# CHAPTER X

SYNTHETIC POLYMERS

X,1.   BRIEF INTRODUCTION TO SUBJECT

Polymerisation involves the chemical combination of a number of identical or similar molecules to form a complex molecule. The resulting polymer has a high molecular weight. The term synthetic polymer is usually employed to denote these compounds of very high molecular weight.

Compounds which polymerise include :

1. Those which contain a reactive multiple bond ($C=C$, $C\equiv C$, $C=O$, etc.).
2. Polyfunctional molecules (glycols, dibasic acids, hydroxy acids, diamides, etc.).
3. Cyclic compounds capable of undergoing ring opening (alkylene oxides, lactones, lactams, anhydrides, etc.).

Polymers can be classified as addition polymers and condensation polymers. *Addition polymers* are formed by intermolecular reactions of the monomeric units without the elimination of atoms or groups. An example is vinyl chloride, which can be made to combine with itself to yield polyvinyl chloride :

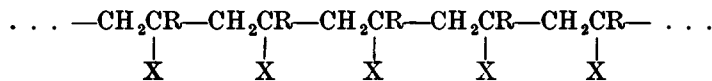$$n CH_2=CHCl \longrightarrow -(CH_2CHCl)_n-$$
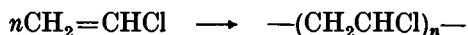
The terminal valencies of the chain are saturated by univalent groups such as hydrogen, halogen, hydroxyl, etc., or an organic fragment derived from the polymerisation catalyst. *Copolymers* are obtained by addition polymerisation of a mixture of two different monomers, for example, butadiene and styrene. The properties of the product depend upon the proportions of the two monomers and upon the average molecular weight of the copolymer. *Condensation polymers* are produced by reactions which are attended by the elimination of some simple molecule (*e.g.*, water, alcohol or ammonia) between functional groups : such reactions are esterification, anhydride formation, amide formation, aldol condensation, and the like. Only a very limited number of examples can, of necessity, be given in this volume.

In practice, synthetic polymers are sometimes divided into two classes, *thermo-setting* and *thermo-plastic*. Those polymers which in their original condition will flow and can be moulded by heat and pressure, but which in their finished or " cured " state cannot be re-softened or moulded are known as thermo-setting (examples: phenol formaldehyde or urea formaldehyde polymer). Thermoplastic polymers can be resoftened and remoulded by heat (examples : ethylene polymers and polymers of acrylic esters).
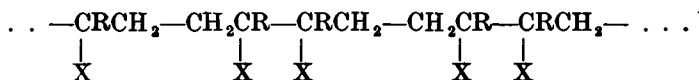
ADDITION POLYMERS

Many of the compounds which undergo addition polymerisation may be represented by the general formula $CH_2=CR-X$, for example, ethylene (R = H, X = H), *iso*butylene (R = CH_3, X = CH_3), vinyl chloride (R = H, X = Cl), vinylidene chloride (R = Cl, X = Cl), vinyl acetate (R = H, X = $OCOCH_3$), methyl acrylate (R = CH_3, X = $COOCH_3$), and styrene (R = H, X = C_6H_5). At least three types
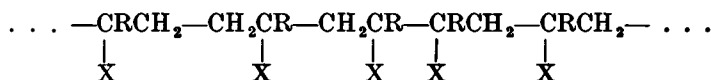
of polymeric structures may result from the polymerisation of unsymmetrical compounds $CH_2=CRX$, depending upon the arrangement of structural units in the chain :

$$\ldots -CH_2CR-CH_2CR-CH_2CR-CH_2CR-CH_2CR- \ldots$$
$$\hspace{0.5cm} | \hspace{1cm} | \hspace{1cm} | \hspace{1cm} | \hspace{1cm} |$$
$$\hspace{0.5cm} X \hspace{1cm} X \hspace{1cm} X \hspace{1cm} X \hspace{1cm} X$$

Type I (X groups in 1 : 3 positions)

$$\ldots -CRCH_2-CH_2CR-CRCH_2-CH_2CR-CRCH_2- \ldots$$
$$| \hspace{1.8cm} | \hspace{0.5cm} | \hspace{1.8cm} | \hspace{0.5cm} |$$
$$X \hspace{1.8cm} X \hspace{0.5cm} X \hspace{1.8cm} X \hspace{0.5cm} X$$

Type II (X groups in 1 : 2 positions)

$$\ldots -CRCH_2-CH_2CR-CH_2CR-CRCH_2-CRCH_2- \ldots$$
$$| \hspace{1.5cm} | \hspace{1cm} | \hspace{0.5cm} | \hspace{1cm} |$$
$$X \hspace{1.5cm} X \hspace{1cm} X \hspace{0.5cm} X \hspace{1cm} X$$

Type III (X groups in random positions)

The structure of the linear polymer formed under a particular set of experimental conditions can be formulated in a number of cases after a detailed examination of its properties.
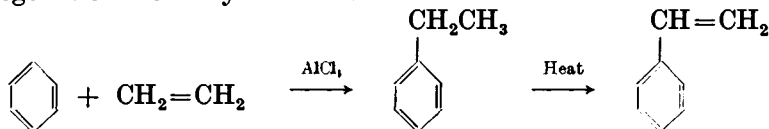
Examples of addition polymers include :

Ethylene. Under the influence of pressure and a catalyst, ethylene yields a white, tough but flexible waxy solid, known as *Polythene*. Polyethylene possesses excellent electrical insulation properties and high water resistance ; it has a low specific gravity and a low softening point (about 110°). The chemical inertness of *Polythene* has found application in the manufacture of many items of apparatus for the laboratory. It is a useful lubricant for ground glass connexions, particularly at relatively high temperatures.
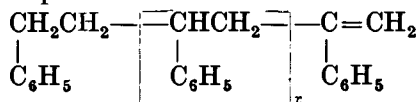
Tetrafluoroethylene. Emulsion polymerisation of tetrafluoroethylene, catalysed by oxygen, yields polytetrafluoroethylene (*Teflon*) as a very tough horn-like material of high melting point. It possesses excellent electrical insulation properties and a remarkable inertness towards all chemical reagents, including aqua regia.

Styrene. Styrene is readily polymerised to a glass-clear resin, polystyrene, but the exact nature of the polymer is influenced by the nature of the catalyst, the temperature, solvent, etc.

Styrene (or vinylbenzene) is prepared technically by the " cracking dehydrogenation " of ethylbenzene :

Polystyrene may be represented as :

$$CH_2CH_2-\overline{}CHCH_2-\overline{}-C=CH_2$$
$$| \hspace{1.5cm} | \hspace{1.5cm} |$$
$$C_6H_5 \hspace{1cm} C_6H_5 \hspace{1cm} C_6H_5$$
$$\hspace{3cm}{}_x$$

Vinyl compounds. Vinyl chloride (prepared from acetylene and hydrogen chloride) yields polyvinyl chloride (*P.V.C.*), which is employed as a rubber substitute and for other purposes. Vinyl acetate (from
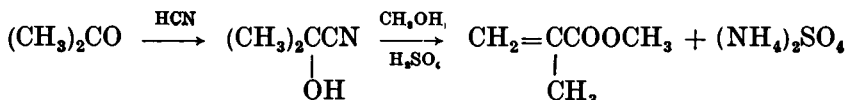
acetylene and acetic acid) similarly gives polyvinyl acetate. Vinylidene chloride $CH_2=CCl_2$ affords polyvinylidene chloride.

Acrylic acid derivatives. Acrylic esters polymerise readily under the influence of oxygen, peroxides, light or heat to give colourless, glass-like plastics.
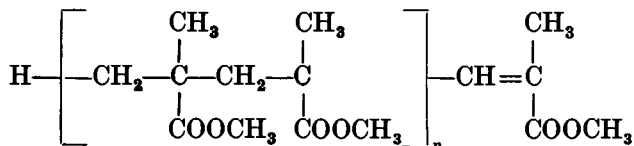
Methyl acrylate is usually prepared from ethylene chlorohydrin thus :

$$CH_2OHCH_2Cl \xrightarrow{NaCN} CH_2OHCH_2CN + NaCl \xrightarrow[H_2SO_4]{CH_3OH,} CH_2=CHCOOCH_3$$
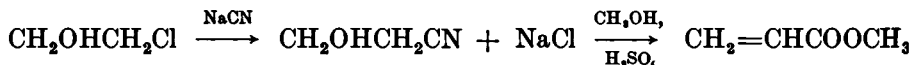
Methyl methacrylate is obtained commercially from acetone cyanohydrin :

$$(CH_3)_2CO \xrightarrow{HCN} \underset{\underset{OH}{|}}{(CH_3)_2CCN} \xrightarrow[H_2SO_4]{CH_3OH,} \underset{\underset{CH_3}{|}}{CH_2=CCOOCH_3} + (NH_4)_2SO_4$$

The action of sulphuric acid alone upon acetone cyanohydrin affords α-methylacrylic acid. The methyl methacrylate polymers are the nearest approach to an organic glass so far developed, and are marketed as *Perspex* (sheet or rod) or *Diakon* (powder) in Great Britain and as *Plexiglass* and *Lucite* in the U.S.A. They are readily depolymerised to the monomers upon distillation. The constitution of methyl methacrylate polymer has been given as :

$$H\left[-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\right]_n -CH=\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}$$

COPOLYMERS

Emulsion polymerisation of a mixture of butadiene and styrene gives a synthetic rubber (*Buna S ; GBS rubber*), which is used either alone or blended with natural rubber for automobile tyres and a variety of other articles.

A mixed polymer of butadiene and acrylonitrile (*Perbunan, Hycar, Chemigum*) may be vulcanised like rubber and possesses good resistance to oils and solvents in general.

Copolymerisation of vinyl acetate and vinyl chloride yields resins of desirable properties : they are strong and adhesive, thermoplastic, and are suitable for the manufacture of synthetic fibre (*Vinyon*).
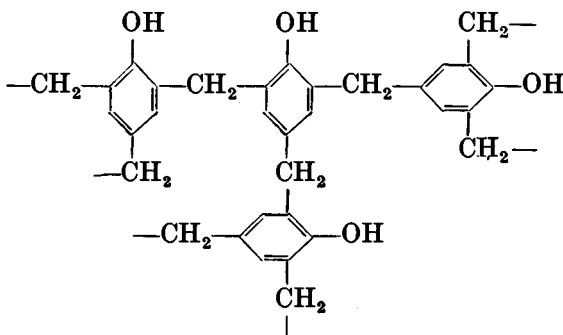
Vinylidene chloride and vinyl chloride lead to the copolymer known as *Saran*. Other commercial copolymers are produced from vinyl chloride and acrylonitrile (*Dynel*), and from maleic anhydride and styrene.

CONDENSATION POLYMERS

These may be produced from a great variety of poly-functional compounds : to obtain satisfactory products, the reactants must be pure. A few examples follow.

Phenol - aldehyde polymers. L. Baekland (1909) first demonstrated the possibilities of the reaction between phenol and formaldehyde from the commercial view point. Condensation in the presence of either
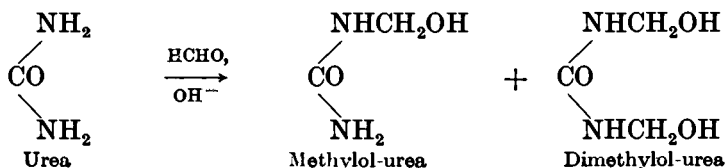
alkaline or acid catalysts gives valuable polymers, covered by the general name *Bakelite*. Baekland recognised three distinct stages in the reaction of phenol and formaldehyde in alkaline solution. The initial product, *Bakelite A*, is a liquid or semi-solid, and is converted by continued heating into an intermediate, *Bakelite B*, a relatively insoluble, fusible solid : when the latter is subjected to heat and pressure, it is converted into *Bakelite C*, an insoluble and infusible plastic. A possible formula is :

$$-CH_2 \overset{OH}{\underset{-CH_2}{\underset{\big|}{\bigcirc}}} -CH_2 \overset{OH}{\underset{CH_2}{\underset{\big|}{\bigcirc}}} -CH_2 \overset{CH_2-}{\underset{CH_2-}{\underset{\big|}{\bigcirc}}} -OH$$

$$-CH_2 \overset{}{\underset{CH_2}{\underset{\big|}{\bigcirc}}} -OH$$

The condensation proceeds somewhat differently with an acid catalyst ; the product is termed *Novolak*.

If formaldehyde is replaced by furfural, the furfural - phenol polymer (U.S.A. *Durite*) results. The above polymers are largely used for moulding purposes.

Urea - formaldehyde polymers. Formalin and urea (usually in the molecular proportions of 3 : 2) condense in the presence of ammonia, pyridine or hexamine to give urea - formaldehyde polymers, known commercially as *Beetle* or *Plaskon*, and are widely used as moulding powders. It is believed that the intermediate products in the condensation are methylol-urea and dimethylol-urea :

$$\underset{\text{Urea}}{\overset{NH_2}{\underset{NH_2}{\overset{\diagup}{CO}\diagdown}}} \xrightarrow[OH^-]{HCHO,} \underset{\text{Methylol-urea}}{\overset{NHCH_2OH}{\underset{NH_2}{\overset{\diagup}{CO}\diagdown}}} + \underset{\text{Dimethylol-urea}}{\overset{NHCH_2OH}{\underset{NHCH_2OH}{\overset{\diagup}{CO}\diagdown}}}$$

Polymerisation may occur as a result of dehydration of these compounds to methylene and dimethylene urea or more probably by a stepwise loss of water between the molecules of methylol and dimethylol-urea.

$$\underset{\text{Methylene urea}}{\overset{NH_2}{\underset{N=CH_2}{\overset{\diagup}{CO}\diagdown}}} \qquad\qquad \underset{\text{Dimethylene urea}}{\overset{N=CH_2}{\underset{N=CH_2}{\overset{\diagup}{CO}\diagdown}}}$$

Melamine - formaldehyde polymers. Melamine (2 : 4 : 6-triamino-1 : 3 : 5-triazine), obtained by heating dicyandiamide under pressure, condenses with formalin to give melamine - formaldehyde polymers (*Beetle - Melamine*), which have similar uses, but better stability to heat

and light, to urea‑formaldehyde plastics. The polymerisation probably proceeds through the intermediate hexamethylol‑melamine :

Dicyandiamide

Melamine

Hexamethylol‑melamine
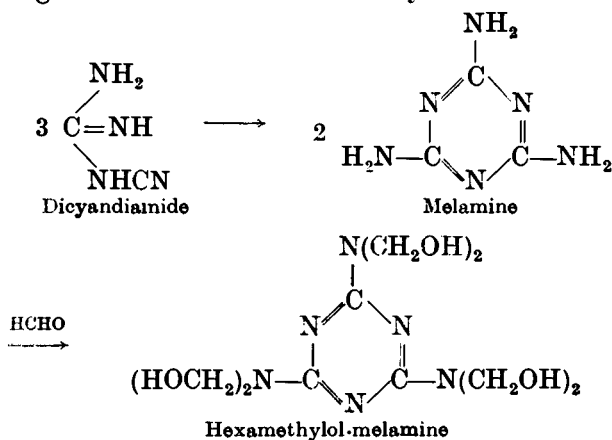
Polyesters from polybasic acids and polyhydric alcohols. Alkyd resins.

The condensation of polyhydric alcohols and polybasic acids or anhydrides leads to polyesters known as *alkyd resins*. The most common member of the group is a glycerol‑phthalic acid polymer, and this has led to the term *glyptal resins* being frequently applied to the whole group.

By controlling the relative amounts of, for example, glycerol and phthalic anhydride and the experimental conditions of the reaction, various polymers of different properties are obtained. Under mild conditions (*ca.* 150°) only the primary alcohol groups are esterified and the secondary alcohol group remains free. The structural unit of the resulting linear polymer is :

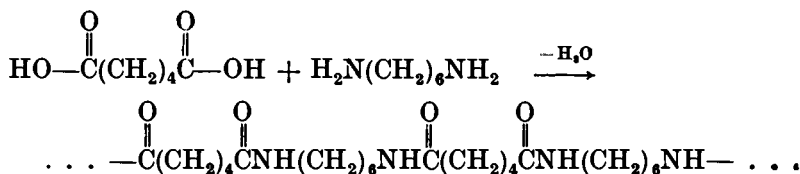$$-CO-C_6H_4-CO-O-CH_2-CHOH-CH_2-OOC-C_6H_4-CO-$$

These are comparatively soft materials and they are soluble in a number of organic solvents. Under more drastic conditions (200–220°) and with a larger proportion of phthalic anhydride, the secondary alcohol groups are esterified and the simple chains become cross-linked ; three dimensional molecules of much higher molecular weight are formed :
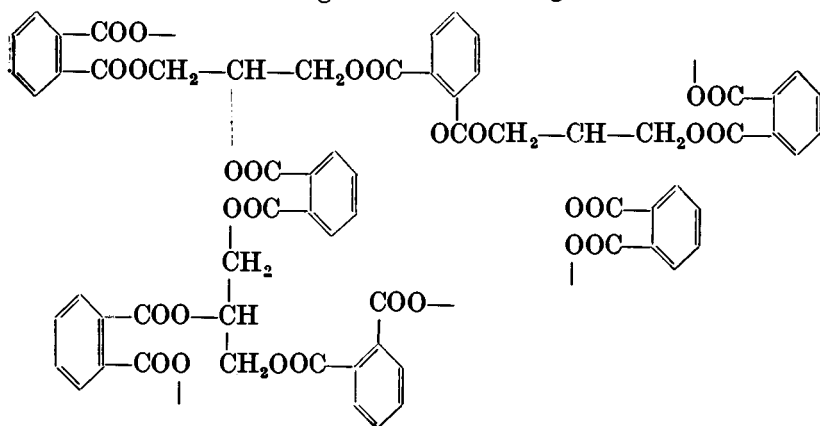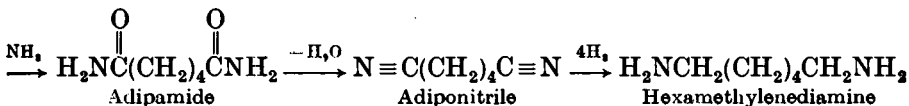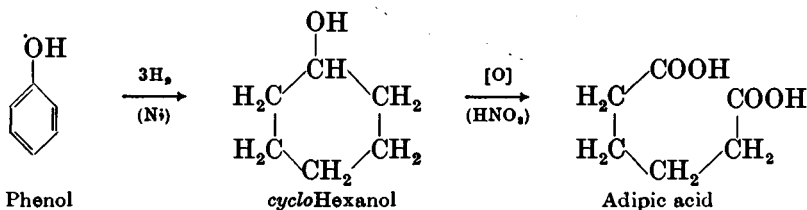
These are relatively infusible, brittle materials that are insoluble in most solvents.

The properties of the polymers may be modified by mixing aliphatic acids or anhydrides with the phthalic anhydride. Many alkyd resins find application in the paint industry.

Polyamides from diamines and dibasic acids. The polyamides formed from aliphatic diamines (ethylene- to decamethylene-diamine) and aliphatic dibasic acids (oxalic to sebacic acid) possess the unusual property of forming strong fibres. By suitable treatment, the fibres may be obtained quite elastic and tough, and retain a high wet strength. These properties render them important from the commercial point of view ; polyamides of this type are called " *nylons* ". The *Nylon* of commerce (a '66' Nylon, named after number of carbon atoms in the two components) is prepared by heating adipic acid and hexamethylenediamine in an autoclave :

$$\text{HO—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{(CH}_2\text{)}_4\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—OH} + \text{H}_2\text{N(CH}_2\text{)}_6\text{NH}_2 \xrightarrow{-\text{H}_2\text{O}}$$

$$\ldots \text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{(CH}_2\text{)}_4\overset{\overset{\text{O}}{\|}}{\text{C}}\text{NH(CH}_2\text{)}_6\text{NH}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{(CH}_2\text{)}_4\overset{\overset{\text{O}}{\|}}{\text{C}}\text{NH(CH}_2\text{)}_6\text{NH—} \ldots$$

The components for *Nylon* are readily produced by the following reactions:

Phenol   cycloHexanol   Adipic acid

$$\xrightarrow{\text{NH}_3} \text{H}_2\text{N}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{(CH}_2\text{)}_4\overset{\overset{\text{O}}{\|}}{\text{C}}\text{NH}_2 \xrightarrow{-\text{H}_2\text{O}} \text{N}\equiv\text{C(CH}_2\text{)}_4\text{C}\equiv\text{N} \xrightarrow{4\text{H}_2} \text{H}_2\text{NCH}_2\text{(CH}_2\text{)}_4\text{CH}_2\text{NH}_2$$

Adipamide   Adiponitrile   Hexamethylenediamine

Polyesters from diols and dicarboxylic acids (polyester fibres). Polymerisation of a diol with a dicarboxylic acid is exemplified by the production of a polyester from ethylene glycol and terephthalic acid either by direct esterification or by a catalysed ester-interchange reaction. The resulting polyester (*Terylene*) is used for the manufacture of fibres and fabrics, and has high tensile strength and resiliency ; its structure is probably :

$$\text{—[OCH}_2\text{CH}_2\text{O—OCC}_6\text{H}_4\text{CO]}_n\text{—}$$
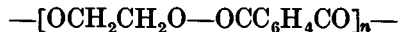
Ion-exchange resins. The constituent phenolic hydroxyl groups in the insoluble phenol-formaldehyde resins react with cations of salts :

$$\text{—OH} + \text{NaCl} \longrightarrow \text{—ONa} + \text{HCl}$$
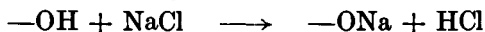
This is the basis of their use as ion exchange resins. The resin can be regenerated by treatment with dilute acids. Further developments have

utilised synthetic resins capable of cation exchange by virtue of the presence of the groups —SO_3H, —COOH and —CH_2COOH.

Anion-exchange resins contain a basic radical, such as —NH_2 and $=NH$, and are prepared by the condensation of formaldehyde with amines such as *m*-phenylenediamine and urea. These resins can absorb acids by the formation of salts, —NH_3Cl and $=NH_2Cl$, and are regenerated by treatment with sodium hydroxide or sodium carbonate.

The exchange resins find application in (i) the purification of water (cation-exchange resin to remove salts, followed by anion-exchange resin to remove free mineral acids and carbonic acid), (ii) removal of inorganic impurities from organic substances, (iii) in the partial separation of amino acids, and (iv) as catalysts in organic reactions (*e.g.*, esterification, Section III,102, and cyanoethylation, Section VI,22).

Organosilicon polymers. Silicon resembles carbon in certain respects and attempts have been made to prepare polymers combining carbon and silicon units in the molecule with the object of increasing the heat resistance of polymers. It has been found that the hydrolysis of a dialkyl-dichlorosilicane or an alkyltrichlorosilicane, or a mixture of the two, leads to polymers (*Silicones*), both solid and liquid, which possess great thermal stability. Thus dimethyldichlorosilicane (I) is rapidly converted by water into the silicol (II), which immediately loses water to give a silicone oil of the type (III):

$$Me_2SiCl_2 \text{ (I)} \rightarrow Me_2Si(OH)_2 \text{ (II)} \rightarrow HO.SiMe_2.[OSiMe_2]_n.O.SiMe_2OH \text{ (III)}$$
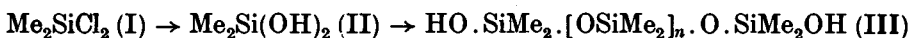
Hydrolysis of mixtures of dialkyldichlorosilicanes and alkyltrichlorosilicanes leads *inter alia* to cross-linked silicones of the type:

$$
\begin{array}{c}
-R_2Si-O-RSi-O-R_2Si-O- \\
| \\
O \\
| \\
-R_2Si-O-RSi-O-RSi-O- \\
| \\
O \\
|
\end{array}
$$
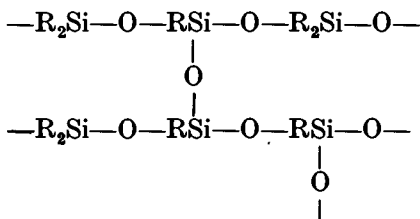
In addition to the above, cyclic polymers, *e.g.* $(R_2SiO)_n$, and also three-dimensional polymers can be formed. The exact nature of the polymer (its structure, and whether it is liquid or solid at room temperatures) will depend upon the substituted chloroalkyl-(or aryl-)silicane, or mixture of substituted silicanes, used and upon the experimental conditions.

The silicone oils and silicone resins find application as (i) lubricants (their change of viscosity with temperature is small), (ii) hydraulic fluids (they are unusually compressible), (iii) dielectric fluids, (iv) for the production of water-repellant surfaces, and (v) in the electrical industry (because of their high insulating properties).

The intermediates may be produced from silicon tetrachloride by interaction with the appropriate Grignard reagent, the composition of the product depending upon the proportions of the reactants:

$$SiCl_4 \xrightarrow{RMgX} RSiCl_3 \xrightarrow{RMgX} R_2SiCl_2 \xrightarrow{RMgX} R_3SiCl$$
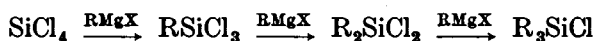
The alkyl- or aryl-halogenosilanes are prepared commercially by passing the vapour of an alkyl or an aryl halide over a heated intimate mixture of powdered silicon and either copper or silver.

Polysulphide rubbers. Ethylene dichloride and excess of sodium tetrasulphide when heated together give a polymeric polysulphide, *Thiokol A*, with properties resembling those of rubber :
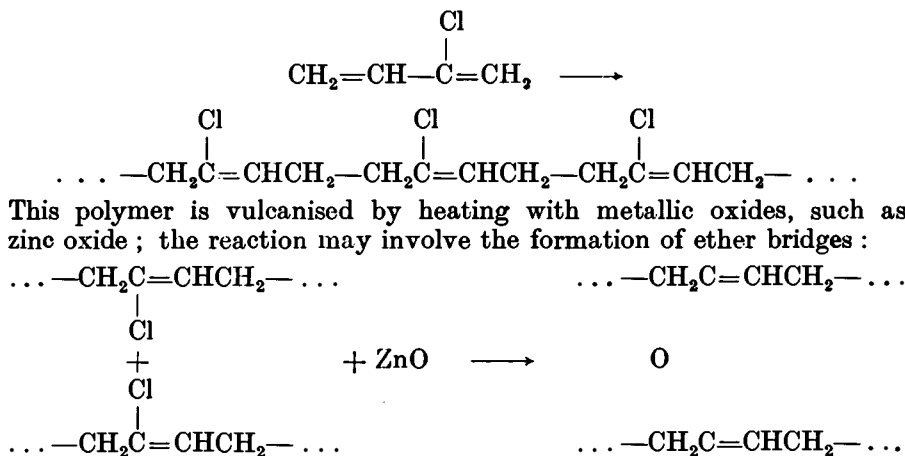
$$ClCH_2CH_2Cl + Na_4S_4 \longrightarrow -\left[CH_2-CH_2-\overset{\downarrow}{S}-\overset{\downarrow}{S} \atop \qquad\qquad S \quad S \right]_n-$$
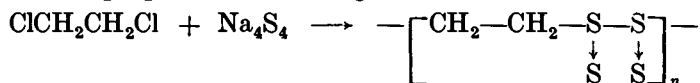
Other polysulphide rubbers are obtained by the use of

ββ'-dichloroethyl ether $O(CH_2CH_2Cl)_2$ (*Thiokol B*),
and glycerol αγ-dichlorohydrin $ClCH_2CH(OH) CH_2Cl$ (*Vulcaplas*).

It is of interest to note that **synthetic rubbers** are produced by the polymerisation of dienes and are therefore examples of additive polymerisation. Thus :
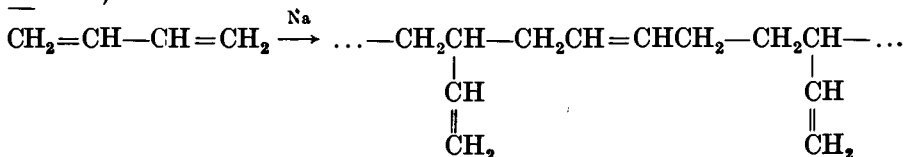
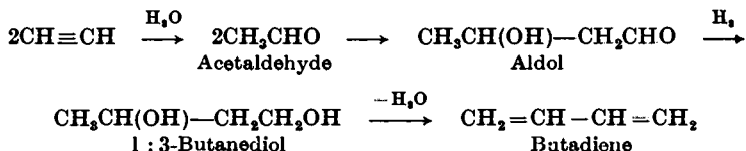(i) **Polychloroprene** (*Neoprene*) is formed from chloroprene or 2-chlorobutadiene :

$$CH_2=CH-\overset{\overset{\displaystyle Cl}{|}}{C}=CH_2 \longrightarrow$$

$$\ldots -CH_2\overset{\overset{\displaystyle Cl}{|}}{C}=CHCH_2-CH_2\overset{\overset{\displaystyle Cl}{|}}{C}=CHCH_2-CH_2\overset{\overset{\displaystyle Cl}{|}}{C}=CHCH_2- \ldots$$

This polymer is vulcanised by heating with metallic oxides, such as zinc oxide ; the reaction may involve the formation of ether bridges :

$$\ldots -CH_2\underset{\underset{\displaystyle Cl}{|}}{C}=CHCH_2- \ldots \qquad\qquad \ldots -CH_2C=CHCH_2- \ldots$$
$$+ \qquad\qquad\qquad + ZnO \longrightarrow \qquad\qquad O$$
$$\ldots -CH_2\overset{\overset{\displaystyle Cl}{|}}{C}=CHCH_2- \ldots \qquad\qquad \ldots -CH_2C=CHCH_2- \ldots$$

2-Chlorobutadiene is prepared commercially by the following reactions :

$$CH{\equiv}CH + CH{\equiv}CH \xrightarrow[\text{(Catalyst)}]{\text{CuCl, NH}_4\text{Cl. aq.}} CH_2=CH-C{\equiv}CH \xrightarrow[\text{(1 : 4-addition)}]{\text{HCl}} \underset{\text{Vinylacetylene}}{}$$

$$\underset{\text{}}{CH_2-CH=C=CH_2} \xrightarrow{\text{Isomerisation}} CH_2=CH-\overset{\overset{\displaystyle Cl}{|}}{C}=CH_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad \text{Chloroprene}$$
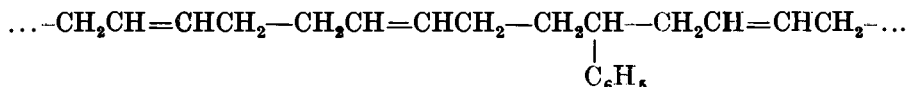
(with the left structure bearing Cl on the first carbon)
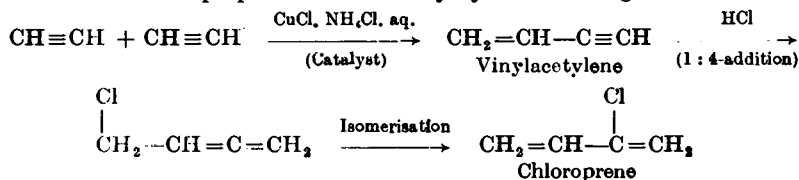
(ii) **Polybutadiene** (*Buna*) is produced by the polymerisation of butadiene in the presence of sodium (the name *Buna* is derived from butadiene - natrium) :

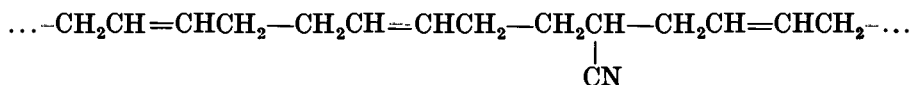$$CH_2=CH-CH=CH_2 \xrightarrow{Na} \ldots -CH_2CH-CH_2CH=CHCH_2-CH_2CH- \ldots$$
$$\qquad\qquad\qquad\qquad\qquad \overset{|}{\underset{\underset{\displaystyle CH_2}{\|}}{CH}} \qquad\qquad\qquad\qquad \overset{|}{\underset{\underset{\displaystyle CH_2}{\|}}{CH}}$$

The following scheme indicates one commercial method for the production of *butadiene* :

$$2CH\equiv CH \xrightarrow{\text{H}_2\text{O}} 2CH_3CHO \longrightarrow CH_3CH(OH)\!-\!CH_2CHO \xrightarrow{\text{H}_2}$$
$$\qquad\qquad\qquad\qquad\text{Acetaldehyde} \qquad\qquad\qquad \text{Aldol}$$

$$CH_3CH(OH)\!-\!CH_2CH_2OH \xrightarrow{-\text{H}_2\text{O}} CH_2\!=\!CH\!-\!CH\!=\!CH_2$$
$$\qquad\text{1 : 3-Butanediol} \qquad\qquad\qquad\qquad \text{Butadiene}$$

By polymerising an emulsified mixture of butadiene and styrene (*ca.* 25 per cent.) *Buna S or GBS rubber* is produced :

$$\ldots\!-\!CH_2CH\!=\!CHCH_2\!-\!CH_2CH\!=\!CHCH_2\!-\!CH_2CH\!-\!CH_2CH\!=\!CHCH_2\!-\ldots$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad C_6H_5$$

Copolymers of butadiene and acrylonitrile $(CH_2\!=\!CH\!-\!C\equiv N)$ are termed *Perbunan, Hycar, Ameripol* and *Chemigum* :
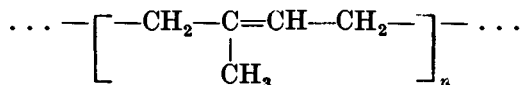
$$\ldots\!-\!CH_2CH\!=\!CHCH_2\!-\!CH_2CH\!=\!CHCH_2\!-\!CH_2CH\!-\!CH_2CH\!=\!CHCH_2\!-\ldots$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad CN$$

Acrylonitrile is prepared from ethylene chlorohydrin :

$$HOCH_2\!-\!CH_2Cl \xrightarrow{\text{NaCN}} CH_2\!=\!CH\!-\!C\equiv N$$
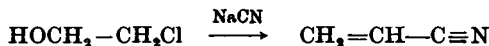
or from acetylene and hydrogen cyanide

$$HC\equiv CH + HC\equiv N \xrightarrow{\text{Catalyst}} H_2C\!=\!CH\!-\!C\equiv N$$

Mention may here be made of the fact that **natural unvulcanised rubber** is poly-isoprene (2-methylbutadiene) :

$$\ldots - \left[-CH_2 - \underset{\underset{\displaystyle CH_3}{|}}{C} = CH - CH_2 - \right] - \ldots _n$$

The preparation of synthetic polymers is hardly suitable for the ordinary organic laboratory. However, a few simple demonstration experiments are described below which, it is hoped, will provide an elementary introduction to the subject.

X,2.   PHENOL-FORMALDEHYDE RESIN

The formation of various types of phenol - formaldehyde resins (the so-called *Bakelite*) may be demonstrated by the following experiments.

1. In a 500 ml. conical flask place 50 ml. of glacial acetic acid, 25 ml. of 40 per cent. formaldehyde solution (formalin) and 20 g. of phenol. Wrap a cloth or towel loosely around the neck and opening of the flask. Pass dry hydrogen chloride gas (Section II,48,*1*) into the mixture. Within 5 minutes, a large mass of pink plastic is formed ; the reaction is sometimes very vigorous. The yield is 36 g. It is frequently necessary to break the flask in order to remove the product completely : for this reason a beaker, or metal flask or beaker, is preferable.

2. Place a mixture of 25 g. of phenol, 50 ml. of formalin and 3 ml. of 40 per cent. sodium hydroxide solution in a 500 ml. conical flask. Attach a reflux condenser to the flask and reflux gently. As the heating proceeds, the mixture acquires a red coloration and becomes increasingly more viscous. After 60–75 minutes the contents of the flask are so viscous that the bubbles which rise through the mass encounter great difficulty in escaping from the surface. At this point remove the flame and immediately pour the viscous mass into a wide test-tube (" boiling tube ") ; upon cooling, an opaque white solid is obtained. (Immediately clean the reaction flask with 40 per cent. sodium hydroxide solution : if it is allowed to stand, the hardened product lining the flask is difficult to remove.) To complete the preparation, place the " boiling tube " in an air oven for 1 hour at 50° and for 4 hours at 60–75° ; when the " baking " process is complete, a hard pink mass of plastic is obtained.

3. In a wide-mouthed test-tube (" boiling tube ") place 5 g. of phenol, 15 ml. of 40 per cent. formaldehyde solution and 3 ml. of concentrated ammonia solution (sp. gr. $0 \cdot 88$). Warm the mixture with a small flame until it becomes opaque. Cool, discard the aqueous layer, but retain the viscous material in the tube. Heat the latter in a water bath at 60° for 30 minutes and then heat the pasty mass in an air oven at 75° for 4–6 hours. A hard solid resin is produced.

X,3.   DEPOLYMERISATION OF METHYL METHACRYLATE RESIN

Place 25 g. of methyl methacrylate polymer (G.B. *Diakon* (powder), *Perspex* (sheet) ; U.S.A. *Lucite, Plexiglass*) in a 100 ml. Claisen flask, attach an efficient condenser (*e.g.*, of the double surface type) and distil with a small luminous flame ; move the flame to and fro around the sides of the flask. At about 300° the polymer softens and undergoes rapid depolymerisation to the monomer, methyl methacrylate, which distils over into the receiver. Continue the distillation until only a small black residue (3–4 g.) remains. Redistil the liquid ; it passes over at 100–110°, mainly at 100–102°. The yield of methyl methacrylate (monomer) is 20 g. If the monomer is to be kept for any period, add $0 \cdot 1$ g. of hydroquinone to act as a stabiliser or inhibitor of polymerisation.

POLYMERISATION OF METHYL METHACRYLATE

Place 10 g. of liquid methyl methacrylate in a test-tube, add 10–20 mg. of benzoyl peroxide (Section IV,196), stopper the test-tube loosely and heat in a boiling water bath. After 20–25 minutes, the liquid suddenly becomes very viscous and soon sets to a hard, colourless mass of the polymer.

X,4.   FORMATION OF A GLYPTAL RESIN

In a 250 ml. beaker place 15 g. of powdered phthalic anhydride and 10 g. of glycerol ; mix thoroughly with a thermometer. Heat the mixture gently to 150–180° on a wire gauze : water vapour is evolved.

Raise the temperature gradually to 200–250° until the mass finally forms large bubbles and puffs up into a voluminous mass. At this point allow the beaker to cool. Remove the brittle mass from the beaker as completely as possible and powder it in a mortar.

Note.

·The solid polymer tends to stick to glass ; for this reason, it is preferable to employ a metal beaker for the experiment.

X,5.   THIOKOL A (POLYETHYLENE POLYSULPHIDE)

Prepare a saturated solution of sodium sulphide, preferably from the fused technical sodium polysulphide, and saturate it with sulphur ; the sulphur content should approximate to that of sodium tetrasulphide. To 50 ml. of the saturated sodium tetrasulphide solution contained in a 500 ml. round-bottomed flask provided with a reflux condenser, add 12·5 ml. of ethylene dichloride, followed by 1 g. of magnesium oxide to act as catalyst. Heat the mixture until the ethylene dichloride commences to reflux and remove the flame. An exothermic reaction sets in and small particles of *Thiokol* are formed at the interface between the tetrasulphide solution and the ethylene chloride ; these float to the surface, agglomerate, and then sink to the bottom of the flask. Decant the liquid, and wash the solid several times with water. Remove the *Thiokol* with forceps or tongs and test its rubber-like properties (stretching, etc.).

X,6.   PHENYLETHYLENE (STYRENE)

Styrene may be conveniently prepared in the laboratory by heating β-phenylethyl alcohol (Section IV,204) with solid sodium or potassium hydroxide when an almost quantitative dehydration occurs :

$$C_6H_5CH_2CH_2OH \xrightarrow{\text{NaOH}} C_6H_5CH=CH_2 + H_2O$$
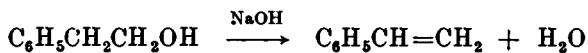
In a 250 ml. distilling flask (1) place 122 g. (119 ml.) of β-phenylethyl alcohol and 40 g. of sodium hydroxide pellets (or 56 g. of potassium hydroxide). Heat is evolved. Warm gently until bubbles commence to form and the mixture separates into two sharply-defined layers. Distil slowly ; water, *etc.* passes over first accompanied by the gradual disappearance of the upper phase. Finally the styrene passes over at 140–160° (mainly 150°) ; collect this separately in a receiver containing about 0·1 g. of hydroquinone. Dry the distillate with a little anhydrous calcium chloride or magnesium sulphate, and then distil under reduced pressure (2). Collect the pure styrene at 42–43°/18 mm. The yield is 80 g. Add about 0·2 g. of hydroquinone (anti-oxidant) if it is desired to keep the phenylethylene.

Notes.

(1) Fused alkalis attack glass ; if several preparations are to be carried out, a copper flask should be used.

(2) Phenylethylene boils at 145–146° at atmospheric pressure, but the high temperature causes a considerable loss by polymerisation. It has been stated that the addition of about 0·1 per cent. by weight of hydroquinone considerably reduces the extent of polymerisation at atmospheric pressure.

X,7.　　　　　　　　　POLYSTYRENE

Heat 20 g. of styrene (Section IX,6) with 0·2 g. of benzoyl peroxide (Section IV,196) on a water bath for 60–90 minutes. A glass-like polymer (polystyrene) is produced. The polymer is soluble in benzene and in dioxan and can be precipitated from its solution by alcohol.

Note.

Great care should be taken in conducting the polymerisation as the reaction may become extremely violent.

X,8.　　ETHYLENEDIAMINE—ADIPIC ACID POLYMER

This is an example of a polymer of the " nylon " type.

Add 40 ml. of ethyl alcohol to 21·5 g. of 70 per cent. ethylenediamine solution (0·25 mol) ; dissolve 36·5 g. of adipic acid (0·25 mol) in 50 ml. of a 6 : 1 mixture of ethyl alcohol and water. Mix the two solutions, stir and cool. Filter off the resulting salt and recrystallise it from 60 ml. of a 6 : 1 ethyl alcohol - water mixture, and dry the salt in the air. Heat the salt in an atmosphere of oxygen-free nitrogen or of carbon dioxide in an oil bath until it melts (ca. 160°) ; the product will solidify after a short time. Reduce the pressure to 15 mm. of mercury or less and raise the temperature of the oil bath until the product remelts (about 290°) and continue the heating for 4–5 hours. Upon cooling, a " nylon " type polymer is obtained.

X,9.　　DEPOLYMERISATION OF A HEXAMETHYLENE-DIAMINE - ADIPIC ACID POLYMER (*NYLON* '66')

Add 10 ml. of concentrated sulphuric acid cautiously to 45 ml. of water contained in a 200 ml. round-bottomed flask, introduce 3 g. of *Nylon* '66' polymer* into the hot solution, and heat under reflux for 6 hours. Allow to stand for 1 hour and cool in ice for a further hour. Filter off the solid and keep the filtrate. Recrystallise the solid (adipic acid) from water m.p. 152°.

Neutralise about one third of the filtrate with 5N sodium hydroxide and add a further 2 ml. of the alkali solution. Add 1 ml. of benzoyl chloride and stir until the odour of the acid chloride disappears. Collect the solid by suction filtration, wash it with water until free from alkali, and then recrystallise it from dilute alcohol. The product is the dibenzoyl derivative of hexamethylenediamine and melts at 159°.

* The '66' polymer refers to the number of carbon atoms in each of the components. I.C.I. "Maranyl" Nylon compound A100 may be used.