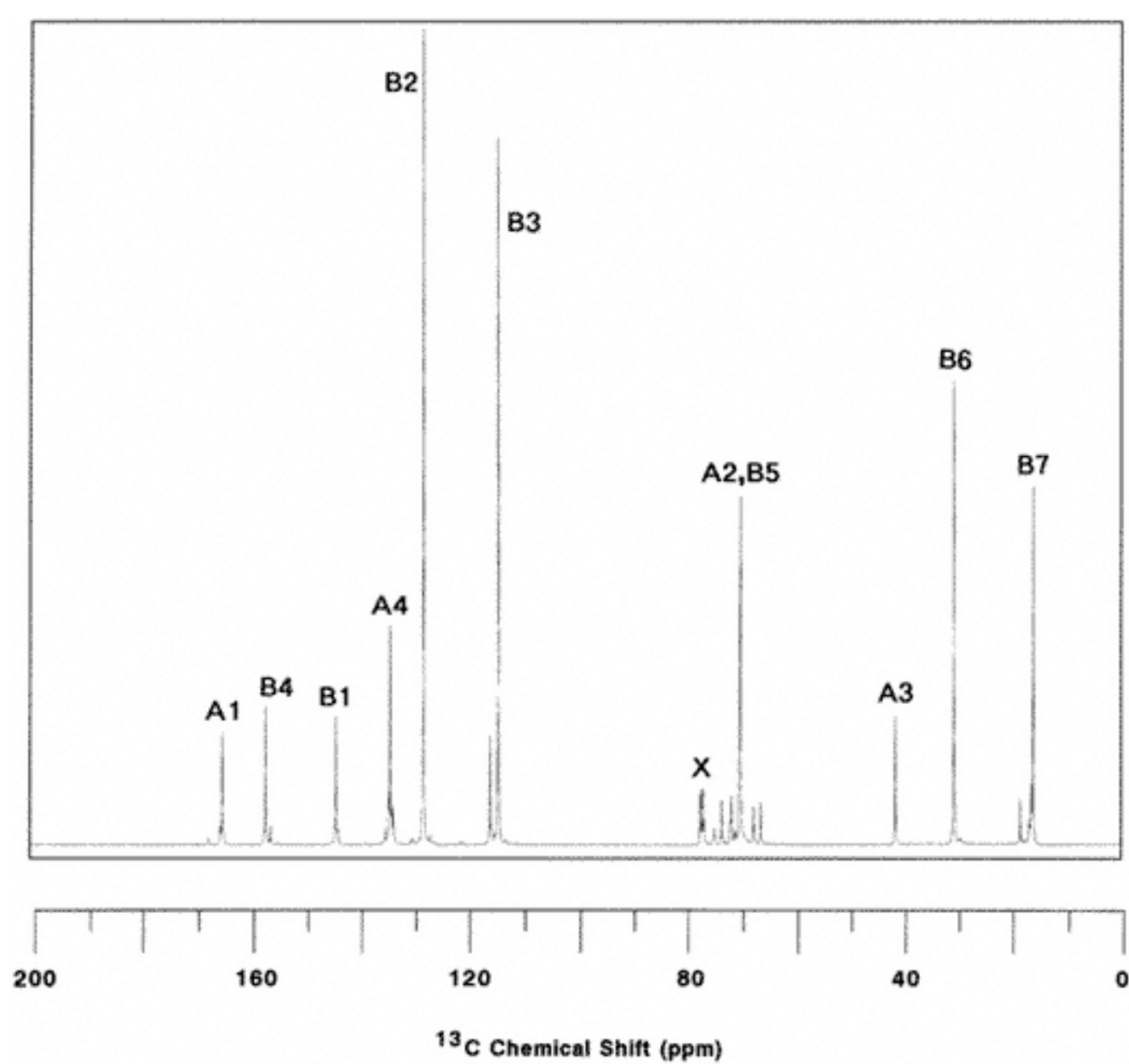
VIII-A-11

VIII-A-11—

Poly(4,4'-Dipropoxy-2,2-Diphenylpropanefumarate)

Comments

Solvent resonances are marked by X. The double bond serves as a potential site for network formation. The non-cross-linked polymer is usually mixed with fibers (often glass) and fillers (such as limestone); after cross-linking, the final product is a fiber-reinforced polyester. These light, strong composites are typically used in appliances, construction materials, and transportation applications.



Code	Shift (ppm)
A1	164.7
A2	70.3
A3	41.9
A4	134.8
B1	143.4
B2	127.9
B3	114.3
B4	156.1
B5	70.3
B6	31.1
B7	16.7

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

References

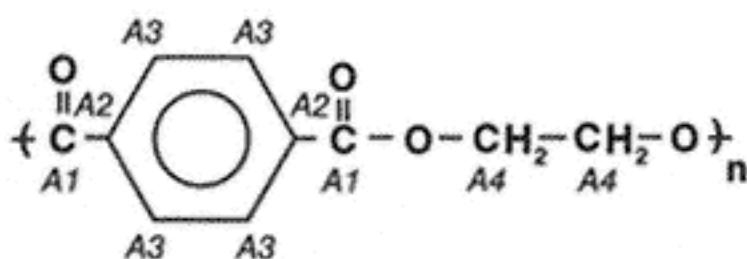
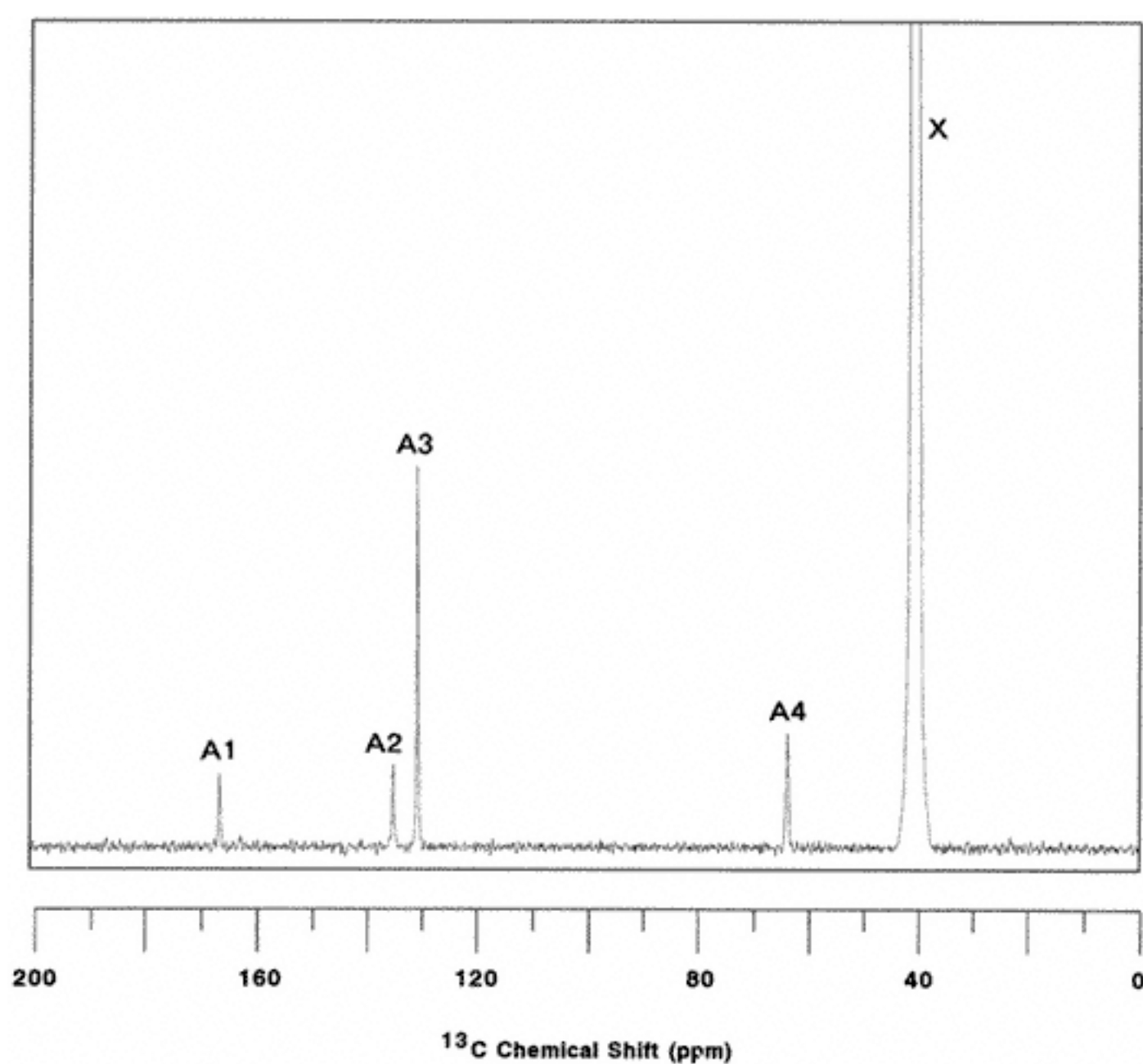
J. Grobelny. *Polymer* 36:4215, 1995; M. Yoshida, A. Matsumoto, and T. Otsu. *Polym. J.* 10:1191, 1991; X. Wang, T. Komoto, I. Ando, and T. Otsu. *Makromol. Chem.* 189:1845, 1988.

VIII-B-1—

Poly(Ethylene Terephthalate) (PET)

Comments

Also commonly known as Mylar (DuPont), Dacron (DuPont), and Valox (General Electric), among other trade names; this is the material commonly referred to as "polyester." Solvent resonances are marked by X. PET is primarily used to make films (such as tape and photographic film backing), synthetic fibers, and soft-drink bottles. It is also found in electrical insulation, food packaging, and appliances.



Code	Shift (ppm)
A1	166.0
A2	134.9
A3	130.5
A4	63.9

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: DMSO- d_6

Concentration: 2% w/w

Scans: 25,000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

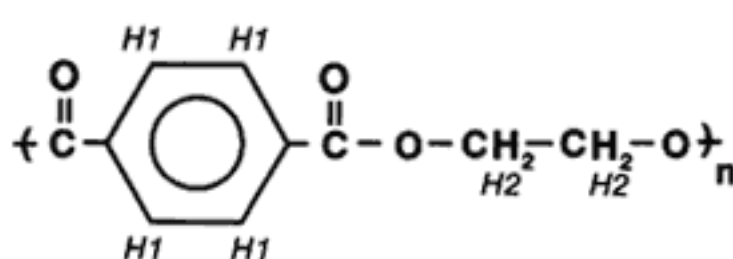
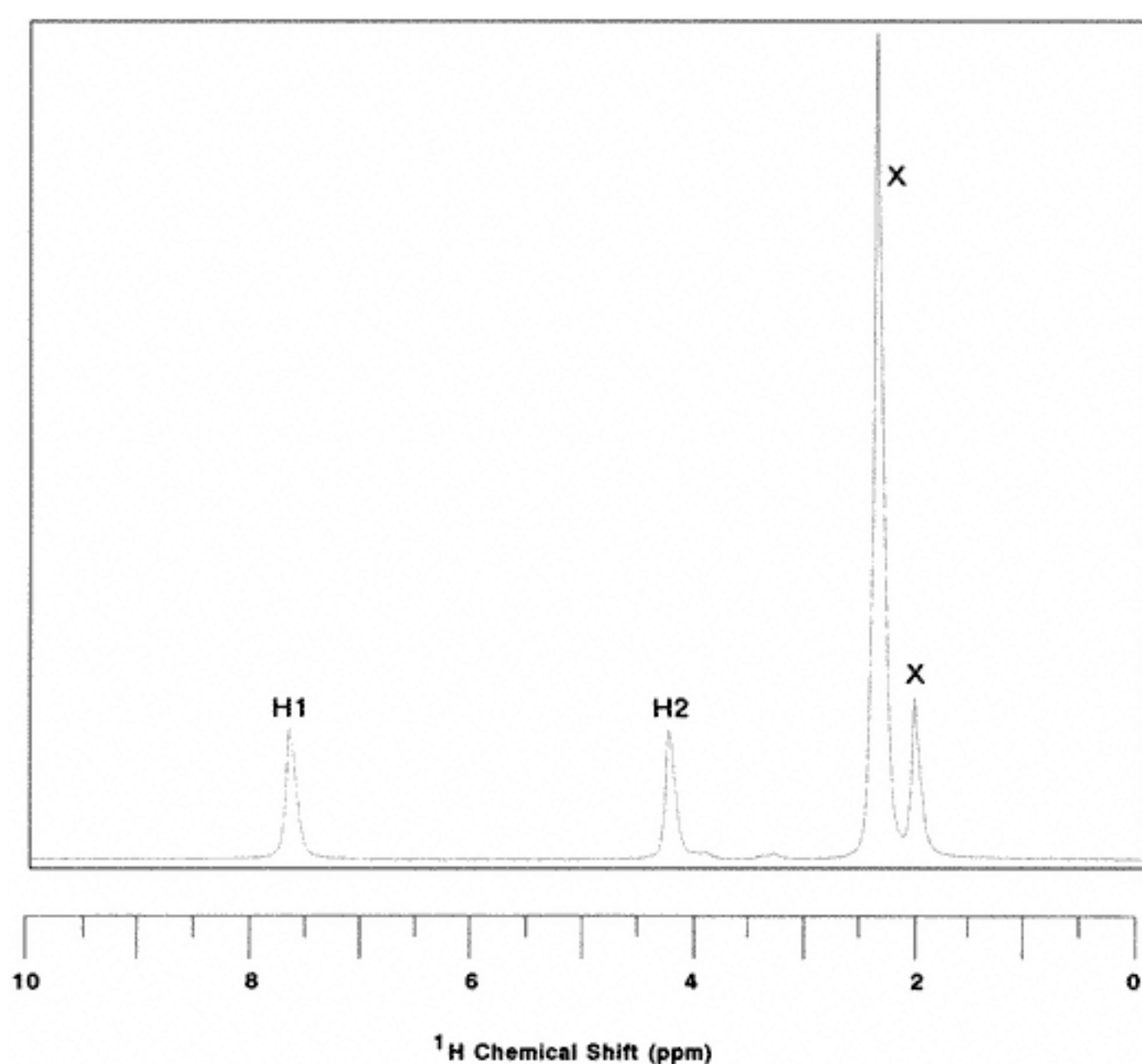
References

F. Khorshahi, S. Lim, A. Jensen, and D. Kwok. *Polym. Bull.* 28:451, 1992; R. Petiaud, H. Waton, and Q.-T. Pham. *Polymer* 33:3144, 1992; R. Po, P. Cioni, L. Abis, E. Occhielli, and F. Garbassi. *Polym. Commun.* 32:208, 1991.

**VIII-B-1H—
Poly(Ethylene Terephthalate) (PET)**

Comments

Also commonly known as Mylar (DuPont), Dacron (DuPont), and Valox (General Electric), among other trade names; this is the material commonly referred to as "polyester." Solvent resonances are marked by **X**. PET is used primarily to make films (such as tape and photographic film backing), synthetic fibers, and soft-drink bottles. It is also found in electrical insulation, food packaging, and appliances.



Code	Shift (ppm)
H1	7.6
H2	4.3

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 130°C

Solvent: DMSO- d_6

Concentration: 2% w/w

Scans: 24

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

Reference

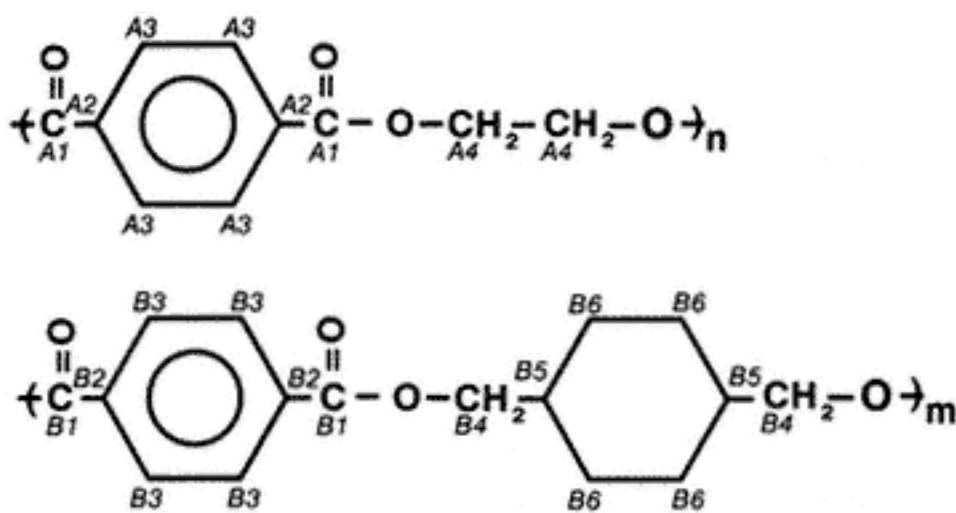
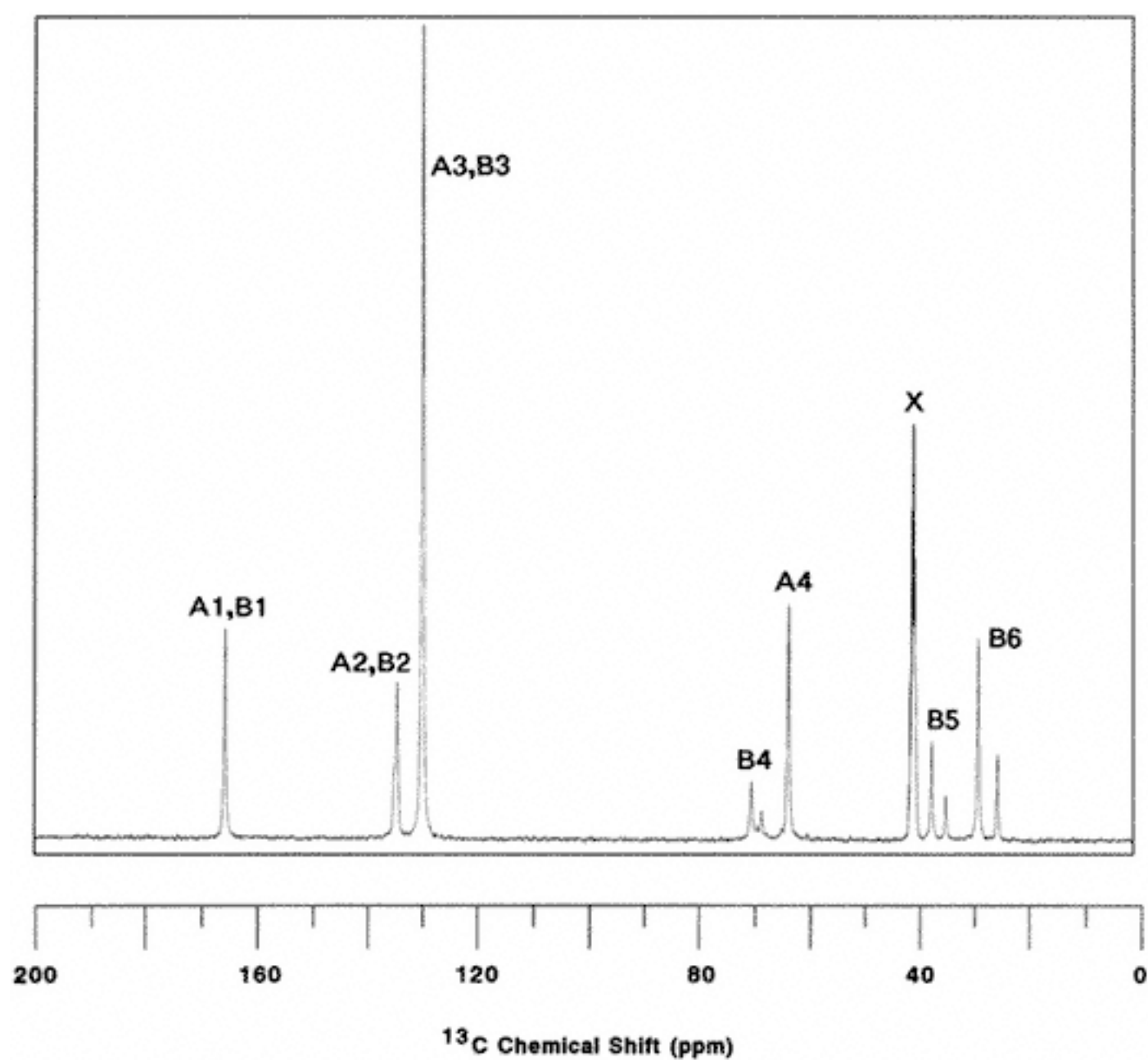
R. Petiaud, H. Waton, and Q.-T. Pham. *Polymer* 33:3144, 1992.

VIII-B-2—

Poly(Ethylene Terephthalate-Co-1,4-Cyclohexane Dimethylene Terephthalate)

Comments

Also known as Spectar (Eastman). Two peaks appear for resonances **B4**, **B5**, and **B6** because of the *cis* and *trans* placements across the cyclohexyl ring. The blocky copolymer structure makes the spectrum look like a composite of the homopolymer spectra, poly(ethylene terephthalate) {VIII-B-1} and poly(1,4-cyclohexanedimethylene terephthalate) {VIII-B-6}. Solvent resonances are marked by **X**. This high-clarity material is often used in packaging and display materials.



Code	Shift (ppm)
A1	166.0
A2	135.1
A3	130.2
A4	64.0
B1	166.0
B2	135.1
B3	130.2
B4	70.7
B5	37.4, 35.3
B6	29.5, 25.6

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: DMSO- d_6

Concentration: 10% w/w

Scans: 800

Spectral Width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

Source

Eastman Chemical, Kingport, TN.

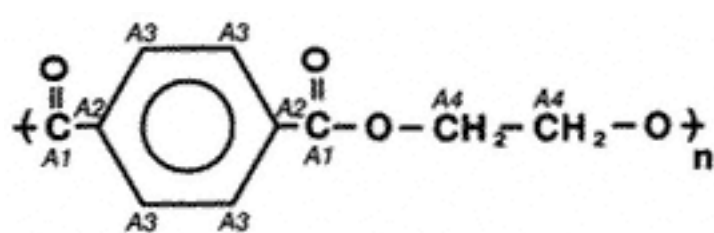
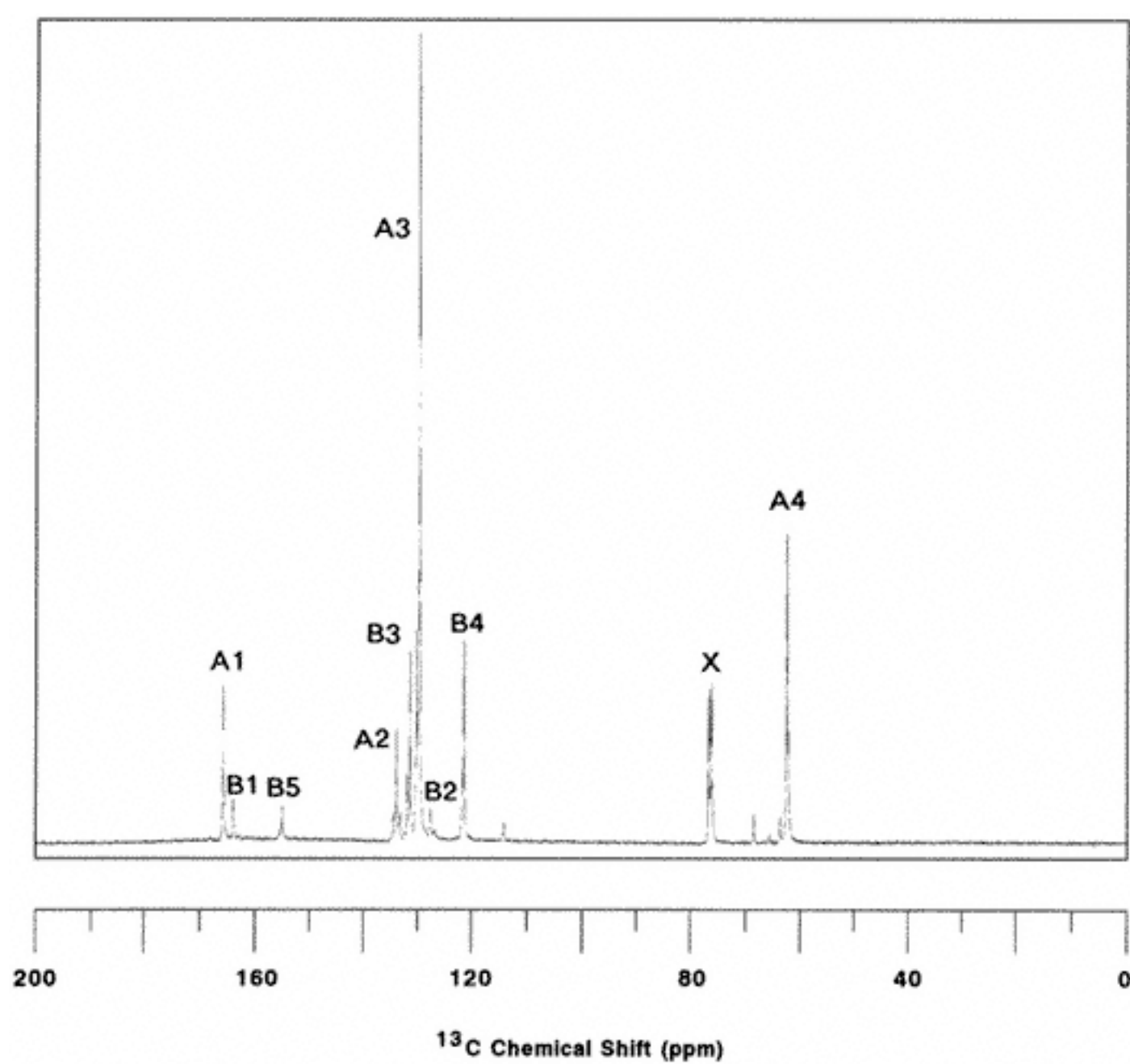
ReferenceF. Khorshahi, S. Lim, A. Jensen, and D. Kwoh. *Polym. Bull.* 28:451, 1992.

VIII-B-3—

Poly(Ethylene Terephthalate-Co-4-Hydroxybenzoic Acid)

Comments

The blocky copolymer structure makes the spectrum look like a composite of the homopolymer spectra, poly(ethylene terephthalate) {VIII-B-1} and poly(4-hydroxybenzoic acid). Solvent resonances are marked by X. This is a liquid-crystalline polymer, which is highly ordered in both the melt and the solid. Such polymers find many electrical and automotive uses.



Code	Shift (ppm)
A1	166.1
A2	134.6
A3	130.4
A4	62.8
B1	163.7
B2	128.0
B3	131.6
B4	121.6
B5	154.7

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

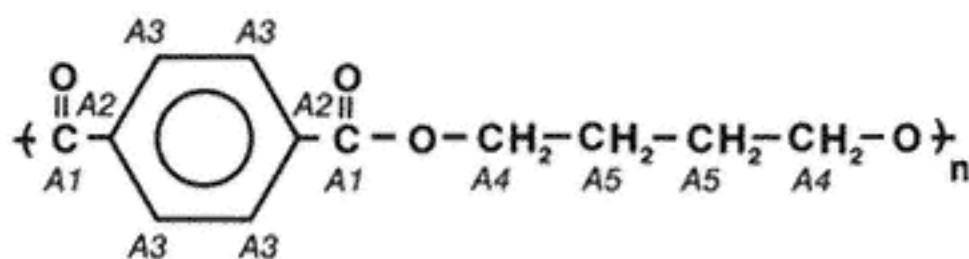
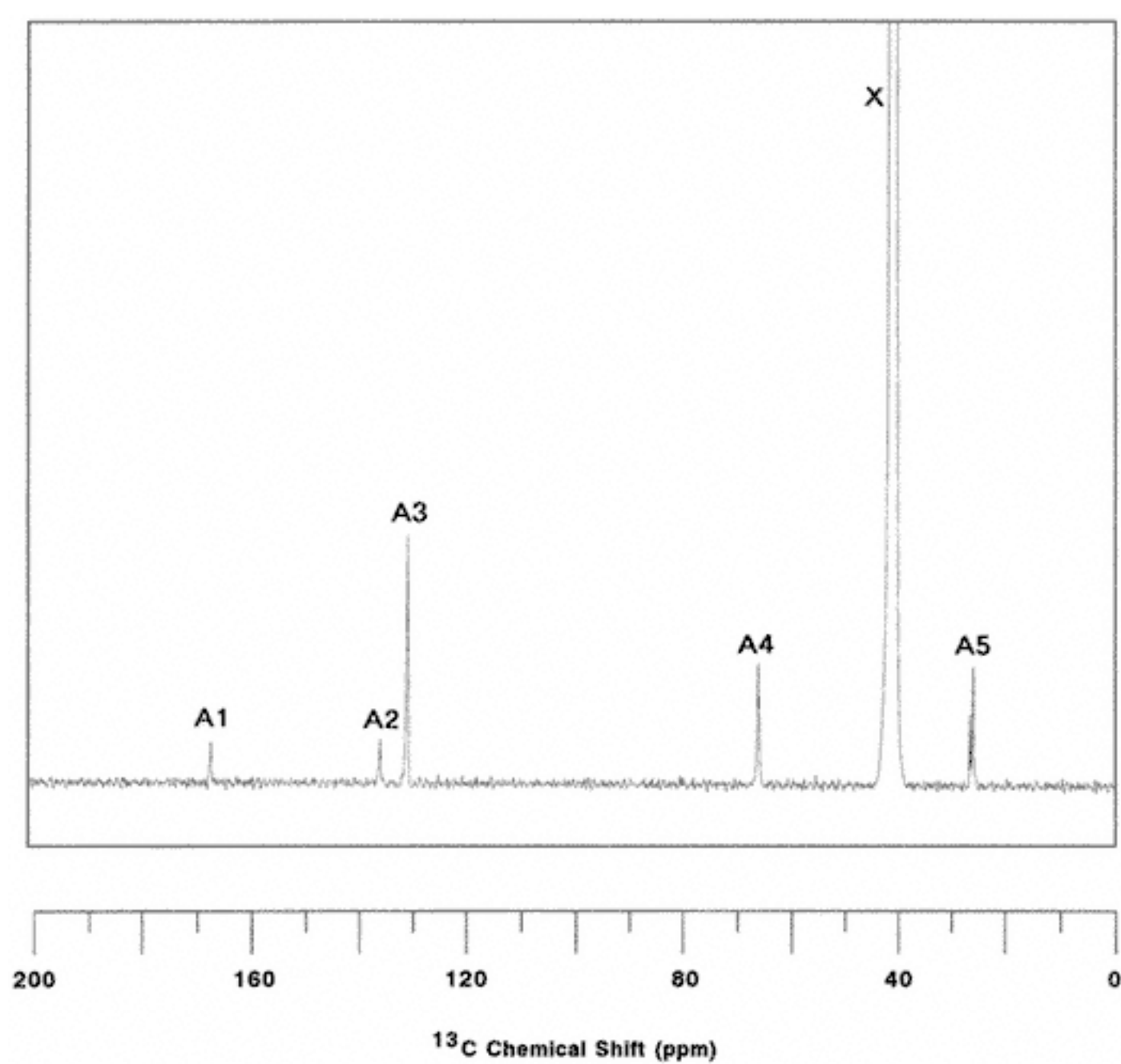
Source

M. J. Stachowski, University of Connecticut, Storrs, CT.

**VIII-B-4—
Poly(Butylene Terephthalate) (PBT)**

Comments

Solvent resonances are marked by **X**. This engineering resin is used primarily in molded applications: automobile exterior and under-hood parts, electrical components, and appliance and power-tool housings. It is sometimes reinforced with glass to improve its properties.



Code	Shift (ppm)
A1	166.0
A2	135.0
A3	130.1
A4	65.7
A5	26.0

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: DMSO- d_6

Concentration: 2% w/w

Scans: 9600

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

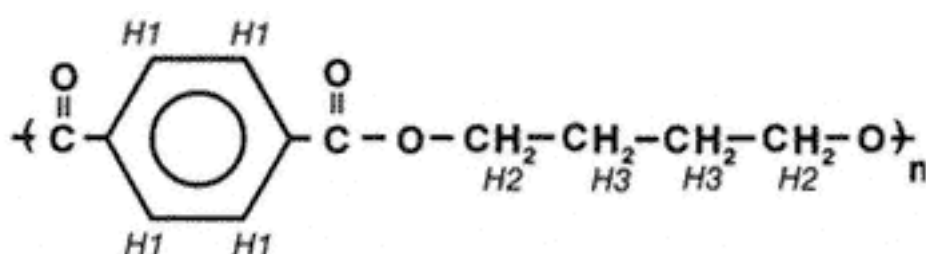
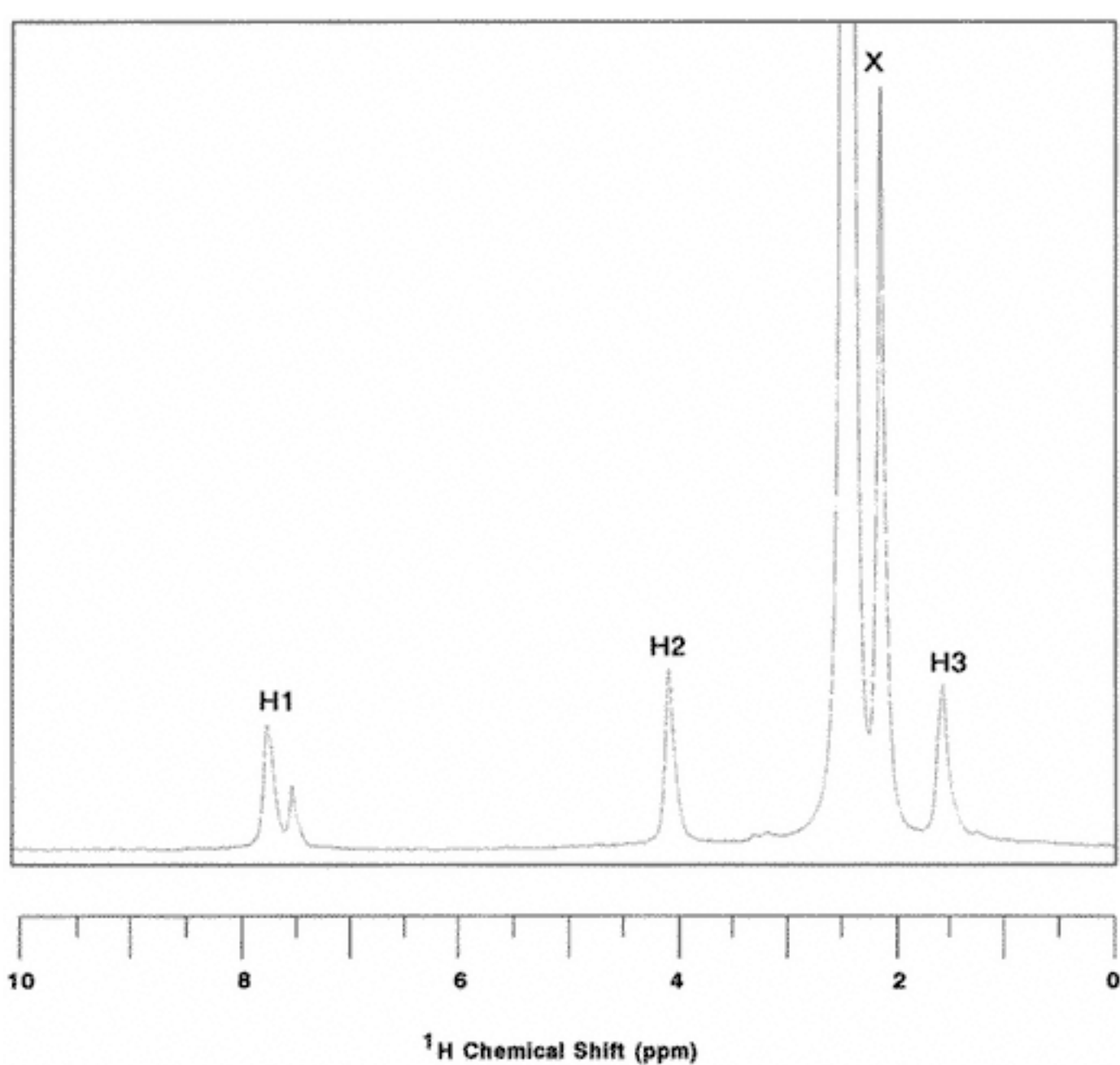
Broadening: 2 Hz

Pulse delay: 5 s

**VIII-B-4H—
Poly(Butylene Terephthalate) (PBT)**

Comments

Solvent resonances are marked by **X**. This engineering resin is used primarily in molded applications: automobile exterior and under-the-hood parts, electrical components, and appliance and power-tool housings. It is sometimes reinforced with glass to improve its properties.



Code	Shift (ppm)
H1	7.7
H2	4.2
H3	1.0

Experimental Parameters

Nucleus: ¹H (400 MHz)

Temperature: 130°C

Solvent: DMSO-d₆

Concentration: 2% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

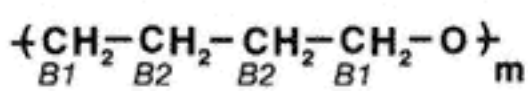
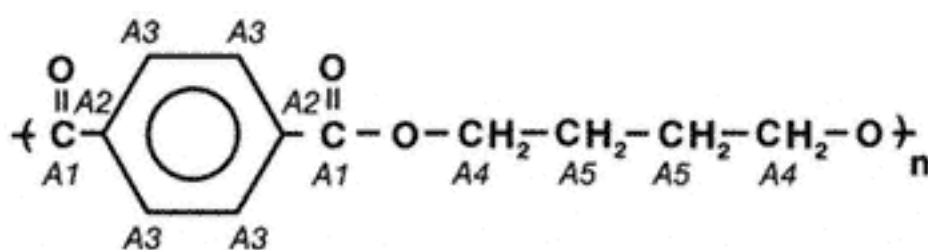
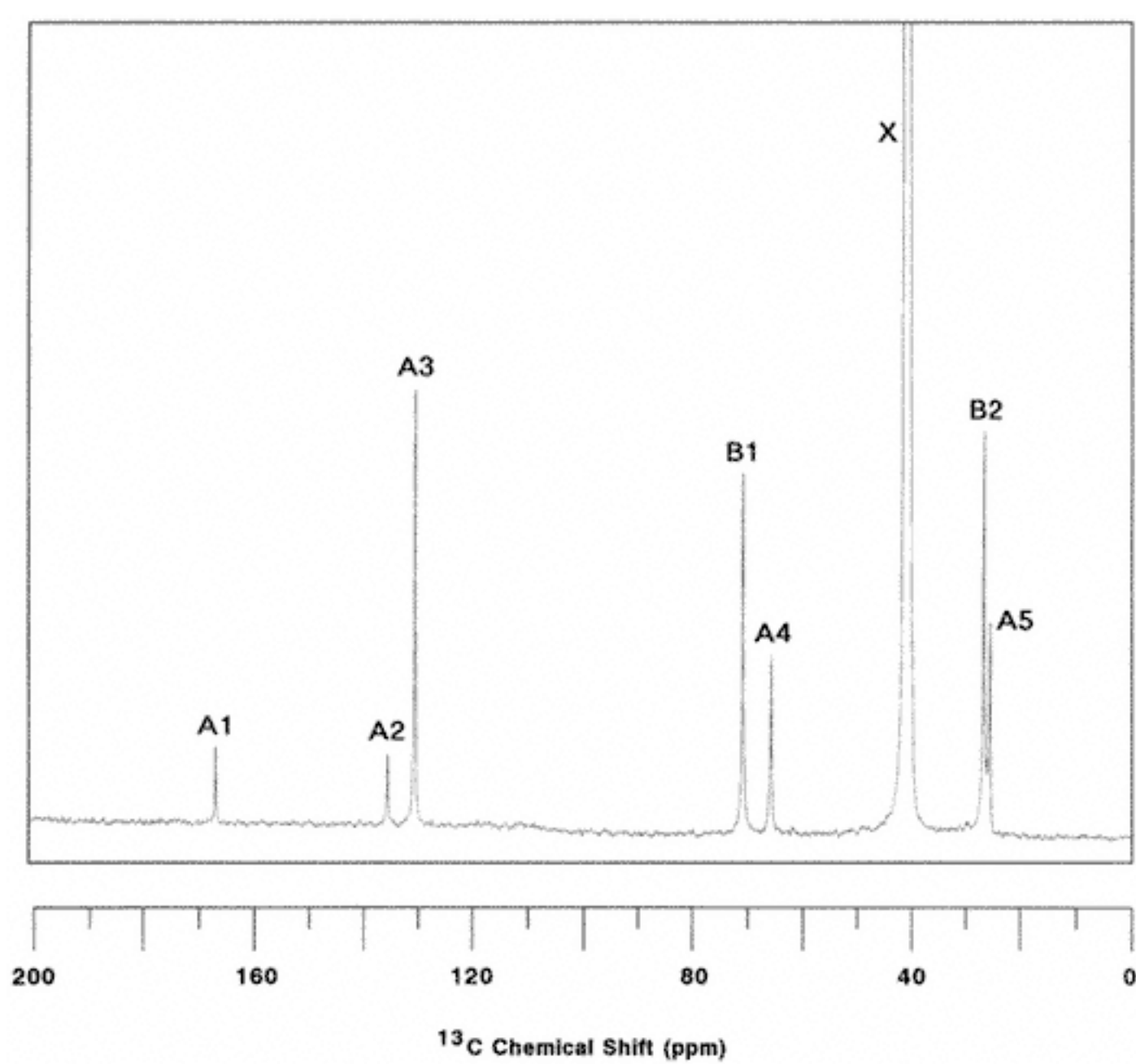
Pulse delay: 5 s

VIII-B-5—

Poly(Butylene Terephthalate-Co-Tetramethylene Glycol)

Comments

Also known as Hytrel (DuPont). Solvent resonances are marked by **X**. This thermoplastic elastomer is a blocky copolymer with both "hard" (butylene terephthalate) and "soft" (tetramethylene glycol) phases; variations in the relative amounts of each change the properties of the resin.



Code	Shift (ppm)
A1	166.2
A2	135.1
A3	130.0
A4	65.8
A5	26.0
B1	71.0
B2	27.1

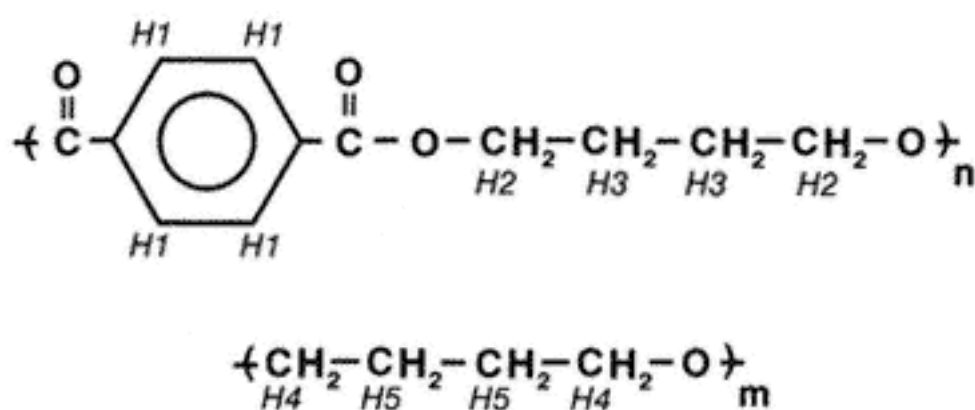
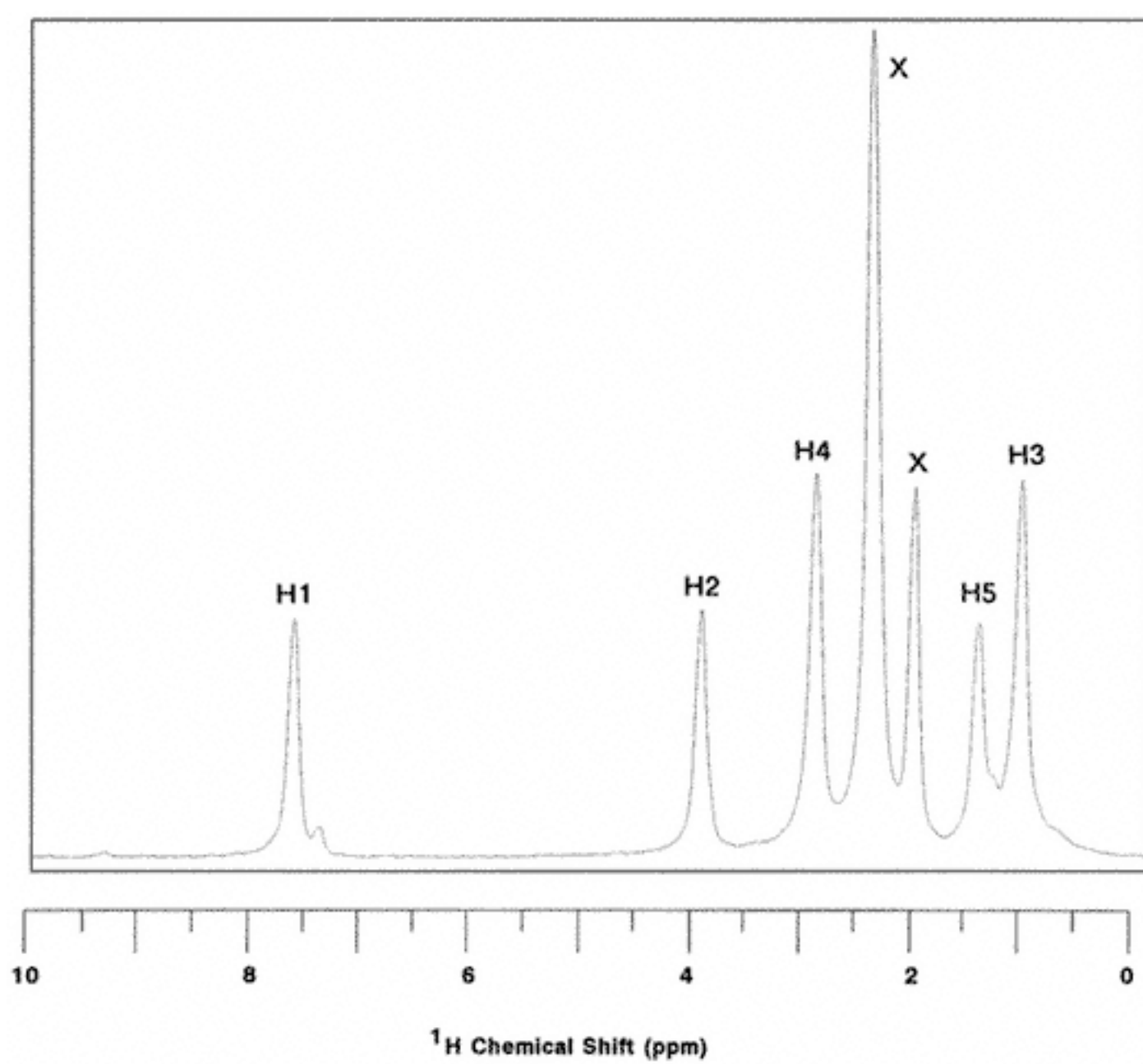
Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 130°
Solvent: DMSO- d_6	Concentration: 2% w/w
Scans: 8000	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 5 s

VIII-B-5H—
Poly(Butylene Terephthalate-Co-Tetramethylene Glycol)

Comments

Also known as Hytrel (DuPont). Solvent resonances are marked by **X**. This thermoplastic elastomer is a blocky copolymer with both "hard" (butylene terephthalate) and "soft" (tetramethylene glycol) phases; variations in the relative amounts of each change the properties of the resin.



Code	Shift (ppm)
H1	7.6
H2	4.0
H3	1.5
H4	3.0
H5	1.1

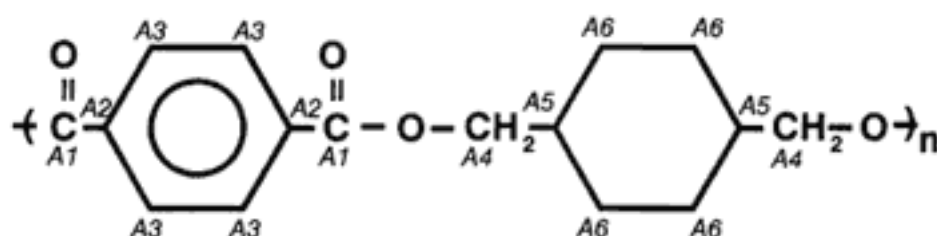
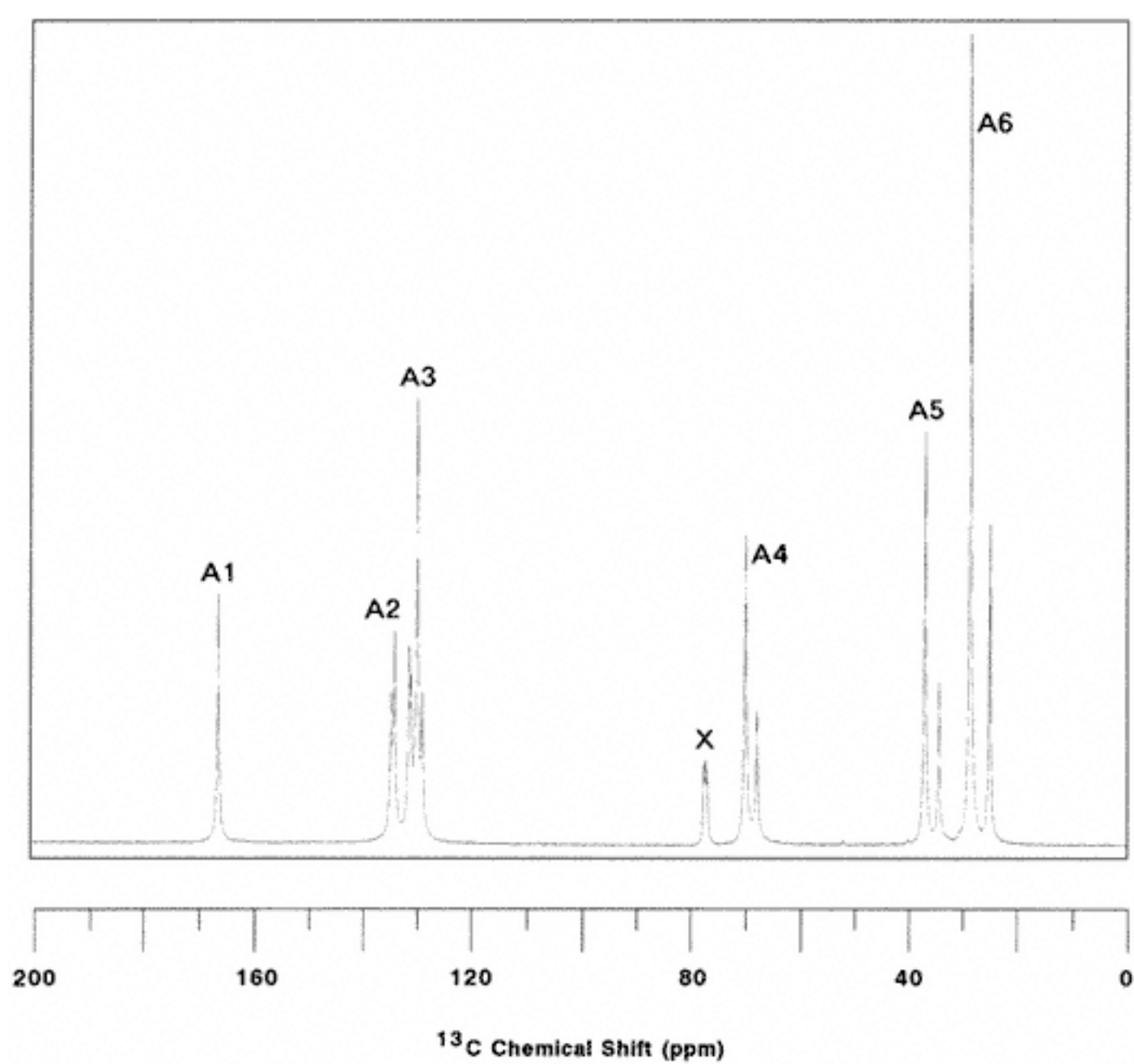
Experimental Parameters

Nucleus: ^1H (400 MHz)	Temperature: 130°C
Solvent: DMSO- d_6	Concentration: 2% w/w
Scans: 48	Spectral width: 8 kHz
Data points: 8192	Pulse width: 10°
Broadening: 5 Hz	Pulse delay: 5 s

**VIII-B-6—
Poly(1,4-Cyclohexanedimethylene Terephthalate)**

Comments

Also known as Kodel (Eastman). Two peaks appear for resonances **A4**, **A5**, and **A6** because there are both *cis* and *trans* placements across the cyclohexyl ring. Solvent resonances are marked by **X**. This material is used to make fiber, film, bottles, and sheet for packaging applications.



Code	Shift (ppm)
A1	165.7
A2	133.7
A3	129.6
A4	70.1, 67.4
A5	37.4, 35.3
A6	29.1, 25.5

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

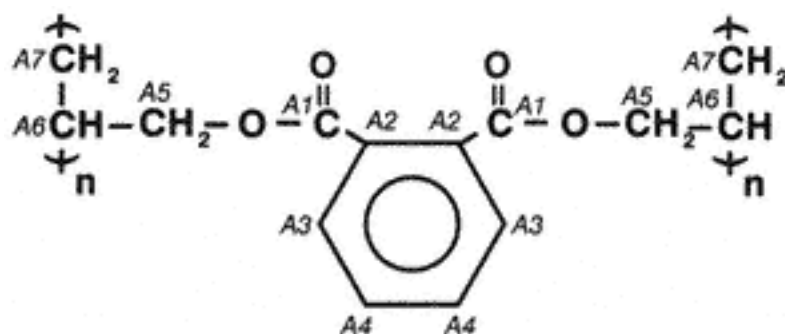
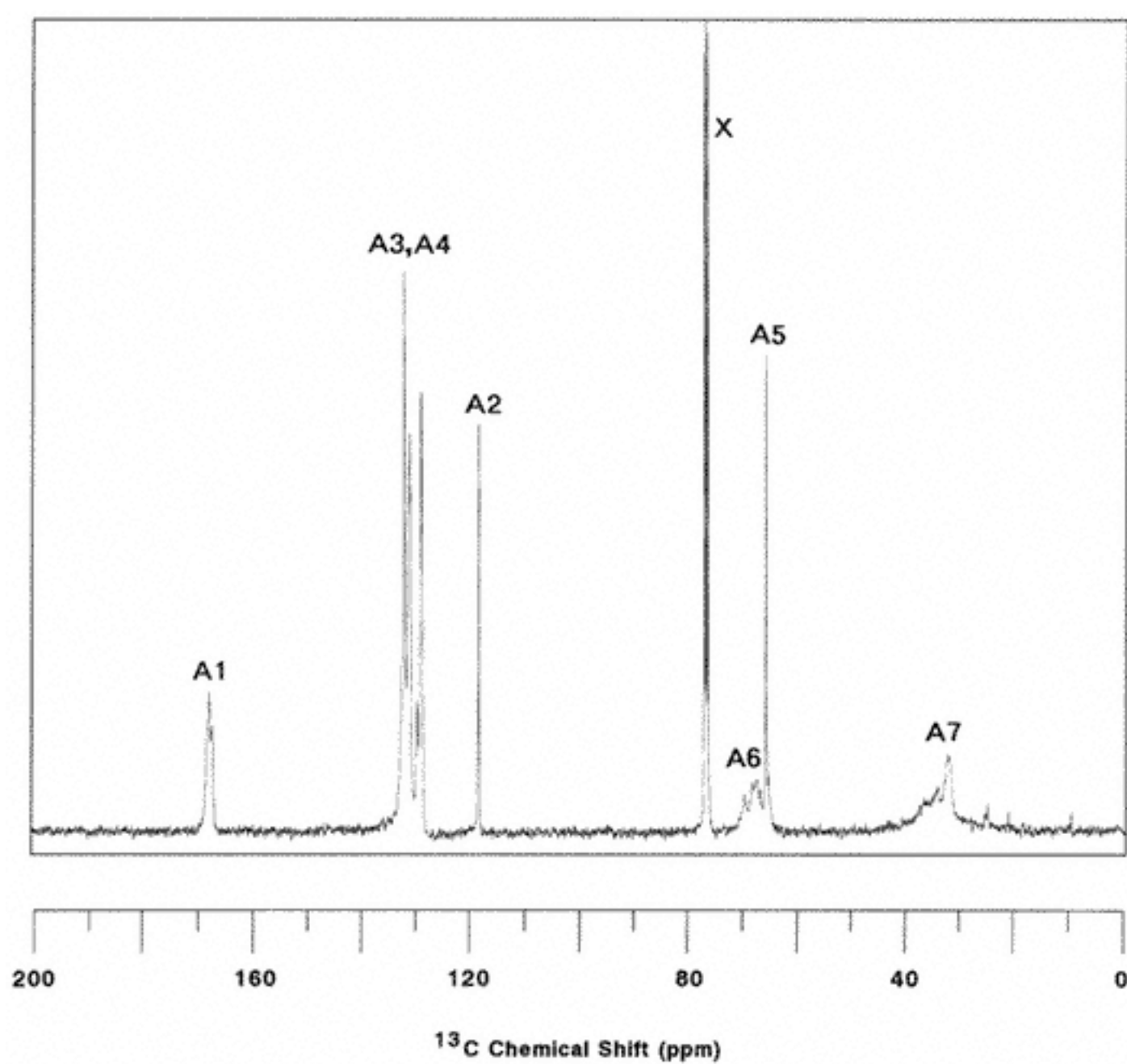
Broadening: 2 Hz

Pulse delay: 5 s

**VIII-B-7—
Poly(Diallyl Phthalate)**

Comments

This low molecular weight oligomer has an irregular structure. Solvent resonances are marked by **X**. It is used as a lamination material or molding compound. When combined with other polyesters, such as PET {VIII-B-1}, it functions as a cross-linking agent.



Code	Shift (ppm)
A1	167.7
A2	119.0
A3	129.9–132.6
A4	129.9–132.6
A5	66.5
A6	67–72
A7	32–38

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 5% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

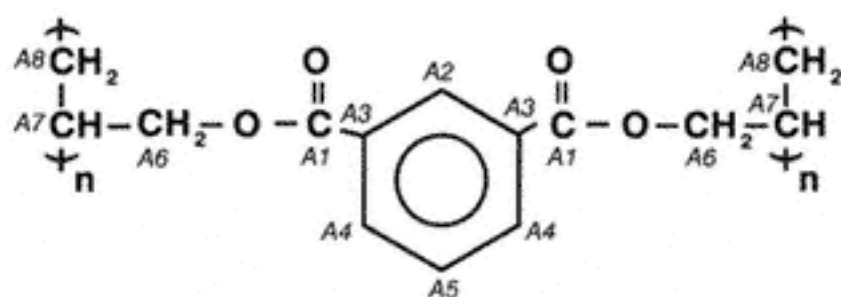
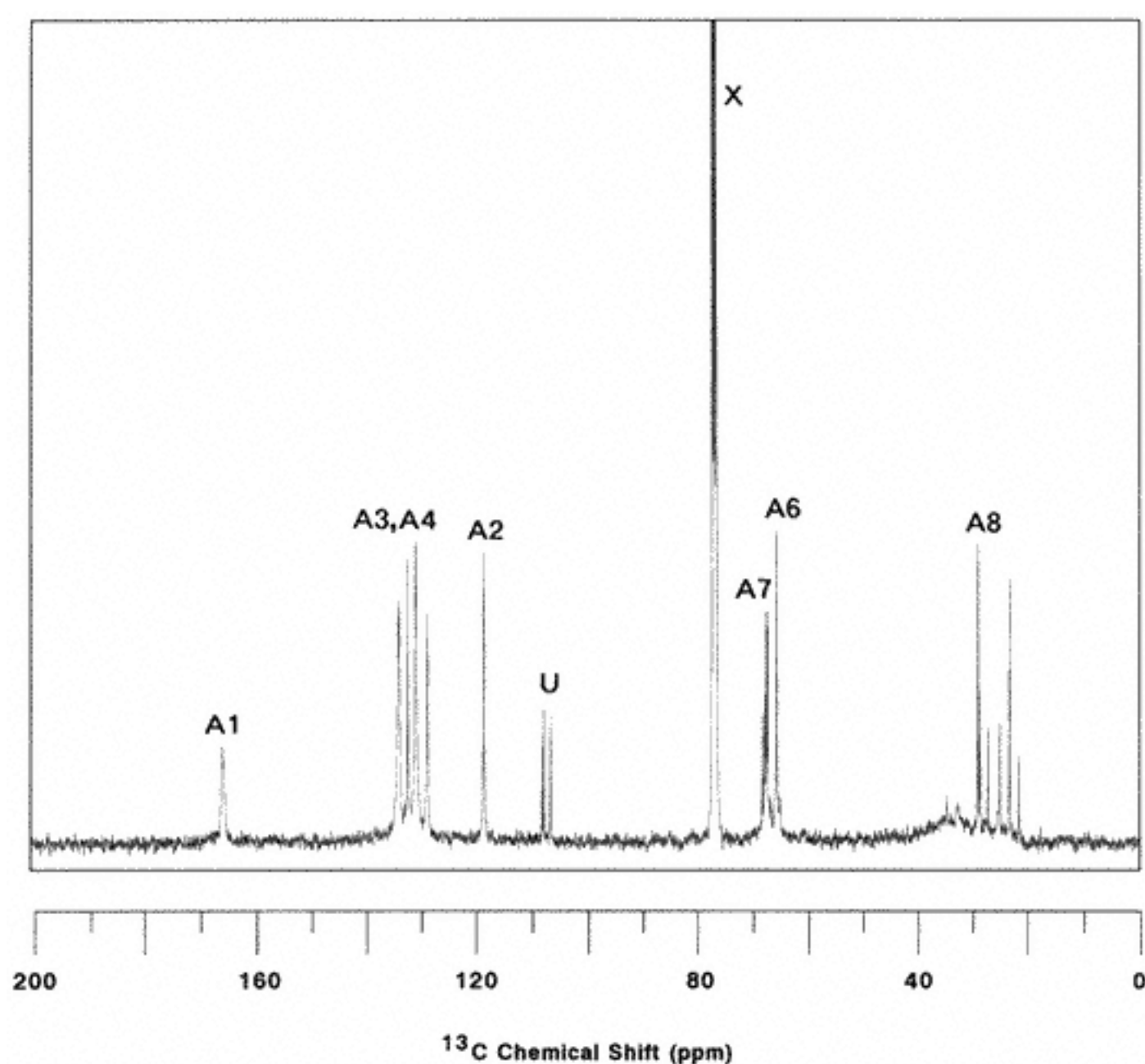
Broadening: 2 Hz

Pulse delay: 5 s

**VIII-B-8—
Poly(Diallyl Isophthalate)**

Comments

This low molecular weight oligomer has an irregular structure. Solvent resonances are marked by **X**; some unassignable peaks, by **U**. It has applications as a lamination material or molding compound. When combined with other polyesters, such as PET { VIII-B-1 }, it functions as a cross-linking agent.



Code	Shift (ppm)
A1	165.4
A2	118.3
A3	128–34
A4	128–34
A5	128–34
A6	65.8
A7	67.9
A8	27.5

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 5% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

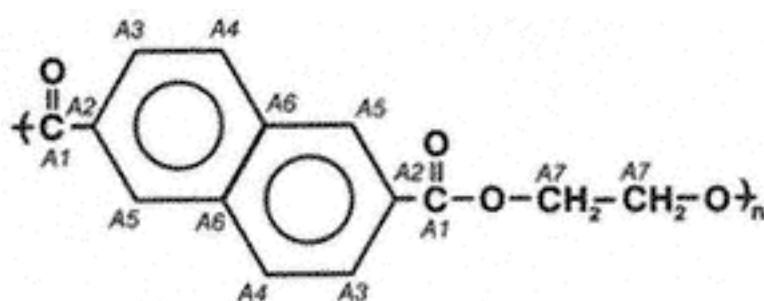
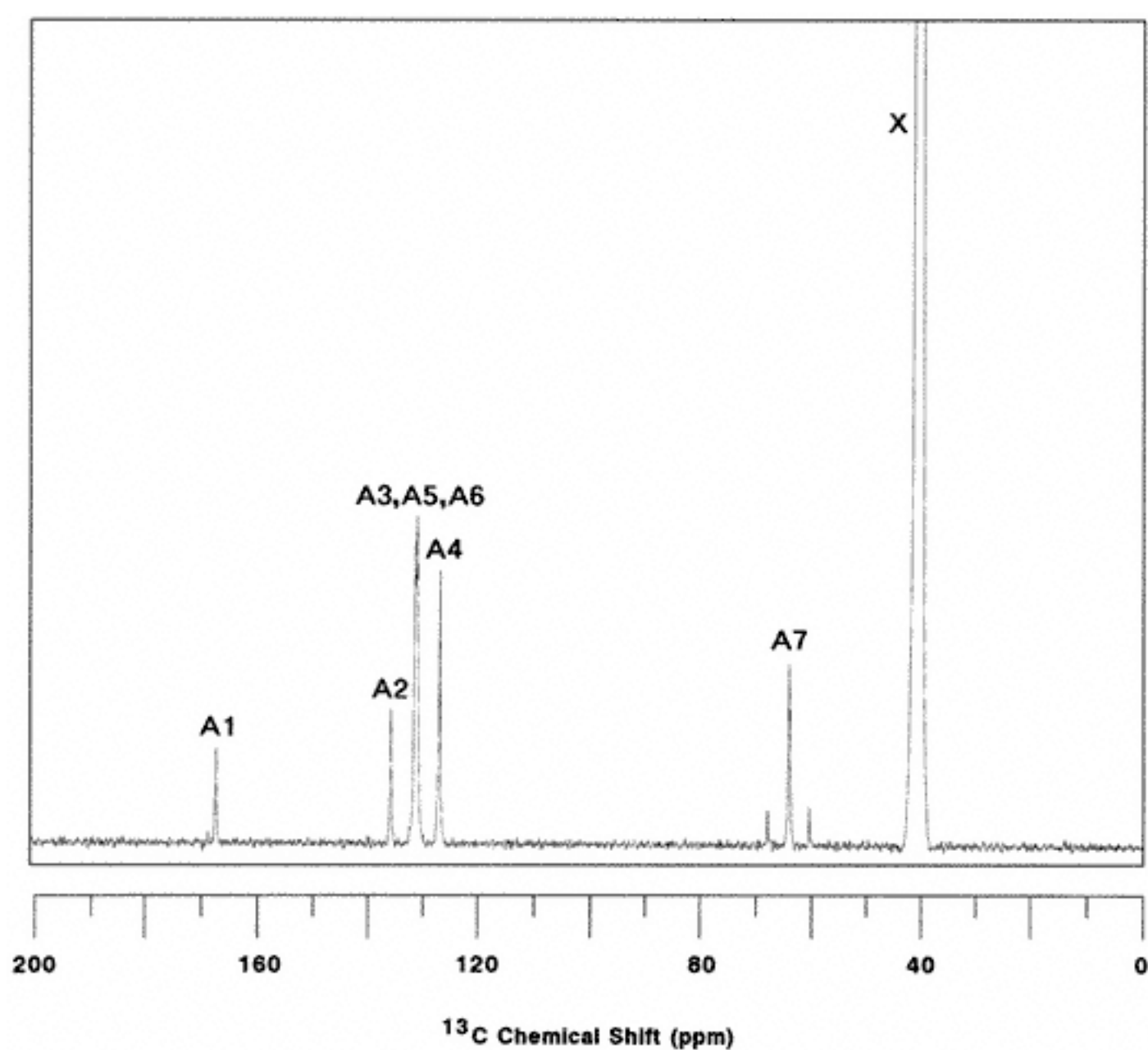
Broadening: 2 Hz

Pulse delay: 5 s

**VIII-B-9—
Poly(Ethylene Naphthoate) (PEN)**

Comments

Solvent resonances are marked by X. This relatively new material is used in applications similar to PET {VIII-B-1}, such as film and bottles, but it has better mechanical properties.



Code	Shift (ppm)
A1	166.4
A2	135.2
A3	131.0
A4	126.5
A5	131.0
A6	131.0
A7	63.7

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 130°C
Solvent: DMSO- d_6	Concentration: 2% w/w
Scans: 9600	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 5 s

Reference

R. Po, P. Cioni, L. Abis, E. Occhielli, and F. Garbassi. *Polym. Commun.* 32:208, 1991.

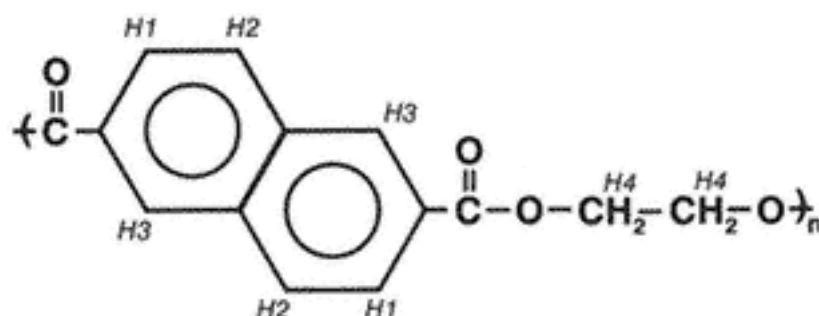
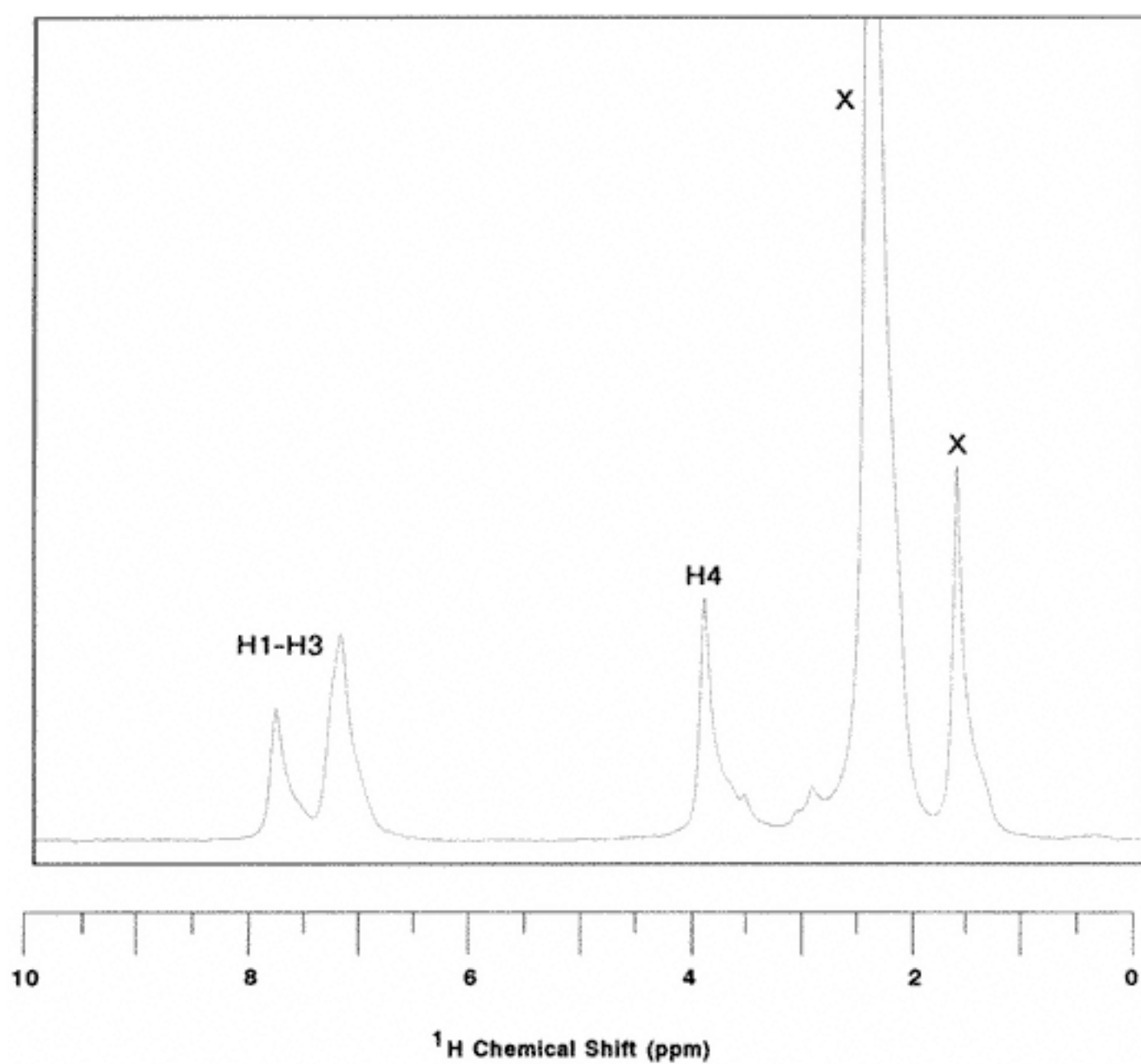
Source

Amoco Chemical, Naperville, IL.

**VIII-B-9H—
Poly(Ethylene Naphthoate) (PEN)**

Comments

Solvent resonances are marked by **X**. This relatively new material is used in applications similar to PET {VIII-B-1}, such as film and bottles, but it has better mechanical properties.



Code	Shift (ppm)
H1	7.0–8.0
H2	7.0–8.0
H3	7.0–8.0
H4	4.1

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 2% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

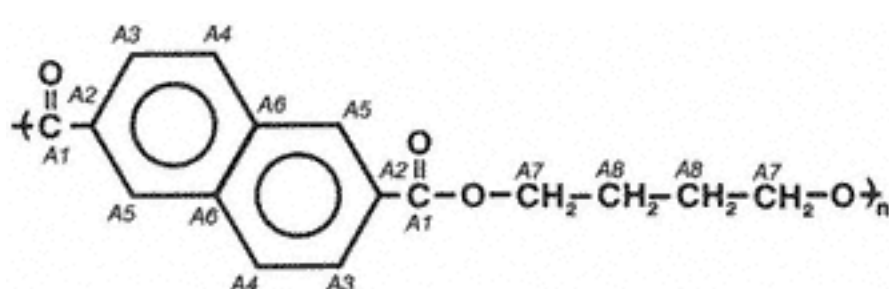
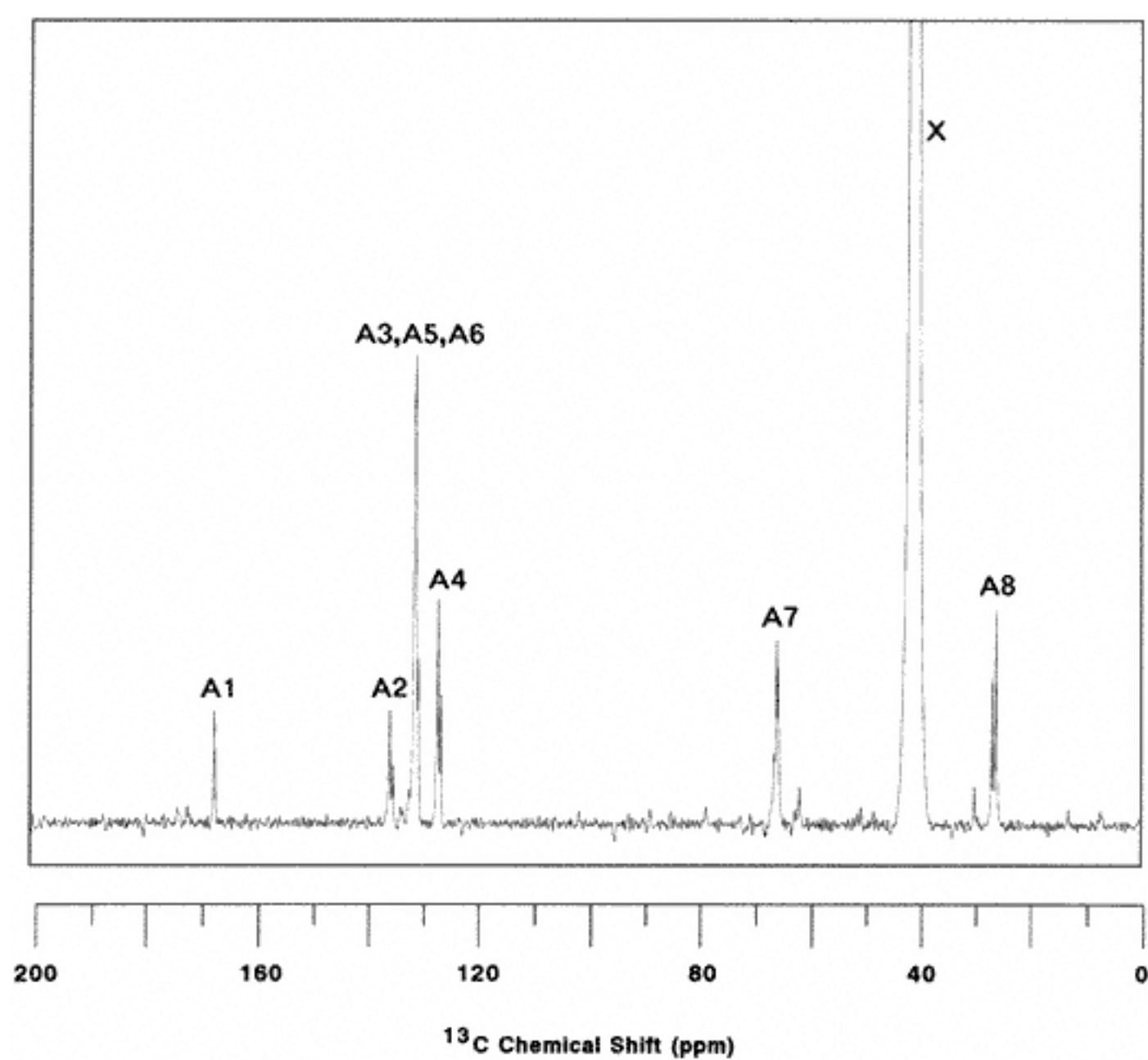
Source

Amoco Chemical, Naperville, IL.

**VIII-B-10—
Poly(Butylene Naphthenoate) (PBN)**

Comments

Solvent resonances are marked by X. This relatively new material is used in applications similar to PBT {VIII-B-4}, such as molded parts, but it has better mechanical properties.



Code	Shift (ppm)
A1	166.7
A2	135.8
A3	130.9
A4	127.0
A5	130.9
A6	130.9
A7	65.8
A8	26.0

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 2% w/w

Scans: 10,000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

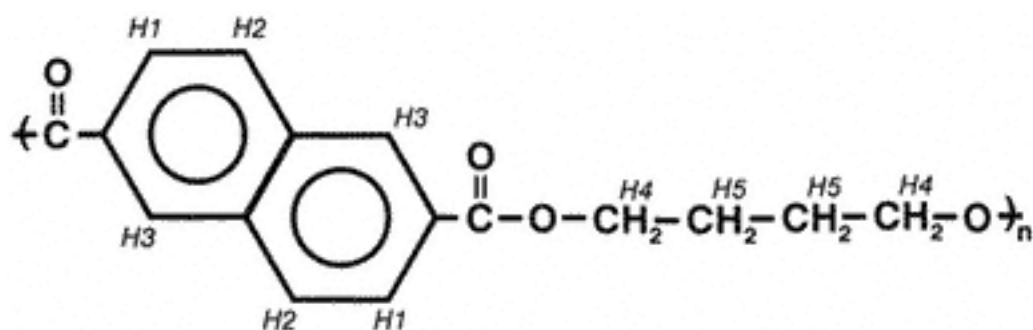
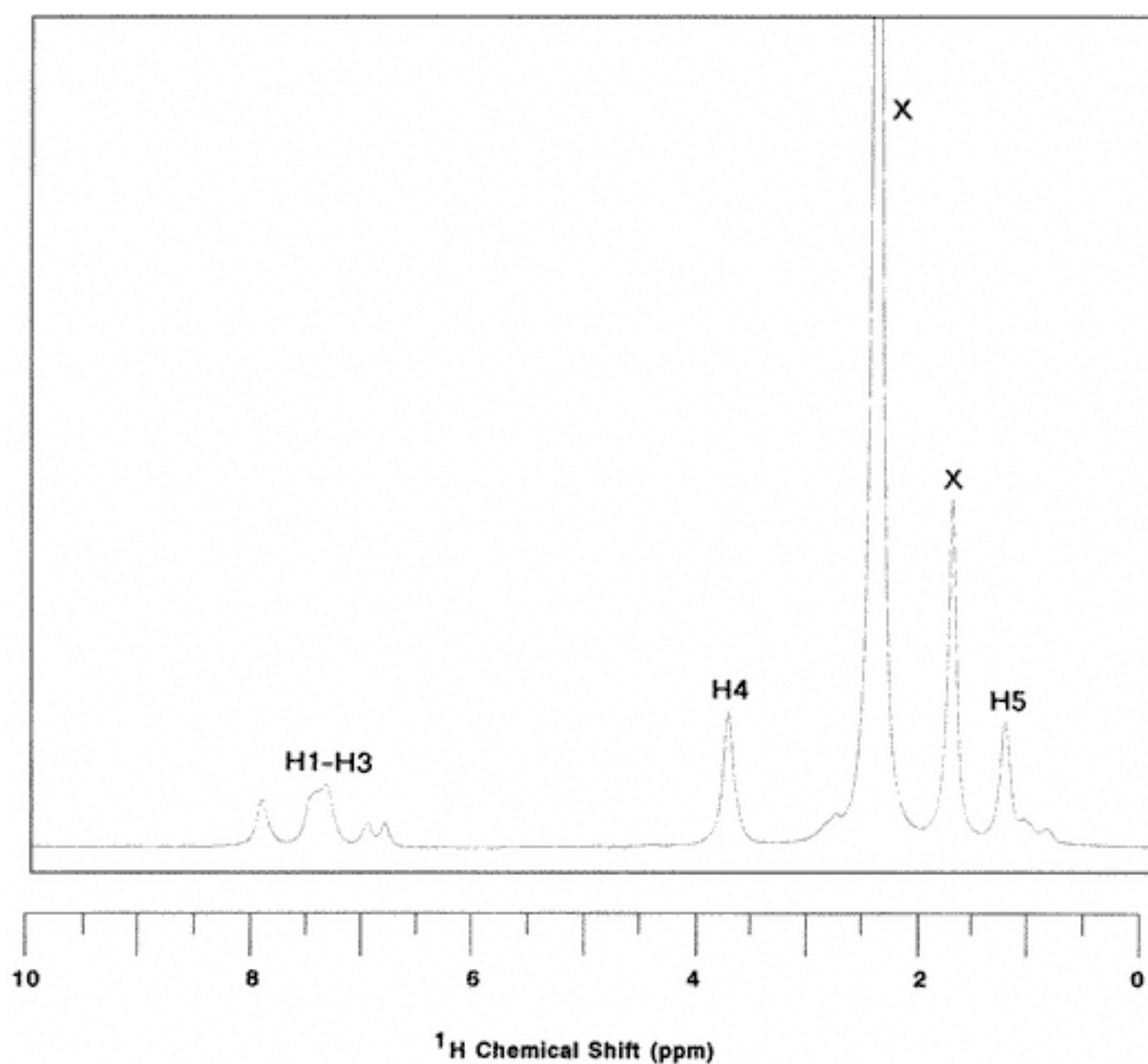
Source

Amoco Chemical, Naperville, IL.

**VIII-B-10H—
Poly(Butylene Naphthoate) (PBN)**

Comments

Solvent resonances are marked by X. This relatively new material is used in applications similar to PBT {VIII-B-3}, such as molded parts, but it has better mechanical properties.



Code	Shift (ppm)
H1	6.8–8.0
H2	6.8–8.0
H3	6.8–8.0
H4	3.8
H5	1.3

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 2% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

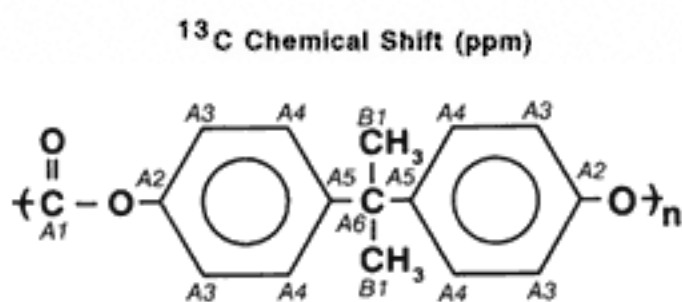
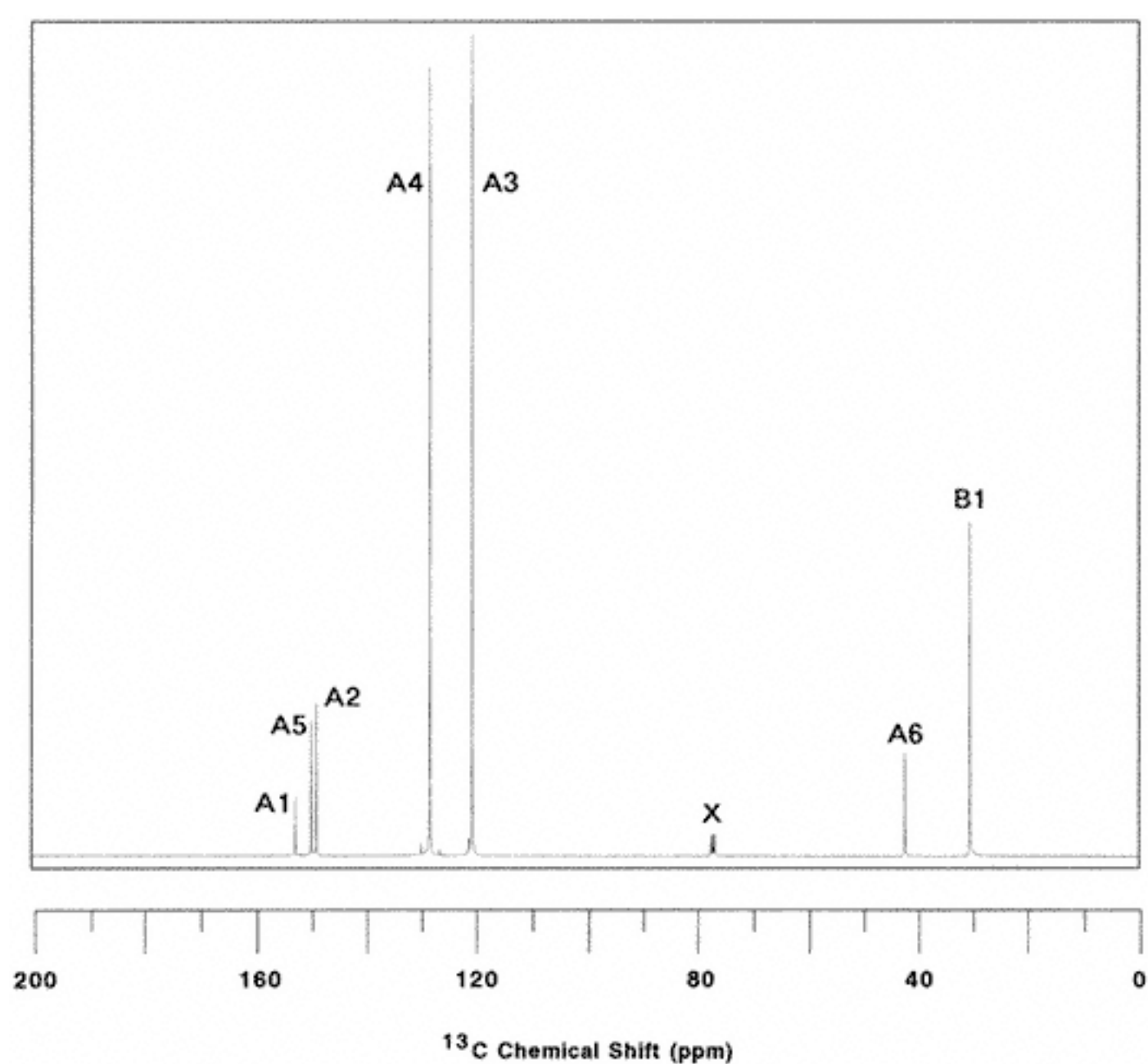
Pulse delay: 5 s

VIII-B-11—

Poly(Bisphenol A Carbonate) (PBPA)

Comments

Also known as Lexan (General Electric). Solvent resonances are marked by **X**. This engineering resin has excellent impact and optical properties, which make it useful as bullet-proof glazing and in jet aircraft windows. The material is sometimes coated to improve its chemical and scratch resistance; glass fibers are sometimes added for additional reinforcement. Specific applications include compact discs, appliance housings, sports helmets, and bottles.



Code	Shift (ppm)
A1	152.1
A2	148.4
A3	120.4
A4	128.3
A5	149.3
A6	42.4
B1	30.9

*Experimental Parameters*Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

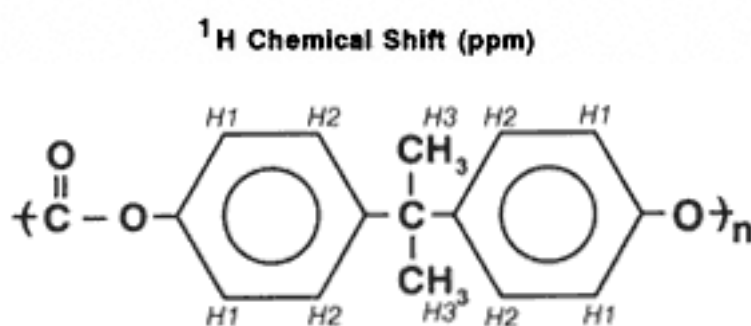
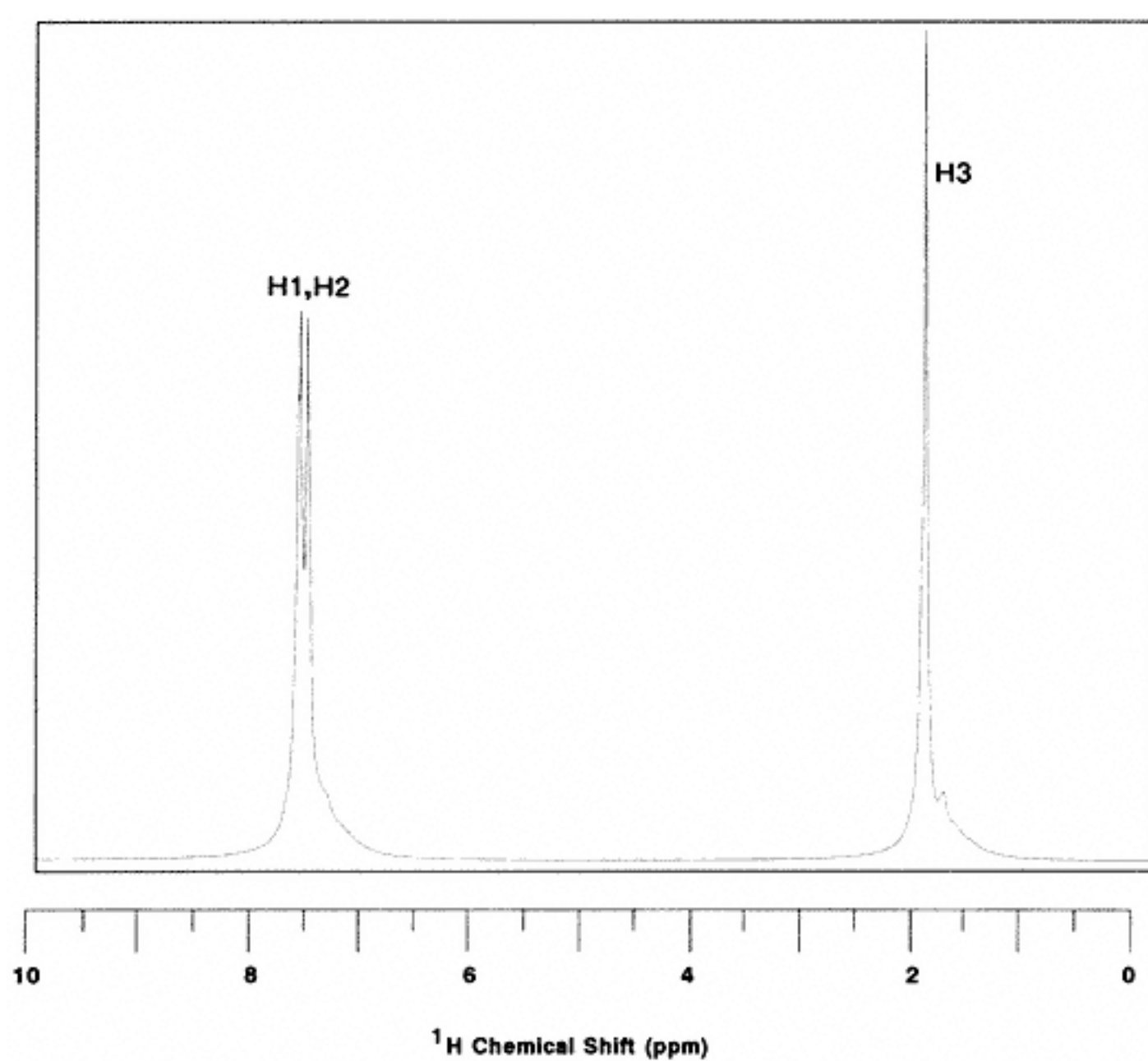
Broadening: 2 Hz

Pulse delay: 5 s

**VIII-B-11H—
Poly(Bisphenol A Carbonate) (PBPAC)**

Comments

Also known as Lexan (General Electric), this engineering resin has excellent impact and optical properties, which make it useful as bullet-proof glazing and in jet aircraft windows. The material is sometimes coated to improve its chemical and scratch resistance; glass fibers are sometimes added for additional reinforcement. Specific applications include compact discs, appliance housings, sports helmets, and bottles.



Code	Shift (ppm)
H1	7.6, 7.7
H2	7.6, 7.7
H3	2.1

Experimental Parameters

Nucleus: ¹H (400 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 20% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

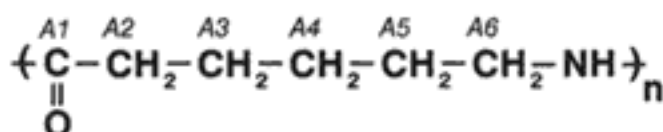
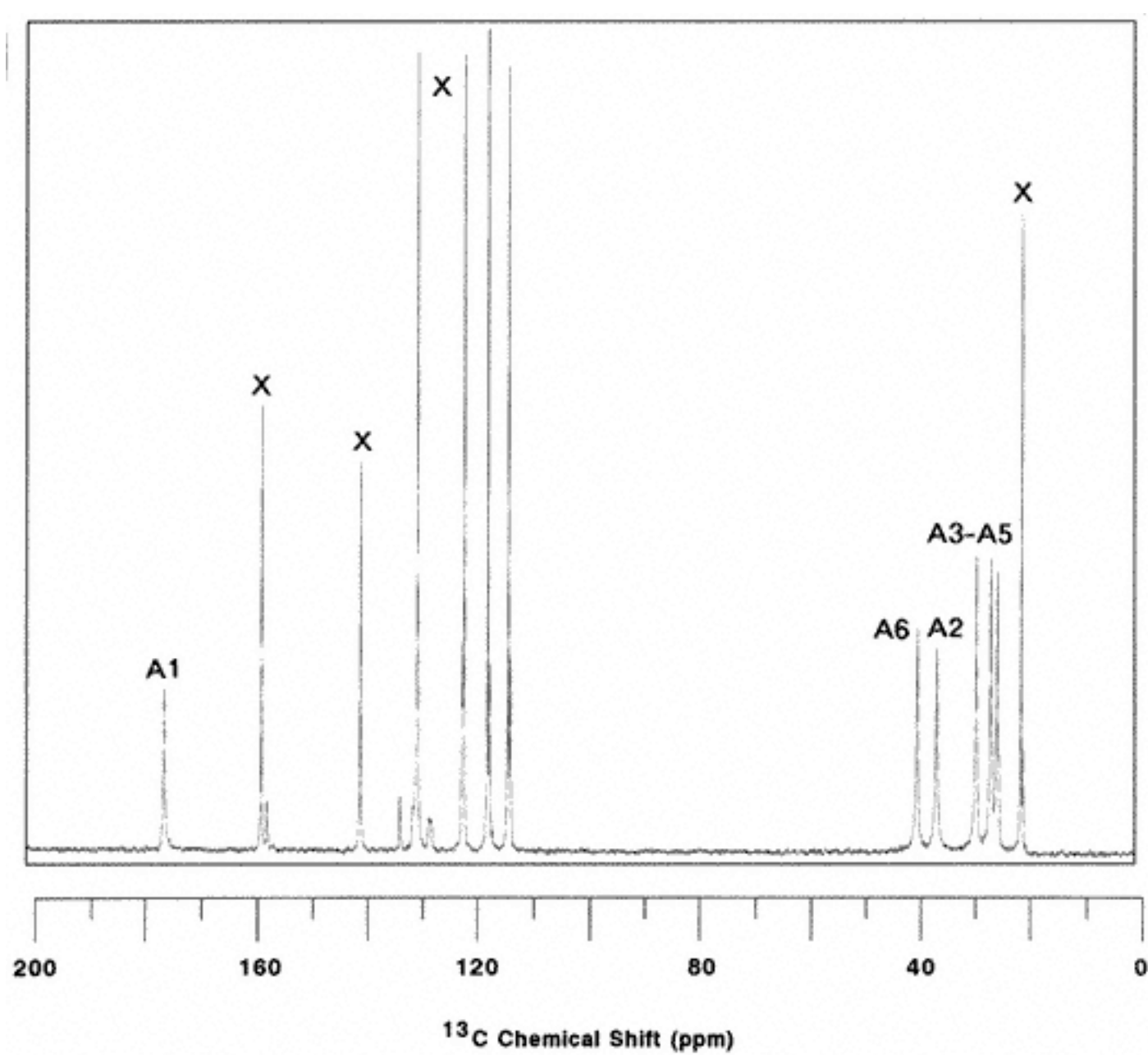
Broadening: 5 Hz

Pulse delay: 5 s

VIII-C-1— Polyhexaneamide (Nylon 6)

Comments

Also known as polycaprolactam. Solvent resonances are marked by X. Nylon 6 melts at 215°C. Similar to most nylons, it is used primarily for fibers in furnishings, clothing, and tire cord. This material and poly(hexamethylene hexaneamide) (nylon 6/6) {VIII-C-4} are the most commonly encountered polyamides; together they constitute 90% of the nylon market.



Code	Shift (ppm)
A1	174.9
A2	36.8
A3	25.8
A4	27.2
A5	29.6
A6	40.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 130°C
Solvent: <i>m</i> -cresol/ODCB- d_4	Concentration: 5% w/w
Scans: 100	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 10 Hz	Pulse delay: 5 s

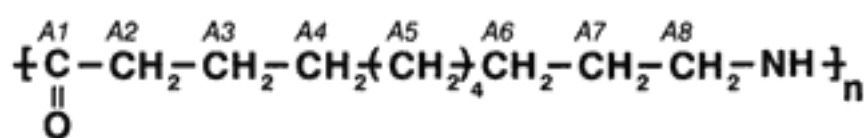
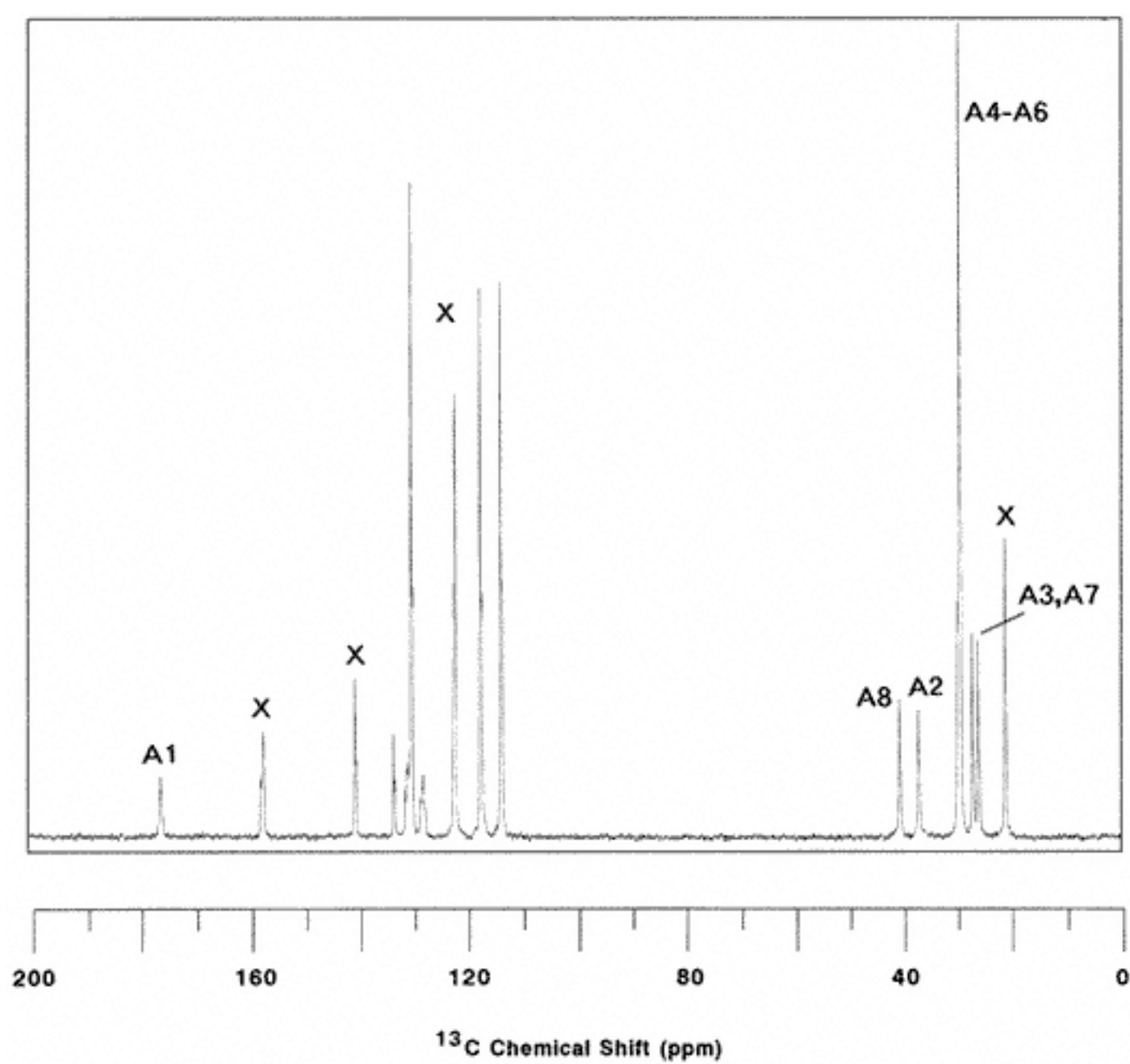
References

K. de Vries, H. Linssen, and G. v. d. Velden. *Macromolecules* 22:1607, 1989; H. Ketels, R. Schellckens, J. Beulen, and G. v. d. Velden. *Polym. Commun.* 29:189, 1988.

VIII-C-2—
Polyundecaneamide (Nylon 11)

Comments

Solvent resonances are marked by X. Nylon 11 melts at 194°C. It is used primarily for the manufacture of vehicle hoses and tubes, and in powder coatings.



Code	Shift (ppm)
A1	174.9
A2	36.8
A3	25.8
A4	29.9
A5	29.9
A6	29.9
A7	26.9
A8	40.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: *m*-cresol/ODCB- d_4

Concentration: 5% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

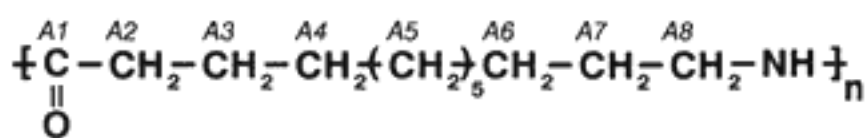
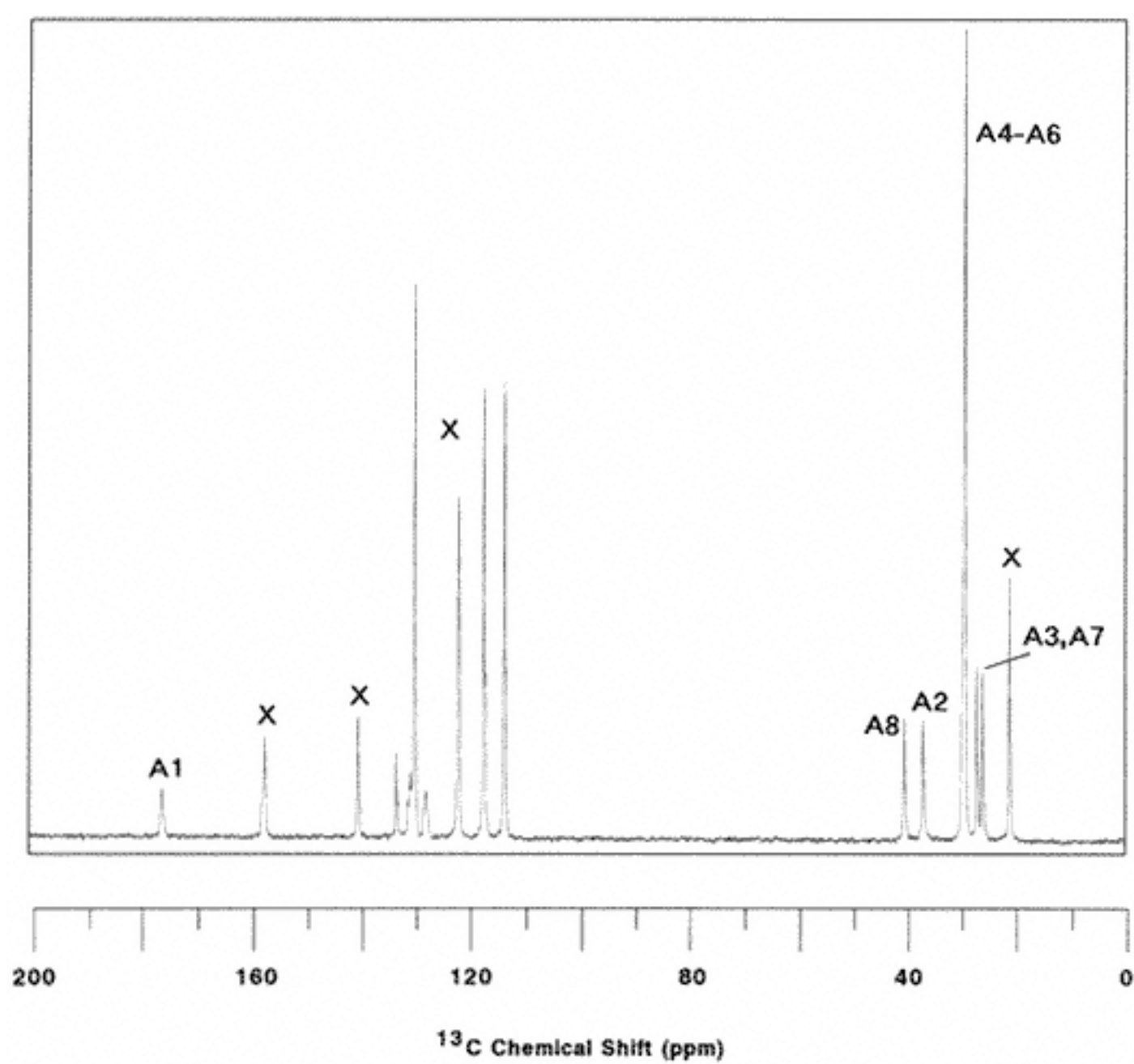
Broadening: 10 Hz

Pulse delay: 5 s

**VIII-C-3—
Polydodecanamide (Nylon 12)**

Comments

Also known as polylauryllactam. Solvent resonances are marked by **X**. Nylon 12 melts at 179°C. It is used primarily for the manufacture of vehicle hoses and tubes, and in powder coatings.



Code	Shift (ppm)
A1	175.5
A2	37.3
A3	26.5
A4	29.9
A5	29.9
A6	29.9
A7	26.9
A8	40.8

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: *m*-cresol/ODCB- d_4

Concentration: 5% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 10 Hz

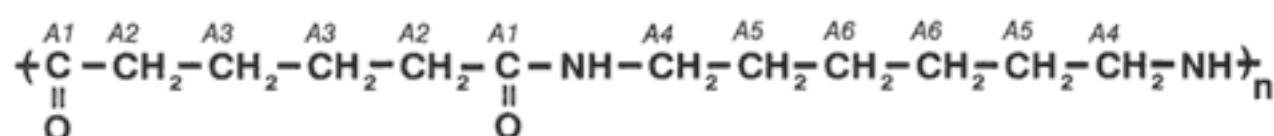
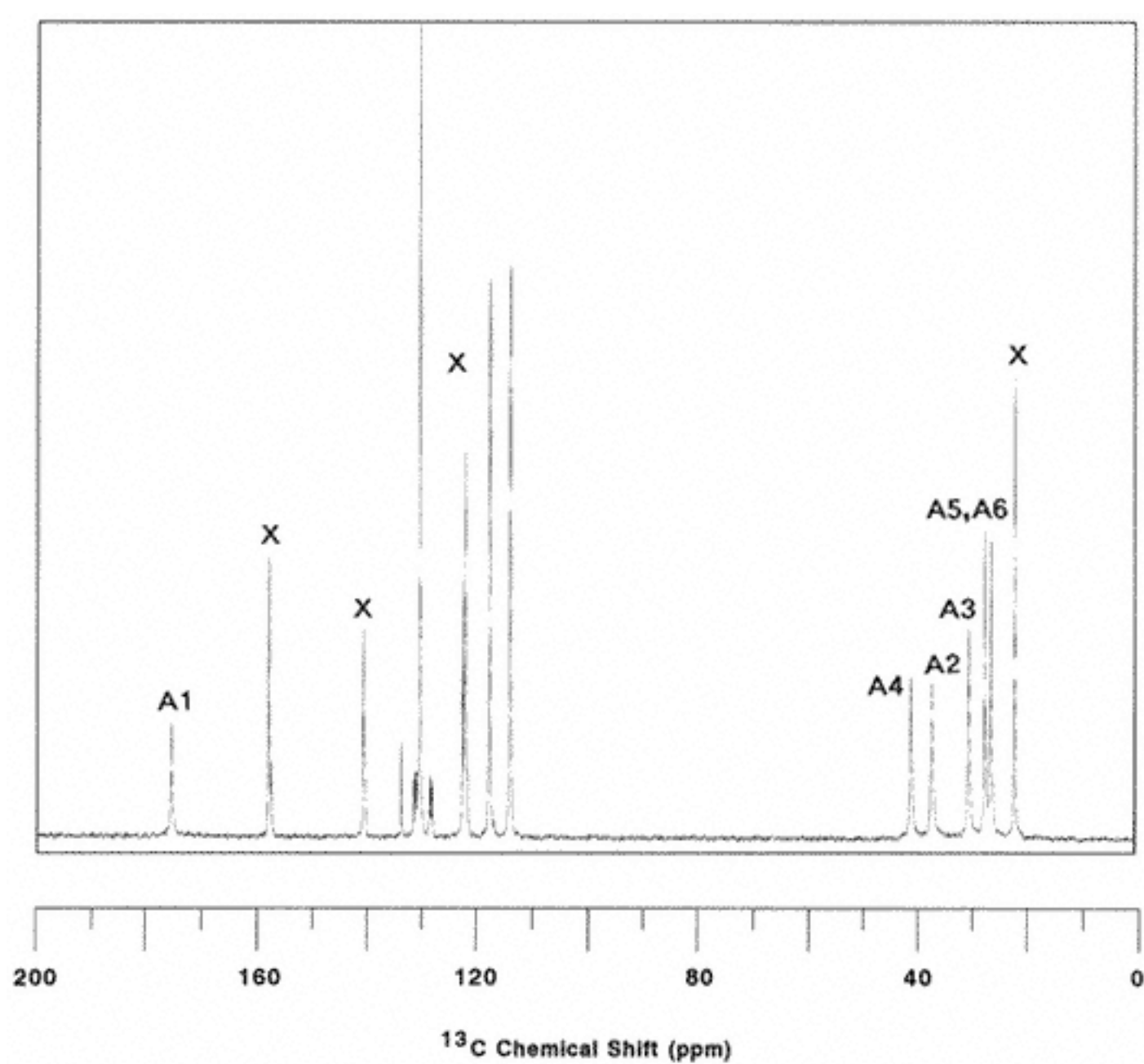
Pulse delay: 5 s

VIII-C-4—

Poly(Hexamethylene Hexaneamide) (Nylon 6/6)

Comments

Solvent resonances are marked by X. Nylon 6/6 melts at 265°C. Similar to most nylons, it is used primarily for fibers in furnishings, clothing, and tire cord. This material and polyhexaneamide (nylon 6) {VIII-C-1} are the most commonly encountered polyamides; together they constitute 90% of the nylon market.



Code	Shift (ppm)
A1	174.9
A2	36.6
A3	29.9
A4	40.4
A5	26.9
A6	25.8

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 130°C
Solvent: <i>m</i> -cresol/ODCB- d_4	Concentration: 5% w/w
Scans: 100	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 10 Hz	Pulse delay: 5 s

Reference

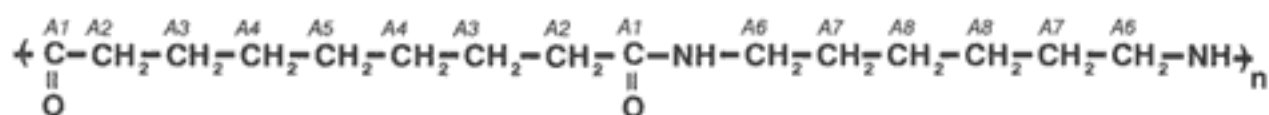
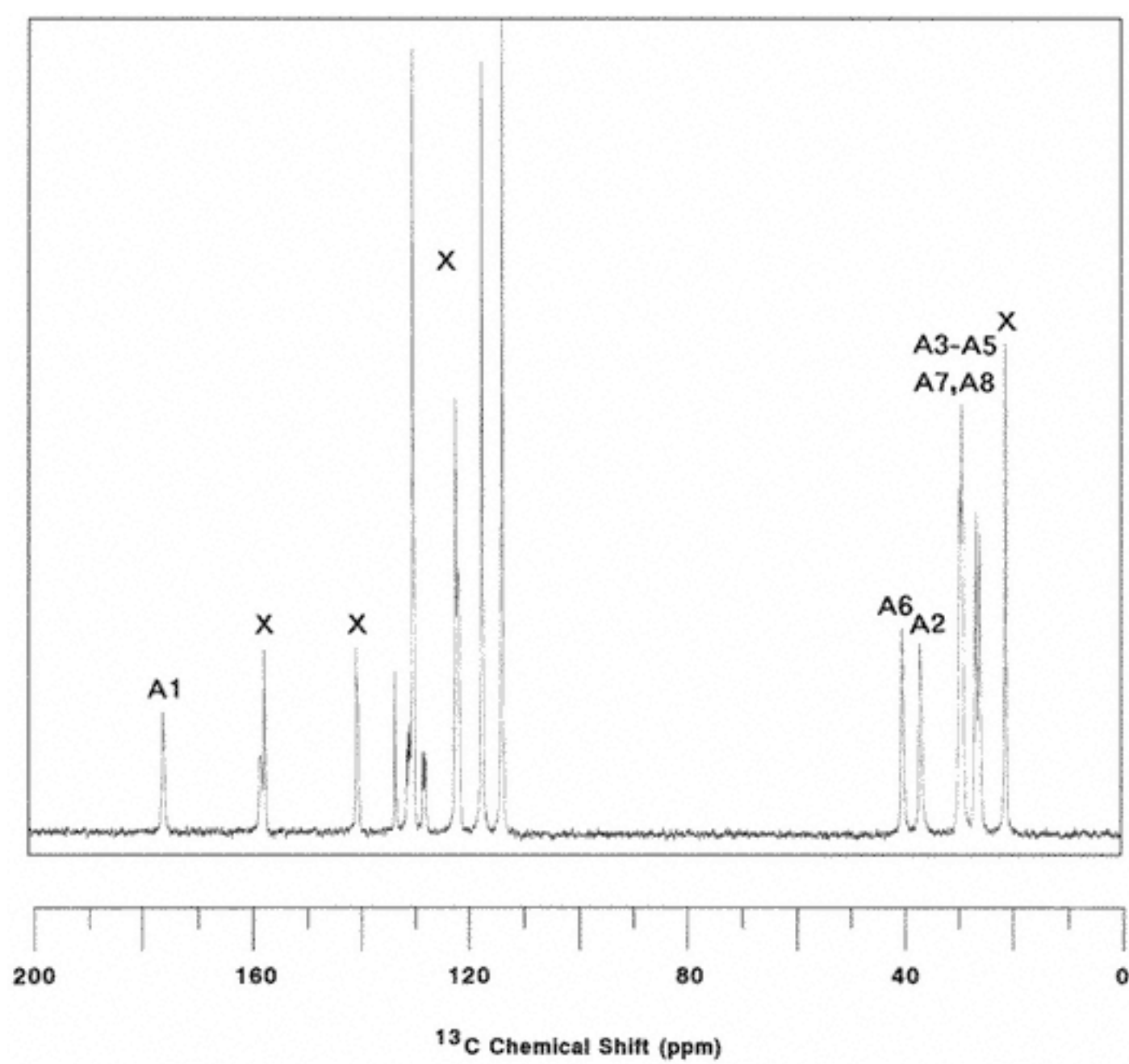
K. de Vries, H. Linssen, and G. v. d. Velden. *Macromolecules* 22:1607, 1989.

VIII-C-5—

Poly(Hexamethylene Nonaneamide) (Nylon 6/9)

Comments

Solvent resonances are marked by X. Nylon 6/9 melts at 205°C. Similar to most nylons, it is used primarily for fibers in furnishings, clothing, and tire cord.



Code	Shift (ppm)
A1	175.2
A2	37.0
A3	26.2
A4	30–31
A5	27.0
A6	40.4
A7	30–31
A8	30–31

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: *m*-cresol/ODCB- d_4

Concentration: 5% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

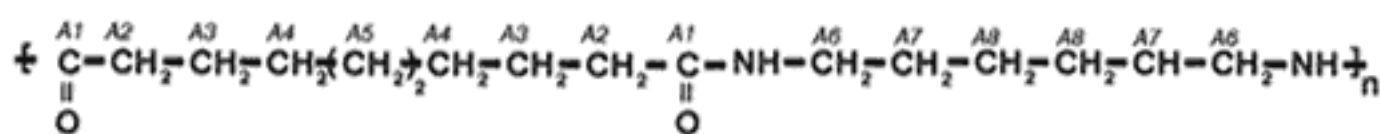
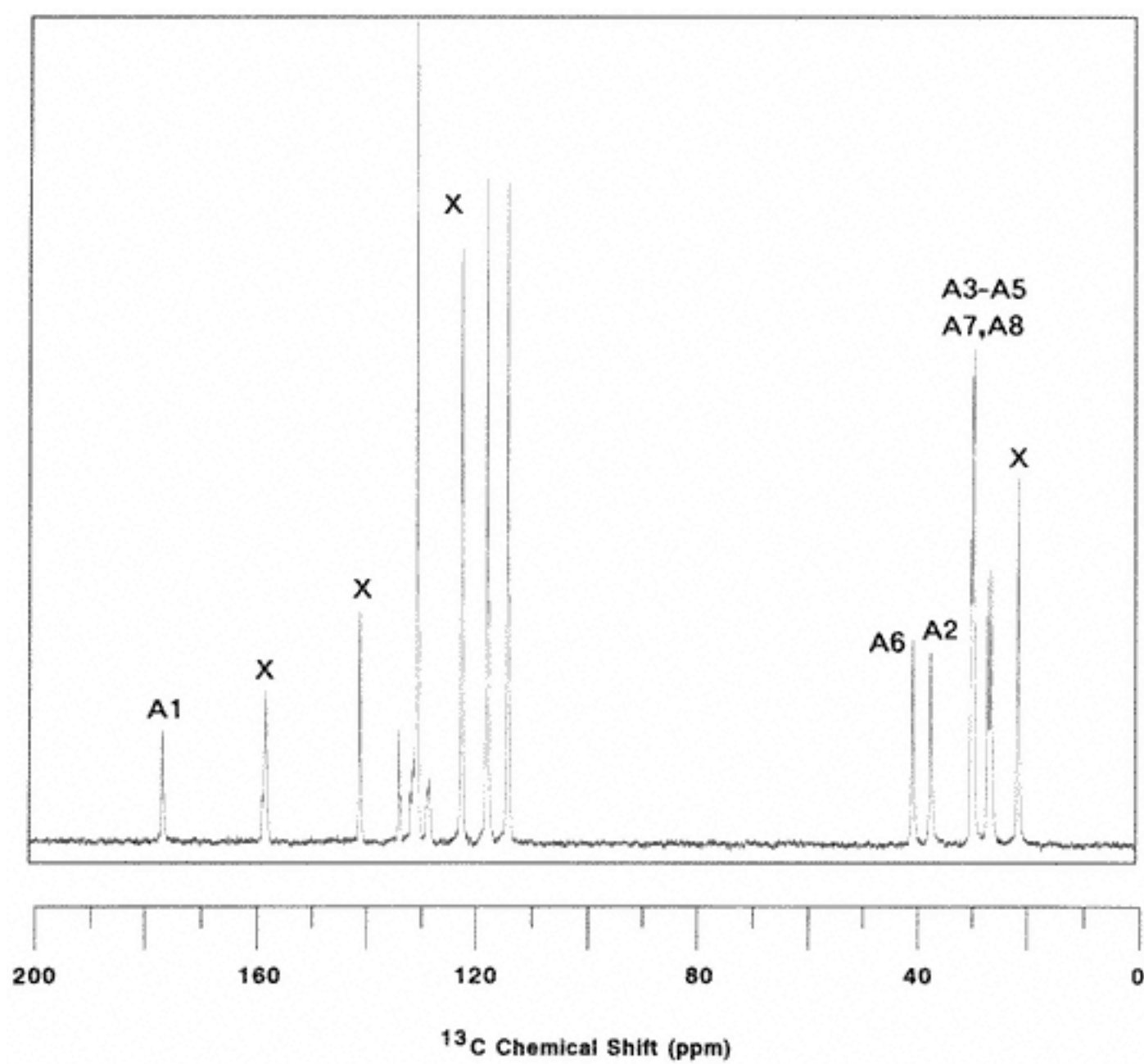
Broadening: 10 Hz

Pulse delay: 5 s

VIII-C-6—
Poly(Hexamethylene Decaneamide) (Nylon 6/10)

Comments

Solvent resonances are marked by X. Nylon 6/10 melts at 225°C. Similar to most nylons, it is used primarily for fibers in furnishings, clothing, and tire cord.



Code	Shift (ppm)
A1	175.5
A2	37.2
A3	27.0
A4	30–31
A5	27.3
A6	40.9
A7	30–31
A8	30–31

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: *m*-cresol/ODCB- d_4

Concentration: 5% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

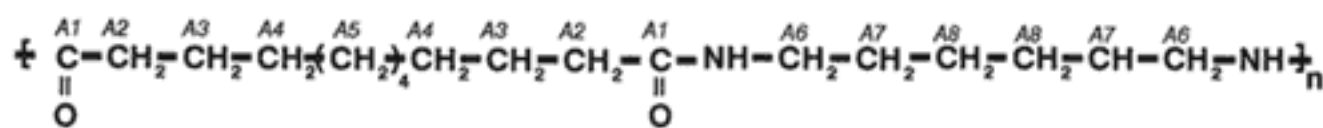
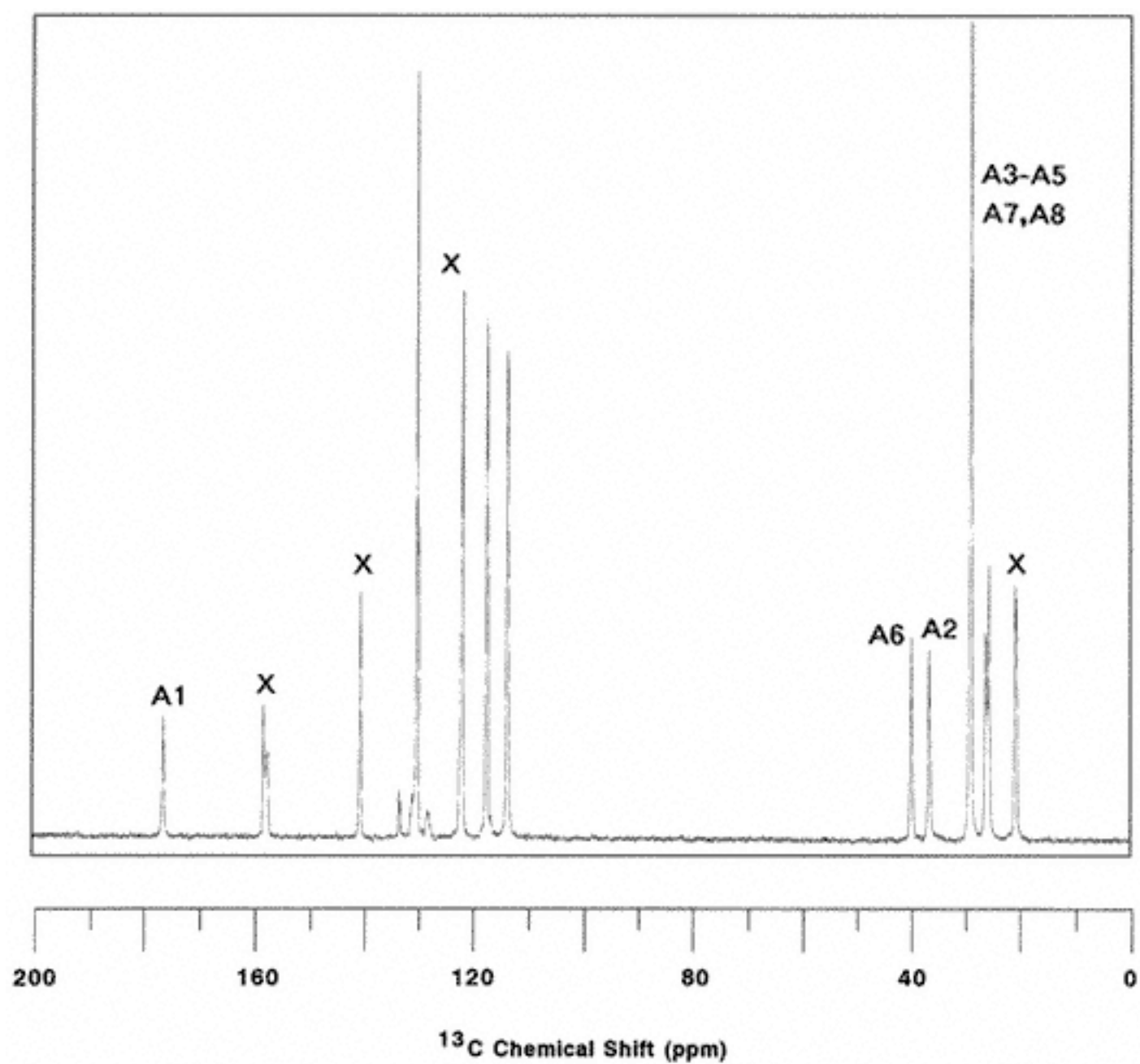
Broadening: 10 Hz

Pulse delay: 5 s

VIII-C-7—
Poly(Hexamethylene Dodecanamide) (Nylon 6/12)

Comments

Solvent resonances are marked by X. Nylon 6/12 melts at 217°C. Similar to most nylons, it is used primarily for fibers in furnishings, clothing, and tire cord.



Code	Shift (ppm)
A1	175.6
A2	37.3
A3	26.5
A4	29–30
A5	26.9
A6	40.5
A7	29–30
A8	29–30

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: *m*-cresol/ODCB- d_4

Concentration: 5% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 10 Hz

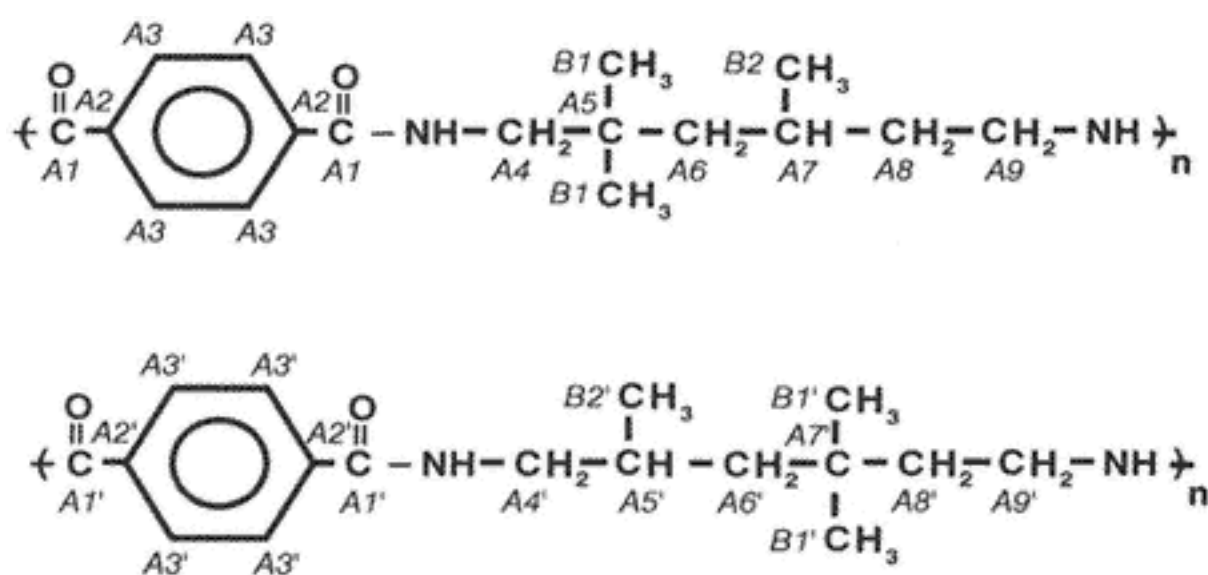
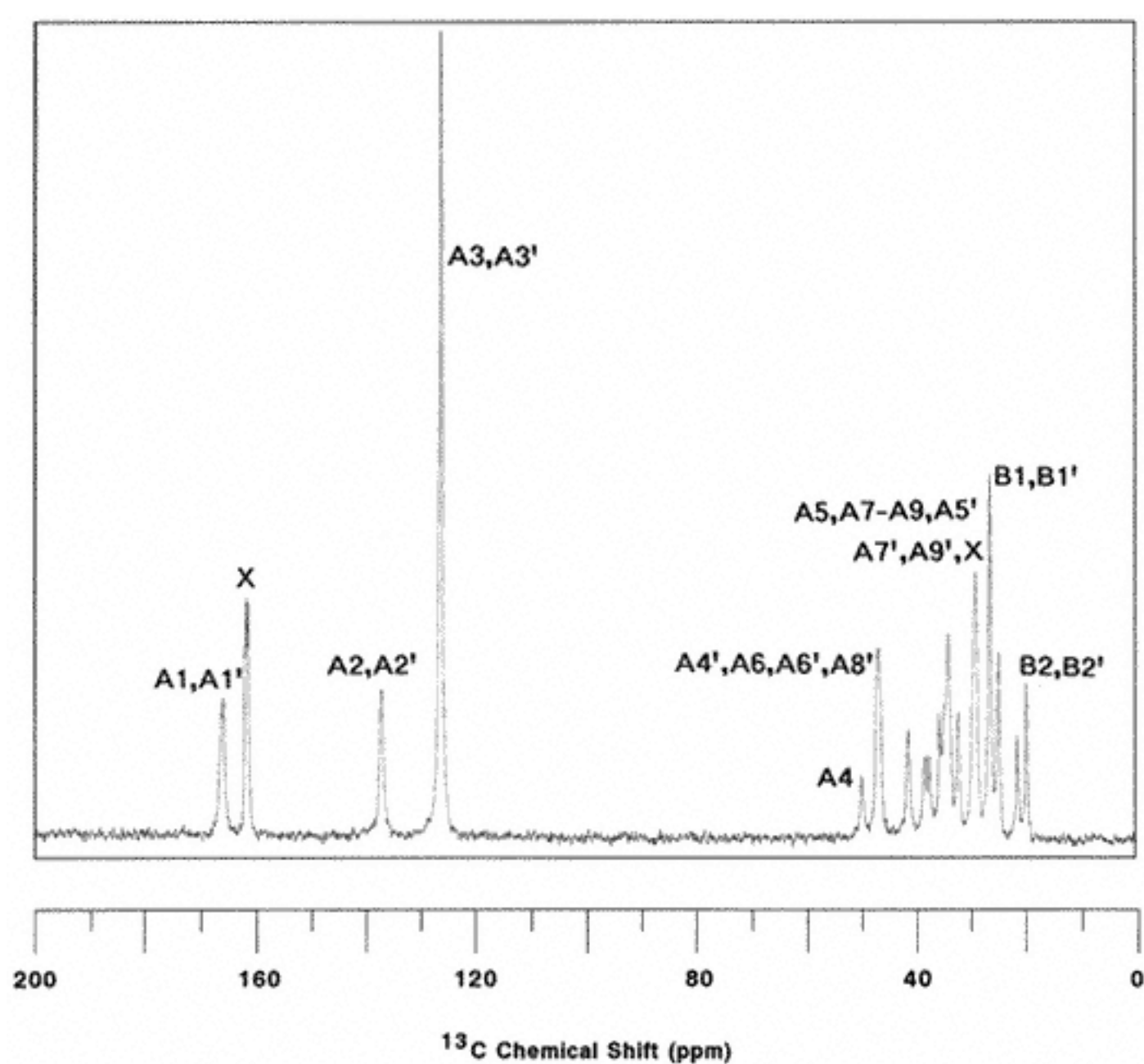
Pulse delay: 5 s

VIII-C-8—

Poly(2,2,4-Trimethylhexamethylene Terephthalamide-Co-2,4,4-Trimethylhexamethylene Terephthalamide) (Nylon 6/T)

Comments

Solvent resonances are marked by X. Nylon 6/T is an amorphous material, with no distinct melting point. Because of its chemical resistance, it is used primarily for tubing.



Code	Shift (ppm)
A1, A1'	166.1
A2, A2'	137.2
A3, A3'	126.7
A4	50.6
A4'	46.8
A5	28–44
A5'	28–44
A6, A6'	46.8
A7, A7'	28–44
A8	28–44
A8'	46.8
A9, A9'	28–44
B1, B1'	26.7, 25.0
B2, B2'	21.7, 20.0

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 130°C

Solvent: dimethylformamide- d_7

Concentration: 10% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

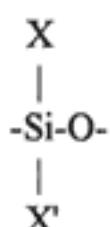
Pulse width: 90°

Broadening: 10 Hz

Pulse delay: 5 s

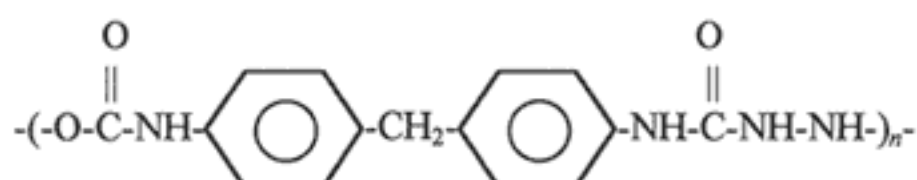
IX—**Miscellaneous Backbones**

Polymers in this group are based on chain backbones not included in any of the previous chapters. Most of these materials are polysiloxanes:



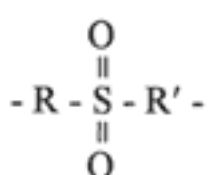
A

in which X and X' can be either a hydrogen atom or an organic group, such as alkyl, phenyl, or ether. Other materials in this chapter are: (1) polyurethane elastomers, in which urethane segments, such as:



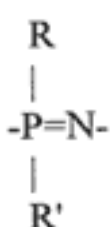
B

alternate with polyether or polyester segments; (2) polymers with sulfur-containing backbones, such as the polysulfone engineering resins:



C

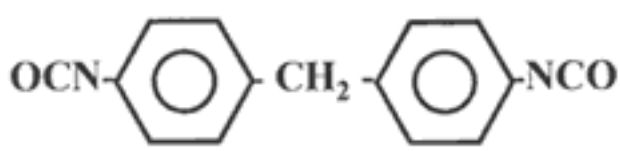
and polysulfide robber; and (3) polyphosphazenes:



D

The polysiloxanes are also known as silicones, and are commonly used as elastomers, waxes, lubricants, and coatings [1]. The most common polymer of this type is polydimethylsiloxane (PDMS) {IX-A-1}, in which both R and R' of Structure A are methyl groups; it is commonly known as *silicone rubber* or *oil*. Silicone materials, which are produced in a wide variety of molecular weights, are prepared from chlorosilane (R_2SiCl_2) monomers. Silicones are chemically inert and stable under high-temperature conditions, so they are often found in demanding applications, such as medical devices, gaskets, and seals. Polysiloxanes designed for use as coatings generally have complex side groups with additional functionalities that improve adhesion to the surface, or that permit cross-linking.

The basic structure of a urethane polymer arises from the condensation reaction of an aromatic diisocyanate, $R(NCO)_2$, such as 4,4'-diphenylenemethane diisocyanate (MDI):



E

and a diol or polyether glycol. This alternating polymer may be further functionalized with a polyglycol or hydroxyl-terminated polyester. The properties of these materials vary according to the relative lengths of the polyether and polyester segments. The most common applications of polyurethanes are foam (both flexible and rigid), elastic fibers (spandex), sealants, coatings, and adhesives. Over 1 billion lb (4.5 billion kg) were produced in the United States in 1996 [2].

Polymers with sulfone linkages in the backbone are high-performance engineering plastics with excellent high-temperature properties; they are found in very demanding applications, such as appliance and tool housings, and automotive components [1]. They are formed by the polycondensation of sulfonyl chlorides or sulfones with reactive end groups. Polysulfides and polyphosphazenes are elastomers, with highly specialized uses in which their chemical resistance is advantageous, such as gaskets, seals, and hoses [1]. Sulfide rubber is produced from alkyl halides and inorganic polysulfides; polyphosphazenes, from poly(phosphonitrilic chlorides).

IX.A—

Sample Preparation and Spectral Acquisition

Most silicone, polysulfone, polysulfide, and polyphosphazene materials are soluble in many widely available organic solvents, such as chloroform or methylene chloride [3]. Polyurethanes dissolve in dimethylformamide (DMF) and swell in some other solvents, although the quality of the spectra of swollen polymers may not be adequate for identification or quantitation of the individual components. ^{13}C NMR spectra of all these materials are easily obtained, and quantitative results can be achieved with typical acquisition parameters: 15-s pulse delay, 90° pulse, and gated 1H decoupling. Quantitative 1H spectra are obtained with a 5-s delay after a 45° pulse. Multinuclear NMR provides further opportunities for the characterization of silicones (^{29}Si) and polyphosphazenes (^{31}P) [4,5]. The negative gyromagnetic ratio of the ^{29}Si nucleus can lead to negative or null signals if continuous (nongated) 1H decoupling is used. Furthermore, these nuclei tend to have very long spin-lattice (T_1) relaxation times, which can render experiments prohibitively long. To circumvent these problems, samples prepared for ^{29}Si NMR usually contain a small amount (0.05 M or less) of a paramagnetic relaxation agent, such as chromium (III) acetoacetate [$Cr(acac)_3$]. The presence of a paramagnetic species significantly decreases T_1 , and eliminates the nuclear Overhauser enhancement (NOE). Quantitative conditions can then be achieved with a 5-s delay following a 90° pulse, with gated 1H decoupling. ^{31}P NMR is an easily observed nucleus because of its high natural abundance [4,5]. No relaxation agent is needed, and correct peak areas can usually be obtained with a 10-s delay, 90° pulse, and complete 1H decoupling.

IX.B—

Spectral Features

Because such a wide variety of structures is included in this chapter, it is not possible to make chemical-shift generalizations for the group.

IX.B.1—

Siloxane Polymers and Copolymers

Alkyl ^{13}C nuclei attached directly to silicon ($Si-C$) resonate between 0 and 20 ppm, with the exact position depending on the type of carbon: 0–2 ppm for CH_3 , 10–20 ppm for CH_2 , and higher shifts for other carbon types. Aromatic carbons bonded

to silicon appear at 130–140 ppm. Carbons located farther from the silicon atom are proportionately less affected by its presence [6]. Similarly, ^1H spectral features are observed at about 0 ppm for $\text{CH}_3\text{-Si}$ and 0.5 ppm for $\text{CH}_2\text{-Si}$, and at somewhat higher shifts for other types of protons. ^{13}C and ^1H data reveal many details about the pendant groups in a silicone polymer, but more direct information about the backbone structure and length can be obtained from the ^{29}Si spectrum. ^{29}Si resonance positions depend most strongly on the number of oxygens bonded to the silicon: -110 to -90 ppm for SiO_4 ; -90 to -40 ppm for RSiO_3 ; -30 to 20 ppm for R_2SiO_2 ; and 0 – 50 ppm for R_3SiO . It is, therefore, simple to distinguish the $(\text{CH}_3)_3\text{SiO}$ end groups in many polydimethylsiloxanes, such as {IX-A-3Si through IX-A-15Si}, from interior $(\text{CH}_3)_2\text{SiO}_2$ units [7], and so determine the chain length (i.e., molecular weight). The identity of the R group has little effect on the ^{29}Si chemical shift.

IX.B.2—

Other Polymers and Copolymers

The ^{13}C spectra of polyurethanes {IX-B-1 through IX-B-4} contain contributions from each component of the system: isocyanate, polyether, and (in some cases) polyester. MDI-based urethane segments (see Structure E) are characterized by a carbonyl resonance at 155 ppm, aromatic peaks at 139, 137, 130, and 120 ppm, and a methylene resonance at 41 ppm. Because the polyether and any polyester segments occur as blocks, their spectra will be essentially identical to those of the homopolymers (such as many of the materials in Chapters VII and VIII). Quantitative spectra can be used to determine the exact composition of these materials.

The ^{13}C spectra of sulfur- and phosphorus-containing polymers do not exhibit any resonances that immediately distinguish these materials. A polyphosphazene will exhibit a ^{31}P signal around -20 ppm.

References

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3. J. Brandup and E. H. Immergut. *Polymer Handbook*. New York: Wiley, 1975.
4. R. K. Harris and B. E. Mann. *NMR and the Periodic Table*. London: Academic Press, 1978.
5. J. Mason, ed., *Multinuclear NMR*, New York: Plenum Press, 1987.
6. E. Breitmaier and W. Voelter. *Carbon-13 NMR Spectroscopy*. New York: VCH Publishers, 1987.
7. G. L. Marshall. *Br. Polym. J.* 14:19, 1982.

MISCELLANEOUS BACKBONES*A. Siloxane Polymers and Copolymers*

IX-A-1	Polydimethylsiloxane
IX-A-1H	Polydimethylsiloxane
IX-A-1Si	Polydimethylsiloxane
IX-A-2	Polydimethylsiloxane, hydroxyl-terminated
IX-A-2H	Polydimethylsiloxane, hydroxyl-terminated
IX-A-2Si	Polydimethylsiloxane, hydroxyl-terminated
IX-A-3	Polydimethylsiloxane, amine-terminated
IX-A-3Si	Polydimethylsiloxane, amine-terminated
IX-A-4	Polydimethylsiloxane, amine-terminated
IX-A-4Si	Polydimethylsiloxane, amine-terminated
IX-A-5	Polydimethylsiloxane, epoxy-modified
IX-A-5Si	Polydimethylsiloxane, epoxy-modified
IX-A-6	Polydimethylsiloxane, poly(ethylene glycol)-modified
IX-A-6Si	Polydimethylsiloxane, poly(ethylene glycol)-modified
IX-A-7	Polydimethylsiloxane, poly(propylene glycol)-modified
IX-A-7Si	Polydimethylsiloxane, poly(propylene glycol)-modified
IX-A-8	Polydimethylsiloxane, poly(ethylene glycol)/poly(propylene glycol)-modified
IX-A-8Si	Polydimethylsiloxane, poly(ethylene glycol)/poly(propylene glycol)-modified
IX-A-9	Polydimethylsiloxane, amine-modified
IX-A-9Si	Polydimethylsiloxane, amine-modified
IX-A-10	Polydimethylsiloxane, mercaptan-modified
IX-A-10Si	Polydimethylsiloxane, mercaptan-modified
IX-A-11	Poly(methyldodecylsiloxane-co-methyl-2-phenylpropylsiloxane)
IX-A-11Si	Poly(methyldodecylsiloxane-co-methyl-2-phenylpropylsiloxane)
IX-A-12	Poly(methyldodecylsiloxane-co-methyl-2-phenylpropylsiloxane), amine-modified
IX-A-12Si	Poly(methyldodecylsiloxane-co-methyl-2-phenylpropylsiloxane), amine-modified
IX-A-13	Poly(methyldodecylsiloxane-co-methyl-2-phenylpropylsiloxane), mercaptan-modified
IX-A-13Si	Poly(methyldodecylsiloxane-co-methyl-2-phenylpropylsiloxane), mercaptan-modified
IX-A-14	Polymethyloctadecylsiloxane
IX-A-14H	Polymethyloctadecylsiloxane
IX-A-14Si	Polymethyloctadecylsiloxane
IX-A-15	Polymethylphenylsiloxane
IX-A-15H	Polymethylphenylsiloxane
IX-A-15Si	Polymethylphenylsiloxane
IX-A-16	Poly(ethyl silicate)
IX-A-16H	Poly(ethyl silicate)
IX-A-16Si	Poly(ethyl silicate)

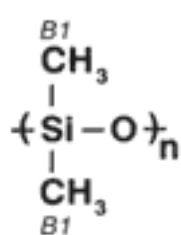
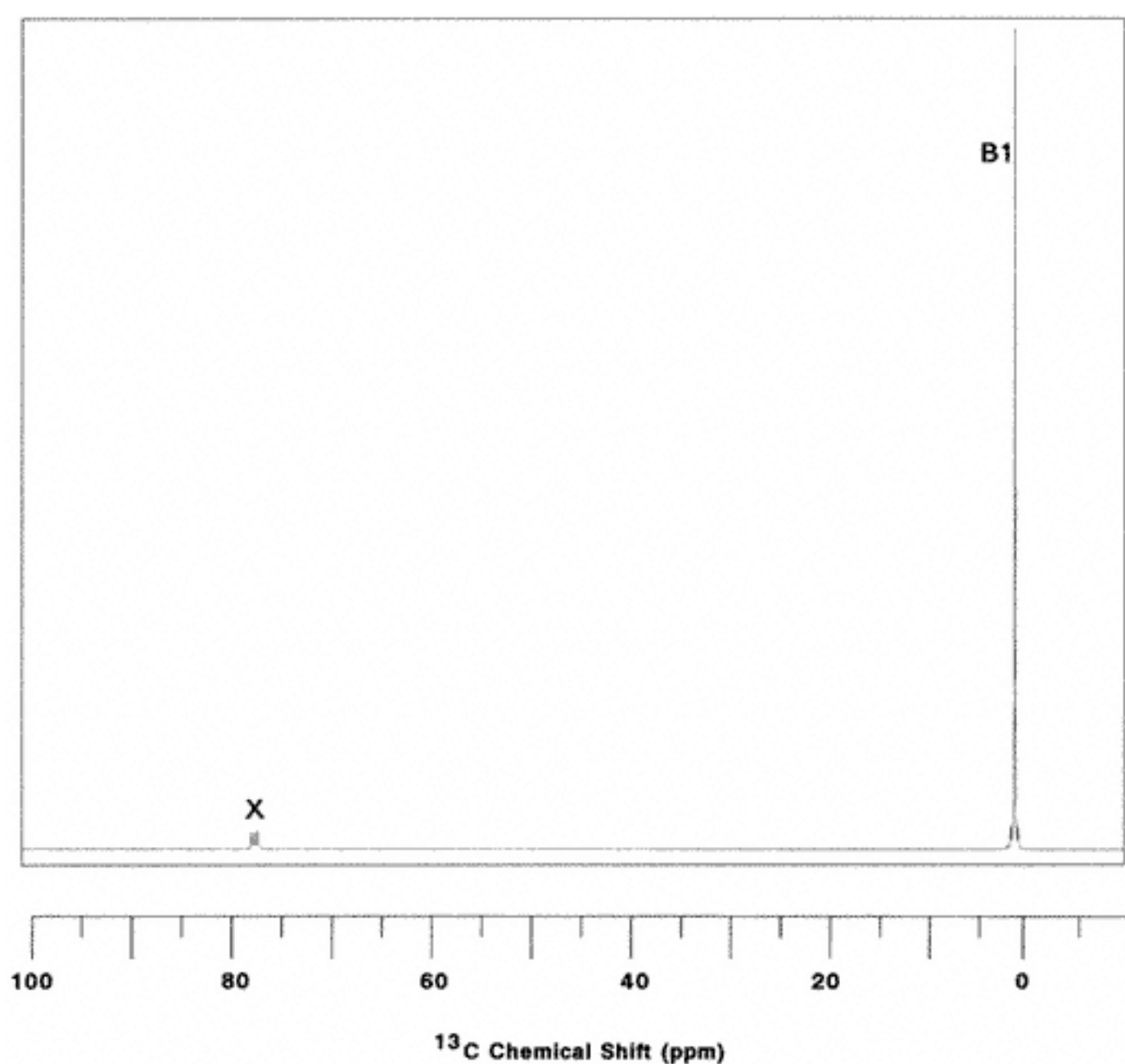
B. Other Polymers and Copolymers

IX-B-1	Poly[4,4'-methylenebis(phenyl isocyanate)-alt-1,4-butanediol/tetrahydrofuran]
IX-B-2	Poly[4,4'-methylenebis(phenyl isocyanate)-alt-1,4-butanediol/propylene glycol]
IX-B-3	Poly[4,4'-methylenebis(phenyl isocyanate)-alt-1,4-butanediol/poly(butylene adipate)]
IX-B-4	Poly[4,4'-methylenebis(phenyl isocyanate)-alt-1,4-butanediol/polycaprolactone]
IX-B-5	Poly(phenyl isocyanate-co-formaldehyde)
IX-B-6	Poly(phenyl glycidyl ether-co-formaldehyde)
IX-B-7	Poly(ethyl formal sulfide)
IX-B-8	Poly(phenylene ether sulfone)
IX-B-9	Poly(Bisphenol A-co-phenylene ether sulfone)
IX-B-10	Polydiphenoxyphosphazene
IX-B-10P	Polydiphenoxyphosphazene

**IX-A-1—
Polydimethylsiloxane (PDMS)**

Comments

Also known as silicone rubber or fluid. Because of the relatively high molecular weight, end-group resonances are not observed. The slight splitting of the single peak is due to ^{13}C - ^{29}Si coupling. Solvent resonances are marked by **X**. These materials have good chemical resistance, and can be cross-linked. The elastomeric form is used for rubber molds, seals, caulking, gaskets, and electrical insulation. Liquid silicones are used as lubricants, hydraulic fluids, heat-exchange fluids, antifoam agents, glass treatment, surfactants, water repellent, and in cosmetics and medical implants.



Code	Shift (ppm)
B1	1.0

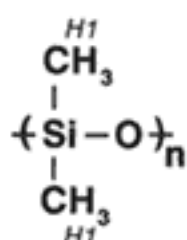
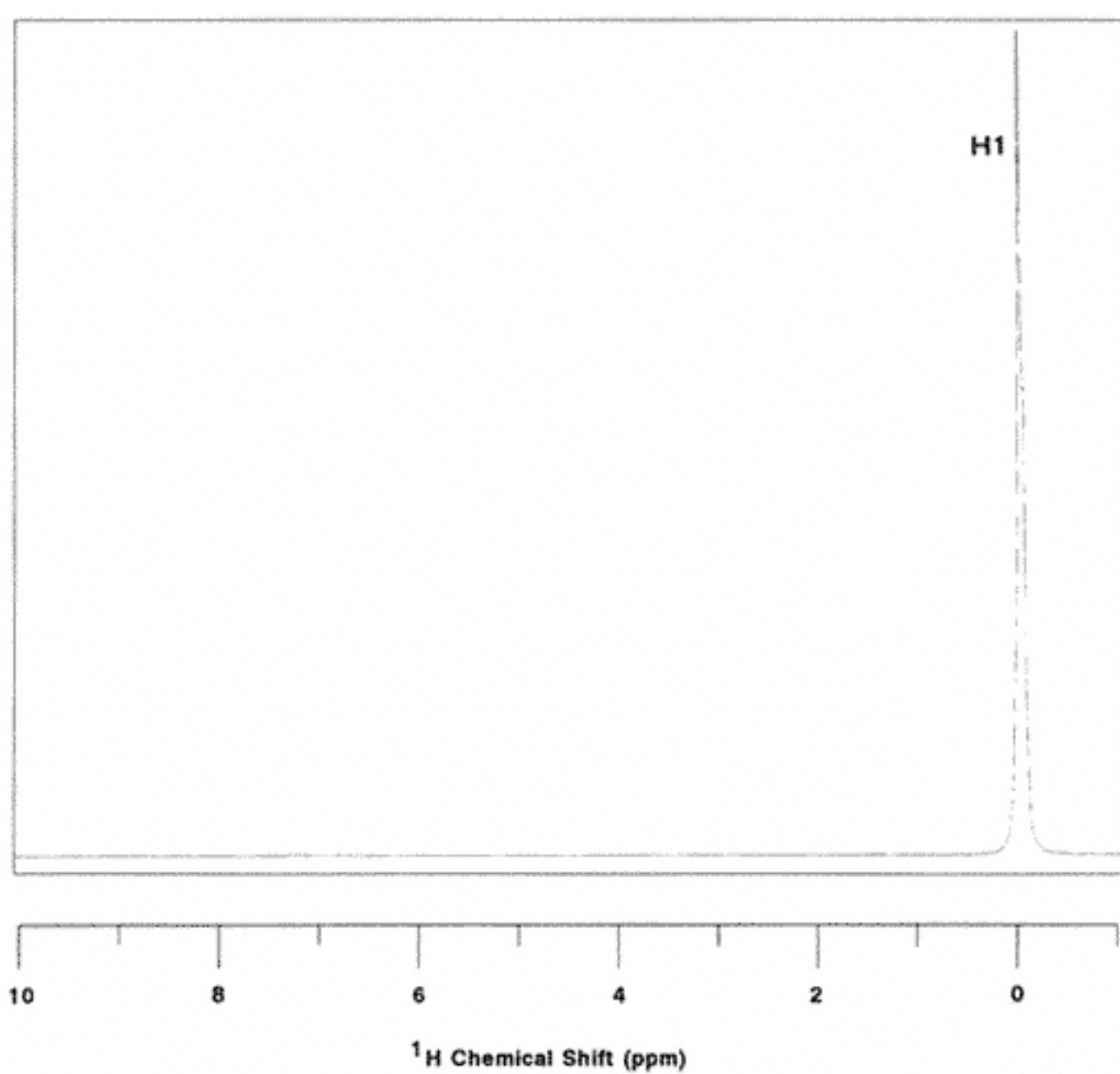
Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 20% w/w
Scans: 3200	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 5 s

**IX-A-1H—
Polydimethylsiloxane**

Comments

Also known as silicone rubber or fluid. These materials have good chemical resistance and can be cross-linked. The elastomeric form is used for rubber molds, seals, caulking, gaskets, and electrical insulation. Liquid silicones are used as lubricants, hydraulic fluids, heat-exchange fluids, antifoam agents, glass treatment, surfactants, water repellent, and in cosmetics and medical implants.



Code	Shift (ppm)
H1	0.04

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

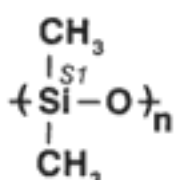
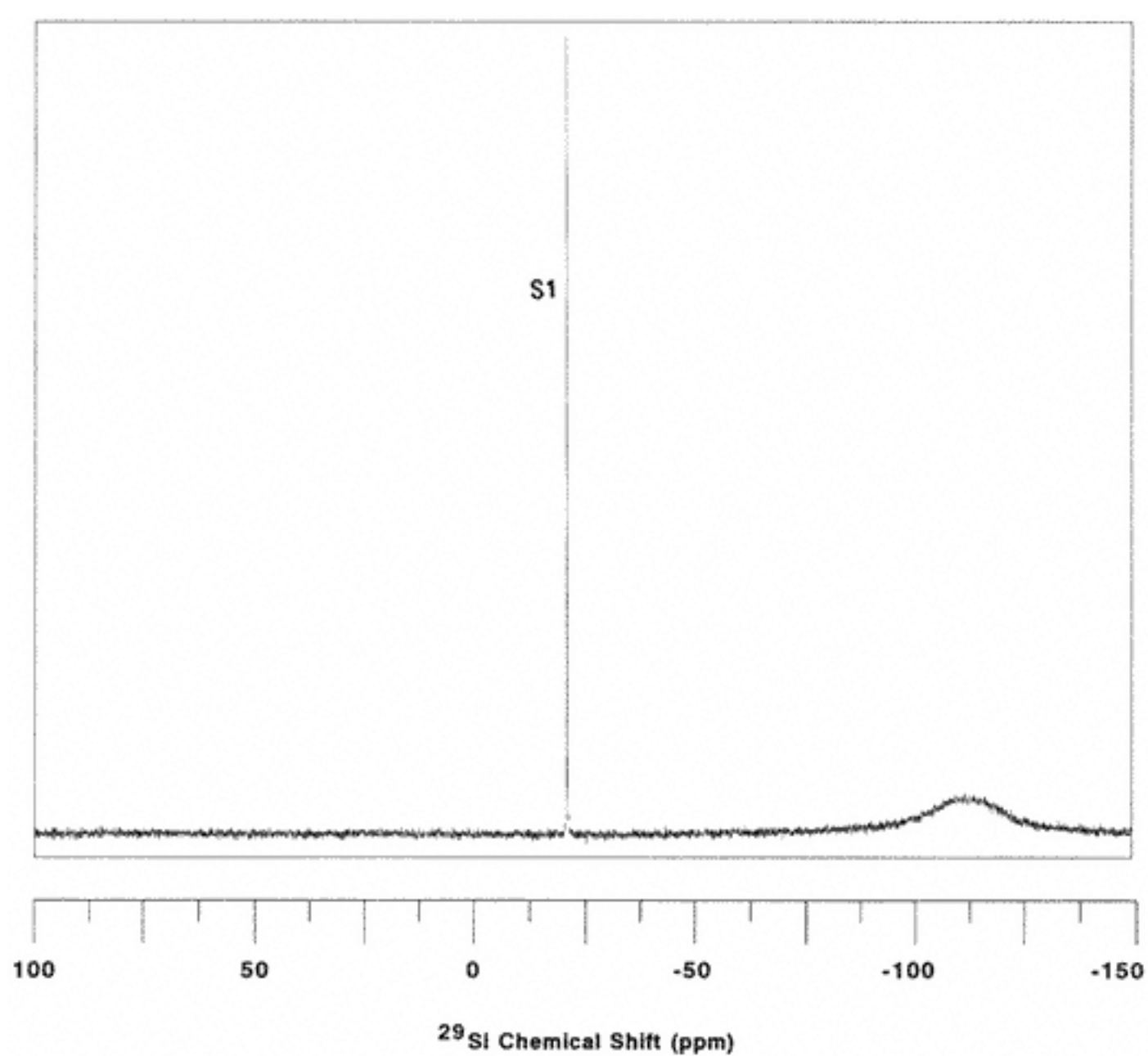
Broadening: 5 Hz

Pulse delay: 5 s

IX-A-1Si— Polydimethylsiloxane

Comments

Also known as silicone rubber or fluid. The broad resonance centered near -110 ppm is due to the glass sample tube. These materials have good chemical resistance, and can be cross-linked. The elastomeric form is used for rubber molds, seals, caulking, gaskets, and electrical insulation. Liquid silicones are used as lubricants, hydraulic fluids, heat-exchange fluids, antifoam agents, glass treatment, surfactants, water repellent, and in cosmetics and medical implants.



Code	Shift (ppm)
S1	-21.3

Experimental Parameters

Nucleus: ^{29}Si (79.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 50 kHz

Data points: 8192

Pulse width: 90°

Broadening: 5 Hz

Pulse delay: 5 s

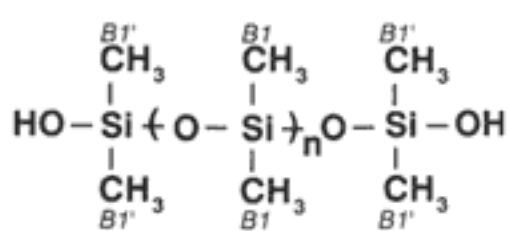
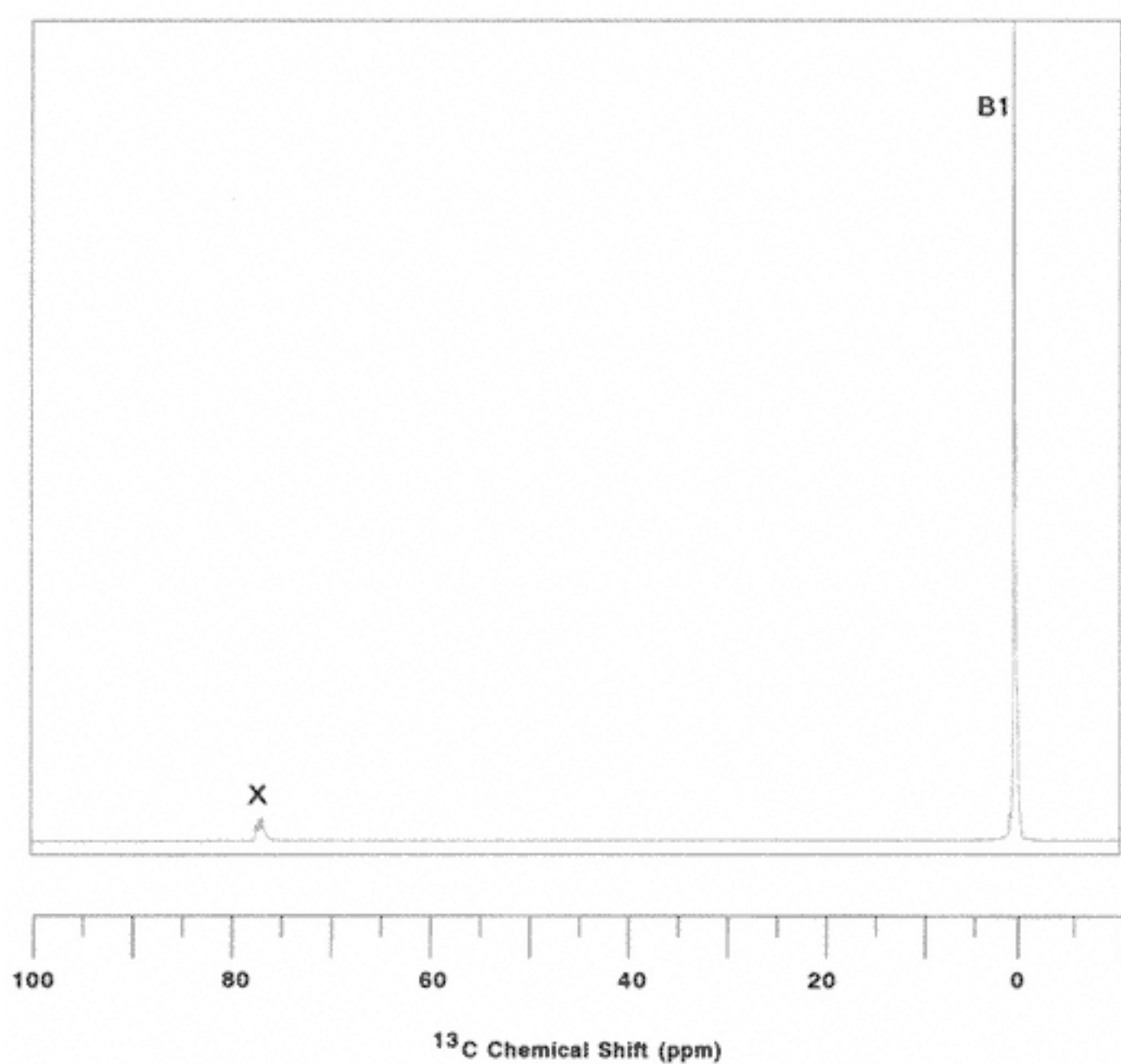
Reference

G. L. Marshall. *Br. Polym. J.* 14:19, 1982.

**IX-A-2—
Polydimethylsiloxane, Hydroxyl-Terminated**

Comments

Also known as silicone rubber or fluid. Because of the relatively high molecular weight (110,000), end-group resonances **B1'** are not observed. Solvent resonances are marked by **X**. These materials have good chemical resistance and can be cross-linked. The hydroxyl end groups permit reaction with other species. The elastomeric form is used for rubber molds, seals, caulking, gaskets, and electrical insulation. Liquid silicones are used as lubricants, hydraulic fluids, heat-exchange fluids, antifoam agents, glass treatment, surfactants, water repellent, and in cosmetics and medical implants.



Code	Shift (ppm)
B1	1.1

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 20% w/w

Scans: 4000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

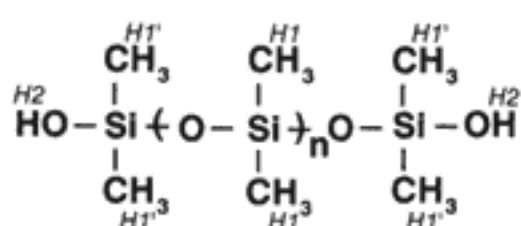
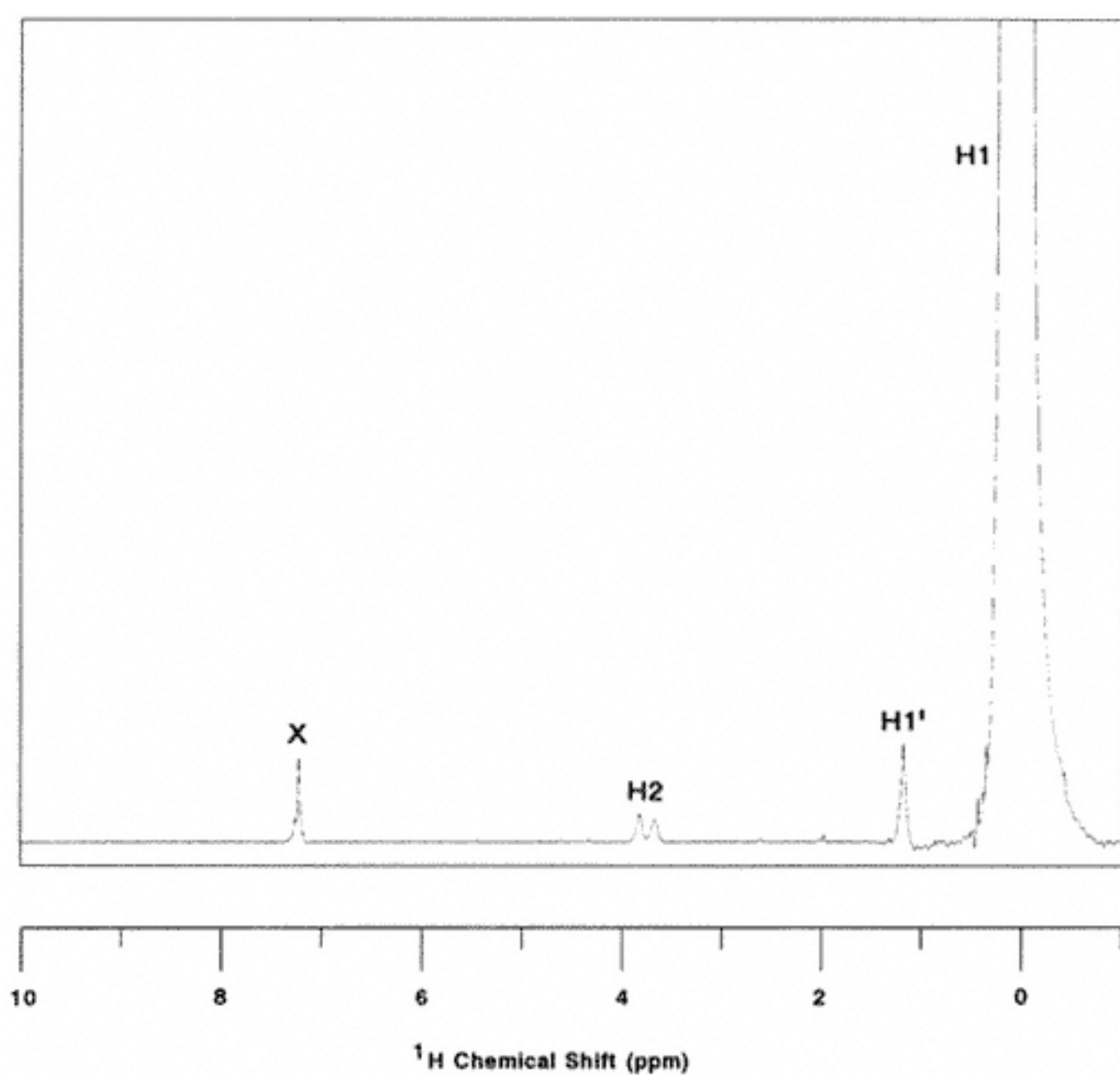
Broadening: 2 Hz

Pulse delay: 5 s

**IX-A-2H—
Polydimethylsiloxane, Hydroxyl-Terminated**

Comments

Also known as silicone rubber or fluid. End-group peaks (**H1'**, **H2**) are small because of the relatively high molecular weight (110,000). Residual solvent resonances are marked by **X**. These materials have good chemical resistance and can be cross-linked. The hydroxyl end groups permit reaction with other species. The elastomeric form is used for rubber molds, seals, caulking, gaskets, and electrical insulation. Liquid silicones are used as lubricants, hydraulic fluids, heat-exchange fluids, antifoam agents, glass treatment, surfactants, water repellent, and in cosmetics and medical implants.



Code	Shift (ppm)
H1	0.05
H1'	1.2
H2	3.7–3.8

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

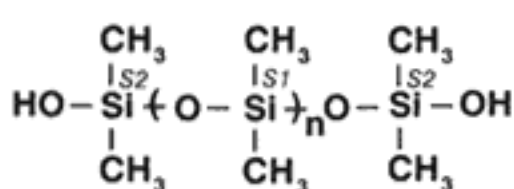
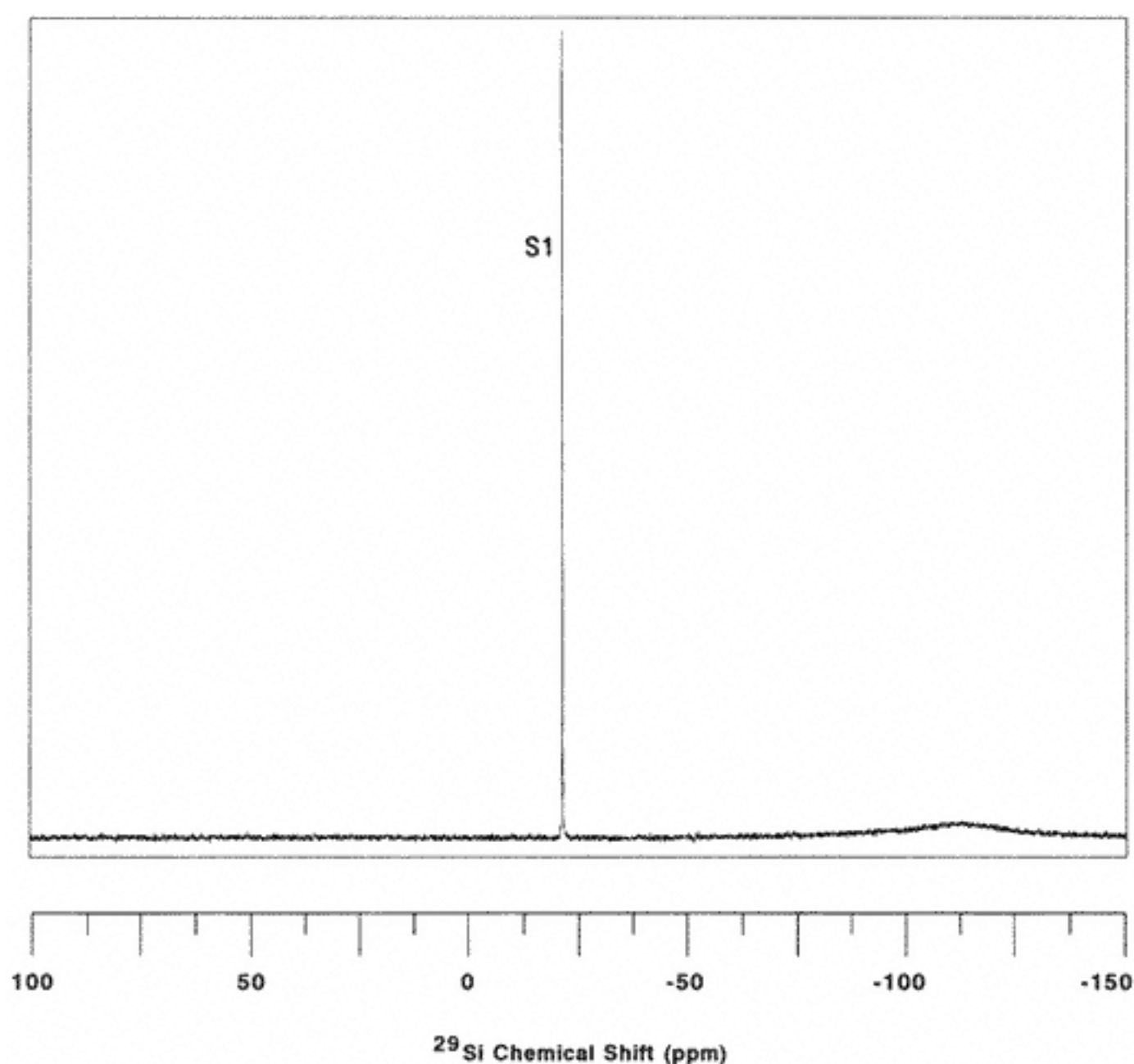
Broadening: 5 Hz

Pulse delay: 5 s

IX-A-2Si—
Polydimethylsiloxane, Hydroxyl-Terminated

Comments

Also known as silicone rubber or fluid. End-group resonances **S2** are not observed because of the relatively high molecular weight (110,000). The broad resonance centered near -110 ppm is due to the glass sample tube. These materials have good chemical resistance, and can be cross-linked. The hydroxyl end groups permit reaction with other species. The elastomeric form is used for rubber molds, seals, caulking, gaskets, and electrical insulation. Liquid silicones are used as lubricants, hydraulic fluids, heat-exchange fluids, antifoam agents, glass treatment, surfactants, water repellent, and in cosmetics and medical implants.



Code	Shift (ppm)
H1	-21.3

Experimental Parameters

Nucleus: ^{29}Si (79.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 20% w/w
Scans: 100	Spectral width: 50 kHz
Data points: 8192	Pulse width: 90°
Broadening: 5 Hz	Pulse delay: 5 s

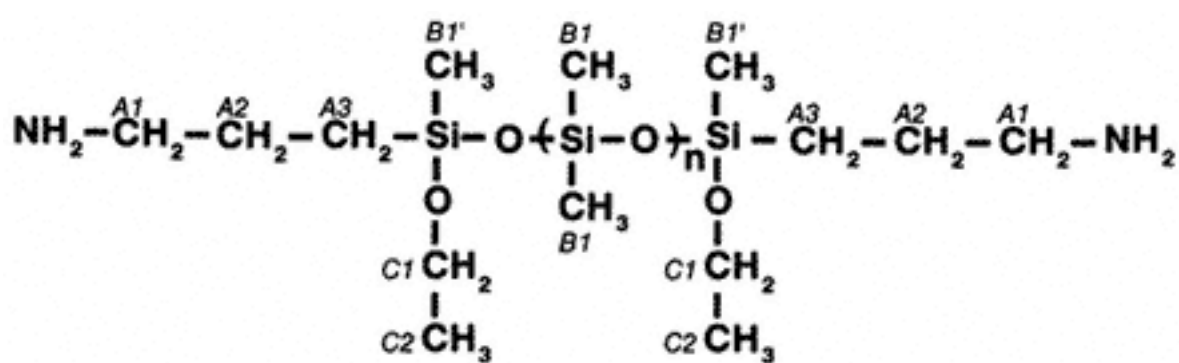
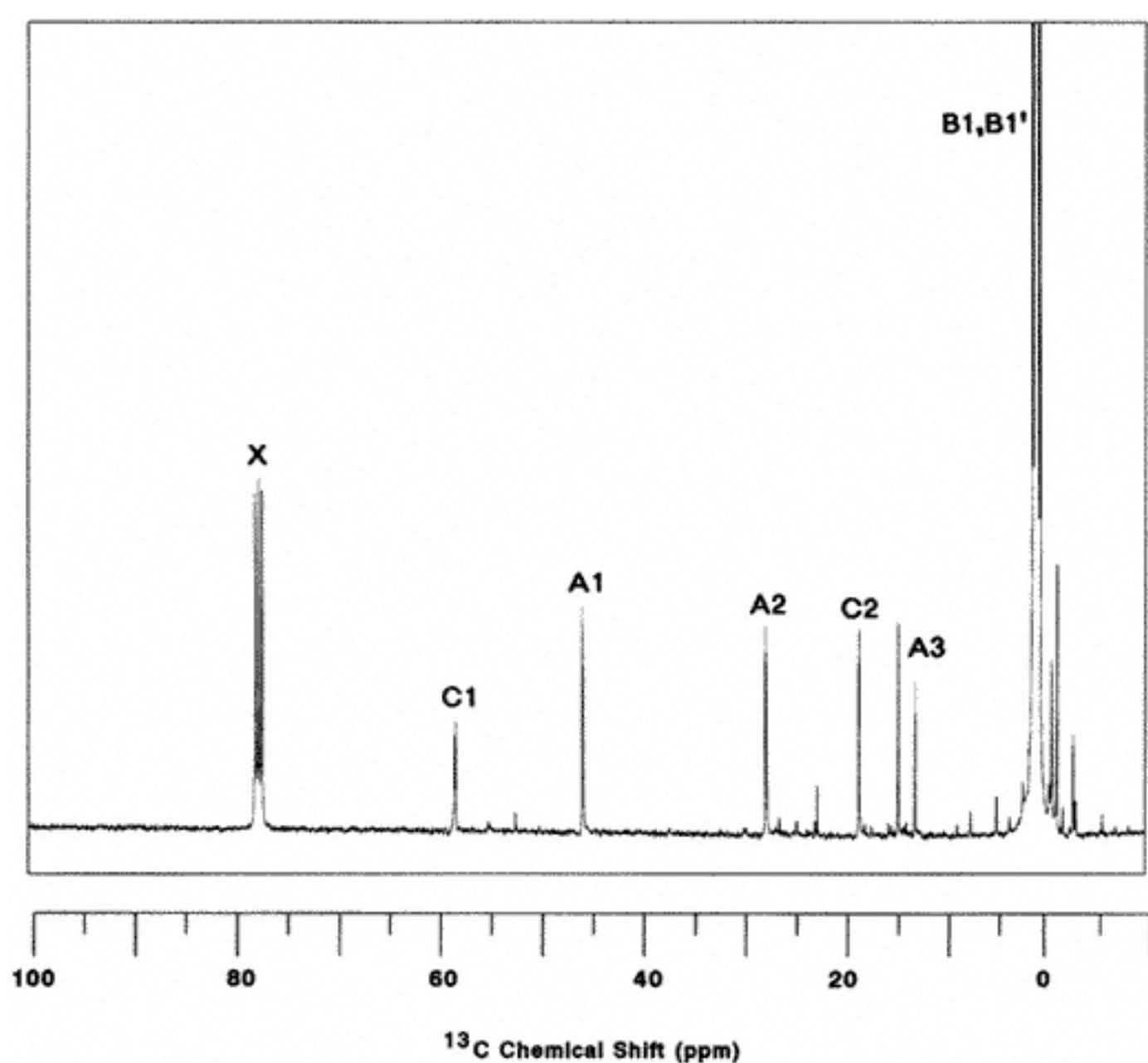
Reference

G. L. Marshall. *Br. Polym. J.* 14:19, 1982.

IX-A-3— Polydimethylsiloxane, Amine-Terminated

Comments

Also known as GP-145 (Genesee Polymers); the length (n) of the interior dimethylsiloxane block is 243 units. Solvent resonances are marked by **X**. Amino-derivatization enhances water solubility. These materials are used in waxes and polishes, and they improve the durability of the finish.



Code	Shift (ppm)
A1	45.3
A2	27.5
A3	14.6
B1	0.9
B1'	0.9
C1	57.6
C2	19.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: $CDCl_3$	Concentration: 20% w/w
Scans: 400	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 5 s

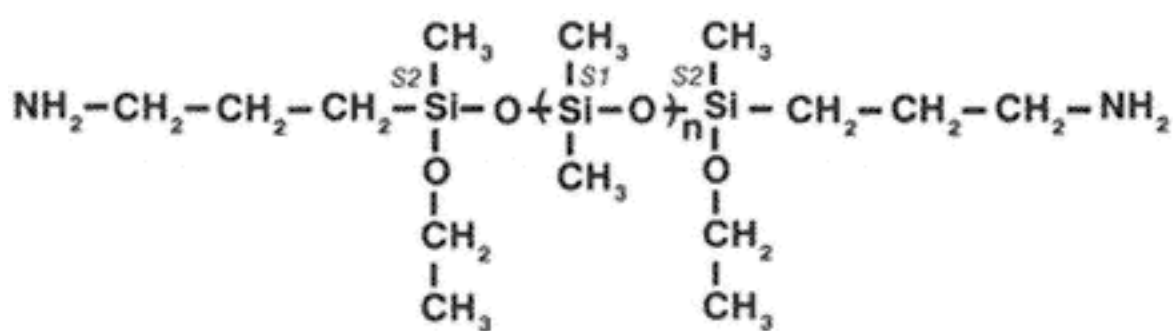
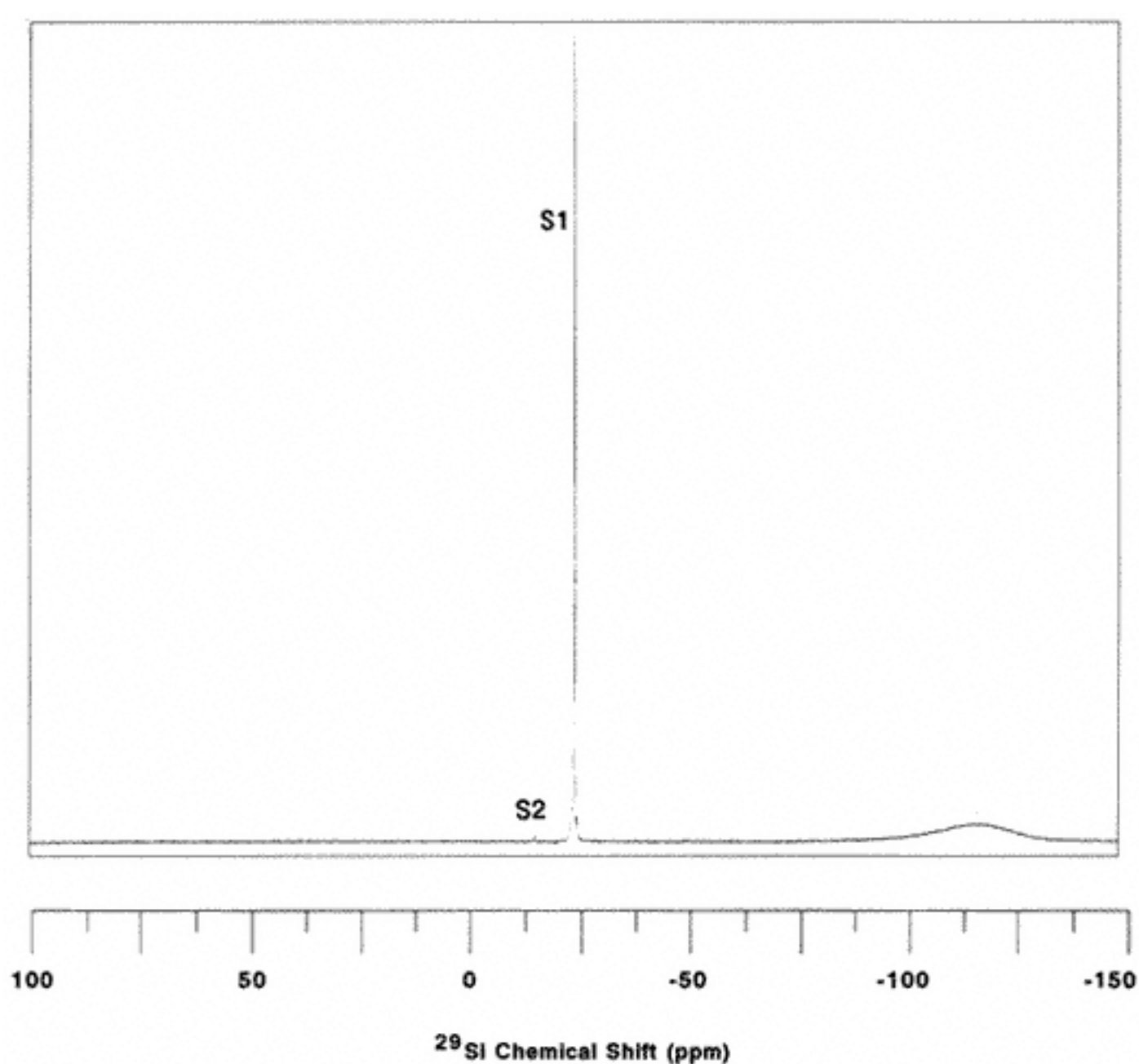
Source

Genesee Polymers, Flint, MI.

IX-A-3Si— Polydimethylsiloxane, Amine-Terminated

Comments

Also known as GP-145 (Genesee Polymers); the length (n) of the interior dimethylsiloxane block is 243 units. The broad resonance centered near -110 ppm is due to the glass sample tube. Amino-derivatization enhances water solubility. These materials are used in waxes and polishes, and they improve the durability of the finish.



Code	Shift (ppm)
S1	-21.7
S2	-13.3

Experimental Parameters

Nucleus: ²⁹Si (79.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 20% w/w

Scans: 2000

Spectral width: 20 kHz

Data points: 8192

Pulse width: 90°

Broadening: 5 Hz

Pulse delay: 5 s

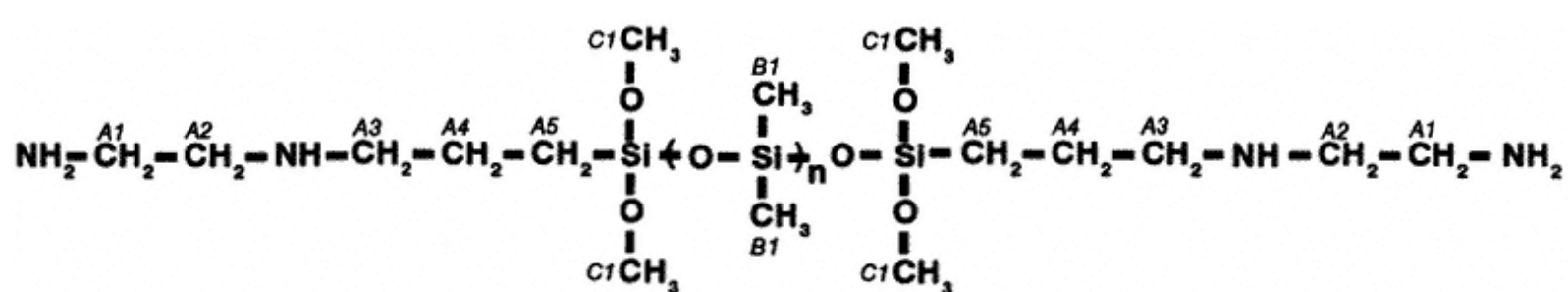
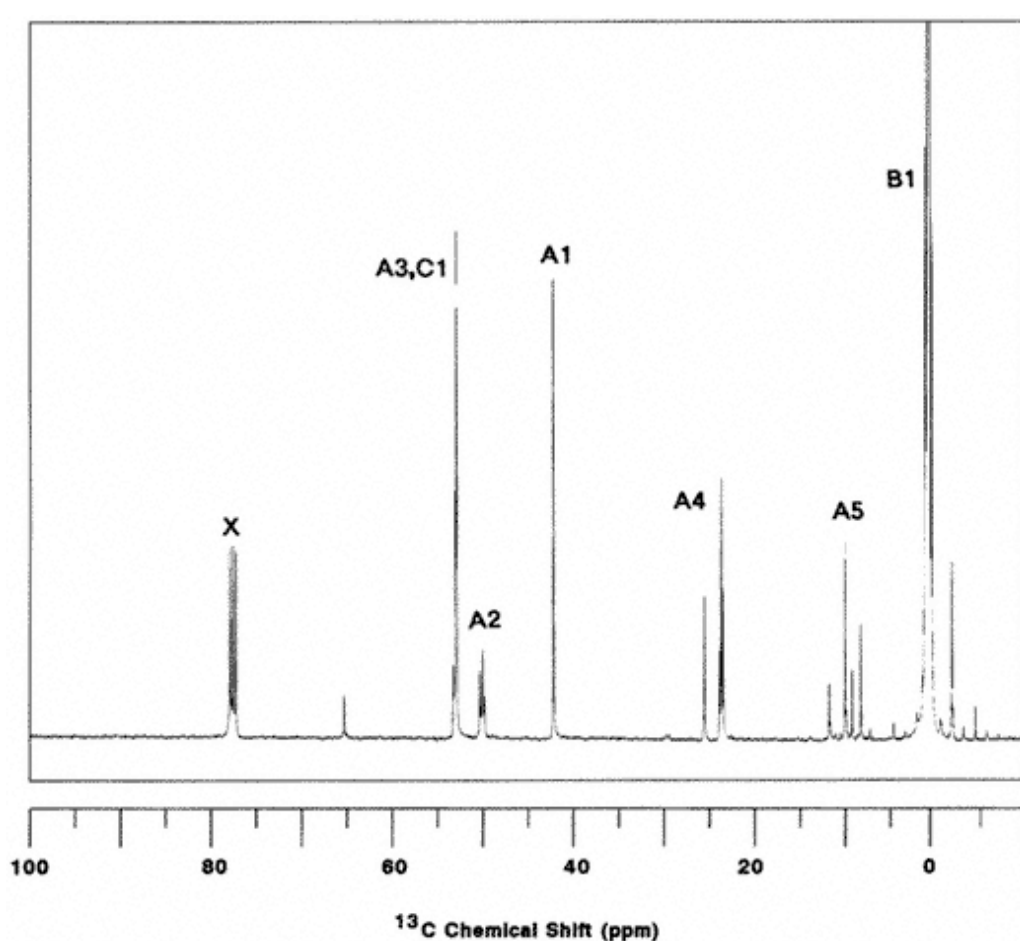
Source

Genesee Polymers, Flint, MI.

**IX-A-4—
Polydimethylsiloxane, Amine-Terminated**

Comments

Also known as GP-134 (Genesee Polymers); the length (n) of the interior dimethylsiloxane block is 46 units. Solvent resonances are marked by **X**. Amino-derivatization enhances water solubility. These materials are used in waxes and polishes, and they improve the durability of the finish.



Code	Shift (ppm)
A1	42.1
A2	49.5
A3	53.5
A4	23.7–25.6
A5	8.1–11.6
B1	1.0
C1	53.5

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 20% w/w
Scans: 400	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 5 s

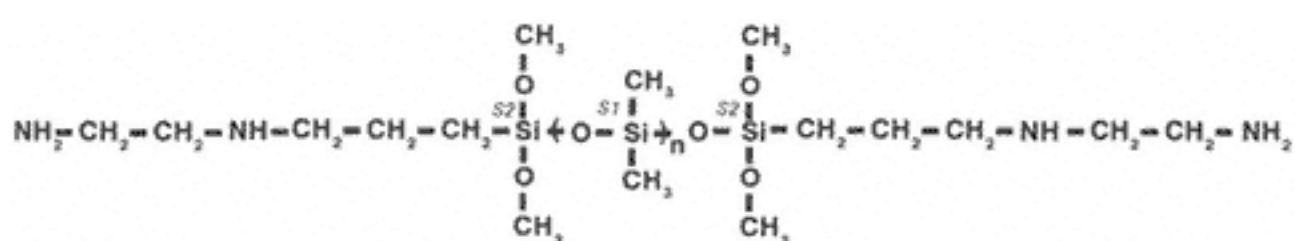
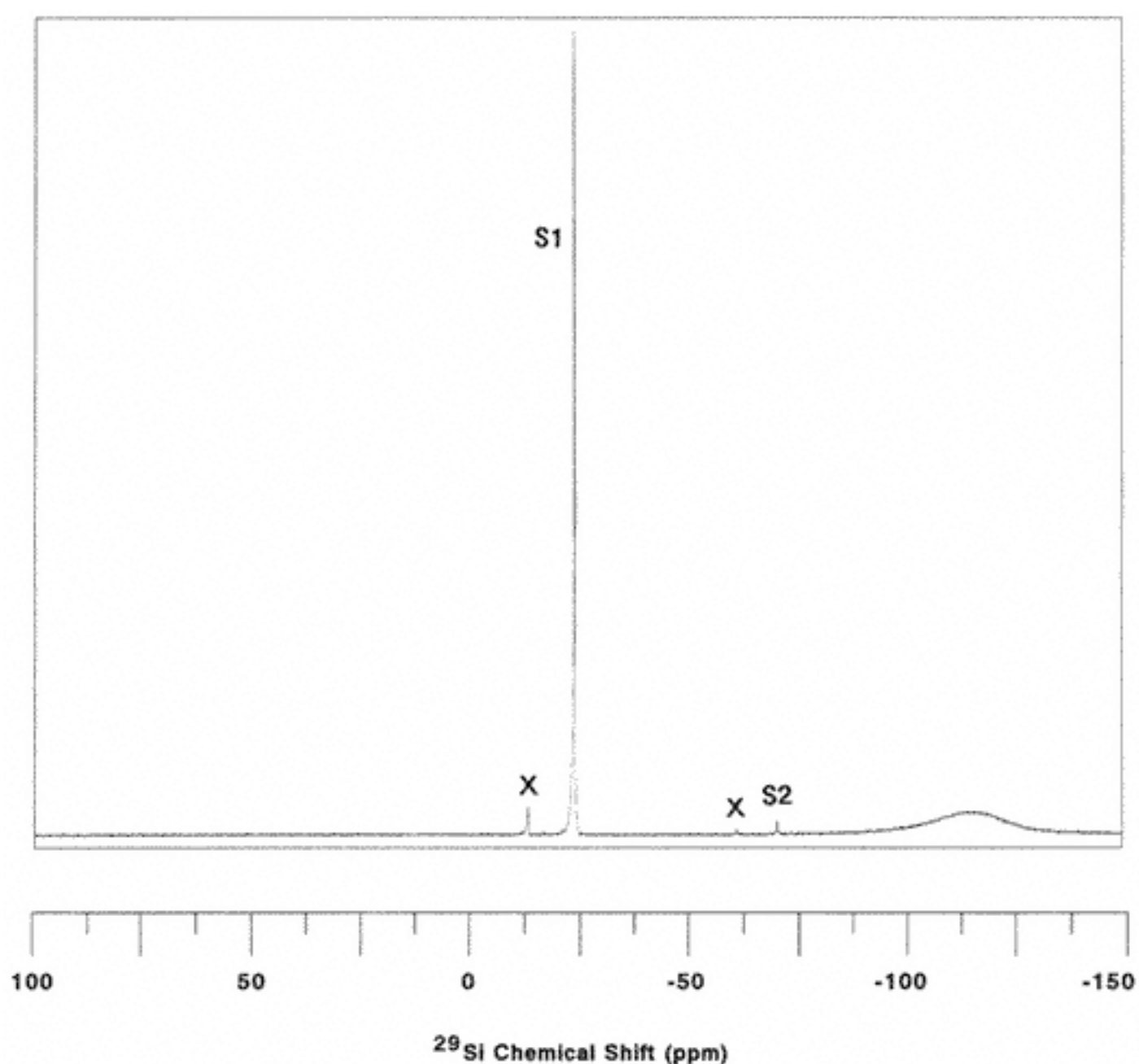
Source

Genesee Polymers, Flint, MI.

IX-A-4Si— Polydimethylsiloxane, Amine-Terminated

Comments

Also known as GP-134 (Genesee Polymers); the length (n) of the interior dimethylsiloxane block is 46 units. The broad resonance centered near -110 ppm is due to the glass sample tube. Small amounts of other silicon-containing species contribute resonances marked by **X**. Amino-derivatization enhances water solubility. These materials are used in waxes and polishes, and they improve the durability of the finish.



Code	Shift (ppm)
S1	-21.3
S2	-67.5

Experimental Parameters

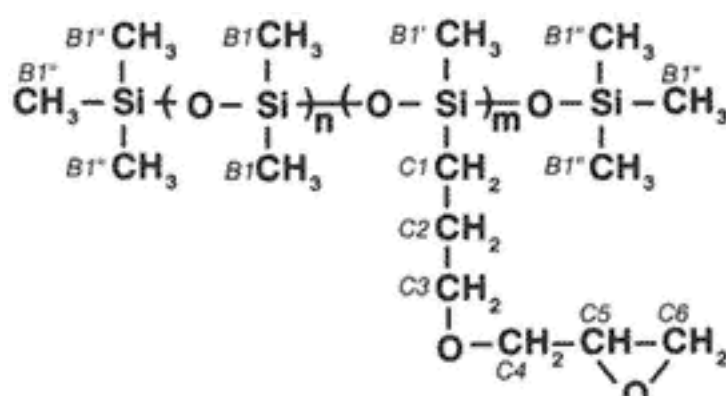
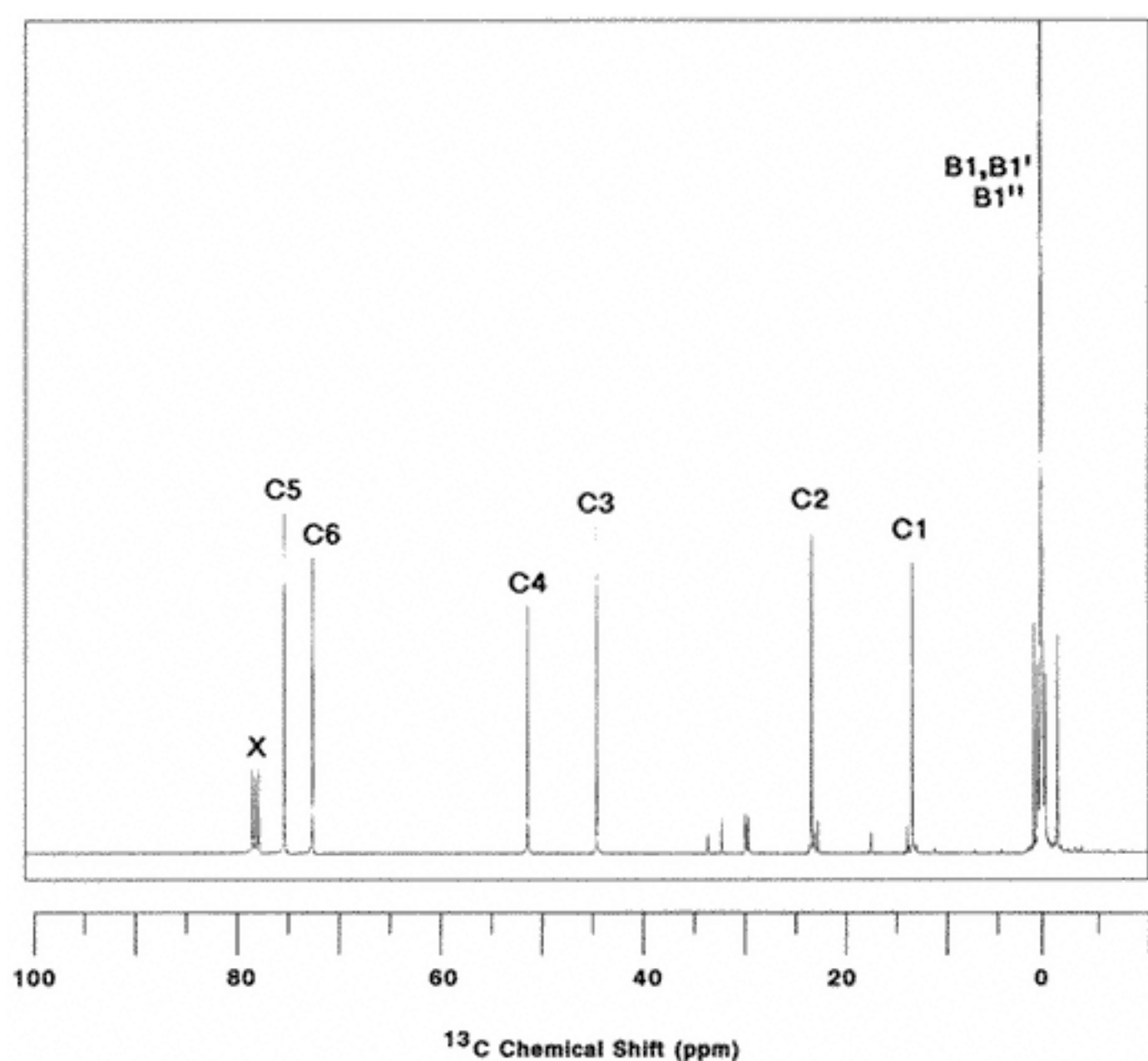
Nucleus: ^{29}Si (79.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 20% w/w
Scans: 2000	Spectral width: 20 kHz
Data points: 8192	Pulse width: 90°
Broadening: 5 Hz	Pulse delay: 5 s

Source

Genesee Polymers, Flint MI.

**IX-A-5—
Polydimethylsiloxane, Epoxy-Modified**
Comments

Also known as EXP-32 (Genesee Polymers). In this polymer, $n = 96.5$ and $m = 5.5$. Solvent resonances are marked by **X**. The reactive epoxy group permits cross-linking and improved bonding to substrates.



Code	Shift (ppm)
B1	1.0
B1'	1.0
B1''	1.0
C1	13.5
C2	23.2
C3	44.0
C4	50.7
C5	74.4
C6	72.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 20% w/w
Scans: 400	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 5 s

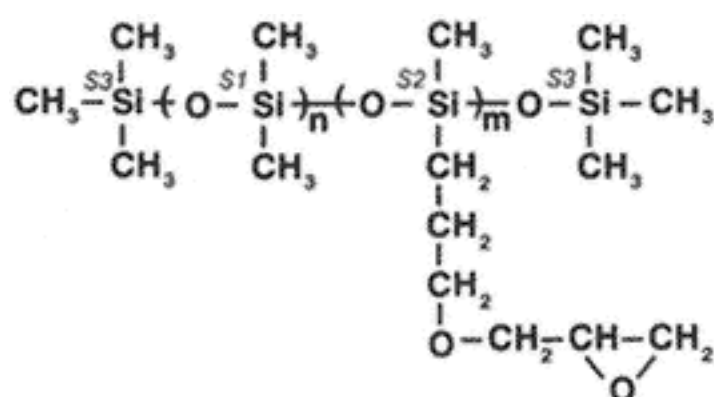
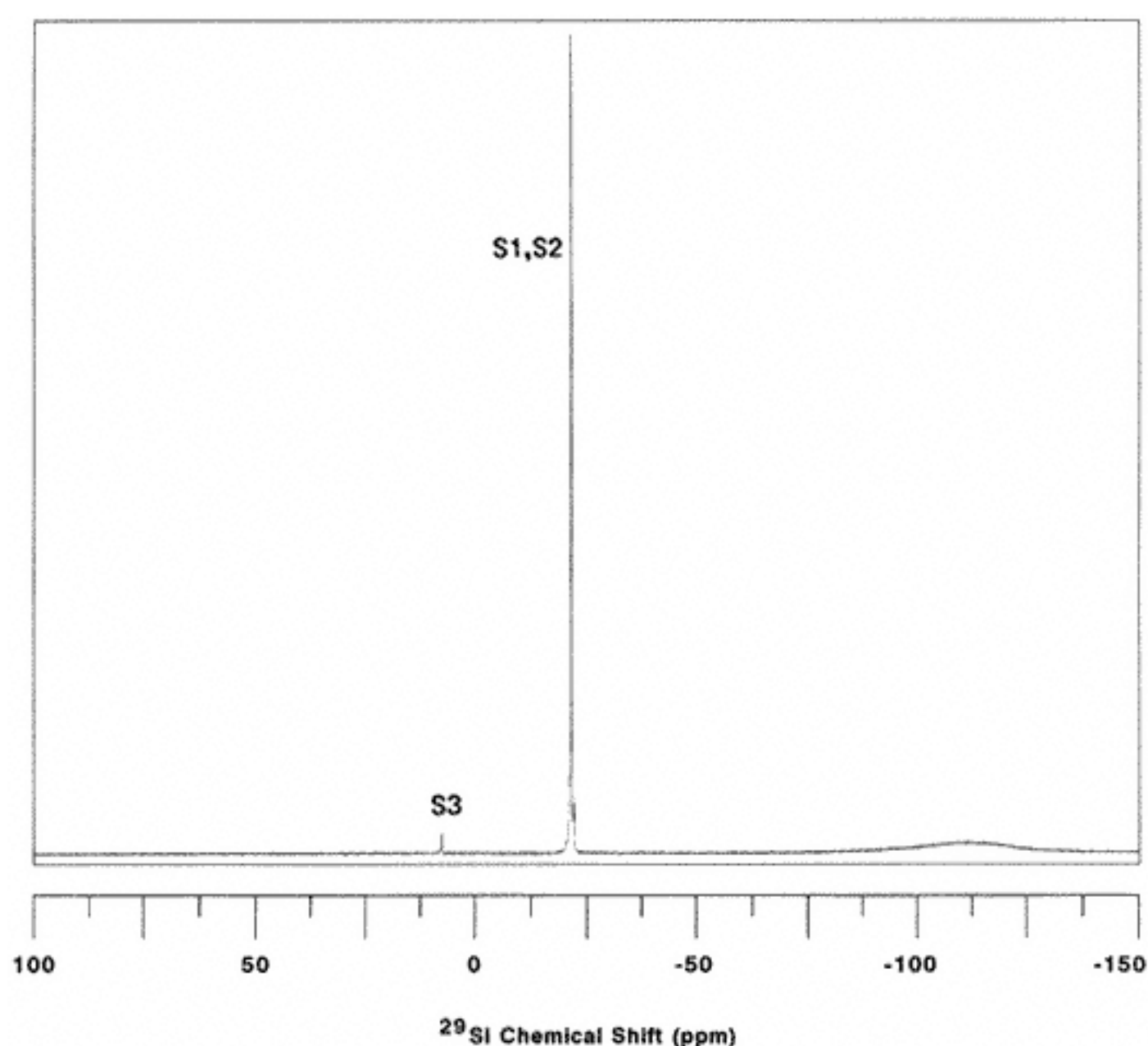
Source

Genesee Polymers, Flint MI.

**IX-A-5Si—
Polydimethylsiloxane, Epoxy-Modified**

Comments

Also known as EXP-32 (Genesee Polymers). In this polymer, $n = 96.5$ and $m = 5.5$. The broad resonance centered near -110 ppm is due to the glass sample tube. The reactive epoxy group permits cross-linking and improved bonding to substrates.



Code	Shift (ppm)
S1	-21.7
S2	-21.7
S3	7.4

Experimental Parameters

Nucleus: ^{29}Si (79.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 2000

Spectral width: 20 kHz

Data points: 8192

Pulse width: 90°

Broadening: 5 Hz

Pulse delay: 5 s

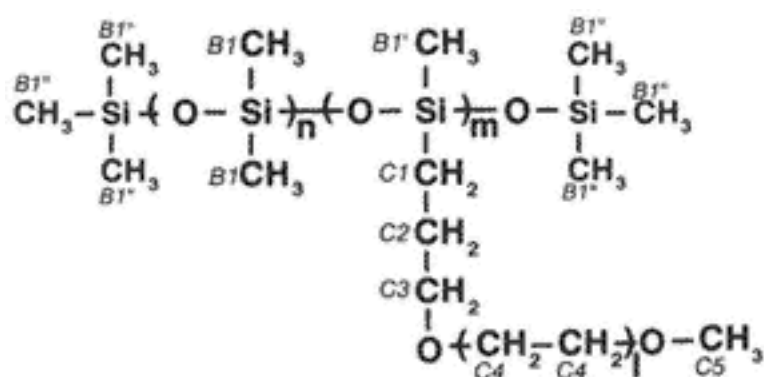
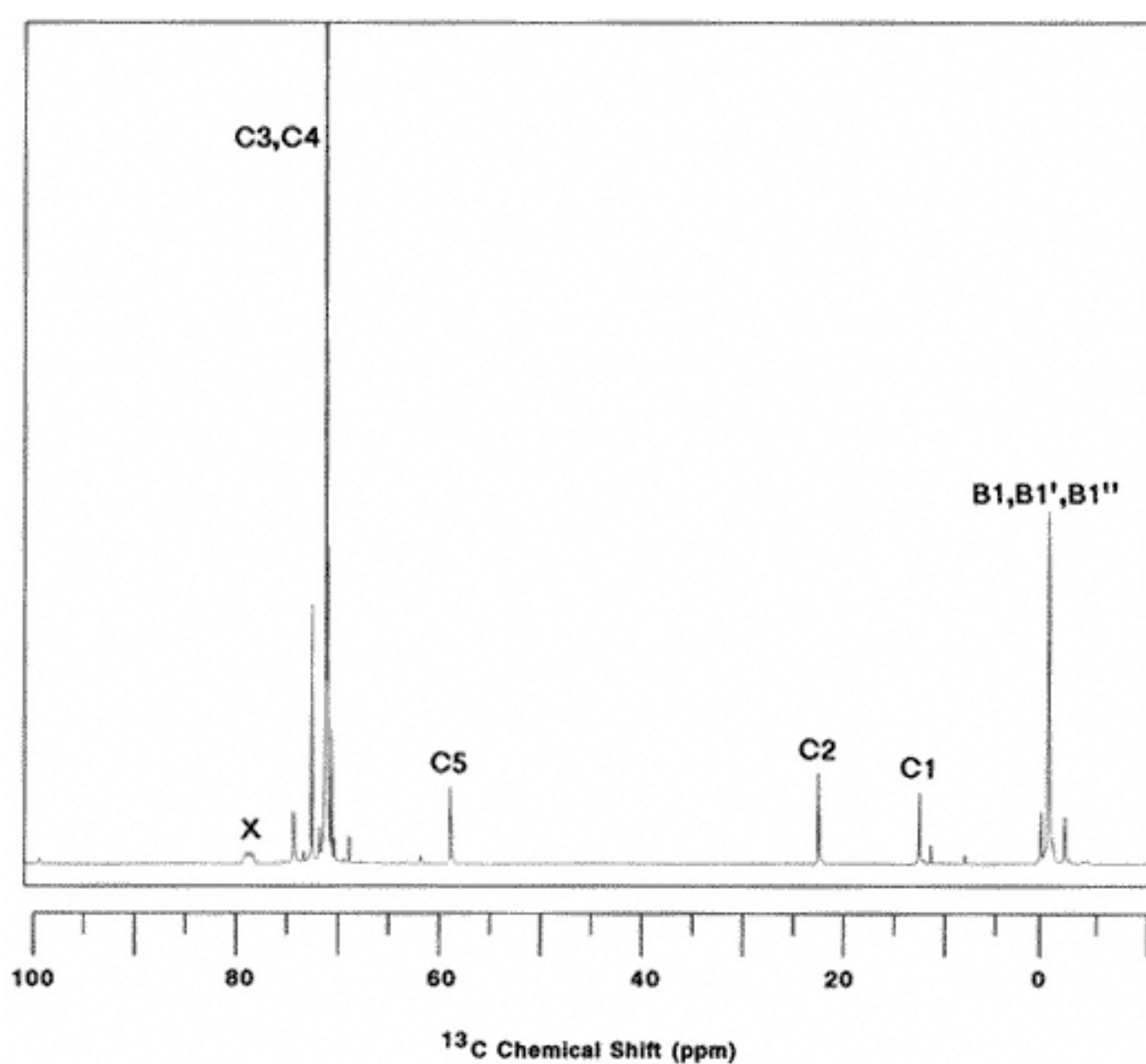
Source

Genesee Polymers, Flint, MI.

**IX-A-6—
Polydimethylsiloxane, Poly(Ethylene Glycol)-Modified**

Comments

Also known as GP-226 (Genesee Polymers). In this polymer, $n = 20$, $m = 6$, and $l = 7.2$. Solvent resonances are marked by **X**. Silicone-polyether copolymers are water-soluble and have improved lubricating properties. They are also useful as surfactants.



Code	Shift (ppm)
B1	0.8
B1'	0.9
B1''	0.5
C1	13.4
C2	22.9
C3	70.6
C4	70.6
C5	58.6

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: $CDCl_3$

Concentration: 20% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

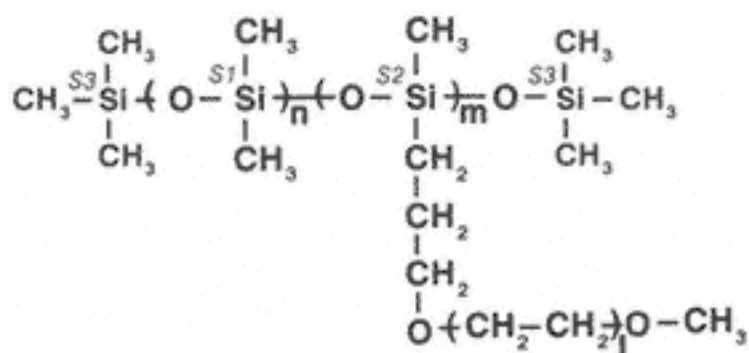
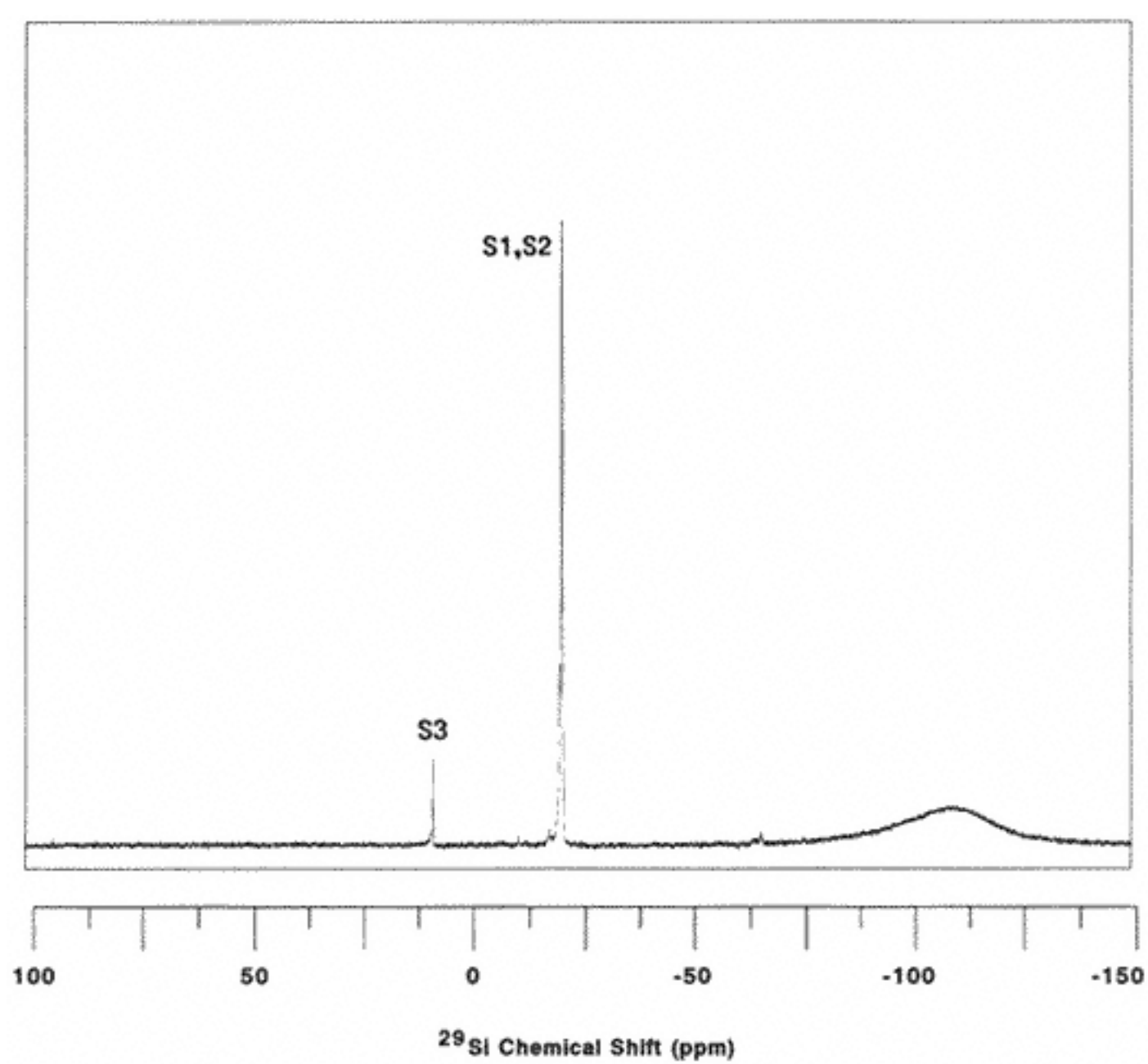
Source

Genesee Polymers, Flint, MI.

**IX-A-6Si—
Polydimethylsiloxane, Poly(Ethylene Glycol)-Modified**

Comments

Also known as GP-226 (Genesee Polymers). In this polymer, $n = 20$, $m = 6$, and $l = 7.2$. Silicone-polyether copolymers are water-soluble and have improved lubricating properties. They are also useful as surfactants.



Code	Shift (ppm)
S1	-21.7
S2	-21.7
S3	7.5

Experimental Parameters

Nucleus: ^{29}Si (79.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 2000

Spectral width: 20 kHz

Data points: 8192

Pulse width: 90°

Broadening: 5 Hz

Pulse delay: 5 s

Source

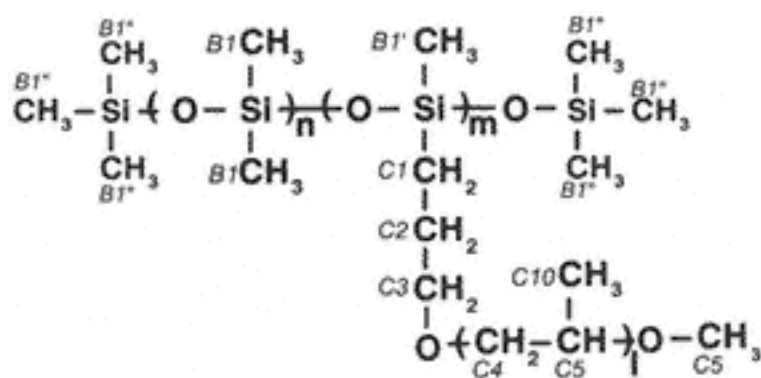
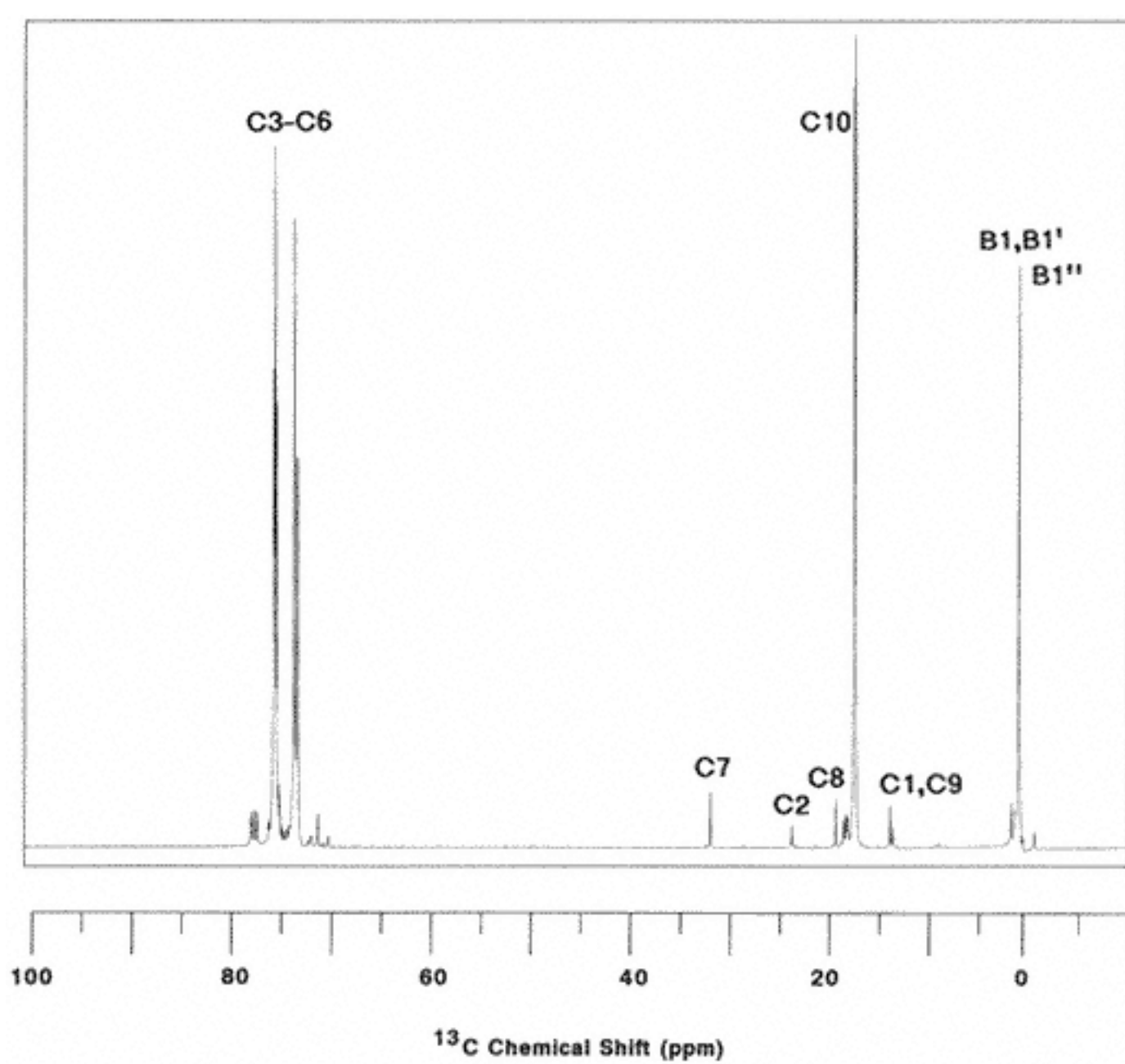
Genesee Polymers, Flint, MI.

IX-A-7

**IX-A-7—
Polydimethylsiloxane, Poly(propylene Glycol)-Modified**

Comments

Also known as GP-218 (Genesee Polymers). In this polymer, $n = 20-60$, $m = 2-10$ and $l = 25-35$. Silicone-polyether copolymers are water-soluble and have improved lubricating properties. They are also useful as surfactants.



Code	Shift (ppm)
B1	0.8
B1'	0.8
B1''	0.8
C1	13.8
C2	23.0
C3	73-76
C4	73-76
C5	73-76
C6	73-76
C7	31.7
C8	19.7
C9	13.8
C10	17.4

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

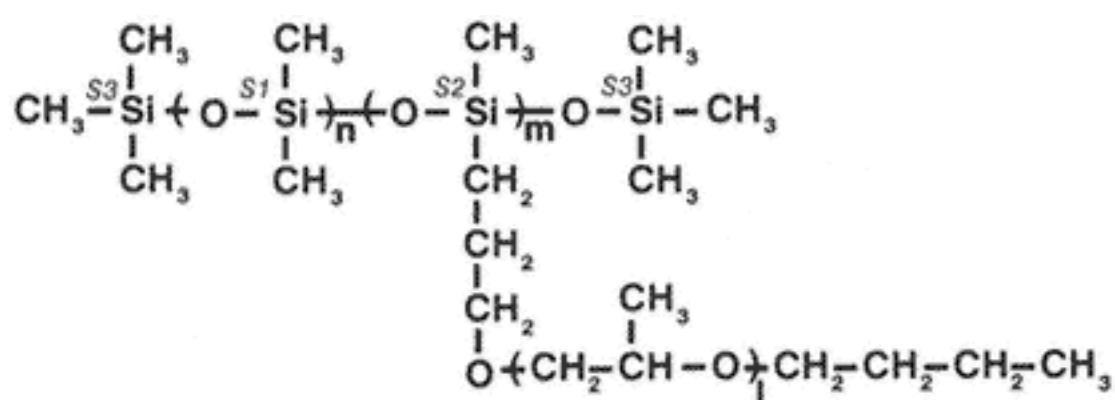
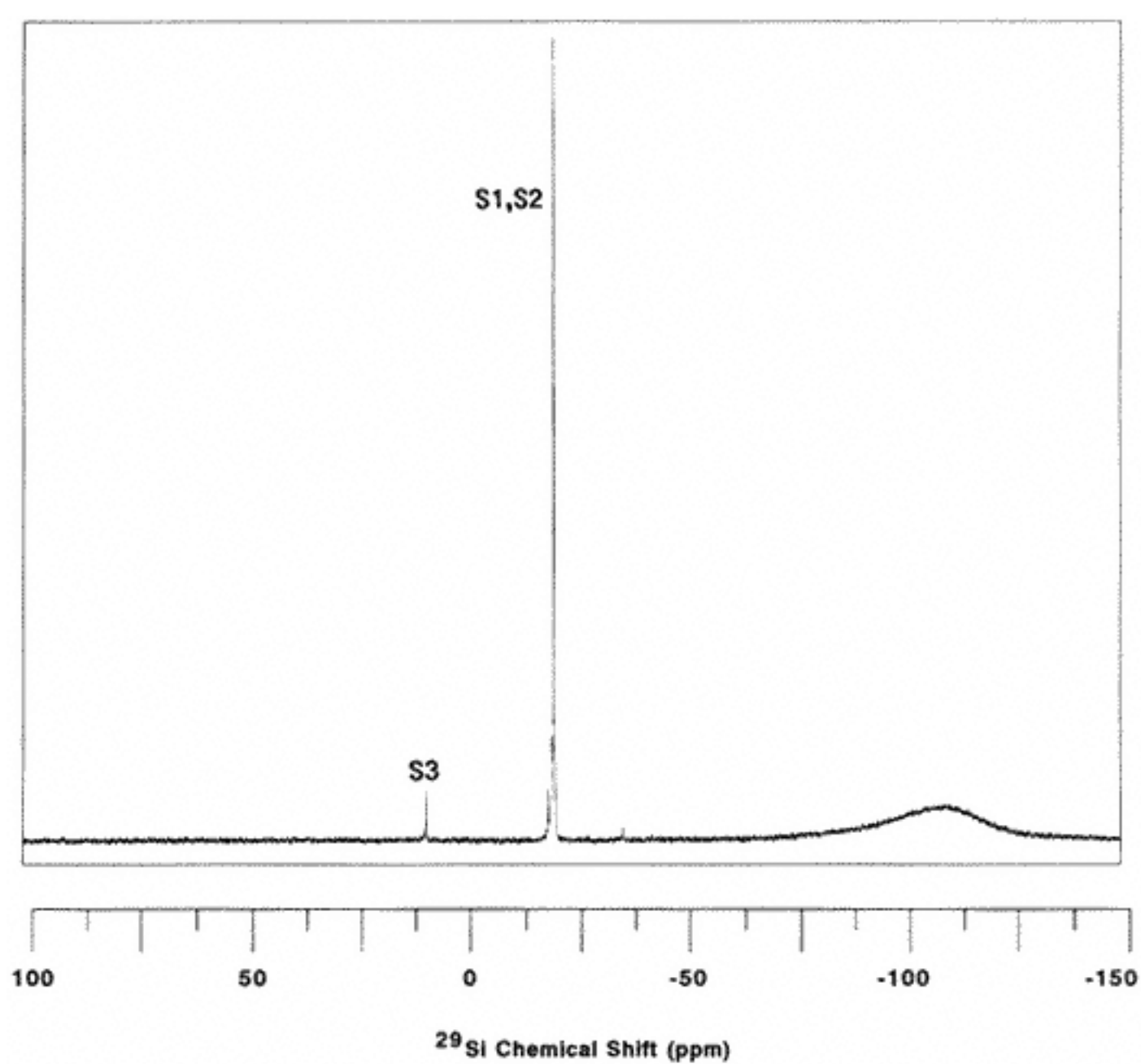
Source

Genesee Polymers, Flint, MI.

**IX-A-7 Si—
Polydimethylsiloxane, Poly(propylene Glycol)-Modified**

Comments

Also known as GP-218 (Genesee Polymers). In this polymer, $n = 20-60$, $m = 2-10$ and $l = 25-35$. The broad resonance centered near -110 ppm is due to the glass sample tube. Silicone-polyether copolymers are water-soluble and have improved lubricating properties. They are also useful as surfactants.



Code	Shift (ppm)
S1	-21.7
S2	-21.7
S3	7.3

Experimental ParametersNucleus: ^{29}Si (79.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 2000

Spectral width: 20 kHz

Data points: 8192

Pulse width: 90°

Broadening: 5 Hz

Pulse delay: 5 s

Source

Genesee Polymers, Flint, MI.

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

Source

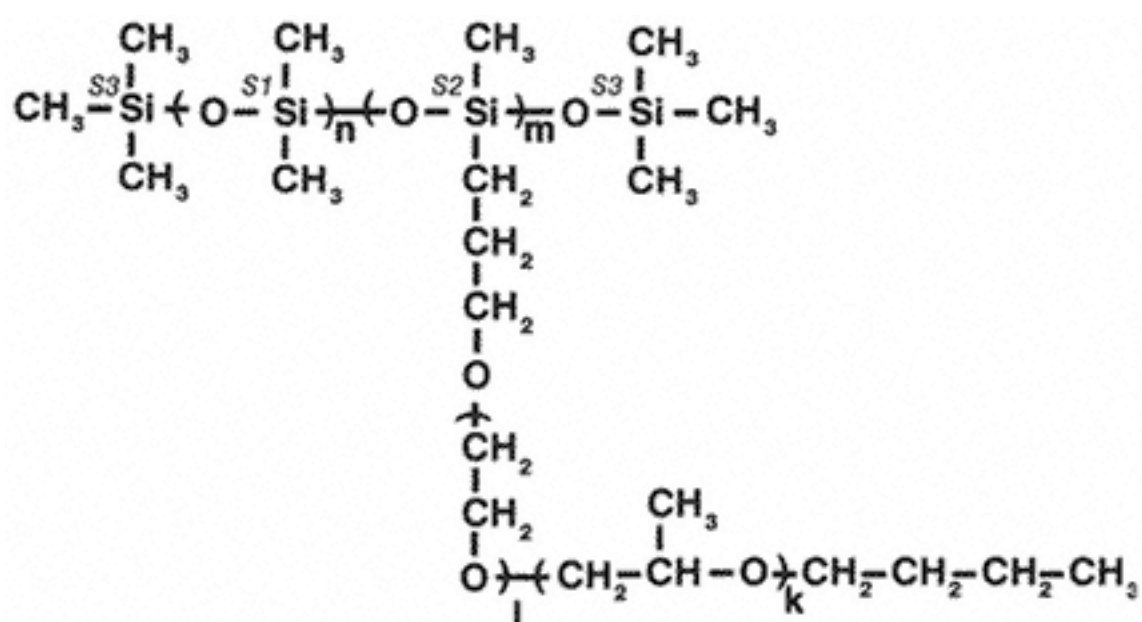
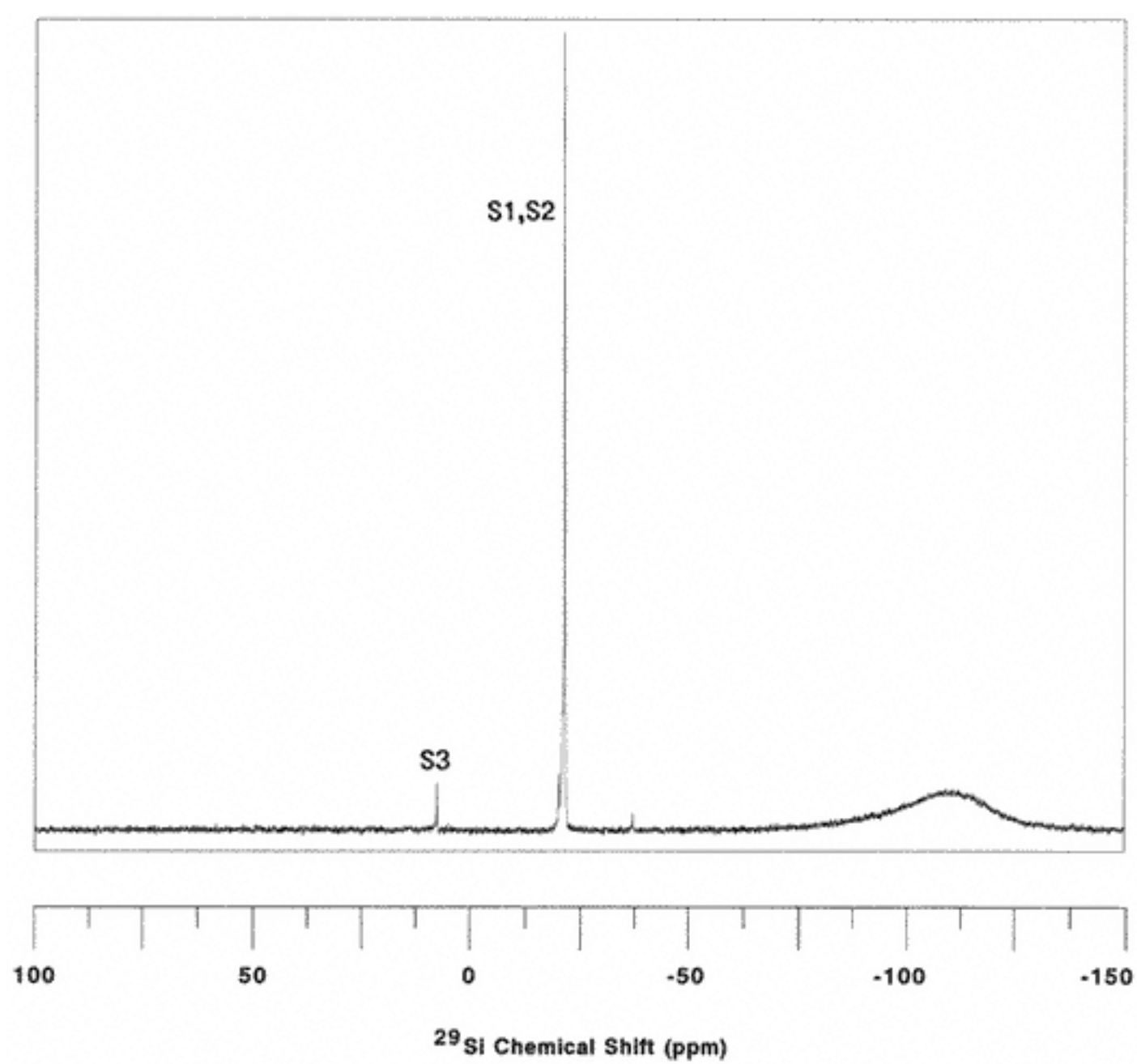
Genesee Polymers, Flint, MI.

IX-A-8Si—

Polydimethylsiloxane, Poly(Ethylene Glycol)/Poly(Propylene Glycol)-Modified

Comments

Also known as GP-214 (Genesee Polymers). In this polymer, $n = 50$, $m = 4$, $l = 20.5$, and $k = 15.5$. The broad resonance centered near -110 ppm is due to the glass sample tube. Silicone-polyether copolymers are water-soluble and have improved lubricating properties. They are also useful as surfactants.



Code	Shift (ppm)
S1	-21.7
S2	-21.7
S3	7.5

Experimental ParametersNucleus: ^{29}Si (79.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 2000

Spectral width: 20 kHz

Data points: 8192

Pulse width: 90°

Broadening: 5 Hz

Pulse delay: 5 s

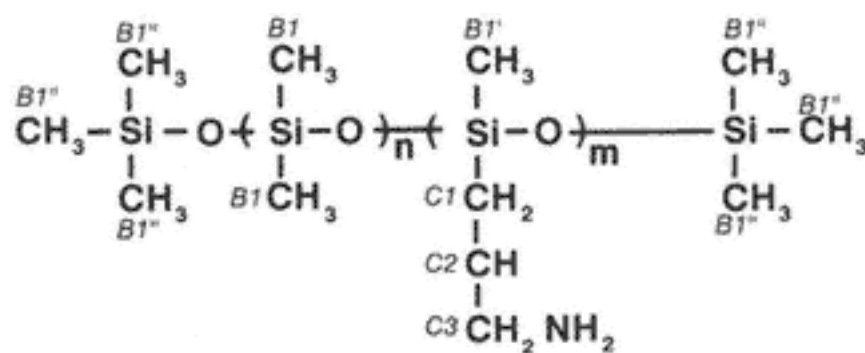
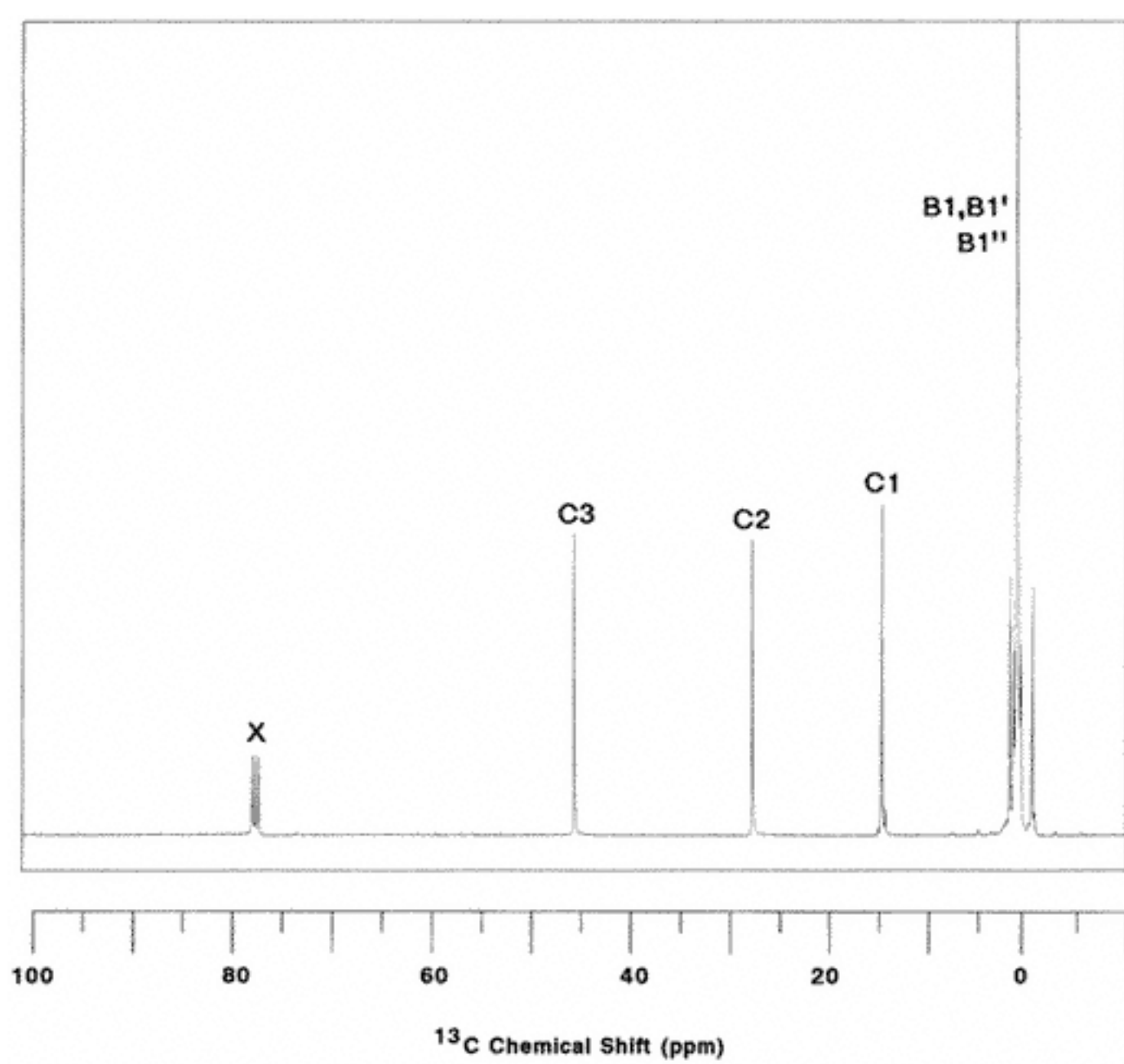
Source

Genesee Polymers, Flint, MI.

**IX-A-9—
Polydimethylsiloxane, Amine-Modified**

Comments

Also known as GP-4 (Genesee Polymers). In this polymer, $n = 58$ and $m = 4$. Solvent resonances are marked by **X**. Amino-derivatization enhances water solubility. These materials are used in waxes and polishes, and they improve the durability of the finish.



Code	Shift (ppm)
B1	0.9
B1'	0.9
B1''	0.9
C1	14.5
C2	27.4
C3	45.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

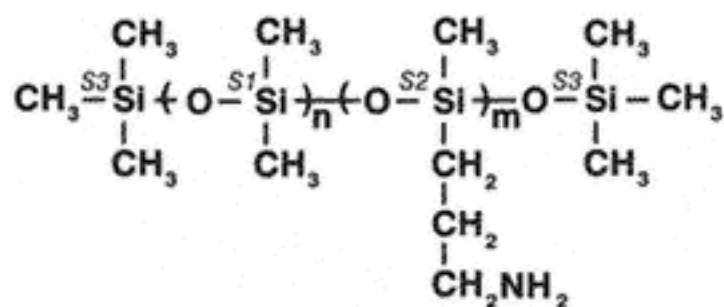
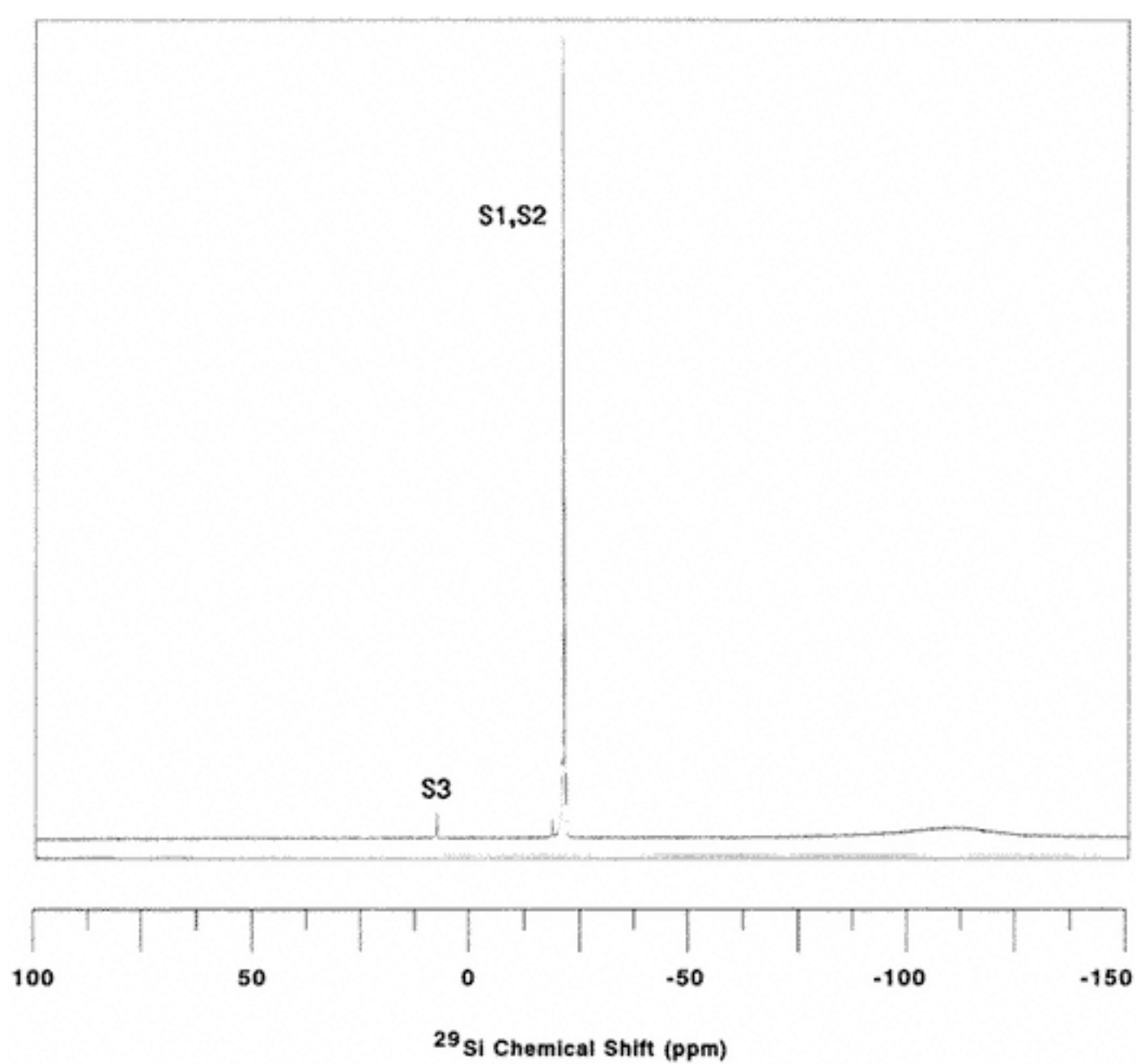
Source

Genesee Polymers, Flint, MI.

IX-A-9Si— Polydimethylsiloxane, Amine-Modified

Comments

Also known as GP-4 (Genesee Polymers). In this polymer, $n = 58$ and $m = 4$. The broad resonance centered near -110 ppm is due to the glass sample tube. Amino-derivatization enhances water solubility. These materials are used in waxes and polishes, and they improve the durability of the finish.



Code	Shift (ppm)
S1	-21.8
S2	-21.8
S3	7.5

Experimental Parameters

Nucleus: ^{29}Si (79.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 20% w/w
Scans: 2000	Spectral width: 20 kHz
Data points: 8192	Pulse width: 90°
Broadening: 5 Hz	Pulse delay: 5 s

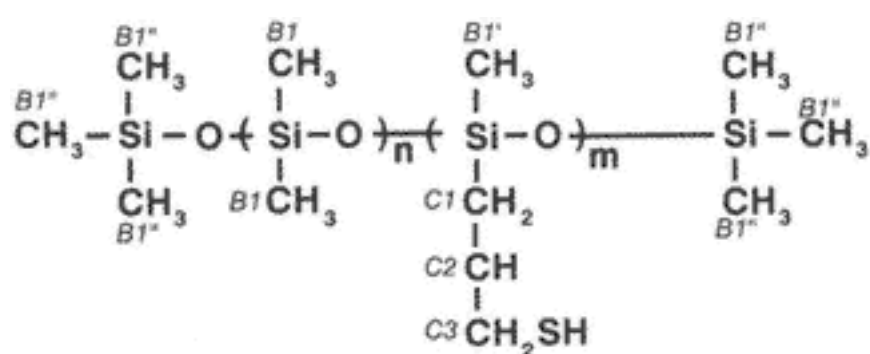
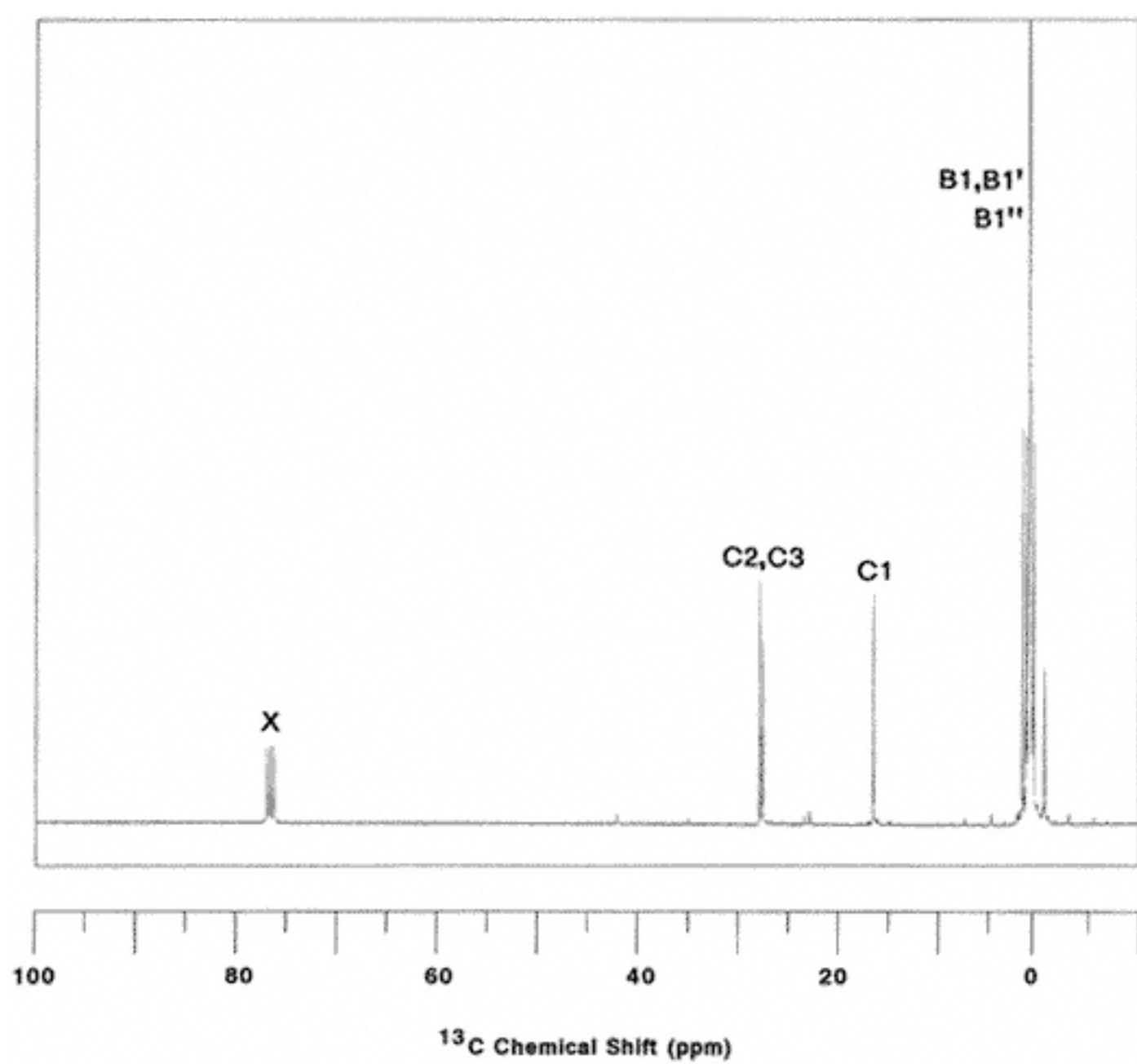
Source

Genesee Polymers, Flint, MI

**IX-A-10—
Polydimethylsiloxane, Mercaptan-Modified**

Comments

Also known as GP-71-SS (Genesee Polymers). In this polymer, $n = 83$ and $m = 2$. Solvent resonances are marked by **X**. The inclusion of a mercaptan improves surface properties.



Code	Shift (ppm)
B1	0.9
B1'	0.9
B1''	0.9
C1	10.6
C2	28.0
C3	28.0

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 20% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

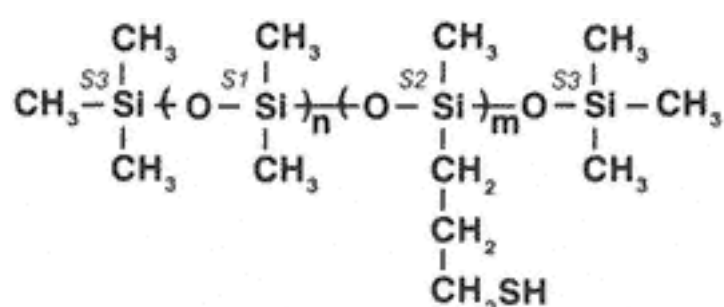
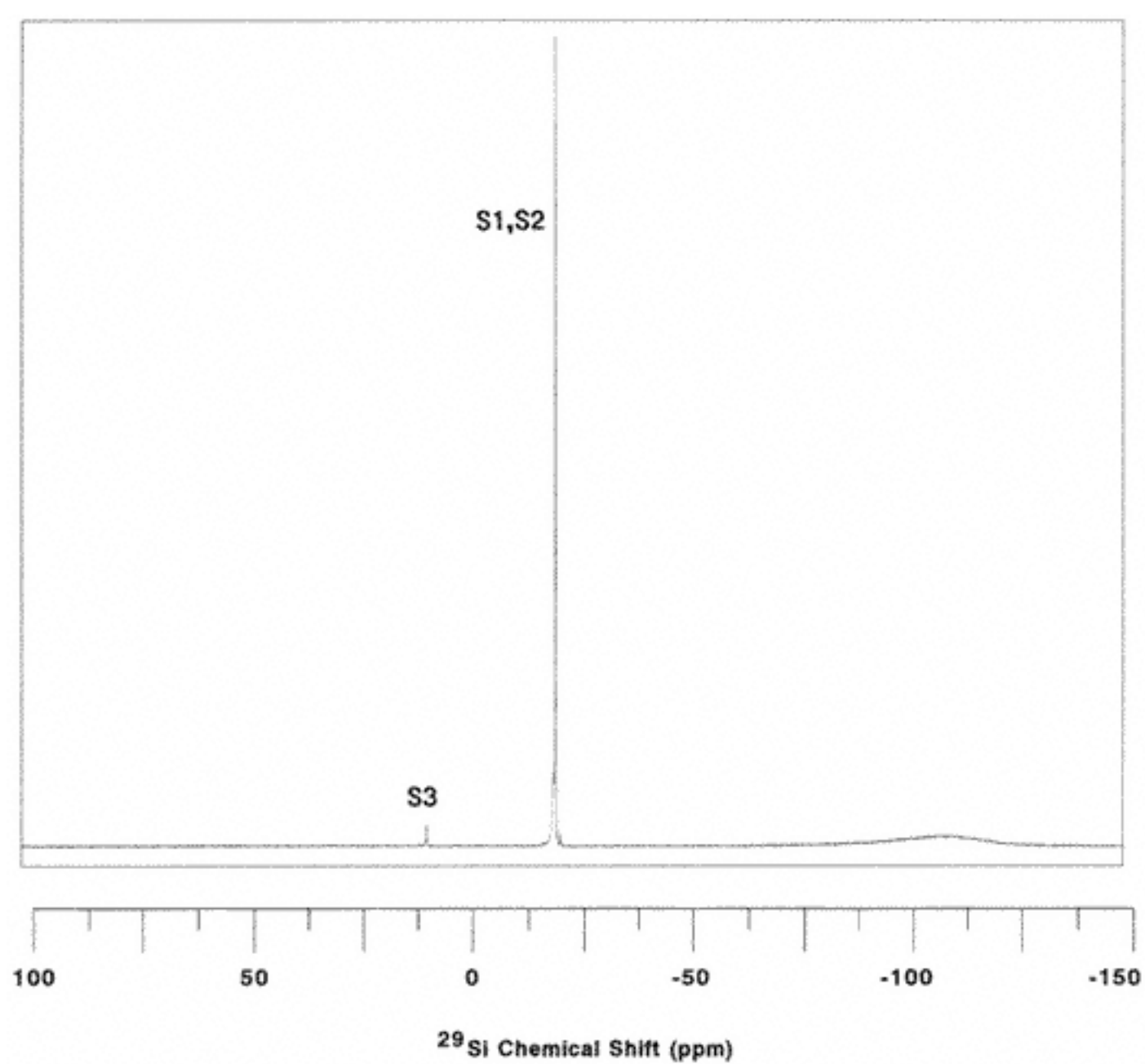
Source

Genesee Polymers, Flint, MI

IX-A-10Si— Polydimethylsiloxane, Mercaptan-Modified

Comments

Also known as GP-71-SS (Genesee Polymers). In this polymer, $n = 83$ and $m = 2$. The broad resonance centered near -105 ppm is due to the glass sample tube. The inclusion of a mercaptan improves surface properties.



Code	Shift (ppm)
S1	-21.9
S2	-21.9
S3	7.5

Experimental Parameters

Nucleus: ^{29}Si (79.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 20% w/w
Scans: 2000	Spectral width: 20 kHz
Data points: 8192	Pulse width: 90°
Broadening: 5 Hz	Pulse delay: 5 s

Source

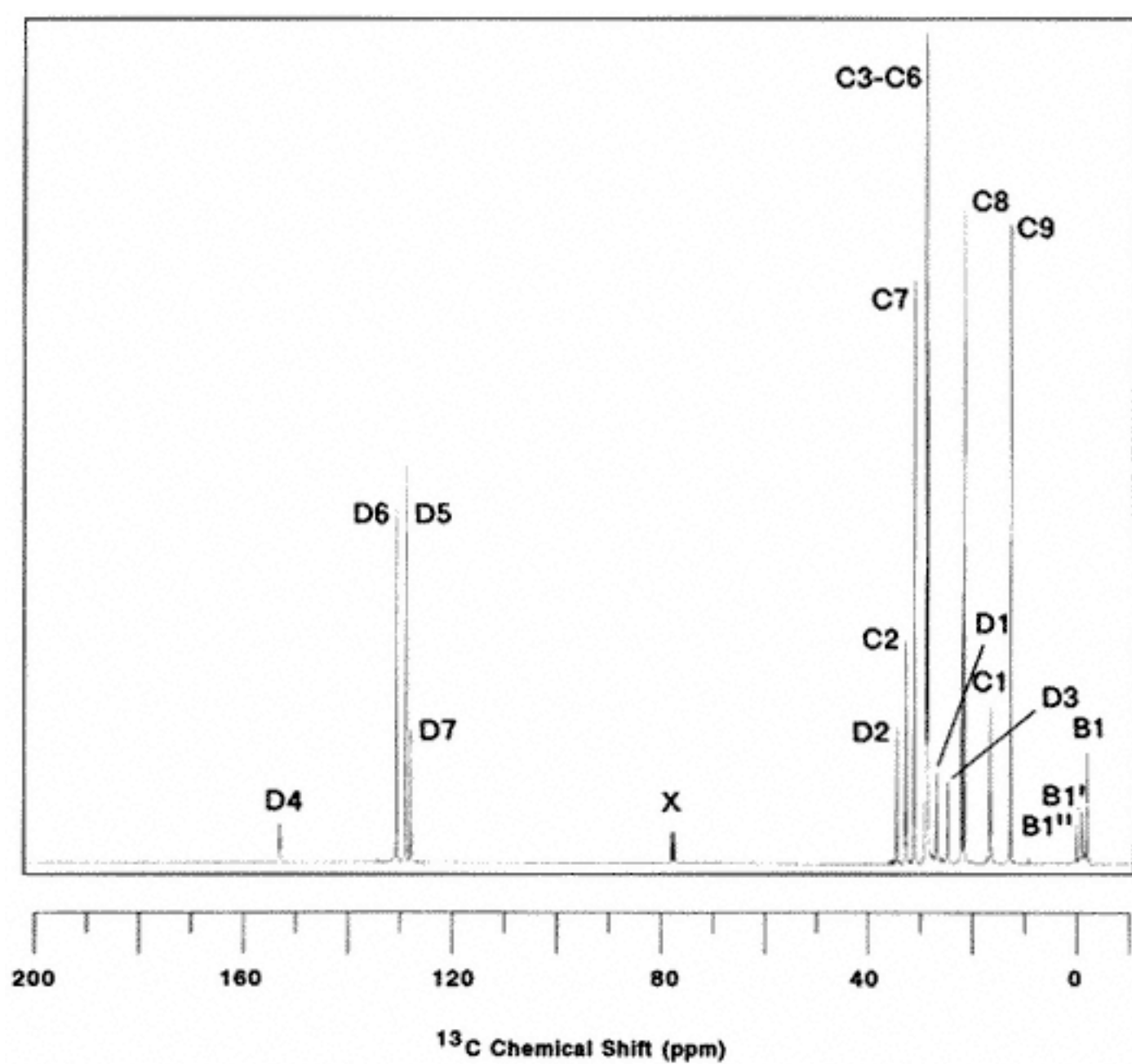
Genesee Polymers, Flint, MI.

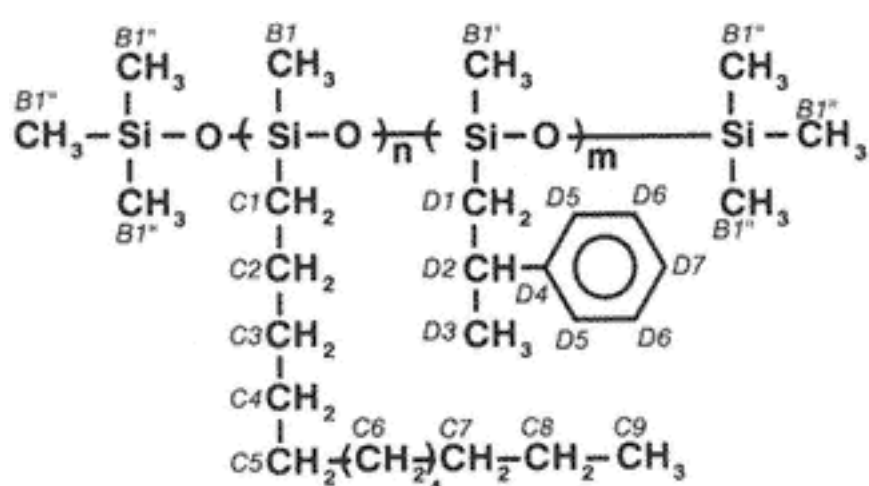
IX-A-11—

Poly(Methyldodecylsiloxane-Co-Methyl-2-Phenylpropylsiloxane)

Comments

Also known as GP-70-S (Genesee Polymers). In this polymer, $n = 26.5$ and $m = 13.5$. Solvent resonances are marked by **X**. The inclusion of longer alkyl and aromatic pendant groups increases miscibility with organic solvents.





Code	Shift (ppm)
B1	-0.05
B'	0.9
B1''	2.0
C1	18.0
C2	33.7
C3	30
C4	30
C5	30
C6	30
C7	32.2
C8	22.9
C9	14.2
D1	28.1
D2	35.4
D3	25.8
D4	149.9
D5	126.6
D6	128.4
D7	125.7

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

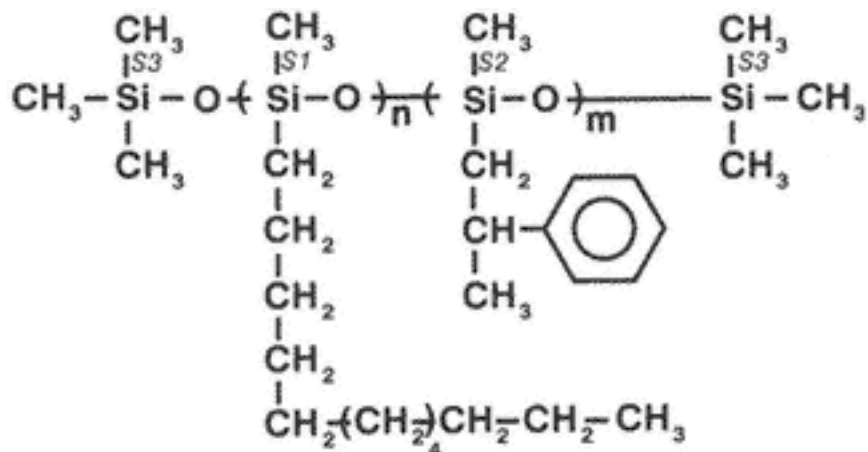
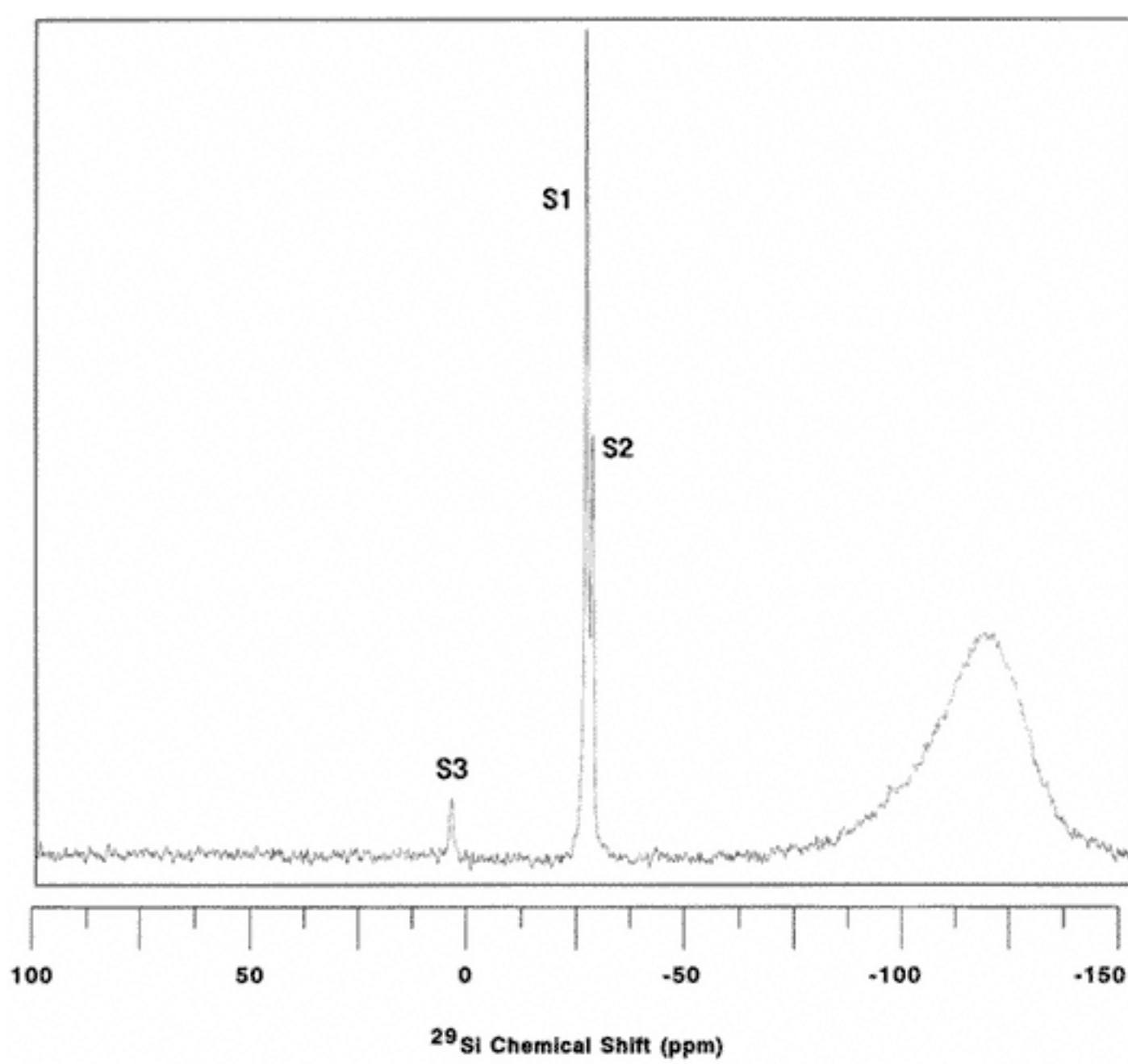
Pulse delay: 5 s

Source

Genesee Polymers, Flint, MI.

**IX-A-11Si—
Poly(Methyldodecylsiloxane-Co-Methyl-2-Phenylpropylsiloxane)**
Comments

Also known as GP-70-S (Genesee Polymers). In this polymer, $n = 26.5$ and $m = 13.5$. The broad resonance centered near – 110 ppm is due to the glass sample tube. The inclusion of longer alkyl and aromatic pendant groups increases miscibility with organic solvents.



Code	Shift (ppm)
S1	-22.1
S2	-23.3
S3	7.5

Experimental ParametersNucleus: ^{29}Si (79.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 2000

Spectral width: 20 kHz

Data points: 8192

Pulse width: 90°

Broadening: 10 Hz

Pulse delay: 5 s

Source

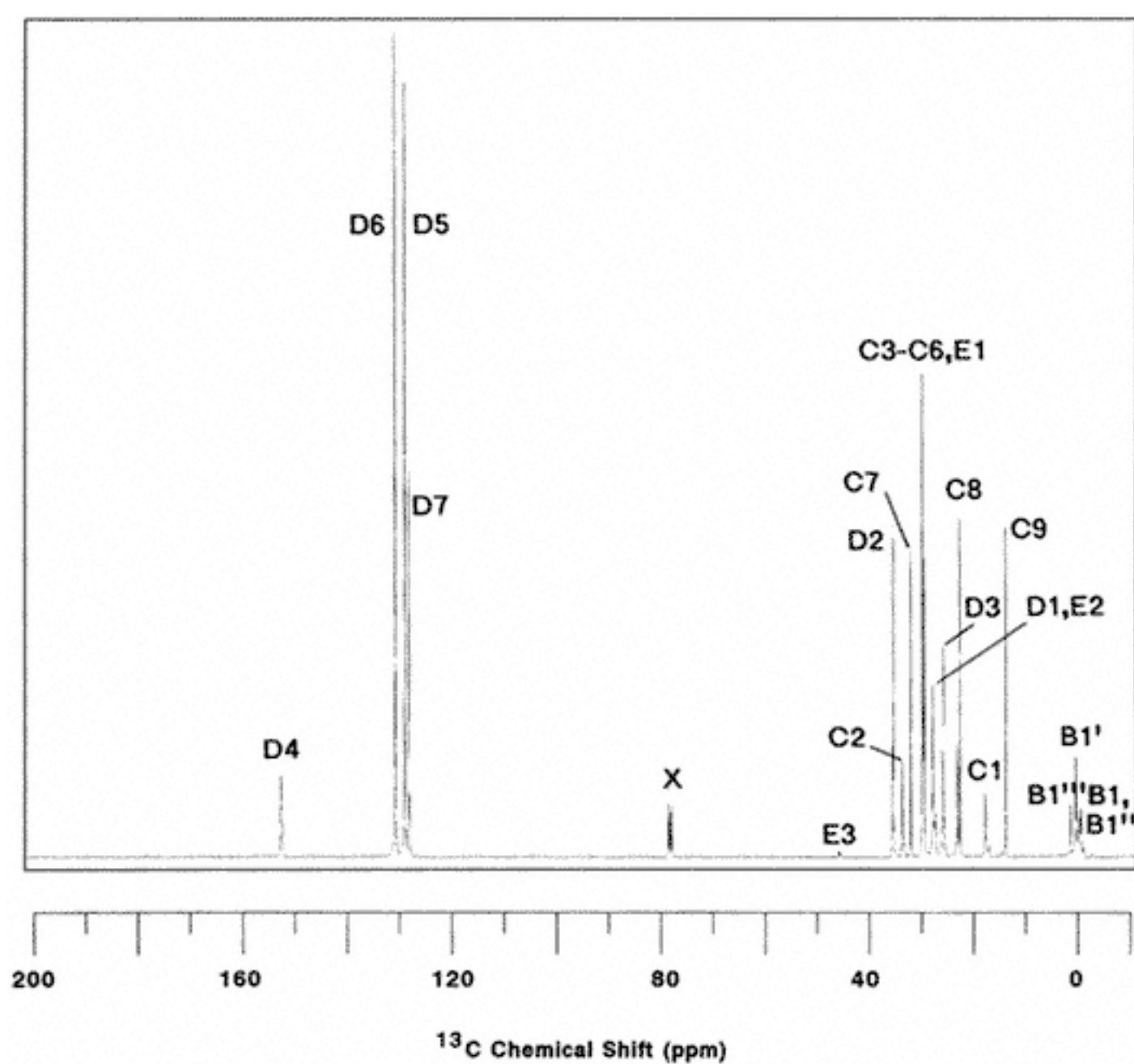
Genesee Polymers, Flint, MI.

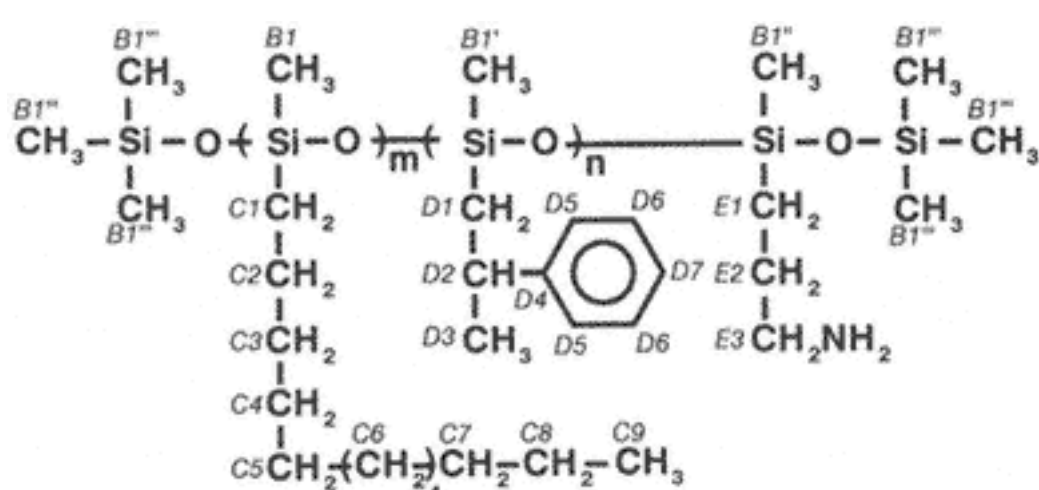
IX-A-12—

Poly(Methyldodecylsiloxane-Co-Methyl-2-Phenylpropylsiloxane), Amine-Terminated

Comments

Also known as GP-7100 (Genesee Polymers). In this polymer, $n = 32$ and $m = 8$. Solvent resonances are marked by **X**. Amino-derivatization enhances water solubility. The inclusion of longer alkyl and aromatic pendant groups increases miscibility with organic solvents. These materials are used in waxes and polishes, and they improve the durability of the finish.





Code	Shift (ppm)
------	-------------

B1	-0.03
----	-------

B1'	0.9
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B1''	-0.02
------	-------

B1'''	2.0
-------	-----

C1	18.1
----	------

C2	33.6
----	------

C3	30
----	----

C4	30
----	----

C5	30
----	----

C6	30
----	----

C7	32.0
----	------

C8	22.7
----	------

C9	14.2
----	------

D1	27.8
----	------

D2	35.4
----	------

D3	25.8
----	------

D4	149.7
----	-------

D5	126.5
----	-------

D6	128.3
----	-------

D7	125.8
----	-------

E1	30
----	----

E2	27.2
----	------

E3	45.1
----	------

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz) Temperature: 50°C

Solvent: CDCl_3 Concentration: 10% w/w

Scans: 400 Spectral width: 25 kHz

Data points: 16384 Pulse width: 90°

Broadening: 2 Hz Pulse delay: 5

Source

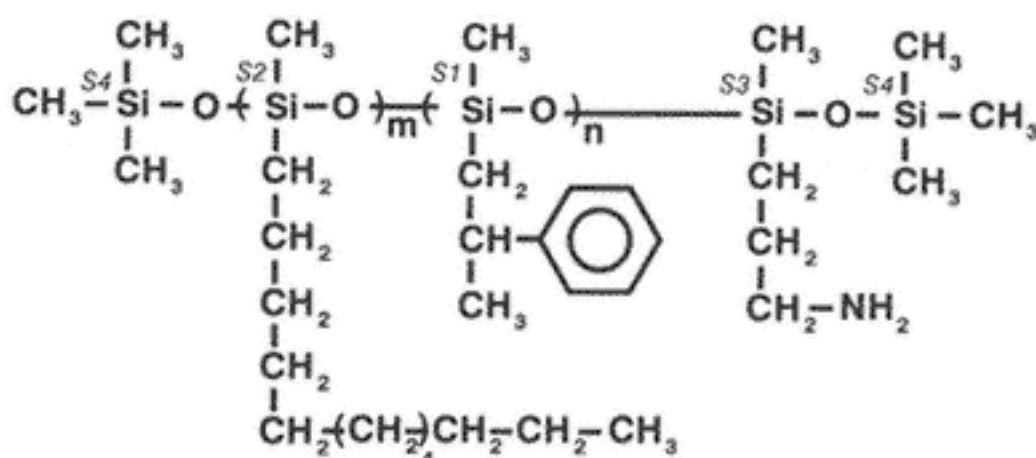
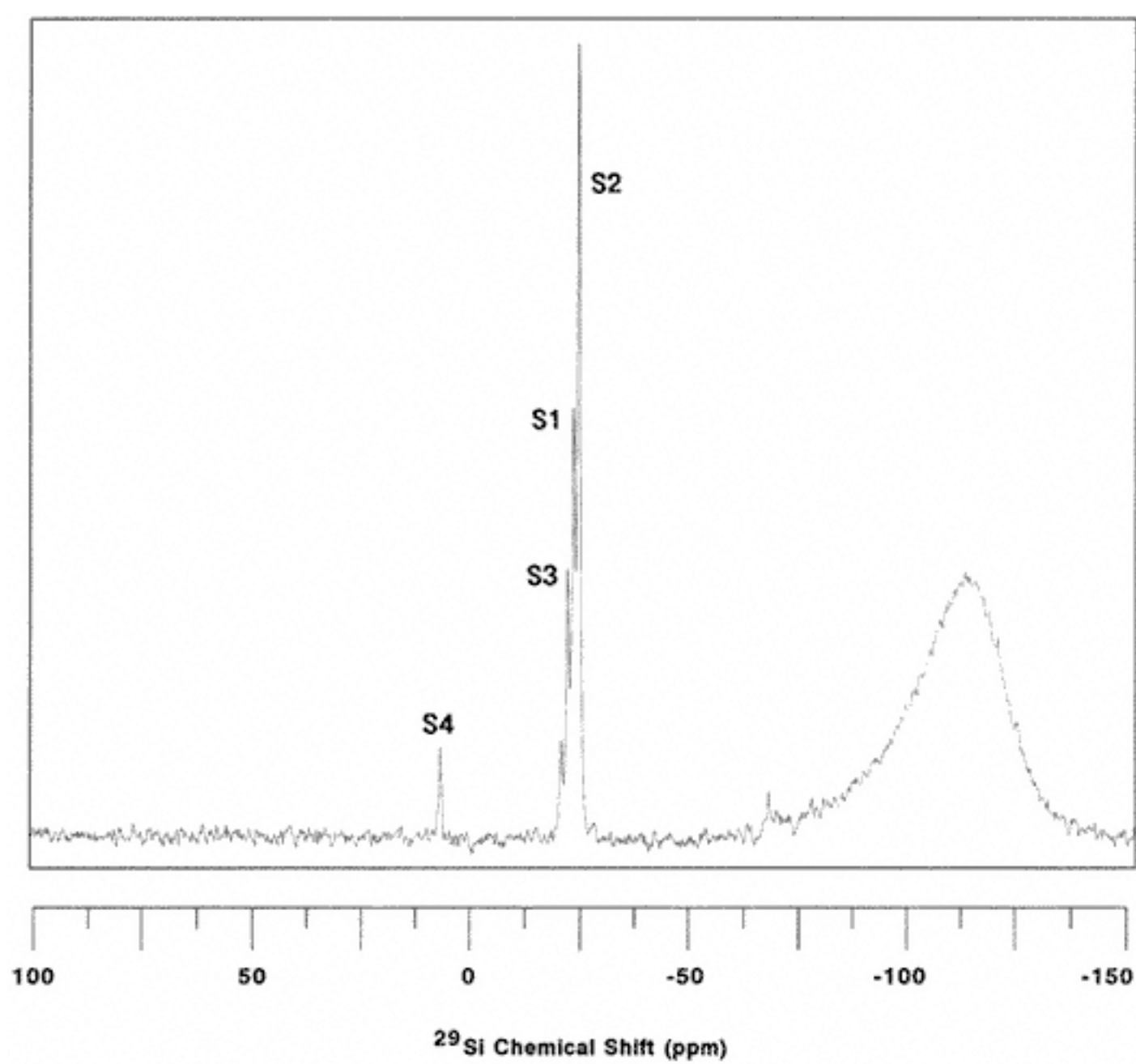
Genesee Polymers, Flint, MI.

IX-A-12Si—

Poly(Methyldodecylsiloxane-Co-Methyl-2-Phenylpropylsiloxane), Amine-Terminated

Comments

Also known as GP-7100 (Genesee Polymers). In this polymer, $n = 32$ and $m = 8$. The broad resonance centered near -110 ppm is due to the glass sample tube. Amino-derivatization enhances water solubility. The inclusion of longer alkyl and aromatic pendant groups increases miscibility with organic solvents. These materials are used in waxes and polishes, and they improve the durability of the finish.



Code	Shift (ppm)
S1	-21.0
S2	-22.1
S3	-19.7
S4	7.5

Experimental ParametersNucleus: ^{29}Si (79.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 2000

Spectral width: 20 kHz

Data points: 8192

Pulse width: 90°

Broadening: 10 Hz

Pulse delay: 5 s

Source

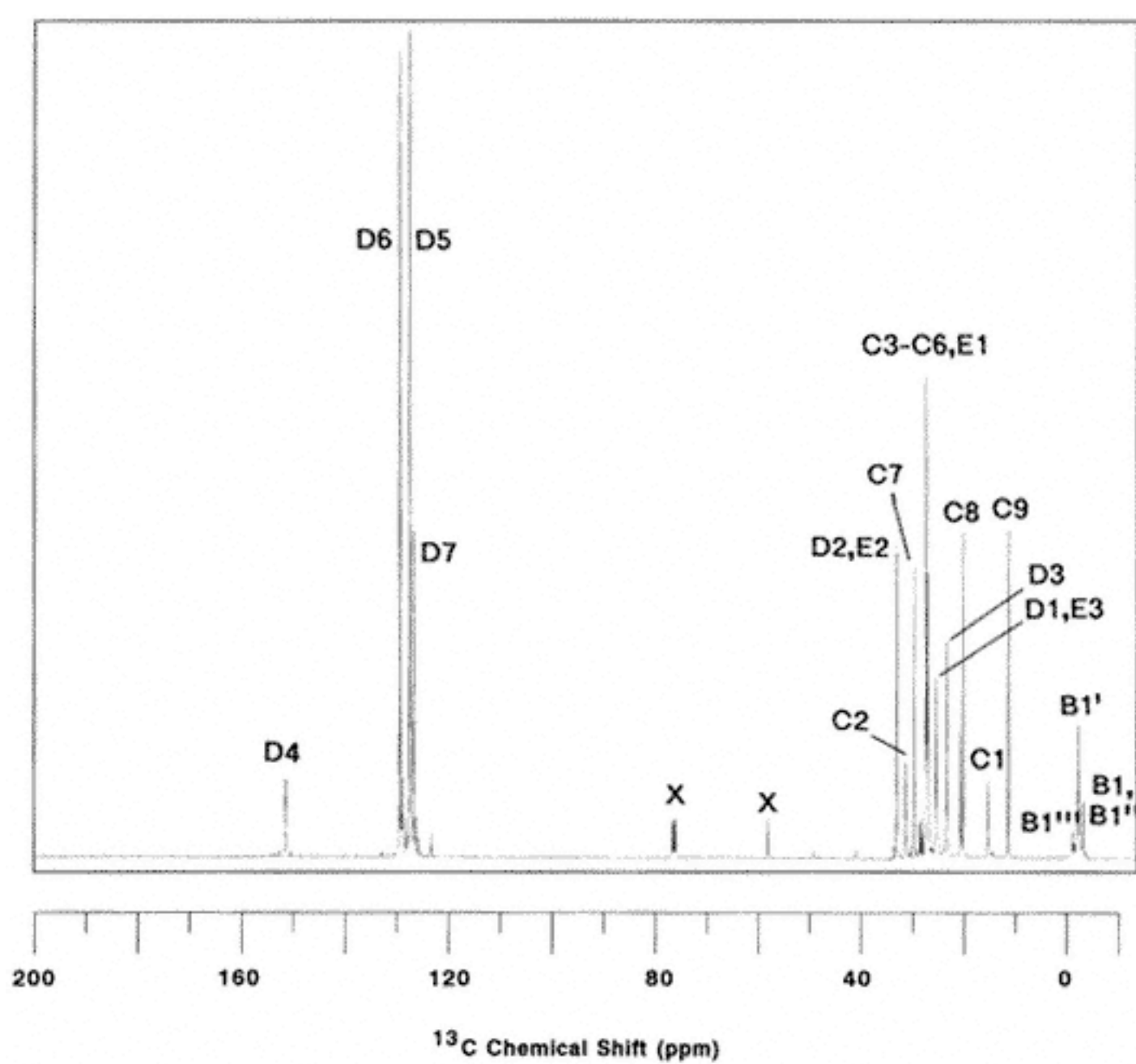
Genesee Polymers, Flint, MI.

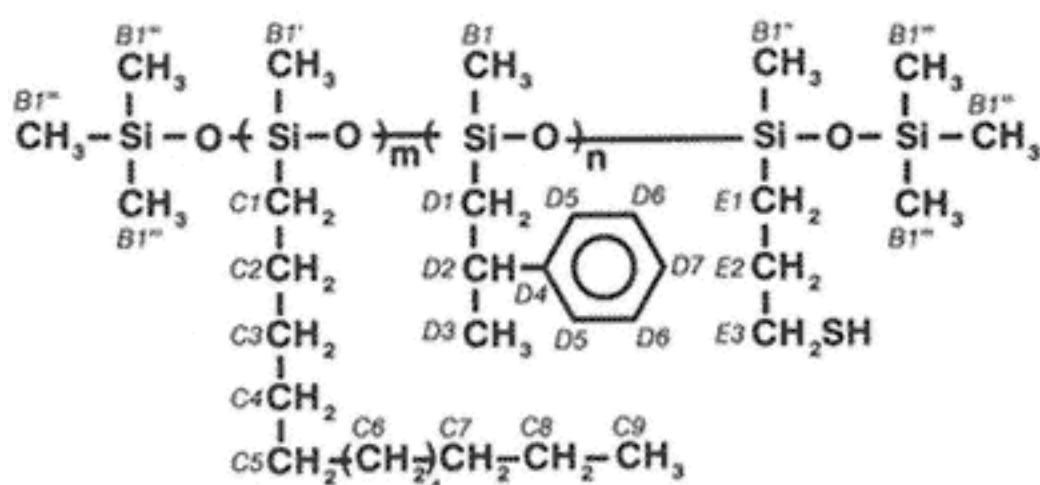
IX-A-13—

Poly(Methyldodecylsiloxane-Co-Methyl-2-Phenylpropylsiloxane), Mercaptan-Modified

Comments

Also known as GP-7200 (Genesee Polymers). In this polymer, $n = 32$ and $m = 8$. Solvent resonances are marked by X. The inclusion of longer alkyl and aromatic pendant groups increases miscibility with organic solvents. The mercaptan improves surface properties.





Code	Shift (ppm)
------	-------------

B1	0
B1'	.09
B1''	0.9
B1'''	2.1
C1	18.0
C2	33.7
C3	30
C4	30
C5	30
C6	30
C7	32.1
C8	22.8
C9	14.2
D1	27.9
D2	35.3
D3	25.8
D4	149.7
D5	126.7
D6	128.4
D7	125.8
E1	30
E2	35.3
E3	27.9

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 10% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

Source

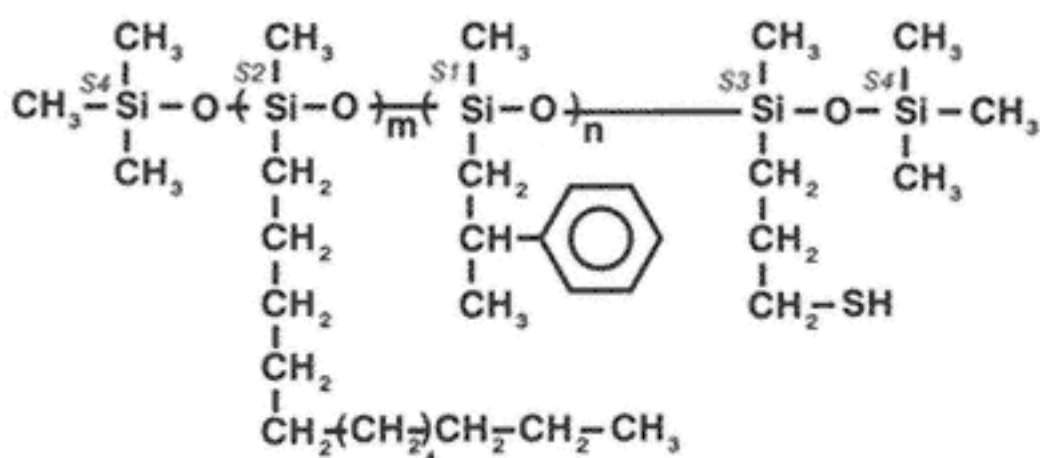
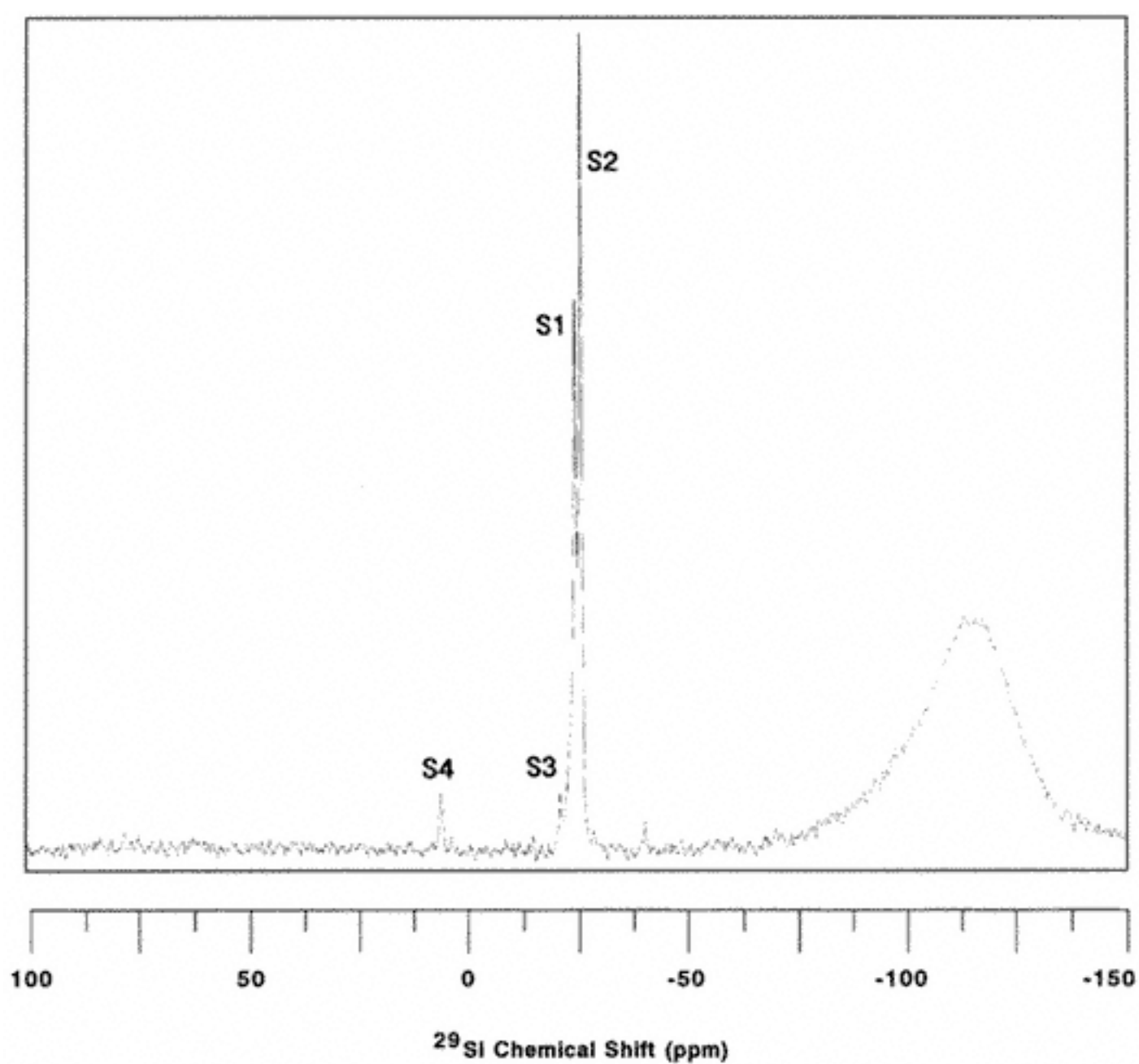
Genesee Polymers, Flint, MI.

IX-A-13Si—

Poly(Methyldodecylsiloxane-Co-Methyl-2-Phe Nylpropylsiloxane), Mercaptan-Modified

Comments

Also known as GP-7200 (Genesse Polymers), In this polymer, $n = 32$ and $m = 8$. The broad resonance centered near -110 ppm is due to the glass sample tube. The inclusion of longer alkyl and aromatic pendant groups increases miscibility with organic solvents. The mercaptan improves surface properties.



Code	Shift (ppm)
S1	-22.1
S2	-23.3
S3	-18.4
S4	7.5

Experimental ParametersNucleus: ^{29}Si (79.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 2000

Spectral width: 20 kHz

Data points: 8192

Pulse width: 90°

Broadening: 10 Hz

Pulse delay: 5 s

Source

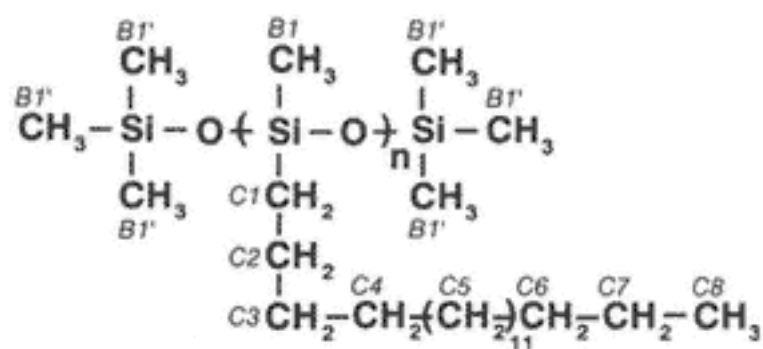
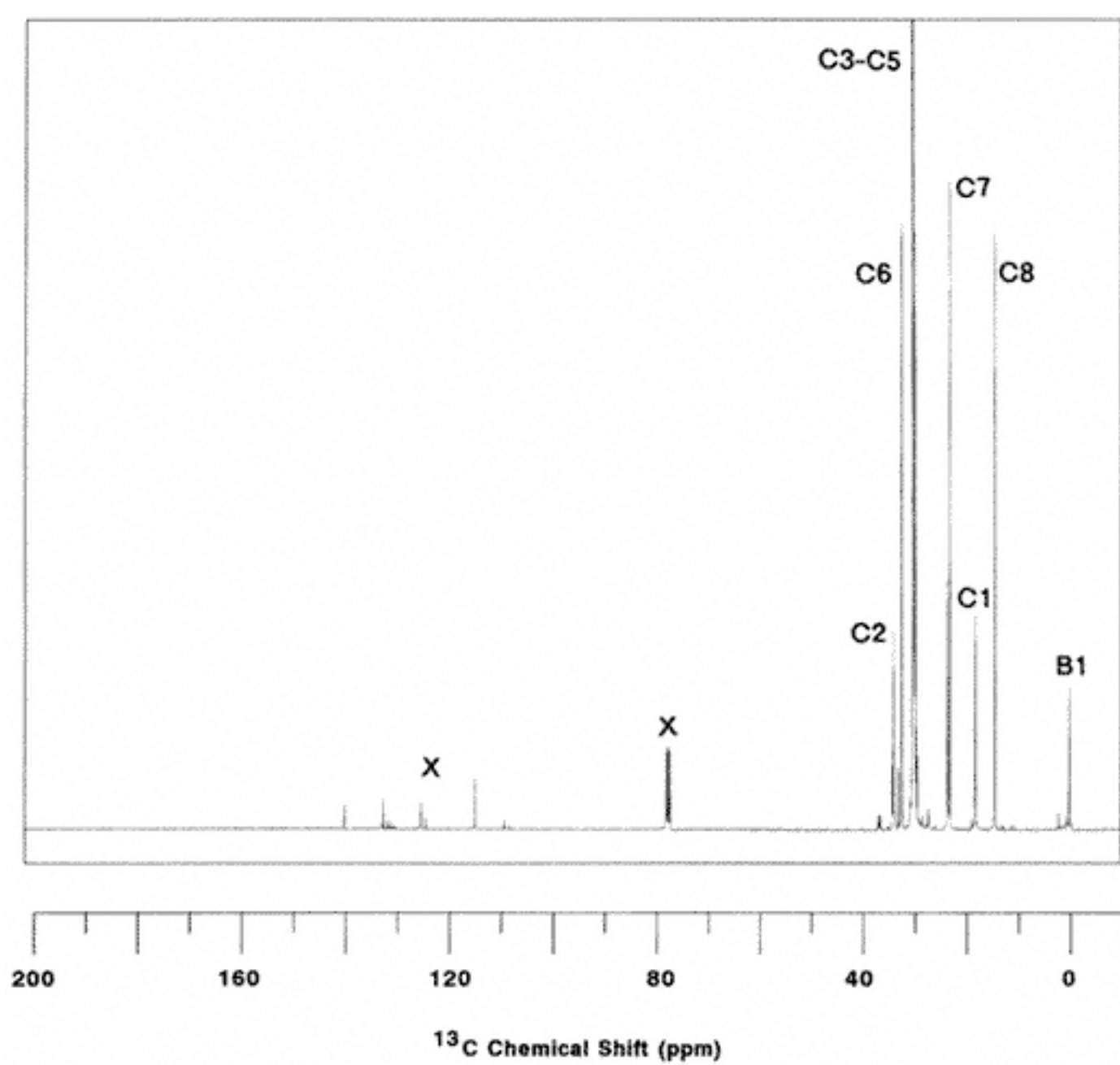
Genesee Polymers, Flint, MI.

IX-A-14—

Polymethyloctadecylsiloxane

Comments

Also known as EXP-58 (Genesee Polymers); the length (n) of the interior methyloctadecylsiloxane block is 40 units. End-group resonances **B1'** are not observed. Solvent resonances are marked by **X**. Substitution of one methyl group with a longer alkyl chain increases miscibility with organic solvents but decreases overall stability.



Code	Shift (ppm)
B1	-0.2
B1'	2.0
C1	18.0
C2	33.7
C3	30
C4	30
C5	30
C6	32.2
C7	22.8
C8	14.2

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 5% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

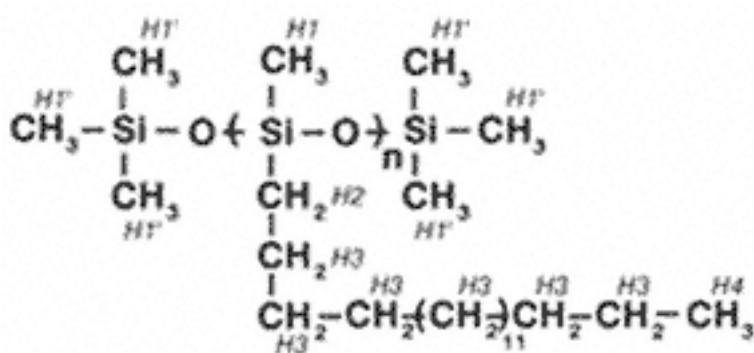
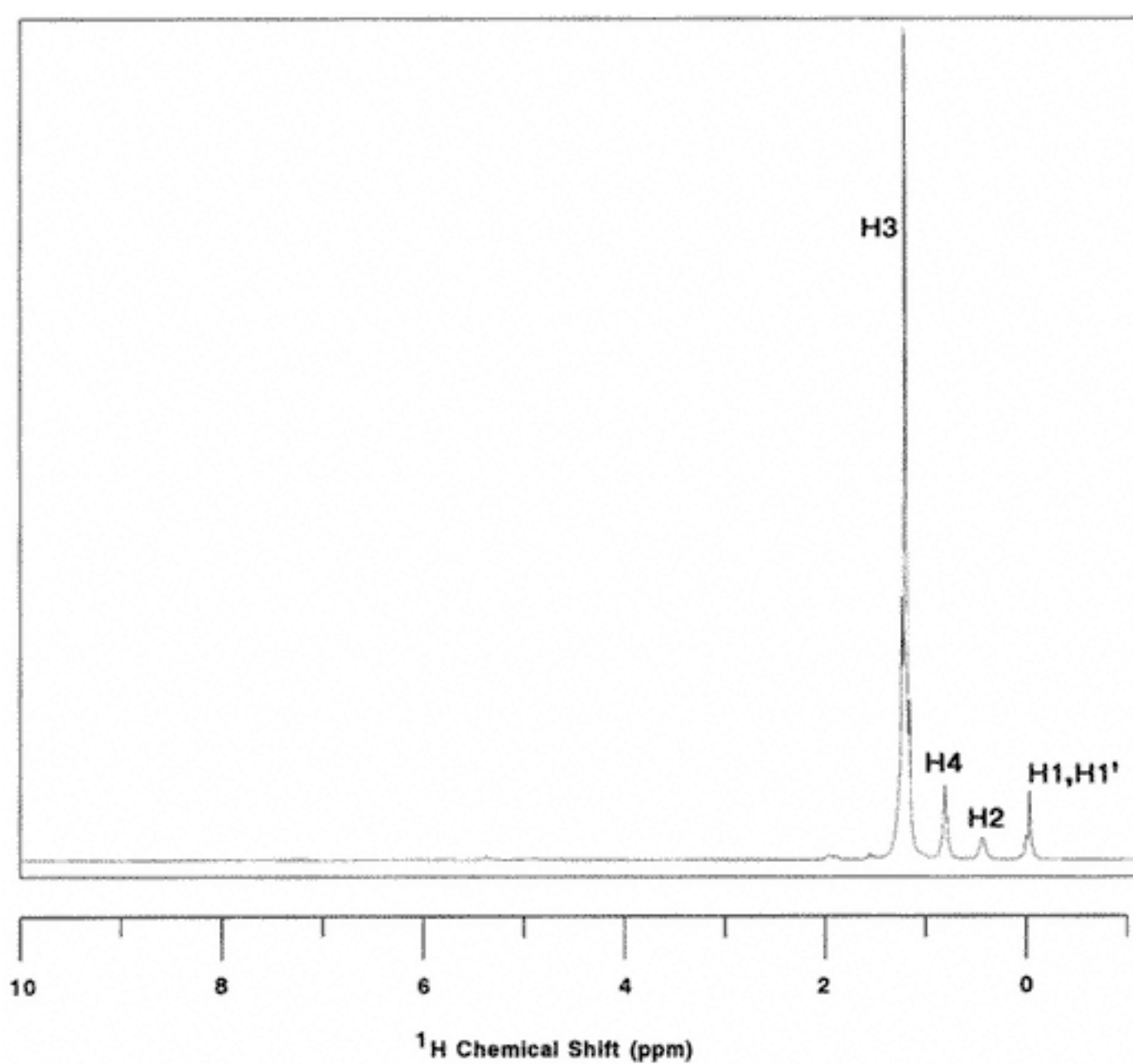
Source

Genesee Polymers, Flint, MI.

IX-A-14H—
Polymethyloctadecylsiloxane

Comments

Also known as EXP-58 (Genesee Polymers); the length (n) of the interior methyloctadecylsiloxane block is 40 units. Substitution of one methyl group with a longer alkyl chain increases miscibility with organic solvents, but decreases overall stability.



Code	Shift (ppm)
H1	0.1
H2	0.5
H3	1.3
H4	0.9

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 5% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

Broadening: 5 Hz

Pulse delay: 5 s

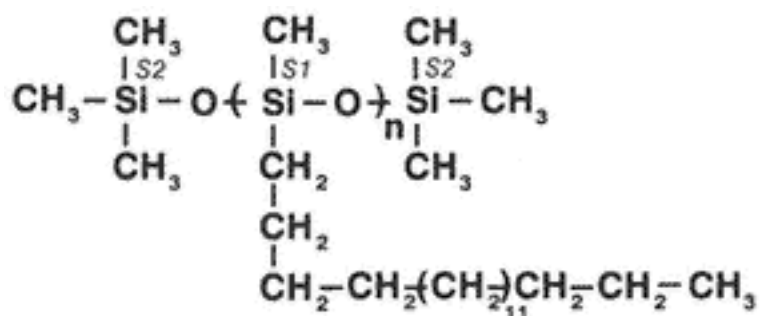
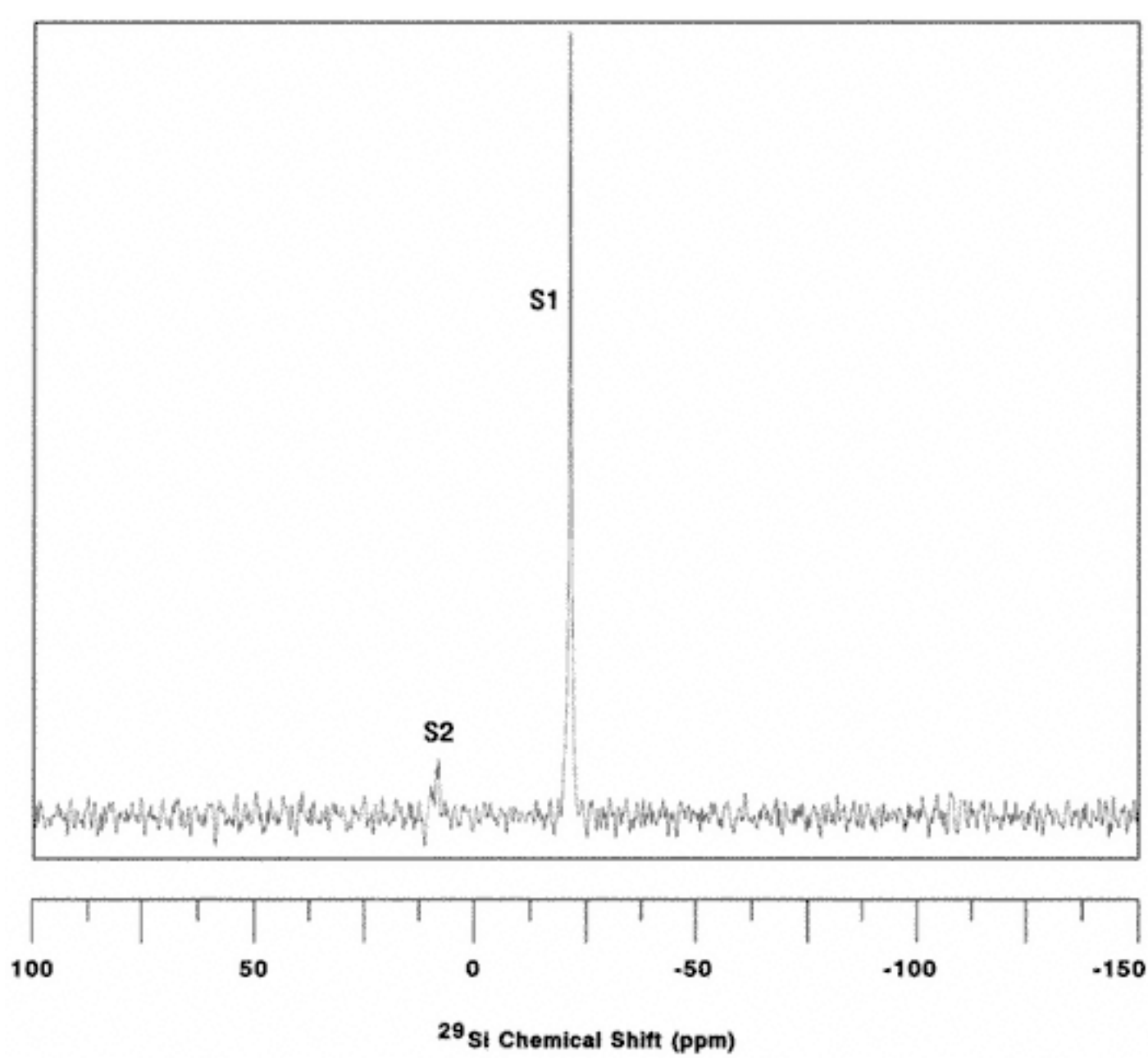
Source

Genesee Polymers, Flint, MI.

IX-A-14Si—
Polymethyloctadecylsiloxane

Comments

Also known as EXP-58 (Genesee Polymers); the length (n) of the interior methyloctadecylsiloxane block is 40 units. The broad resonance centered near — 110 ppm, caused by the glass sample tube, was removed by baseline correction. Substitution of one methyl group with a longer alkyl chain increases miscibility with organic solvents but decreases overall stability.



Code	Shift (ppm)
S1	-22.3
S2	9.1

Experimental Parameters

Nucleus: ^{29}Si (79.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 5% w/w
Scans: 100	Spectral width: 50 kHz
Data points: 8192	Pulse width: 90°
Broadening: 20 Hz	Pulse delay: 5 s

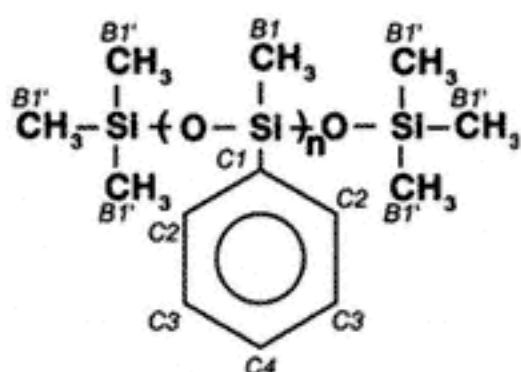
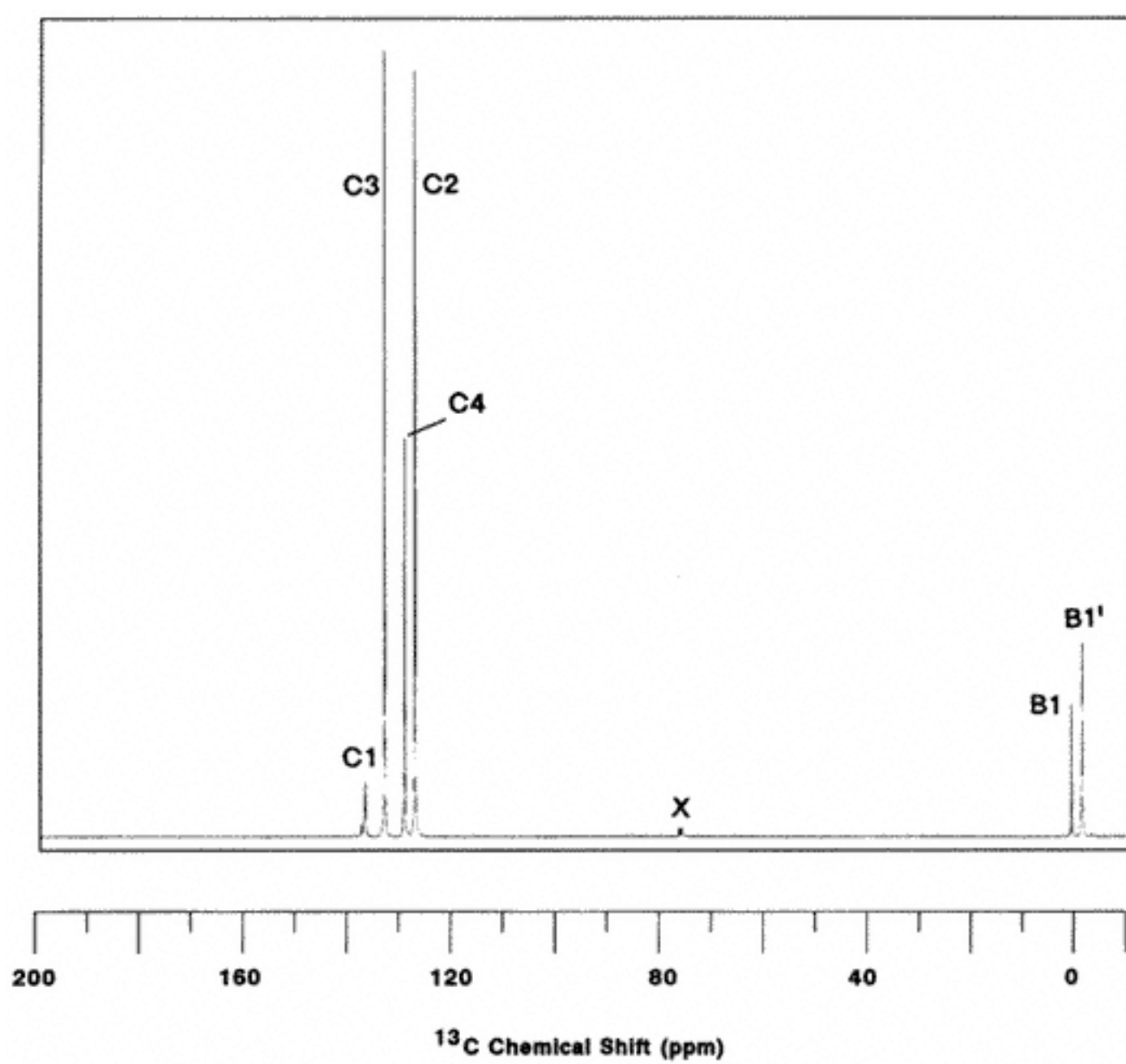
Source

Genesee Polymers, Flint, MI.

**IX-A-15—
Polymethylphenylsiloxane**

Comments

Trimethyl end groups are observed because of the relatively low molecular weight (2600). The splitting of peak **C1** is due to tacticity effects; solvent resonances are marked by **X**. Substitution of one methyl group of PDMS {IX-A-1} with a phenyl ring increases miscibility with organic solvents and improves oxidative stability.



Code	Shift (ppm)
B1	0.2
B1'	0.8
C1	138.0
C2	127.6
C3	133.7
C4	130.0

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

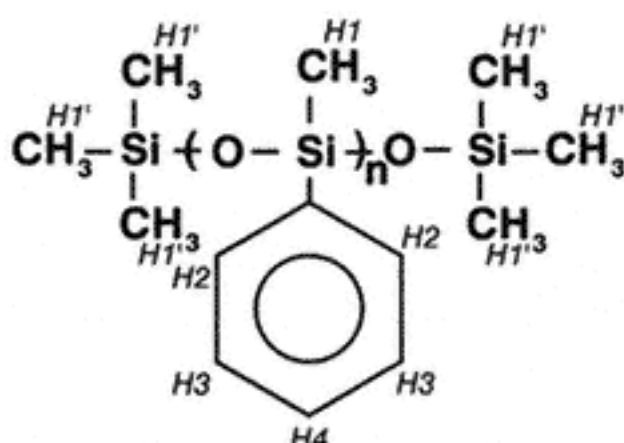
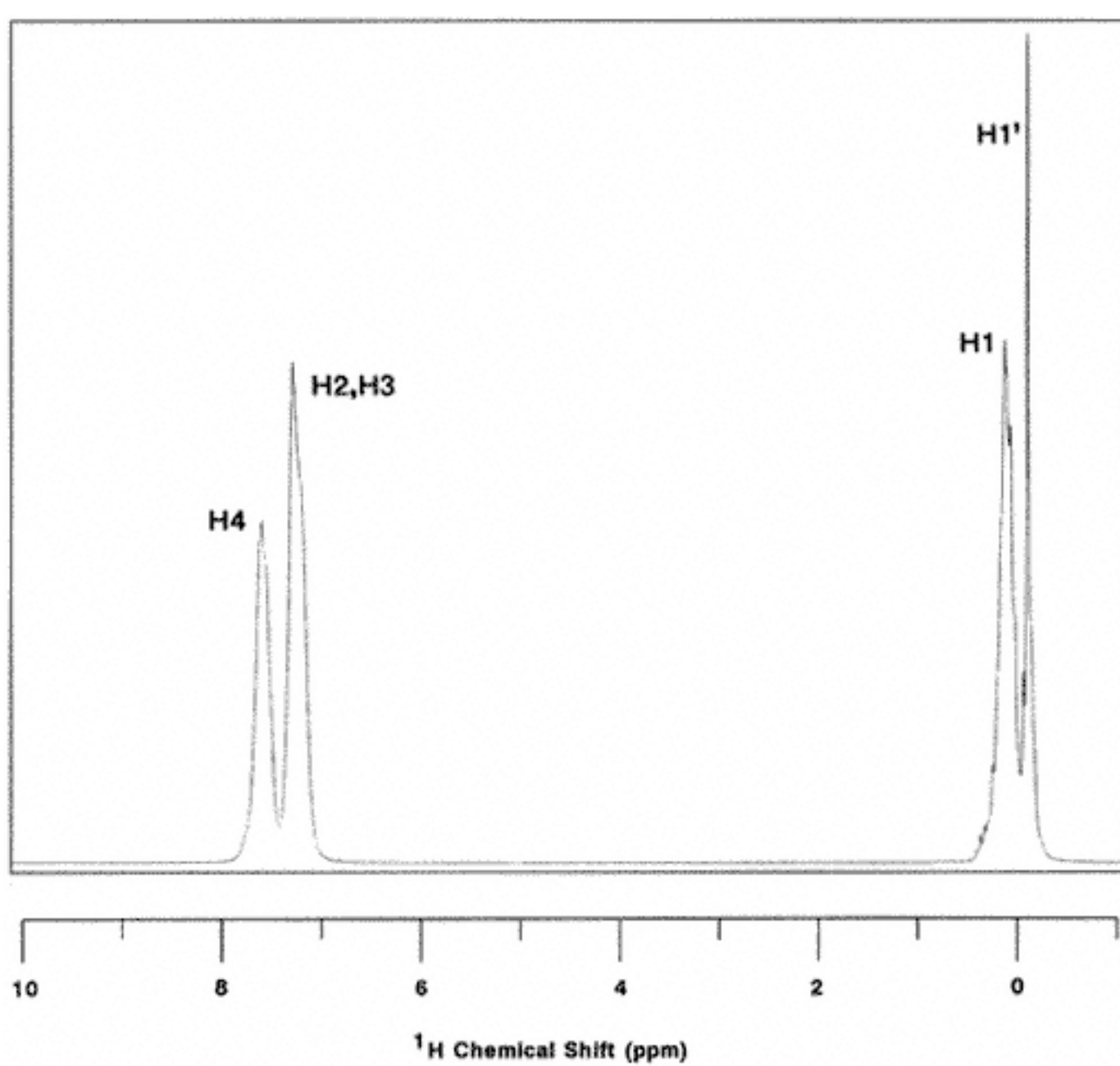
Broadening: 2 Hz

Pulse delay: 5 s

**IX-A-15H—
Polymethylphenylsiloxane**

Comments

Trimethyl end groups are observed because of the relatively low molecular weight (2600). Substitution of one methyl group of PDMS with a phenyl ring increases miscibility with organic solvents and improves oxidative stability.



Code	Shift (ppm)
H1	0.26
H1'	0.04
H2	7.2
H3	7.2
H4	7.5

Experimental Parameters

Nucleus: ^1H (400 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 48

Spectral width: 8 kHz

Data points: 8192

Pulse width: 10°

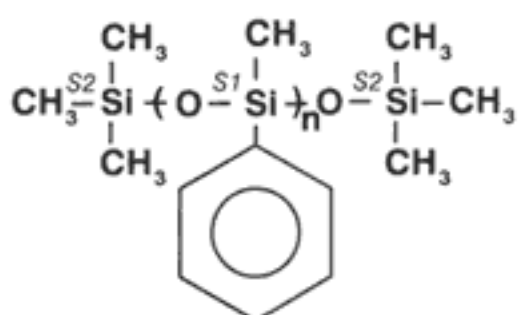
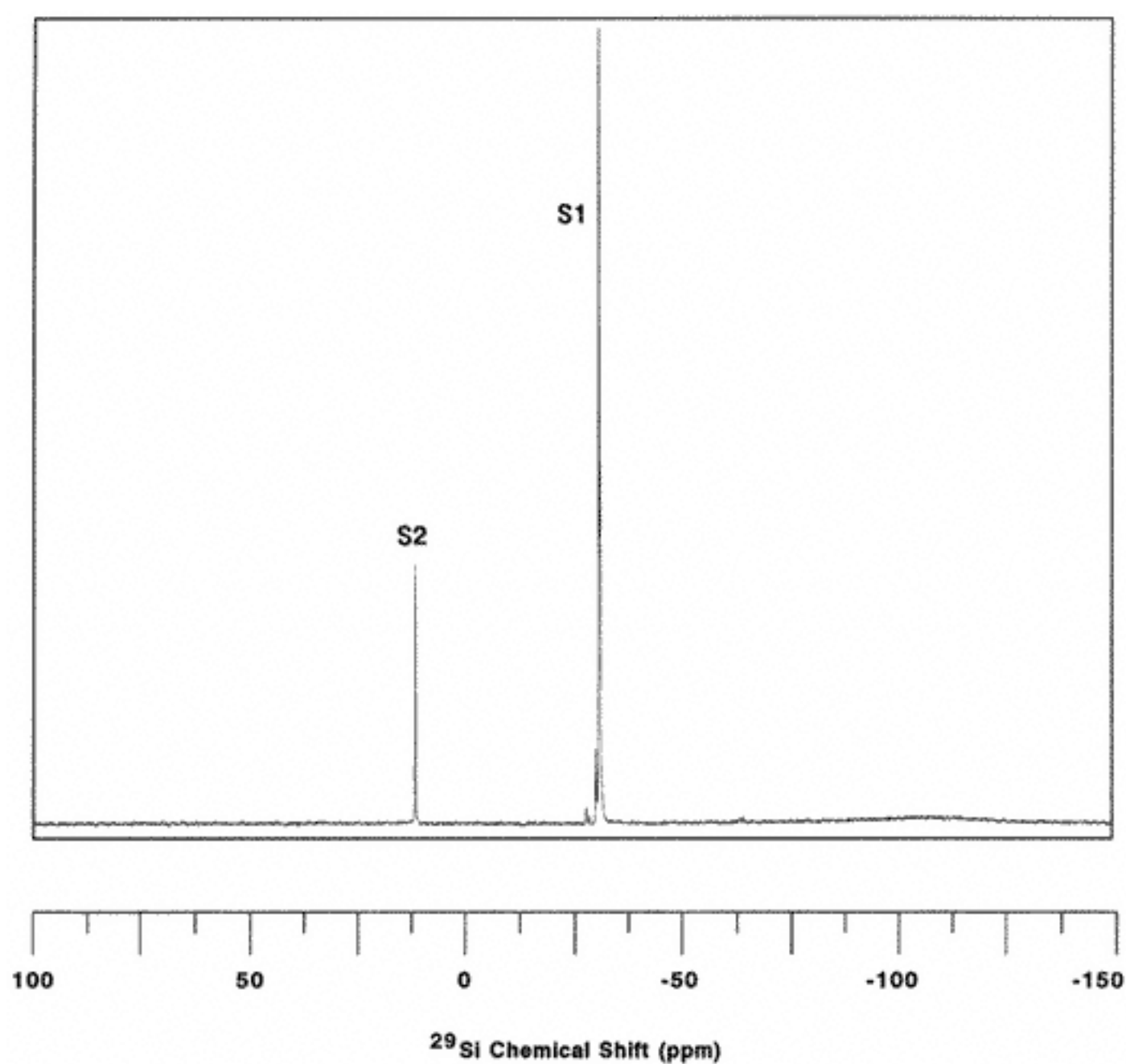
Broadening: 5 Hz

Pulse delay: 5 s

IX-A-15Si—
Polymethylphenylsiloxane

Comments

Trimethyl end groups are observed because of the relatively low molecular weight (2600). The broad resonance centered near – 110 ppm is due to the glass sample tube. Substitution of one methyl group of PDMS with a phenyl ring increases miscibility with organic solvents and improves oxidative stability.



Code	Shift (ppm)
S1	-31.6
S2	9.0

Experimental Parameters

Nucleus: ^{29}Si (79.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 50 kHz

Data points: 8192

Pulse width: 90°

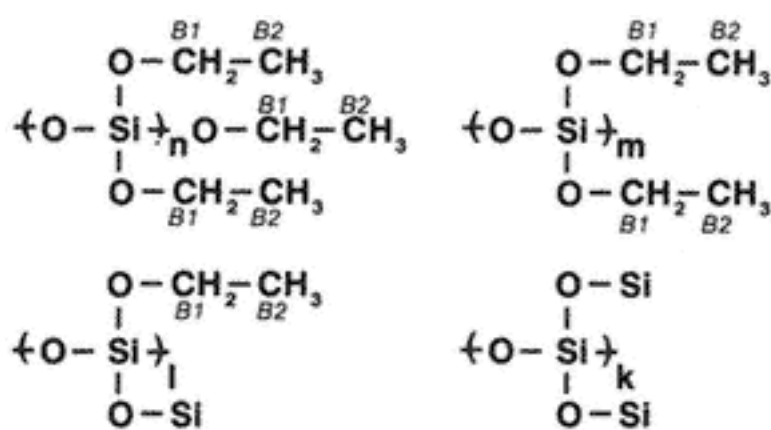
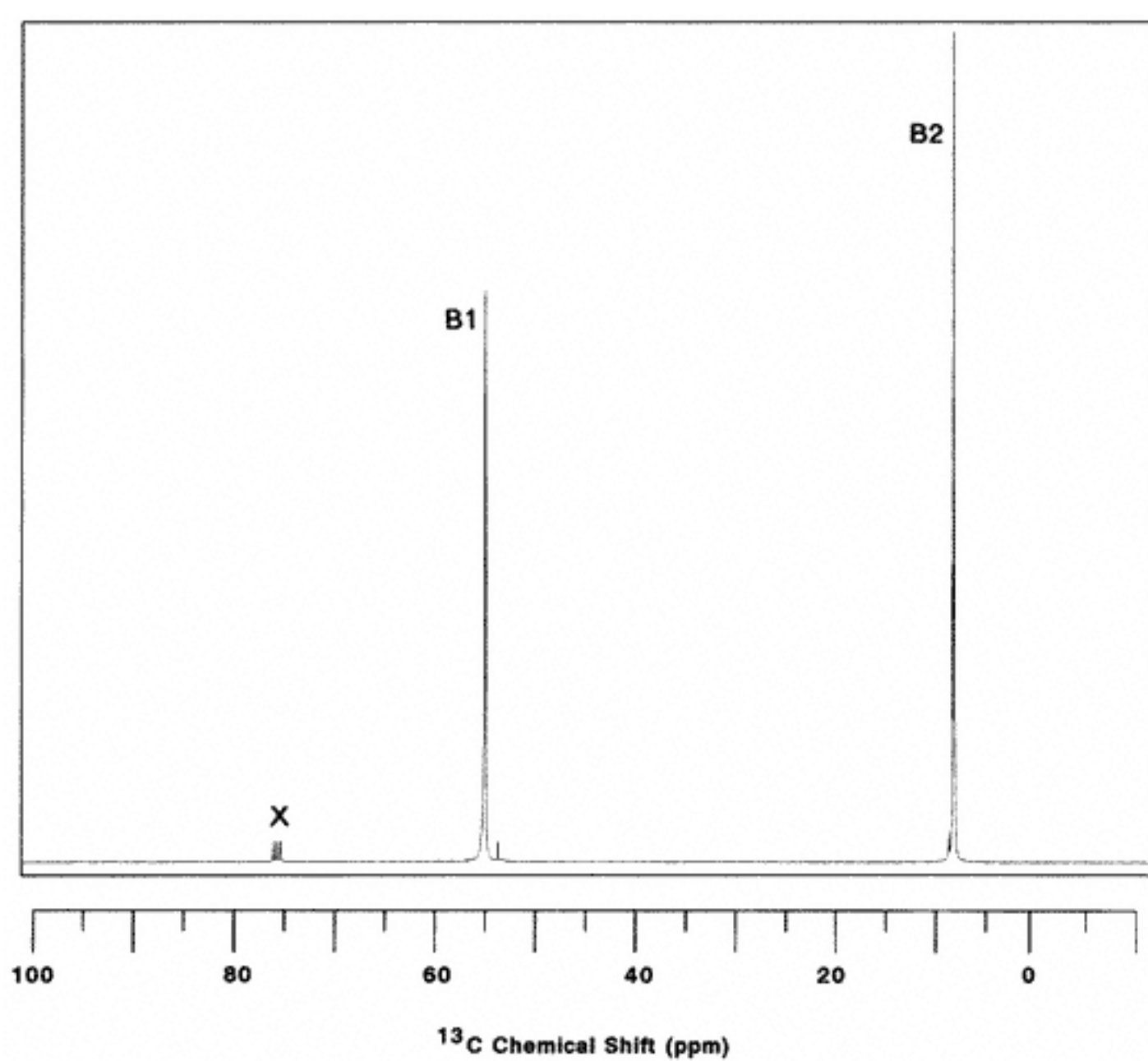
Broadening: 5 Hz

Pulse delay: 5 s

**IX-A-16—
Poly(Ethyl Silicate)**

Comments

Also known as polydiethoxysiloxane. The highly branched, irregular structure leads to the presence of species with 0, 1, 2, or 3 ethoxy groups; however, these differences are not reflected in the ^{13}C spectrum. Solvent resonances are marked by **X**. This material is used to make paints and other coatings that are resistant to heat, water, and many other chemicals.



Code	Shift (ppm)
B1	58.8
B2	13.6

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 5% w/w

Scans: 400

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

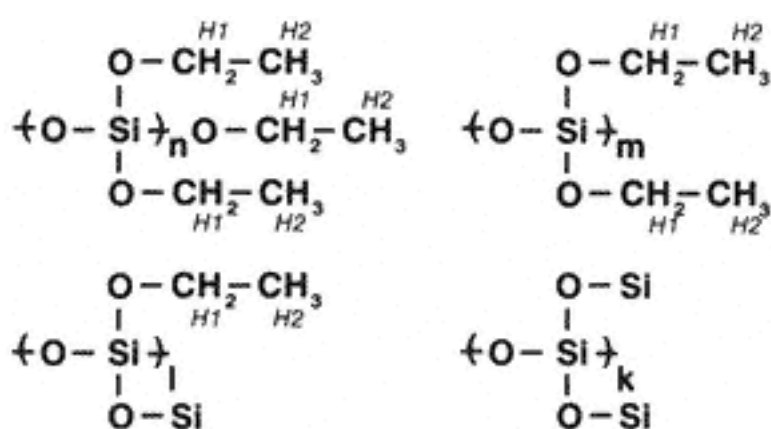
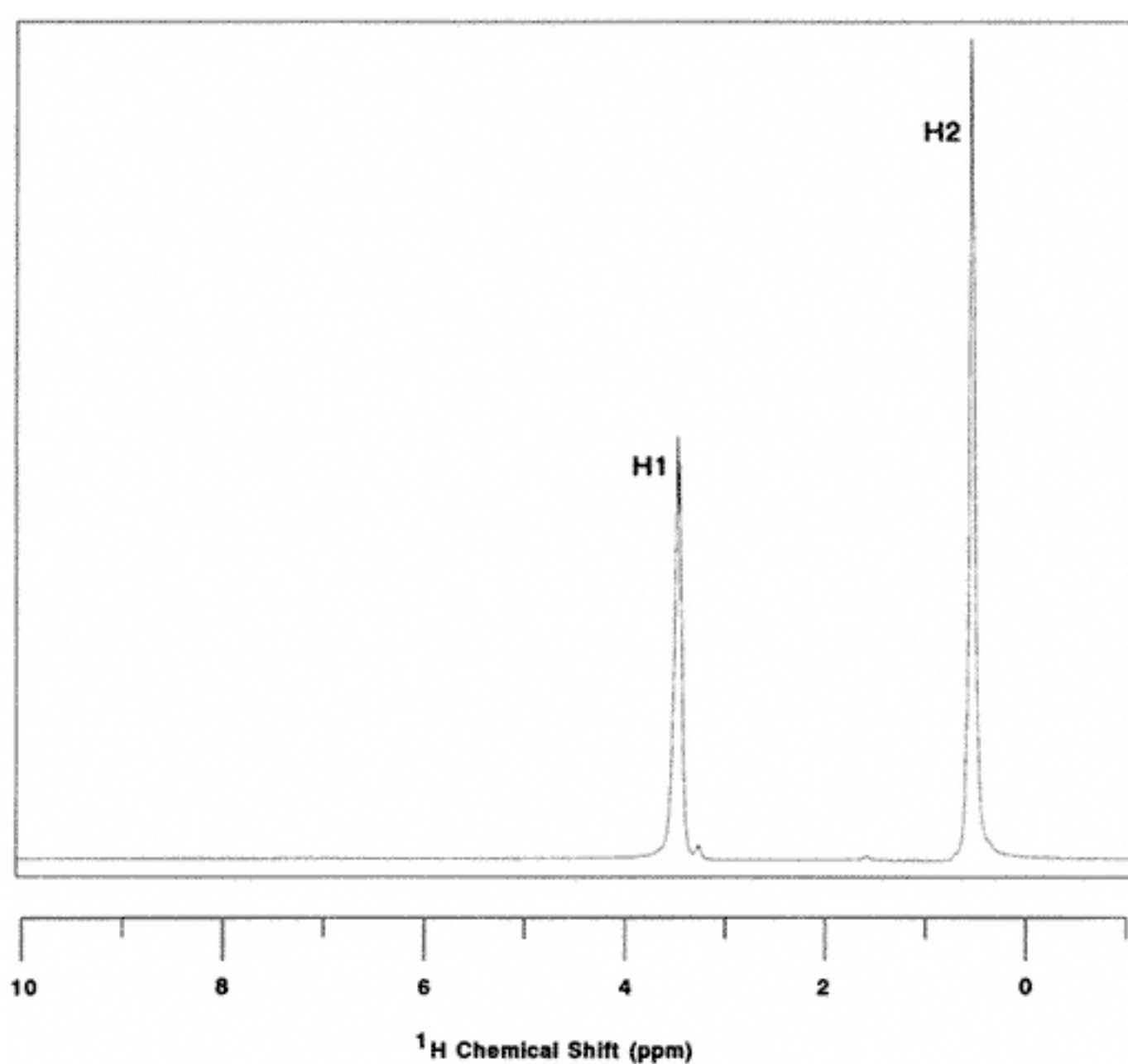
Broadening: 2 Hz

Pulse delay: 5 s

IX-A-16H—
Poly(Ethyl Silicate)

Comments

Also known as polydiethoxysiloxane. The highly branched, irregular structure leads to the presence of species with 0, 1, 2, or 3 ethoxy groups; however, these differences are not reflected in the ^1H spectrum. This material is used to make paints and other coatings that are resistant to heat, water, and many other chemicals.



Code	Shift (ppm)
H1	3.3
H2	0.7

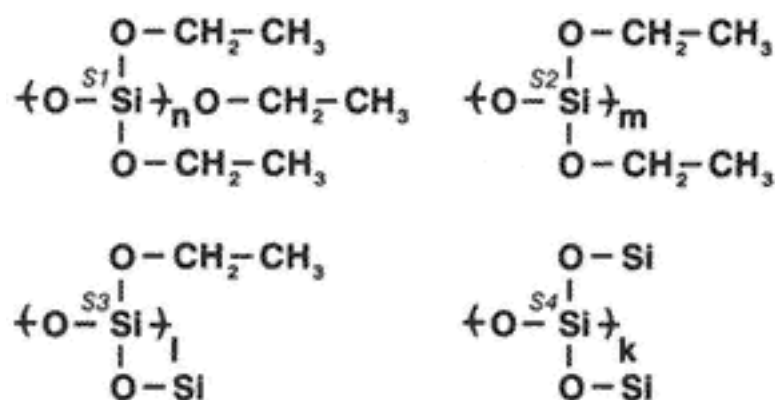
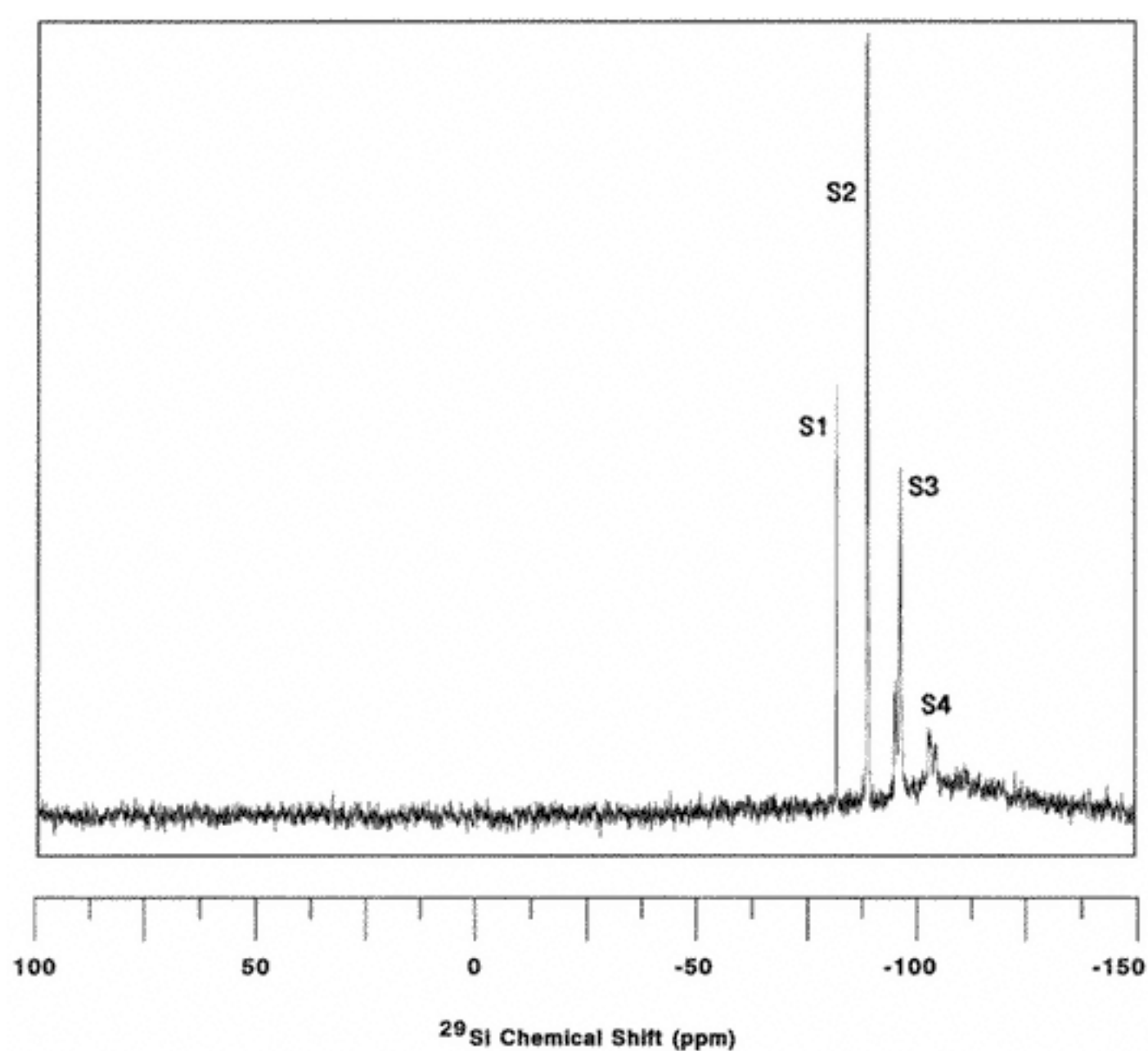
Experimental Parameters

Nucleus: ^1H (400 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 5% w/w
Scans: 48	Spectral width: 8 kHz
Data points: 8192	Pulse width: 10°
Broadening: 5 Hz	Pulse delay: 5 s

**IX-A-16Si—
Poly(Ethyl Silicate)**

Comments

Also known as polydiethoxysiloxane. The highly branched, irregular structure leads to the presence of species with 0, 1, 2, or 3 ethoxy groups; each gives rise to a distinct resonance. The broad resonance centered near -110 ppm is due to the glass sample tube. This material is used to make paints and other coatings that are resistant to heat, water, and many other chemicals.



Code	Shift (ppm)
S1	-81.3
S2	-88.4
S3	-96.8
S4	-102.5

Experimental Parameters

Nucleus: ^{29}Si (79.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 5% w/w

Scans: 100

Spectral width: 50 kHz

Data points: 8192

Pulse width: 90°

Broadening: 5 Hz

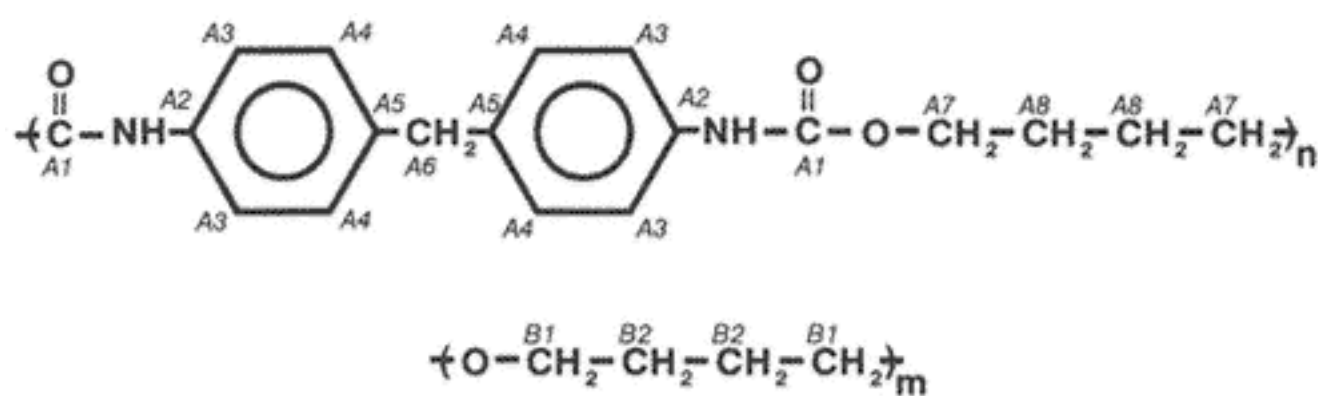
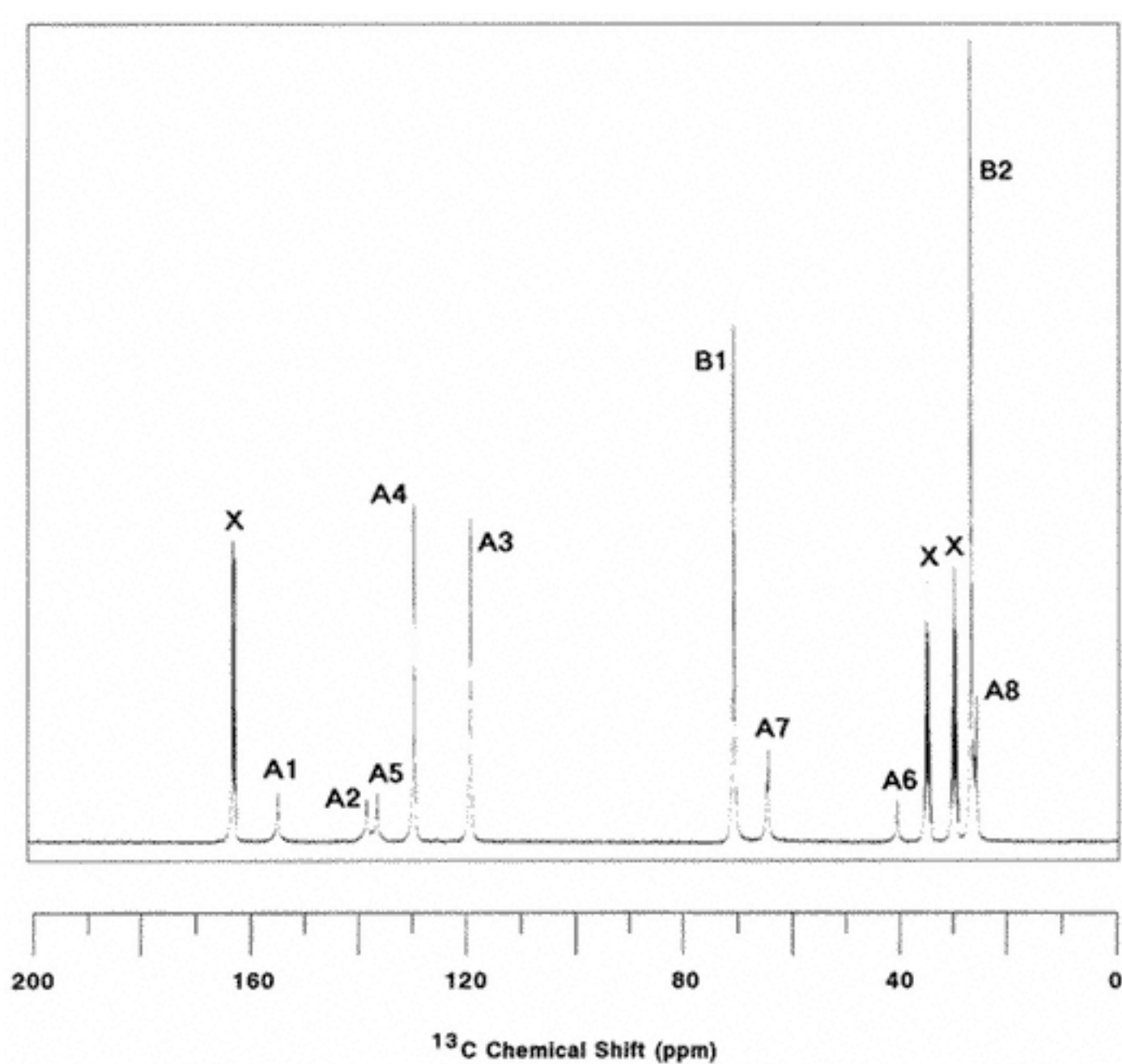
Pulse delay: 5 s

IX-B-1—

Poly[4,4'-Methylenebis(Phenyl Isocyanate)-Alt-1,4-Butanediol/Tetrahydrofuran]

Comments

Solvent resonances are marked by **X**. This material is a polyether urethane thermoplastic elastomer containing both stiff (carbons **A1–A8**) and flexible (carbons **B1** and **B2**) segments. It has good hydrolytic stability, and is found in sporting goods, tubing, cable jackets, gears, automotive parts, and as spandex fibers in hosiery and other clothing.



Code	Shift (ppm)
A1	155.1
A2	139.2
A3	119.6
A4	129.9
A5	136.7
A6	41.2
A7	65.0
A8	27.4
B1	71.5
B2	27.7

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: dimethylformamide- d_7

Concentration: 10% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

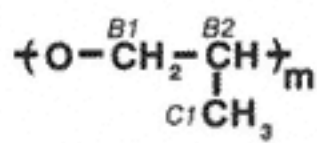
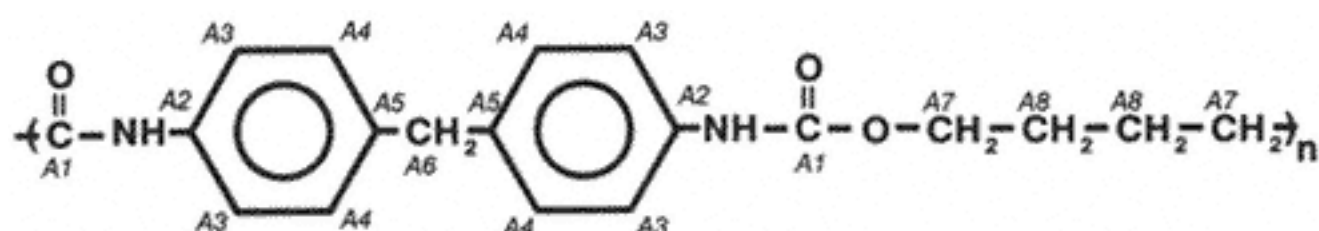
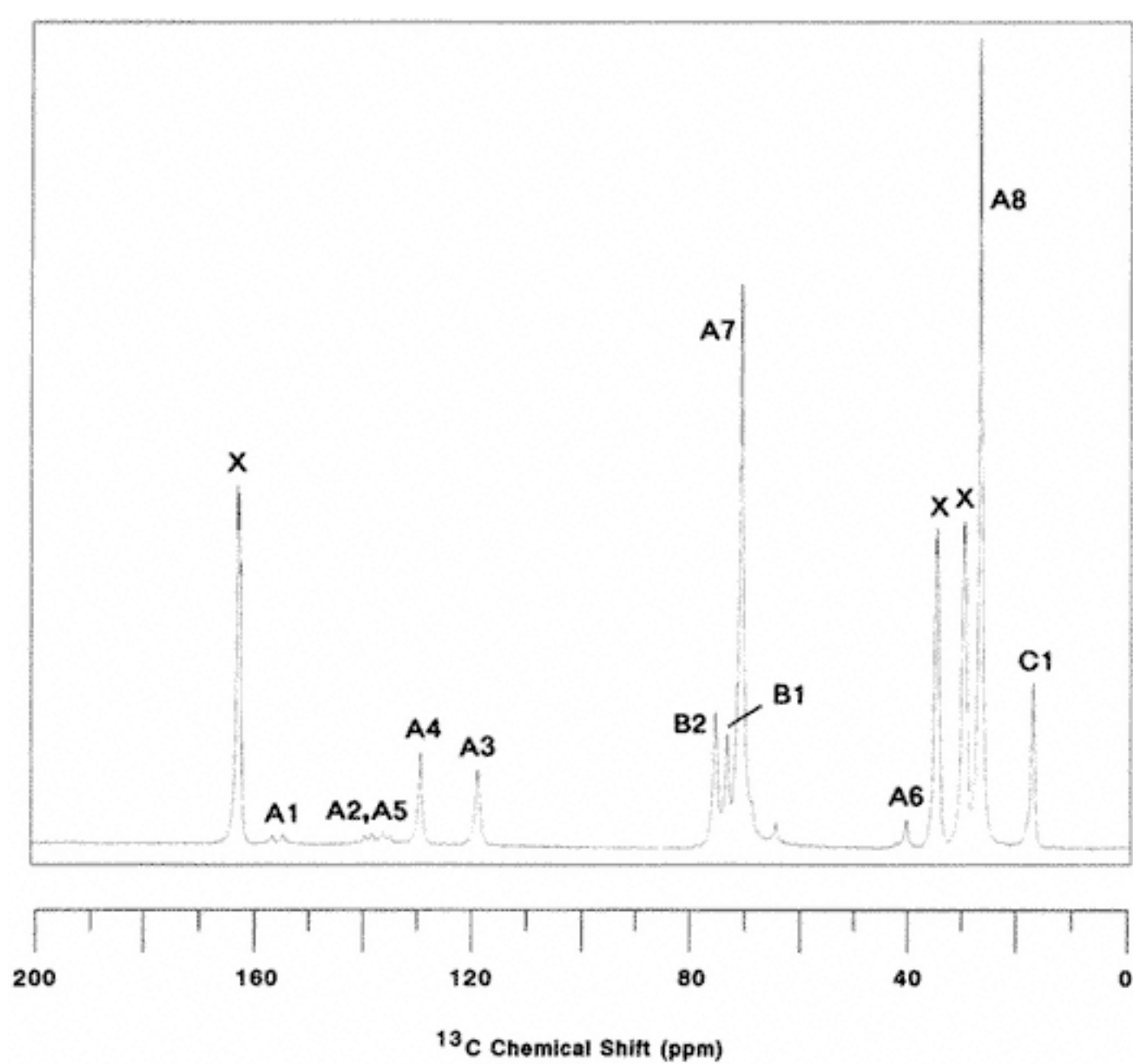
Pulse delay: 5 s

IX-B-2—

Poly[4,4'-Methylenebis(Phenyl Isocyanate)-Alt-1,4-Butanediol/Propylene Glycol]

Comments

Solvent resonances are marked by **X**. This material is a polyether urethane thermoplastic elastomer containing both stiff (carbons **A1–A8**) and flexible (carbons **B1, B2, and C1**) segments. It has good hydrolytic stability. It is found in sporting goods, tubing, cable jackets, gears, automotive parts, and as spandex fibers in hosiery and other clothing.



Code	Shift (ppm)
A1	155.8
A2	135–142
A3	119.3
A4	130.6
A5	135–142
A6	41.8
A7	71.3
A8	28.4
B1	74.0
B2	76.9
C1	17.4

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: dimethylformamide- d_7

Concentration: 10% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

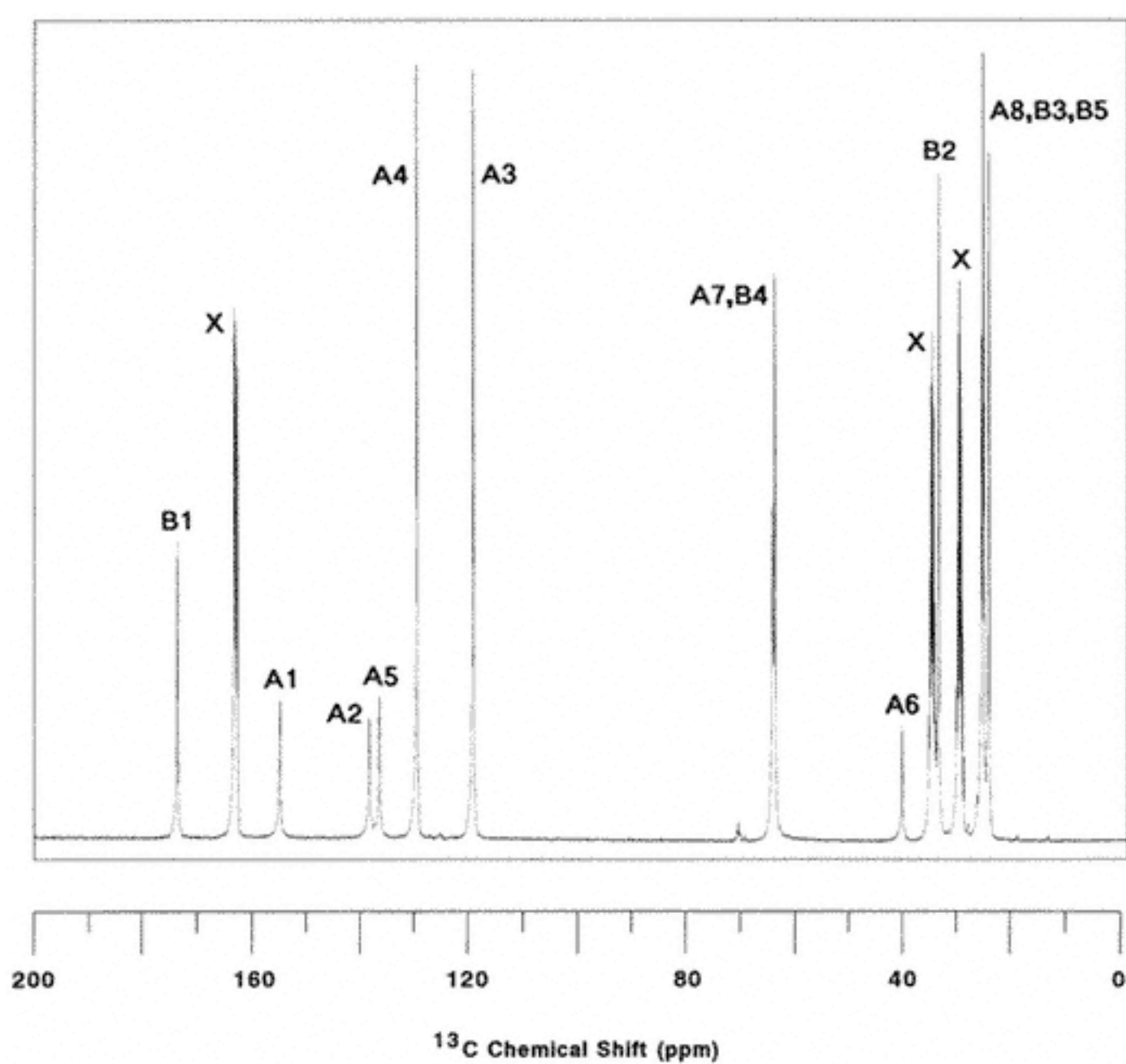
Pulse delay: 5 s

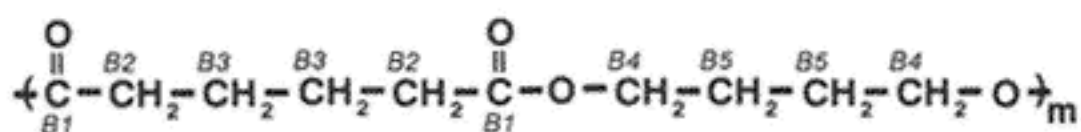
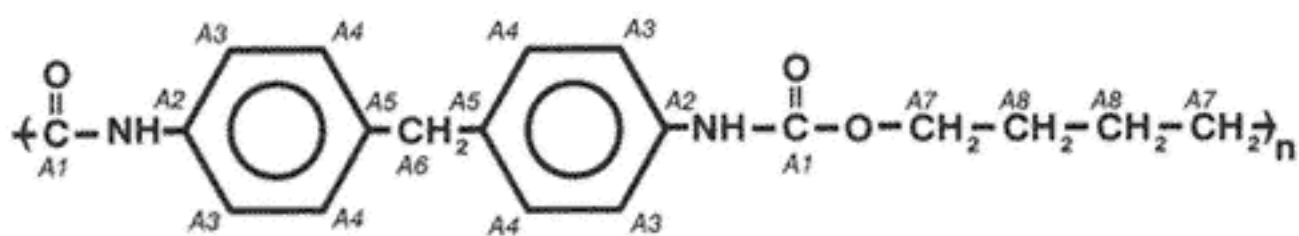
IX-B-3—

Poly[4,4'-Methylenebis(Phenyl Isocyanate)-Alt-1,4-Butanediol/Poly(butylene Adipate)]

Comments

Solvent resonances are marked by **X**. This material is a polyester urethane thermoplastic elastomer containing both stiff (carbons **A1–A8**) and flexible (carbons **B1–B5**) segments. It has good hydrolytic stability and oil resistance, and is found in sporting goods, tubing, cable jackets, gears, automotive parts, and as spandex fibers in hosiery and other clothing.





Code	Shift (ppm)
A1	155.0
A2	139.1
A3	119.3
A4	130.2
A5	136.8
A6	41.4
A7	65.0
A8	26.3
B1	174.0
B2	34.8
B3	25–26
B4	65.0
B5	25–26

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: dimethylformamide- d_7

Concentration 10% w/w

Scans: 8000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

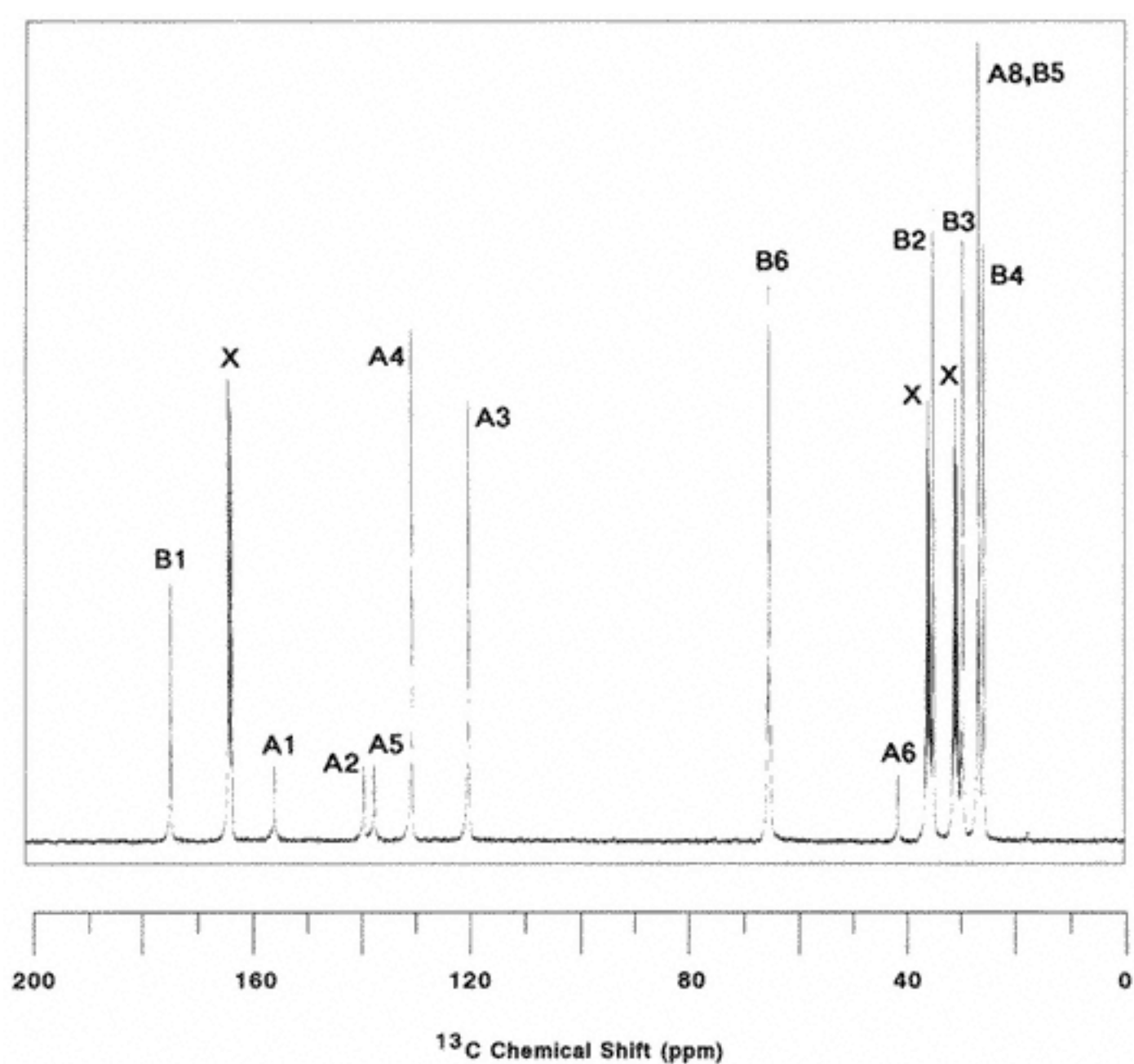
Pulse delay: 5 s

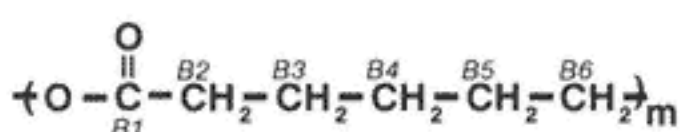
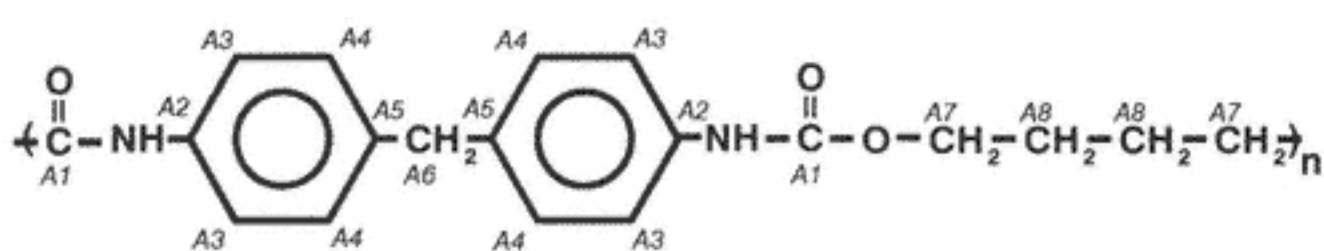
IX-B-4—

Poly[4,4'-Methylenebis(Phenyl Isocyanate)-Alt-1,4-Butanediol/Polycaprolactone]

Comments

Solvent resonances are marked by **X**. This material is a polyether ester urethane thermoplastic elastomer containing both stiff (carbons **A1–A8**) and flexible (carbons **B1–B6**) segments. It has good oil resistance, and is found in sporting goods, tubing, cable jackets, gears, automotive parts, and as spandex fibers in hosiery and other clothing.





Code	Shift (ppm)
A1	155.5
A2	139.1
A3	120.1
A4	130.1
A5	137.0
A6	40.7
A7	65.1
A8	26.3
B1	174.4
B2	34.8
B3	30.2
B4	24.7
B5	30.2
B6	65.1

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: dimethylformamide- d_7

Concentration: 10% w/w

Scans: 1000

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

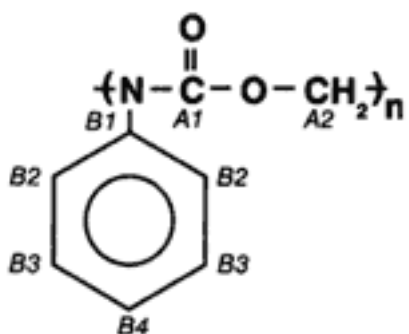
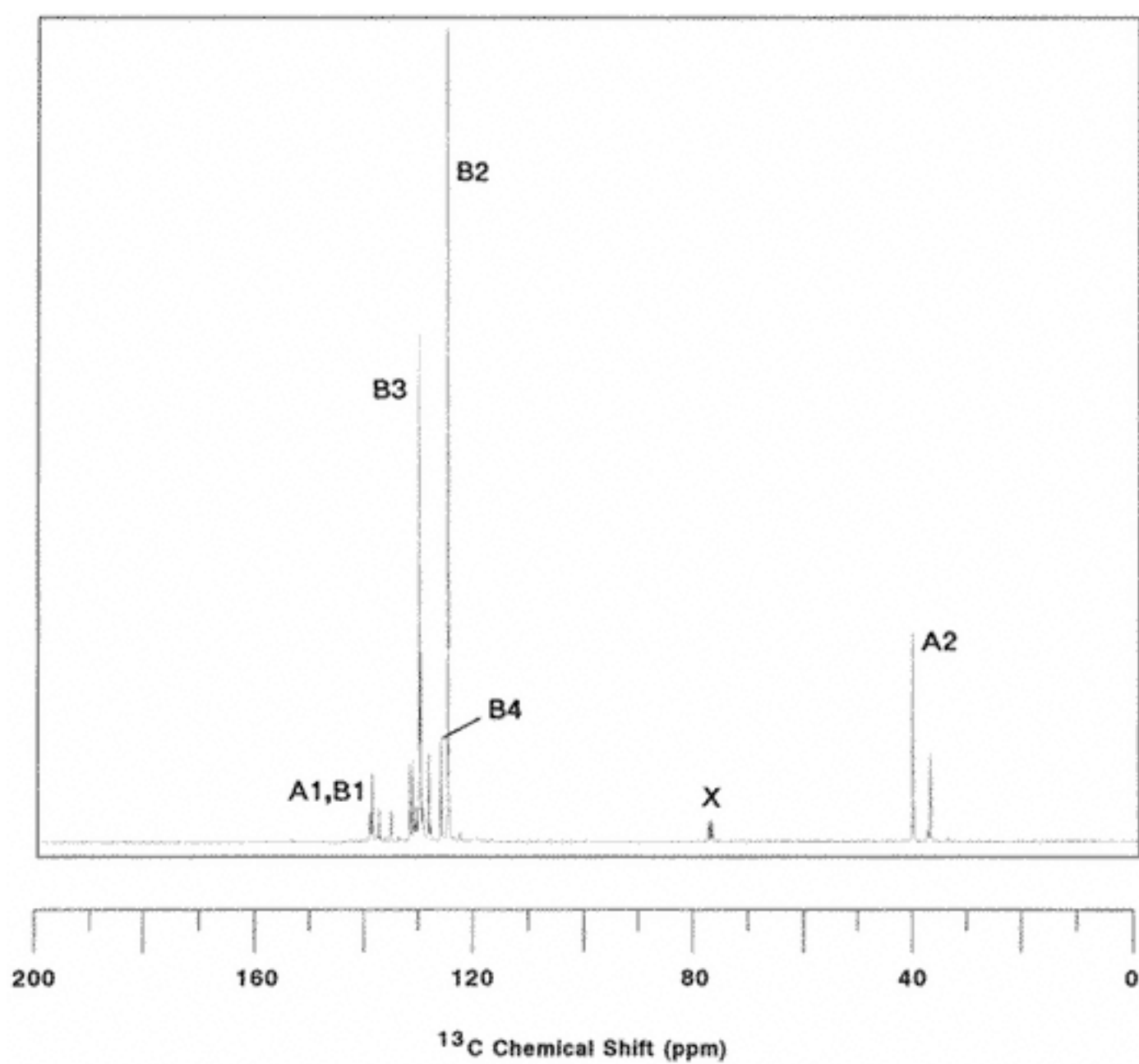
Broadening: 2 Hz

Pulse delay: 5 s

**IX-B-5—
Poly(Phenyl Isocyanate-Co-Formaldehyde)**

Comments

Solvent resonances are marked by X. This polymer has an aliphatic urethane backbone.



Code	Shift (ppm)
A1	136–139
A2	37–40
B1	136–139
B2	124.4
B3	129.6
B4	125.8

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 800

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

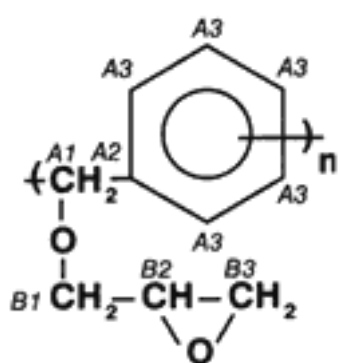
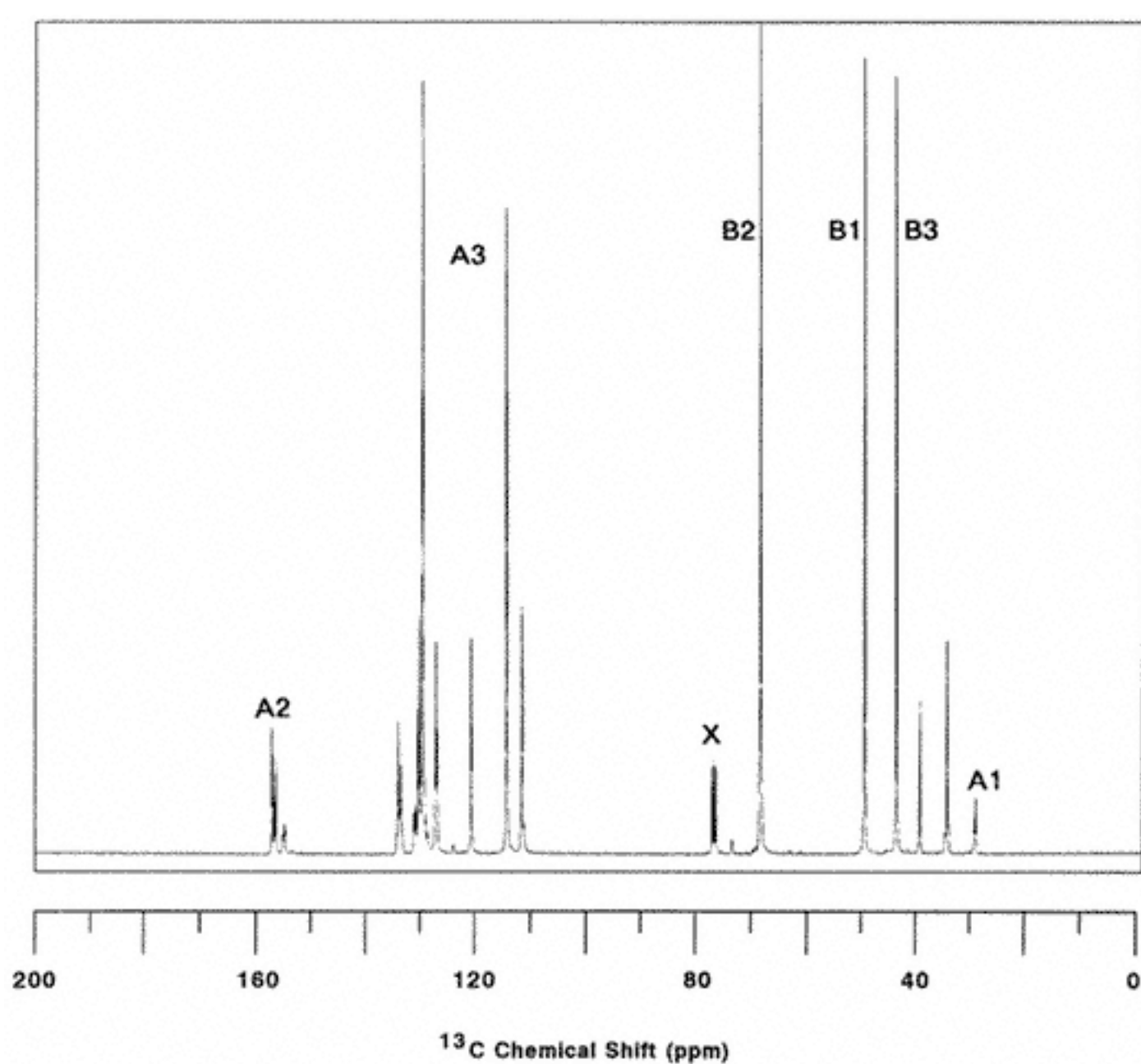
Broadening: 2 Hz

Pulse delay: 5 s

**IX-B-6—
Poly(Phenyl Glycidyl Ether-Co-Formaldehyde)**

Comments

The spectrum is complex because of the variability of ring substitution. Solvent resonances are marked by **X**. This is an epoxy prepolymer. The final, cross-linked materials are used in surface coatings, laminates, composites, molding, flooring, and adhesives.



Code	Shift (ppm)
A1	30–40
A2	~157
A3	112–135
B1	50.7
B2	69.4
B3	44.8

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 20% w/w
Scans: 800	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 5 s

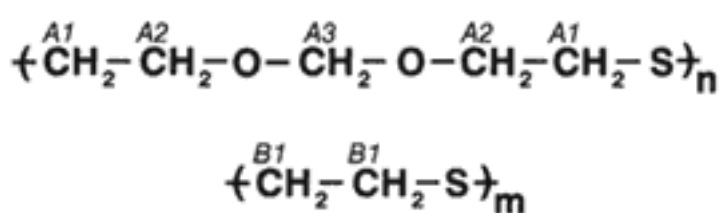
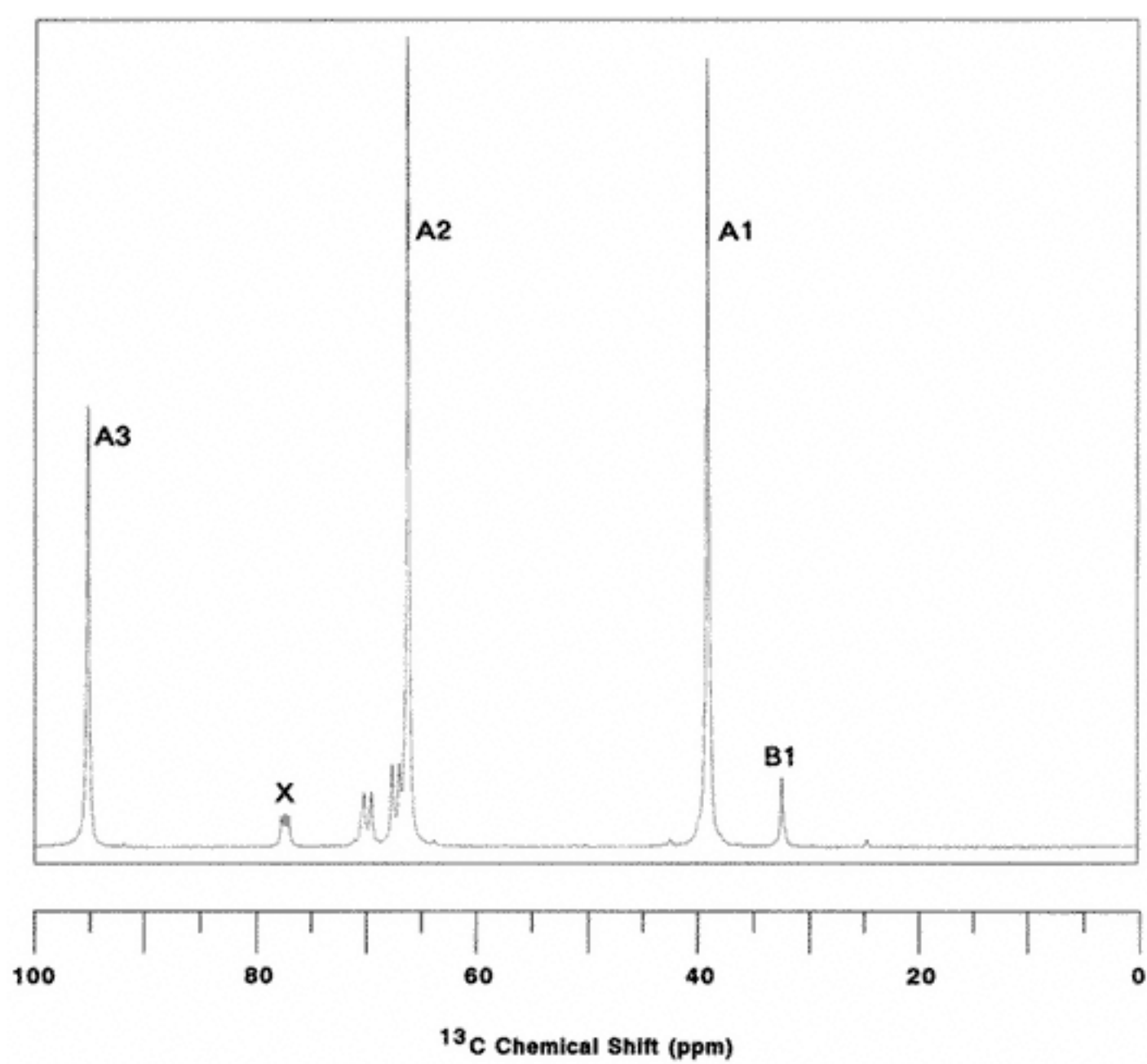
Reference

R. K. Harris, R. R. Yeung, P. Johncock, and D. A. Jones. *Polymer* 37:721, 1996.

**IX-B-7—
Poly(Ethyl Formal Sulfide)**

Comments

Also known as Thiokol (Morton Thiokol) or polysulfide rubber. Solvent resonances are marked by **X**. This material has excellent oil and chemical resistance and high-temperature properties. It is used in fuel hoses, tubing, binders, caulking compounds, sealants, and casting.



Code	Shift (ppm)
A1	39.1
A2	66.3
A3	95.4
B1	32.3

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 10% w/w
Scans: 1000	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 5 s

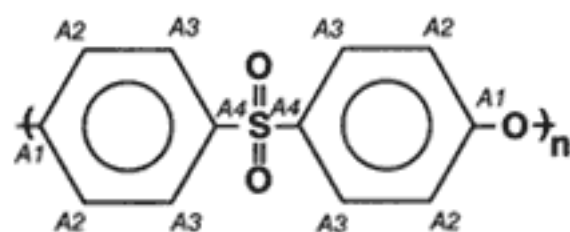
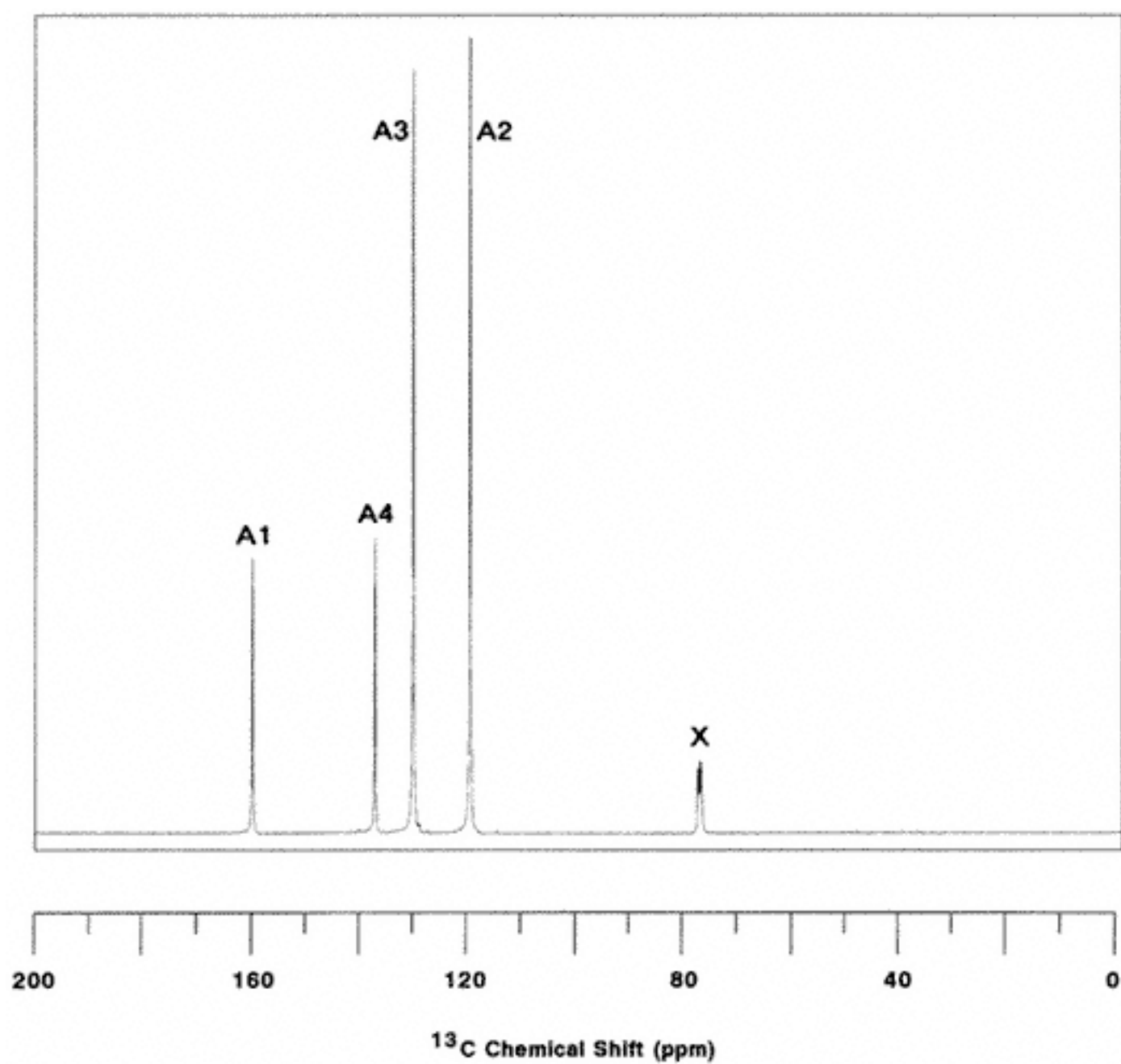
Reference

W. Mazurek and A. G. Moritz. *Macromolecules* 24:3261, 1991.

**IX-B-8—
Poly(Phenylene Ether Sulfone)**

Comments

Solvent resonances are marked by **X**. This high-performance engineering resin is used to make mechanical parts, appliance housings, and electrical connectors.



Code	Shift (ppm)
A1	160.1
A2	120.1
A3	130.6
A4	137.6

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 10% w/w
Scans: 800	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 5 s

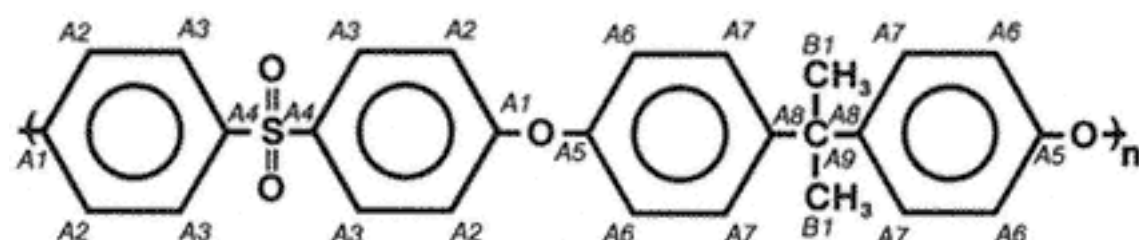
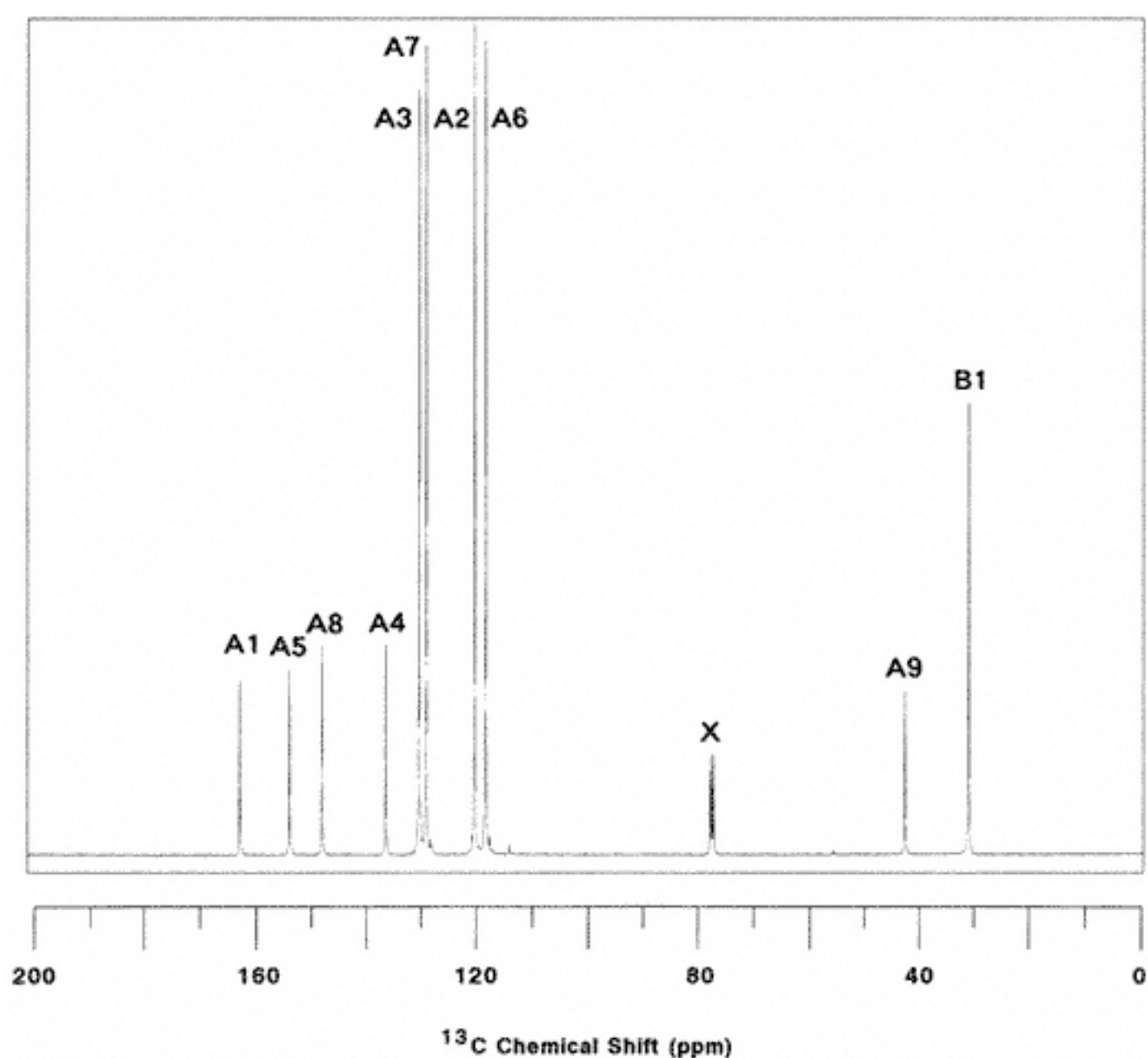
Reference

F. H. Roos, W. H. Daly, M. N. Aniano-Ilaio, and I. I. Negulescu. *J. Macromol. Sci. Pure Appl. Chem.* A33:275, 1996.

**IX-B-9—
Poly(Bisphenol A-Co-phenylene Ether Sulfone)**

Comments

Also known as Udel (Union Carbide). Solvent resonances are marked by **X**. This high-performance engineering resin is used to make mechanical parts, appliance housings, and electrical connectors.



Code	Shift (ppm)
A1	162.1
A2	120.1
A3	130.0
A4	136.0
A5	153.3
A6	118.0
A7	128.6
A8	147.4
A9	42.6
B1	31.1

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 800

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

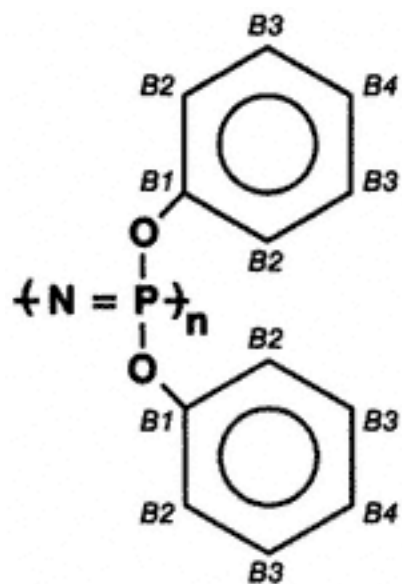
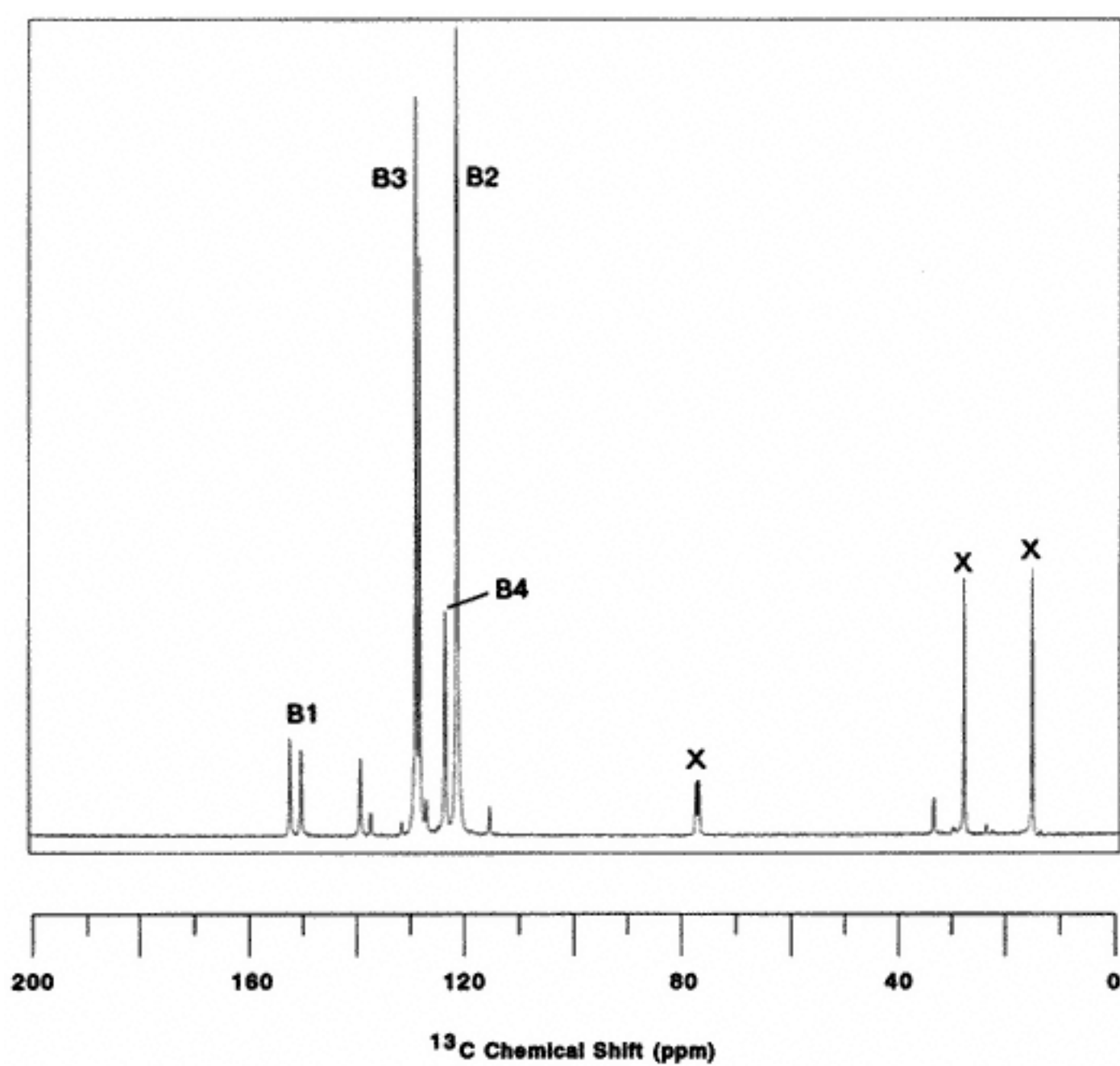
Pulse delay: 5 s

IX-B-10

**IX-B-10—
Polydiphenoxyphosphazene**

Comments

Solvent resonances are marked by **X**. This elastomer is used in high-performance applications because of its excellent resistance to oil, fuel, and chemicals, and its ability to maintain good mechanical properties over a wide temperature range. It is used for O-rings, gaskets, and hydrocarbon fuel hoses.



Code	Shift (ppm)
B1	150–153
B2	121.6
B3	129.3
B4	124.1

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 800

Spectral width: 25 kHz

Data points: 16384

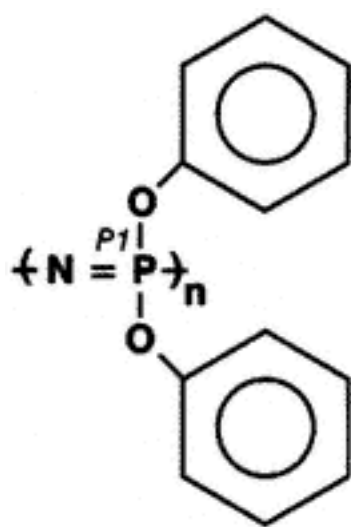
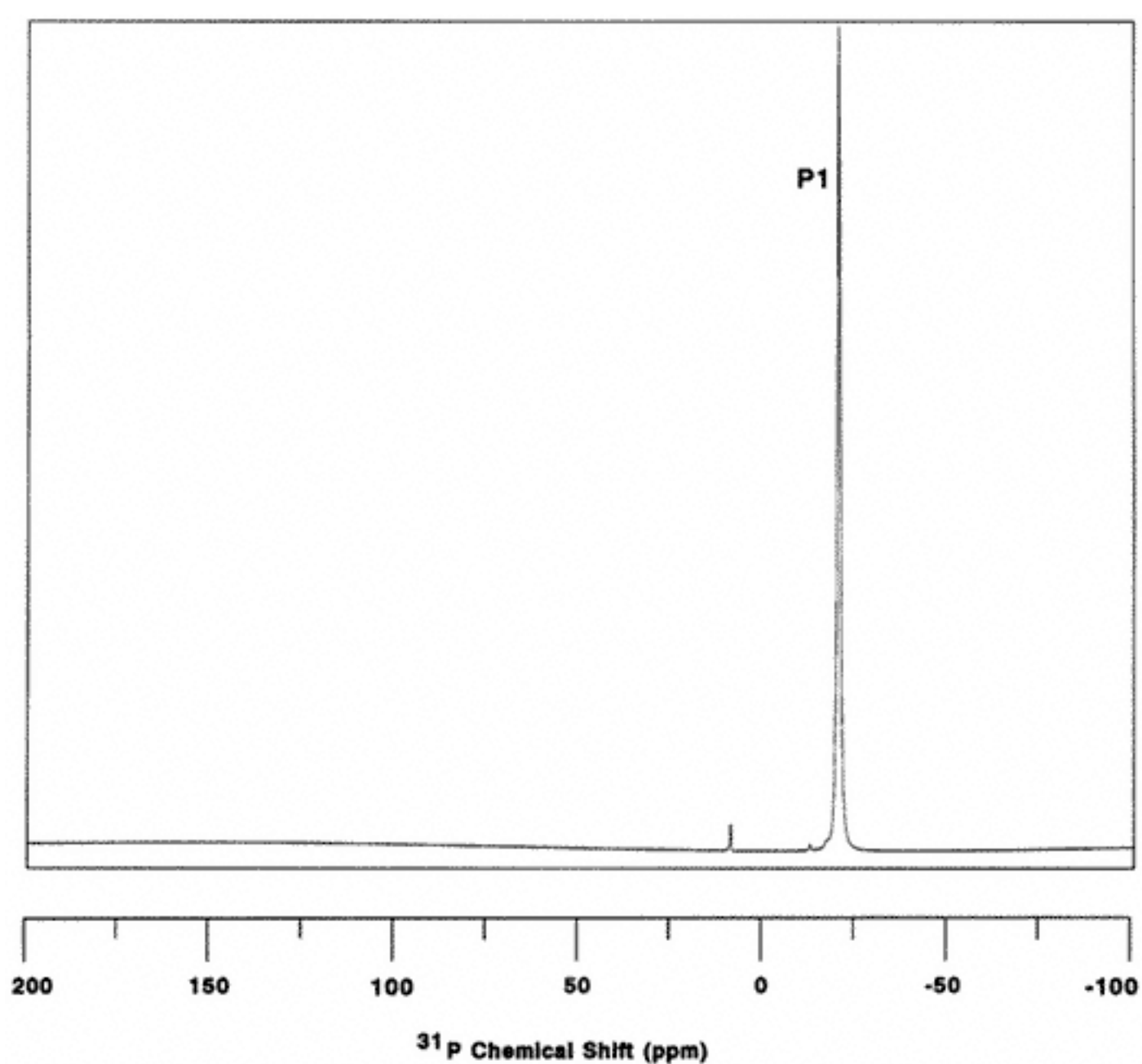
Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

**IX-B-10P—
Polydiphenoxyphosphazene****Comments**

This elastomer is used in high-performance applications because of its excellent resistance to oil, fuel, and chemicals, and its ability to maintain good mechanical properties over a wide temperature range. It is used for O-rings, gaskets, and hydrocarbon fuel hoses.



Code	Shift (ppm)
P1	-19.3

Experimental ParametersNucleus: ^{31}P (161.8 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 48

Spectral width: 70 kHz

Data points: 8192

Pulse width: 30°

Broadening: 5 Hz

Pulse delay: 5 s

X—

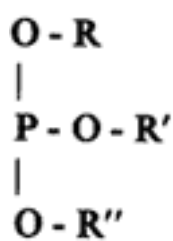
Polymer Additives

This chapter includes a variety of polymer additives, which are compounded into base resins in concentrations ranging from a few parts per million (ppm) to several percent. The additives included in this chapter are: (1) esters of saturated acids; (2) esters of unsaturated acids; (3) esters of aromatic di- or triacids; (4) phosphates and phosphites; and (5) other compounds, such as alkanes (halogenated and nonhalogenated) and sulfonamides. Sometimes, low molecular weight (MW) forms of polymers described in previous chapters are also used as additives; in such cases, these uses are noted in the comments for those entries.

Most finished polymer products contain a variety of additives that modify polymer properties by, for example, lowering the glass-transition temperature, imparting stability, or improving melt-flow behavior [1,2]. Some of the major classes of polymer additives and their target properties are listed in Table X-1; not all are amenable to NMR analysis. Many of the organic additives are used at very low levels (< 0.5 wt%), so that their carbon and hydrogen signals are lost among the polymer resonances under normal spectral-acquisition conditions. Other nuclei that are found in many additives, such as oxygen, nitrogen, and sulfur, have very unfavorable NMR properties; their signals are difficult to acquire and/or different species are not well resolved. This chapter includes some of the additives that can be readily observed by NMR, either because they are used at relatively high concentrations, or because they contain a unique element with favorable NMR properties.

Additives that lower the glass-transition temperature T_g are called *plasticizers*, and they are used in many polymers, such as polystyrene (PS) {III-A-2}, poly(vinyl chloride) (PVC) {V-A-8}, poly(vinyl acetate) (PVA) {IV-A-1}, poly(methyl methacrylate) {IV-C-1} (PMMA), and cellulosic materials {VII-B-1 through VII-B-10} [1,2]. Not all plasticizer-resin combinations exhibit stability; Table X-2 lists several plasticizers and the materials with which they are compatible. A polymer that is normally brittle at its intended use temperature becomes more flexible when a plasticizer is added. For example, unplasticized poly(vinyl chloride) (referred to as "rigid PVC") is found in pipe and building siding. This is obviously quite a different material from the "flexible PVC" used in upholstery and waterproof clothing. The most commonly encountered plasticizer for PVC is di(2-ethylhexyl phthalate) (DEHP) {X-C-8}, also known as dioctyl phthalate (DOP). Many of these additives impart other advantageous properties, such as stabilization, or are used as ingredients in other formulations, such as perfumes or detergents; these other applications are also given in Table X-2.

Many materials contain *antioxidants* (AOs) that protect a resin from oxidative degradation [1,2]. The most widely used AOs are hindered phenolics, which contain only carbon, hydrogen, and oxygen. Other *secondary AOs* are phosphorus-containing; these additives are often used in conjunction with hindered phenolics [1,2]. ^{31}P nuclei are easily observed by NMR, even at low levels (~50 μg phosphorus per gram) [3,4]. The original phosphite form:

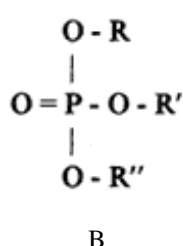


A

where R, R' and R'' may be the same or different, is oxidized to a phosphate species during normal processing:

Table X.1 Common Types of Polymer Additives

Class	Property affected	Typical chemical species
Antioxidants	Oxidative stability	Hindered phenols, lactones, thiodipropionates, phosphites
Light stabilizers	Light/color stability	Hindered amines, benzophenones, benzotriazoles, organotin compounds
Flame retardants	Flammability	Antimony trioxide, zinc borate, brominated compounds, chlorinated compounds, organophosphorus compounds
Impact modifiers	Toughness	Elastomers, such as polyisobutylene, poly(ethylene-co-propylene)
Plasticizers	Flexibility	Fatty acid esters, phthalate esters, phosphates, toluenesulfonamides, citrate esters, acetate esters, chlorinated paraffins
Tackifiers	Film surface tackiness	Polyisobutylene, glycerol monooleate
Antiblock agents	Film surface roughness	Silica, talc
Slip agents	Film surface slipperiness	Fatty acid amides
Antistatic agents	Static charge	Hydroxylated amines
Processing aids	Melt viscosity	Poly(ethylene glycol), polyacrylates, poly(vinylidene fluoride), fluoroelastomers, low-MW hydrocarbon waxes, poly(styrene-co-butadiene)
Dyes/pigments	Color, opacity	Titanium dioxide, carbon black, phthalocyanines, various other organic and inorganic compounds
Fillers/extenders	Mechanical strength, opacity	Aluminas, silicates, kaolinites, glass, calcium carbonate, diatomite, clays, talcs, ellulosics
Dispersants	Pigment/filler uniformity	Low-MW polyethylenes, poly(ethylene-co-vinyl acetate), low-MW polyacrylates, succinimides
Adhesion promoters	Polymer/filler adhesion	Silanes, phosphates, acrylate esters
Bactericides/fungicides	Resistance to bacterial or fungal growth	Isothiazolins, organotin compounds, organomercury compounds, organoarsenic compounds
Blowing agents	Foam structure	Chlorofluorocarbons, hydrocarbons, azodicarbonamides



where R, R' or R'' can be either an organic group or hydrogen. ^{31}P NMR is easily able to distinguish these different forms.[5].

X.A—

Sample Preparation and Spectral Acquisition

Most of these additives are soluble in a number of common solvents, such as chloroform, benzene, toluene, or acetone. However, if the presence of an additive is to be detected, the solubility of the polymer matrix must also be considered. Typically, a 30-s pulse delay following a 45° pulse, with gated ^1H decoupling, will ensure that relative ^{13}C peak areas are quantitative, whether the additive is neat or in a polymer. Appropriate ^1H quantitative conditions are the same as outlined for most other materials in this collection: 5-s delay after a 45° pulse. For ^{31}P NMR, correct relative areas result from 10-s delay following a 45° pulse, usually with continuous ^1H decoupling.

X.B—

Spectral Features

The list of additives included in this chapter indicates that most are esters. Their ^{13}C NMR spectrum will, therefore, have many similarities: a $\text{C}=\text{O}$ resonance at 165–180 ppm, $\text{C}-\text{O}$ at 50–75 ppm, and a variety of other resonances corresponding to the remaining carbons. ^{13}C chemical shifts for this chapter's entries are summarized in Tables X-3, X-4, and X-5.

Table X.2 Plasticizer Uses^a

Plasticizer	Code	PS	PVA	PVC	PMMA	EC	CA	CAB	CN	Others ^b
Glycerol triacetate	X-A-1		x		x	x	x	x	x	7,8
Methyl laurate	X-A-2		x			x	x			9–13
Isopropyl myristate	X-A-3					x		x	x	
Methyl palmitate	X-A-4					x			x	
Butyl stearate	X-A-5				x		x	x	x	4,5,13–17
Propylene glycol monostearate	X-A-6								x	9
2-Ethylhexyl epoxystearate	X-A-7			x			x			10
Diethyl succinate	X-A-8						x	x	x	18
Di(2-ethylhexyl) adipate	X-A-9	x	x	x	x	x	x	x	x	1,2
Dinonyl adipate	X-A-10	x	x	x	x	x	x	x		1,2
Di(<i>n</i> -hexyl) azelate	X-A-11		x	x		x	x	x	x	1,2
Di(2-ethylhexyl) azelate	X-A-12		x	x	x	x	x	x	x	1,2,13
Di(2-ethylhexyl) sebacate	X-A-13	x	x	x	x	x	x	x	x	1,2
Tri(<i>n</i> -butyl) citrate	X-A-14	x	x	x	x	x	x	x	x	1,2,19
Acetyl tri(<i>n</i> -butyl) citrate	X-A-15	x	x	x		x	x	x	x	1,2
Di(<i>n</i> -butyl) maleate	X-B-1		x							
Di(<i>n</i> -butyl) fumarate	X-B-3		x	x						1
Methyl oleate	X-B-4	x	x	x	x	x			x	1,2,9,11,12,17,20
Glycerol monooleate	X-B-5	x	x	x	x	x	x	x	x	1,2,10,11,14,15,21
Butyl ricinoleate	X-B-6	x	x			x		x	x	1,2
Propylene glycol ricinoleate	X-B-7	x				x			x	6,13,14,22
Glycerol tri(12-acetyl ricinoleate)	X-B-8	x	x	x		x			x	1
Methyl linoleate	X-B-9									9–13,23
Epoxidized linseed oil	X-B-10			x						10
Epoxidized soybean oil	X-B-11			x		x		x	x	1,10
Dimethyl phthalate	X-C-1	x	x	x	x	x	x	x	x	1,2,4,5,15,24
Diethyl phthalate	X-C-2	x	x	x	x	x	x	x	x	1,2
Di(<i>i</i> -butyl) phthalate	X-C-3	x	x	x		x		x	x	2
Butyl 2-ethylhexyl phthalate	X-C-4	x		x	x	x		x	x	1,2
Butyl benzyl phthalate	X-C-5	x		x	x	x	x	x		1,2
Dihexyl phthalate	X-C-6			x			x	x	x	1
Dicyclohexyl phthalate	X-C-7	x	x	x	x	x	x	x	x	1,2,5
Di(2-ethylhexyl) phthalate	X-C-8	x		x	x	x	x		x	1
Diisooctyl phthalate	X-C-9	x		x	x	x		x	x	1,2,4
Diundecyl phthalate	X-C-10		x							
Dimethyl isophthalate	X-C-11	x		x		x		x	x	1,2
Diphenyl isophthalate	X-C-13									25
Tri(2-ethylhexyl) trimellitate	X-C-14			x						
Tributyl phosphate	X-D-1	x	x		x	x	x	x	x	1,2
2-Ethylhexyl diphenyl phosphate	X-D-2									26
Triphenyl phosphate	X-D-3	x	x	x	x	x	x	x	x	1,26
Tricresyl phosphate	X-D-4	x	x	x		x	x	x	x	1,2
Tributoxyethyl phosphate	X-D-5	x	x	x		x	x	x	x	1,2
Mineral oil	X-E-1	x								
Chloroparaffin	X-E-2			x						12,13,16,26
<i>o</i> , <i>p</i> -Toluenesulfonamide	X-E-3		x			x	x	x	x	15
<i>N</i> -Ethyl- <i>o</i> , <i>p</i> -toluenesulfonamide	X-E-4		x			x	x	x	x	15

^a PS, polystyrene {III-A-2}; PVA, poly(vinyl acetate) {IV-A-1}; PVC, poly(vinyl chloride) {V-A-8}; PMMA, poly(methyl methacrylate) {IV-C-1}; EC, ethylcellulose {VII-B-3}; CA, cellulose acetate {VII-B-4}; CAB, cellulose acetate butyrate {VII-B-5}; CN, cellulose nitrate {VII-B-8}.

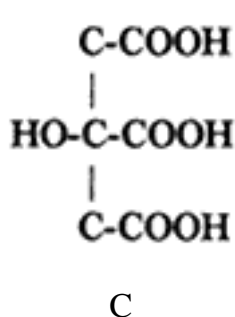
^b (1) poly(vinyl chloride-co-vinyl acetate) {V-A-9}; (2) poly(vinyl butyral) {V-B-6}; (3) poly(styrene-co-butadiene) {VI-A-4, VI-A-5}; (4) polyisoprene {VI-B-1}; (5) chlorinated polyisoprene {VI-B-3}; (6) polyurethanes {IX-B-1 through IX-B-4}; (7) perfumes; (8) fixatives; (9) emulsifiers; (10) stabilizers; (11) textile finishes; (12) detergents; (13) lubricants; (14) cosmetics; (15) lacquers, paints, coatings; (16) water sealants; (17) polishes, waxes; (18) flavorings; (19) antifoam additives; (20) inks; (21) tackifiers; (22) hydraulic fluids; (23) wetting agents; (24) molding resins; (25) polyimidazoles; (26) flame retardants.

Phosphorus-containing additives may also be studied by ^{31}P NMR. Phosphites, $\text{P}(\text{OR})_3$, resonate between 100 and 150 ppm, whereas the phosphates, $\text{O}=\text{P}(\text{OR})_3$, appear between 20 and -20 ppm. Further details about the relevant chemical shifts are given in the following.

X.B.1—

Aliphatic Acid Ester Additives

The plasticizers in this category include an acetic acid ester, esters of small polyfunctional acids, such as succinic (butanedioic) acid, adipic (hexanedioic) acid, or citric acid:



and esters of saturated fatty acids, such as lauric (dodecanoic) acid, palmitic (hexadecanoic) acid, or stearic (octadecanoic) acid. They are recognized from the resonances typical of aliphatic esters: $\text{C}=\text{O}$ at 170–175 ppm and $\text{C}-\text{O}$ at 50–75 ppm. As can be seen from Table X-3, the spectra of the fatty acid esters are very similar, because it is difficult to determine the length of the hydrocarbon chain by chemical shift alone. The carbons of the end groups are distinctive: 14.0 ppm for the methyl, 22.9 for the first methylene, and 32.2 for the second. A carbon adjacent to the carbonyl in the acid moiety usually appears at about 34 ppm. The particular fatty acid component of the ester can be identified by calculating the relative ratio of the areas of the group of resonances near 30 ppm (discounting any resonances associated with the alcohol part), compared with distinctive peaks, such as the end-group methylene at 22.9 ppm. These ratios are summarized in Table X-4 for several different fatty acids.

X.B.2—

Unsaturated Acid Ester Additives

The plasticizers in this group are esters of unsaturated mono- or difunctional acids. The diacids include maleic (*cis*-butenedioic) and fumaric (*trans*-butenedioic) acids. The monofunctional acids are monounsaturated fatty acids, such as oleic (*cis*-9-octadecenoic) or ricinoleic (*cis*-12-hydroxyoctadec-9-enoic) acids. Polyunsaturated acid esters, such as linseed or soybean oil, also fall into this category. ^{13}C spectra of unsaturated acids exhibit carbonyl resonances at 160–175 ppm, $\text{C}-\text{O}$ at 50–75 ppm, and olefinic resonances between 120 and 140 ppm. Shifts are summarized in Table X-5. The specific acid component can, again, be identified based on relative peak areas, as illustrated in Table X-4.

X.B.3—

Aromatic Ester Additives

The most commonly encountered plasticizers belong to this group; in fact, one material, di(2-ethylhexyl) phthalate (DEHP, also known as dioctyl phthalate or DOP) {X-C-8} accounts for 25% of all plasticizer use [6]. This category also includes phthalic (*o*-benzene dicarboxylic), isophthalic (*m*-benzene dicarboxylic), and trimellitic (1,2,4-benzene tricarboxylic) acid esters. Their carbonyl resonances occur at 165–170 ppm; their aromatic carbons, between 125 and 135 ppm; and $\text{C}-\text{O}$, between 50 and 75 ppm. Some of the higher alcohols (hexyl, octyl, and so on) found in these esters are mixtures of isomers, which lead to very complex patterns in the alkyl region of the spectrum. ^{13}C chemical shifts are listed in Table X-6.

X.B.4—

Phosphorus-Containing Additives

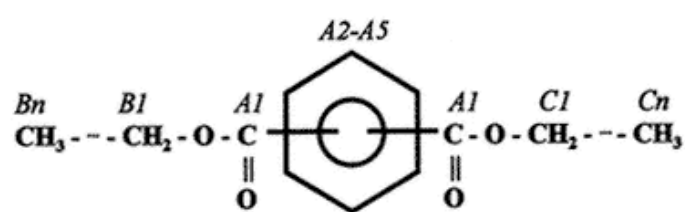
Phosphoric acid esters may also be used as plasticizers. The ^{13}C spectrum of a phosphate ester may be confused with that of the corresponding alcohol; they may be distinguished by the presence of a ^{31}P signal that appears between 20 and -20 ppm. At typical plasticizer levels (1–10 wt%), the concentration of phosphorus in the sample is about 0.05–0.5 wt%; ^{31}P signals are readily observed at these levels.

Table X.3 ¹³C Chemical Shifts of Saturated-Acid Ester Plasticizers

Plasticizer	Code	$\begin{array}{c} \text{An} \quad \text{A2} \quad \text{A1} \quad \text{B1} \quad \text{Bn} \\ \text{CH}_3 - \text{---} - \text{CH}_2 - \text{C} - \text{O} - \text{CH}_2 - \text{---} - \text{CH}_3 \\ \parallel \\ \text{O} \end{array}$														
		A1	A2	A3	A4	A5	A6	A7	B1	B2	B3	B4	B5	B6	B7	B8
Glyceroltriacetate	X-A-1	170.2	19.6	—	—	—	—	—	61.6	68.8	—	—	—	—	—	—
Methylaurate	X-A-2	173.9	34.0	24.7	29.1	31.9	22.6	13.7	50.8	—	—	—	—	—	—	—
Isopropylmyristate	X-A-3	173.0	34.2	24.8	29.1	30.6	22.5	13.5	66.8	21.5	—	—	—	—	—	—
Methylpalmitate	X-A-4	173.1	33.9	24.6	29.1	31.9	22.5	13.1	50.7	—	—	—	—	—	—	—
Butylstearate	X-A-5	173.0	34.4	25.8	30.6	32.0	22.4	13.5	64.4	30.9	18.9	13.5	—	—	—	—
Propyleneglycolmonostearate	X-A-6	173.5	34.2	25.3	30.0	32.2	22.9	14.3	65–71	65–71	19.1	—	—	—	—	—
Diethylsuccinate	X-A-8	172.2	28.7	—	—	—	—	—	60.0	13.5	—	—	—	—	—	—
Di(2-ethylhexyl)adipate	X-A-9	172.2	33.7	24.2	—	—	—	—	66.3	38.7	30.3	28.7	22.6	13.4	23.0	10.4
Dinonyladipate	X-A-10	172.7	33.7	22.0	—	—	—	—	62.5	37.1	50.8	26.1	29.7	24.2	—	—
Di(<i>n</i> -hexyl)azelate	X-A-11	173.1	34.0	26.4	28.4	28.4	—	—	64.0	28.4	25.3	31.1	22.2	13.5	—	—
Di(2-ethylhexyl)azelate	X-A-12	173.1	34.0	24.7	28.4	—	—	—	66.4	38.7	30.3	28.4	22.6	13.5	23.6	10.6
Di(2-ethylhexyl)sebacate	X-A-13	173.1	34.0	24.7	28.7	—	—	—	66.2	38.6	30.3	28.7	22.6	13.6	23.6	10.6

Table X.4 Relative Peak Areas for Fatty-Acid Esters

Type	No. Carbons	No. COOH's	No. (C=)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---CH}_2\text{---CH}_2\text{---CH}_2\text{---} \text{---} \text{---CH}_2\text{---CH}_2\text{---CH}_3 \\ \text{A} \quad \text{B} \quad \text{C} \quad \text{---} \quad \text{C} \quad \text{D} \quad \text{E} \end{array}$				
				A (28–34 ppm)	B (24–25 ppm)	C (~30 ppm)	D (22–23 ppm)	E (13–14 ppm)
Laurate	12	1	0	1	1	7	1	1
Myristate	14	1	0	1	1	9	1	1
Palmitate	16	1	0	1	1	11	1	1
Stearate	18	1	0	1	1	13	1	1
Succinate	4	2	0	2	0	0	0	0
Adipate		2	0	2	2	0	0	0
Azelate	9	2	0	2	2	3	0	0
Sebacate	10	2	0	2	2	4	0	0
Oleate	18	1	2	1	1	11	1	1
Linoleate	18	1	4	1	1	9	1	1



Plasticizer	Code	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5	B6	B7	B8	C1	C2	C3	C4	C5	C6	C7	C8
Dimethyl phthalate	X-C-1	169.7	131.5	128.0	130.6	—	51.8	—	—	—	—	—	—	—	51.8	—	—	—	—	—	—	—
Diethyl phthalate	X-C-2	167.2	132.4	128.6	130.3	—	60.8	13.0	—	—	—	—	—	—	60.8	13.0	—	—	—	—	—	—
Di(<i>i</i> -butyl) phthalate	X-C-3	166.7	132.2	128.9	131.1	—	71.2	27.4	18.5	—	—	—	—	—	71.2	27.4	18.5	—	—	—	—	—
Butyl 2-ethylhexyl phthalate	X-C-4	166.9	132.7	128.3	130.3	—	64.7	30.0	18.3	13.5	—	—	—	—	67.4	38.4	30.0	28.4	22.0	13.5	23.4	10.4
Butyl benzyl phthalate	X-C-5	167.0	132.2	128.6	130.6	—	64.6	29.4	18.8	13.0	—	—	—	—	67.0	135.9	128.0	128.0	131.6	—	—	—
Dihexyl phthalate	X-C-6	167.9	138.6	127.8	130.9	—	63-66	10-40	—	—	—	—	—	—	63-66	10-40	—	—	—	—	—	—
Dicyclohexyl phthalate	X-C-7	167.4	133.5	128.5	130.9	—	75.2	30.9	23.5	25.6	—	—	—	—	75.2	30.9	23.5	25.6	—	—	—	—
Di(2-ethylhexyl) phthalate	X-C-8	168.0	132.9	129.3	130.9	—	67.8	38.7	30.1	28.7	22.8	13.5	23.4	10.7	67.8	38.7	30.1	28.7	22.8	13.5	23.4	10.7
Diocetyl phthalate	X-C-9	167.5	132.6	128.8	130.8	—	63-76	10-47	—	—	—	—	—	—	63-76	10-47	—	—	—	—	—	—
Diundecyl phthalate	X-C-10	167.4	133.0	128.6	130.5	—	65.4	10-34	—	—	—	—	—	—	65.4	10-34	—	—	—	—	—	—
Dimethyl isophthalate	X-C-11	166.4	130.9	130.9	133.4	128.4	51.2	—	—	—	—	—	—	—	51.2	—	—	—	—	—	—	—
Di(2-ethylhexyl isophthalate)	X-C-12	165.0	130.3	130.3	133.3	128.2	67.4	38.8	30.4	28.8	22.7	13.6	23.8	10.8	67.4	38.8	30.4	28.8	22.7	13.6	23.8	10.8
Diphenyl isophthalate	X-C-13	163.8	129.9	131.6	134.7	129.4	150.7	121.4	130.4	125.9	—	—	—	—	150.7	121.4	130.4	125.9	—	—	—	—

Organic phosphites, $P(OR)_3$, are used as antioxidants [1,2]. Because these additives {X-D-6P through X-D-10P} are used at very low concentrations (typically 0.1–0.5 wt%), it is virtually impossible to detect them by ^{13}C NMR. ^{31}P NMR is much more useful for this purpose, and it is also a powerful tool for characterizing the extent of degradation of the antioxidant [5]. If the antioxidant is not properly stored, it may become hydrolyzed to phosphoric acid (H_3PO_4), the ^{31}P signal of which appears at 0 ppm. As the polymer is processed, phosphites are oxidized to mono-, di-, and triesters. Because the additive is likely to be the only phosphorus-containing component of the material, and because ^{31}P is naturally abundant, an informative spectrum can be obtained even at low levels of P ($< 100 \mu\text{g/g P}$). The original, nondegraded phosphites resonate between 120 and 150 ppm; the degraded products, between 20 and –20 ppm, and relative peak areas directly reflect the degree of degradation the antioxidant has undergone during processing.

X.B.5—

Other Additives

Aside from the chemicals discussed on the foregoing, many other materials are used as polymer additives, a number of which were included in earlier chapters (see also Appendix 1). Low molecular weight hydrocarbons and their derivatives, such as mineral oil {X-E-1} and chloroparaffin {X-E-2}, exhibit complex ^{13}C spectra because of their highly irregular structures. ^{13}C spectra of toluenesulfonamides {X-E-3 and X-E-4} exhibit chemical shifts in the aromatic and aliphatic resonances; they are difficult to distinguish from non-sulfur-containing compounds [7].

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4. J. Mason, ed. *Multinuclear NMR*. New York: Plenum Press, 1987.
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6. J. K. Sears and N. W. Touchette. Plasticizers. In: *Encyclopedia of Polymer Science and Engineering*. New York: John Wiley & Sons, 1989.
7. E. Breitmaier and W. Voelter. *Carbon-13 NMR Spectroscopy*. New York: VCH Publishers, 1987.

POLYMER ADDITIVES*A. Aliphatic Esters*

X-A-1	Glycerol triacetate
X-A-2	Methyl laurate
X-A-3	Isopropyl myristate
X-A-4	Methyl palmitate
X-A-5	Butyl stearate
X-A-6	Propylene glycol monostearate
X-A-7	2-Ethylhexyl epoxystearate
X-A-8	Diethyl succinate
X-A-9	Di(2-ethylhexyl) adipate
X-A-10	Dinonyl adipate
X-A-11	Di(<i>n</i> -hexyl) azelate
X-A-12	Di(2-ethylhexyl) azelate
X-A-13	Di(2-ethylhexyl) sebacate
X-A-14	Tri- <i>n</i> -butyl citrate
X-A-15	Acetyl tri- <i>n</i> -butyl citrate

B. Unsaturated Esters

X-B-1	Di(<i>n</i> -butyl) maleate
X-B-2	Di(2-ethylhexyl) maleate
X-B-3	Di(<i>n</i> -butyl) fumarate
X-B-4	Methyl oleate
X-B-5	Glycerol monooleate
X-B-6	Butyl ricinoleate
X-B-7	Propylene glycol ricinoleate
X-B-8	Glycerol tri(12-acetyl ricinoleate)
X-B-9	Methyl linoleate
X-B-10	Epoxidized linseed oil
X-B-11	Epoxidized soybean oil

C. Aromatic Esters

X-C-1	Dimethyl phthalate
X-C-2	Diethyl phthalate
X-C-3	Diisobutyl phthalate
X-C-4	Butyl 2-ethylhexyl phthalate
X-C-5	Butyl benzyl phthalate
X-C-6	Diethyl phthalate
X-C-7	Dicyclohexyl phthalate
X-C-8	Di(2-ethylhexyl) phthalate
X-C-9	Diethyl phthalate
X-C-10	Diundecyl phthalate
X-C-11	Dimethyl isophthalate
X-C-12	Di(2-ethylhexyl) isophthalate
X-C-13	Diphenyl isophthalate
X-C-14	Tri(2-ethylhexyl) trimellitate

D. Phosphorus-Containing Additives

X-D-1	Tributyl phosphate
X-D-1P	Tributyl phosphate
X-D-2	2-Ethylhexyl diphenyl phosphate
X-D-2P	2-Ethylhexyl diphenyl phosphate
X-D-3	Triphenyl phosphate
X-D-3P	Triphenyl phosphate
X-D-4	Tricresyl phosphate
X-D-4P	Tricresyl phosphate
X-D-5	Tributoxyethyl phosphate
X-D-5P	Tributoxyethyl phosphate
X-D-6P	Bis(2,4-di- <i>t</i> -butylphenyl) pentaerythritol diphosphite
X-D-7P	Bis(2,4-di- <i>t</i> -butyl-6-methylphenyl)ethyl phosphite
X-D-8P	2,2',2''-Nitrilo triethyl-tris(3,3',5,5'-tetra- <i>t</i> -butyl-1,1'-biphenyl-2,2'-diyl) phosphite
X-D-9P	Tris(2,4-di- <i>t</i> -butylphenyl) phosphite
X-D-10P	Tris(nonylphenyl) phosphite

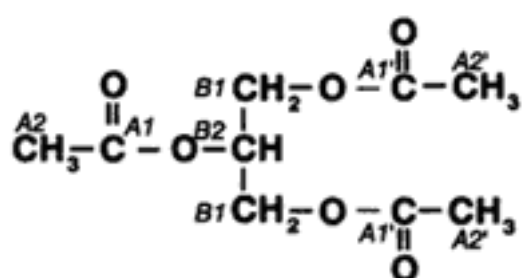
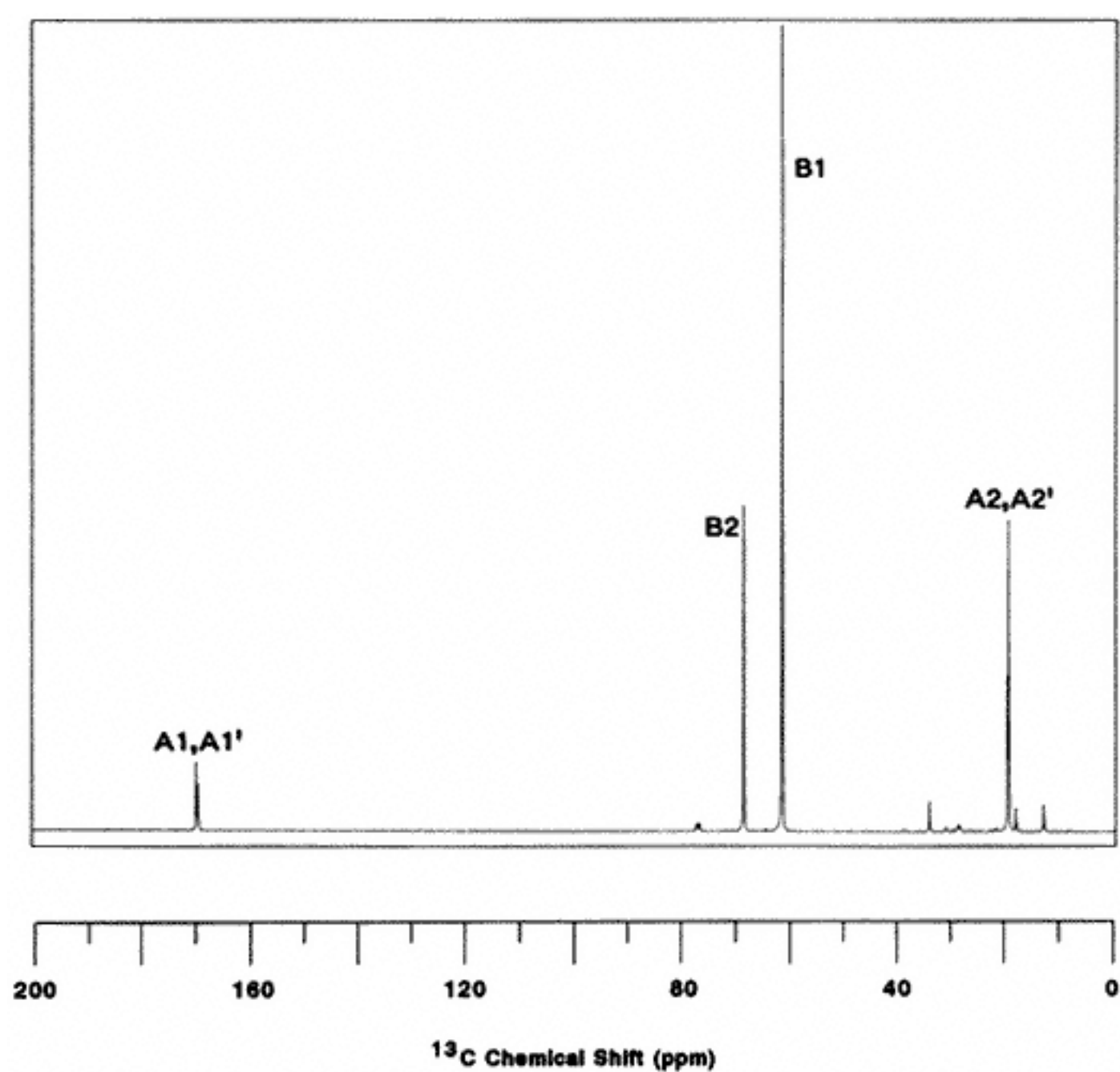
E. Other Additives

X-E-1	Mineral oil
X-E-2	Chloroparaffin
X-E-3	<i>o,p</i> -Toluenesulfonamide
X-E-4	<i>N</i> -Ethyl- <i>o,p</i> -toluenesulfonamide

**X-A-1—
Glycerol Triacetate**

Comments

Also known as triacetin. Solvent resonances are marked by **X**. This material is used as a plasticizer for poly(vinyl acetate) {IV-A-1}, poly(methyl methacrylate) {IV-C-1}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}, and as a fixative in perfumes and cosmetics.



Code	Shift (ppm)
A1	170.2
A1'	170.2
A2	19.6
A2'	19.6
B1	61.6
B2	68.8

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

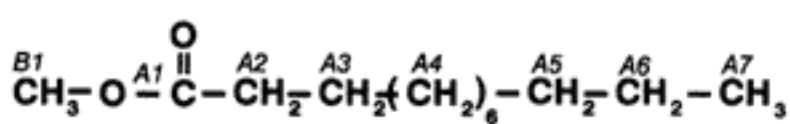
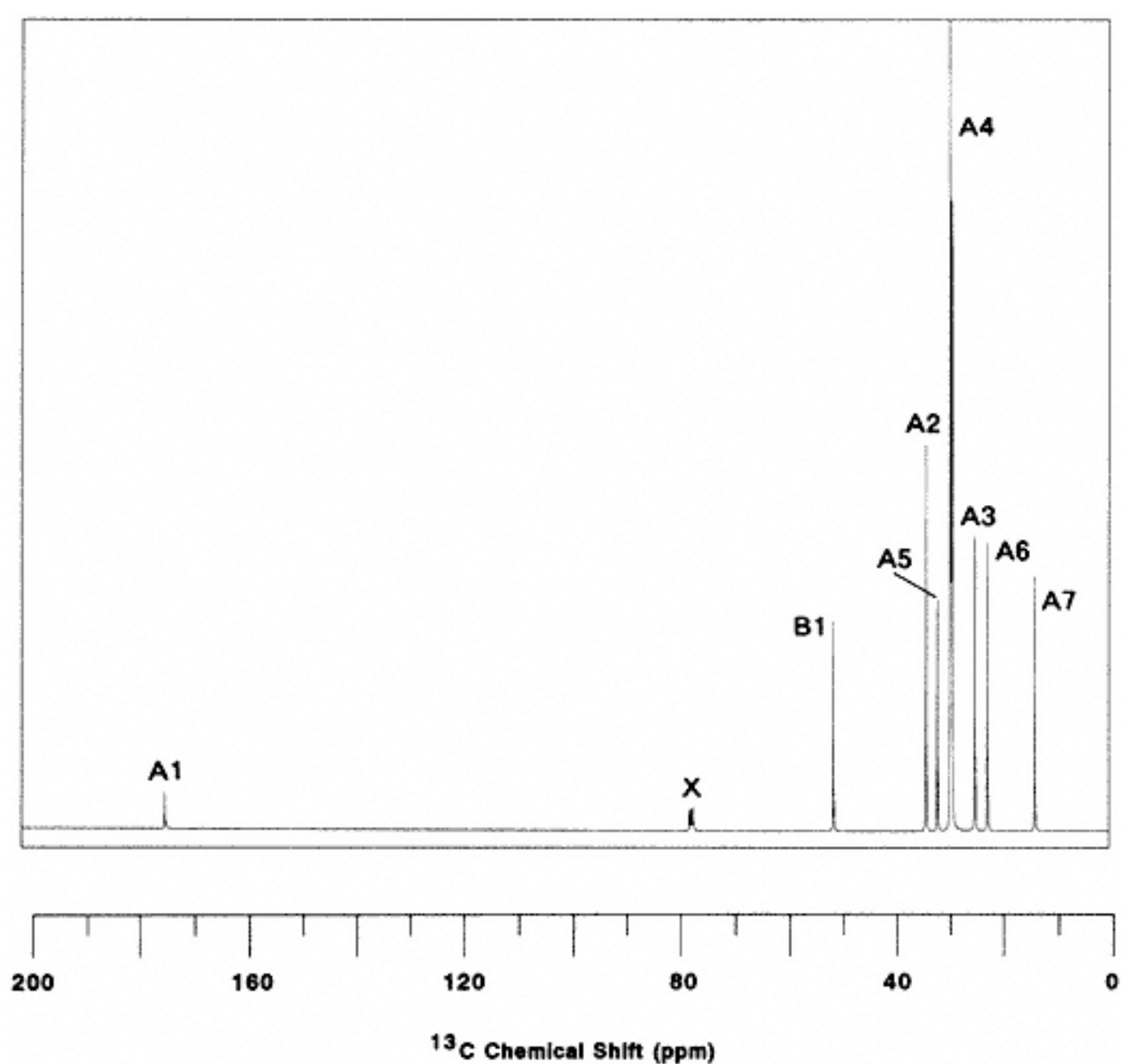
Broadening: 2 Hz

Pulse delay: 5 s

**X-A-2—
Methyl Laurate**

Comments

Also known as methyl dodecanoate. Solvent resonances are marked by **X**. This material is used in detergents, emulsifiers, stabilizers, lubricants, and textile finishes.



Code	Shift (ppm)
A1	173.9
A2	34.0
A3	24.7
A4	29.1
A5	31.9
A6	22.6
A7	13.7
B1	50.8

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

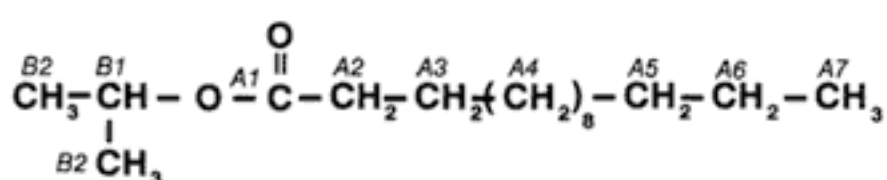
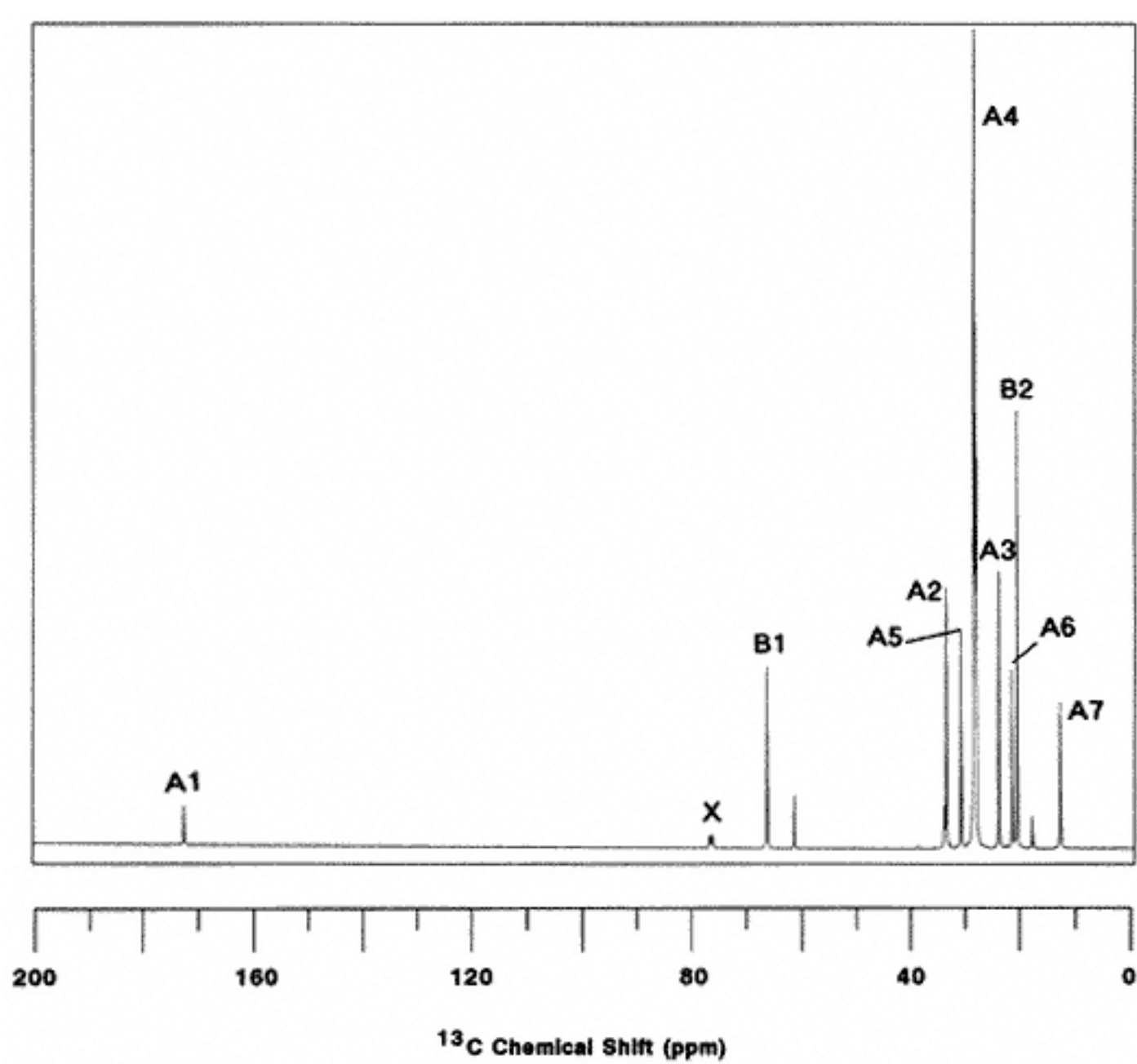
Broadening: 2 Hz

Pulse delay: 5 s

**X-A-3—
Isopropyl Myristate**

Comments

Also known as isopropyl tetradecanoate. Solvent resonances are marked by **X**. This material is used as a plasticizer in ethyl cellulose {VII-B-3}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
A1	173.0
A2	34.2
A3	24.8
A4	29.1
A5	30.6
A6	22.5
A7	13.5
B1	66.8
B2	21.5

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

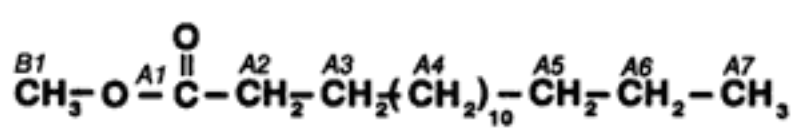
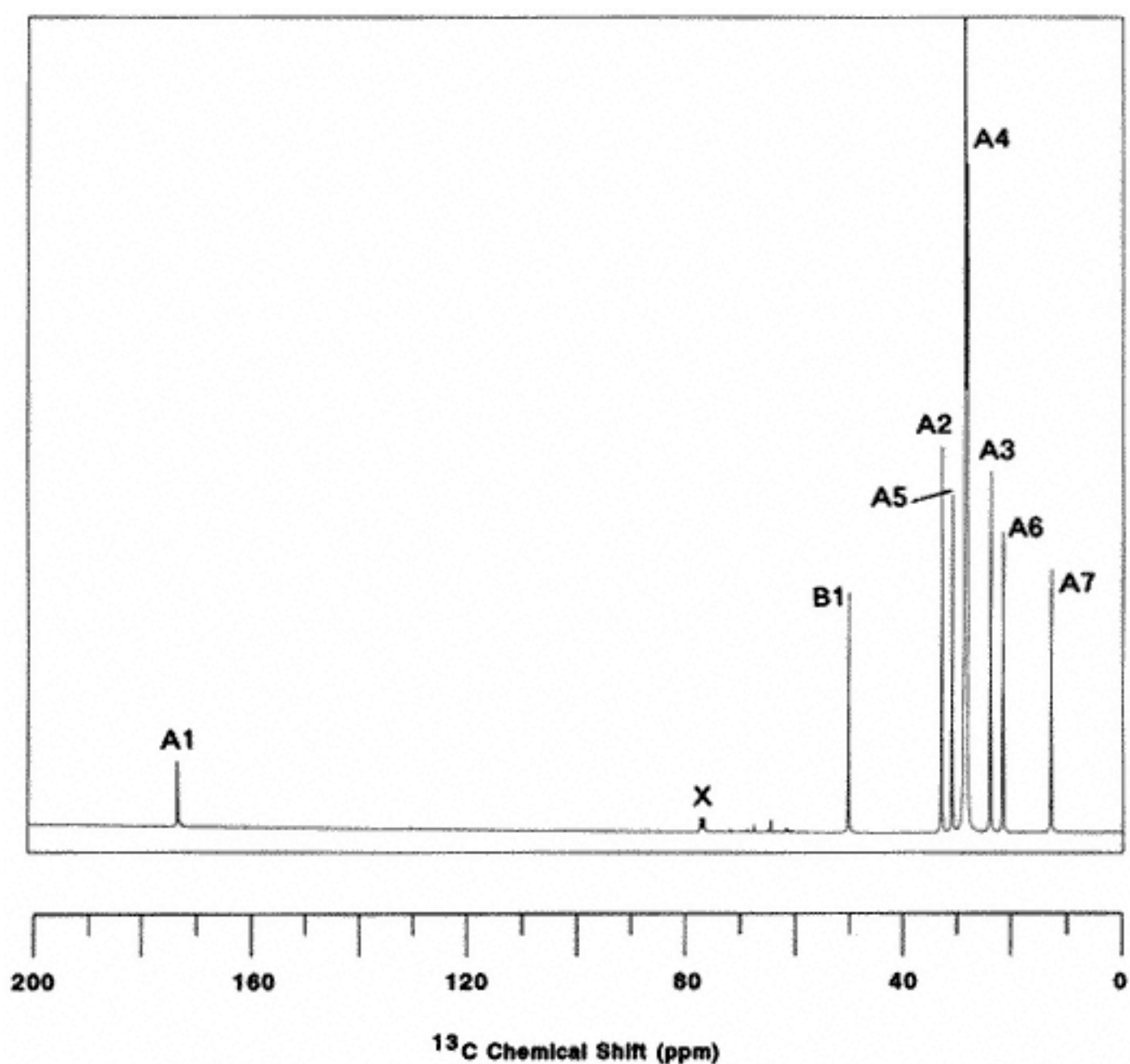
Broadening: 2 Hz

Pulse delay: 5 s

**X-A-4—
Methyl Palmitate**

Comments

Also known as methyl hexadecanoate. Solvent resonances are marked by **X**. This material is used as a plasticizer in ethyl cellulose {VII-B-3} and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
A1	173.1
A2	33.9
A3	24.6
A4	29.1
A5	31.9
A6	22.5
A7	13.1
B1	50.7

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

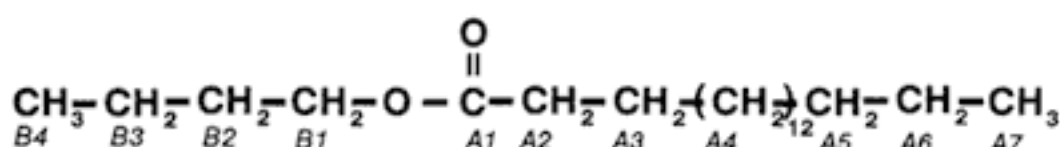
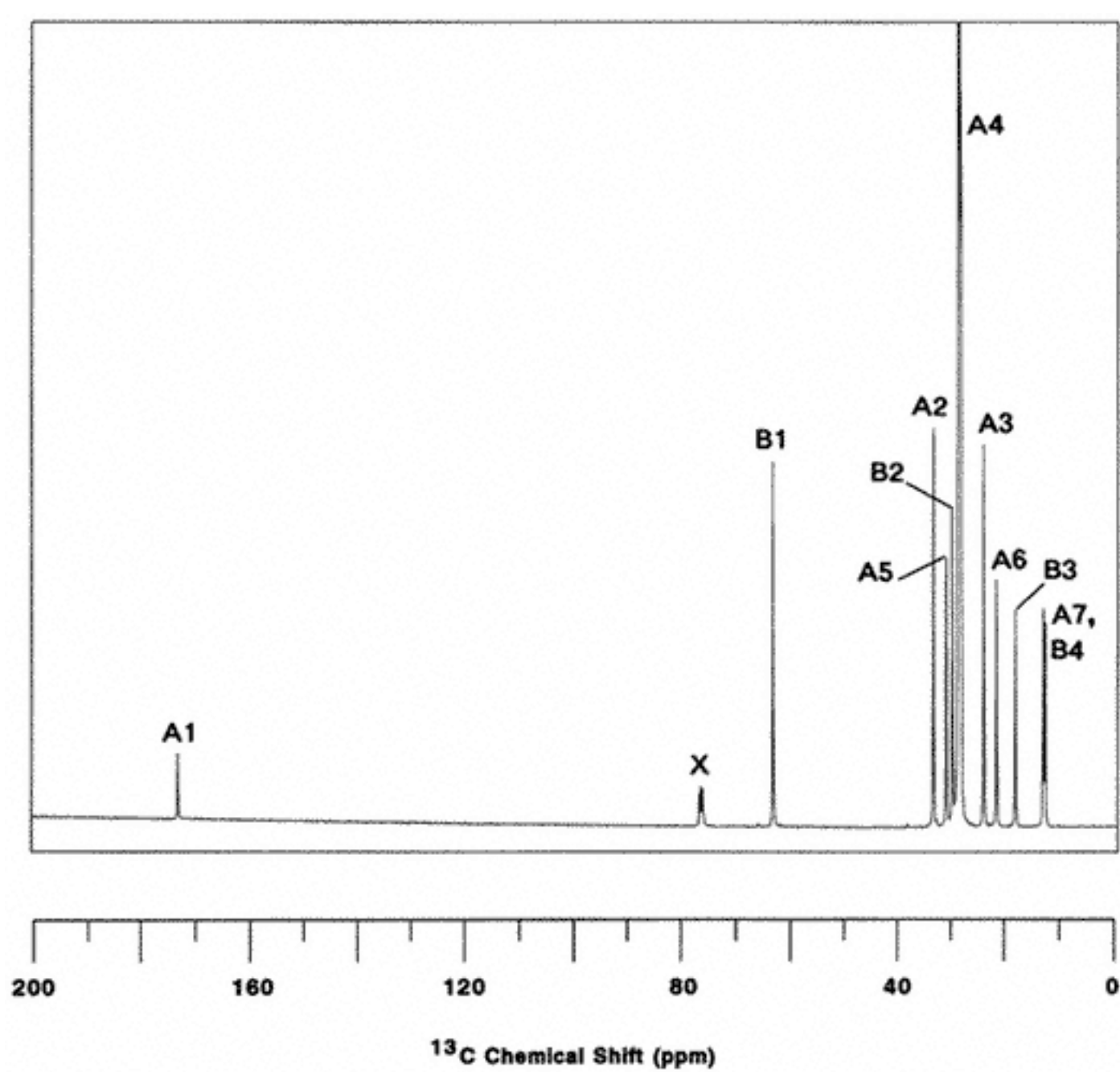
Pulse delay: 5 s

X-A-5

**X-A-5—
Butyl Stearate**

Comments

Also known as butyl octadecanoate. Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, polyisoprene {VI-B-1}, chlorinated polyisoprene {VI-B-3}, ethyl cellulose {VII-B-3}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}, and in polishes, lubricants, cosmetics, water sealants, and lacquers.



Code	Shift (ppm)
A1	173.0
A2	34.4
A3	25.8
A4	30.6
A5	32.0
A6	22.4
A7	13.5
B1	64.4
B2	30.9
B3	18.9
B4	13.5

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

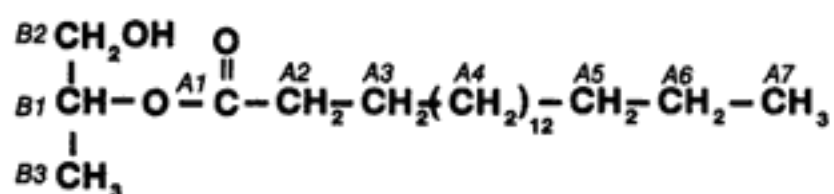
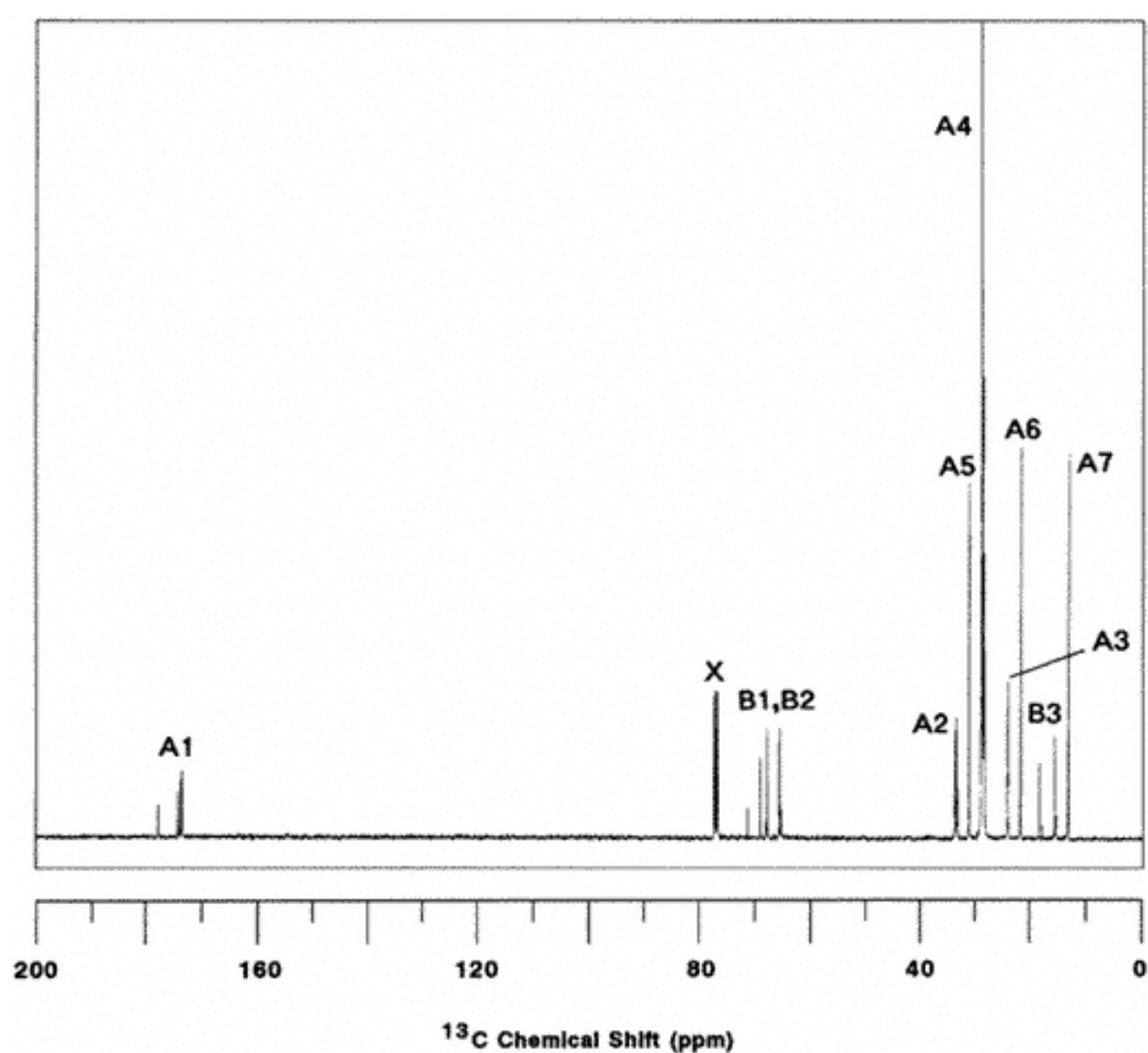
Broadening: 2 Hz

Pulse delay: 5 s

X-A-6—
Propylene Glycol Monostearate

Comments

Esterification occurs primarily at carbon **B1**; other resonances in the spectrum are due to reaction at carbon **B2**. Solvent resonances are marked by **X**. This material is used as a plasticizer for cellulose nitrate {VII-B-8} and as an emulsifier.



Code	Shift (ppm)
A1	173.5
A2	34.2
A3	25.3
A4	30.0
A5	32.2
A6	22.9
A7	14.3
B1	65–71
B2	65–71
B3	19.1

Experimental Parameters

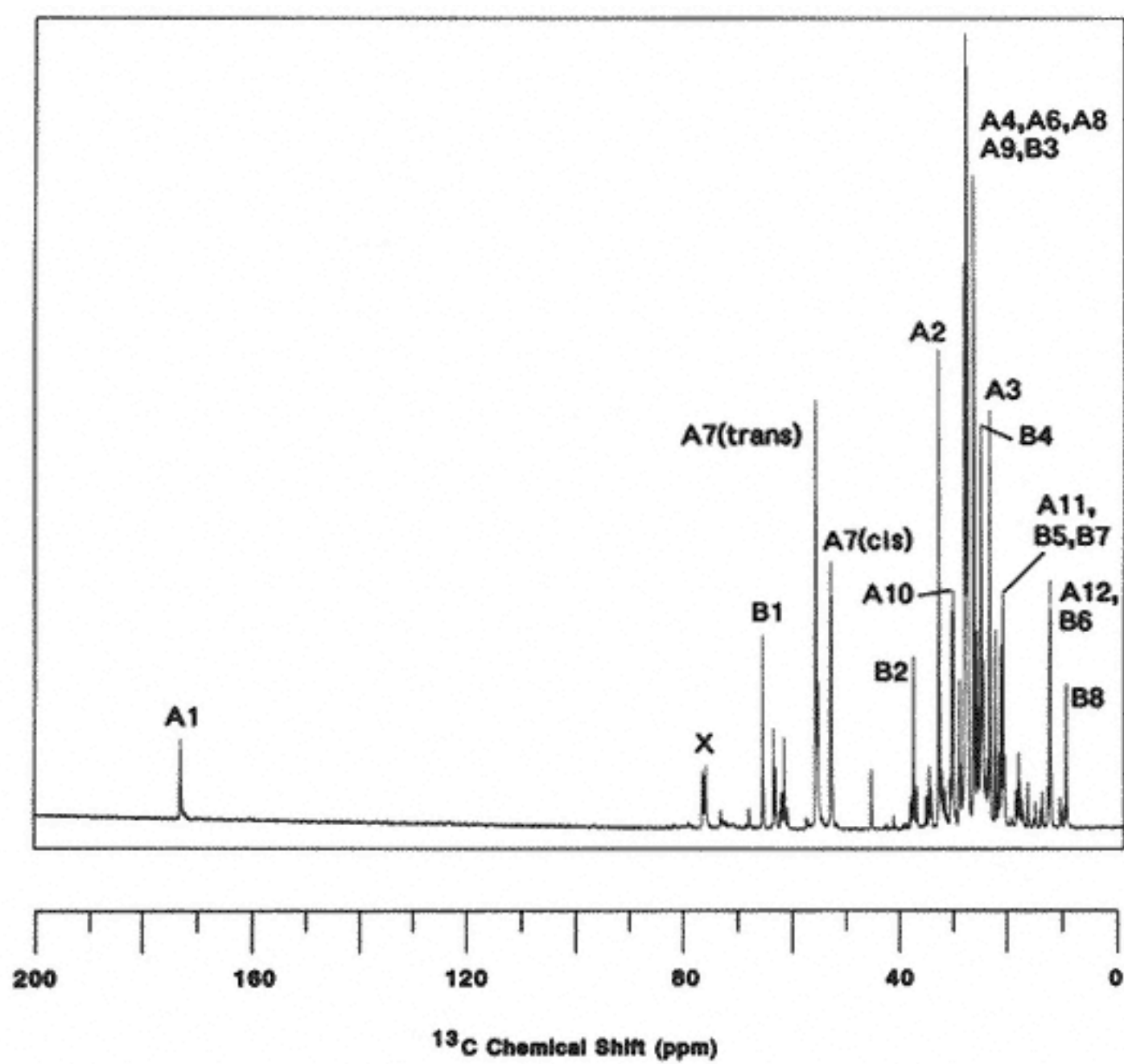
Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 20% w/w
Scans: 100	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 5 s

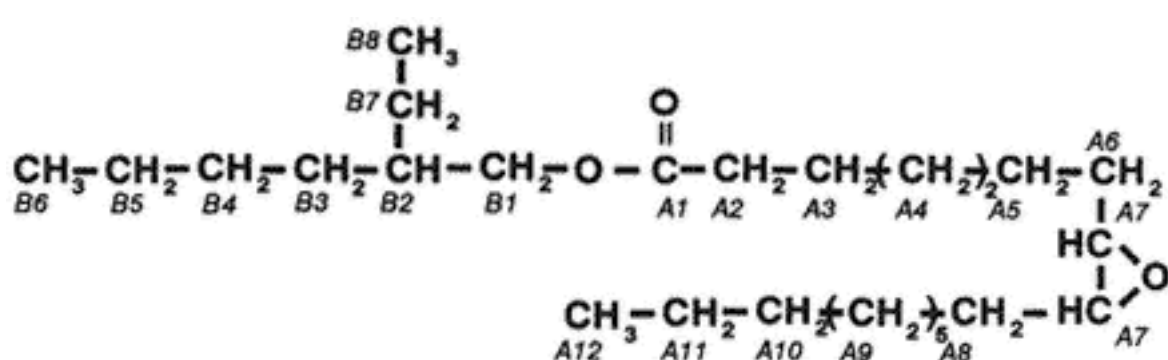
X-A-7

X-A-7—
2-Ethylhexyl Epoxystearate

Comments

Solvent resonances are marked by X. This material is used as a plasticizer for poly(vinyl chloride) (PVC) {V-A-8}, and acts as a stabilizer, scavenging the HCl produced as PVC degrades.





Code	Shift (ppm)
A1	173.2
A2	34.1
A3	27.0
A4	29.5
A5	29.5
A6	28.7
A7 (<i>cis</i>)	53.9
A7 (<i>trans</i>)	56.7
A8	29.5
A9	29.5
A10	32.1
A11	22.0
A12	13.6
B1	66.3
B2	39.0
B3	29.5
B4	28.7
B5	22.0
B6	13.6
B7	23.4
B8	10.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

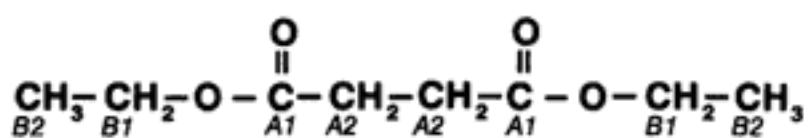
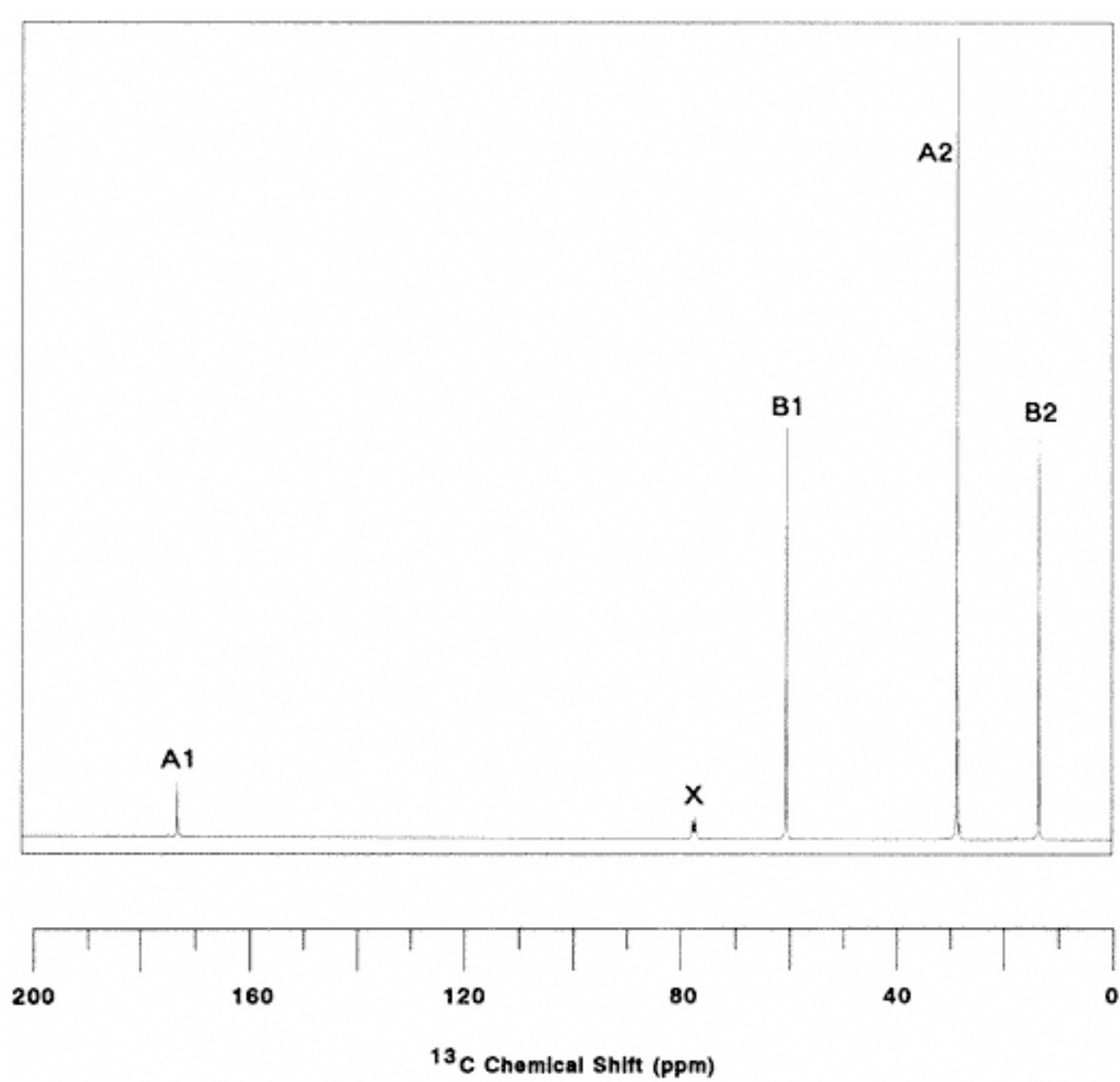
Broadening: 2 Hz

Pulse delay: 5 s

**X-A-8—
Diethyl Succinate**

Comments

Solvent resonances are marked by **X**. This material is used as a plasticizer in cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}, and as an ingredient in flavorings.



Code	Shift (ppm)
A1	172.2
A2	28.7
B1	60.0
B2	13.5

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

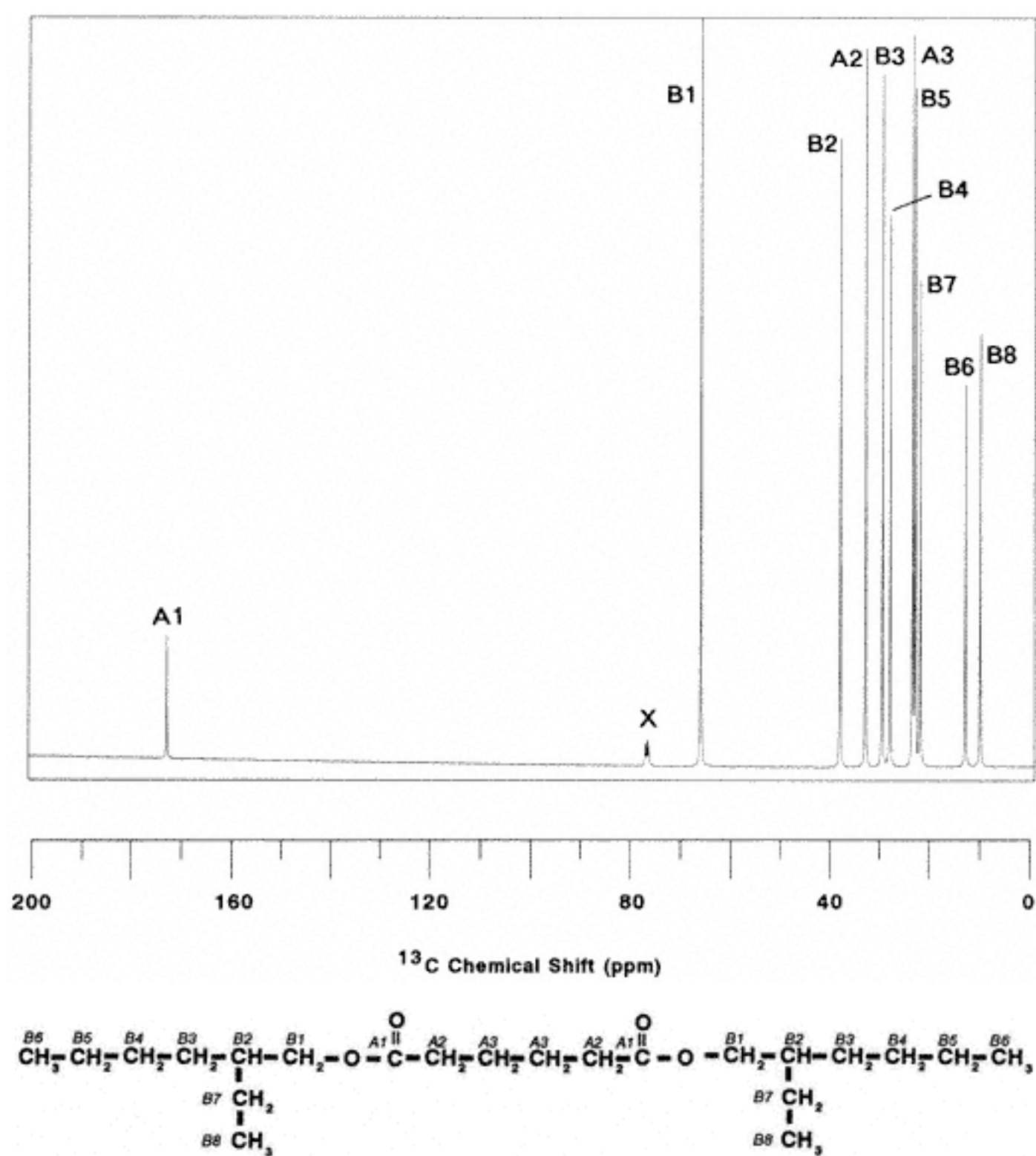
Pulse delay: 5 s

X-A-9

**X-A-9—
Di(2-Ethylhexyl) Adipate**

Comments

Also known as dioctyl adipate (DOA). Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate, {VII-B-5}, and cellulose nitrate {VII-B-8}. It is often combined with di(2-ethylhexyl phthalate) {X-C-8} and dioctyl phthalate {X-C-9}, and is particularly effective at improving low-temperature properties.



Code	Shift (ppm)
A1	172.2
A2	33.7
A3	24.2
B1	66.3
B2	38.7
B3	30.3
B4	28.7
B5	22.6
B6	13.4
B7	23.0
B8	10.4

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

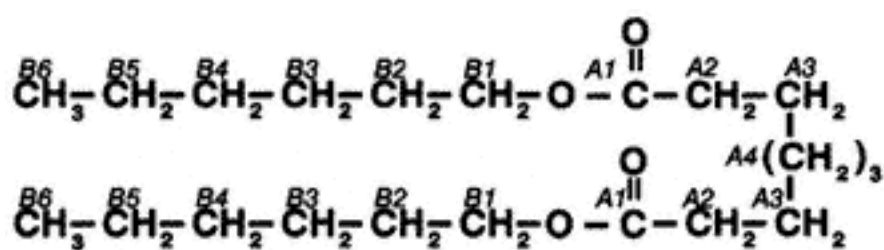
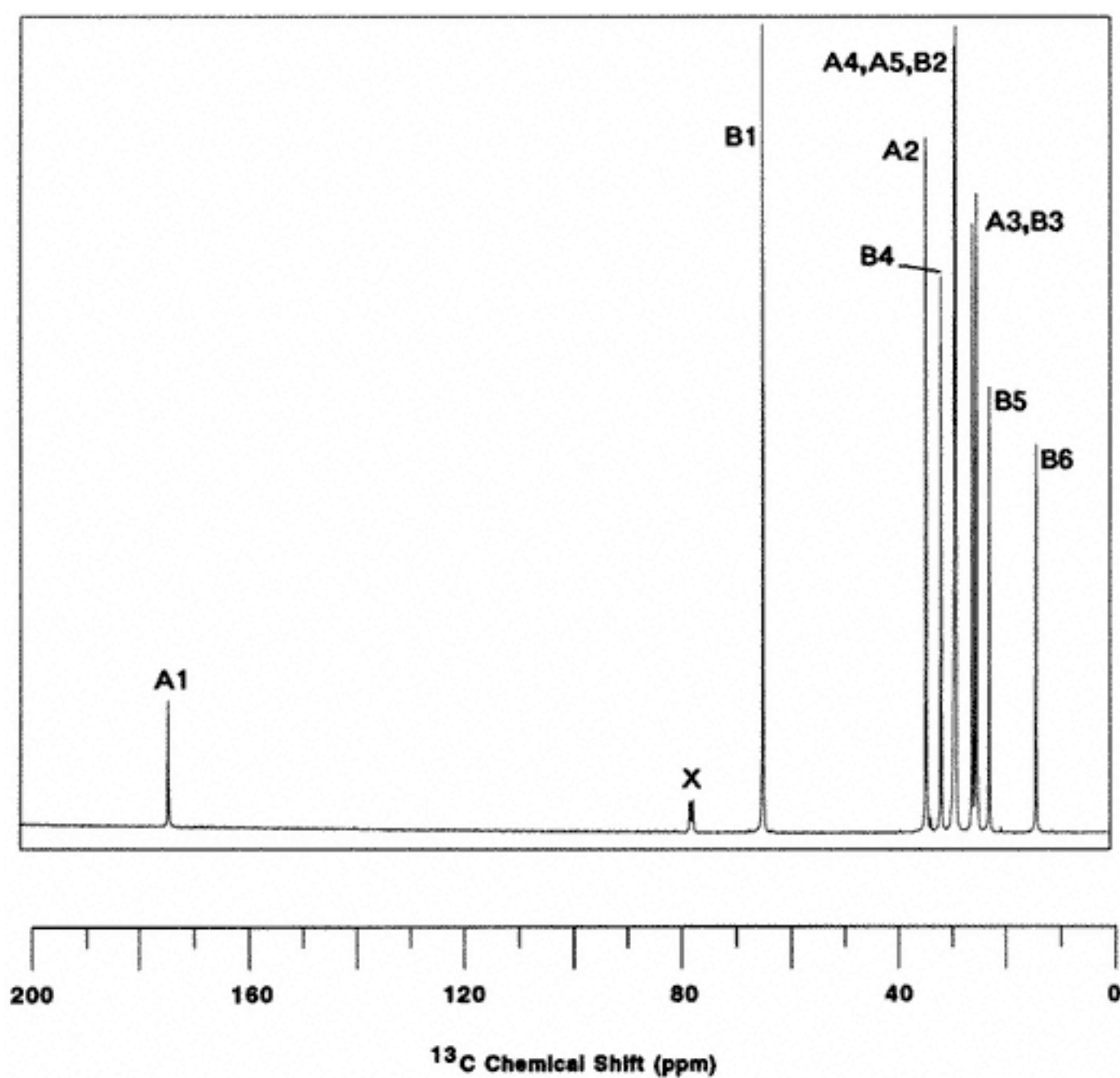
Broadening: 2 Hz

Pulse delay: 5 s

**X-A-11—
Di(*n*-Hexyl) Azelate**

Comments

Solvent resonances are marked by **X**. This material is used as a plasticizer in poly(vinyl acetate) {IV-A-1}, poly(vinyl chloride) {IV-A-8}, poly(vinyl chloride-co-vinyl acetate) {IV-A-9}, poly(vinyl butyral) {IV-B-6}, poly(styrene-co-butadiene) {VI-A-4}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}. It is particularly effective at improving low-temperature properties.



Code	Shift (ppm)
A1	173.1
A2	34.0
A3	26.4
A4	28.4
A5	28.4
B1	64.0
B2	28.4
B3	25.3
B4	31.1
B5	22.2
B6	13.5

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

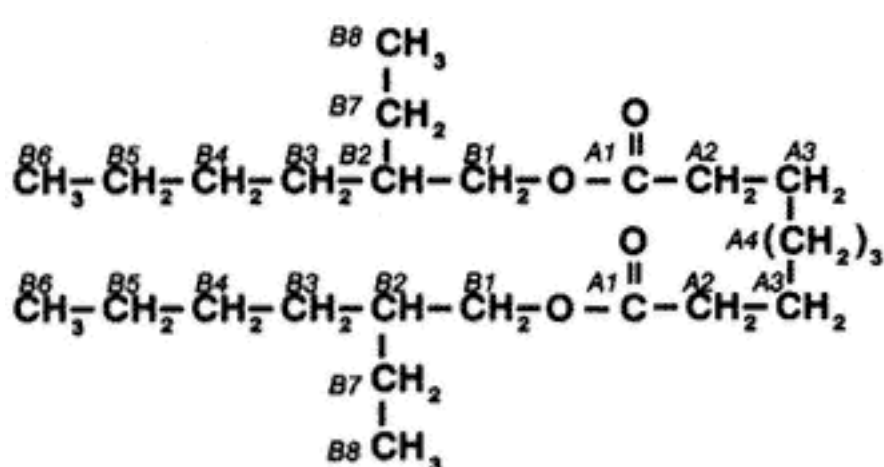
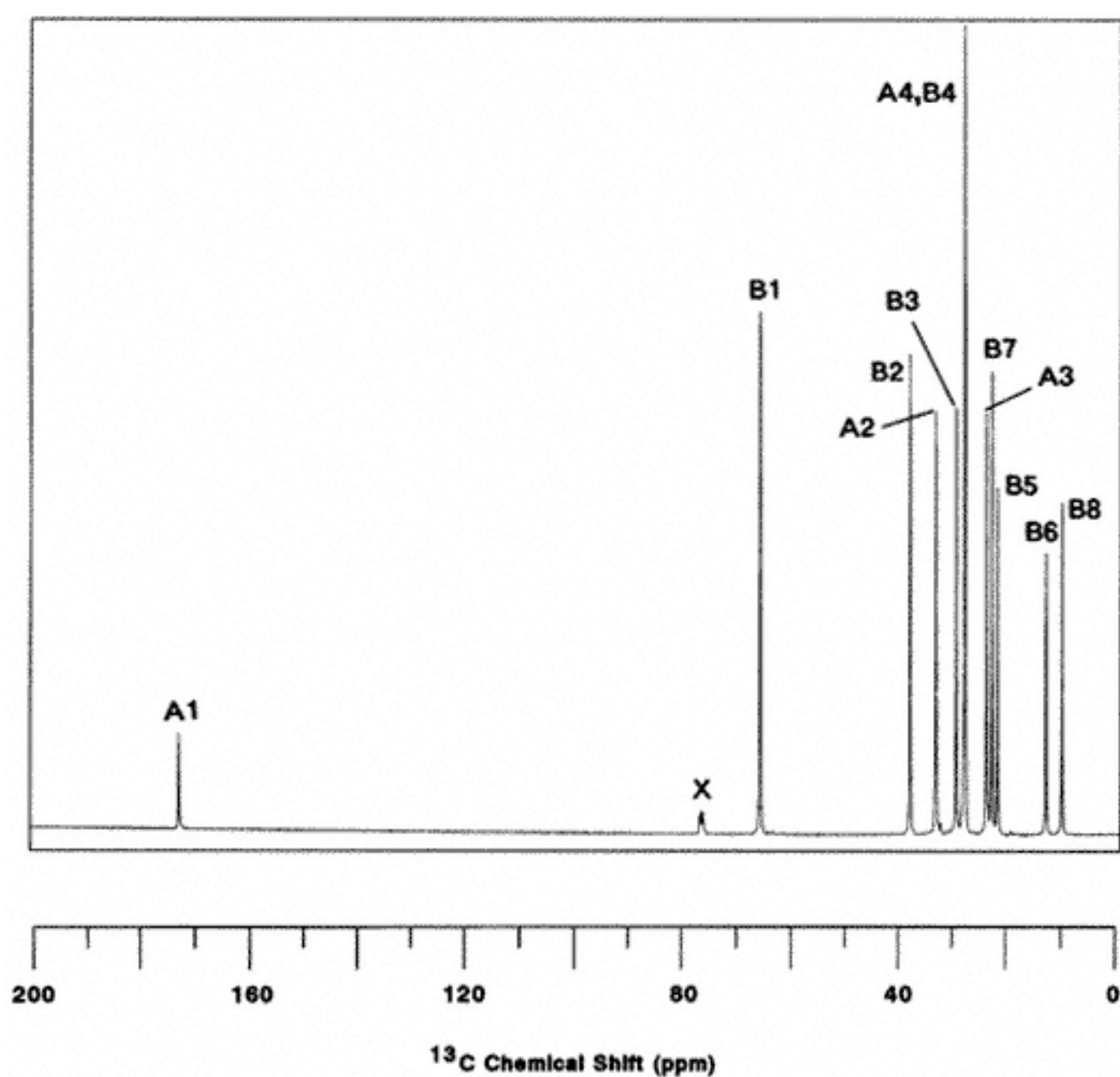
Broadening: 2 Hz

Pulse delay: 5 s

**X-A-12—
Di(2-Ethylhexyl) Azelate**

Comments

This material is used as a plasticizer in poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}, and in lubricants. It is particularly effective at improving low-temperature properties.



Code	Shift (ppm)
A1	173.1
A2	34.0
A3	24.7
A4	28.4
B1	66.4
B2	38.7
B3	30.3
B4	28.4
B5	22.6
B6	13.5
B7	23.6
B8	10.6

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

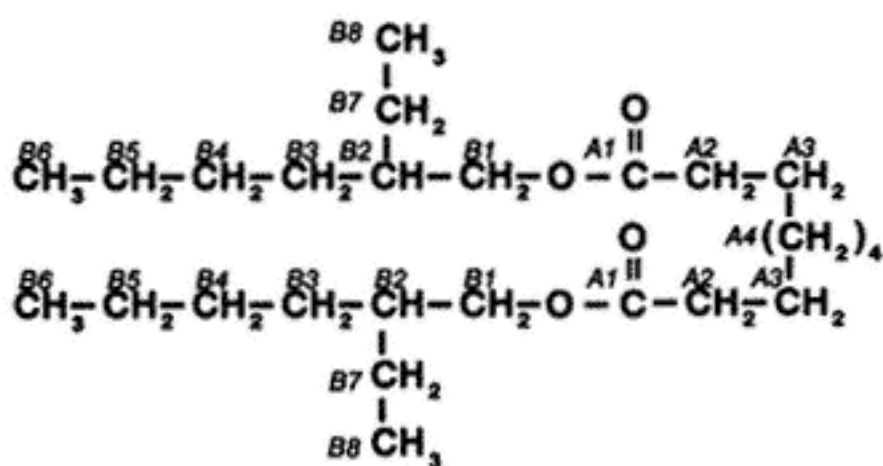
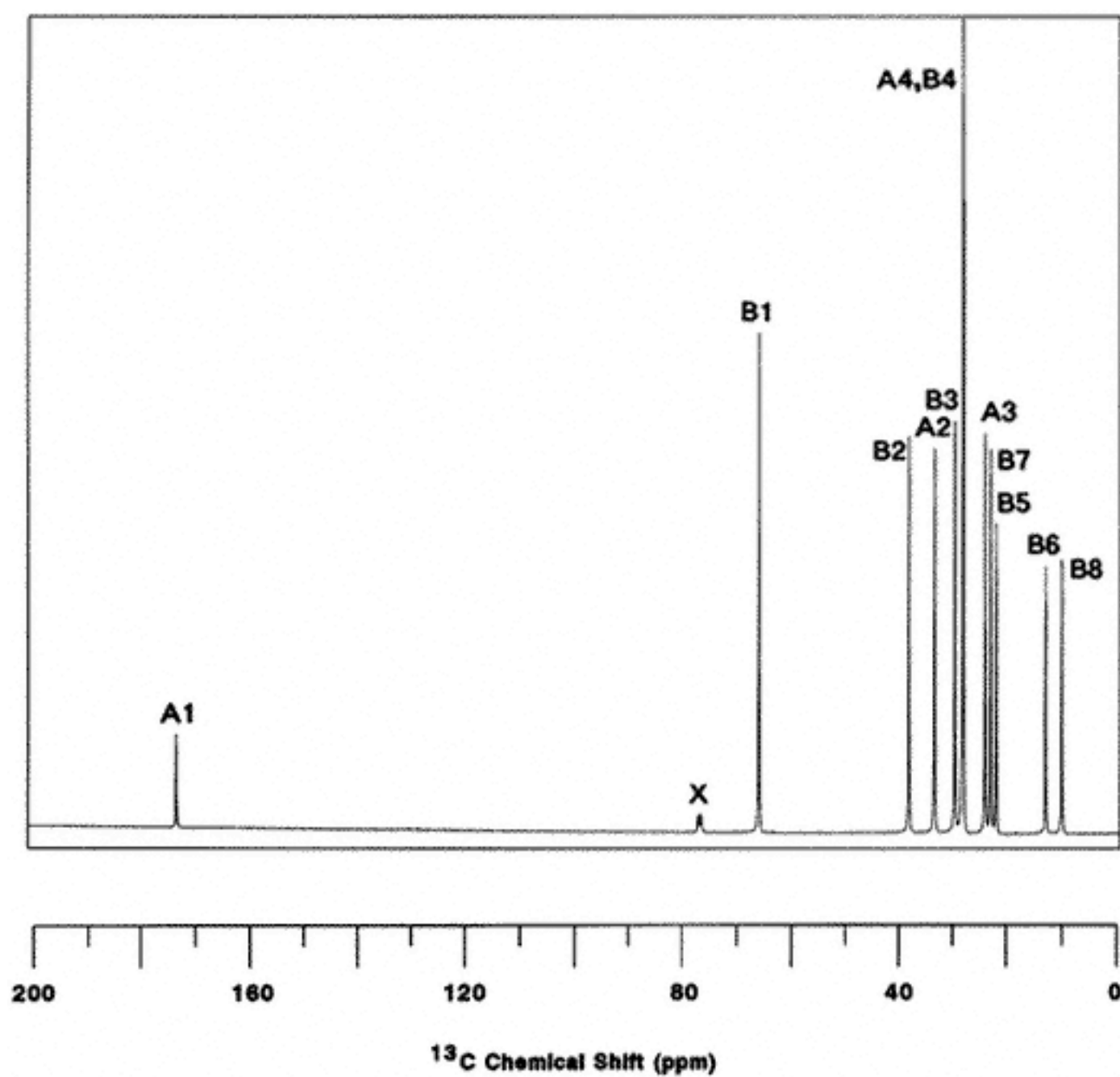
Pulse delay: 5 s

X-A-13—

Di(2-Ethylhexyl) Sebacate

Comments

Solvent resonances are marked by X. This material is used as a plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}. It is particularly effective at improving low-temperature properties.



Code	Shift (ppm)
A1	173.1
A2	34.0
A3	24.7
A4	28.7
B1	66.2
B2	38.6
B3	30.3
B4	28.7
B5	22.6
B6	13.6
B7	23.6
B8	10.6

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

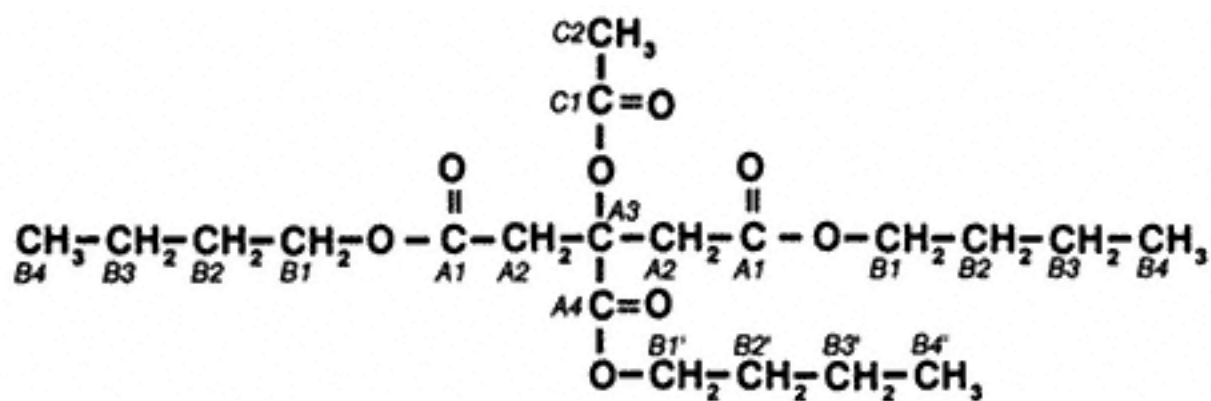
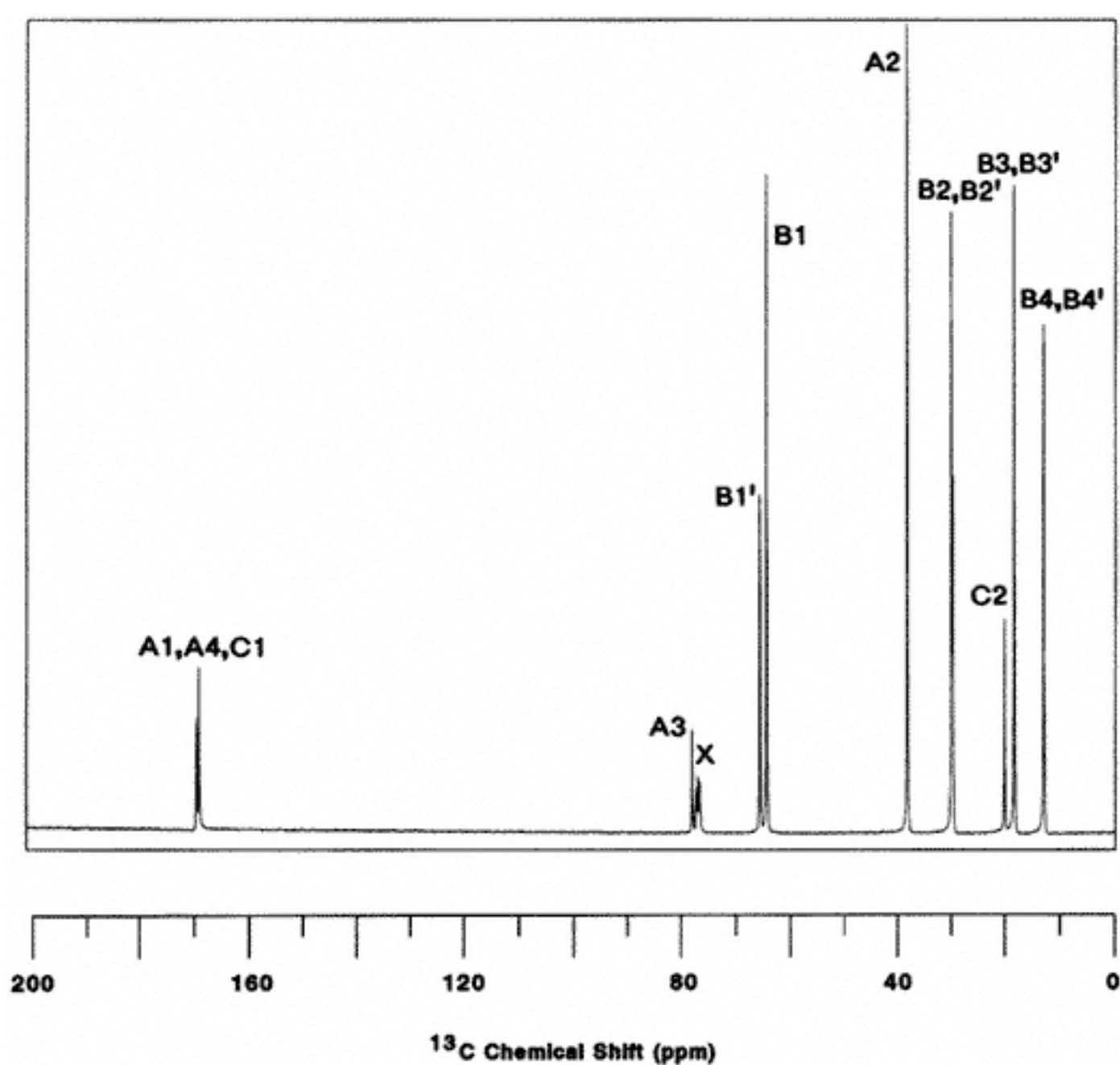
Broadening: 2 Hz

Pulse delay: 5 s

**X-A-15—
Acetyl Tri-*n*-Butyl Citrate**

Comments

Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
A1	169.1
A2	38.3
A3	79.2
A4	169.1
B1	64.3
B1'	65.6
B2	30.9
B2'	30.9
B3	18.6
B3'	18.6
B4	13.2
B4'	13.2
C1	169.1
C2	20.5

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

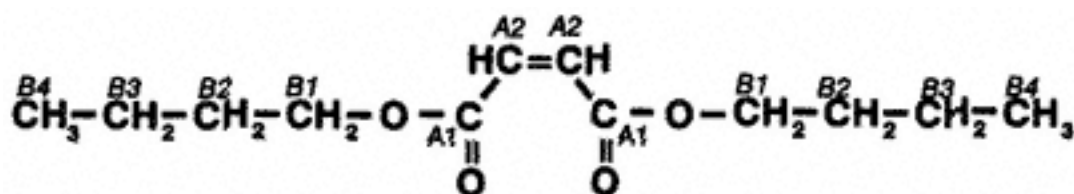
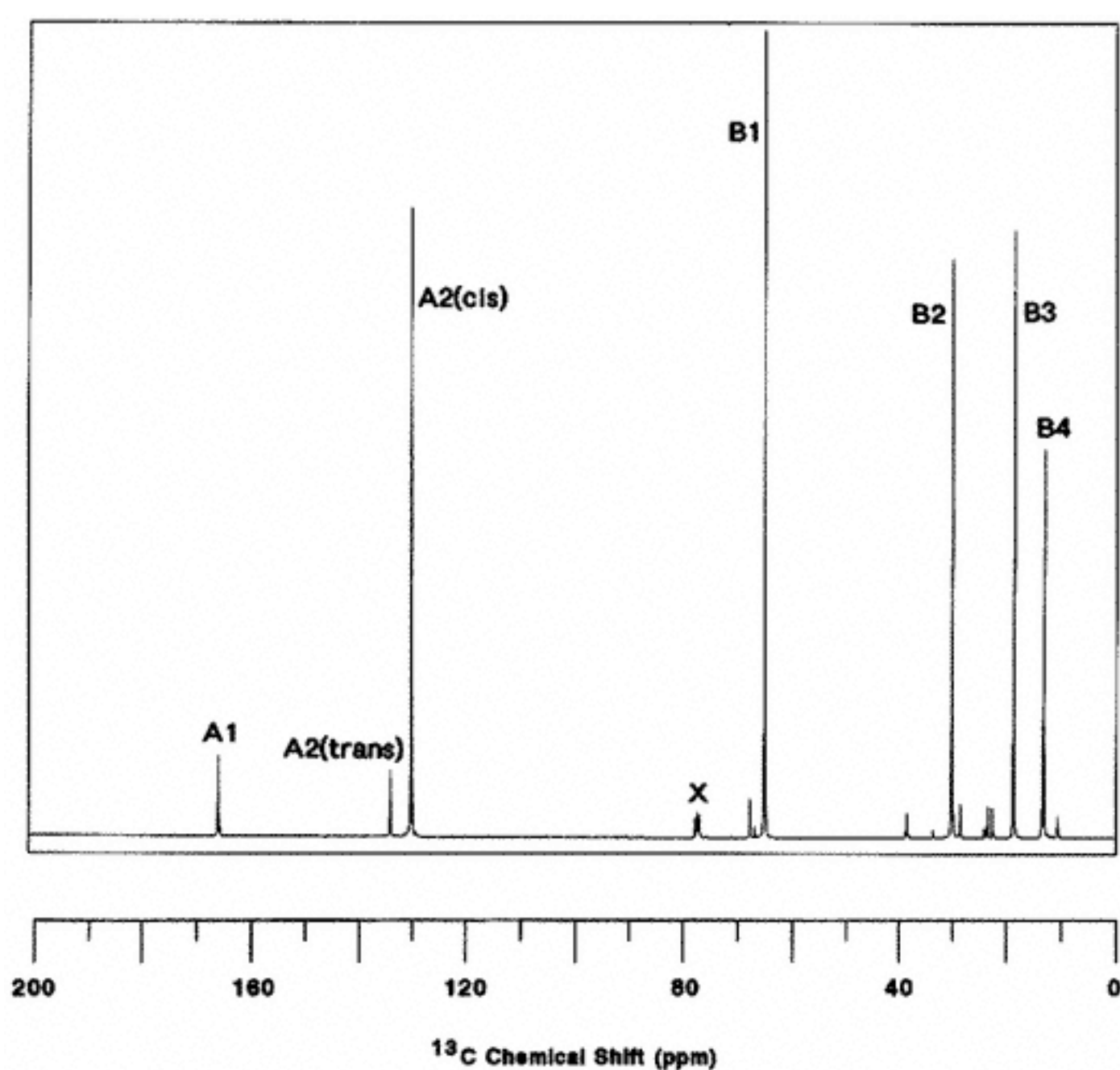
Broadening: 2 Hz

Pulse delay: 5 s

**X-B-1—
Di(*n*-Butyl) Maleate**

Comments

The acid moiety is primarily *cis* (maleate); some *trans* (fumarate) isomer {X-B-3} is also present. Solvent resonances are marked by **X**. This material is used as a plasticizer for poly(vinyl acetate) {IV-A-1}.



Code	Shift (ppm)
A1	165.1
A2 (<i>cis</i>)	129.7
As (<i>trans</i>)	133.5
B1	64.7
B2	30.3
B3	18.8
B4	13.3

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

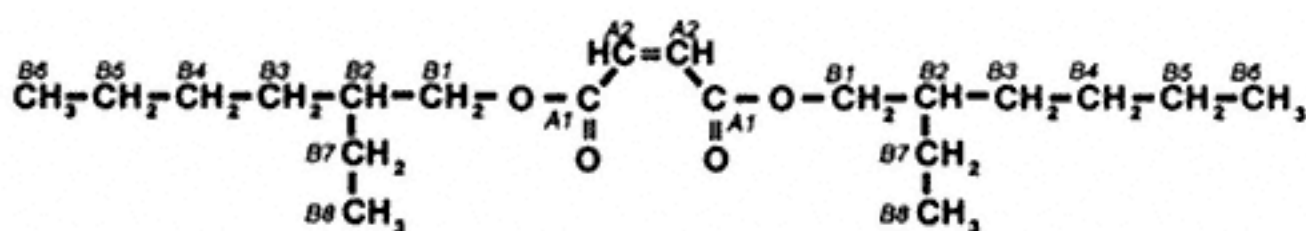
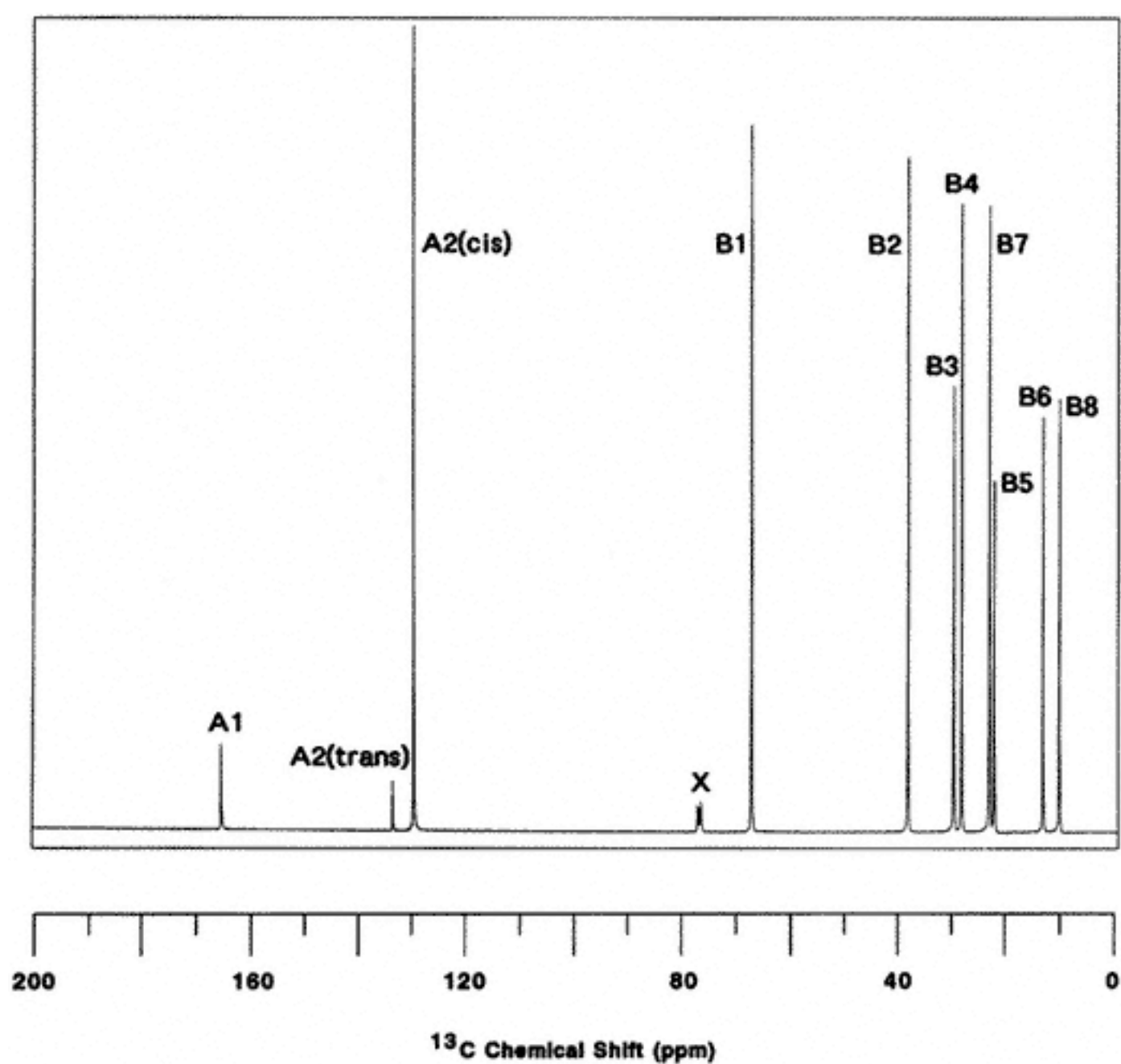
Pulse delay: 5 s

X-B-2

**X-B-2—
Di(2-Ethylhexyl) Maleate**

Comments

Also known as dioctyl maleate (DOM). The acid moiety is primarily *cis* (maleate); some *trans* (fumarate) isomer is also present. Solvent resonances are marked by **X**.



Code	Shift (ppm)
A1	164.9
A2 (<i>cis</i>)	129.7
A2 (<i>trans</i>)	133.5
B1	67.4
B2	38.3
B3	30.2
B4	28.7
B5	22.7
B6	13.7
B7	23.3
B8	10.6

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

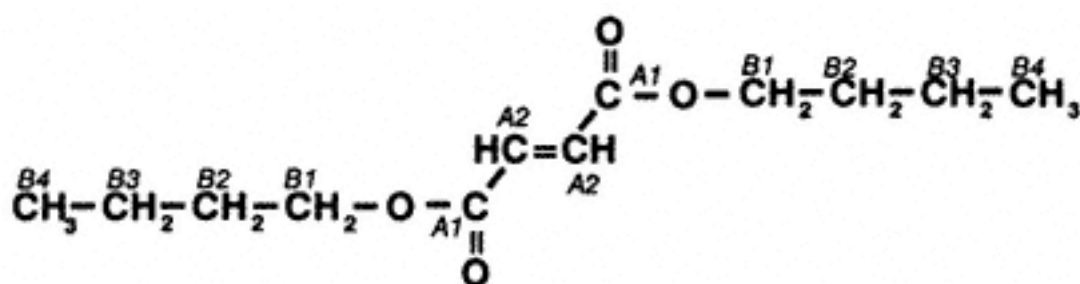
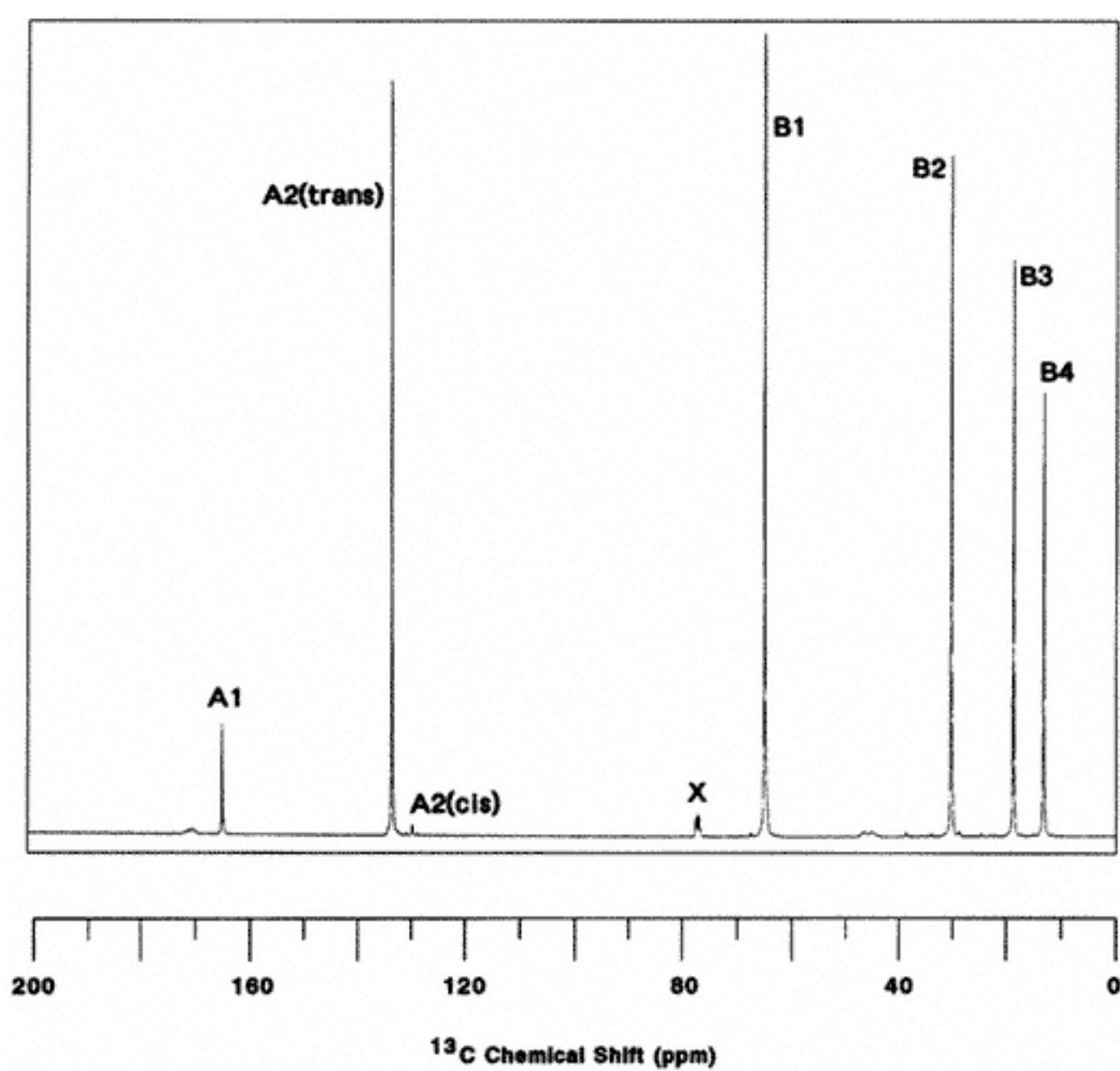
Broadening: 2 Hz

Pulse delay: 5 s

**X-B-3—
Di(*n*-Butyl) Fumarate**

Comments

The acid moiety is primarily *trans* (fumarate); some *cis* (maleate) isomer {X-B-1} is also present. Solvent resonances are marked by **X**. This material is used as a plasticizer in poly(vinyl acetate) {IV-A-1}, poly(vinyl chloride) {V-A-8}, and poly(vinyl chloride-co-vinyl acetate) {V-A-9}.



Code	Shift (ppm)
A1	164.8
A2 (<i>cis</i>)	129.5
A2 (<i>trans</i>)	133.6
B1	64.7
B2	30.1
B3	18.8
B4	13.3

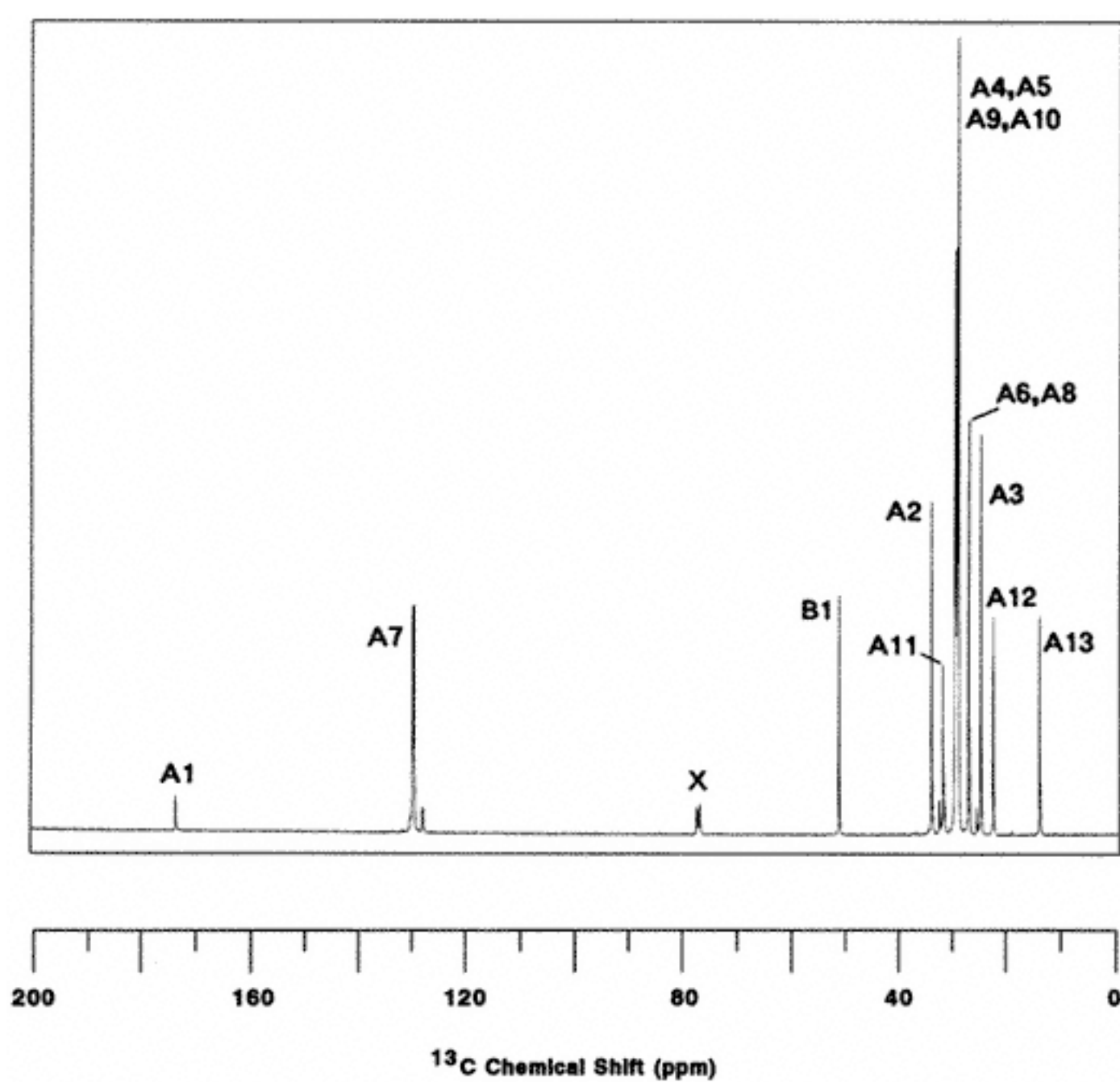
Experimental Parameters

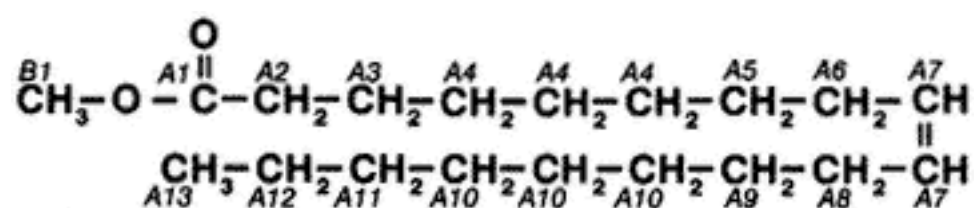
Nucleus: ^{13}C (100.4 MHz)	Temperature: 50°C
Solvent: CDCl_3	Concentration: 50% w/w
Scans: 100	Spectral width: 25 kHz
Data points: 16384	Pulse width: 90°
Broadening: 2 Hz	Pulse delay: 5 s

X-B-4

**X-B-4—
Methyl Oleate****Comments**

The acid moiety is primarily *cis*. Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, and cellulose nitrate {VII-B-8}. It is also found in detergents, emulsifiers, wetting agents, textile finishes, waxes, and inks.





Code	Shift (ppm)
A1	173.6
A2	34.1
A3	24.7
A4	28.9
A5	28.9
A6	26.9
A7	129.4
A8	26.9
A9	28.9
A10	28.9
A11	31.7
A12	22.4
A13	13.7
B1	50.9

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

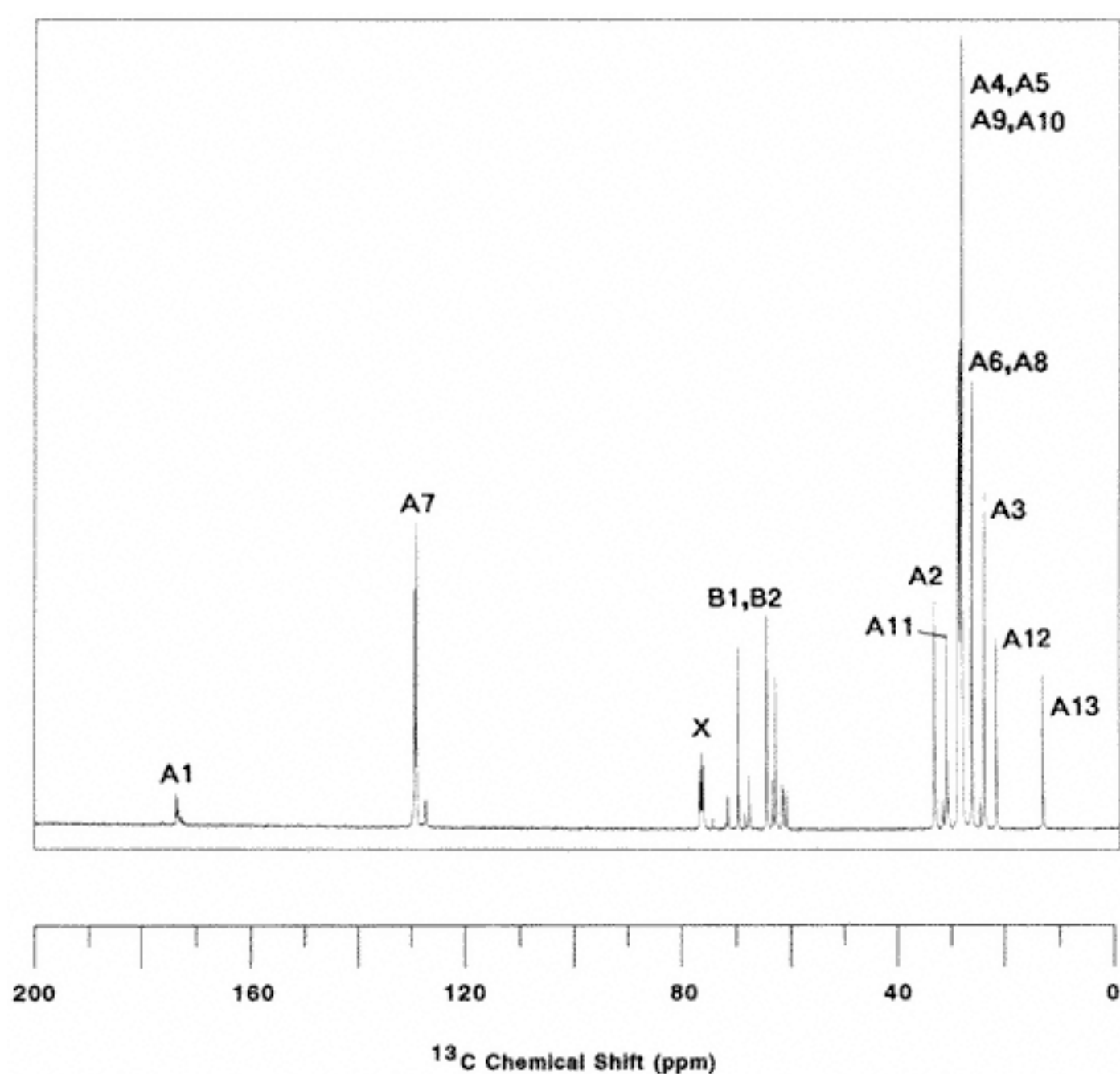
Pulse width: 90°

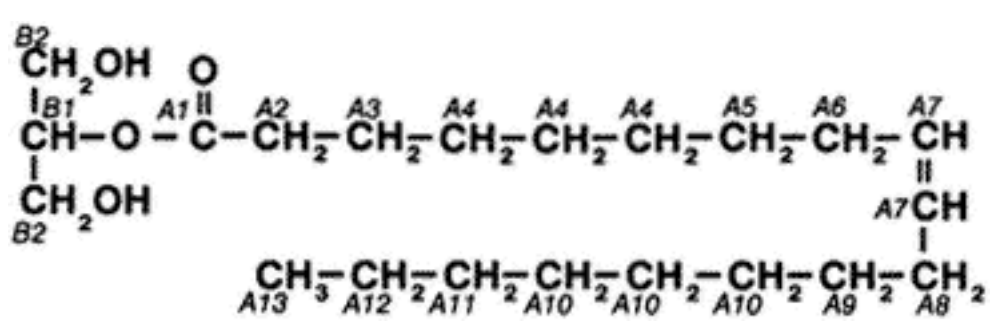
Broadening: 2 Hz

Pulse delay: 5 s

**X-B-5—
Glycerol Monooleate****Comments**

The acid moiety is primarily *cis*. Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {IV-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}. It is also employed as a tackifier; it is found in cosmetics, rust preventatives, textiles, paints, and light stabilizers.





Code	Shift (ppm)
A1	174.0
A2	33.9
A3	24.7
A4	29.1
A5	29.1
A6	27.0
A7	129.5
A8	27.0
A9	29.1
A10	29.1
A11	31.7
A12	22.4
A13	13.9
B1	60–72
B2	60–72

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16,384

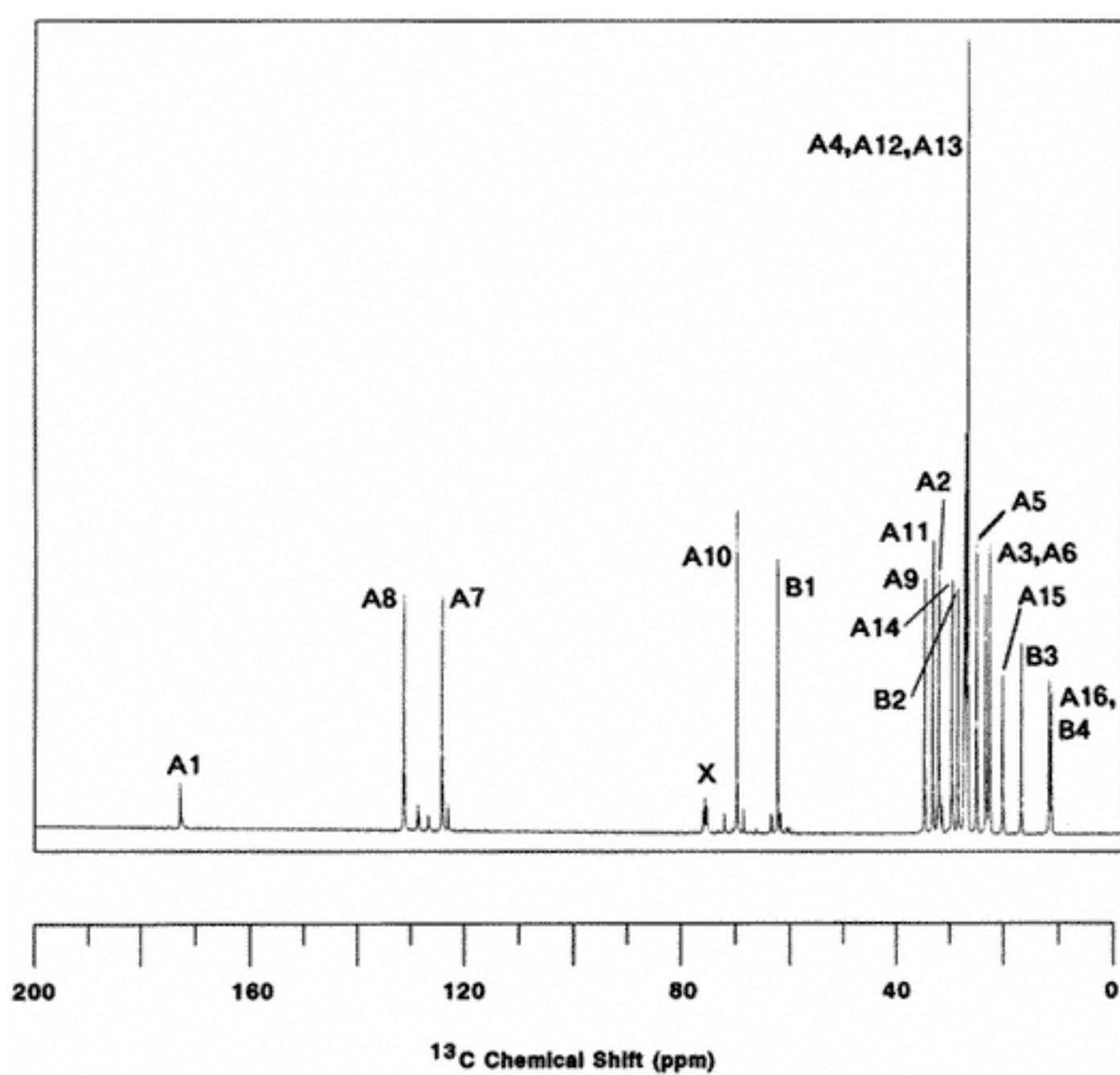
Pulse width: 90°

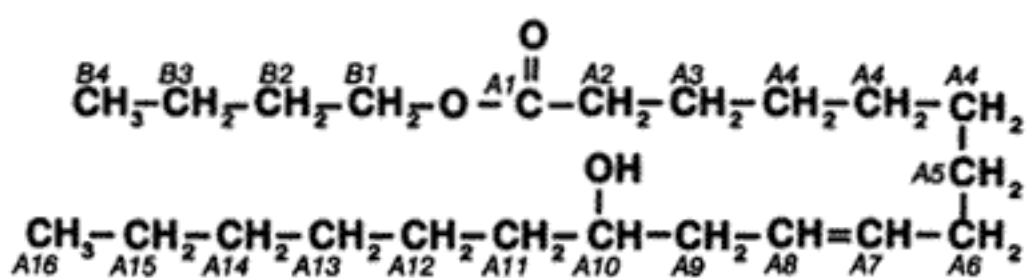
Broadening: 2 Hz

Pulse delay: 5 s

**X-B-6—
Butyl Ricinoleate****Comments**

Esterification has occurred primarily at carbon **B1**; some reaction at carbon **B2** is also observed. The acid moiety is primarily *cis*. Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}, and in lubricants.





Code	Shift (ppm)
A1	173.5
A2	34.1
A3	24.6
A4	28.8
A5	27.1
A6	25.4
A7	125.9
A8	133.0
A9	36.6
A10	71.2
A11	35.2
A12	28.8
A13	28.8
A14	31.8
A15	23.0
A16	13.7
B1	63.7
B2	28.8
B3	18.3
B4	13.7

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

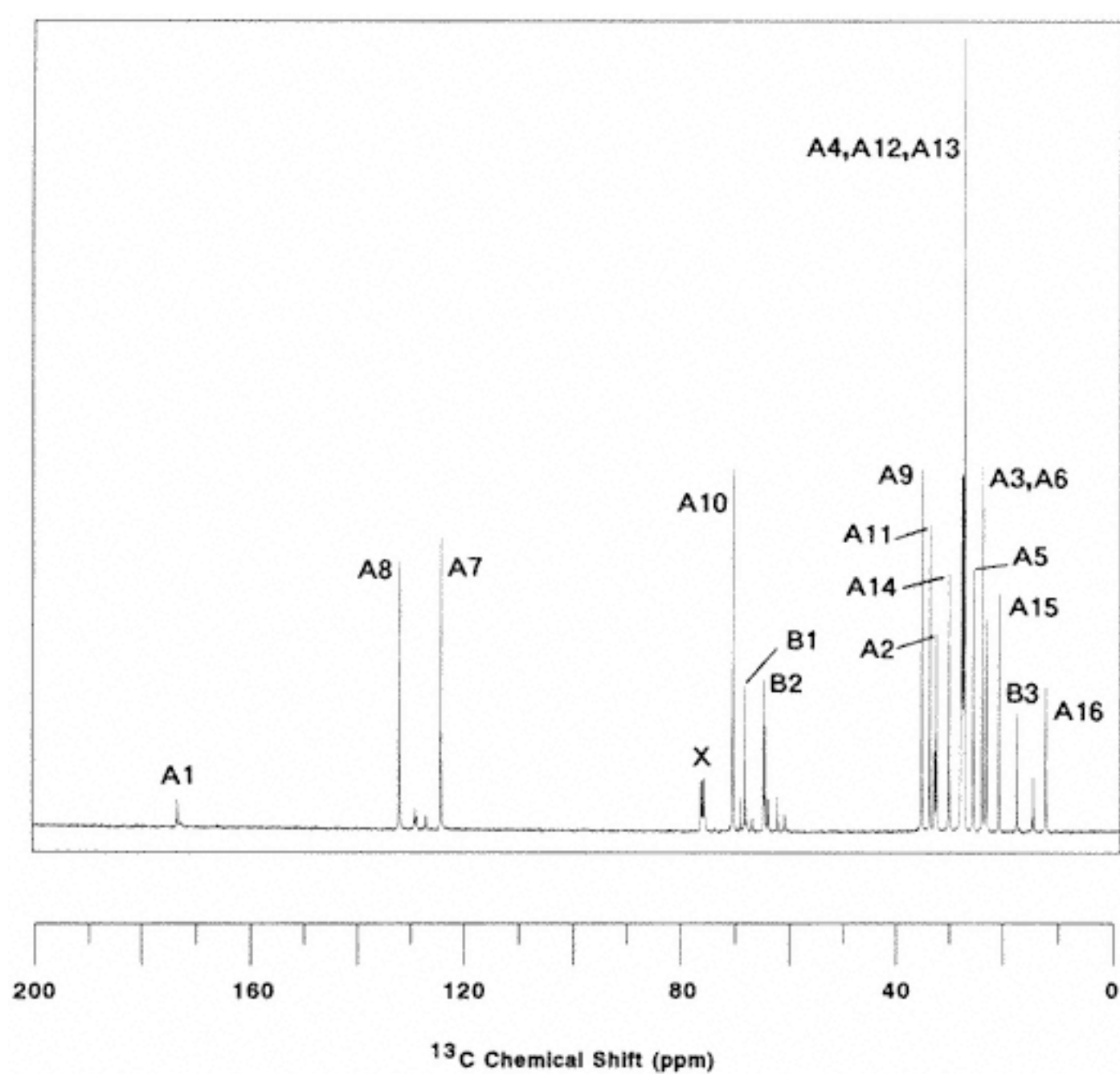
Broadening: 2 Hz

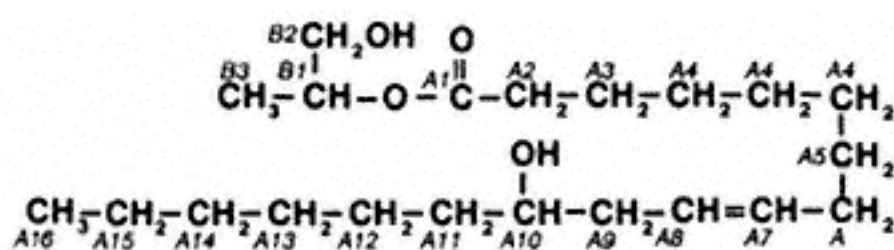
Pulse delay: 5 s

**X-B-7—
Propylene Glycol Ricinoleate**

Comments

Esterification has occurred primarily at carbon **B1**; some reaction at carbon **B2** is also observed. The acid moiety is primarily *cis*. Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, ethyl cellulose {VII-B-3}, and cellulose nitrate {VII-B-8}, and in lubricants, cosmetics, hydraulic fluids, and polyurethanes {IX-B-1 through IX-B-4}.





Code	Shift (ppm)
A1	173.7
A2	34.0
A3	24.6
A4	28.8
A5	27.0
A6	25.0
A7	125.9
A8	132.7
A9	36.7
A10	71.4
A11	34.4
A12	28.8
A13	28.8
A14	31.8
A15	22.4
A16	13.7
B1	69.2
B2	65.5
B3	18.4

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

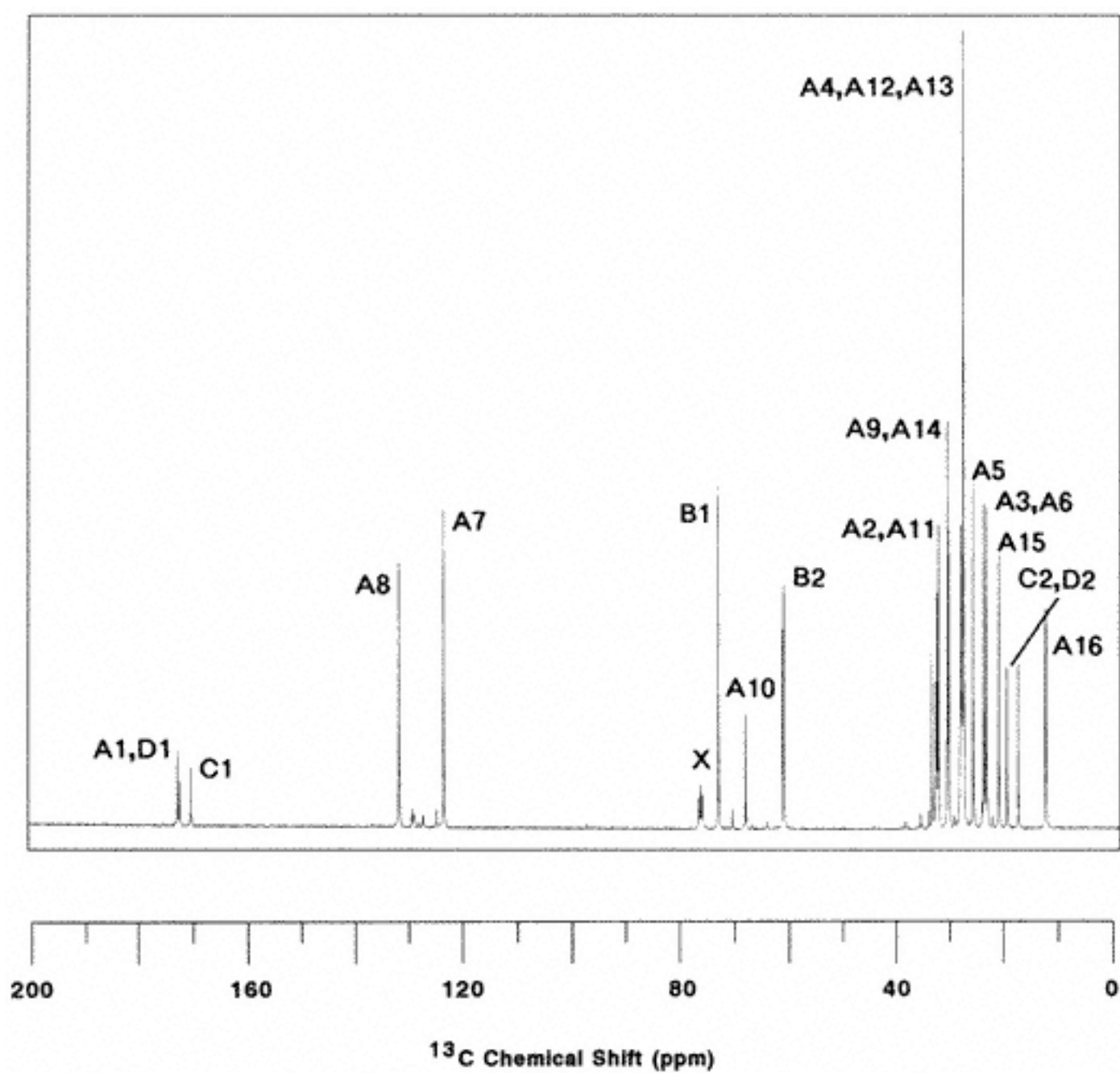
Broadening: 2 Hz

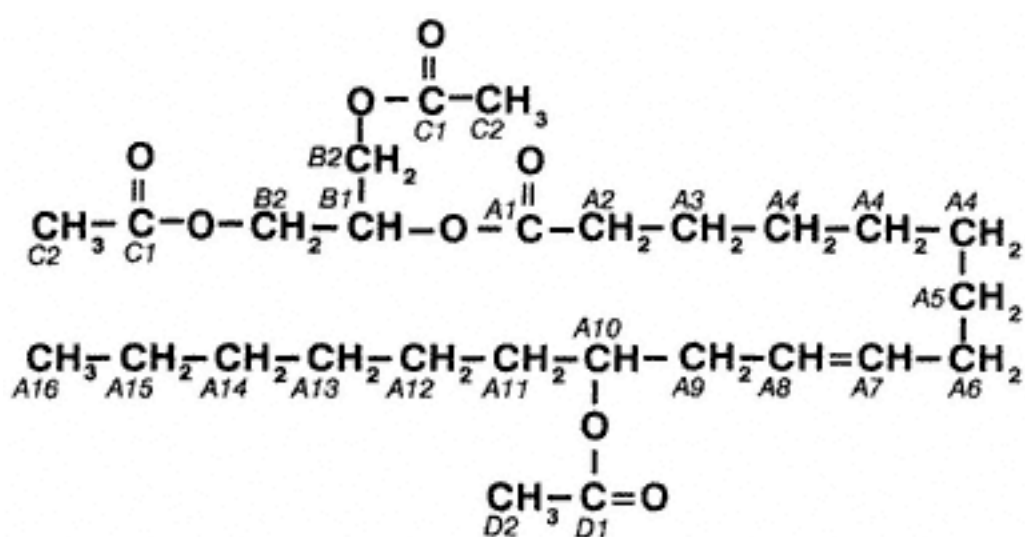
Pulse delay: 5 s

X-B-8—
Glycerol Tri(12-Acetyl Ricinoleate)

Comments

Also known as acetylated castor oil. Esterification has occurred primarily at carbon **B1**; some reaction at carbon **B2** is also observed. The acid moiety is primarily *cis*. Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, ethyl cellulose {VII-B-3}, and cellulose nitrate {VII-B-8}, and in lubricants and protective coatings.





Code	Shift (ppm)
A1	172.8
A2	33.3
A3	24.5
A4	28.7
A5	26.4
A6	25.0
A7	124.5
A8	132.7
A9	31.8
A10	68.8
A11	33.3
A12	28.7
A13	28.7
A14	31.8
A15	22.1
A16	13.5
B1	75.6
B2	62.2
C1	170.4
C2	22.1
D1	172.8
D2	23.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

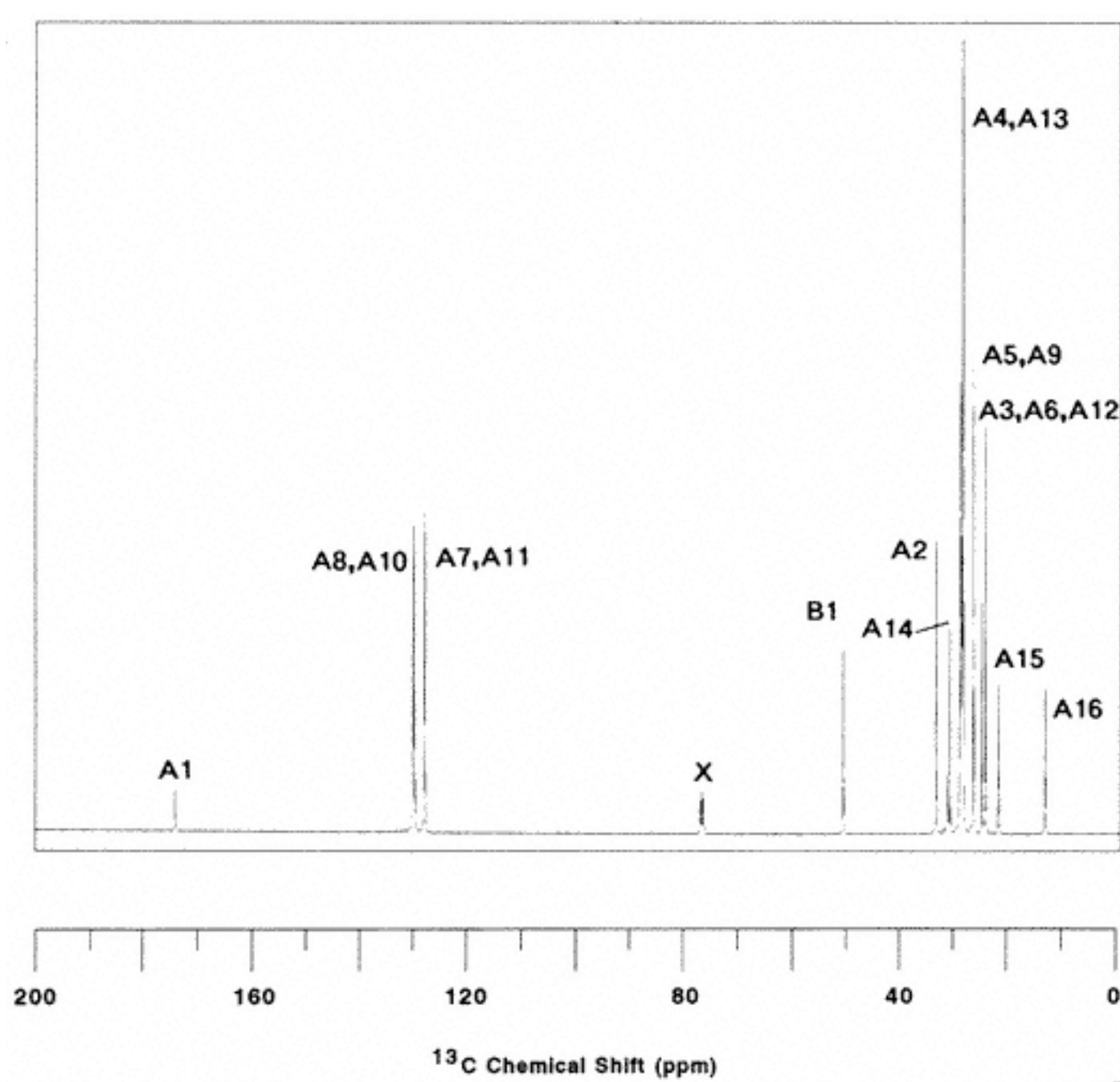
Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

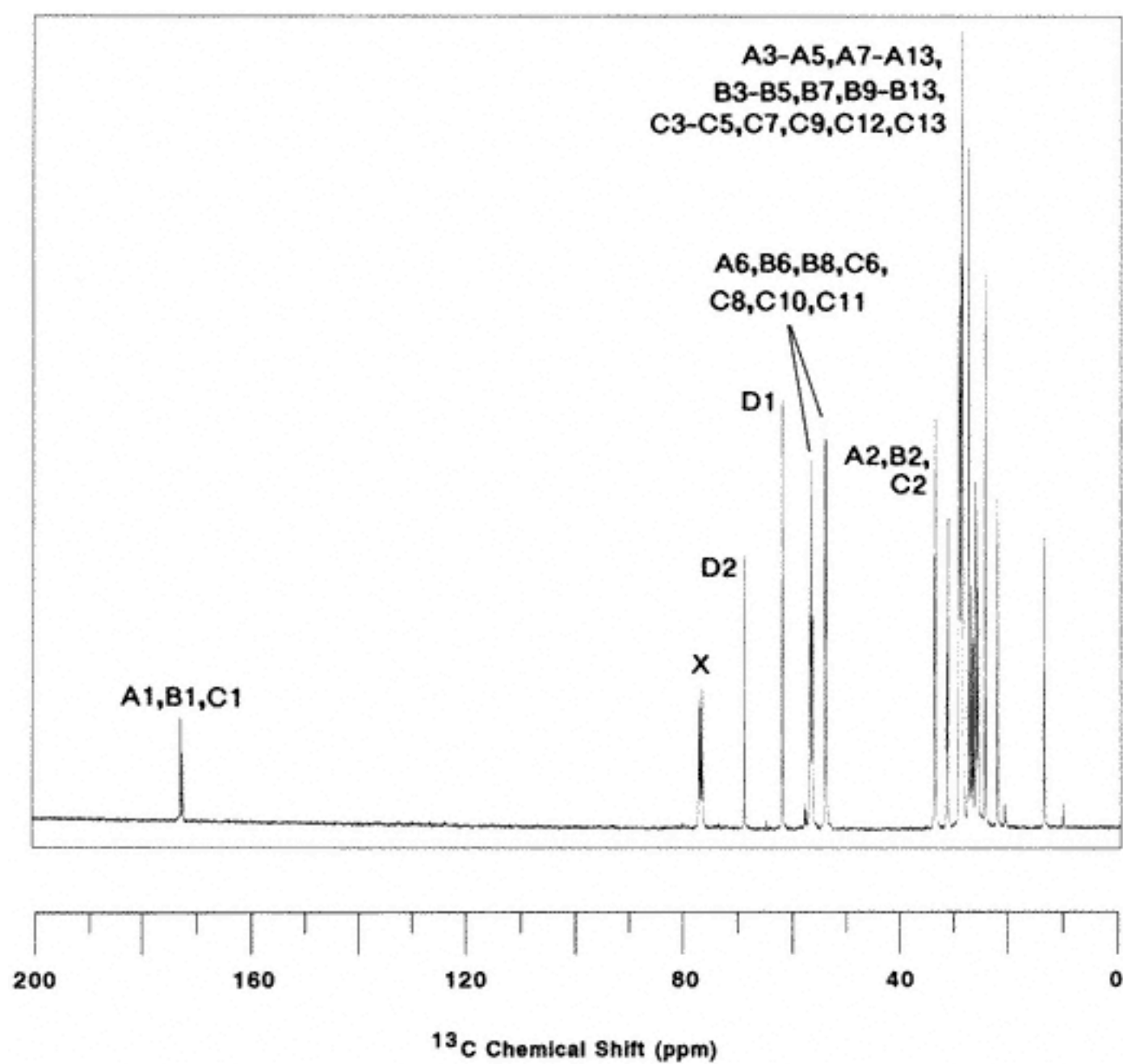
**X-B-9—
Methyl Linoleate****Comments**

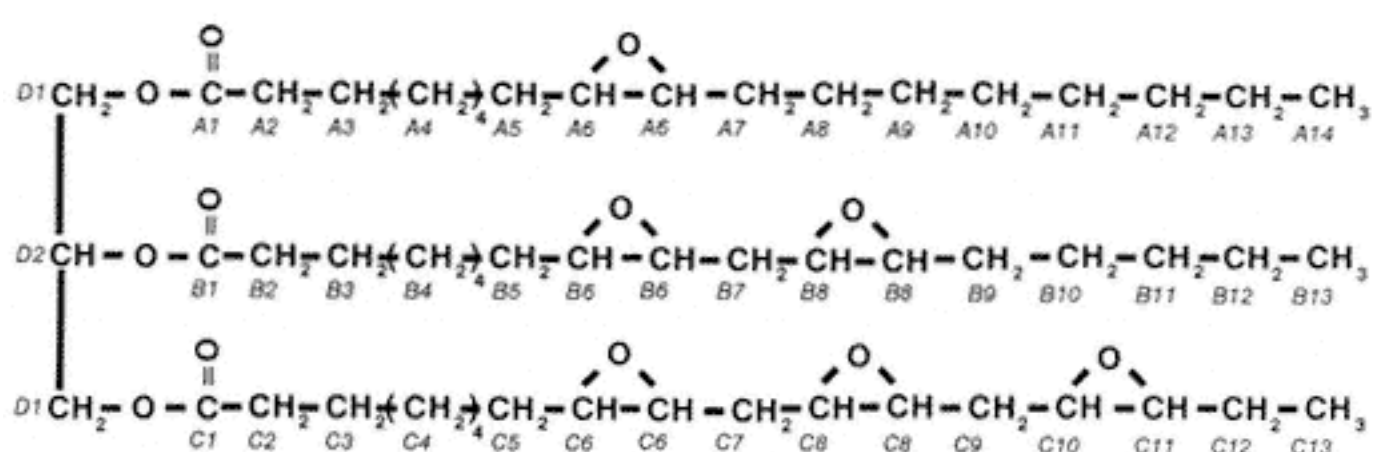
The acid moiety is primarily *cis/cis*. Solvent resonances are marked by **X**.



**X-B-10—
Epoxidized Linseed Oil (ELO)****Comments**

The acid moieties are primarily *cis* at each double bond. This material can be differentiated from epoxidized soybean oil (ESO) {X-B-11} by relative peak ratios. Solvent resonances are marked by **X**. This material is employed as a plasticizer for poly(vinyl chloride) (PVC) {V-A-8}, but its use can lead to aging problems at high concentrations. ELO also serves as stabilizer, scavenging HCl produced as PVC degrades.





Code	Shift (ppm)
A1	172.7
A2	34.3
A3–A5	10–34
A6	53–58
A7–A14	10–34
B1	172.7
B2	34.3
B3–B5	10–34
B6	53–58
B7	10–34
B8	53–58
B9–B13	10–34
C1	172.7
C2	34.3
C3–C5	10–34
C6	53–58
C7	10–34
C8	53–58
C9	10–34
C10	53–58
C11	53–58
C12, C13	10–34
D1	61.8
D2	68.8

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

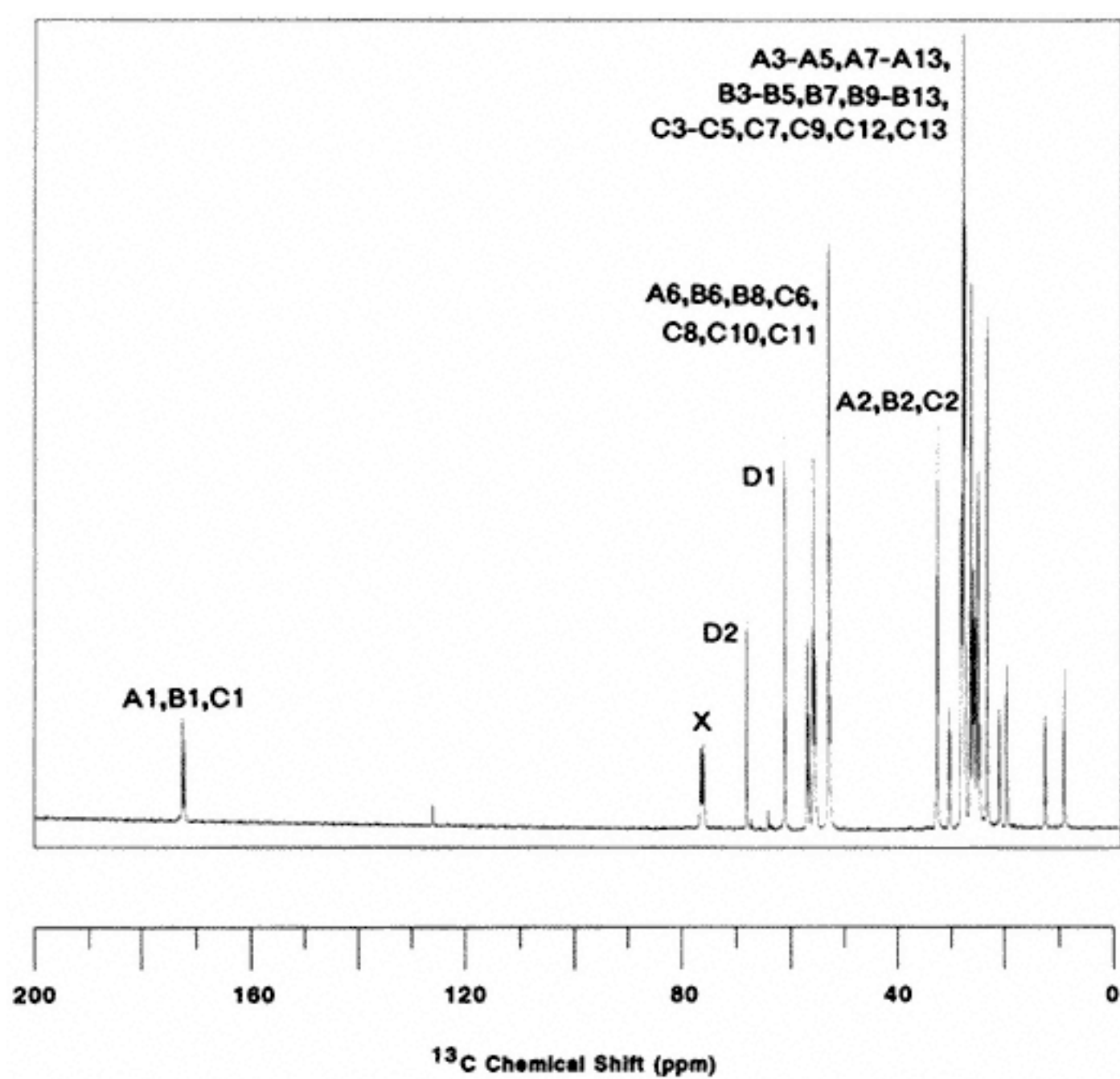
Pulse width: 90°

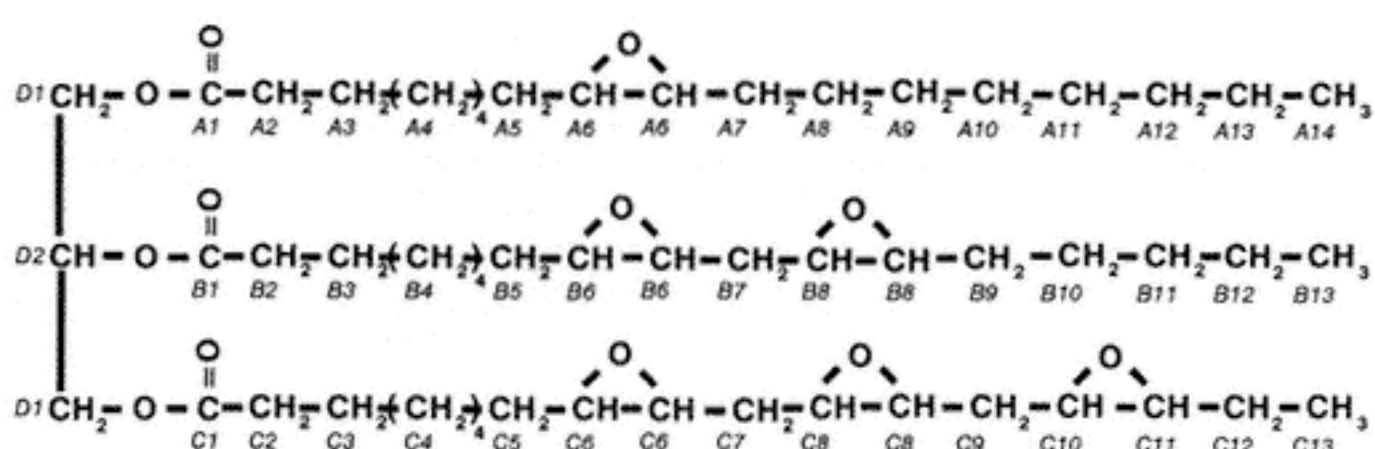
Broadening: 2 Hz

Pulse delay: 5 s

**X-B-11—
Epoxidized Soybean Oil (ESO)****Comments**

The acid moieties are primarily *cis* at each double bond. This material can be differentiated from epoxidized linseed oil (ELO) {X-B-10} by relative peak ratios. Solvent resonances are marked by **X**. This material is employed as a plasticizer in poly(vinyl chloride) (PVC) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) (VC/VA) {V-A-9}, ethylcellulose {VII-B-3}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}, but its use can lead to aging problems at high concentrations. ESO also serves as stabilizer, scavenging HCl produced as PVC or VC/VA degrades.





Code	Shift (ppm)
A1	172.7
A2	34.3
A3–A5	10–34
A6	53–58
A7–A14	10–34
B1	172.7
B2	34.3
B3–B5	10–34
B6	53–58
B7	10–34
B8	53–58
B9–B13	10–34
C1	172.7
C2	34.3
C3–C5	10–34
C6	53–58
C7	10–34
C8	53–58
C9	10–34
C10	53–58
C11	53–58
C12, C13	10–34
D1	61.8
D2	68.8

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

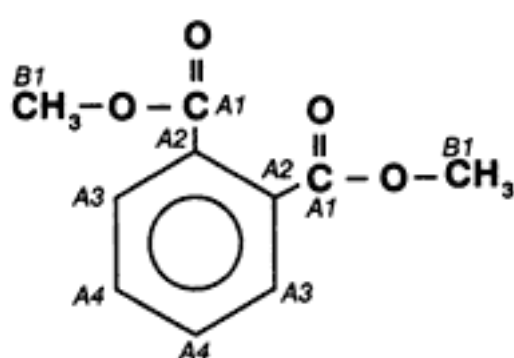
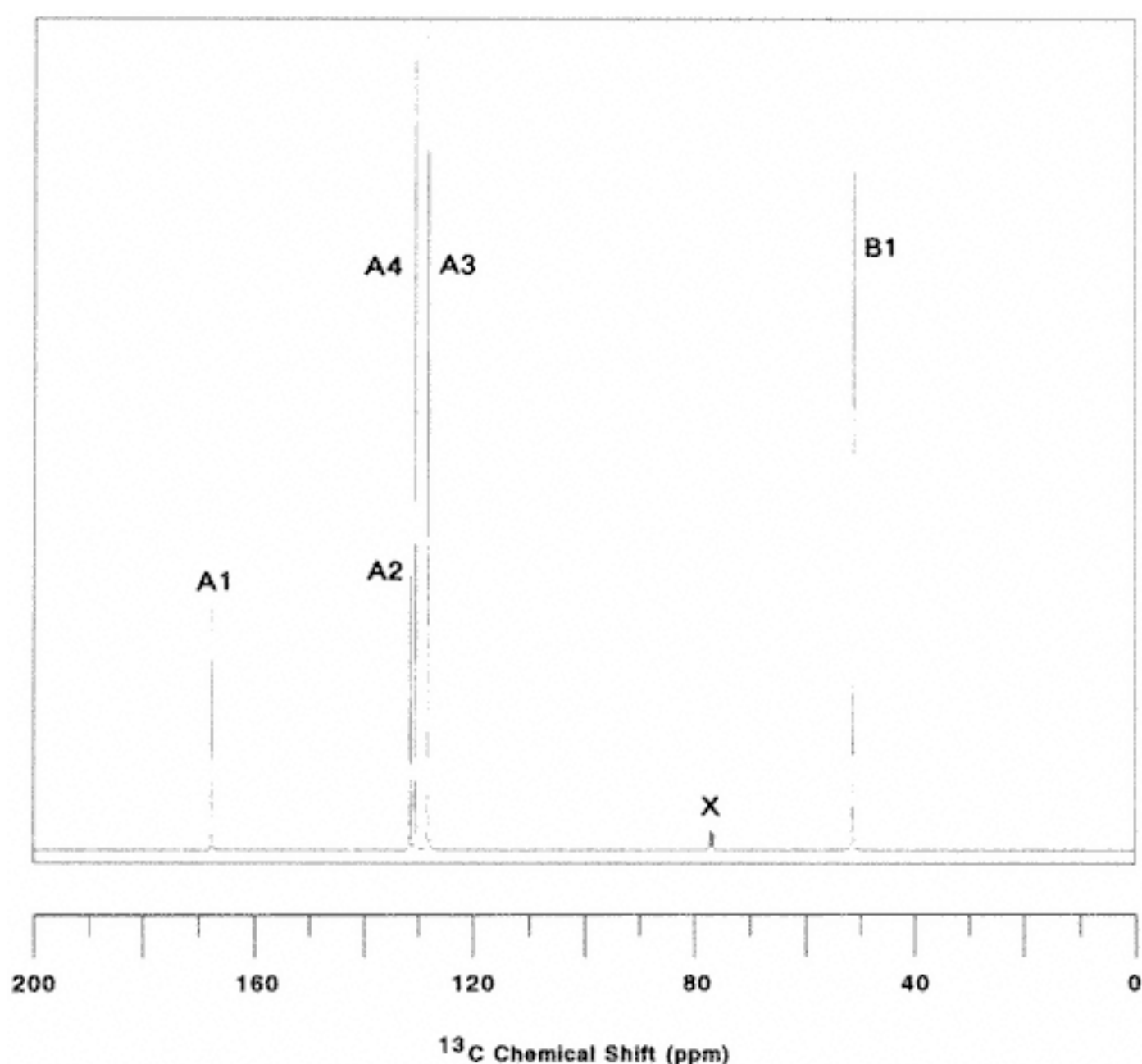
Broadening: 2 Hz

Pulse delay: 5 s

**X-C-1—
Dimethyl Phthalate**

Comments

Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, polyisoprene {VI-B-1}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}. It is also found in lacquers, coatings, and molding powders.



Code	Shift (ppm)
A1	169.7
A2	131.5
A3	128.0
A4	130.6
B1	51.8

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

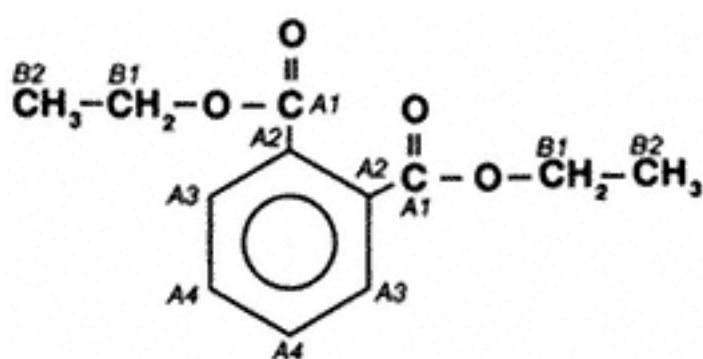
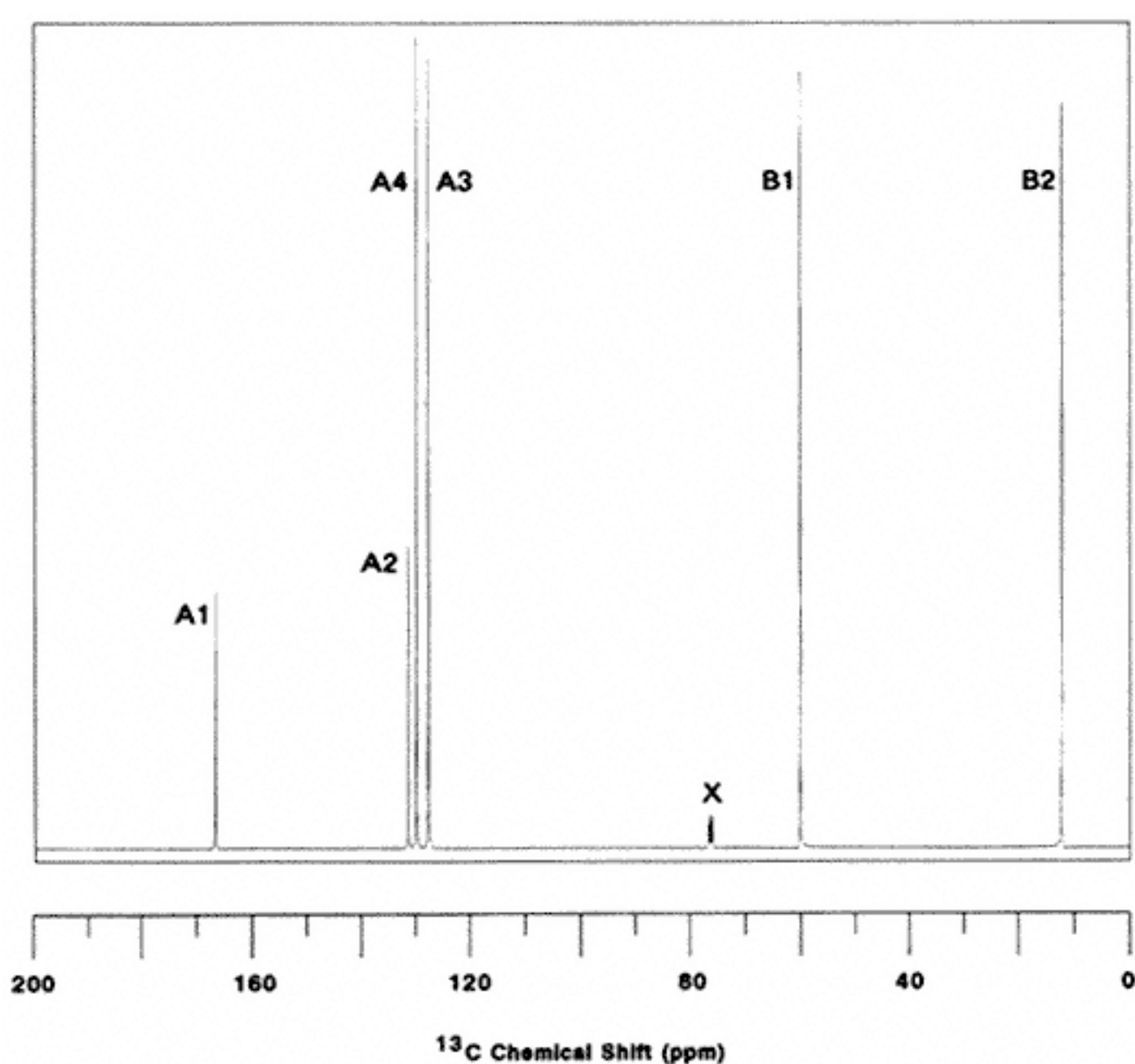
Broadening: 2 Hz

Pulse delay: 5 s

**X-C-2—
Diethyl Phthalate**

Comments

Solvent resonances are marked by **X**. It is used as a plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
A1	167.2
A2	132.4
A3	128.6
A4	130.3
B1	60.8
B2	13.0

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

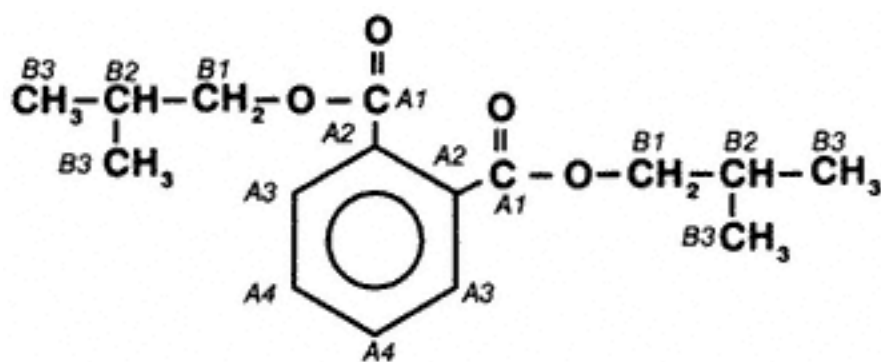
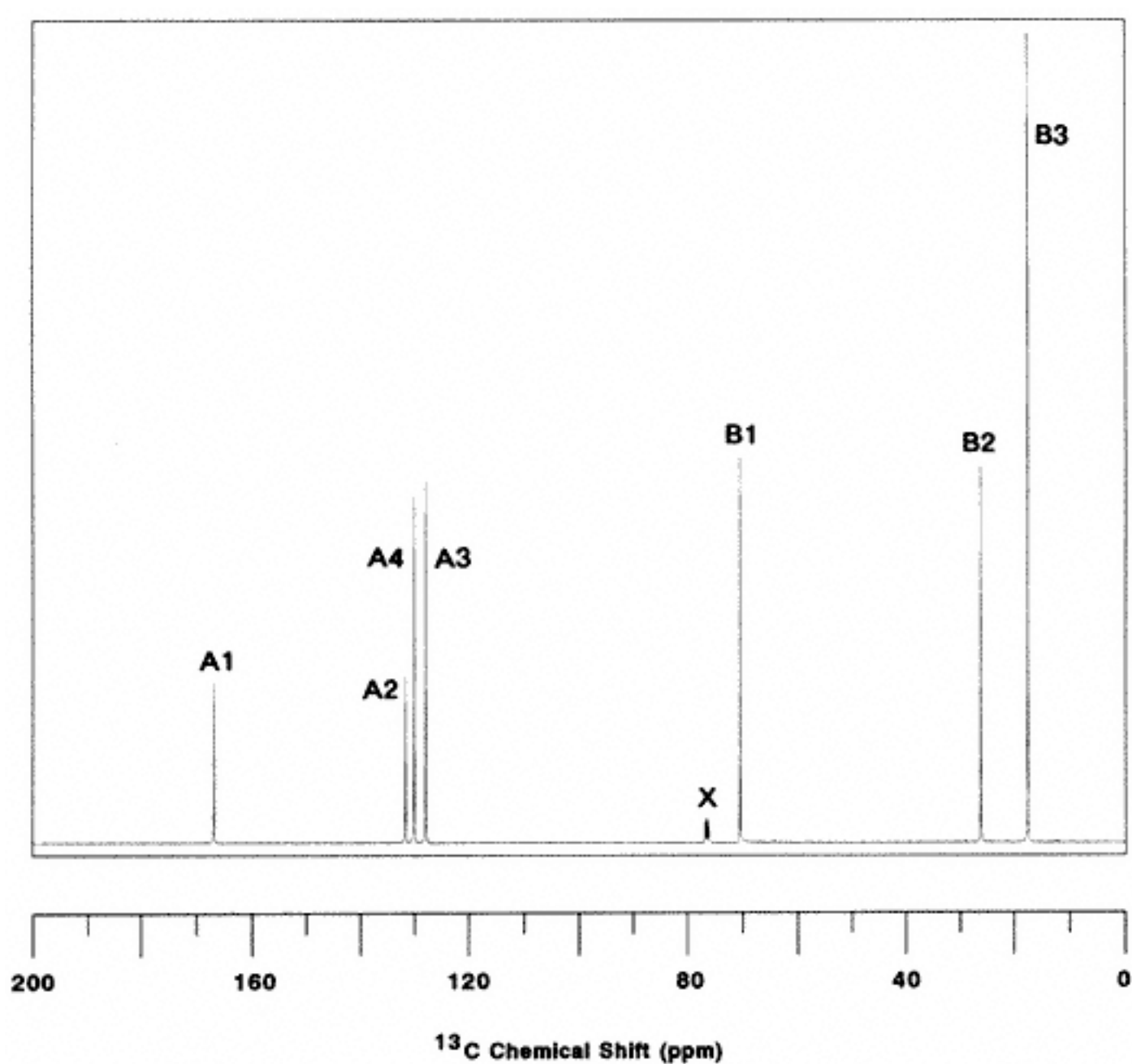
Broadening: 2 Hz

Pulse delay: 5 s

**X-C-3—
Diisobutyl Phthalate**

Comments

Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
A1	166.7
A2	132.2
A3	128.9
A4	131.1
B1	71.2
B2	27.4
B3	18.5

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

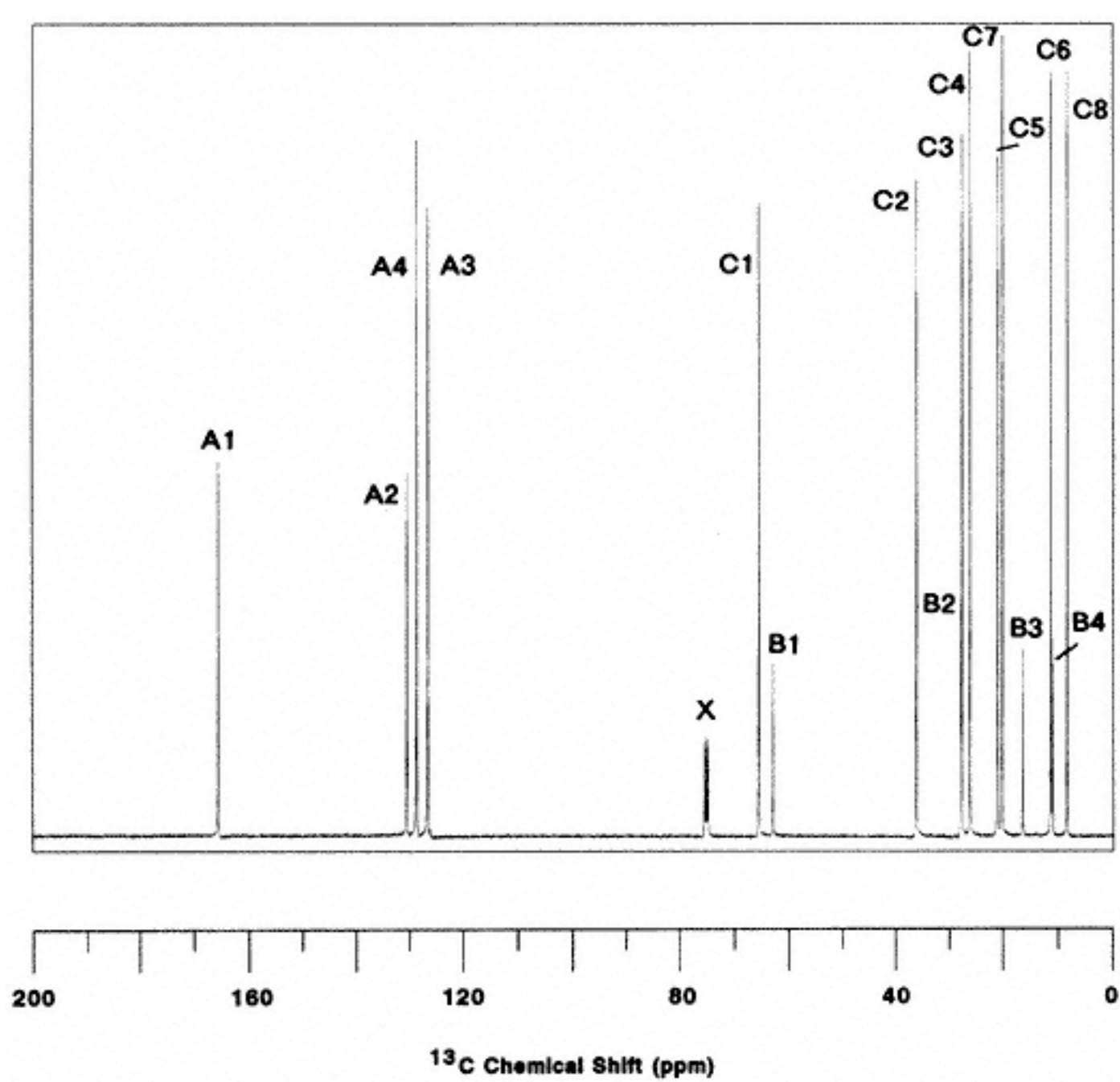
X-C-4

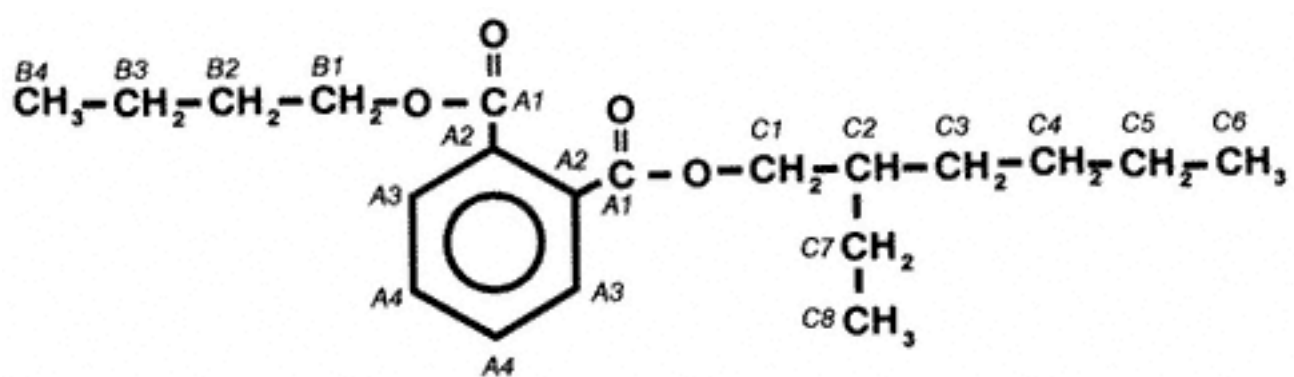
X-C-4—

Butyl 2-Ethylhexyl Phthalate

Comments

Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.





Code	Shift (ppm)
A1	166.9
A2	132.7
A3	128.3
A4	130.3
B1	64.7
B2	30.0
B3	18.3
B4	13.4
C1	67.4
C2	38.4
C3	30.0
C4	28.4
C5	22.0
C6	13.5
C7	23.4
C8	10.4

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

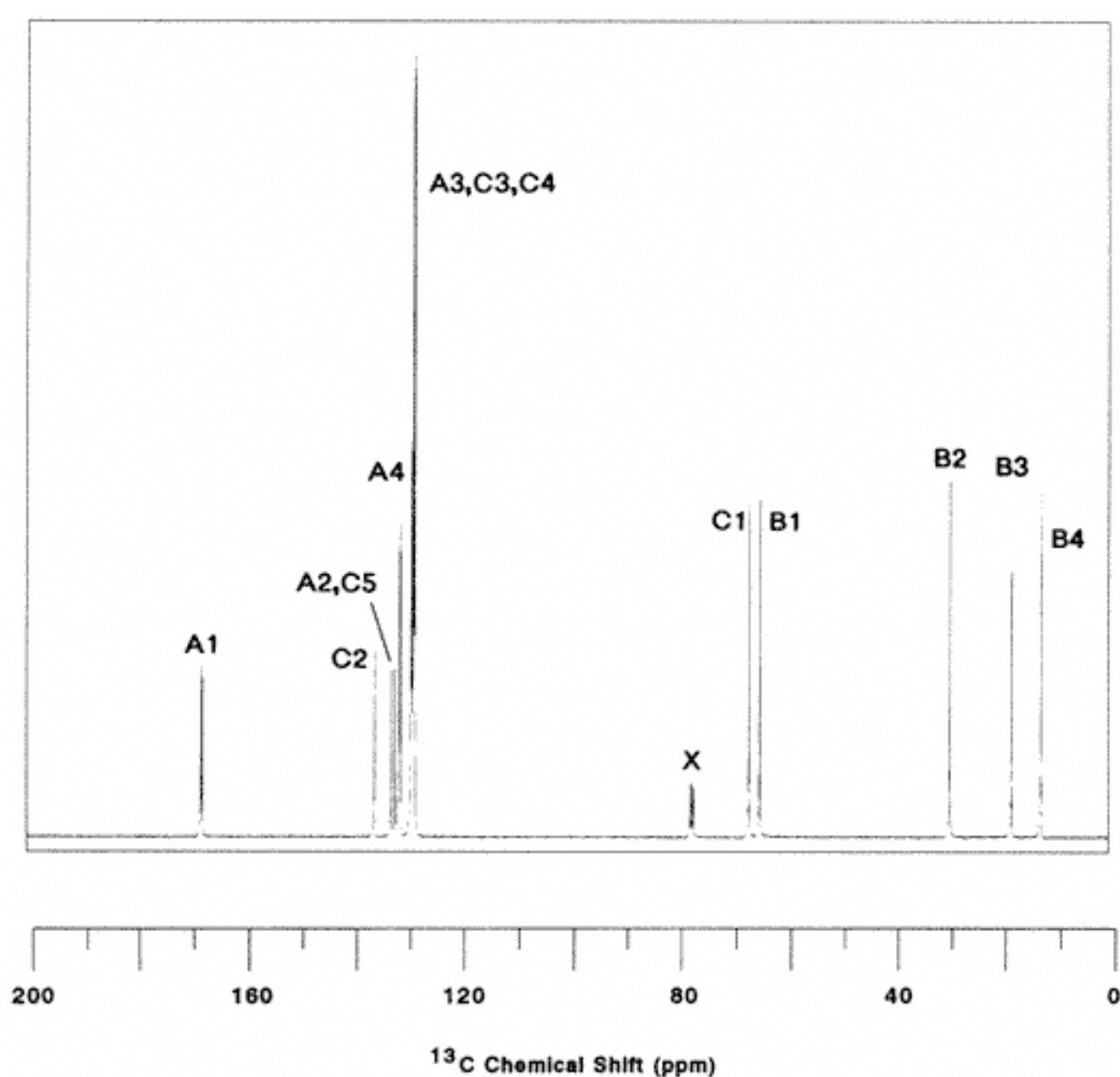
Pulse width: 90°

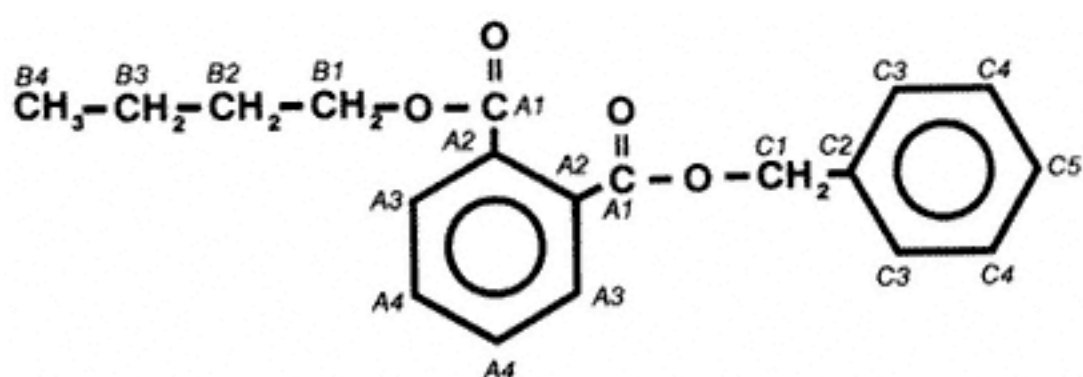
Broadening: 2 Hz

Pulse delay: 5 s

**X-C-5—
Butyl Benzyl Phthalate****Comments**

Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene [III-A-2), poly (methyl methacrylate) {IV-C-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, and cellulose acetate butyrate, {VII-B-5}. It also improves stain resistance.





Code	Shift (ppm)
A1	167.0
A2	132.2
A3	128.6
A4	130.6
B1	64.6
B2	29.4
B3	18.8
B4	13.0
C1	67.0
C2	135.9
C3	128.0
C4	128.0
C5	131.6

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

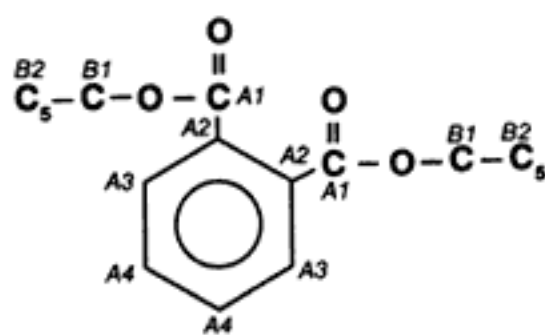
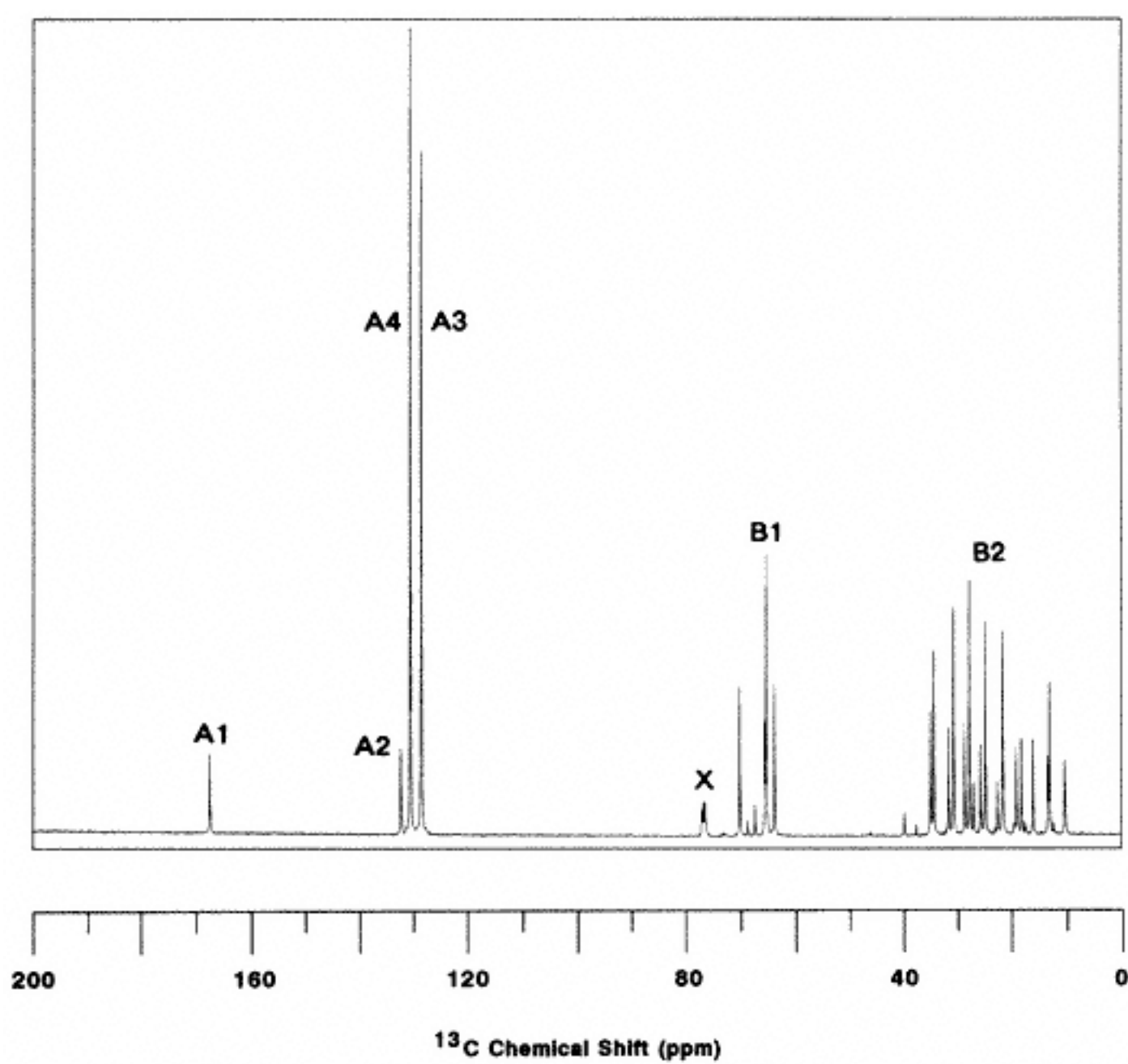
Broadening: 2 Hz

Pulse delay: 5 s

**X-C-6—
Dihexyl Phthalate**

Comments

The spectrum is complex because of the variety of C₆ isomers present. Solvent resonances are marked by **X**. This material is used as a plasticizer in poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
A1	167.9
A2	138.6
A3	127.8
A4	130.9
B1	63–66
B2	10–40

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

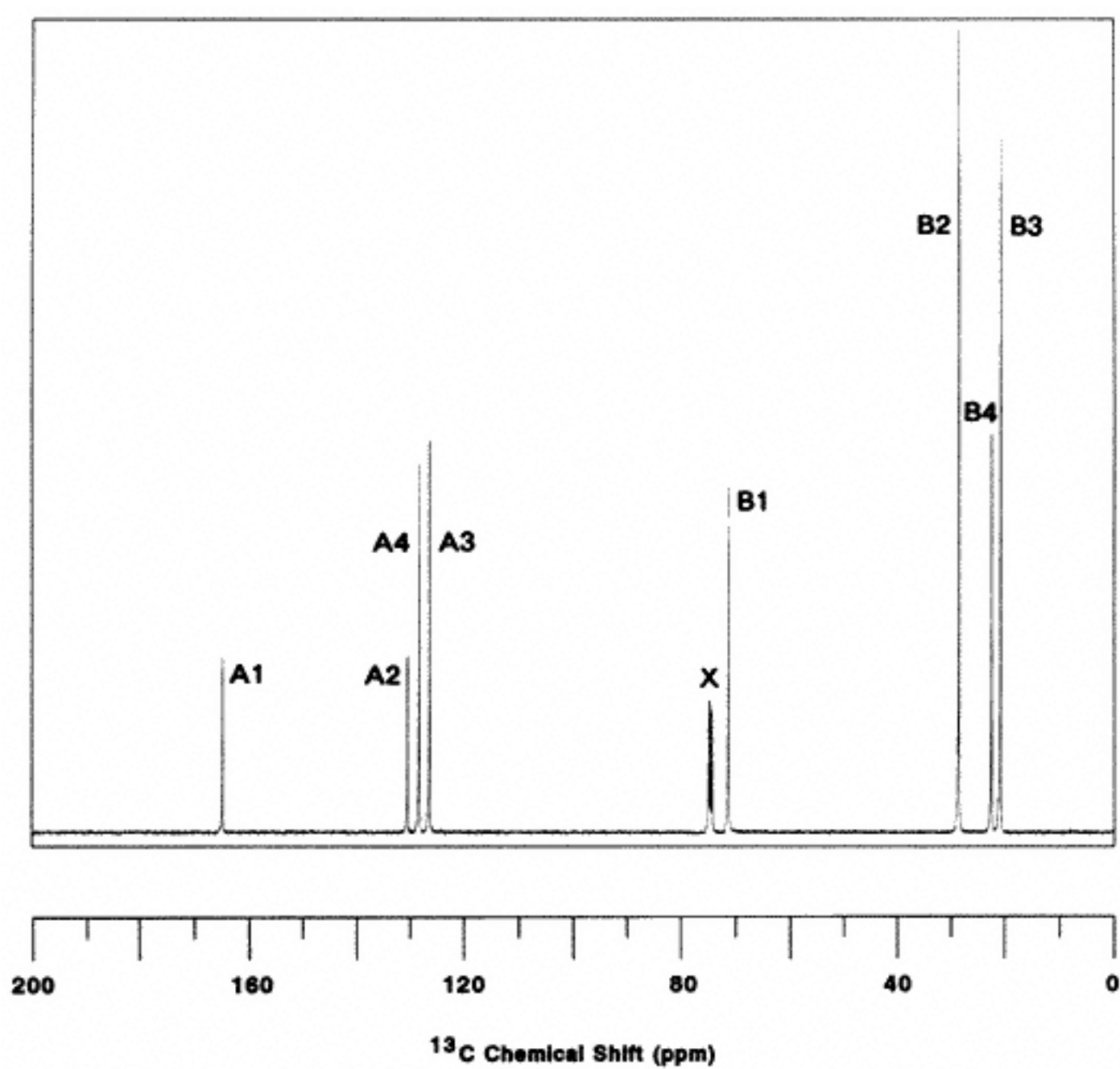
Broadening: 2 Hz

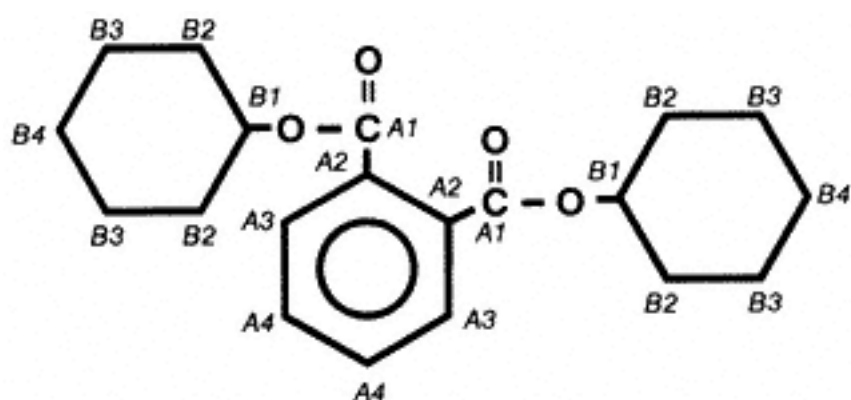
Pulse delay: 5 s

X-C-7

**X-C-7—
Dicyclohexyl Phthalate****Comments**

Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, chlorinated polyisoprene {VI-B-3}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.





Code	Shift (ppm)
A1	167.4
A2	133.5
A3	128.5
A4	130.9
B1	75.2
B2	30.9
B3	23.5
B4	25.6

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

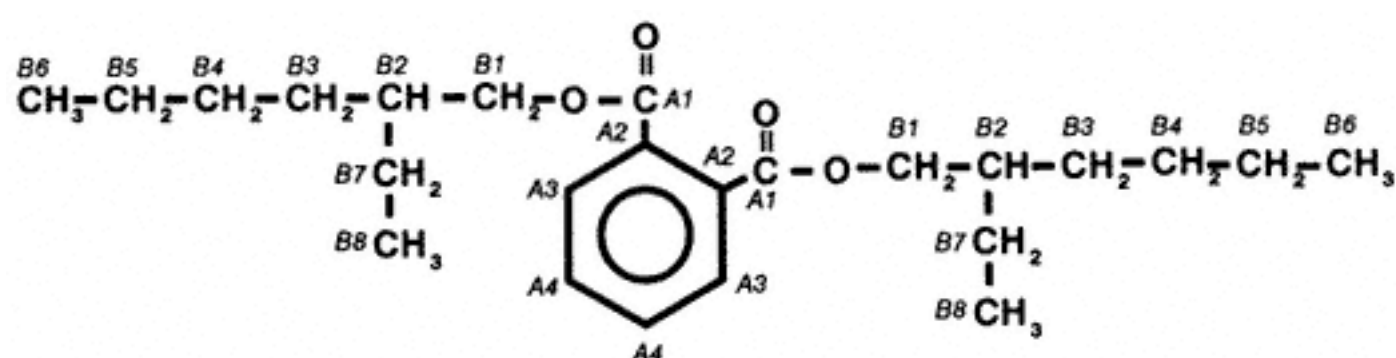
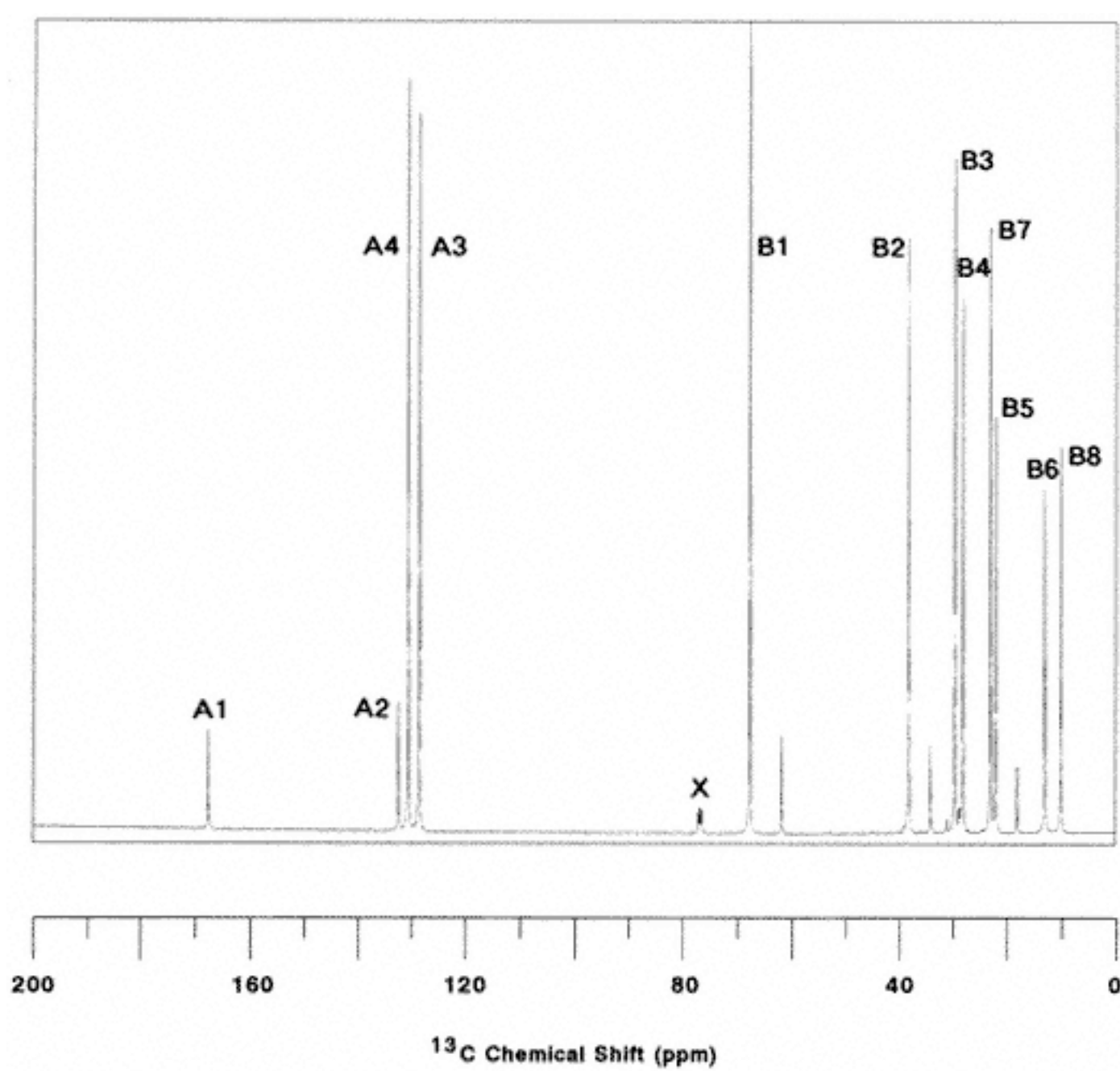
Pulse delay: 5 s

X-C-8—

Di(2-Ethylhexyl) Phthalate (DEHP)

Comments

Also known as dioctyl phthalate (DOP). Solvent resonances are marked by X. This material accounts for one-quarter of all plasticizer volume. It is used as a plasticizer in polystyrene {III-A-2}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, ethyl cellulose {VII-B-3}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
A1	168.0
A2	132.9
A3	129.3
A4	130.9
B1	67.8
B2	38.7
B3	30.1
B4	28.7
B5	22.8
B6	13.5
B7	23.4
B8	10.7

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

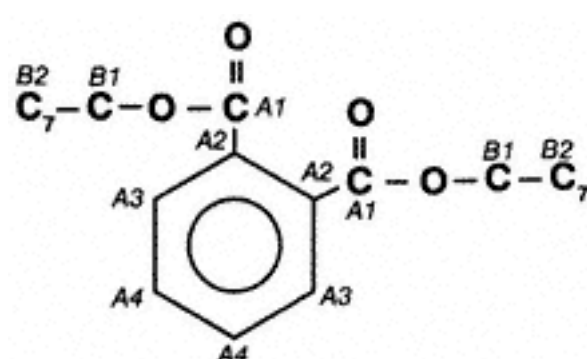
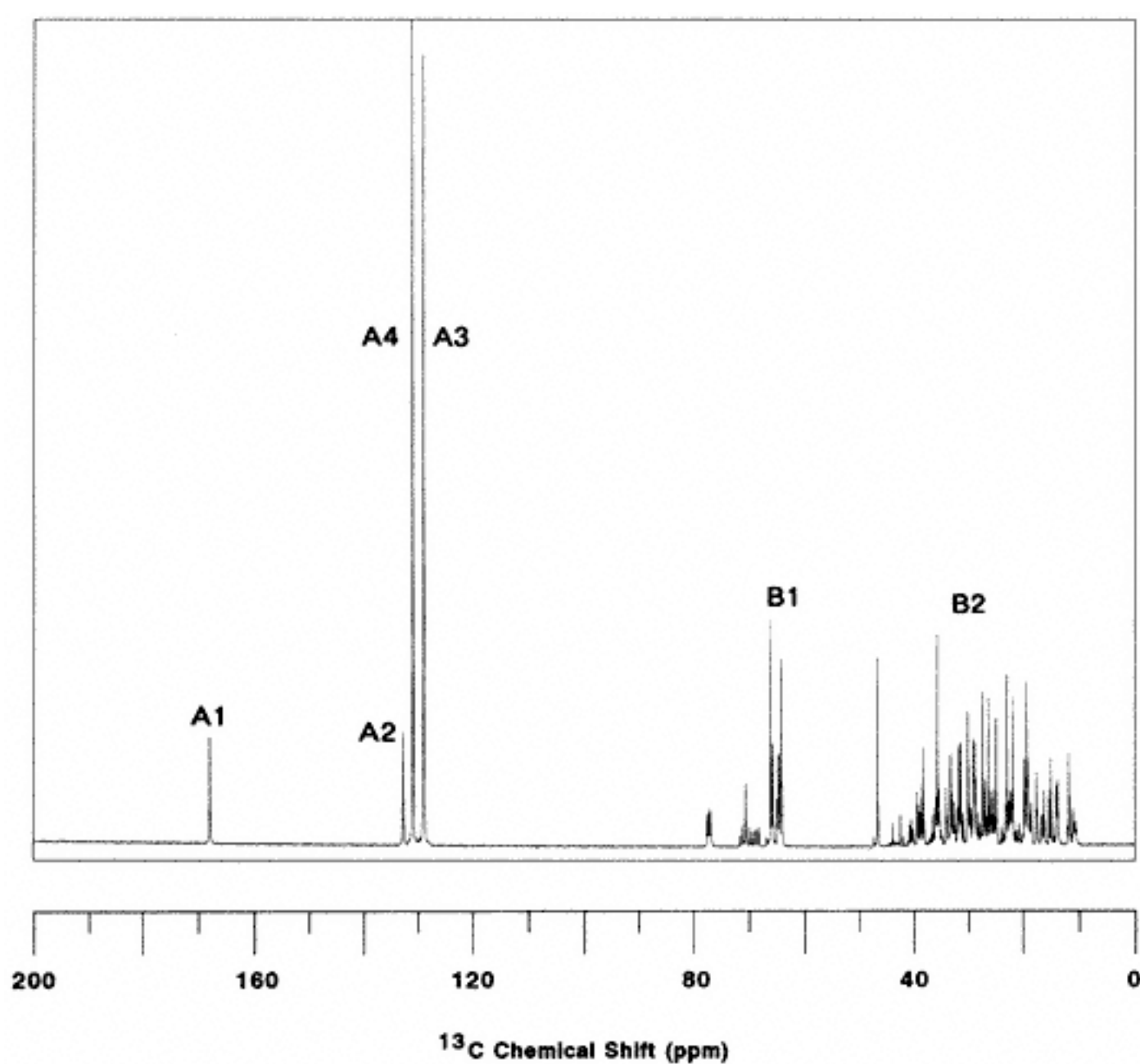
Broadening: 2 Hz

Pulse delay: 5 s

**X-C-9—
Diethyl Phthalate**

Comments

The spectrum is complex because of the variety of C₈ isomers present. Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, polyisoprene {VI-B-1}, ethyl cellulose {VII-B-3}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
A1	167.5
A2	132.6
A3	128.8
A4	130.8
B1	63–66
B2	10–47

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

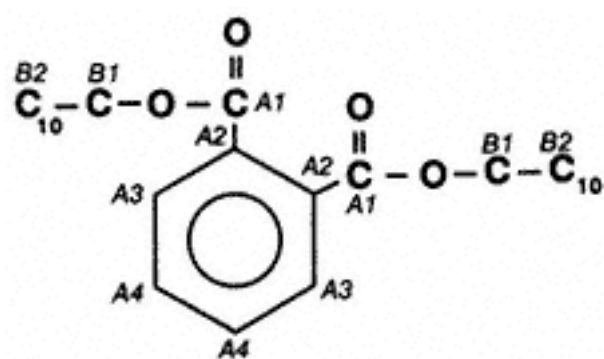
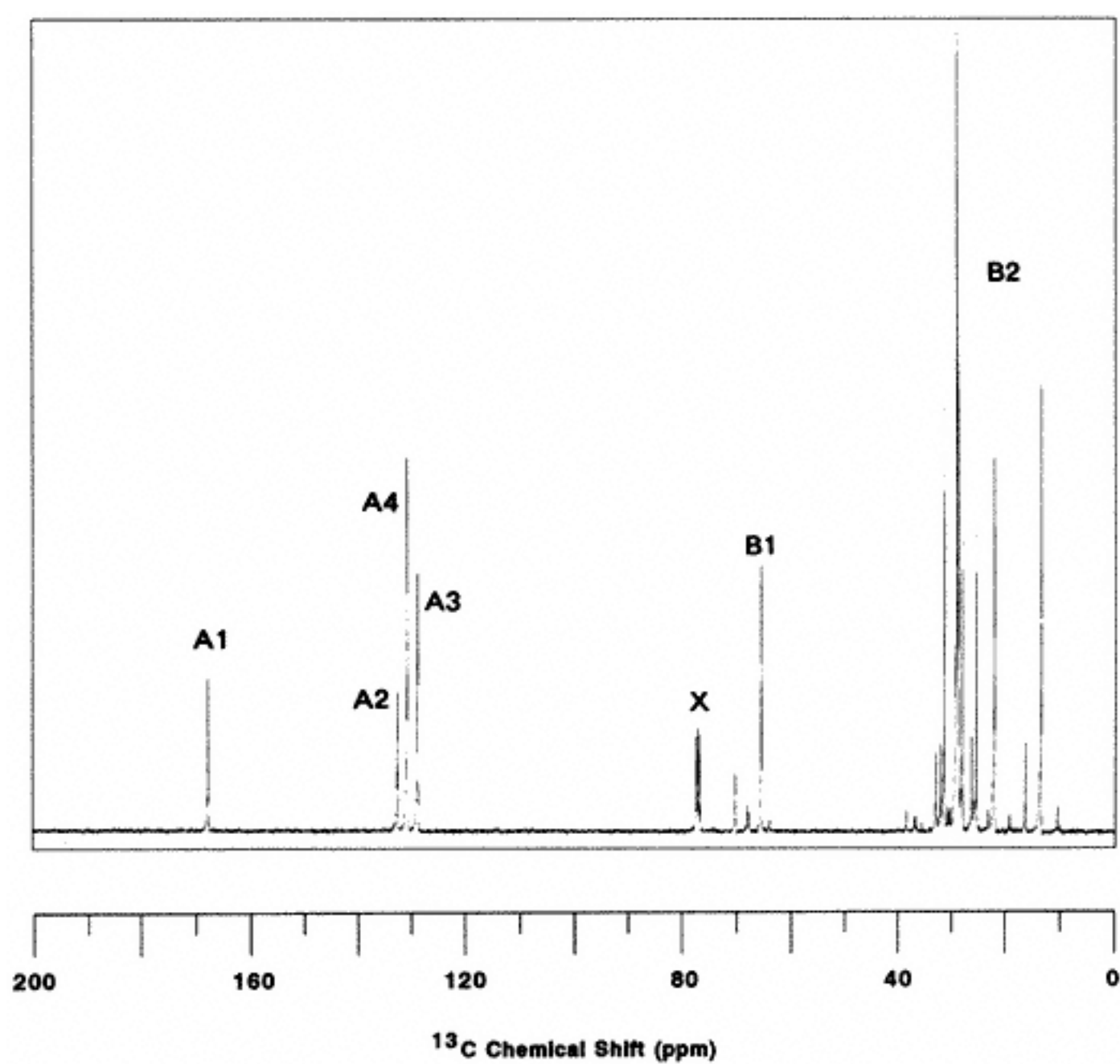
Broadening: 2 Hz

Pulse delay: 5 s

**X-C-10—
Diundecyl Phthalate (DUP)**

Comments

The spectrum is complex because of the variety of C₁₁ isomers present. Solvent resonances are marked by **X**. This material is used as a plasticizer for poly(vinyl chloride) {V-A-8}, particularly for automobile interiors and electrical insulation. It exhibits good performance over a wide temperature range.



Code	Shift (ppm)
A1	167.4
A2	133.0
A3	128.6
A4	130.5
B1	65.4
B2	10–34

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 20% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

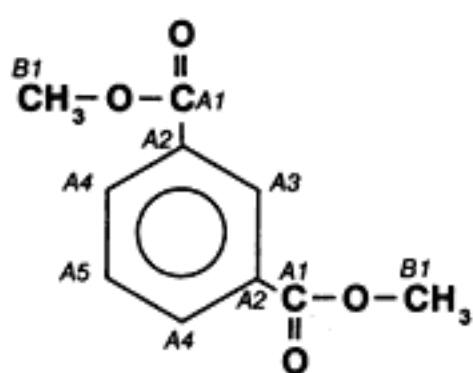
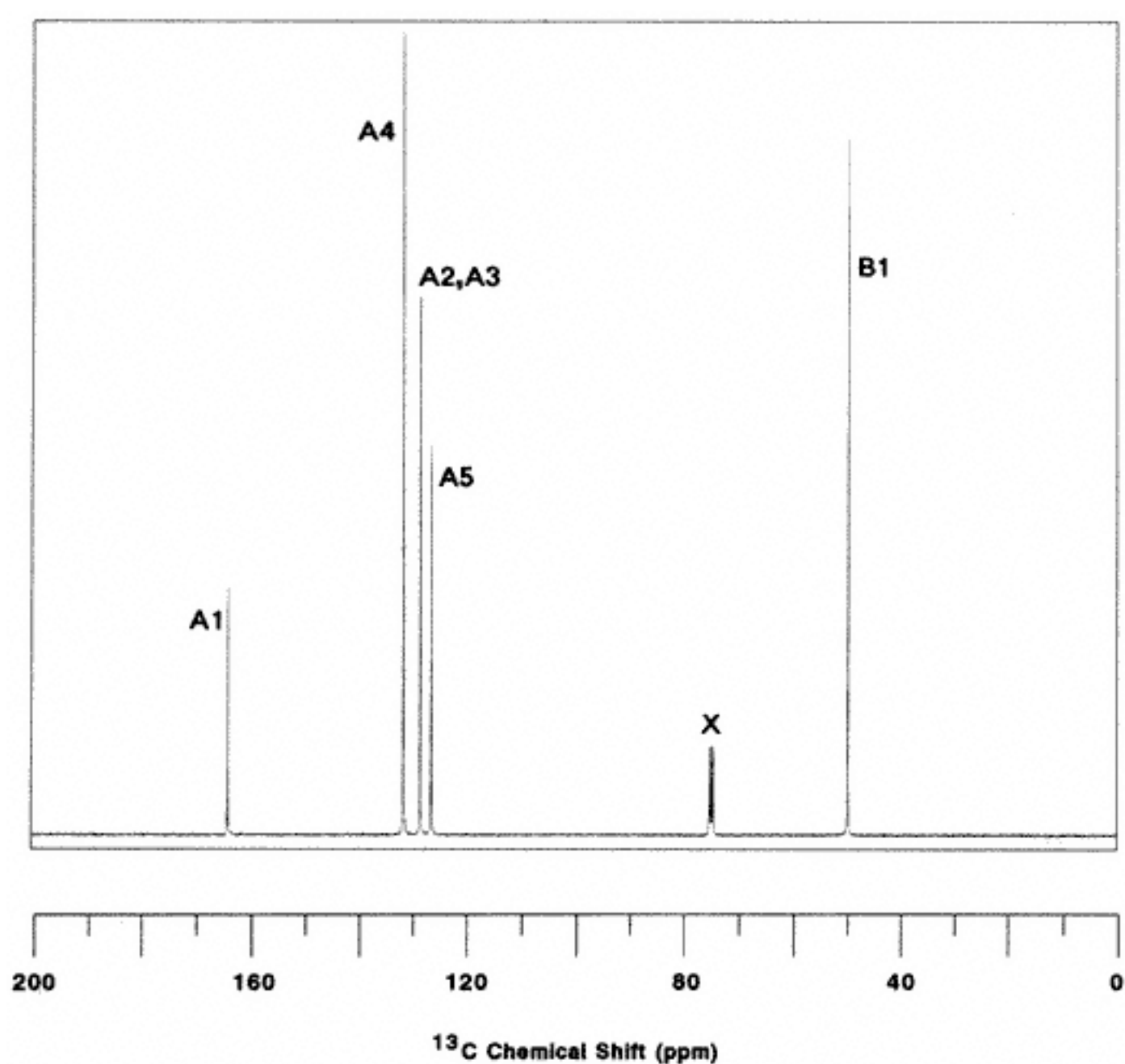
Broadening: 2 Hz

Pulse delay: 5 s

**X-C-11—
Dimethyl Isophthalate**

Comments

Solvent resonances are marked by **X**. This material is used as a plasticizer in polystyrene {III-A-2}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
A1	166.4
A2	130.9
A3	130.9
A4	133.4
A5	128.4
B1	51.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

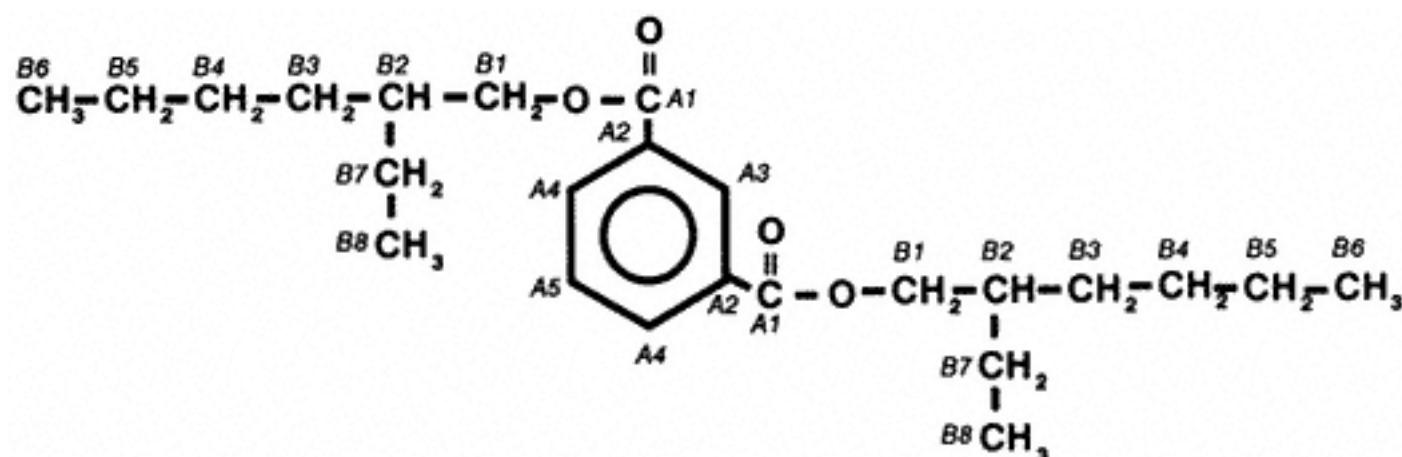
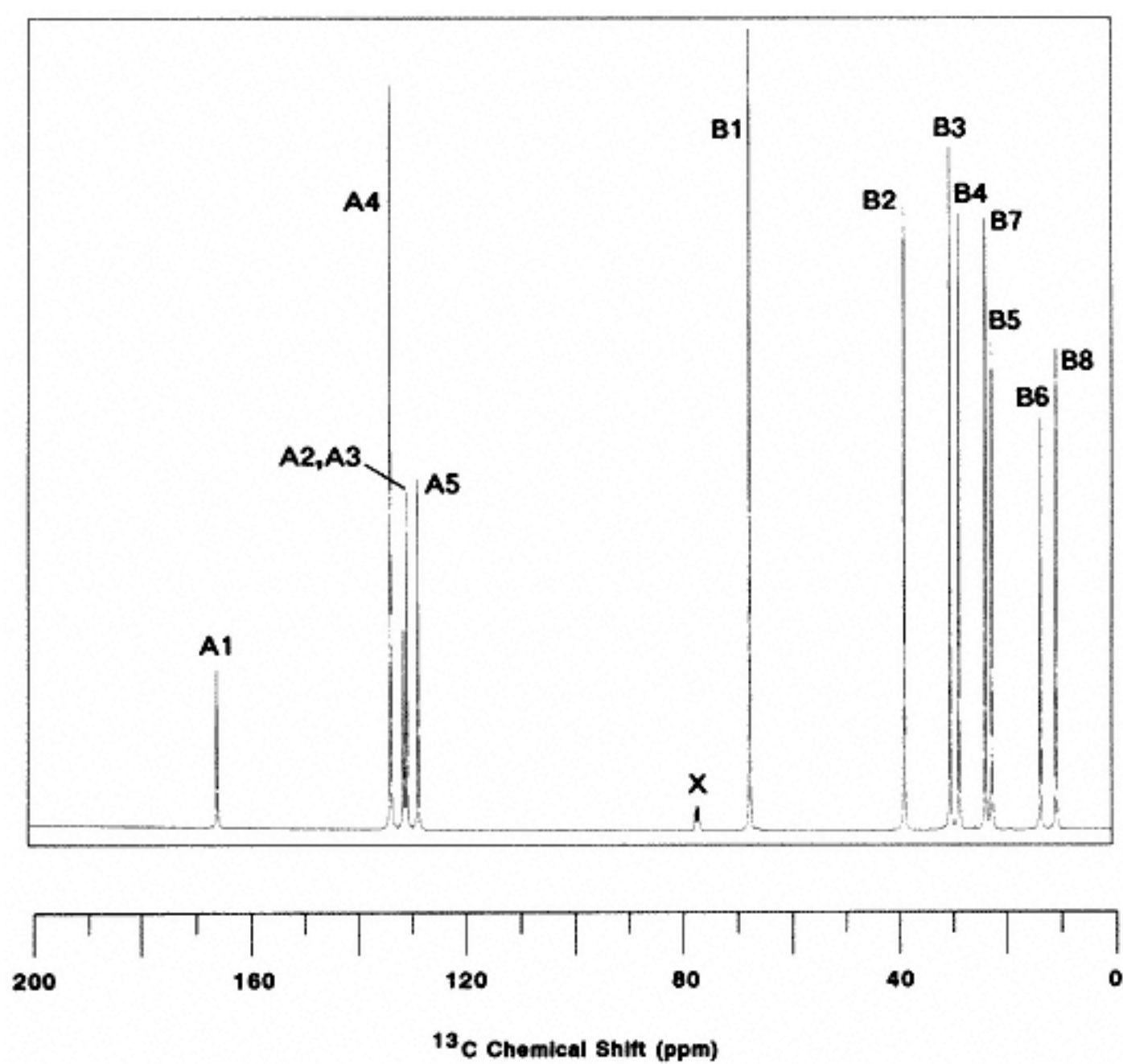
Pulse delay: 5 s

X-C-12

X-C-12—
Di(2-Ethylhexyl) Isophthalate

Comments

Also known as dioctyl isophthalate. Solvent resonances are marked by X.



Code	Shift (ppm)
A1	165.0
A2	130.3
A3	130.3
A4	133.3
A5	128.2
B1	67.4
B2	38.8
B3	30.4
B4	28.8
B5	22.7
B6	13.6
B7	23.8
B8	10.8

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 50% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

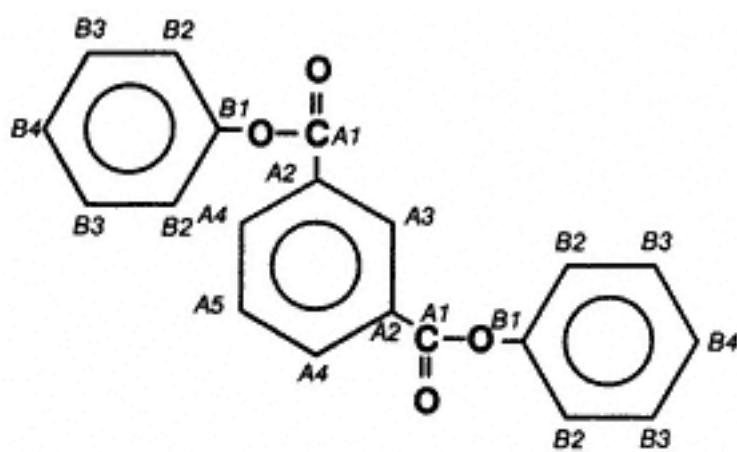
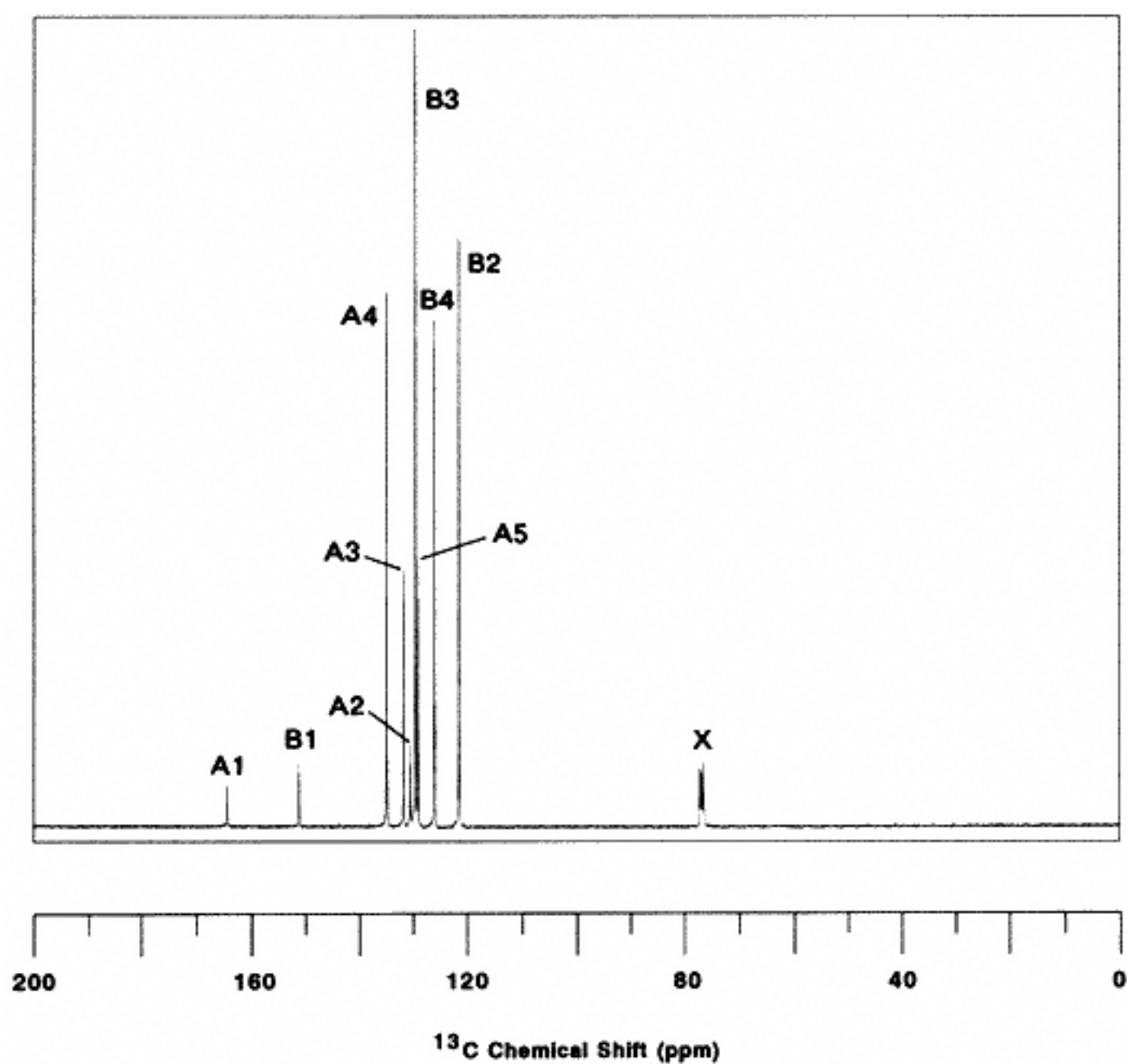
Broadening: 2 Hz

Pulse delay: 5 s

**X-C-13—
Diphenyl Isophthalate**

Comments

Solvent resonances are marked by X. This material is used in the manufacture of polyimidazoles and other high-performance polymers.



Code	Shift (ppm)
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A1	163.8
----	-------

A2	129.9
----	-------

A3	131.6
----	-------

A4	134.7
----	-------

A5	129.4
----	-------

B1	150.7
----	-------

B2	121.4
----	-------

B3	130.4
----	-------

B4	125.9
----	-------

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

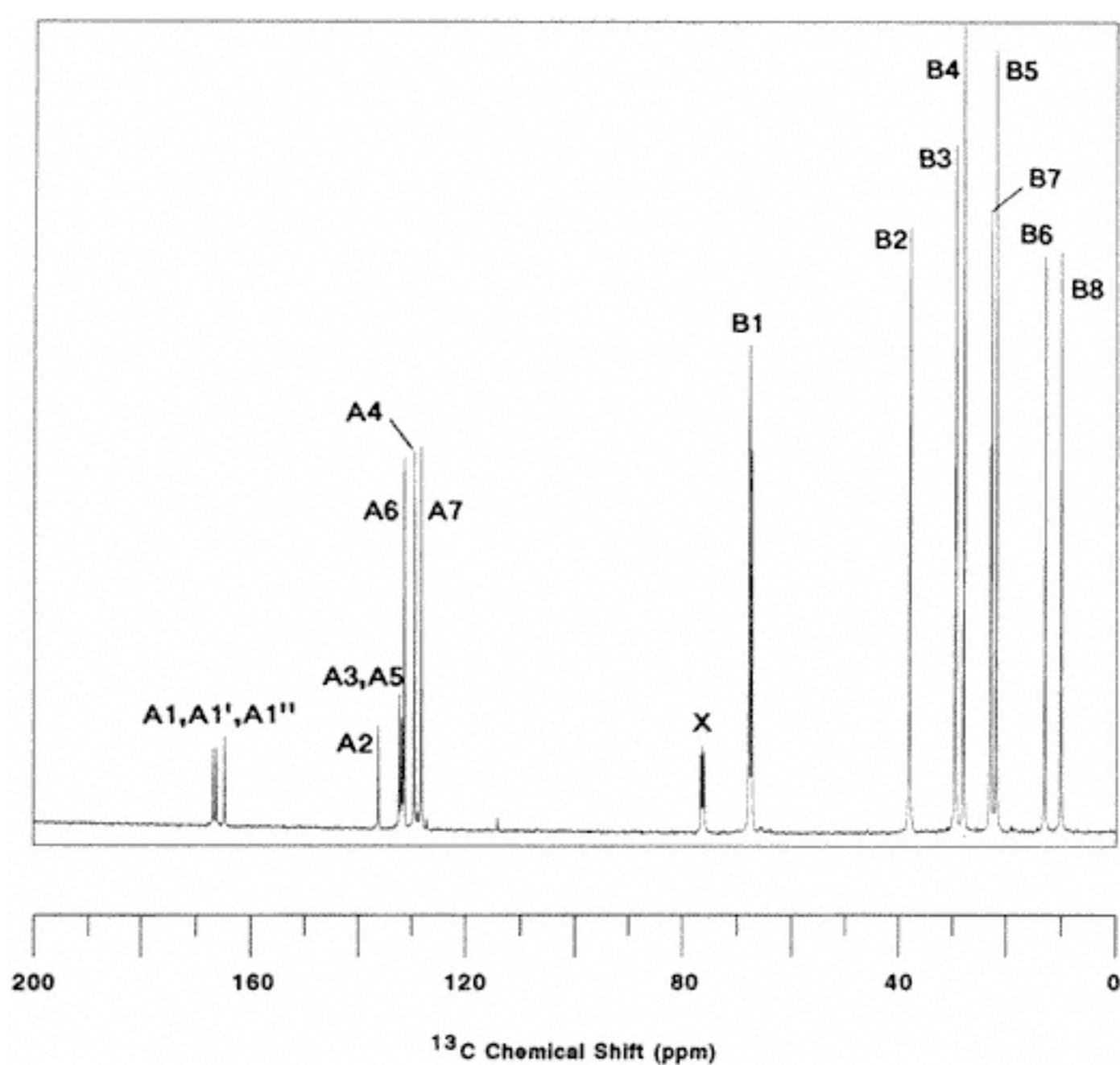
Pulse width: 90°

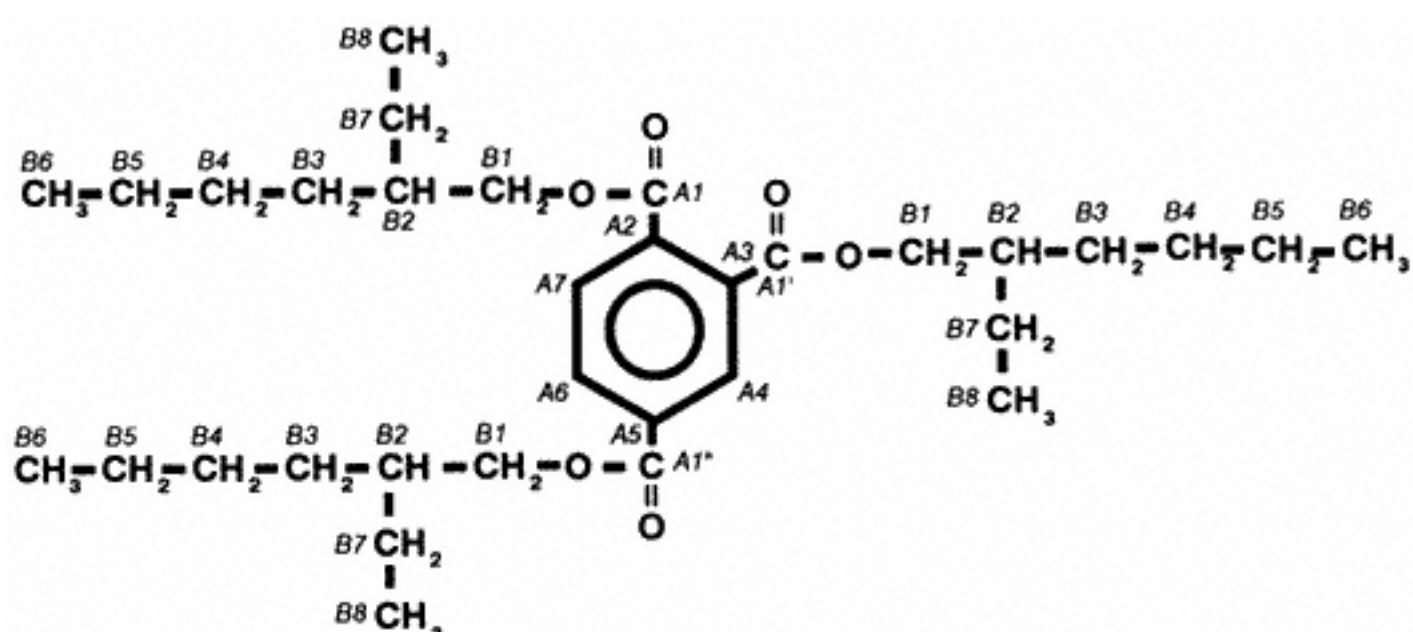
Broadening: 2 Hz

Pulse delay: 5 s

**X-C-14—
Tri(2-Ethylhexyl) Trimellitate****Comments**

Solvent resonances are marked by **X**. This material is used as a plasticizer for poly(vinyl chloride) {V-A-8}, resulting in good balance of properties and oxidative resistance, particularly in wire and cable jacketing.





Code	Shift (ppm)
A1	164–168
A1'	164–168
A1''	164–168
A2	136.5
A3	~132
A4	129.8
A5	~132
A6	131.7
A7	128.4
B1	68.2
B2	38.8
B3	30.4
B4	28.8
B5	22.8
B6	13.7
B7	23.7
B8	10.9

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

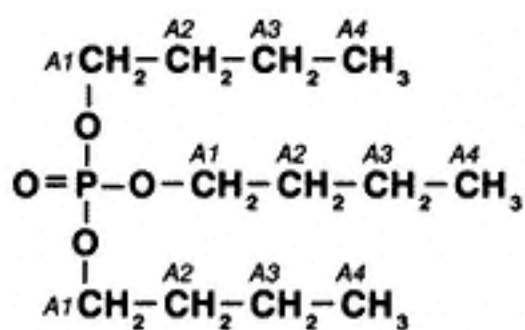
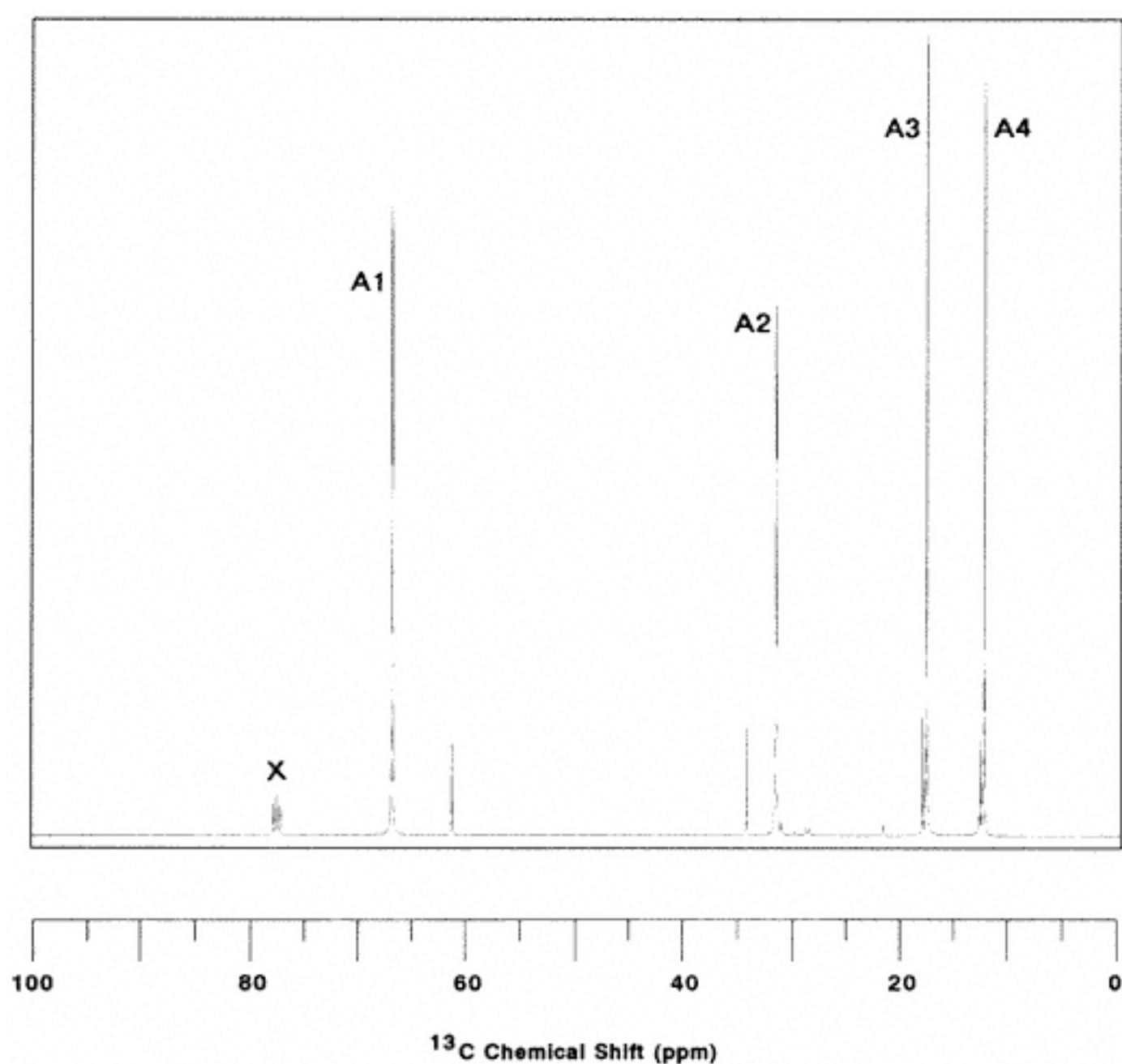
Broadening: 2 Hz

Pulse delay: 5 s

**X-D-1—
Tributyl Phosphate (TBP)**

Comments

Solvent resonances are marked by **X**; some residual *n*-butanol is also observed. This material is used as a flame-retardant plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
A1	66.6
A2	31.8
A3	18.1
A4	13.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

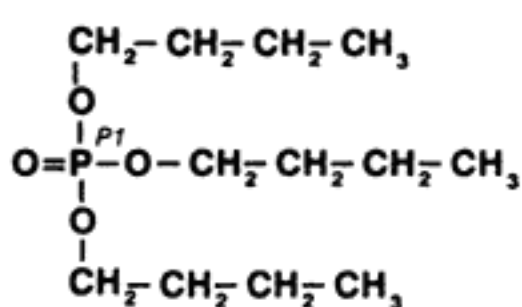
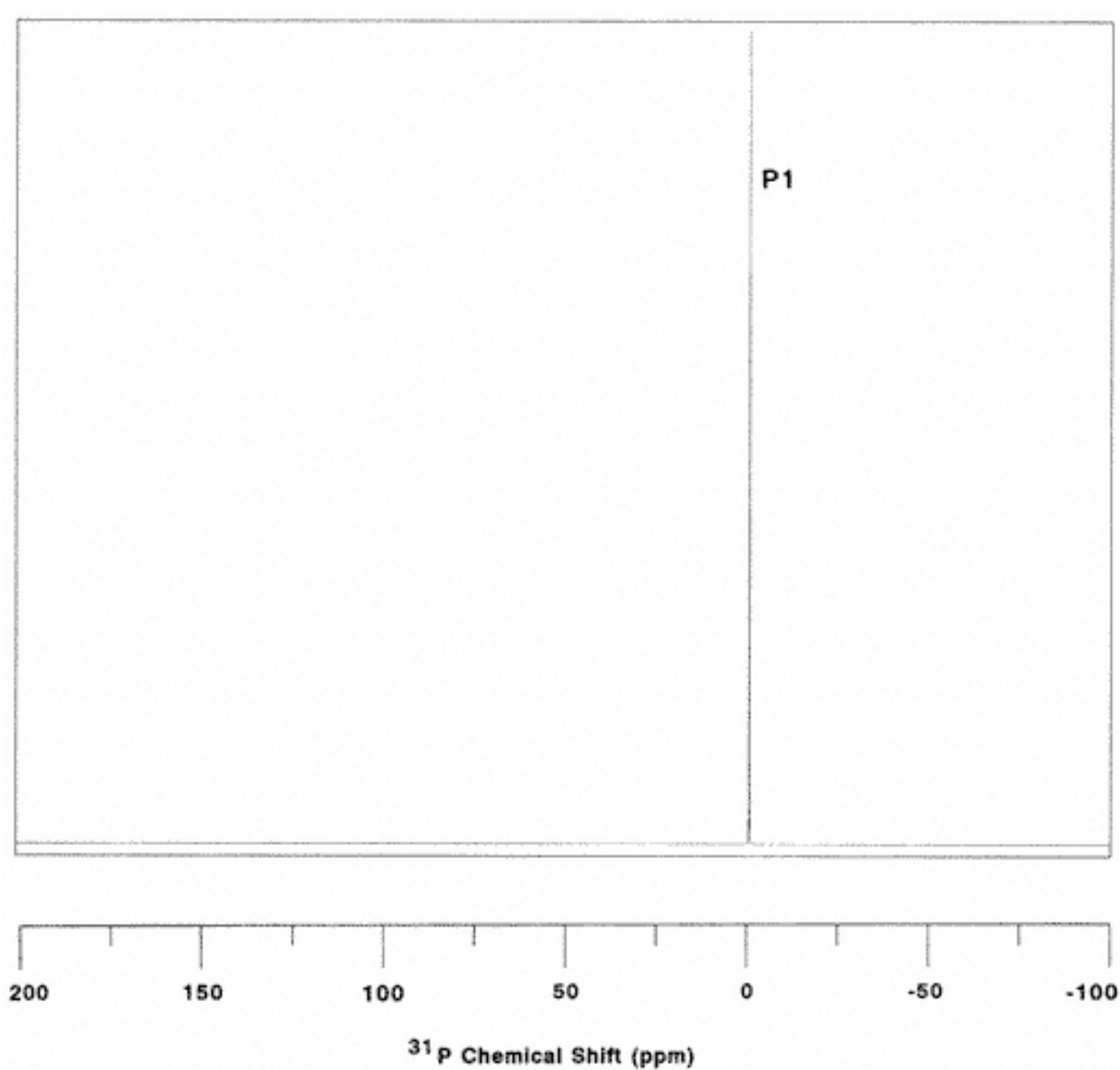
Broadening: 2 Hz

Pulse delay: 5 s

**X-D-1P—
Tributyl Phosphate (TBP)**

Comments

This material is used as a flame-retardant plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
P1	0.3

Experimental Parameters

Nucleus: ³¹P (161.8 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 20% w/w

Scans: 48

Spectral width: 70 kHz

Data points: 8192

Pulse width: 30°

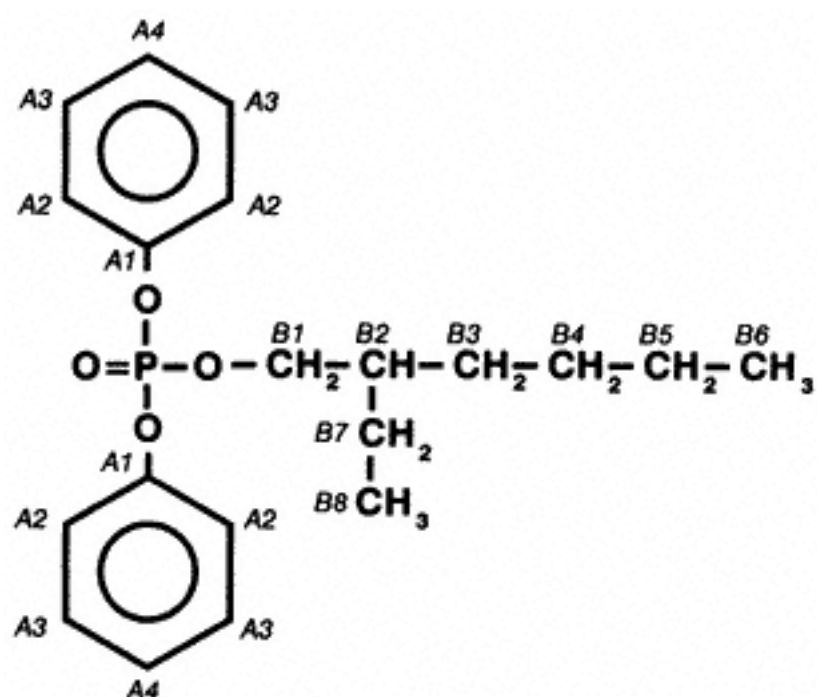
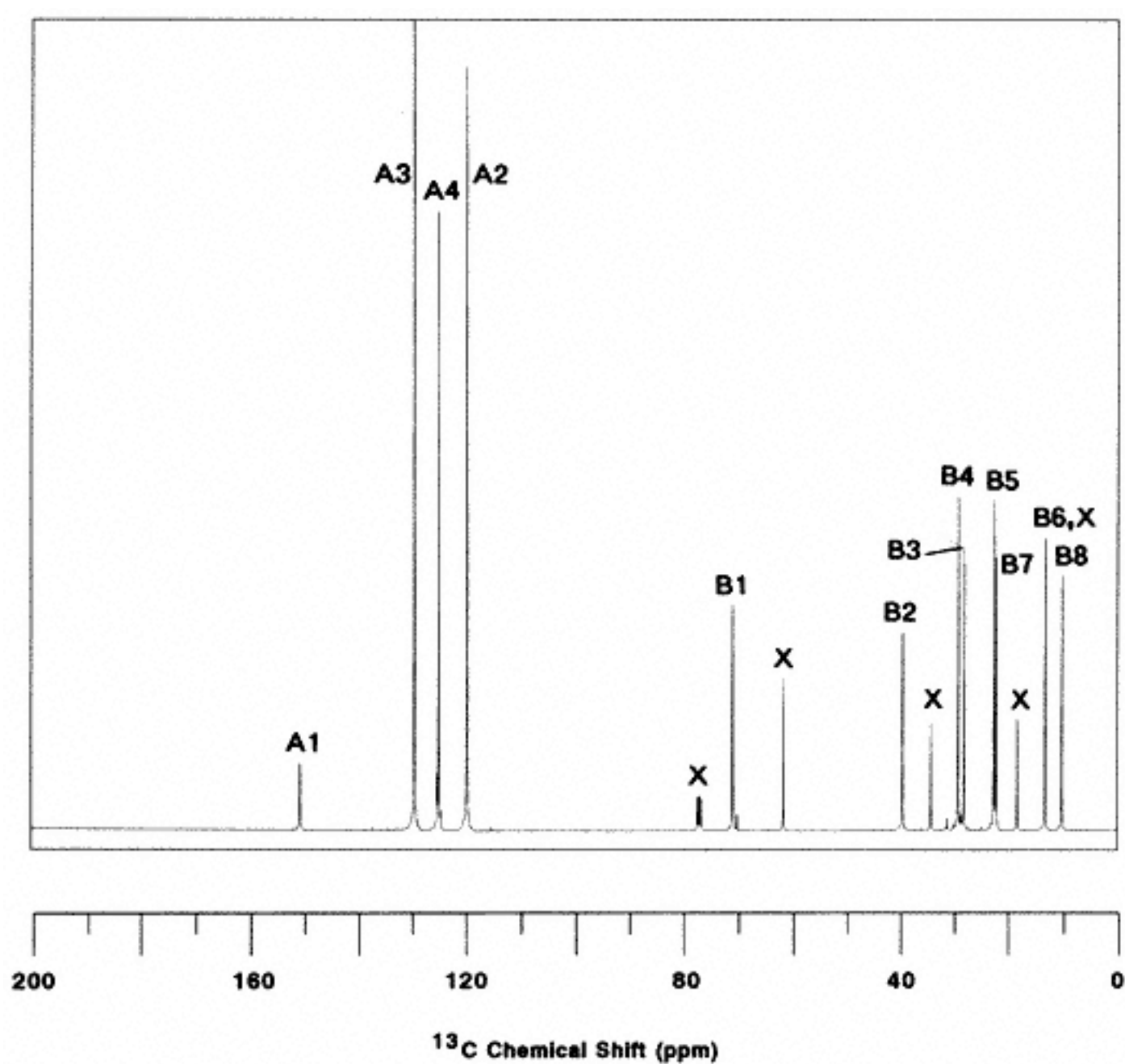
Broadening: 5 Hz

Pulse delay: 5 s

**X-D-2—
2-Ethylhexyl Diphenyl Phosphate**

Comments

Solvent resonances are marked by X; some *n*-butanol solvent is also observed. This material is used as a flame-retardant plasticizer.



Code	Shift (ppm)
A1	150.1
A2	119.8
A3	129.6
A4	125.4
B1	71.2
B2	40.0
B3	28.5
B4	29.1
B5	22.7
B6	13.7
B7	22.4
B8	10.6

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

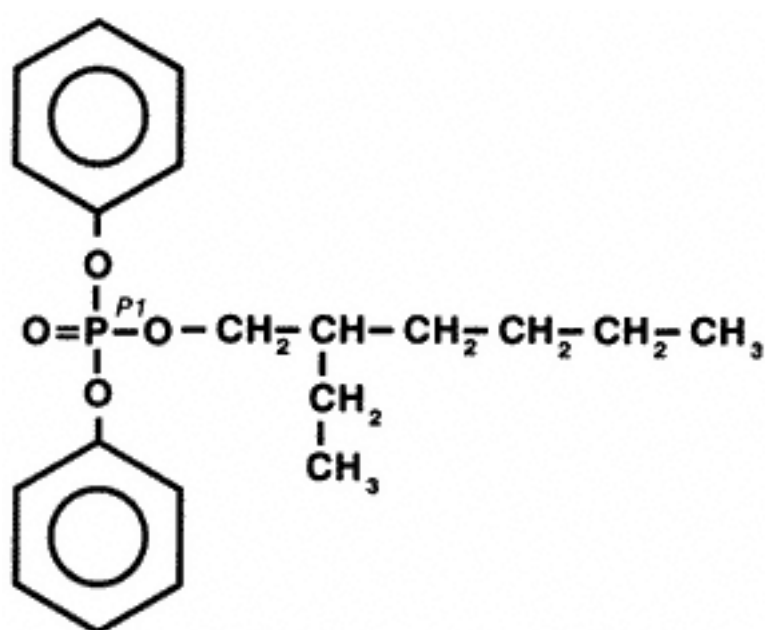
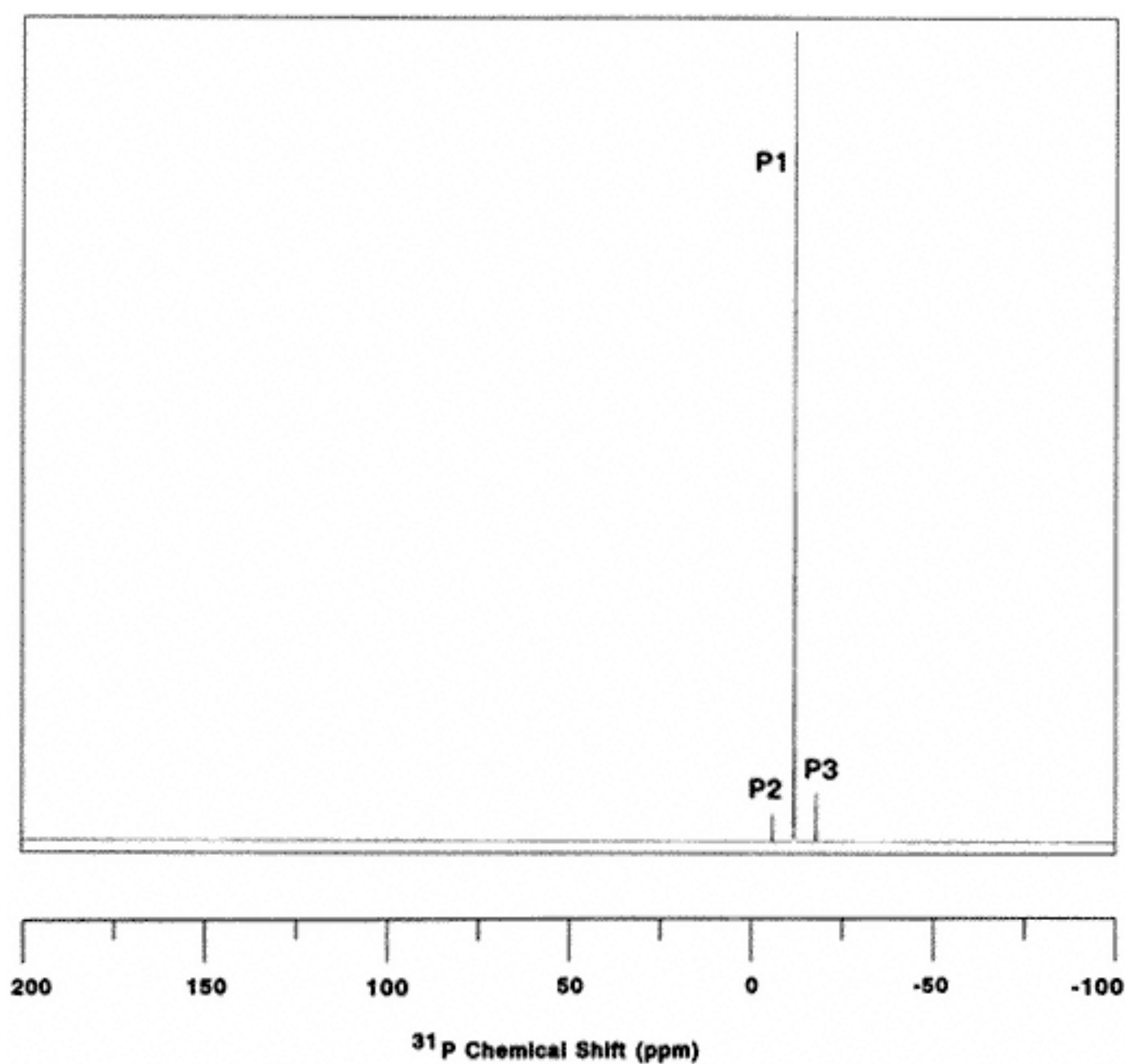
Pulse delay: 5 s

X-D-2P—

2-Ethylhexyl Diphenyl Phosphate

Comments

This sample also contains some tri(2-ethylhexyl) phosphate (**P2**) and triphenyl phosphate (**P3**) {X-D-3P}. This material is used as a flame-retardant plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
P1	-10.3
P2	-4.3
P3	-16.8

Experimental ParametersNucleus: ^{31}P (161.8 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 48

Spectral width: 70 kHz

Data points: 8192

Pulse width: 30°

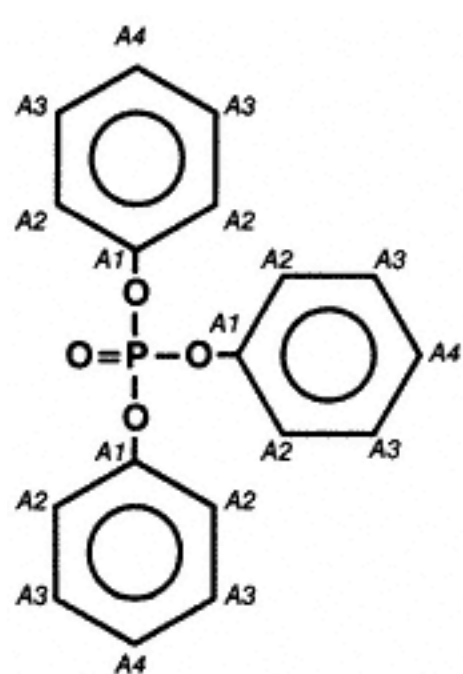
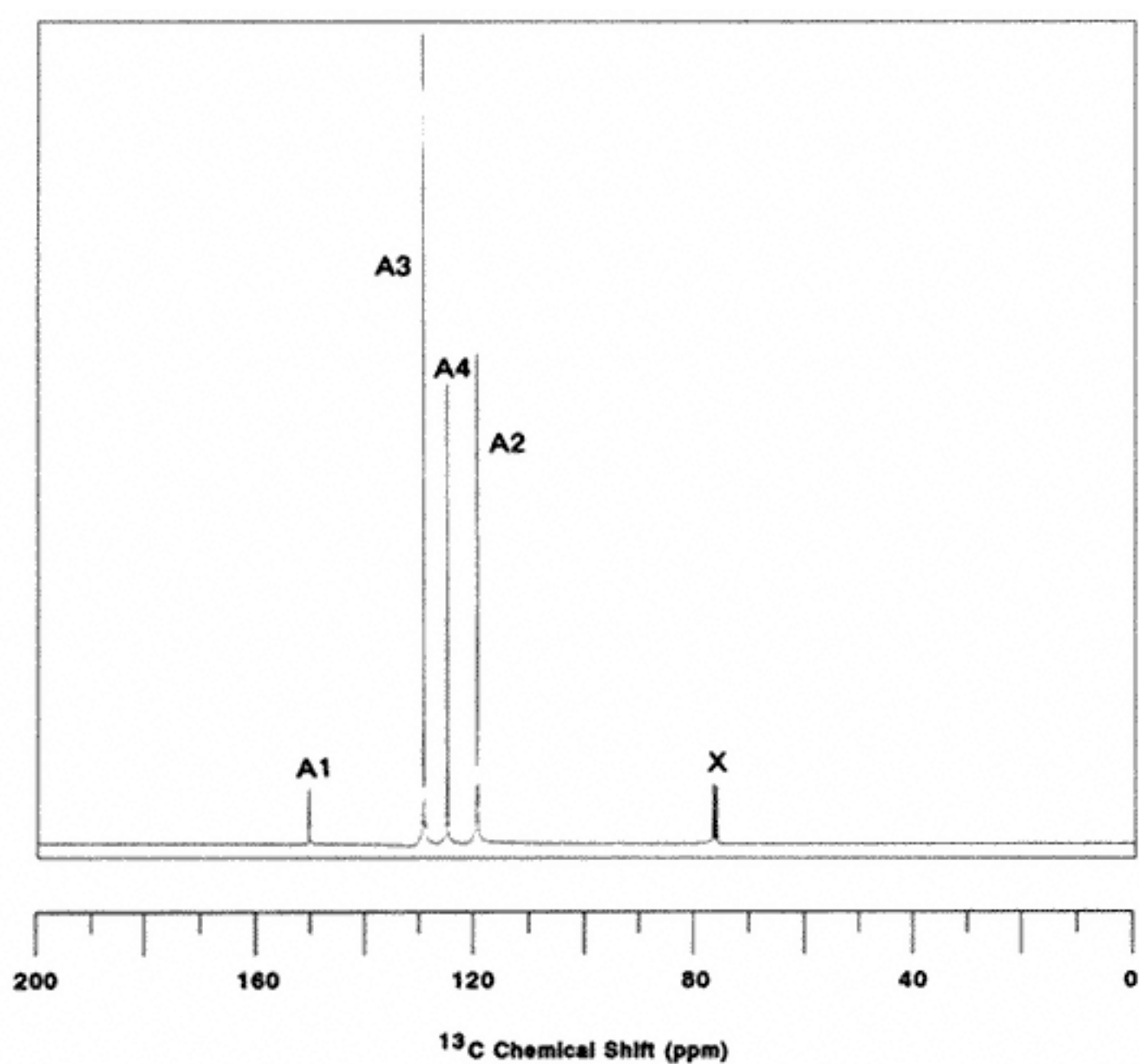
Broadening: 5 Hz

Pulse delay: 5 s

**X-D-3—
Triphenyl Phosphate (TPP)**

Comments

Solvent resonances are marked by **X**. This material is used as a flame-retardant plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {IV-A-9}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
A1	150.4
A2	119.9
A3	129.8
A4	125.6

Experimental ParametersNucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

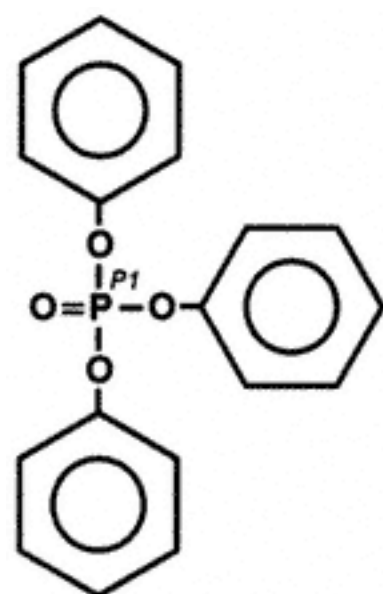
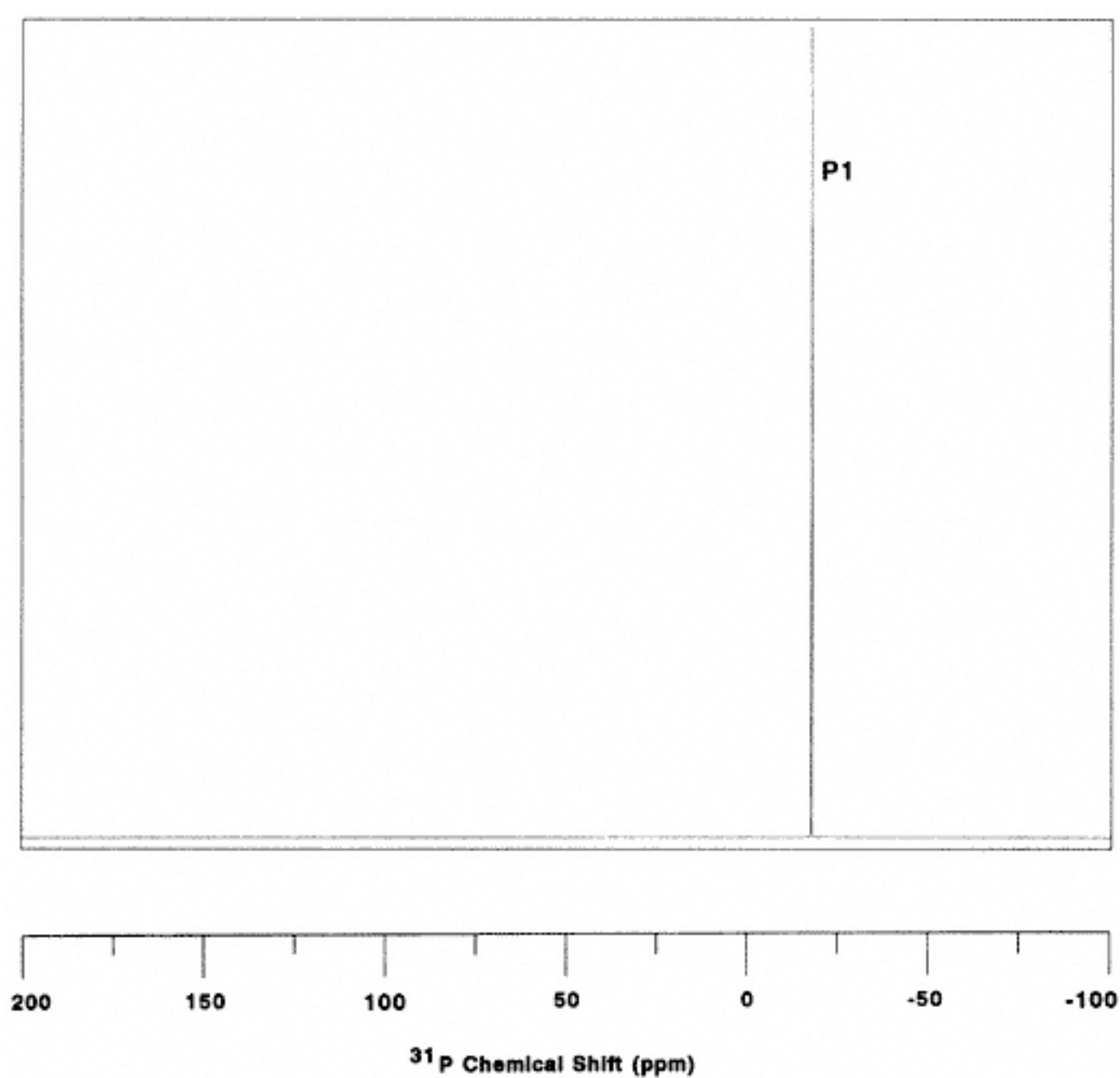
Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

**X-D-3P—
Triphenyl Phosphate****Comments**

This material is used as a flame-retardant plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(methyl methacrylate) {IV-C-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
P1	-16.7

Experimental ParametersNucleus: ^{31}P (161.8 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 48

Spectral width: 70 kHz

Data point: 8192

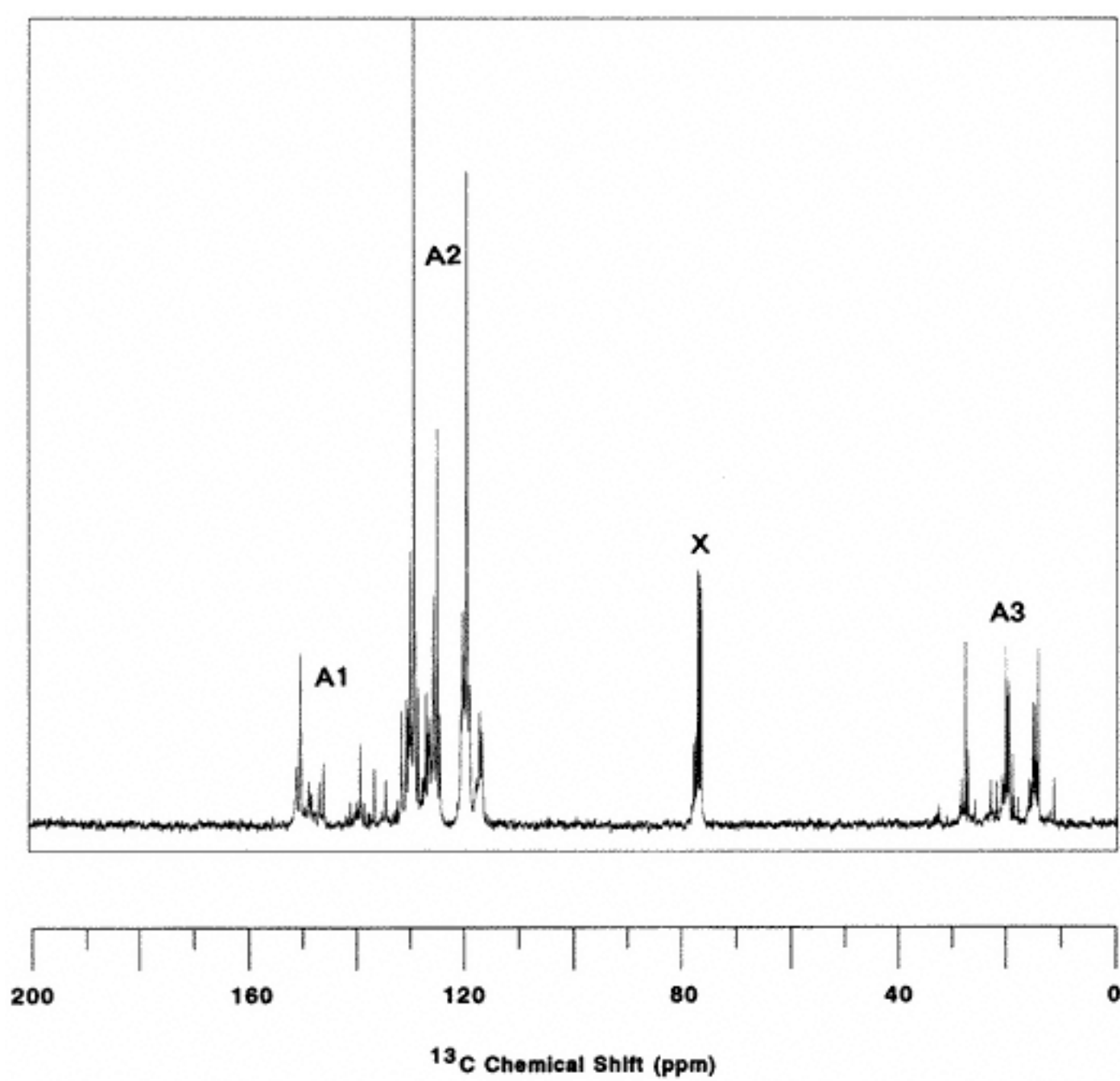
Pulse width: 30°

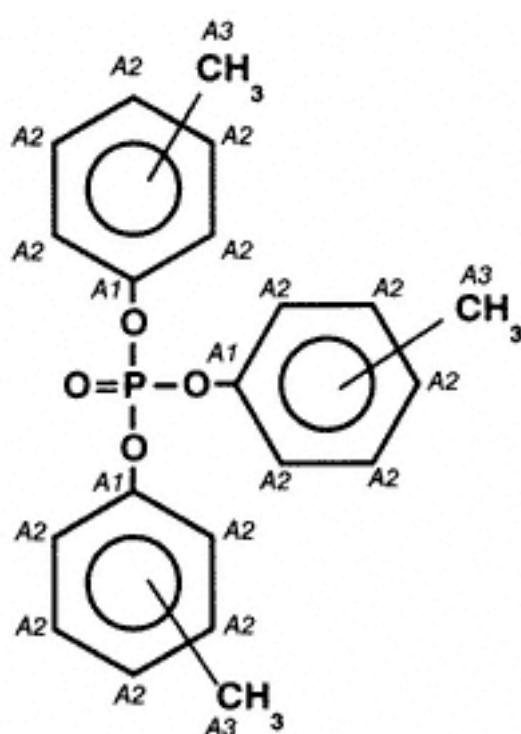
Broadening: 5 Hz

Pulse delay: 5 s

**X-D-4—
Tricresyl Phosphate (TCP)****Comments**

The spectrum is complex because of the various ring substitutions (primarily *m*- and *p*-) observed. Solvent resonances are marked by **X**. This material is used as a flame-retardant plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.





Code	Shift (ppm)
A1	146–150
A2	116–142
A3	10–34

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

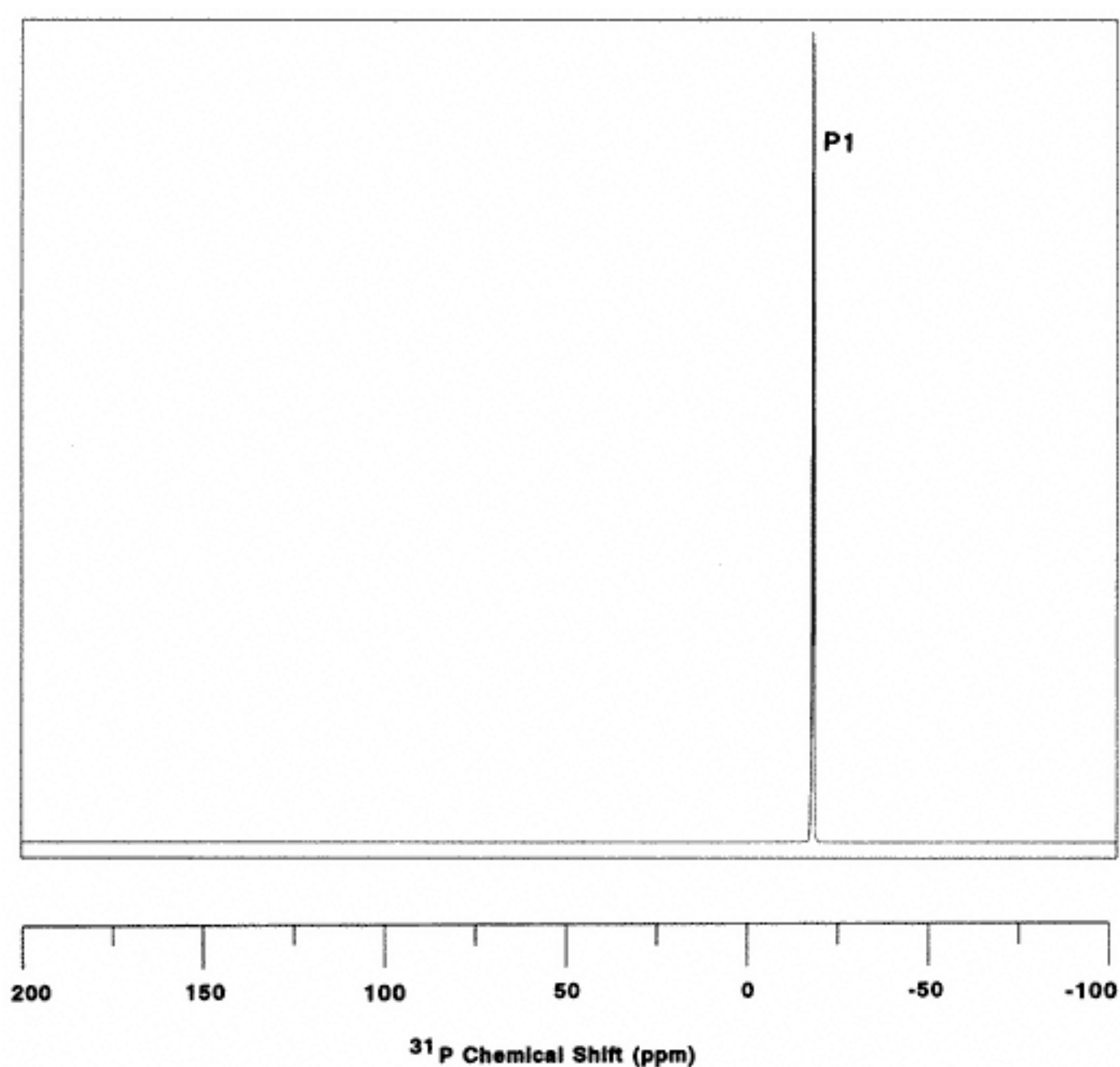
Broadening: 2 Hz

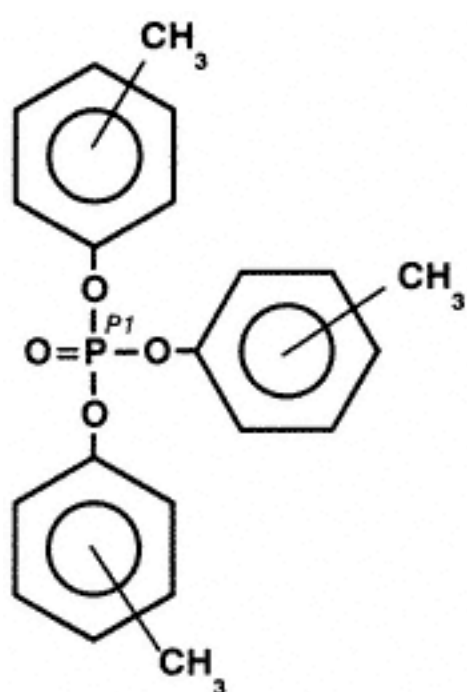
Pulse delay: 5 s

X-D-4P—
Tricresyl Phosphate (TCP)

Comments

This material is used as a flame-retardant plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.





Code	Shift (ppm)
P1	-15.8

Experimental Parameters

Nucleus: ³¹P (161.8 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 10% w/w

Scans: 48

Spectral width: 70 kHz

Data points: 8192

Pulse width: 30°

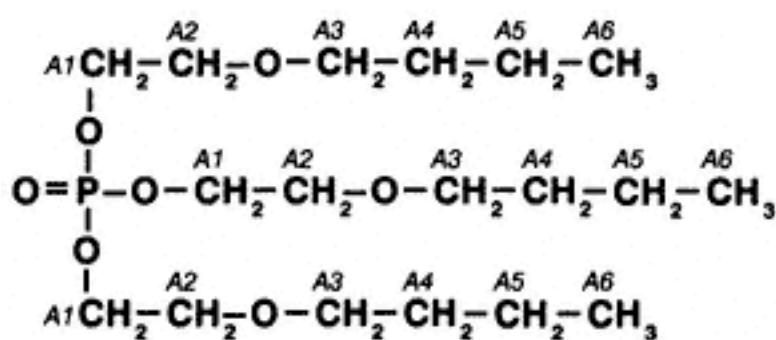
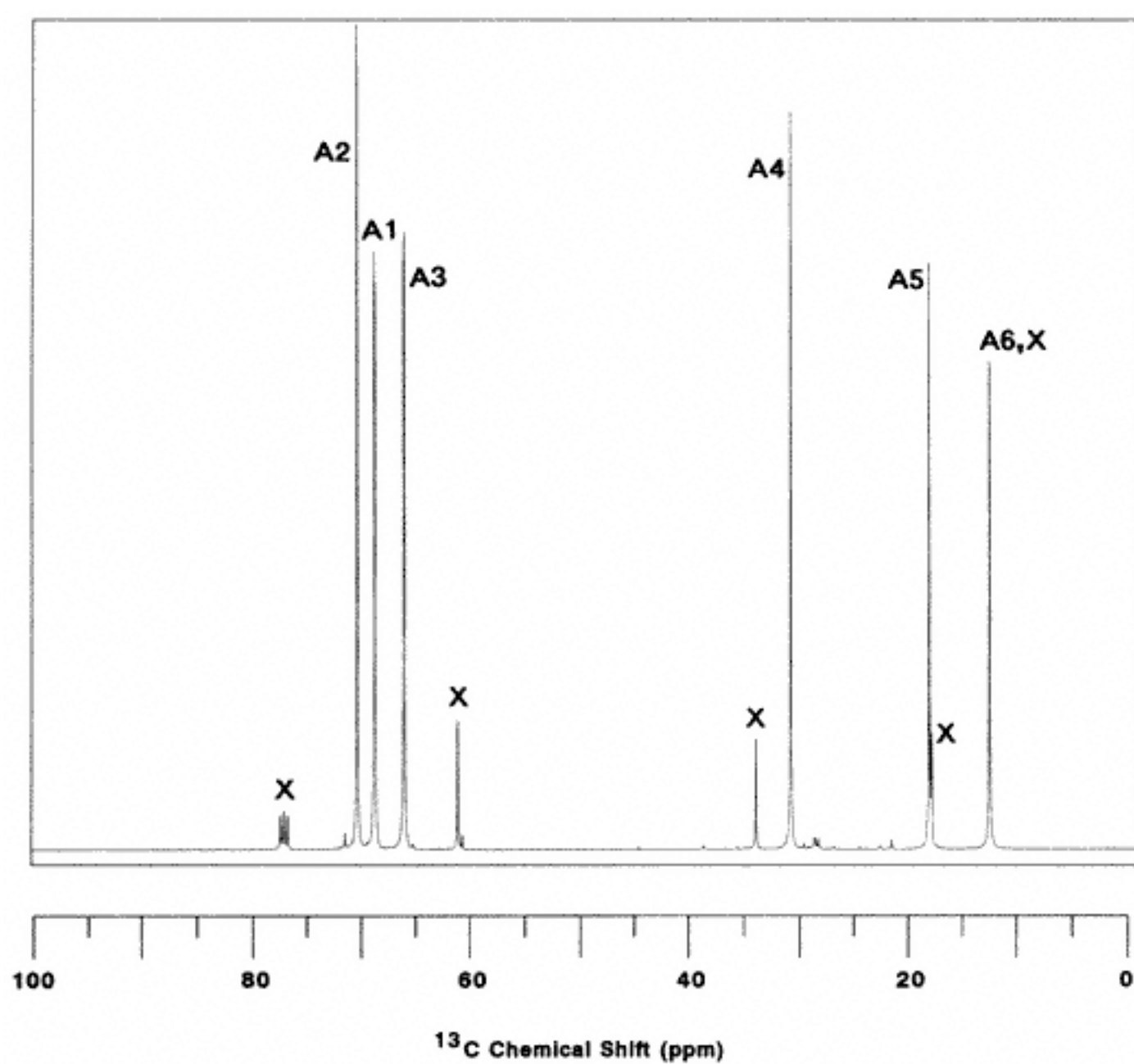
Broadening: 5 Hz

Pulse delay: 5 s

**X-D-5—
Tributoxyethyl Phosphate**

Comments

Solvent resonances are marked by **X**. This material is used as a flame-retardant plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
A1	69.0
A2	70.6
A3	66.3
A4	31.3
A5	18.8
A6	13.2

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

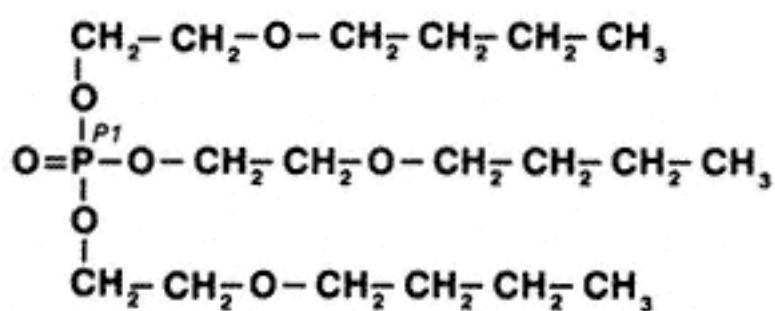
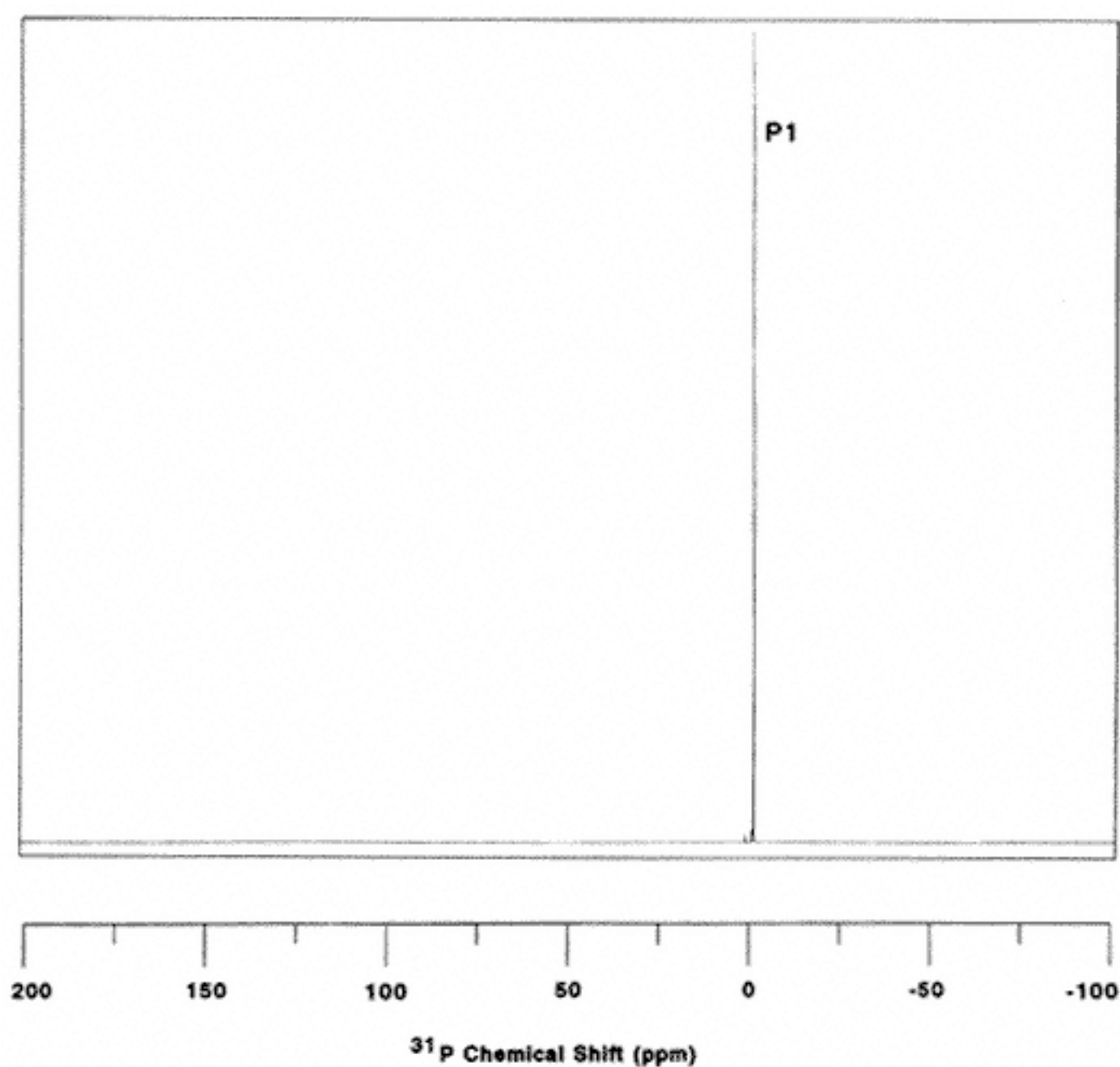
Broadening: 2 Hz

Pulse delay: 5 s

**X-D-5P—
Tributoxyethyl Phosphate**

Comments

This material is used as a flame-retardant plasticizer in polystyrene {III-A-2}, poly(vinyl acetate) {IV-A-1}, poly(vinyl chloride) {V-A-8}, poly(vinyl chloride-co-vinyl acetate) {V-A-9}, poly(vinyl butyral) {V-B-6}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}.



Code	Shift (ppm)
P1	-0.2

Experimental Parameters

Nucleus: ^{31}P (161.8 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 20% w/w

Scans: 48

Spectral width: 70 kHz

Data points: 8192

Pulse width: 30°

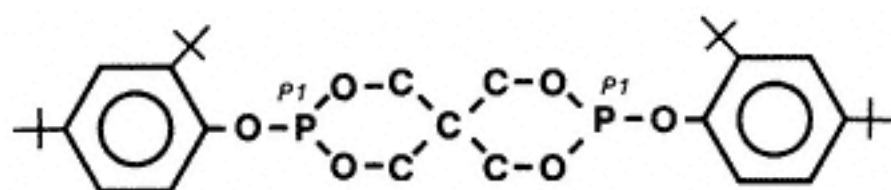
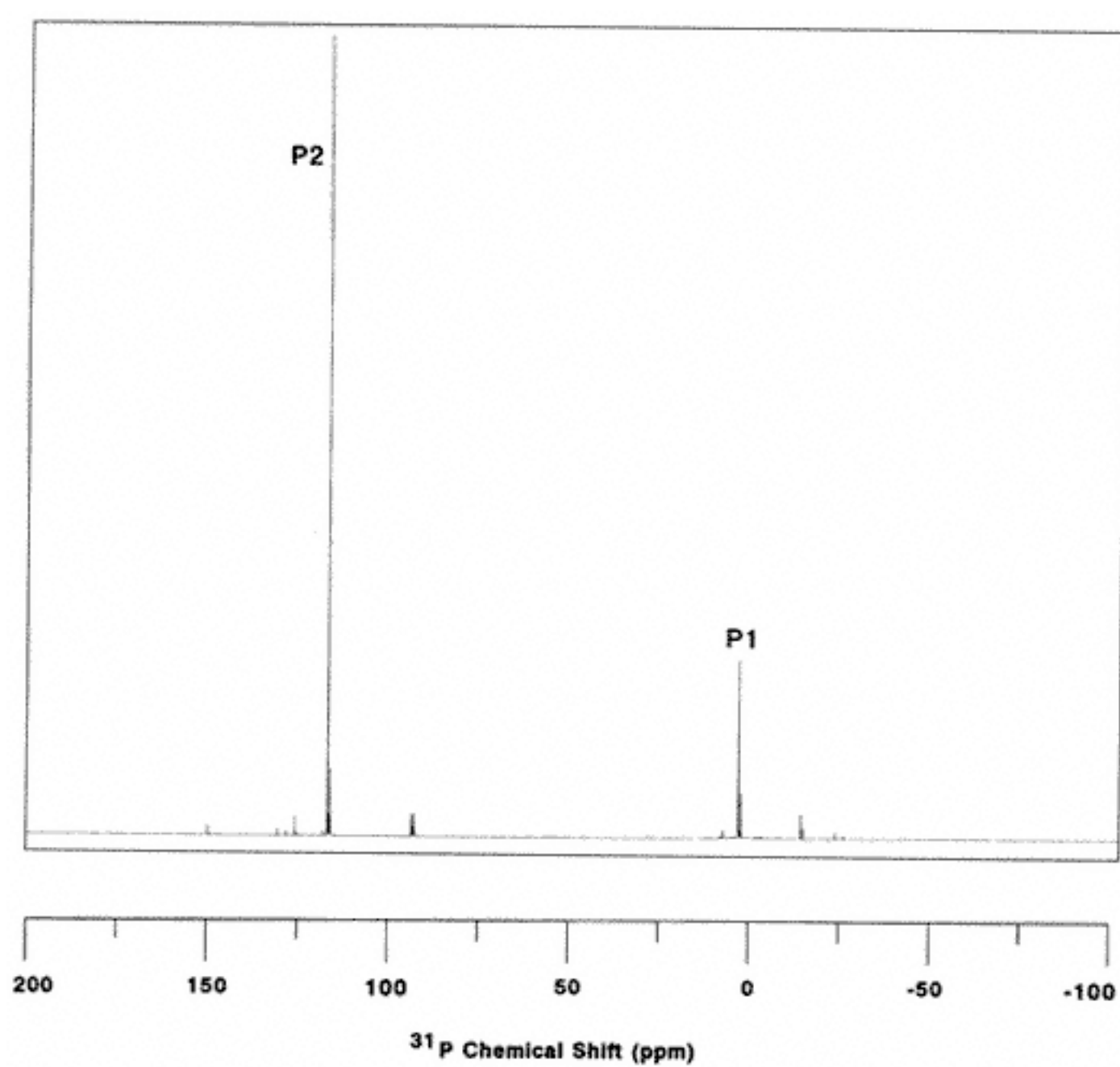
Broadening: 5 Hz

Pulse delay: 5 s

X-D-6P—
Bis(2,4-Di-*t*-Butylphenyl) Pentaerythritol Diphosphite

Comments

Also known as Ultrinox 626 (General Electric). Some conversion of phosphite (**P1**) species to phosphate (**P2**) has occurred as a result of storage conditions. This material is a secondary antioxidant used primarily in polyolefins.



Code	Shift (ppm)
P1	117.8
P2	5.1

Experimental Parameters

Nucleus: ^{31}P (161.8 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

cans: 48

Spectral width: 70 kHz

Data points: 8192

Pulse width: 30°

Broadening: 5 Hz

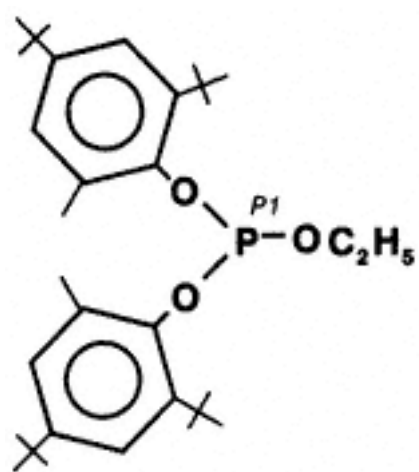
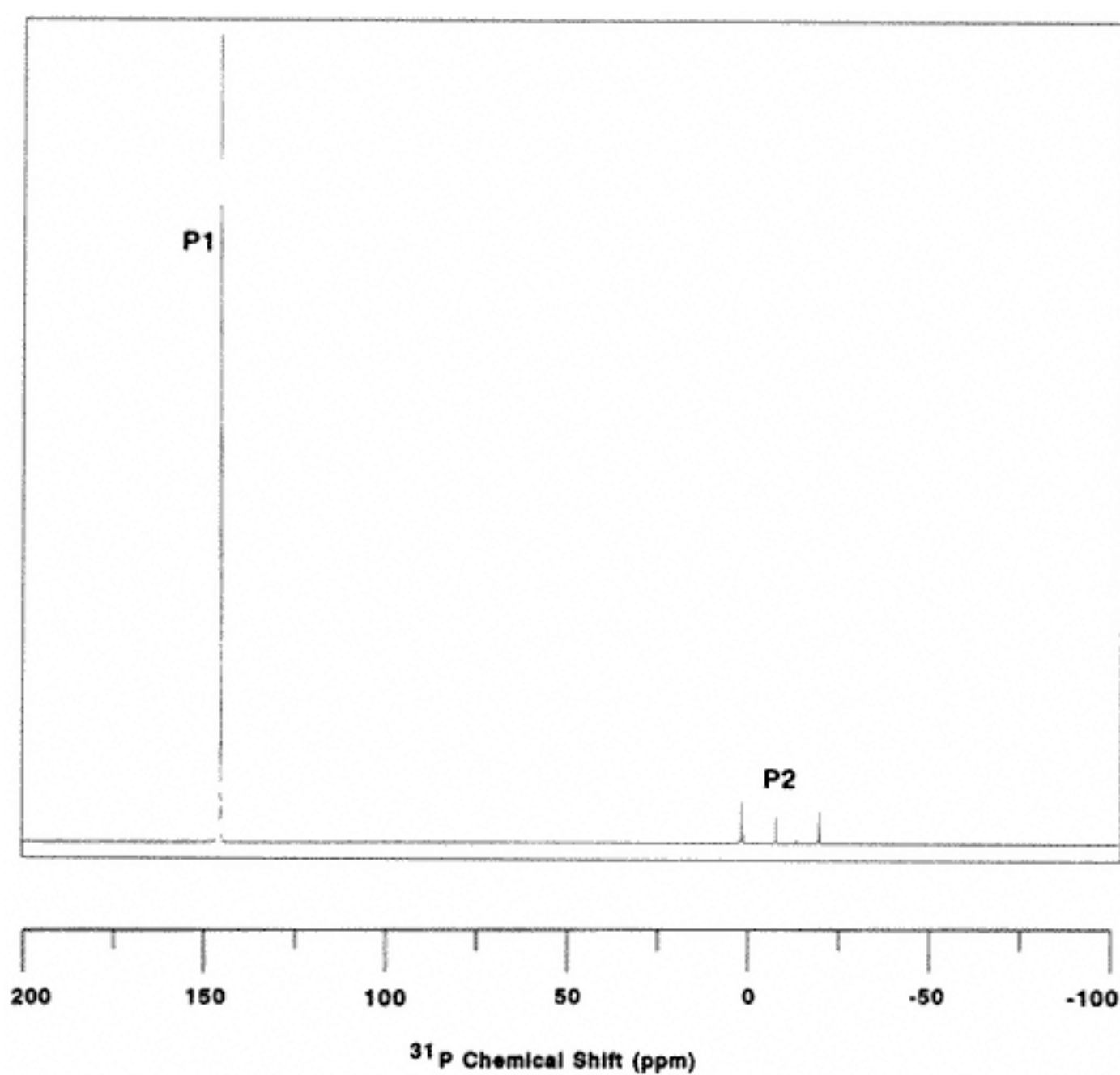
Pulse delay: 5 s

X-D-7P

X-D-7P—
Bis(2,4-Di-*t*-Butyl-6-Methylphenyl) Ethyl Phosphite

Comments

Also known as Irgafos 38 (Ciba Specialties). Some conversion of phosphite (**P1**) species to phosphate (**P2**) has occurred as a result of storage conditions. This material is a secondary antioxidant used primarily in polyolefins.



Code	Shift (ppm)
P1	143.2
P2	3.2, -6.1, -17.8

Experimental ParametersNucleus: ^{31}P (161.8 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 48

Spectral width: 70 kHz

Data points: 8192

Pulse width: 30°

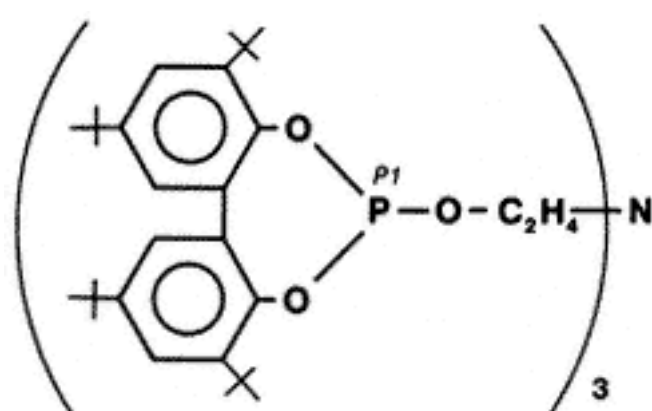
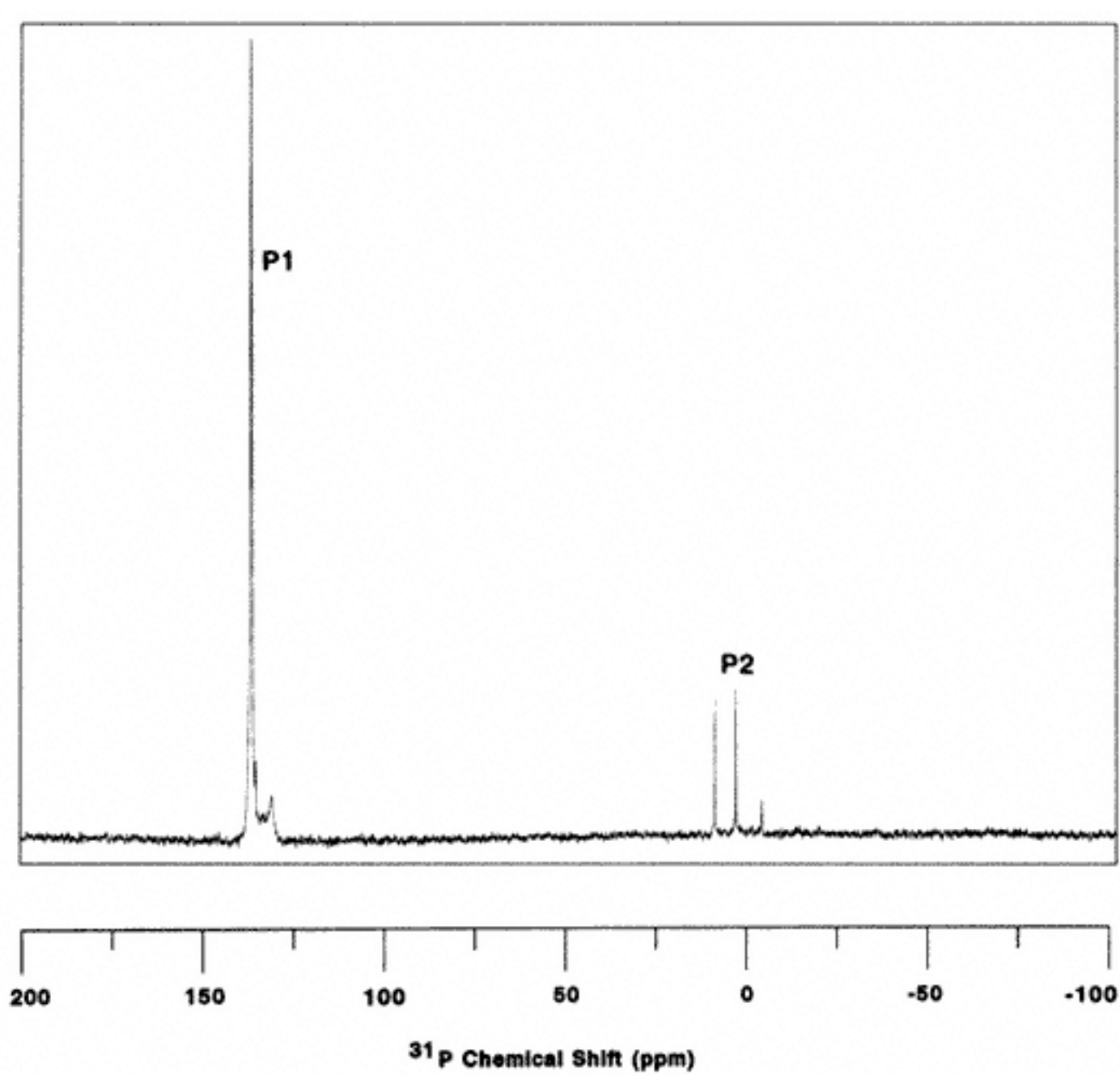
Broadening: 5 Hz

Pulse delay: 5 s

X-D-8P—

2,2',2''-Nitrilo Triethyl-Tris(3,3',5,5',-Tetra-*t*-Butyl-1,1'-Biphenyl-2,2'-Diyl) Phosphite*Comments*

Also known as Irgafos 12 (Ciba Specialties). Some conversion of phosphite (**P1**) species to phosphate (**P2**) has occurred as a result of storage conditions. This material is a secondary antioxidant used primarily in polyolefins.



Code	Shift (ppm)
P1	138.7
P2	10.0, 4.1, -3.0

Experimental ParametersNucleus: ^{31}P (161.8 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 48

Spectral width: 70 kHz

Data points: 8192

Pulse width: 30°

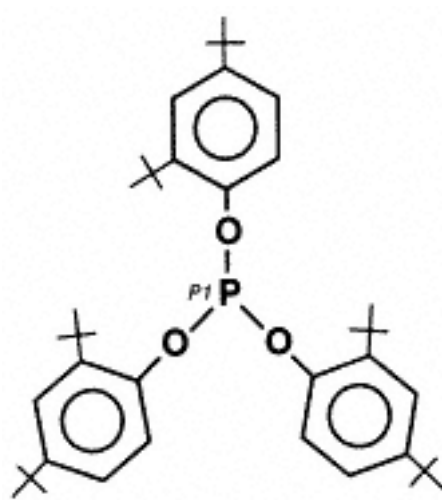
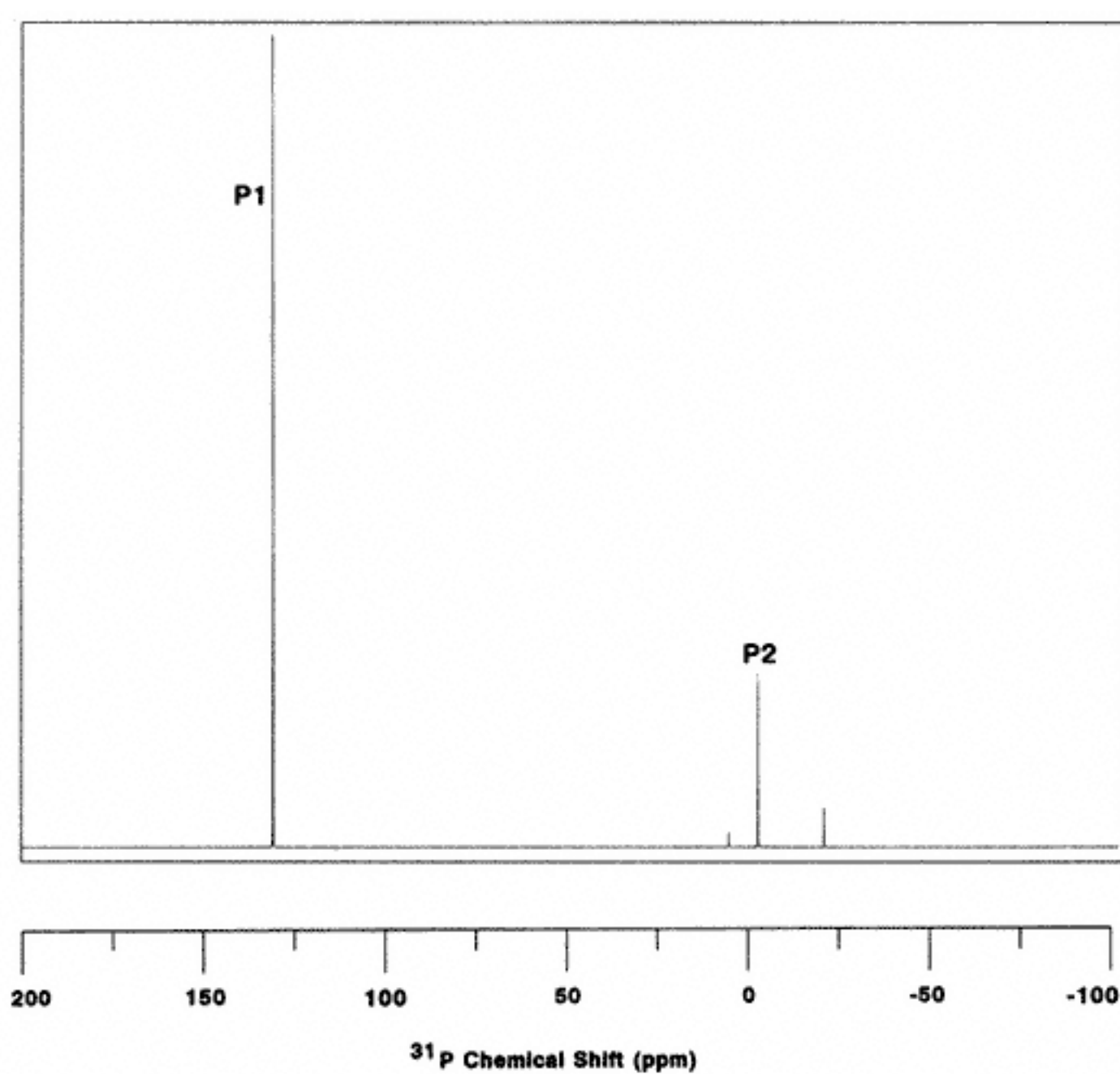
Broadening: 5 Hz

Pulse delay: 5 s

X-D-9P—
Tris(2,6-Di-*t*-Butylphenyl) Phosphite

Comments

Also known as Irgafos 168 (Ciba Specialties). Some conversion of phosphite (**P1**) species to phosphate (**P2**) has occurred as a result of storage conditions. This material is a secondary antioxidant used primarily in polyolefins.



Code	Shift (ppm)
P1	131.6
P2	7.7, -0.8, -19.0

Experimental ParametersNucleus: ^{31}P (161.8 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 48

Spectral Width: 70 kHz

Data points: 8192

Pulse Width: 30°

Broadening: 5 Hz

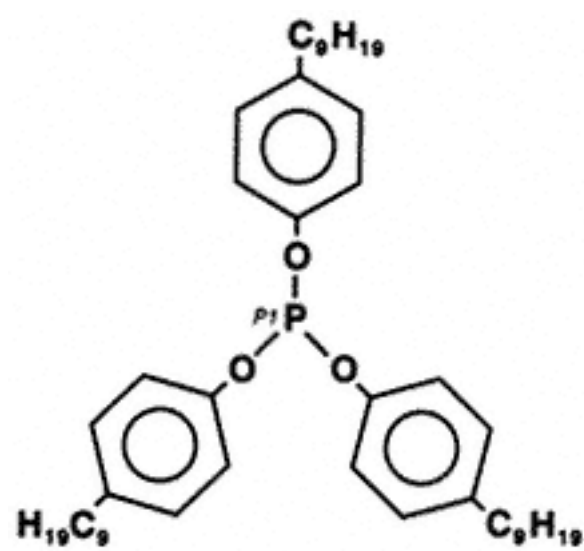
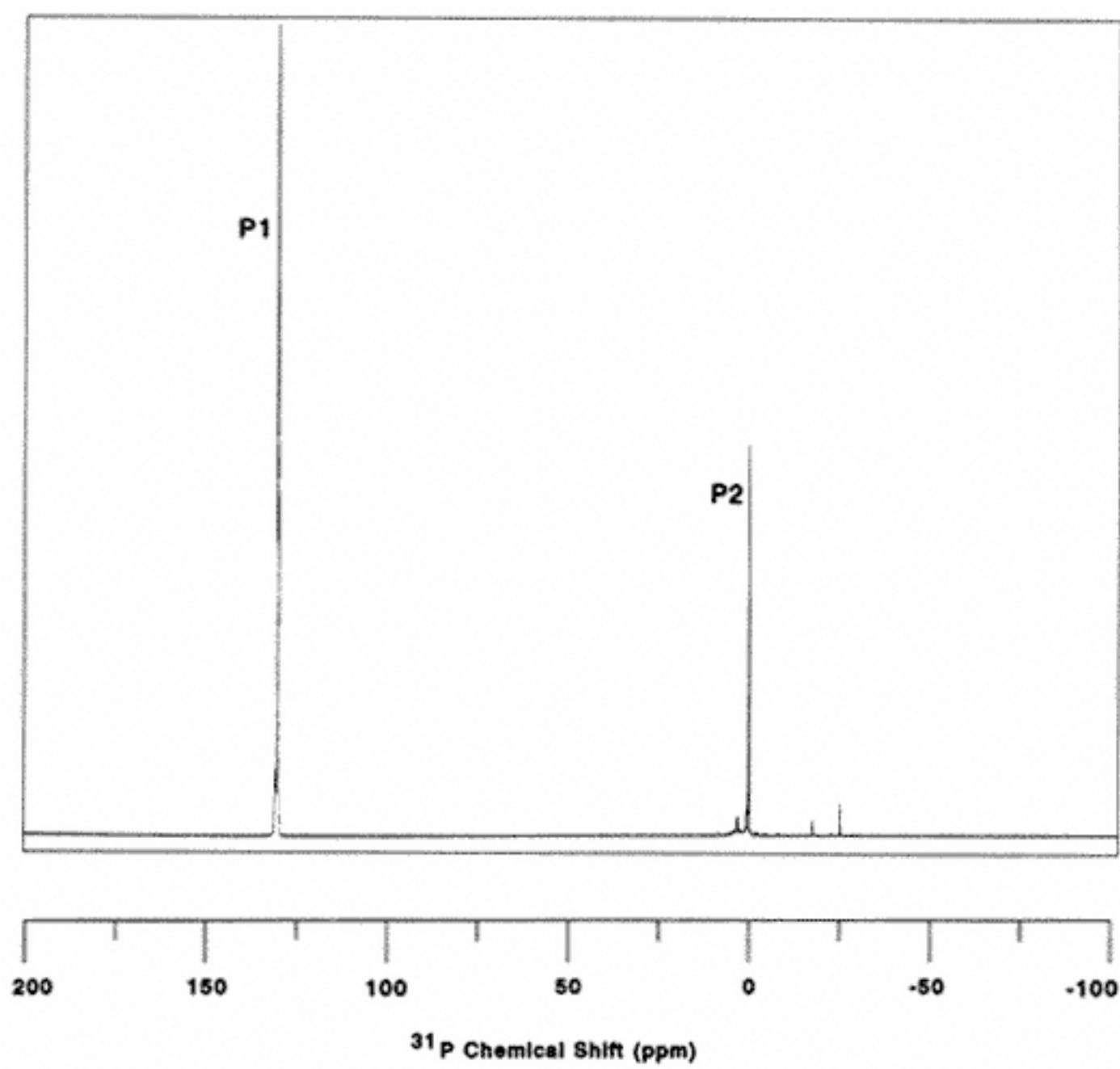
Pulse Delay: 5 s

X-D-10P—

Tris(Nonylphenyl) Phosphite (TNPP)

Comments

Some conversion of phosphite (**P1**) species to phosphate (**P2**) has occurred as a result of storage conditions. This material is a secondary antioxidant used primarily in polyolefins.



Code	Shift (ppm)
P1	130.3
P2	1.0, -16.7, -23.8

Experimental ParametersNucleus: ^{31}P (161.8 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 48

Spectral Width: 70 kHz

Data points: 8192

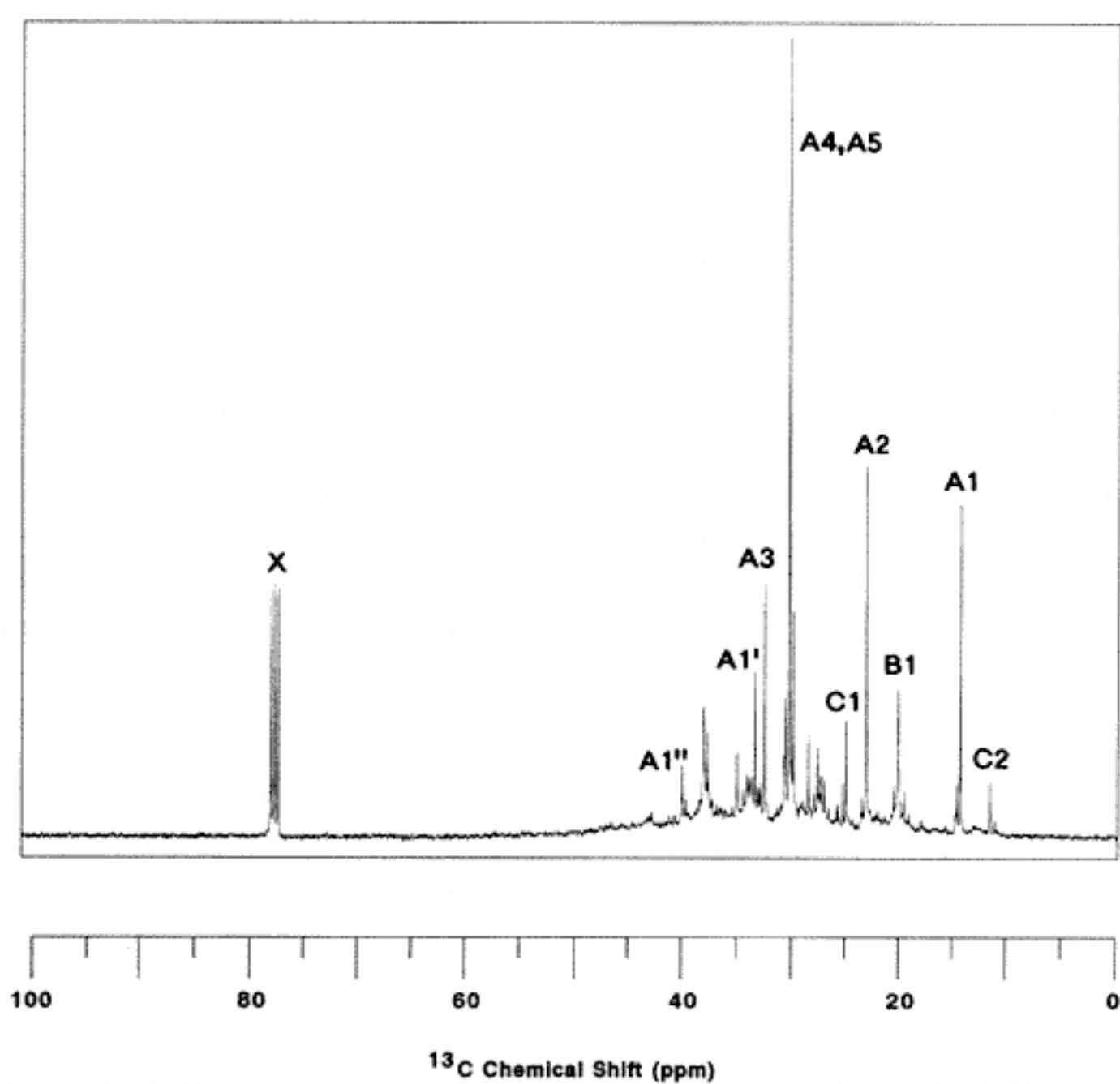
Pulse Width: 30°

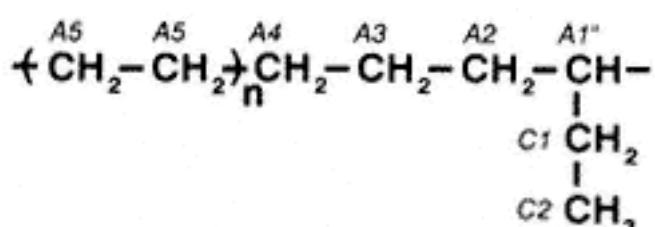
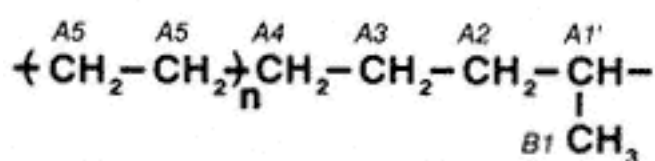
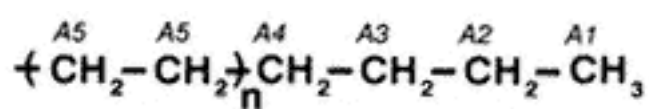
Broadening: 5 Hz

Pulse Delay: 5 s

**X-E-1—
Mineral Oil****Comments**

This material is primarily a straight-chain alkane, with some branching; its structure is similar to that of low-density polyethylene (LDPE) {II-A-3.}. Mineral oil is used in polymers such as polystyrene {III-A-2} as a plasticizer and processing aid.





Code	Shift (ppm)
A1	14.4
A1'	33.7
A1''	40.1
A2	23.0
A3	32.4
A4	30.2
A5	30.2
B1	19.8
C1	26.8
C2	11.6

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

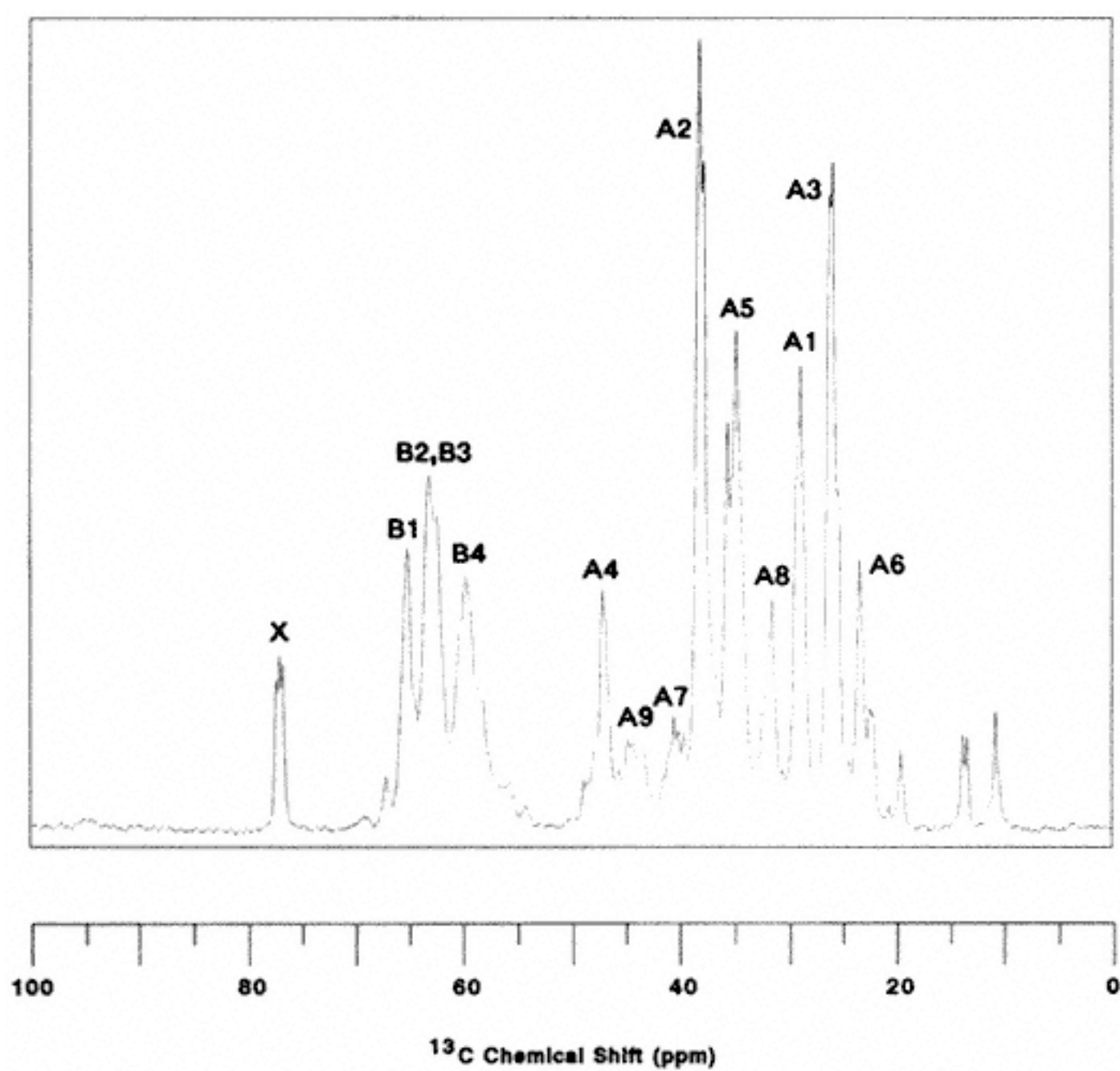
Pulse width: 90°

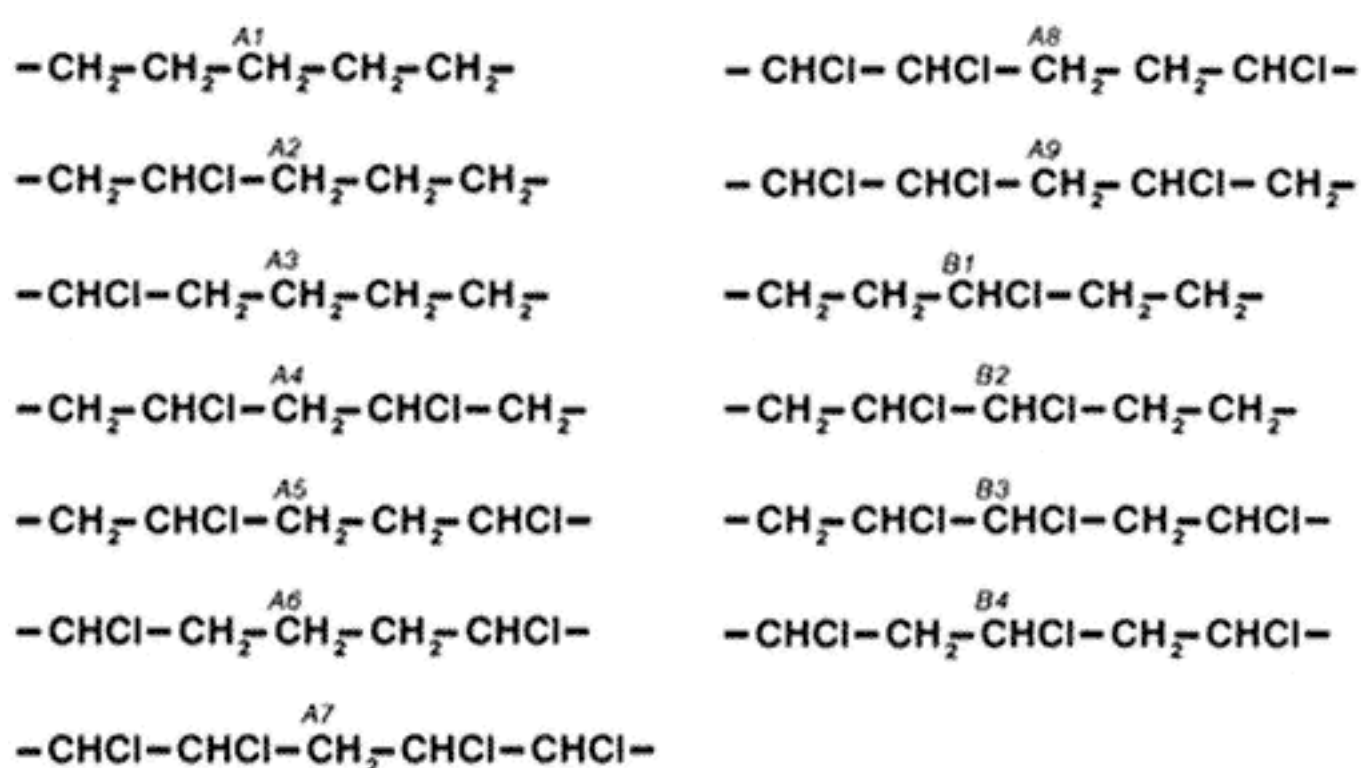
Broadening: 2 Hz

Pulse delay: 5 s

**X-E-2—
Chloroparaffin****Comments**

Solvent resonances are marked by **X**. The structure is similar to that of chlorinated polyethylene {II-A-5}. This material is used as a flame-retardant and plasticizer in poly(vinyl chloride) {V-A-8}, and in sealants, lubricants, and detergents.





Code	Shift (ppm)
A1	28.4
A2	38.1
A3	26.8
A4	47.5
A5	34.5
A6	23.1
A7	40.2
A8	31.3
A9	45.1
B1	64.0
B2	66.1
B3	64.0
B4	59.3

Experimental Parameters

Nucleus: ^{13}C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl_3

Concentration: 10% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

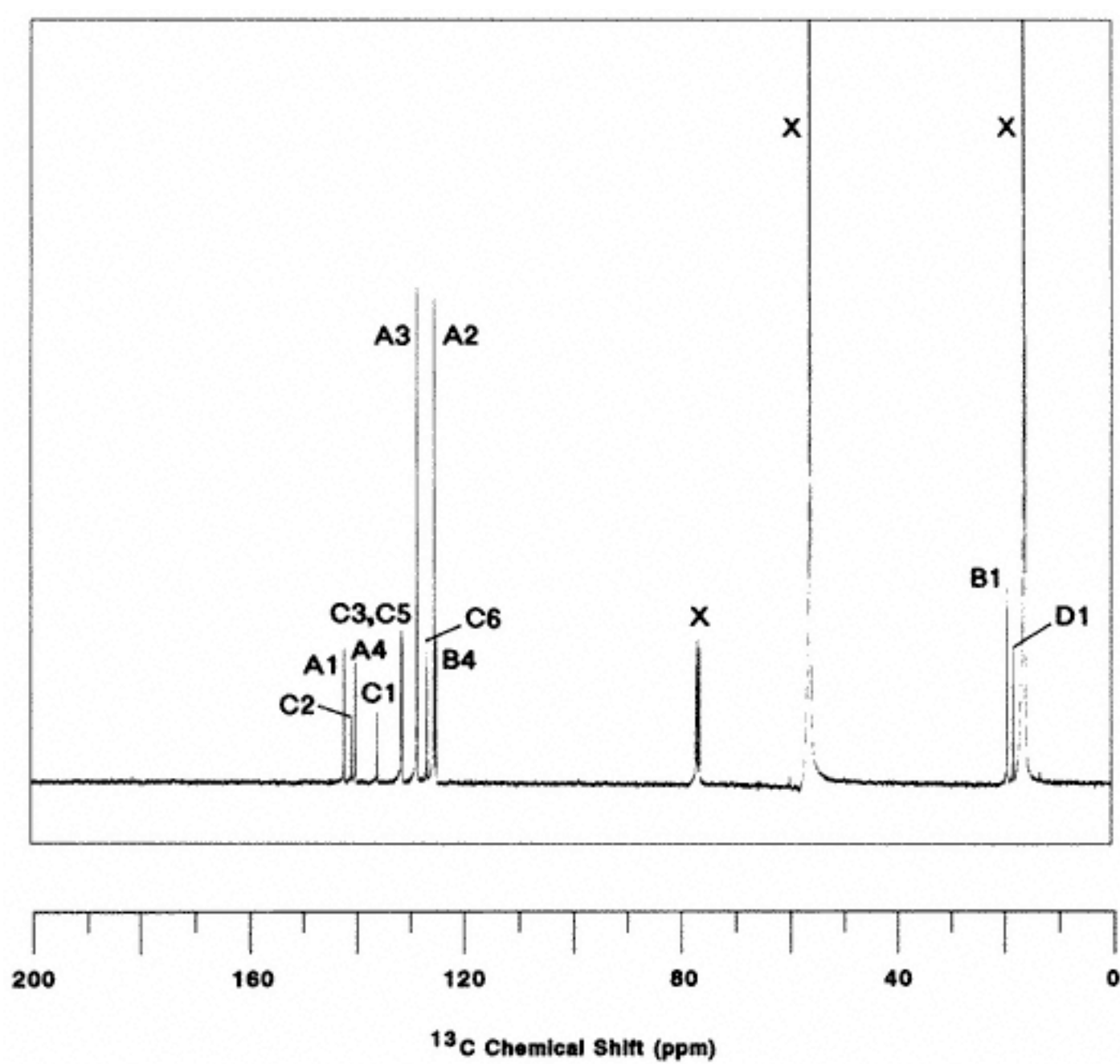
Pulse width: 90°

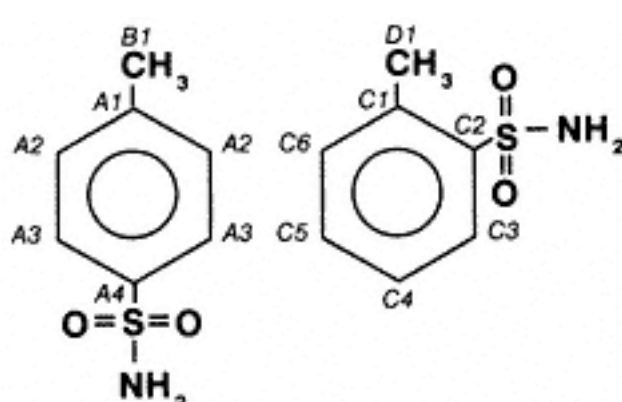
Broadening: 10 Hz

Pulse delay: 5 s

**X-E-3—
o,p-Toluenesulfonamide****Comments**

Solvent resonances are marked by **X**; some residual ethanol is also observed. This material is used as a plasticizer in poly(vinyl acetate) {IV-A-1}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8}. It is also employed as a fungicide and antimildew agent in paints and other coatings.





Code	Shift (ppm)
A1	143.5
A2	127.6
A3	130.5
A4	141.9
B1	21.5
C1	138.1
C2	142.2
C3	133.4
C4	127.3
C5	133.4
C6	128.8
D1	20.7

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 10% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

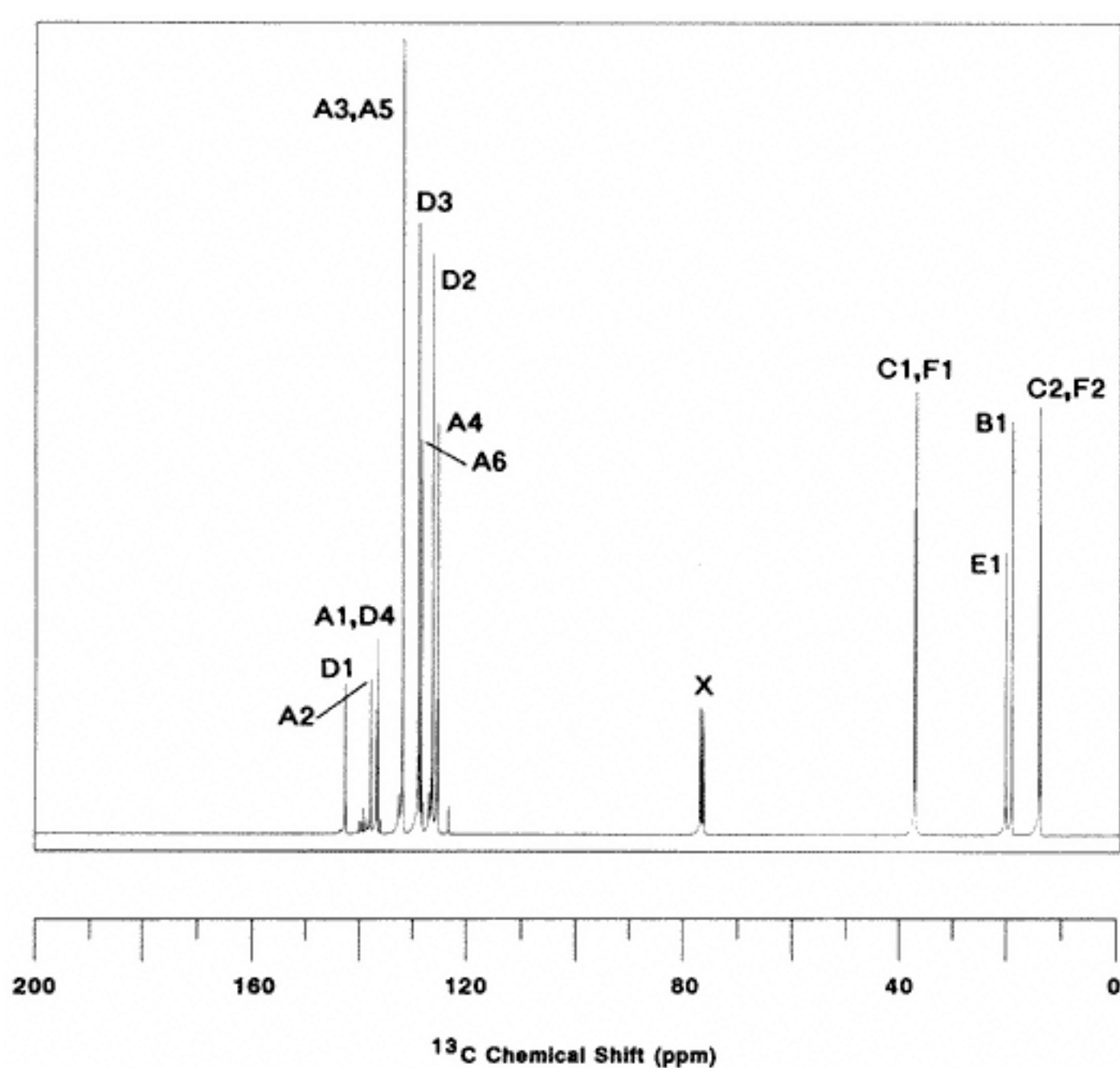
Broadening: 2 Hz

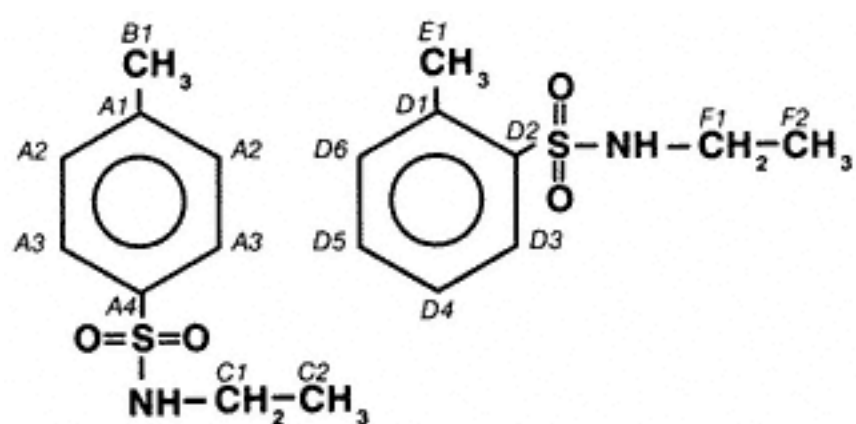
Pulse delay: 5 s

X-E-4—

N-Ethyl-*o,p*-Toluenesulfonamide*Comments*

Solvent resonances are marked by **X**. This material is used as a plasticizer in poly(vinyl acetate) {IV-A-1}, ethyl cellulose {VII-B-3}, cellulose acetate {VII-B-4}, cellulose acetate butyrate {VII-B-5}, and cellulose nitrate {VII-B-8.}. It is also employed as a fungicide and antimildew agent in paints and other coatings.





Code	Shift (ppm)
A1	138.9
A2	139.5
A3	132.8
A4	126.1
A5	132.8
A6	129.1
B1	20.2
C1	38.0
C2	14.9
D1	143.5
D2	126.7
D3	129.9
D4	137.6
E1	21.5
F1	38.0
F2	14.9

Experimental Parameters

Nucleus: ¹³C (100.4 MHz)

Temperature: 50°C

Solvent: CDCl₃

Concentration: 10% w/w

Scans: 100

Spectral width: 25 kHz

Data points: 16384

Pulse width: 90°

Broadening: 2 Hz

Pulse delay: 5 s

Appendix 1— Major End-Use Applications for Some Commercially Significant Polymers

This appendix lists major end-use applications for many of the polymers presented in Chapters 2 through 10. This type of list can never be completely comprehensive, as new materials are constantly being developed and as new applications of old materials are devised. However, it is often helpful, when faced with an unknown material, to have some information about its likely composition. The application areas listed include:

Additives and Blend Components

These may be low-molecular weight polymers that are added at low levels ($\leq 10\%$) to modify the properties of a base resin. Or, they may be higher-molecular weight materials that are commonly found blended with one or more other components; blend compositions can vary widely.

Adhesives and Binders

These polymers are commonly used as in various types of formulations, as glues, pressure-sensitive adhesives, or as binders that hold other components together, as in fiberboard or laminated materials.

Automotive

Many components of automobiles, trucks, and other vehicles are made of polymeric materials because of their relatively low weight. These include mechanical and electrical components, as well as interior and exterior parts, such as seats, body panels, and bumpers.

Caulk, Gaskets, Seals

Polymers in this category are used as seals that exclude unwanted chemicals or environmental conditions. Examples include O-rings and weatherstripping.

Coatings, Paints, Varnishes

Various types of decorative, protective, and functional coatings, such as latex paints, water repellants, and metal finishes are based on these materials.

Construction Materials and Pipe

These polymers are found in construction materials and plumbing supplies. Some are intended for outdoor use (such as building siding, cement modifiers, and swimming-pool liners); others, for indoor applications (e.g., flooring, molding, and wall coverings).

Containers and Bottles

This category encompasses plastic dishware and flatware, as well as many types of storage containers, particularly those for food, detergents, personal-care products, and other household and industrial chemicals.

Cosmetics

Many personal-care products, such as nail polish and hair-styling mousse, are polymer-based. Others contain polymeric ingredients that modify the product's viscosity or provide a smooth feel; examples include moisturizers, makeup foundations, shampoos, and hair conditioners.

Degradable Materials

Materials that slowly degrade when exposed to light, air, or microbes are considered by many to be more environmentally "friendly" than nondegradable polymers. Some of these polymers have acceptable physical prop-

erties, and can be used as the primary component of a product; others are included as additives that hasten the degradation of the base material.

Elastomers and Rubbers/Tires

Elastomeric, or rubbery, materials do not exhibit permanent deformation after stretching or compression; they quickly return to their original dimensions. Such polymers obviously have many applications in which their flexibility and resilience are important. The production of tires for various wheeled vehicles is one of the most significant applications of these materials.

Electronic and Electrical Equipment

These polymers are used to manufacture electrical connectors, battery cases, telephone housings, wire and cable insulation, and other parts for electronic and electrical equipment.

Engineering Resins

This is a generic term used to describe materials that can withstand extreme conditions. In general, they are hard, strong, heat-resistant, chemically inert, and machinable.

Fibers, Textiles, Clothing

These applications include synthetic or chemically modified natural fibers and yarns that can then be woven or knitted into fabric for clothing. Other materials in this category are used as textile modifiers or finishes, for example, to provide water repellency or to promote dye fixation.

Films, Sheet, Packaging

Polymers of this type can be processed into relatively thin, flat sheets, which may be further manipulated: Examples of specific products are merchandise bags, beverage and condiment pouches, trash-can liners, protective coverings, barrier films, adhesive and recording tapes, photographic-film backing, blister packs, and other types of flexible packaging.

Foam and Insulation

The cellular structures of foams are formed by the expansion of a pressurized gas, the evaporation of a volatile chemical, or the evolution of gaseous products during a chemical reaction. Foams are commonly used as protective packaging because they absorb shocks well, and as insulation because the entrapped air bubbles do not conduct heat well.

Furniture and Carpet

Many plastic materials are found in the frames of furniture pieces, particularly seating. Other polymers are used to produce upholstery fabrics and carpet fibers. Nonslip carpet backing is generally made of elastomeric materials, for comfort as well as safety.

Glazing and Lenses

Optically clear materials can make suitable windows, skylights, eyeglass lenses, illuminated display signs, and other products requiring effective light transmission. Specialty glazing, such as bullet-proof and safety glass, also incorporate polymeric components.

Hoses and Tubing

Such items obviously require materials that are flexible and exhibit good chemical and heat resistance.

Lubes, Waxes, Greases

These are generally relatively low in molecular weight, and are suitable for applications such as lubricants, viscosity modifiers, and hydraulic, heat-exchange, and transformer fluids.

Mechanical Parts

Materials used to make gears, switches, pumps, valves, and other mechanical components must be physically strong and chemically and thermally inert.

Medical and Pharmaceutical

A wide variety of modern medical and pharmaceutical products incorporate polymeric components because of their desirable properties. For example, the biocompatibility of some materials is useful for surgical sutures, medicine capsules, implants, and contact lenses. The relative inertness and good mechanical properties of others make them appropriate for prosthetic devices and dental applications.

Recreational Equipment and Toys

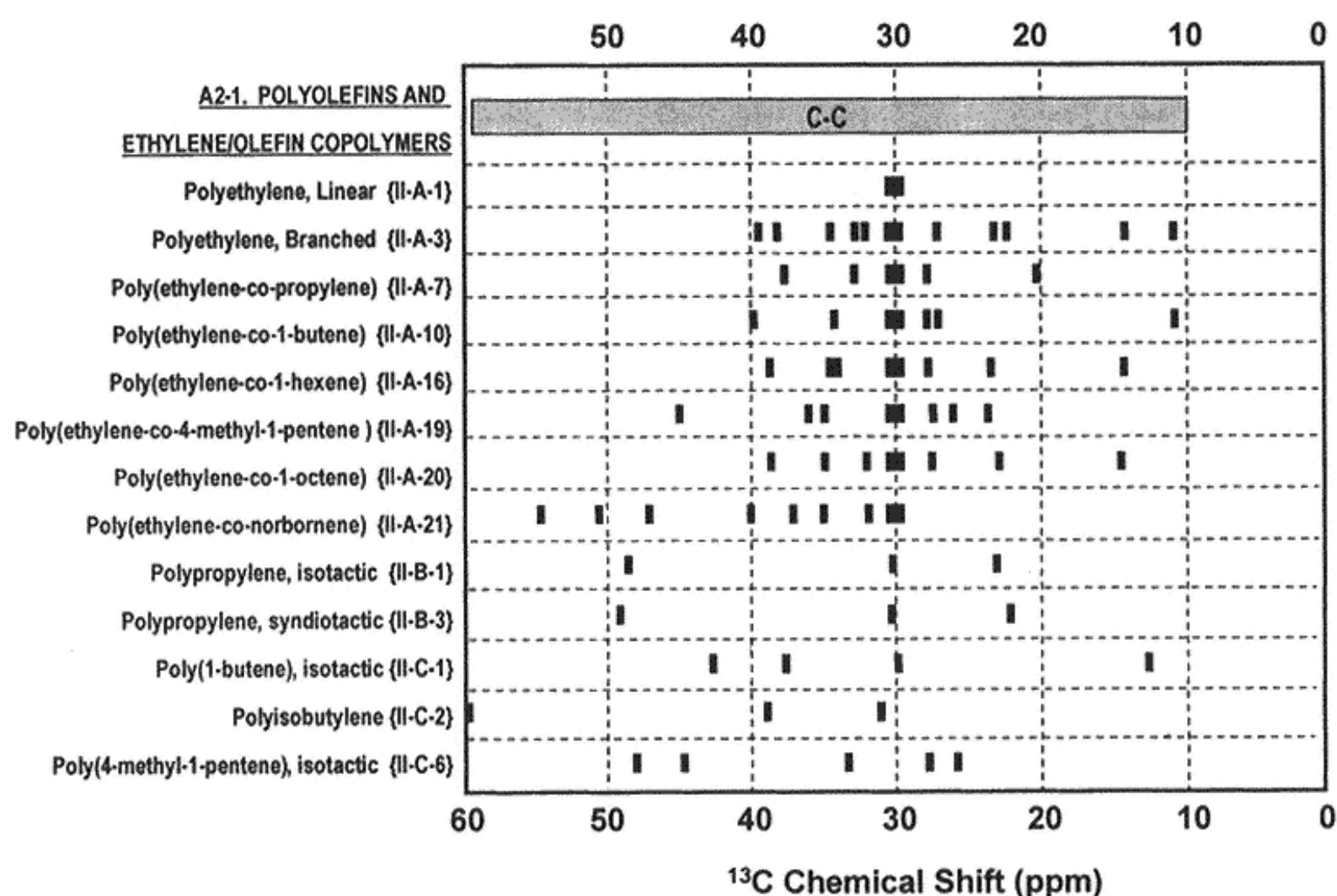
Materials used in sporting goods, such as balls and athletic footwear, or in toys usually exhibit good impact resistance and an attractive appearance. Other applications include recording media (e.g., compact discs) and luggage.

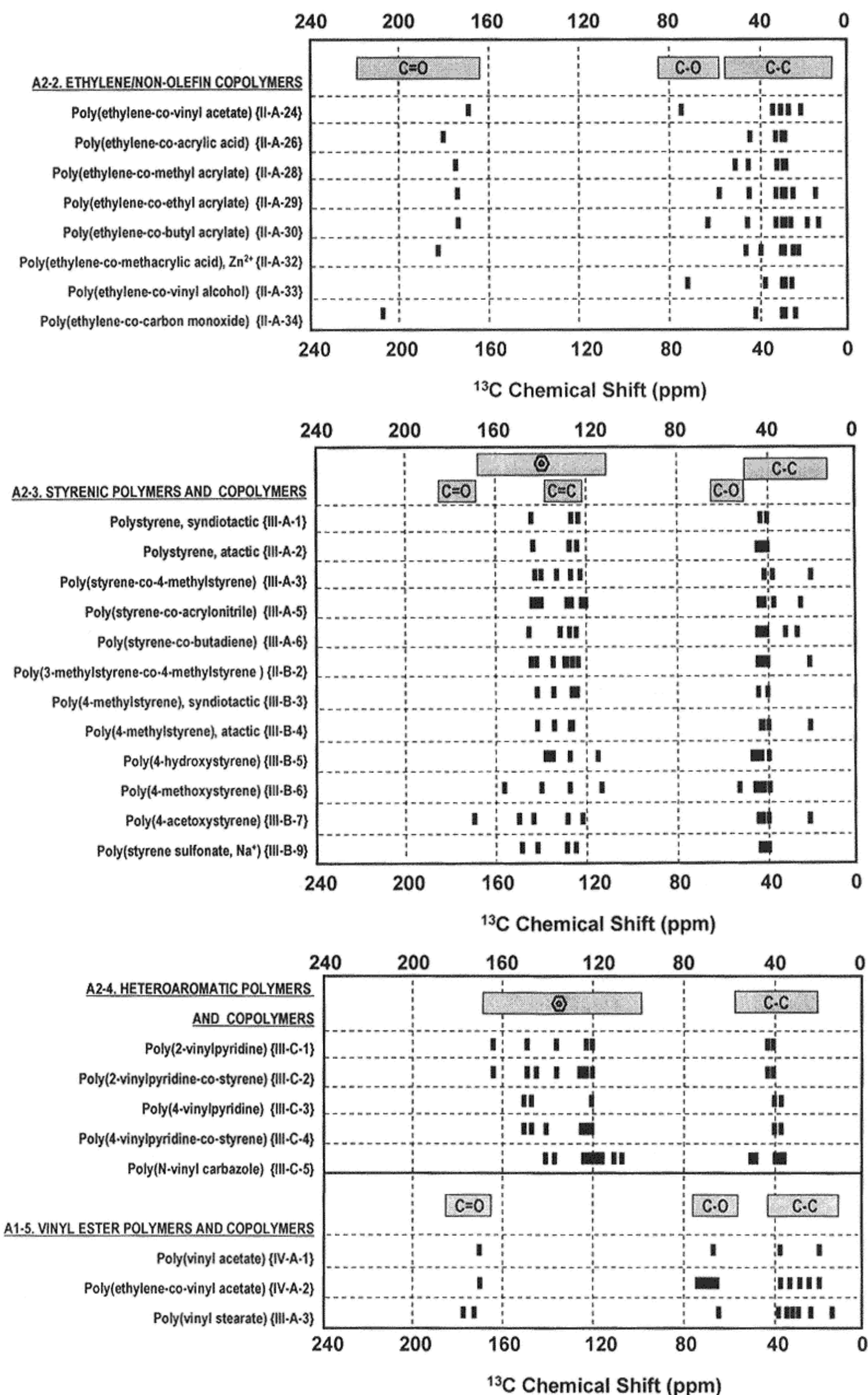
Polymer name	Ref No.	Additives/blend components	Adhesives/binders	Automotive components	Caulk/gaskets/seals	Coatings/paints/varnishes	Construction materials/pipe	Containers/bottles	Cosmetics	Degradable materials	Elastomers/rubbers/tires	Electronic/electrical equipment	Engineering resins	Fibers/textiles/clothing	Films/sheet/packaging	Foam/insulation	Furniture/carpet	Glazing/lenses	Hoses/tubing	Lubes/waxes/greases	Mechanical parts	Medical/pharmaceutical	Recreational equipment/toys	Tools/appliances	Water treatment
Polydimethylsiloxane	IX-A-1				●																				
Polydimethylsiloxane, hydroxyl terminated	IX-A-2				●				●												●				
Polymethyloctadecylsiloxane	IX-A-14																				●				
Poly(ethyl silicate)	IX-A-16				●																				
Poly[4,4'-methylenebis(phenyl isocyanate)-alt-1,4-butanediol/tetrahydrofuran]	IX-B-1			●							●	●		●		●					●		●		
Poly[4,4'-methylenebis(phenyl isocyanate)-alt-1,4-butanediol/propylene glycol]	IX-B-2			●							●	●		●		●					●		●		
Poly[4,4'-methylenebis(phenyl isocyanate)-alt-1,4-butanediol/poly(butylene adipate)]	IX-B-3			●							●	●		●		●					●		●		
Poly[4,4'-methylenebis(phenyl isocyanate)-alt-1,4-butanediol/ polycaprolactone]	IX-B-4			●							●	●		●		●					●		●		
Poly(phenylglycidyl ether-co-formaldehyde)	IX-B-6	●				●	●																		
Poly(ethylformal sulfide)	IX-B-7			●	●						●									●					
Poly(phenylene ether sulfone)	IX-B-8											●	●								●				●
Poly(Bisphenol A-co-phenylene ether sulfone)	IX-B-9											●	●								●				●
Polydiphenoxyposphazene	IX-B-10			●	●						●								●						

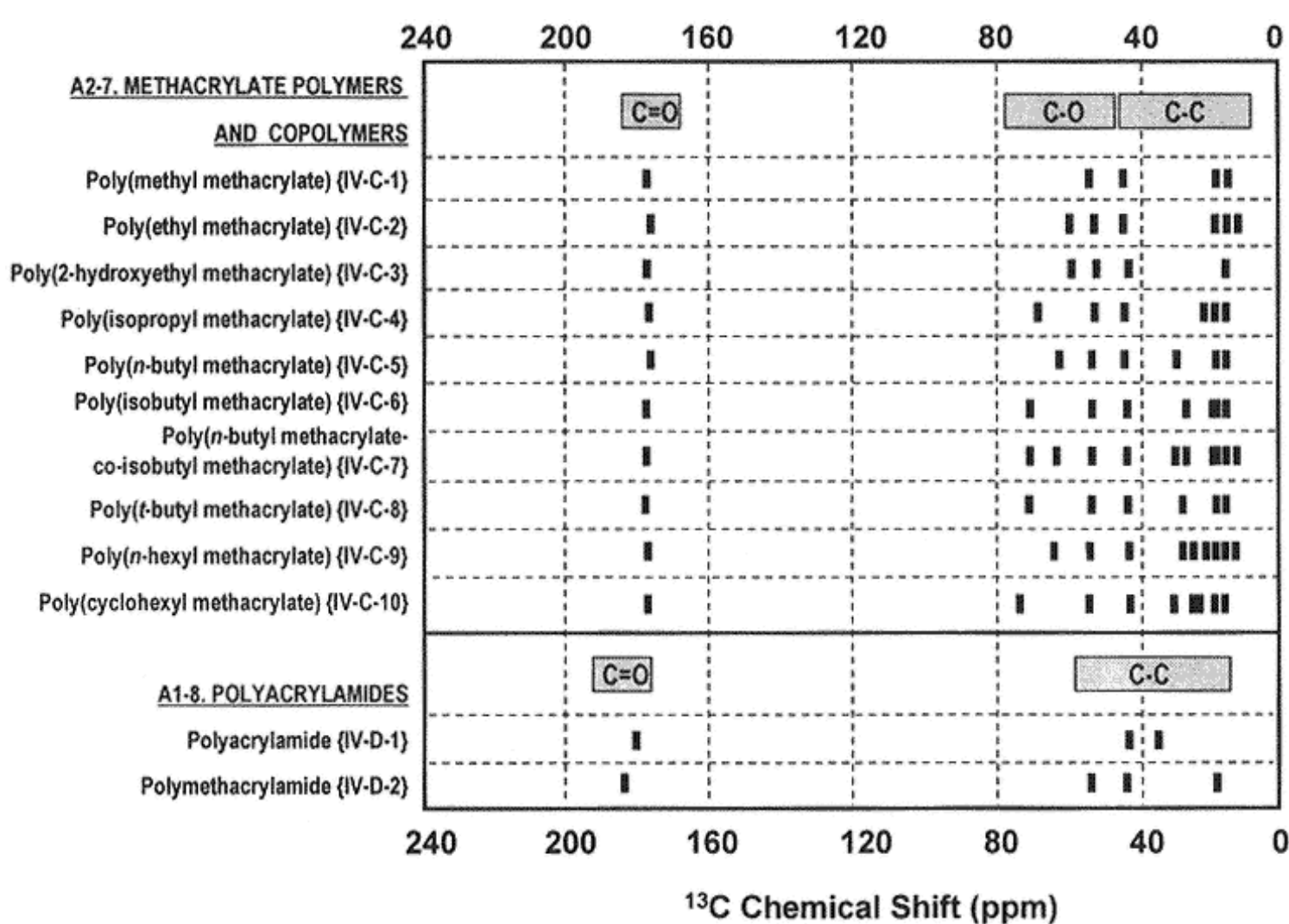
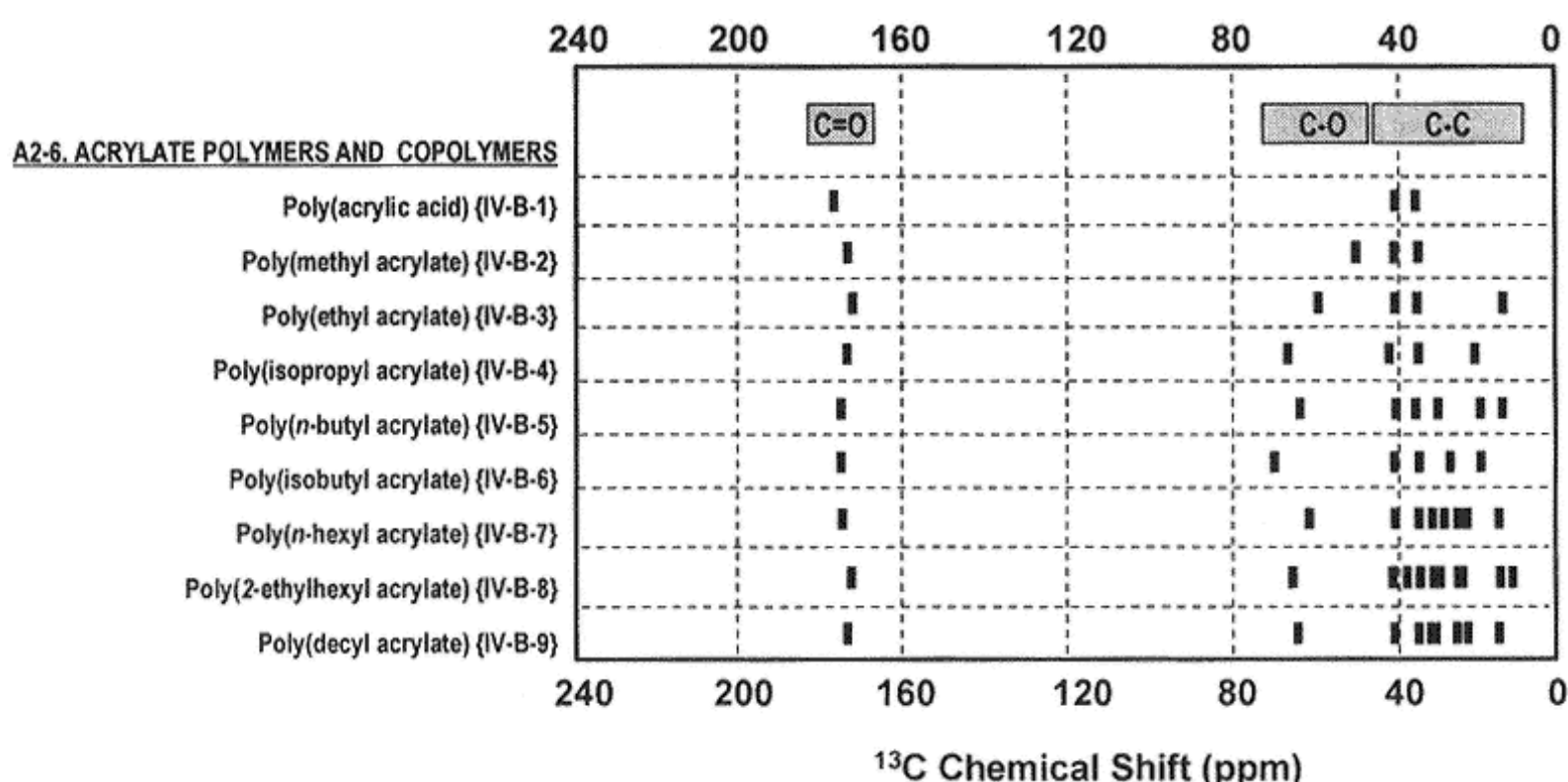
Appendix 2—

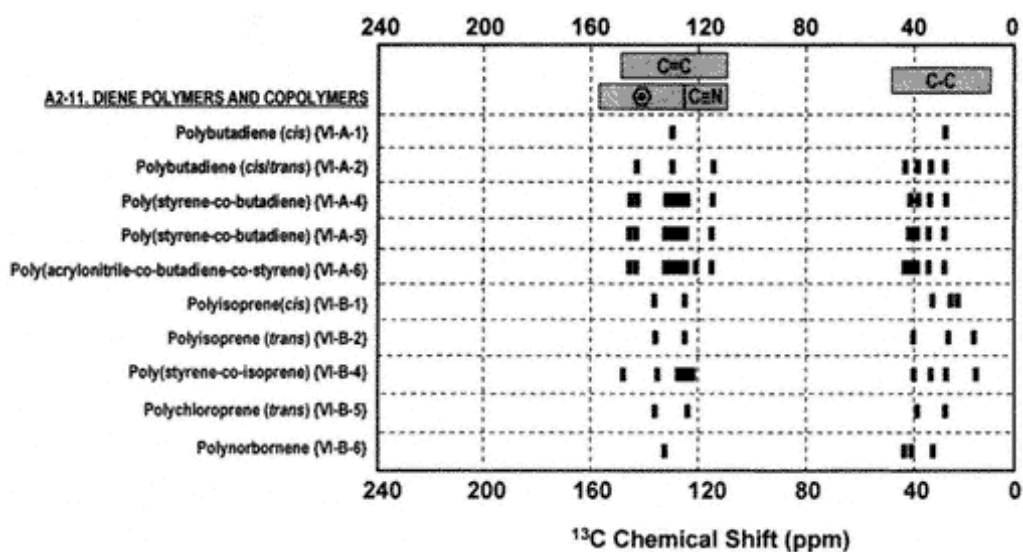
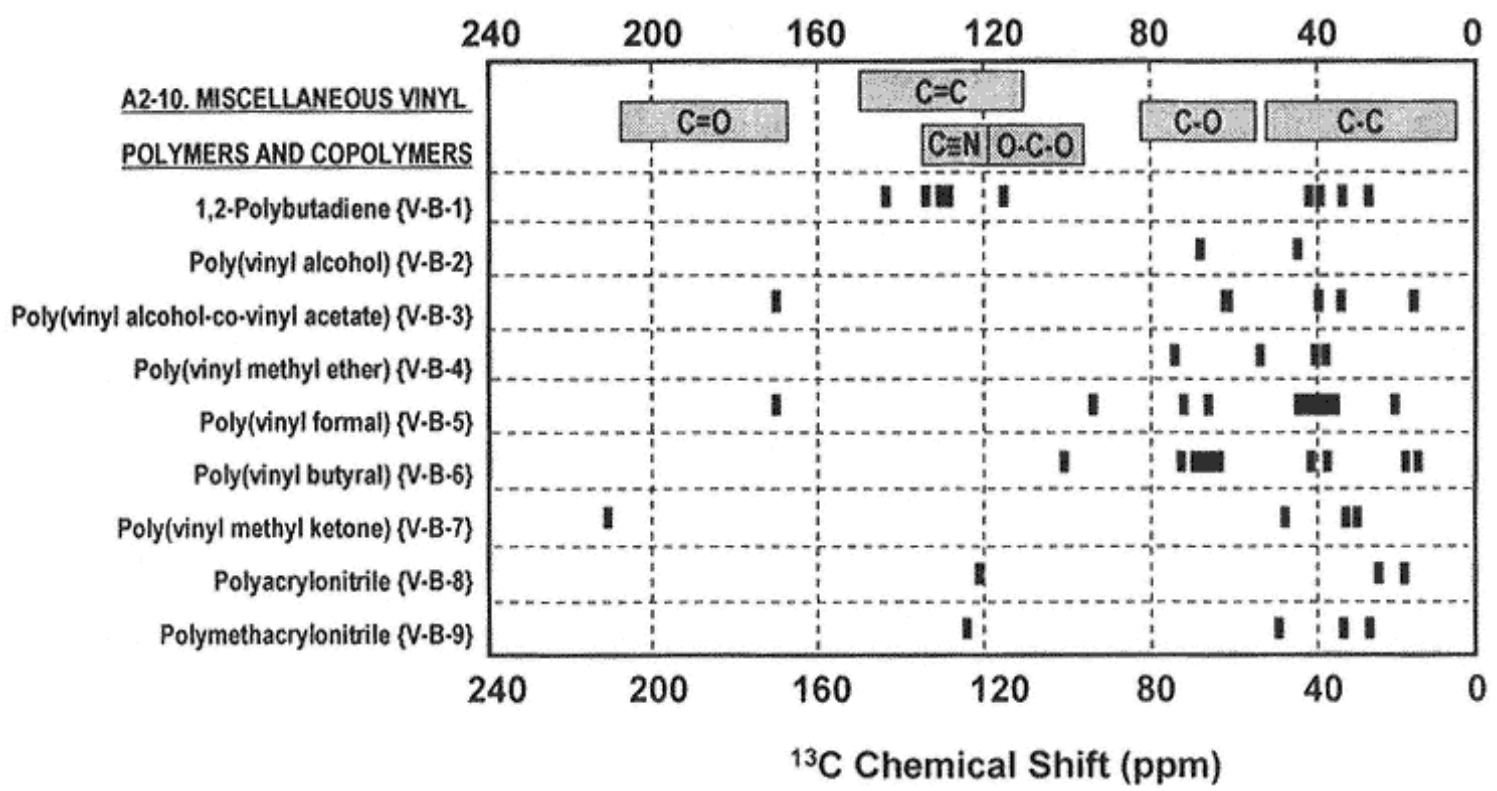
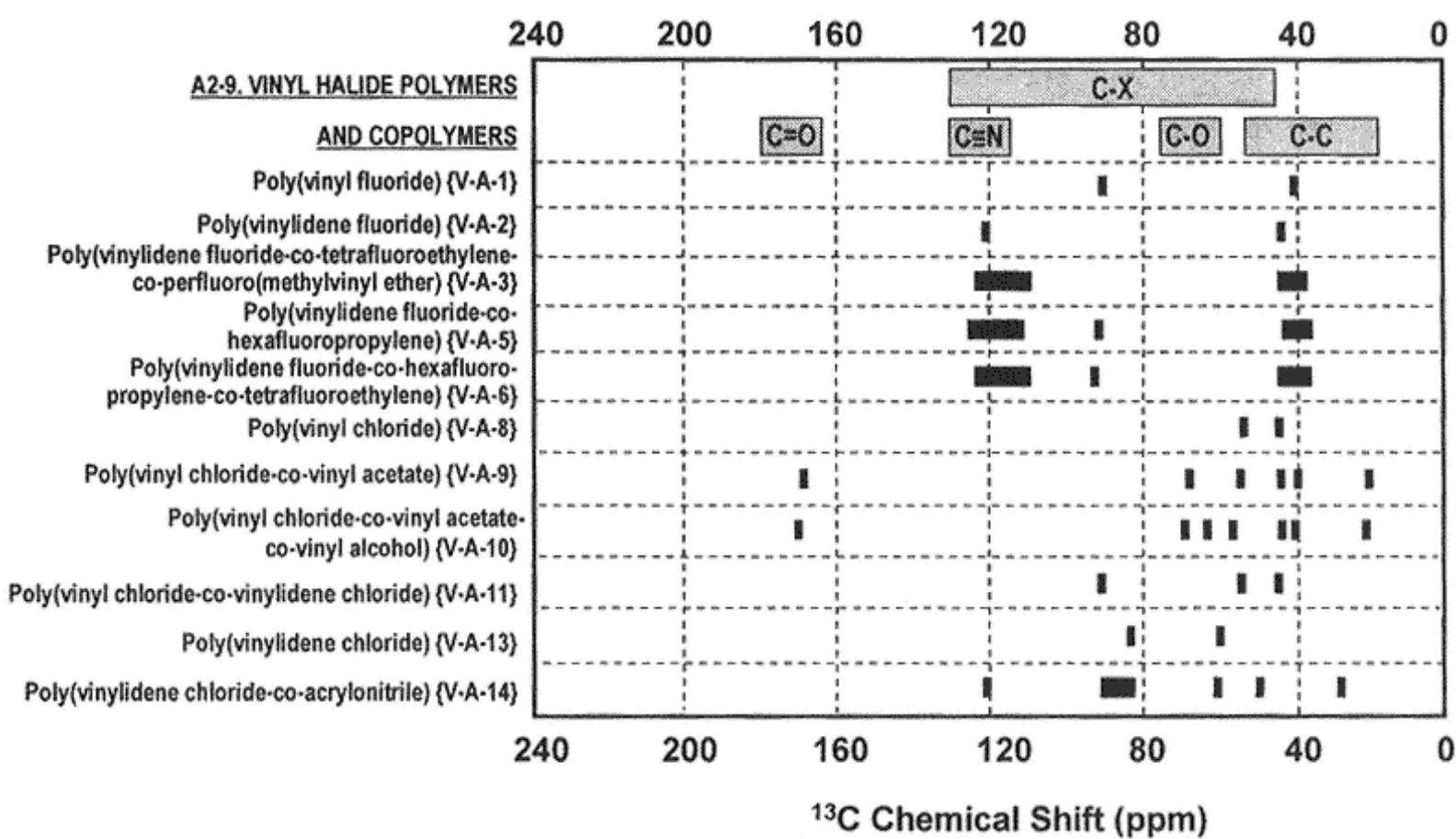
Graphic Summary of ^{13}C Chemical Shifts for Common Polymers

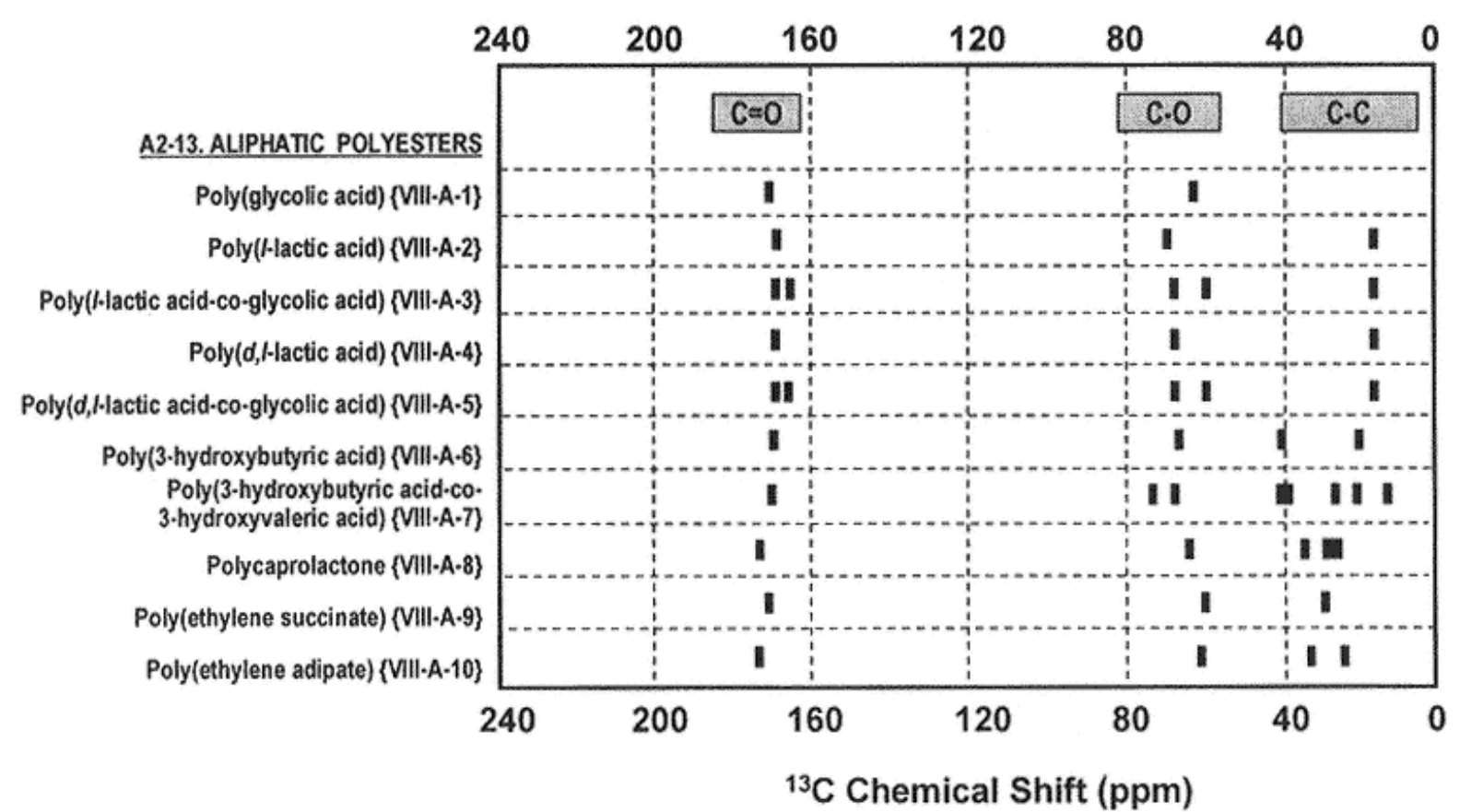
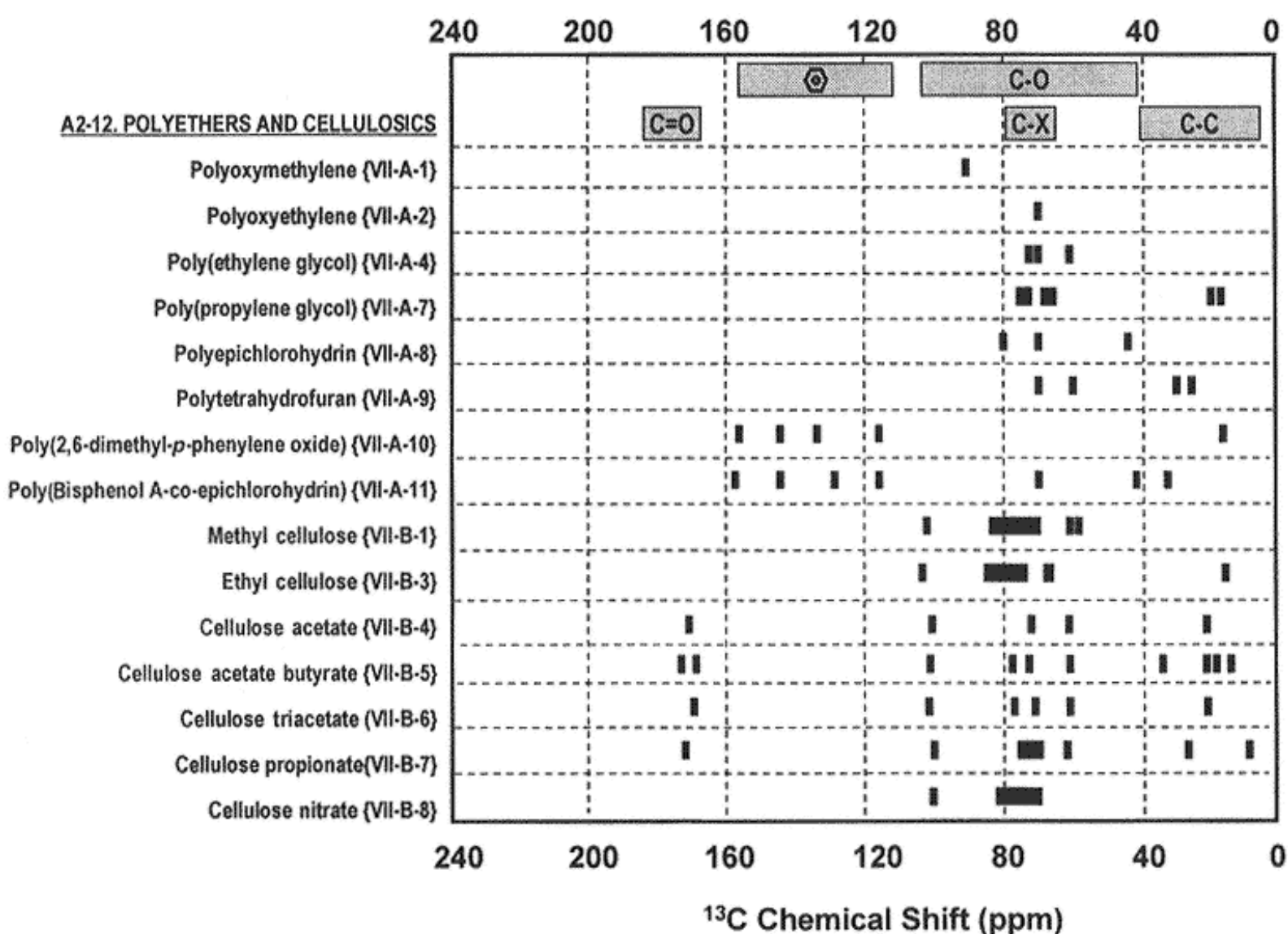
The following figures graphically illustrate the major resonances observed in the ^{13}C spectra of the most common materials of Chapters 2 through 10. The chemical-shift ranges observed for the carbon types (aliphatic, aromatic, or other) included in each group of polymers are shown by gray bars. For individual polymers, peak positions are indicated by black lines, which will permit a quick survey of the materials that exhibit signals in particular δ_{C} regions. When a particular carbon resonates over a range of shifts, a black bar spans the appropriate range. Closely spaced peaks are often marked by a single line. Because these tables give no indication of relative intensities, possible identifications should be checked against the actual spectrum.

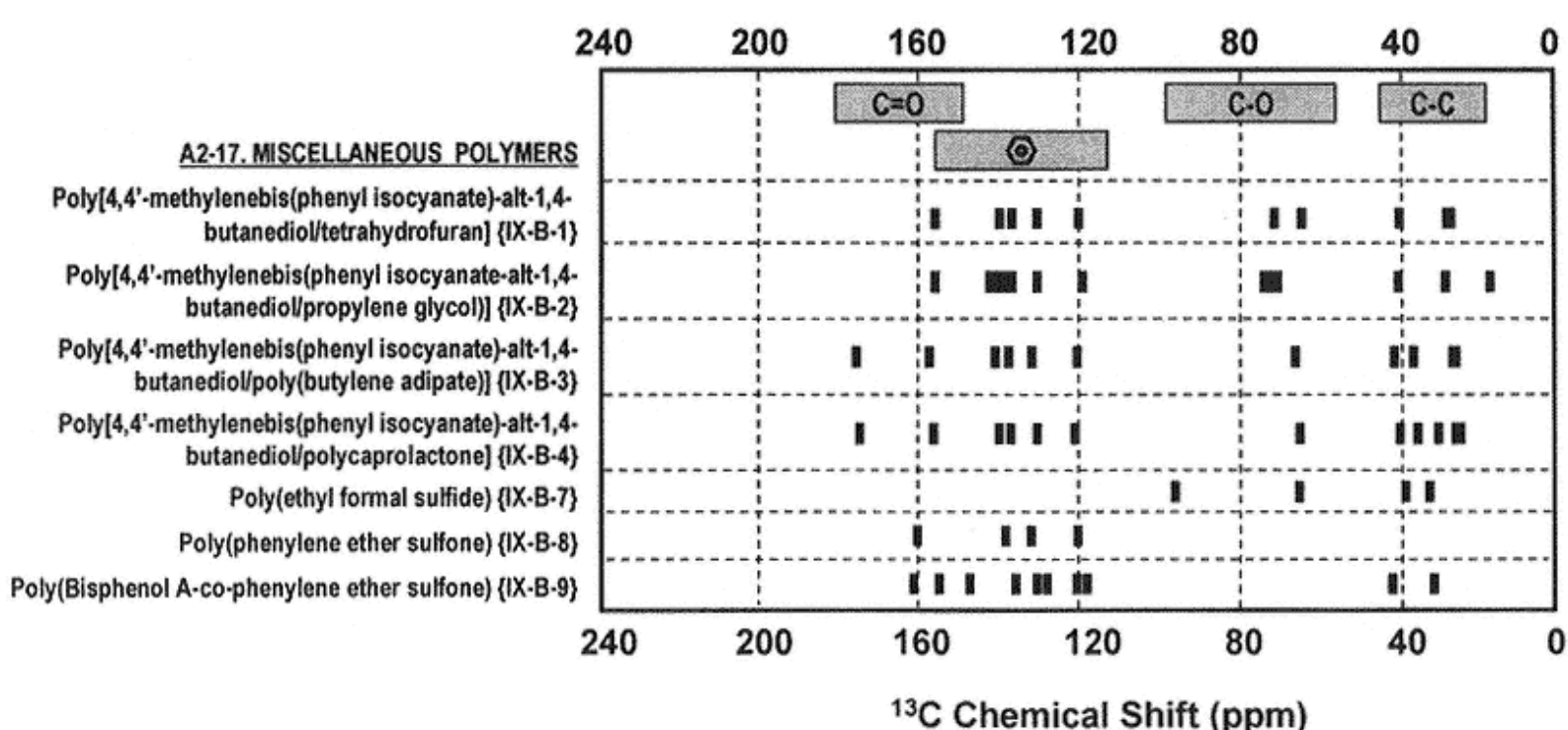
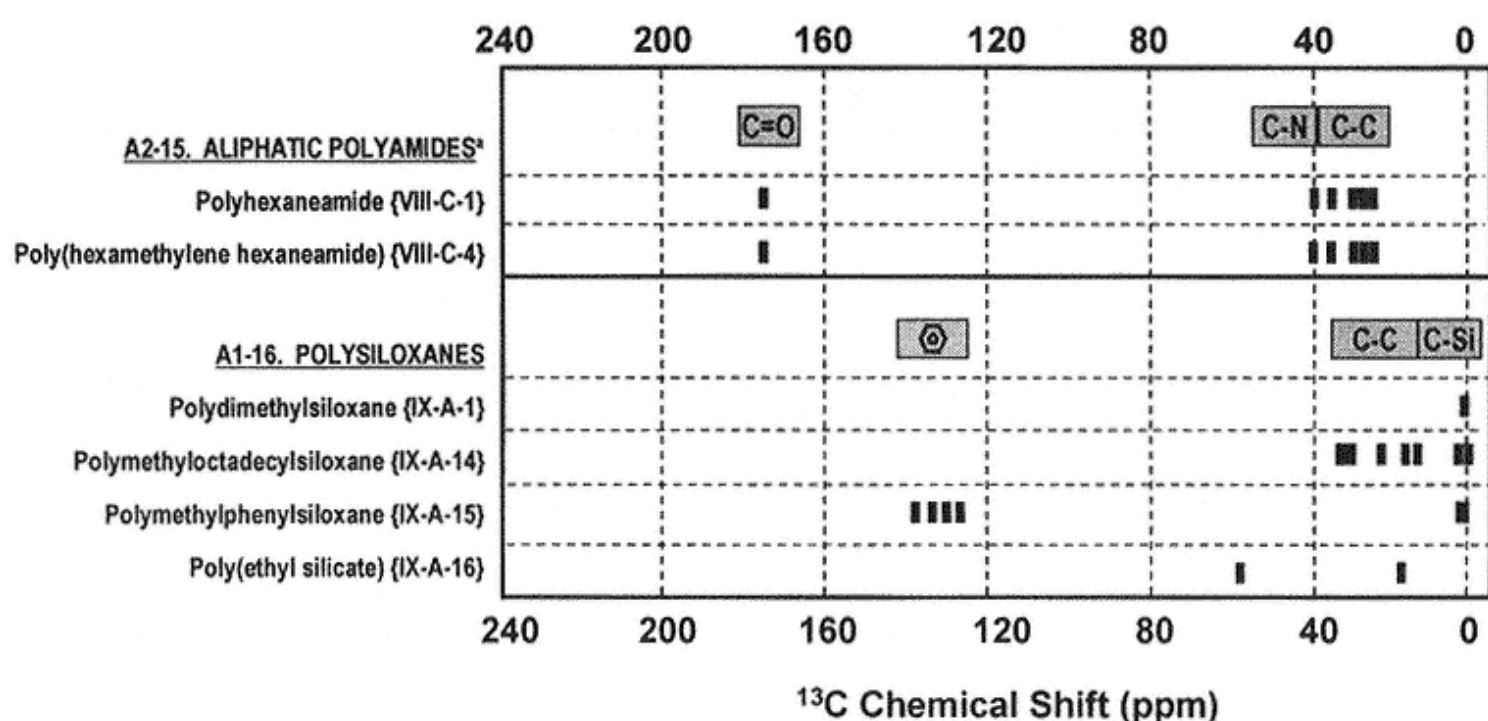
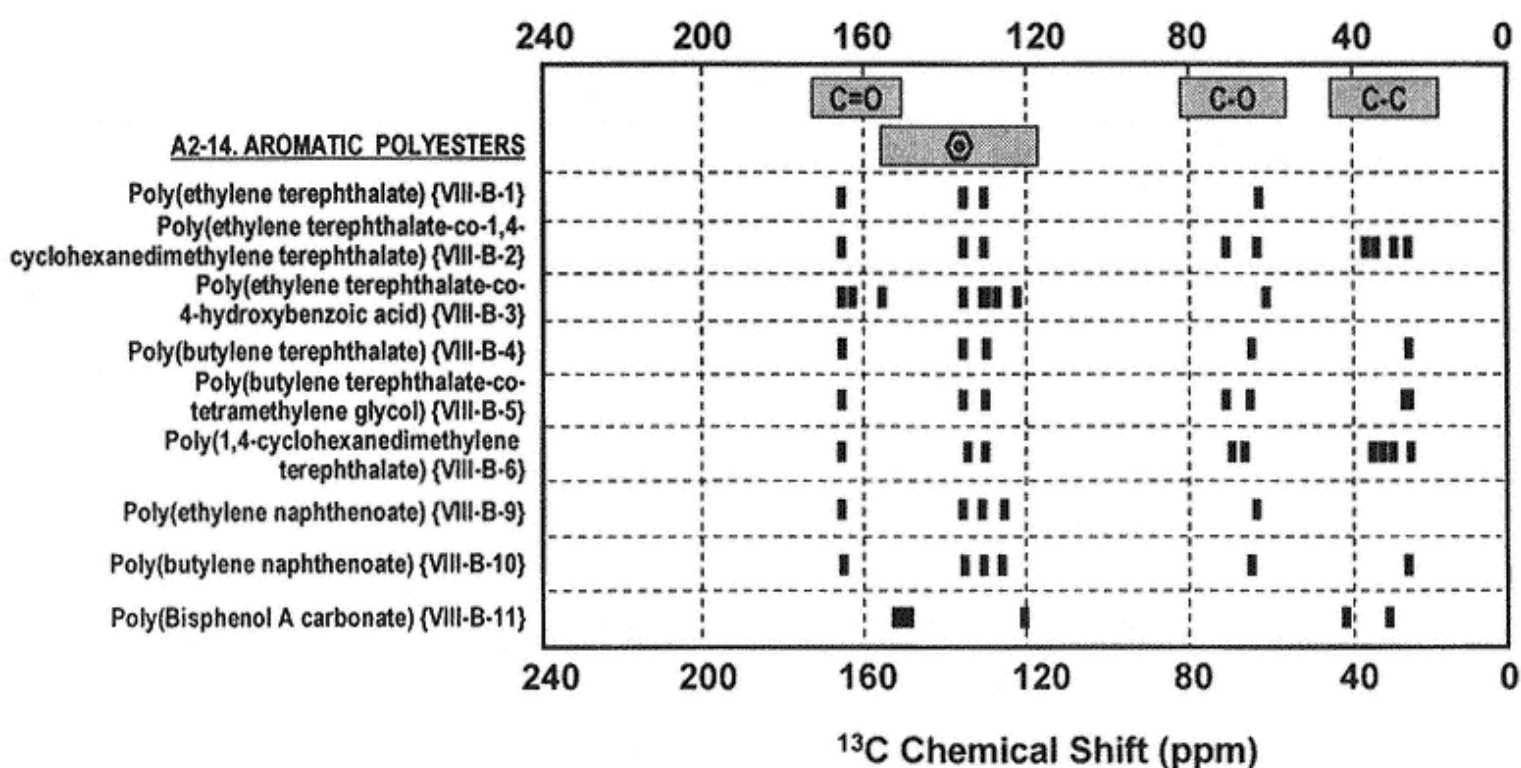












Appendix 3— Some Suppliers of Polymers and Polymer Additives

The information summarized below is correct, to the best of our knowledge, as of the winter of 1999. Because of mergers, acquisitions, and spinoffs, company names and locations may change. Suppliers in **boldface** contributed materials to this collection.

Material Codes:

AC = Acrylates and methacrylates	FL = Fluoropolymers
AD = Additives	HA = Heteraromatic vinyl polymers
AM = Polyamides	MI = Miscellaneous polymers
CE = Cellulosics	OL = Polyolefins
CL = Chloropolymers	SI = Polysiloxanes
DI = Polydienes	ST = Styrenics
EP = Epoxies	SU = Polysulfones
ES = Polyesters	UR = Polyurethanes
ET = Polyethers	VI = Miscellaneous vinyl polymer types

Company: Advanced Elastomer Systems

Address: 388 S. Main Street
Akron, OH 44331-1059

Phone: (800) 305-8070

Web site: www.aestpe.com

Materials: OL

Company: Air Products and Chemicals

Address: 7201 Hamilton Parkway
Allentown, PA 18195-1501

Phone: (800) 345-3148

Web site: www.airproducts.com

Materials: AC, UR, VI

Company: Akcros Chemicals America

Address: 500 Jersey Avenue
New Brunswick, NJ 08903

Phone: (732) 247-2202

Web site: www.akcros.com

Materials: AD, EP, ES

Company: Akzo Nobel Chemicals, Inc.

Address: 300 S. Riverside Plaza
Chicago, IL 60626

Phone: (800) 666-1200

Web site: www.akzonobel.com

Materials: AD, FL, MI

Company: Albemarle Corporation

Address: 451 Florida Blvd.
Baton Rouge, LA 70801

Phone: (800) 535-3030

Web site: www.albemarle.com

Materials: AD

Company: Albright & Wilson Americas

Address: P. O. Box 4439
Glen Allen, VA 23058

Phone: (804) 968-6300

Web site: www.albright-wilson.com

Materials: AD

Company: Allied Signal Inc., Specialty Chemicals

Division Address: 101 Columbia Road
Morristown, NJ 07962

Phone: (800) 222-0094

Web site: www.specialtychem.com

Materials: AM, ES, FL, OL

Company: Aristech Chemical Corporation

Address: 600 Grant Street
Pittsburgh, PA 15230

Phone: (412) 433-2747

Web site: www.aristechchem.com

Materials: AC, AD, ES, OL

Company: A. Schulman

Address: 3550 W. Market Street
Akron, OH 44333

Phone: (800) 662-3 751

Web site: www.aschulman.com

Materials: AM, CL, DI, ES, OL, ST, UR

Company: Ashland Chemical, Industrial Chemicals and
Solvents Division

Address: P. O. 2219
Columbus, OH 43216

Phone: (888) 274-2436

Web site: www.ashchem.com

Materials: AC, AD, DI, EP, ES, ET, HA, OL, SI, ST,
UR, VI

Company: Ashley Polymers

Address: 5114 Fort Hamilton Parkway
Brooklyn, NY 11219

Phone: (718) 851-8111

Web site: www.ashleypoly.com

Materials: AM, DI, ES, ET, ST

Company: AT Plastics, Inc.

Address: 142 Kennedy Road S.
Brampton, ON, Canada L6W 3G4

Phone: (800) 788-4073

Web site: www.atplas.com

Materials: OL

Company: AtoHaas Americas Inc.

Address: 100 Independence Mall West
Philadelphia, PA 19106

Phone: (800) 217-3258

Web site: www.atohaas.com

Materials: AC, ES

Company: Ausimont U.S.A., Inc.

Address: 10 Leonards Lane
Thorofare, NJ 08086

Phone: (800) 323-2874

Web site: www.ausiusa.inter.net

Materials: FL

Company: BASF Corporation

Address: 3000 Continental Drive North
Mount Olive, NJ 07828-1234

Phone: (800) 669-2273

Web site: www.basf.com

Materials: AC, AD, AM, CL, ES, ET, FL, HA, OL, ST, SU,
UR, VI

Company: Bayer Corporation

Address: 100 Bayer Road
Pittsburgh, PA 15205-9741

Phone: (412) 777-2000

Web site: www.bayer.com/polymers-usa

Materials: AC, AD, AM, DI, ES, ET, OL, SI, ST, UR

Company: B.F. Goodrich, Performance Materials

Address: 9911 Brecksville Road
Cleveland, OH 44141-3247

Phone: (800) 331-1144

Web site: www.bfgoodrich.com

Materials: AC, CL, DI, MI, OL, ST, UR

Company: BP Amoco Chemicals

Address: 801 Warrenville Road
Lisle, IL 60532

Phone: (800) 621-4567

Web site: www.bpamoco.com

Materials: AD

Company: BP Amoco Polymers

**Address: 4500 McGinnis Ferry Road
Alpharetta, GA 30202-3914**

Phone: (800) 621-4557

Web site: www.bpamoco.com

Materials: AC, AM, EP, ES, MI, OL, ST, SU

Company: Cabot Corporation

Address: 1751 Diehl Road
Suite 160
Naperville, IL 60563

Phone: (800) 222-6745

Web site: www.cabot-corp.com

Materials: UR

Company: Calgene Chemical Inc.
Address: 7247 N. Central Park Avenue
Skokie, IL 60076
Phone: (800) 432-7187
Web site: www.calgene.com

Materials: ET

Company: Chevron Chemical Company, U.S.
Chemicals

Address: P. O. Box 3766
1301 McKinney
Houston, TX 77253

Phone: (800) 231-3260

Web site: www.chevron.com

Materials: OL, ST

Company: Ciba Specialty Chemicals, Additives Division

**Address: P. O. Box 2005
540 White Plains Road
Tarrytown, NY 10591**

Phone: (800) 431-1900

Web site: www.cibasc.com

Materials: AD

Company: Ciba Specialty Chemicals, Performance
Polymers Division

Address: 281 Fields Lane
Brewster, NY 10509

Phone: (800) 222-1906

Web site: www.cibasc.com

Materials: AC, AM, CL, EP, FL, MI

Company: Clariant Corp., Advanced Materials Group

Address: 90 Morris Avenue
Summit, NJ 07901-3914

Phone: (800) 626-4960

Web site: www.clariant.com

Materials: AC, AM, ES, FL, MI, OL

Company: ComAlloy International Company

Address: 481 Allied Drive
Nashville, TN 37211

Phone: (615) 333-3453

Web site: www.aschulman.com/about/comalloy.htm

Materials: AM, DI, ES, ET, MI, OL, SU, ST

Company: Conap, Inc.

Address: 1405 Buffalo Street
Olean, NY 14760

Phone: (800) 836-3666

Web site: www.conap.com

Materials: EP, UR

Company: CONDEA Company
Address: 900 Threadneedle
Houston, TX 77079-2990
Phone: (800) 841-4877
Web site: www.condea.com

Materials: CL, DI, ST

Company: C. P. Hall Company
Address: 311 S. Wacker Drive
Suite 4700
Chicago, IL 60606
Phone: (312) 554-7400
Web site: www.cphall.com

Materials: AD

Company: Creanova, Inc.
Address: 220 Davidson Avenue
Somerset, NJ 08873
Phone: (732) 560-6000
Web site: www.creanovainc.com

Materials: AM, CL, ES, ET, SI

Company: Cytec Industries, Inc.
Address: Five Garret Mountain Plaza
West Paterson, NJ 07424
Phone: (800) 652-6213
Web site: www.cytec.com

Materials: AC, AD, EP, ES, MI, SI

Company: Dover Chemical Corporation
Address: 3676 Davis Road NW
Dayton, OH 44622
Phone: (800) 821-4369
Materials: AD, EP

Company: Dow Corning Corporation
Address: Box 0994
Midland, MI 48646-4586
Phone: (517) 496-4000
Materials: SI

Company: Dow Plastics
Address: 690 Building
Midland, MI 48640
Phone: (800) 441-4369
Web site: www.dow.com
Materials: CE, CL, DI, EP, ES, ST, OL, UR

Company: DSM Copolymer, Inc.

Address: P. O. Box 2591
5955 Scenic Highway
Baton Rouge, LA 70821-2591

Phone: (800) 535-9990

Web site: www.dsmna.com

Materials: AM, DI, ES, ET, MI, OL, SU, ST

Company: DuPont Chemicals
Address: 15305 Brandwine Building
Wilmington, DE 19801
Phone: (800) 441-9493
Web site: www.dupont.com
Materials: AC, AM, ES, ET, FL, MI, OL

Company: DuPont Dow Elastomers
Address: 300 Bellevue Parkway
Wilmington, DE 19809
Phone: (800) 853-5515
Web site: www.dupont-dow.com
Materials: CL, DI, FL, MI, OL

Company: Dyneon
Address: 6744 33rd Street N.
Oakdale, MN 55128
Phone: (800) 863-9374
Web site: www.dyneon.com
Materials: FL

Company: Eastman Chemical Company
Address: P. O. Box 431
Kingsport, TN 37662-5371
Phone: (800) 327-8626
Web site: www.eastman.com
Materials: AC, AD, CE, CL, ES, OL

Company: ELF Atochem North America Inc.
Address: 2000 Market Street
Philadelphia, PA 19103
Phone: (800) 225-7788
Web site: www.elf-atochem.com
Materials: AD, AM, CL, DI, ET, FL

Company: Emerson & Cuming Specialty Polymers
Address: 46 Manning Road
Billerica, MA 01821
Phone: (800) 832-4929
Materials: EP, SI, UR

Company: EniChem America
Address: 2000 West Loop South
Suite 2010
Houston, TX 77027
Phone: (800) 441-3546
Web site: www.enichemea.com
Materials: AD, DI, EP, OL, VI

Company: Epsilon Products Company
Address: Post Road and Blueball Avenue
Marcus Hook, PA 19061
Phone: (800) 522-7509
Web site: www.epsilonproducts.com

Materials: OL

Company: Equistar Chemicals
Address: 1221 McKinney Street
Suite 1600
Houston, TX 77252-2583
Phone: (888) 777-0232
Web site: www.equistarchem.com

Materials: AD, OL, VI

Company: EVAL Company of America
Address: 1001 Warrenville Road
Suite 201
Lisle, IL 60532-1359

Phone: (800) 423-9762

Materials: OL

Company: Exxon Chemical Company

**Address: P. O. Box 3272
13501 Katy Highway
Houston, TX 77079-1398**

Phone: (713) 870-6000

Web site: www.exxon.com

Materials: AD, OL

Company: Ferro Corporation, Polymer Additives Division

Address: 1000 Lakeside Avenue
P. O. Box 147000
Cleveland, OH 44114-6958

Phone: (216) 641-8580

Web site: www.ferro.com

Materials: AD, AM, DI, ES, ET, MI, OL, SU, ST

Company: Fina Oil and Chemical Company

Address: P. O. Box 2159
Dallas, TX 75221

Phone: (800) 344-3462

Web site: www.fina.com

Materials: DI, OL, ST

Company: Firestone Synthetic Rubber and Latex Company

Address: P. O. Box 26611
381 W. Wilbeth Road
Akron, OH 44319-0006

Phone: (800) 282-0222

Web site: www.firesyn.com

Materials: DI, ST

Company: FMC Corporation, Chemical Products Group

Address: 1735 Market Street
Philadelphia, PA 19103

Phone: (215) 299-6000

Web site: www.fmc.com

Materials: AC, AD

Company: Formosa Plastics Corporation U.S.A.

Address: 9 Peach Tree Hill Road
Livingston, NJ 07039

Phone: (800) 363-1823

Web site: www.fpcusa.com

Materials: CL

Company: Genesee Polymers Corporation

**Address: G-5251
P. O. Box 7047
Flint, MI 48507**

Phone: (810) 238-4966

Materials: SI

Company: GE Plastics

Address: One Plastics Avenue
Pittsfield, MA 01201

Phone: (800) 845-0600

Web site: www.geplastics.com

Materials: AD, DI, ES, ET, MI, OL, ST

Company: GE Silicones

Address: 260 Hudson River Road
Waterford, NY 12188

Phone: (800) 255-8886

Web site: www.ge.com/plastics

Materials: SI

Company: Geon Company

Address: One Geon Center
Avon Lake, OH 44012

Phone: (800) 438-4366

Web site: www.geon.com

Materials: CL

Company: Georgia Gulf Corporation

Address: P.O. Box 105197
Atlanta, GA 30348

Phone: (770) 395-4500

Materials: CL

Company: Georgia Pacific Resins, Inc.

Address: 300 W. Laurel Street
Bellingham, WA 98225

Phone: (360) 650-6171

Web site: www.gp.com

Materials: MI

Company: Goodyear Tire and Rubber Co., Chemical Division

Address: 1452 E. Archwood Avenue
Building 240
Akron, OH 44306

Phone: (800) 321-2416

Web site: www.goodyear.com

Materials: AC, AD, CL, DI, MI

Company: Great Lakes Chemical Corporation

Address: One Great Lakes Boulevard
P. O. Box 2000
West Lafayette, IN 47906-0220

Phone: (800) 428-7947

Web site: www.greatlakeschem.com

Materials: FL, ST

Company: Hatco Corporation

Address: 1020 King Georges Post Road
Fords, NJ 08863

Phone: (732) 738-1000

Materials: AD

Company: Henkel Corporation

Address: 300 Brookside Avenue
Ambler, PA 19002

Phone: (215) 628-1311

Web site: www.henkelcorp.com

Materials: AC, AD

Company: Hercules, Inc.

**Address: 1313 N. Market Street
Wilmington, DE 19894-0001**

Phone: (302) 594-5000

Web site: www.herc.com

Materials: AD, CE, MI

Company: Huntsman Corporation

Address: 500 Huntsman Way
Salt Lake City, UT 84108

Phone: (800) 421-2411

Web site: www.huntsman.com

Materials: OL, ST

Company: ICI Acrylics, Inc.

Address: 7275 Goodlette Farms Parkway
Cordova, TN 38018

Phone: (800) 325-9577

Web site: www.ici.com

Materials: AC

Company: ICI Americas, Inc.

Address: Shipley Building
P. O. Box 8340
3411 Silverside Road
Wilmington, DE 19803-8340

Phone: (302) 887-3000

Web site: www.icinorthamerica.com

Materials: ES, FL

Company: ICI Polyurethanes Group
Address: 286 Mantua Grove Road
West Deptford, NJ 08066-1732
Phone: (800) 257-5547
Web site: www.icinorthamerica.com
Materials: AC

Company: Insite Technology Group Inc.
Address: 7055 Engle Road
Building 5
Middleburg Heights, OH 44130
Phone: (800) 446-8665
Web site: www.insite-inc.com
Materials: OL

Company: International Specialty Products
Address: 1361 Alps Road
Wayne, NJ 07470
Phone: (973) 628-3825
Web site: www.ispcorp.com
Materials: AD, ET, HA, VI

Company: ITW Devcon
Address: 30 Endicott Street
Danvers, MA 01923
Phone: (800) 933-8266
Web site: www.devcon.com
Materials: EP, UR

Company: Keil Chemical Division, Ferro Corporation
Address: 3000 Sheffield Avenue
Hammond, IN 46320
Phone: (219) 682-4000
Web site: www.ferro.com
Materials: AD

Company: Kenrich Petrochemicals Inc.
Address: P.O. Box 32
140 E. 22nd Street
Bayonne, NJ 07002-0032
Phone: (201) 823-9000
Materials: AD

Company: LG Chemical America, Inc.
Address: 1000 Sylvan Avenue
Englewood Cliffs, NJ 07632
Phone: (201) 816-2308
Web site: www.lgchem.com
Materials: AC, CL, DI, ET, ST

Company: LNP Engineering Plastics, Inc.
Address: 475 Creamery Way
Exton, PA 19341
Phone: (800) 854-8774
Web site: www.lnp.com
Materials: AM, DI, ES, ET, MI, OL, SI, ST, SU, UR

Company: Lonza Inc.
Address: 17-17 Route 206
Fair Lawn, NJ 07410
Phone: (800) 777-1875
Web site: www.lonza.com
Materials: ET

Company: M.A. Hanna Engineered Materials
Address: 4955 Avalon Ridge Parkway
Suite 300
Norcross, GA 30071
Phone: (770) 243-7000
Web site: www.hanna.com
Materials: AM, ES, ET, MI

Company: Mitsubishi Engineering Plastics America
Incorporated
Address: One N. Lexington Avenue
White Plains, NY 10601
Phone: (914) 286-3680
Web site: www.m-ep.co.jp
Materials: AM, ES, ET, MI

Company: Mitsui Chemicals America
Address: 2500 Westchester Avenue
Suite 110
Purchase, NY 10577
Phone: (800) 682-2377
Web site: www.mitsui.com
Materials: MI, OL

Company: Mobil Chemical Company
Address: P.O. Box 3140
Edison, NJ 08818-3140
Phone: (732) 321-6000
Web site: www.mobil.com
Materials: OL

Company: Monsanto Company
Address: 800 N. Lindbergh Boulevard
St. Louis, MO 63167
Phone: (800) 325-4330
Web site: www.monsanto.com
Materials: AD, ET, MI, ST, VI

Company: Montell North America
Address: 2801 Centerville Road
Wilmington, DE 19808
Phone: (302) 996-6000
Web site: www.montell.com
Materials: MI, OL

Company: Morton International Inc.
Address: 100 N. Riverside Plaza
Chicago, IL 60606
Phone: (800) 789-7258
Web site: www.mortonintl.com
Materials: AC, AD, MI, OL, ST

Company: MRC Polymers, Inc.
Address: 1716 W. Webster Avenue
Chicago, IL 60614
Phone: (773) 276-6345
Web site: www.mrcpolymers.com
Materials: AC, AM, ES

Company: National Institute of Standards and
Technology
Address: Building 221
Room A320
Gaithersburg, MD 20899
Phone: (301) 975-6478
Web site: www.nist.gov
Materials: Standard references

Company: National Starch and Chemical Co.
Address: 10 FINDERNE AVENUE
BRIDGEWATER, NJ 08807
Phone: (800) 797-4992
Web site: www.nationalstarch.com
Materials: AC, ST, VI

Company: Neste Resins Corporation
Address: 1600 Valley River Drive
Suite 390
Eugene, OR 97401
Phone: (800) 862-1332
Web site: www.neste-resins.com
Materials: ET, MI

Company: Neville Chemical Company
Address: 2800 Neville Road
Pittsburgh, PA 15225
Phone: (412) 331-4200
Materials: AD

Company: Nova Chemicals Corporation
Address: 645 Seventh Avenue S. W.
P. O. Box 2518
Station M
Calgary, Alberta, Canada T2P 5C6
Phone: (724) 773-6632
Web site: www.novachem.com

Materials: AC, OL, ST

Company: Occidental Chemical Corporation/OxyChem

Address: 5005 LBJ Freeway
P. O. Box 809050
Dallas, TX 75244

Phone: (972) 404-3800

Web Site: www.oxychem.com

Materials: AD, CL, DI, MI, VI

Company: Olin Corporation

Address: 501 Merritt 7
P. O. Box 4500
Norwich, CT 06856-4500

Phone: (203) 750-3000

Web site: www.olin.com

Materials: ET

Company: Phillips Chemical Company

Address: 1195 Adams Building
Bartlesville, OK 74004

Phone: (800) 537-3746

Web site: www.phillips66.com

Materials: MI, OL, ST

Company: Plaskolite Inc.

Address: P.O. Box 1497
Columbus, OH 43216

Phone: (800) 848-9124

Web site: www.plaskolite.com

Materials: AC

Company: Plastics Engineering Company

Address: 3518 Lakeshore Road
P. O. Box 758
Sheboygan, WI 53082-0758

Phone: (800) 558-7722

Web site: www.plenco.com

Materials: ES, MI

Company: Polifil

Address: 1112 River Street
P. O. Box 509
Woonsocket, RI 02895

Phone: (800) 394-4166

Web site: www.plasticsgroup.com

Materials: AM, ES, OL

Company: Polyply Composites Inc.

Address: 1540 Marion
Grand Haven, MI 49417

Phone: (616) 842-6330

Web site: www.polyplycomposites.com

Materials: ES

Company: Polysciences

Address: 400 Valley Road
Warrington, PA 18976

Phone: (800) 343-3291

Web site: www.polysciences.com

Materials: All types

Company: PPG Industries, Specialty Chemicals
Division

Address: One PPG Place
Pittsburgh, PA 15272

Phone: (412) 434-3131

Web site: www.ppg.com

Materials: AD, SI, VI

Company: Premix Inc.

Address: Route 20 & Hamilton Road
P. O. Box 281
North Kingsville, OH 44068

Phone: (216) 224-2181

Web site: www.premix.fi

Materials: ES

Company: Pressure Chemical Company

Address: 3419 Smallman Street
Pittsburgh, PA 15201

Phone: (412) 682-5882

Web site: www.presschem.com

Materials: All types

Company: Reichhold

Address: P.O. Box 13582
Research Triangle Park, NC 22709-3582

Phone: (800) 448-3482

Web site: www.reichhold.com

Materials: AC, DI, ES, OL, ST, VI

Company: Reilly Industries Inc.

Address: 1500 S. Tibbs Avenue
Indianapolis, IN 46204

Phone: (800) 777-3536

Web site: www.reillyind.com

Materials: HA

Company: Rhodia Inc.
Address: Prospect Plains Road
CN-7500
Cranbury, NJ 08512-7500
Phone: (800) 922-2189
Web site: www.rpsurfactants.com
Materials: AC, AD, EP, ET, SI

Company: Rohm and Haas Company, Polymers,
Resins, and Monomers Group
Address: 100 Independence Mall West
Philadelphia, PA 19106
Phone: (215) 592-3086
Web site: www.rohmmaas.com
Materials: AC, ST, VI

Company: RTP Company
Address: 580 E. Front Street
P. O. Box 5439
Winona, MN 55987-0439
Phone: (800) 433-4787
Web site: www.rtpcompany.com
Materials: AC, AM, DI, ES, ET, FL, MI, ST, SU, UR

Company: Sartomer Company, Inc.
Address: 502 Thomas Jones Way
Exton, PA 19341
Phone: (800) 345-8247
Web site: www.sartomer.com
Materials: AC, AD, EP, ES, OL

Company: Schenectady International Inc.
Address: P.O. Box 1046
Schenectady, NY 12301
Phone: (518) 370-4200
Web site: www.pleo.com/schenectady
Materials: EP, MI

Company: Scientific Polymer Products
Address: 6265 Dean Parkway
Ontario, NY 14519
Phone: (716) 265-0413
Web site: www.scientificpolymer.com
Materials: All types

Company: S. C. Johnson Polymers
Address: 8310 16th Street
Sturtevant, WI 53177
Phone: (414) 631-4120
Web site: www.scjohnsonwax.com
Materials: AC

Company: Shearwater Polymers, Inc.

Address: 1112 Curch Street
Huntsville, AL 35801

Phone: (800) 457-1806

Web site: www.swpolymers.com

Materials: ET

Company: Shell Chemical Company

Address: 910 Louisiana Street
Houston, TX 77252

Phone: (800) 872-7435

Web site: www.shellchemical.com

Materials: DI, EP, ES, MI, OL, ST

Company: Shintech Inc.

Address: 24 Greenway Plaza
Suite 811
Houston, TX 77046

Phone: (713) 965-0713

Web site: N/A

Materials: CL

Company: Shuman Plastics Inc.

Address: 35 Neoga Street
Depew, NY 14043

Phone: (716) 685-2121

Web site: www.shuman-plastics.com

Materials: DI, ET, OL, ST

Company: Solutia, Inc.

Address: 1300 Olive Boulevard
P. O. Box 66760
St. Louis, MO 63166-6760

Phone: (800) 964-5224

Web site: www.solutia.com

Materials: AD, AM, MI, OL

Company: Solvay Polymers Inc.

Address: P.O. Box 27328
Houston, TX 77227-7328

Phone: (800) 231-6313

Web site: www.solvay.com

Materials: CL, ES, FL, OL

Company: Spartech Plastics

Address: 840 Great S. W. Parkway
Arlington, TX 76011

Phone: (817) 640-0621

Web site: www.spartech.com

Materials: OL

Company: Stepan Company
Address: 22 W. Frontage Road
Northfield, IL 60093
Phone: (800) 745-7837
Web site: www.stepan.com

Materials: ET, UR

Company: Thermofil Inc.
Address: 6150 Whitmore Lake Road
Brighton, MI 48116-1990
Phone: (800) 444-4408
Web site: www.thermofil.com

Materials: AM, DI, ES, OL, ST

Company: Ticona
Address: 90 Morris Avenue
Summit, NJ 07901-3914
Phone: (800) 526-4960
Web site: www.hoechst.com

Materials: AM, ES, ET, MI, OL, UR

Company: Union Camp Company
Address: 5220 Belfort Road
Suite 200
Jacksonville, FL 32256-6012
Phone: (904) 332-1800
Web site: www.unioncamp.com

Materials: AD

Company: Union Carbide Corporation
Address: 39 Old Ridgebury Road
Danbury, CT 06817-0001
Phone: (800) 335-8550
Web site: www.unioncarbide.com

Materials: AC, AD, CL, EP, ES, ET, MI, OL, UR, VI

Company: Uniroyal Chemical Co.
Address: World Headquarters
Middlebury, CT 06749
Phone: (203) 573-2000
Web site: www.uniroyalchemical.com

Materials: AD, DI, OL

Company: United Minerals Corporation
Address: Route 1 & Highway 67 N.
P. O. Box 1176
Malvern, AR 72104
Phone: (501) 332-8118
Web site: www.aimgroup.com/aim

Materials: EP

Company: Univation Technologies

Address: 5555 San Felipe
19th Floor
Houston, TX 77056

Phone: (713) 892-3700

Materials: OL

Company: UOP—Food Antioxidants

Address: 25 E. Algonquin Road
Des Plaines, IL 60017-5017

Phone: (800) 348-0832

Materials: AD

Company: U.S. Chemicals, Inc.

Address: 280 Elm Street
New Canaan, CT 06840

Phone: (203) 966-8777

Web site: www.uschemicals.com

Materials: EP

Company: Victrex U.S.A.

Address: 601 Willowbrook Lane
West Chester, PA 19382

Phone: (800) 842-8739

Web site: www.victrex.com

Materials: MI

Company: Wacker Silicones

Address: 3301 Sutton Road
Adrian, MI 49221

Phone: (800) 243-0063

Web site: www.wackersilicones.com

Materials: SI

Company: Westlake Group

Address: 2801 Post Oak Road
Suite 600
Houston, TX 77056

Phone: (800) 545-9577

Web site: www.westlakeplastics.com

Materials: CL, OL

Company: Witco Corporation, Performance Chemical Group

Address: One American Lane
Greenwich, CT 06831-2559

Phone: (800) 494-8673

Web site: www.witco.com

Materials: AC, AD, ES, ET, SI, UR

Appendix 4— List of Abbreviations

ABA	triblock copolymer ($A_xB_yA_z$)
ABS	poly(acrylonitrile-co-butadiene-styrene)
AO	antioxidant
APT	" <u>attached proton test</u> " experiment
Bd	butadiene
BPE	branched polyethylene; same as low-density polyethylene
BR	butyl rubber
CA	cellulose acetate
CAB	cellulose acetate butyrate
CDC1 ₃	chloroform-d
C1PE	chlorinated polyethylene
CN	cellulose nitrate
COC	cyclic olefin copolymer; poly(ethylene-co-norbornene)
COSY	" <u>correlation spectroscopy</u> " experiment
Cr(acac) ₃	Cr(III) acetylacetonate
DEHP	di(2-ethylhexyl) phthalate; dioctyl phthalate
DEPT	" <u>distortionless enhancement by polarization transfer</u> " experiment
DMF-d ₇	dimethylformamide-d ₇
DMSO-d ₆	dimethylsulfoxide-d ₆
D ₂ O	deuterium oxide; deuterated water
DOA	dioctyl adipate; di(2-ethylhexyl) adipate
DOM	dioctyl maleate; di(2-ethylhexyl) maleate
DOP	dioctyl phthalate; di(2-ethylhexyl phthalate)
DUP	diundecyl phthalate
EAA	poly(ethylene-co-acrylic acid)
EBA	poly(ethylene-co-butyl acrylate)
EC	ethyl cellulose
ECO	poly(ethylene-co-carbon monoxide)
EEA	poly(ethylene-co-ethyl acrylate)
ELO	epoxidized linseed oil
EMA	poly(ethylene-co-methyl acrylate)
EMAA	poly(ethylene-co-methacrylic acid)
EPDM	ethylene-propylene-diene rubber
EPR	ethylene-propylene rubber
ESO	epoxidized soybean oil
EVA	poly(ethylene-co-vinyl acetate)
EVA1	poly(ethylene-co-vinyl alcohol)
EVOH	poly(ethylene-co-vinyl alcohol)
HDPE	high-density polyethylene
HIPS	high-impact polystyrene

INEPT	"insensitive nuclei enhanced by polarization transfer" experiment
LDPE	low-density polyethylene
LLDPE	linear, low-density polyethylene
LPE	linear polyethylene; high-density polyethylene
MDI	4,4'-diphenylenemethane diisocyanate
M_n	number-average molecular weight
M_w	weight-average molecular weight
MW	molecular weight
MWD	molecular-weight distribution
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser enhancement
ODCB-d ₄	<i>o</i> -dichlorobenzene-d ₄
PAA	poly(acrylic acid)
P α MS	poly(α -methylstyrene)
PAN	polyacrylonitrile
PB	poly(1-butene)
PBA	poly(<i>n</i> -butyl acrylate)
PBd	polybutadiene

PBMA	poly(<i>n</i> -butyl methacrylate)
PBN	poly(butylene naphthenoate)
PBPAC	poly(Bisphenol A carbonate)
PBT	poly(butylene terephthalate)
PCL	polycaprolactone
PDMS	polydimethylsiloxane
PE	polyethylene
PEA	poly(ethyl acrylate)
PEG	poly(ethylene glycol)
PEMA	poly(ethyl methacrylate)
PEN	poly(ethylene naphthenoate)
PET	poly(ethylene terephthalate)
PHB	poly(3-hydroxybutyric acid)
PHBV	poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid)
PI	polyisoprene
PIB	polyisobutylene
PiBA	poly(isobutyl acrylate)
PiBMA	poly(isobutyl methacrylate)
PiPA	poly(isopropyl acrylate)
PMA	poly(methyl acrylate)
PMAN	polymethacrylonitrile
PMMA	poly(methyl methacrylate)
PMP	poly(4-methyl-1-pentene)
PNB	polynorbornene
P <i>n</i> BA	poly(<i>n</i> -butyl acrylate)
P <i>n</i> BMA	poly(<i>n</i> -butyl methacrylate)
PNVC	poly(<i>N</i> -vinyl carbazole)
POE	polyoxyethylene
POM	polyoxymethylene
PP	polypropylene
PPG	poly(propylene glycol)
ppm	parts-per-million (chemical-shift scale, δ)
PPO	poly(2,6-dimethylphenylene oxide)
PS	polystyrene
PTHF	polytetrahydrofuran
PVA	poly(vinyl acetate)
PVC	poly(vinyl chloride)
PVdC	poly(vinylidene chloride)
PVdF	poly(vinylidene fluoride)
PVF	poly(vinyl fluoride)
PVME	poly(vinyl methyl ether)
PVMK	poly(vinyl methyl ketone)
PVOH	poly(vinyl alcohol)
P2VP	poly(2-vinyl pyridine)

P4VP	poly(4-vinyl pyridine)
PVS	poly(vinyl stearate)
PVT	poly(vinyl toluene)
SAN	poly(styrene-co-acrylonitrile)
SBS	styrene-butadiene-styrene block copolymer
SBR	styrene-butadiene rubber
T ₁	spin-lattice relaxation time
T ₂	spin-spin relaxation time
TCB	1,2,4-trichlorobenzene
TCP	tricresyl phosphate
TBP	tributyl phosphate
T _g	glass-transition temperature
THF-d ₈	tetrahydrofuran-d ₈
TNPP	tris(nonylphenyl) phosphite
TPP	triphenyl phosphate
UHMWPE	ultrahigh-molecular weight polyethylene
w/w	weight/weight
VA	vinyl acetate
VOH	vinyl alcohol
v/v	volume/volume

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Organized by chemical structure, this practical reference compiles nearly **400 fully assigned NMR spectra of some 300 polymers and polymer additives** representing all major classes of materials—polyolefins, styrenics, acrylates, methacrylates, vinyl polymers, elastomers, polyethers, polyesters, polyamides, silicones, cellulose, polyurethanes, plasticizers, and antioxidants.

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