TEMPLATE POLYMERIZATION

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ChemTec Publishing

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ISBN 1-895198-15-1

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Printed in Canada

ChemTec Publishing
38 Earswick Drive
Toronto-Scarborough
Ontario M1E 1C6
Canada

Canadian Cataloguing in Publication Data

Polowinski, Stefan
Template polymerization

Includes bibliographical references and index.
ISBN 1-895198-15-1

1. Polymerization. 2. Biochemical templates
I. Title

QD381.P64 1997 547'.28 C96-900763-9

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INTRODUCTION

Template or matrix polymerization can be defined as a method of polymer synthesis in which specific interactions between preformed macromolecule (template) and a growing chain are utilized. These interactions affect structure of the polymerization product (daughter polymer) and the kinetics of the process.[1] The term "template polymerization" usually refers to one phase systems in which monomer, template, and the reaction product are soluble in the same solvent.

The growth of living organisms is associated with very complicated processes of polymerization. Low molecular weight substrates, such as sugars, amino acids, fats, and water in animals and carbon dioxide in plants are precursors of polymers (polypeptides, polynucleic acids, polysaccharides, etc.). They are organized in tissues and can be reproduced. In many biological reactions such as DNA replication or polypeptide creation, low molecular weight substrates and polymeric products are present in the reaction medium together with the macromolecular compounds called matrices or templates controlling the process. In this book, the synthesis of polypeptides or polynucleic acids is not considered in detail. A very broad literature already exists in this field.[2,3] However, it is difficult to avoid some analogies between natural biological processes and template polymerization of simple synthetic polymers or copolymers, especially that some findings are applicable to both fields. Some methods of polypeptide synthesis *in vitro* include aspects of template-type interaction, for instance in enzymatic polypeptide synthesis.[3]

During the basic step of peptide formation, two or more reacting components are pre-bonded by the enzyme molecule. A simple model of such reaction can be represented by the diagram in Figure 1.1.

This simple scheme can help us to understand unusual selectivity and high efficiency of such template reactions. The specific character of the enzyme effectiveness towards a particular substrate becomes obvious. The effect of macromolecular template on the reaction rate and particularly on its selectivity suggests that this type of reaction can be regarded as a catalyzed reaction. The template plays a role of a polymeric catalyst.[1] On the other hand, the template polymerization is a particular case of a more general group of processes such as polymerization in organized systems.[4] Many factors may affect organization of monomer units during polymerization. For example, polymerization in solid state proceeds with molecules of monomer surrounded by molecules already organized in a crystal lattice.

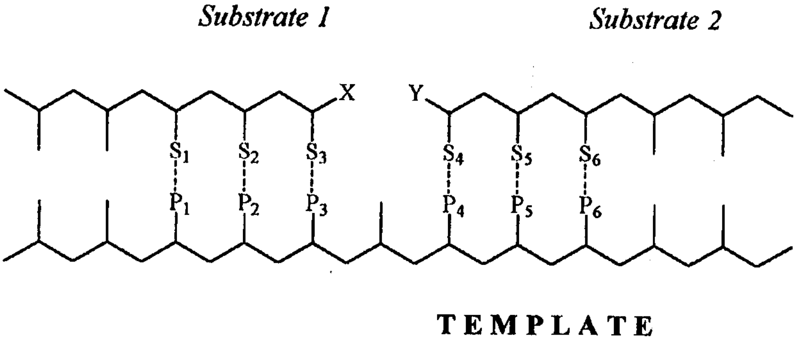

Figure 1.1. Simplified model of enzymatic polypeptide synthesis. X and Y are reacting groups and S_1.... P_1, S_2 ....P_2, etc. alate-substrate. By the selective sorption, the substrate 1 is connected with a specific part of the template (possessing specific sequence of interacting groups P_1, P_2, P_3). The second substrate is adsorbed by another part (with sequence of interacting groups P_4, P_5, P_6). As a consequence of the selective sorption, the reacting groups X and Y are brought closer together and reaction between X and Y is promoted.

A specific type of polymerization occurs on the surface of solids. Numerous monomers with long hydrocarbon chains can form monolayers at the gas-water interface and these are oriented on the surface of water. Polymerization of systems having such an organization leads to the preparation of polymers with peculiar morphology and properties. This is the method of polymer synthesis in ultra-thin films of different forms. For instance, this method is used to produce polymeric microspheres containing drugs. Polymerization in the presence of clays and other minerals was considered to occur on earth before life begun. Montmorillonite was used for polymerization of amino-acid derivatives. Montmorillonite can bind proteins so strongly that they cannot be removed without being destroyed. A polymerization in liquid crystalline state is another example of polymerization in organized system.

In this book the term matrix or template polymerization is used only to one-phase systems.

To study template systems it is important to compare the template process and products of the reaction with conventional polymerization carried out under the same conditions. It is typical to replace template by a low molecular non-polymerizable analogue. The influences of the template on the process and the product are usually called "template effect" or "chain effect".[5,6]

The template effects can be expressed as:

- kinetic effect - usually an enhancement of the reaction rate, change in kinetic equation
- molecular effect - influence on the molecular weight and molecular weight distribution. In the ideal case, the degree of polymerization of daughter polymer is the same as the degree of polymerization of the template used. We can call this case a replication.
- effect on tacticity - the daughter polymer can have the structure complementary to the structure of the template used.
- in the case of template copolymerization, the template effect deals with the sequence distribution of units. This effect is very important in biological synthesis, for instance in the DNA replication.

The template processes can be realized as template polycondensation, polyaddition, ring-opening polymerization, and ionic or radical polymerization.[7,8] These types of template polymerization are fundamentally treated in the separate chapters below.

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GENERAL MECHANISM OF TEMPLATE POLYMERIZATION

It is widely acknowledged that polymerization can proceed according two general mechanisms of reaction: step polymerization and chain polymerization. These two mechanisms are quite different and consequently their kinetics, molecular weight distribution, influence of reaction parameters on the process, etc., are very different in both cases. For the same reasons, the template reactions differ, depending on their mechanisms of the polymerization processes.

Division of all processes leading to the polymer synthesis into the above classes is a simplification - convenient to present general mechanisms of template polymerization.

2.1 TEMPLATE POLYCONDENSATION

Template polycondensation or, more generally speaking, template step polyreaction, is seemingly the most similar to natural synthesis of polypeptides or polynucleotides which occurs in living organisms. Using simple models as macromolecular templates, we can better understand the specificity of natural processes of biopolymer synthesis. It is worth considering the similarities and the differences between natural and simple template polymerization which can be illustrated by the diagram in Figure 2.1.

The synthesis of a new DNA molecule proceeds from the defined point which is designated on the diagram by “G” (replication origin). New DNA molecule grows in the direction of the lower arrow to the so-called leading strand. The second part of single chain of DNA molecule serves also as the template (lagging strand) for the synthesis of shorter fragments of polynucleotides. The synthesis proceeds in the direction indicated by the upper arrow. Even, if we do not consider the complicated mechanism, which contributes monomeric units to the growing center “G”, and the effect of helix structure of the template, we can see that this mechanism is rather far from a simple polycondensation. The natural process begins at a defined point of macromolecular template (for instance, DNA replication). The specific geometric surrounding around a growing center “G” is created by decomposition of a double helix of DNA molecule.

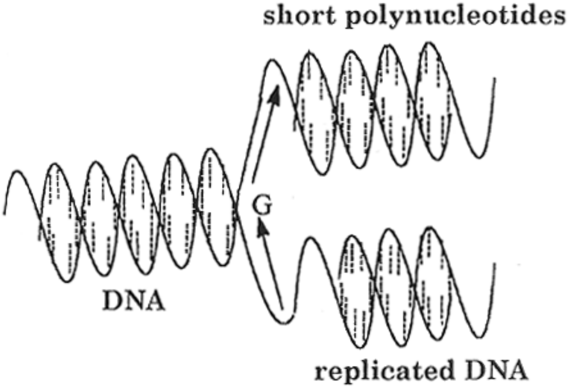


Figure 2.1 Simplified diagram of self-replication of DNA.

Because template polycondensation is not very well studied at present,[1-10] general mechanism is difficult to present. Two main types of polycondensation are well known in the case of conventional polycondensation. They are heteropolycondensation and homopolycondensation. In the heteropolycondensation two different monomers take part in the reaction (e.g., dicarboxylic acid and diamine). In the case of homopolycondensation, one type of monomer molecule is present in the reacting system (e.g., aminoacid). The results published[1] on the template heteropolycondensation indicate that monomer (dicarboxylic acid) is incorporated into a structure of the matrix (prepared from N-phosphonium salt of poly-4-vinyl pyridine) and then the second monomer (diamine) can react with so activated molecules of the first monomer. The mechanism can be represented as in Figure 2.2.

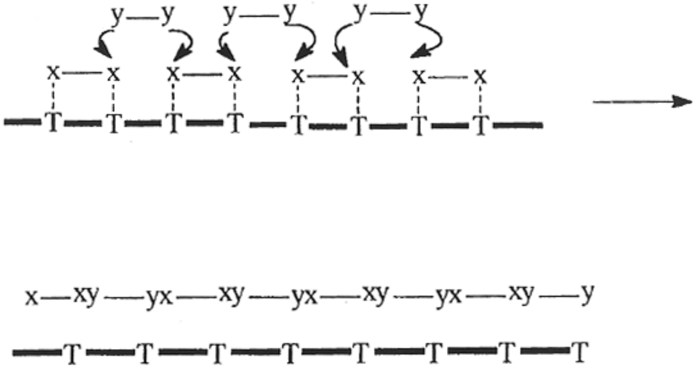


Figure 2.2. Template heteropolycondensation.

In this case one monomer with groups x (e.g., COOH) can be absorbed on the template -T-T-. The second monomer with groups y (e.g., amine) reacts, forming a daughter polymer having groups xy and the template is available for further reaction. Low molecular weight product is not indicated in this scheme.

In another case of template heteropolycondensation two reagents with groups x (e.g., COOH) and y (e.g., amine) can be adsorbed on the template. A hypothetical scheme of this process is represented by the Figure 2.3.

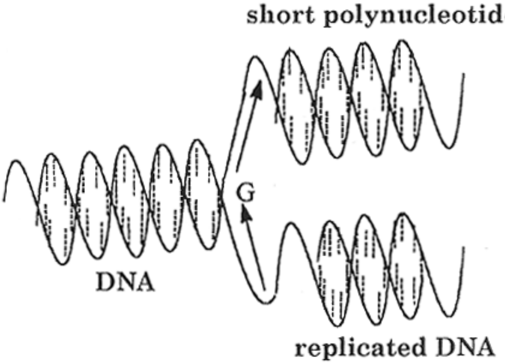


Figure 2.3. Heteropolycondensation with two substrates absorbed on the template.

If groups in monomer molecule, which interact with the matrix, are not located at the ends of the molecule as is the case of dimethyl tartrate and dimethyl muconate,[6,7] we can imagine that ordering of monomer molecules on the template takes place according to the scheme given in Figure 2.4. The mechanism of template homopolycondensation can be represented in Figure 2.5. The monomer molecule has two different reacting groups x and y (e.g., COOH and NH_2 as in aminoacids). One (as shown by the scheme) or both groups can interact with the template. In all cases of template polycondensation, the reaction begins at a randomly selected point of template. Usually a simple linear macromolecule of template interacts from one side without creating a three dimensional growing center. It is very probable that some template irregularities complicate mechanism (Figure 2.6). The same questions regarding mechanism of matrix homopolycondensation are waiting for answer and future studies.

Mathematical description of the polymerization of biological macromolecules on templates, based on simple models, has been published by Simha *et al*.[11] Two types of reaction were discussed. The first type of reaction was initiated by polymerization of two monomers on each template. The reaction proceeded throughout the addition of monomer to the growing ends or by the coupling of the growing chains. In the second type of re-

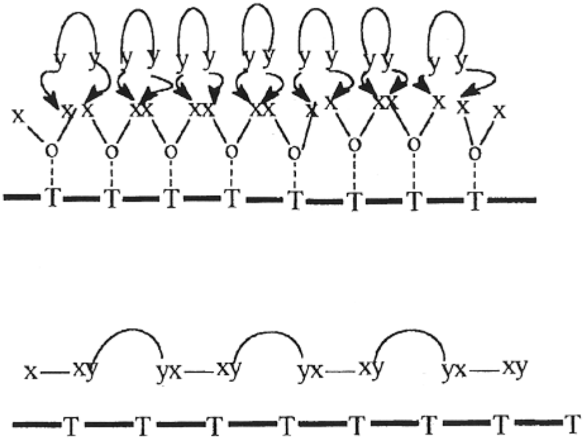


Figure 2.4 Mechanism of template polyheterocondensation in which groups located inside one monomer molecule interact with the template.

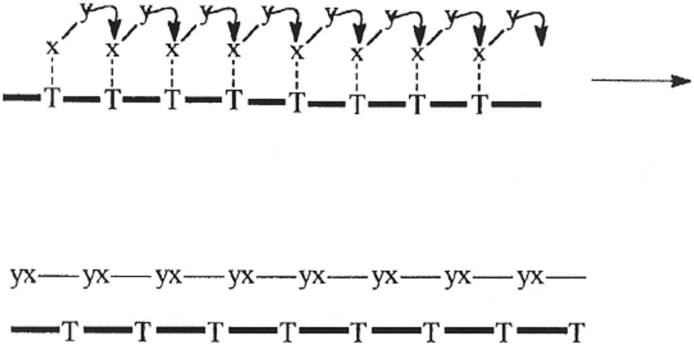


Figure 2.5. Template homopolycondensation.

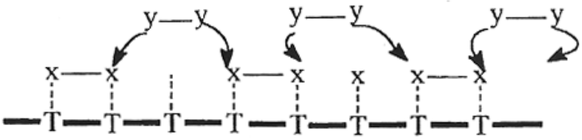


Figure 2.6. Irregular absorption onto the template.

action, the number of growing centers per template was zero or one and growth was achieved through monomer addition only. In both models monomer diffuses to the template surface where polymerization may occur if an adjacent site is suitably occupied. An infinite template length was assumed in both cases. This model is closer to the mechanism of polyaddition than polycondensation. This is not surprising since model was constructed with application to DNA-type synthesis of biopolymers in mind.

Experimental investigation of the kinetics of template step polymerization, determination of average molecular weights of the product, and molecular weight distribution are still available for future studies.

2.2 CHAIN TEMPLATE POLYMERIZATION

The majority of papers published in the field of template polymerization deal with the systems in which both template and monomer are dissolved in a proper solvent and initiation occurs according to the chain mechanism.[12-15] It is generally accepted that, for chain processes, there are at least three elementary processes: initiation, propagation and termination. The mechanism of the addition radical polymerization can be schematically written as follows:

$$\begin{array}{lll} \text{Initiation} & I \rightarrow 2R_p^{\bullet} & R_p^{\bullet} + M \rightarrow M^{\bullet} \\ \text{Propagation} & M_n^{\bullet} + M \rightarrow M_{n+1}^{\bullet} & \\ \text{Termination} & M_n^{\bullet} + M_m^{\bullet} \rightarrow \text{Polymer} & \end{array}$$

where: I - initiator molecule; $R_p^{\bullet}$ - radical from initiator decomposition; $M_n^{\bullet}$ and $M_m^{\bullet}$ - radicals with n and m monomer units, respectively.

In the case of template processes, this mechanism must be completed by terms accounting for interaction between template, monomer, and polymer. This subject is discussed in more detail in Chapter 8. Intermolecular forces lead to absorption of the monomer on the template or, if interaction between monomer and template is too weak, oligoradicals form complexes with the template. Taking into account these differences in interaction, this case of template polymerization can be divided into two types.[12] In Type I, monomer is preadsorbed by, or complexed with, template macromolecules. Initiation, propagation and perhaps mostly termination take place on the template. The mechanism can be represented by the scheme given in Figure 2.7.

On the template unit, -T-, monomer, M, having double bonds is adsorbed. Radical, $R^{\bullet}$, initiates propagation process which proceeds along the template, and eventually a complex of the template and the daughter polymer, consisting M units, is created. In the extreme case of template polymerization, proceeding according to mechanism I, the monomer units are attached to the template by covalent bonding. The substrate of this reaction can be called multimonomer, the product after template polymerization - lad-

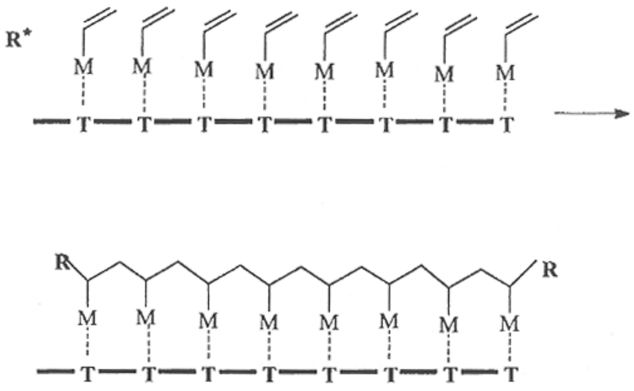


Figure 2.7. Chain template polymerization of Type I.

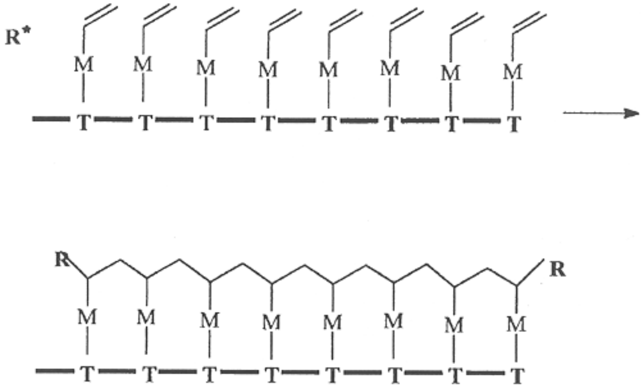


Figure 2.8. Chain polymerization of multimonomer.

der-type polymer. Chain template polymerization of multimonomer, very similar to Figure 2.7, is presented in Figure 2.8.

The only difference between Figures 2.7 and 2.8 is that hydrogen bonding in Figure 2.7 is replaced by covalent bonding between T and M in Figure 2.8 in both the substrate and the product.

In Type II mechanism, the interaction between monomer and template is too weak to form a complex. Initiation begins in a "free" solution. When oligoradicals reach a proper length (critical chain length), the complexation occurs and then oligoradicals continue to propagate along the template by adding monomer molecules from the surrounding solution. The propagation process in the case of Type II template polymerization is shown in Figure 2.9.

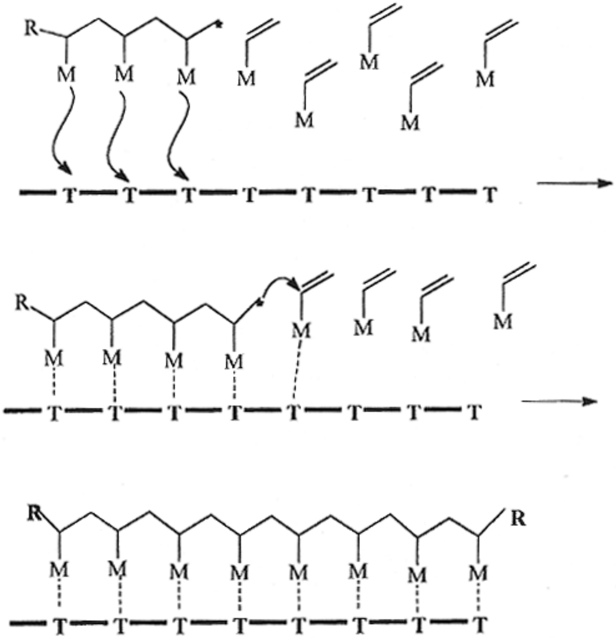


Figure 2.9. Template chain polymerization of Type II.

Termination can be realized both by macroradicals on the template (template-template termination) or by recombination of radicals on the template with macroradicals or oligoradicals not connected with the template (cross-termination). For some systems, it is difficult to decide whether they are type I or type II. The intermediate systems can also exist.

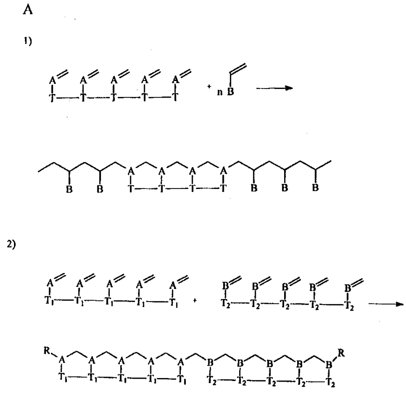
2.3 TEMPLATE COPOLYMERIZATION

The synthesis of biopolymers *in vivo* leads to macromolecules with a defined sequence of units. This effect is very important for living organisms and is different in comparison with random copolymerization in which sequences of units are distributed according to stochastic rules. On the other hand, the predicted sequence of units can be achieved by a set of successive reactions of respective monomer molecule addition. In template copolymerization, the interaction between comonomers and the template could pre-arrange monomer units defining sequence distribution in the macromolecular product.

There is far less information in the scientific literature about template copolymerization than about template homopolymerization. As in the case of template homopolymerization, template copolymerization can be realized according to different types of reaction: stepwise (template polycondensation), copolyaddition, radical or ionic polymerization, ring-opening copolymerization, etc.

Only a few publications have appeared in the literature on template copolycondensation, in spite of the fact, that the process is very important to understand the mechanisms of processes similar to natural synthesis of biopolymers. General mechanism of this reaction can be considered in terms of the examples of template step homopolymerization. A few published systems will be described in the Chapter 5.

Investigation of radical template copolymerization has been slightly more extensive. The classification of template copolymerization systems can be based on the type of interaction between the monomer and the template as was done for homopolymerization. Three basic types of such interactions can be recognized: covalent bonding, strong intermolecular forces, and weak interactions between template and oligomers exceeding the critical length. However, these interactions can vary when two different types of comonomer are used. We may consider the case when one monomer is not interacting with the template at all. From this point of view, the classification of template copolymerization systems is more complex than for homopolymerization.[16] Possible cases of such reactions are presented in Figure 2.10.



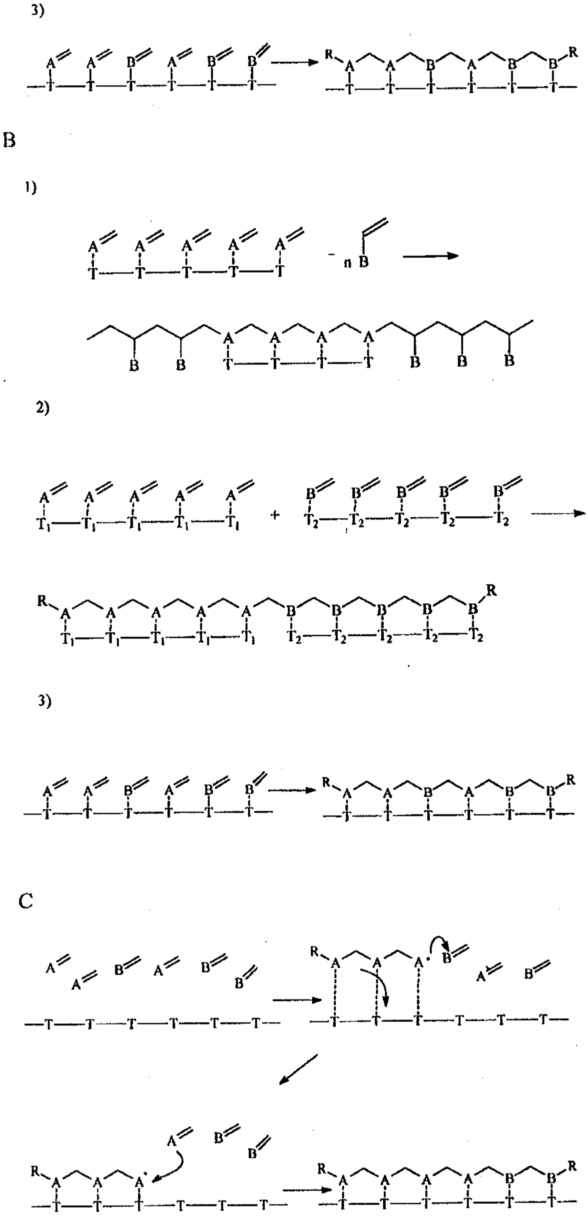


Figure 2.10. Schematic representation of template copolymerization.

Point A deals with the case in which at least one of the comonomers is connected with the template by covalent bonding. In particular: A1 represents the reaction of multimonomer with free monomer B (not connected to the template). One type of units A with double bonds (for instance, acrylic groups) is connected by covalent bonds to the template units, T. As a result of polymerization, a copolymer with ladder blocks is formed.

A2 shows the reaction between two different multimonomers. Two different type of units A and B, containing double bonds, are attached to two different templates. After polymerization, the ladder block copolymer can be formed. However, one cannot exclude formation of a mixture consisting two unconnected ladder homopolymers.

A3 deals with polymerization of multimonomer in which two different types of groups are connected with one template by covalent bonding. In this case, two types of units A and B with double bonds are deposited onto one template. It is worth noticing that the order of units is controlled by process of synthesis of multimonomer, not by copolymerization process, as in conventional copolymerization. Point B deals with the case in which at least one of the comonomers interacts with the template due to strong intermolecular forces. In particular: B1 shows the reaction of one comonomer which is free (i.e., it has no affinity to the template) why the second comonomer A is bound (for instance, hydrogen bonding with the template). B2 represents the reaction of two comonomers adsorbed onto two different templates, B3 shows the reaction of two comonomers connected with the same template.

Point C deals with the case in which interactions between both comonomers and the template are weak and complexation is possible only with oligoradicals. Let us consider this case taking into account the composition of monomers mixture and composition of copolymer created. One or both comonomers can interact weakly with the template. As was the case of Type II template homopolymerization, we can assume that oligomeric radicals are adsorbed by the template and then propagation proceeds, at least partially, in close contact with the template. The cases in which one comonomer or oligomeric radical forms a complex with the template and the other comonomer reveals a weak interaction with the template or is not interacting at all with the template were described.[17] The results of this investigation can be further generalized.

The composition of copolymer and distribution of units in copolymer molecule can be predicted as follows. Let us designate two types of comonomer molecules as A and B; and the respective radicals as $A^{\rceil}$ and $B^{\rceil}$. The symbols with an asterisk deal with the process proceeding on the template. In addition, let us assume that we can neglect the penultimate effect. In this case, the process of propagation is expressed by the following set of reactions and respective rates and rate constants:

$$A\bullet + A = A\bullet \qquad v_{AA} = k_{AA}[A\bullet][A]$$

$$A\bullet^{*} + A = A\bullet^{*} \qquad v_{A^{*}A} = k_{A^{*}A}[A\bullet^{*}][A]$$

$$\begin{array}{ll}
A\bullet + B = B\bullet & v_{AB} = k_{AB}[A\bullet][B] \\
A\bullet^{*} + B = B\bullet^{*} & v_{A^{*}B} = k_{A^{*}B}[A\bullet^{*}][B] \\
B\bullet + A = A\bullet & v_{BA} = k_{BA}[B\bullet^{*}][A] \\
B\bullet^{*} + A = A\bullet^{*} & v_{B^{*}A} = k_{B^{*}A}[B\bullet^{*}][A] \\
B\bullet + B = B\bullet & v_{BB} = k_{BB}[B\bullet][B] \\
B\bullet^{*} + B = B\bullet^{*} & V_{B^{*}B} = k_{B^{*}B}[B\bullet^{*}][B]
\end{array} \qquad [2.1]$$

It was shown that we can define two probabilities P_{AB} and P_{BA}:

$$P_{AB} = 1/(xr_1' + 1); \quad P_{BA} = x/(x + r_2'); \quad [A]/[B] = x \qquad [2.2]$$

where:

$$r'_1 = \frac{k_{AA}[A\bullet] + k_{A^*B}[A\bullet^*]}{k_{AB}[A\bullet] + k_{A^*B}[A\bullet^*]} \qquad [2.3]$$

$$r'_2 = \frac{k_{BB}[B\bullet] + k_{B^*B}[B\bullet^*]}{k_{BA}[B\bullet] + k_{B^*A}[B\bullet^*]}$$

Initial composition of copolymer S can be expressed by S= P_{BA}/P_{AB} which leads to the conventional form of the composition equation:

$$S = x(xr_1' + 1)/(x + r_2') \qquad [2.4]$$

But, in contrast to the conventional Mayo-Levis equation, in this equation $r`_1$ and $r`_2$ depend on the template concentration.

Assuming that the reaction of complex formation is reversible we can write for monomer A:

$$A\bullet + T \leftrightarrow A\bullet^{*} \qquad [2.5]$$

and for monomer B:

$$B\bullet + T \leftrightarrow B\bullet^{*} \qquad [2.6]$$

with equilibrium constants respectively for monomer A:

$$K_A = \frac{[A\bullet *]}{[A\bullet]\,[T]} \qquad [2.7]$$

and for B

$$K_B = \frac{[B\bullet *]}{[B\bullet]\,[T]} \qquad [2.8]$$

We can denote z = $K_A[T]$ and rewrite equation for $r`_1$

$$r_1' = (k_{AA} + z\,k_{A*A}) \big/ (k_{AB} + z\,k_{A*B}) \qquad [2.9]$$

These considerations lead to many important conclusions. If $0 < K_A < \infty$, then $r_1 \neq r_1$. This means that in this case of constant template concentration, [T], $r_1`$ can be computed using conventional procedure (for instance according to Kellen-Tüdös or Fineman-Ross). However, $r_1`$ value depends on the concentration of the template.

If $K_A = \infty$, then $r_1` = k_{A*A}/k_{A*B} = r_{1M}$. It means that propagation of monomer A proceeds only on template and bonds between monomer A and template are very strong. The ratio of rate constants for reactions proceeding along the template can be defined as r_{1M}.

If $K_A = 0$, then $r_1` = k_{AA}/k_{AB} = r_1$. It means that monomer A is not adsorbed by the template and we have the conventional formula for r_1.

Dependence between $r_1`$, r_1, and r_{1M} can be expressed by the equation:

$$r_1' = \alpha r_1 + (1 + \alpha) r_{1M} \qquad [2.10]$$

where:

$$\alpha = 1 \big/ (1 + K_A\,[T] r_{CA}); \quad r_{CA} = k_{A*B} \big/ k_{AB} \qquad [2.11]$$

All these considerations can be repeated for comonomer B.

The conclusion can be drawn that in template copolymerization reactivity ratios depend on the nature and concentration of the template used. Template controls composition and sequence distribution of monomer units in copolymers obtained.

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3

TEMPLATES AND ORIENTATION OF SUBSTRATES ON TEMPLATE

Template polymerization is connected with two similar phenomena: association of monomer units with the template and aggregation of polymerization product with the template. The first phenomenon can be considered in terms of interaction of a macromolecule in a mixed solvent. The system containing monomer, solvent, and template is an initial state of template polymerization. It is well known that two liquids can interact with a macromolecule depending on the forces operating between specific groups (e.g., formation of hydrogen bonds). Composition of solvent in the immediate domain of polymer differs from that in the bulk. This phenomenon can be called preferential solvation or preferential adsorption. Solvation of one solvent through hydrogen bonding with polymer leads to decrease in the concentration of this solvent in the bulk. Stockmayer and Chan[1] described solvation of polymethylene oxide molecules by hexafluoroacetone monohydrate in mixture: hexafluoroacetone/water. Hexafluoroacetone forms with water monohydrate: $(CF_3)_2C(OH)_2$. In the presence of polyoxymethylene, one or both OH groups can be engaged in hydrogen bonding with ether groups. The molecule of hexafluoroacetone can be oriented by a pair of monomer units. Similar orientation can be expected in the case of monomer absorption onto template, for instance, on polyethylene glycol molecules. Specific interaction between protein chain and water in organic solvents was examined in detail by Timasheff and Inoue.[2] The authors constructed a model of protein chain. Depending on the chemical structure of units in the chain, hydrophylic or hydrophobic parts were distinguished. Water adsorption onto these hydrophylic sequences of units caused conformation changes of protein molecule.

A quantitative measure of interaction between polymer and monomer in solution can be expressed by a value of preferential solvation. Preferential solvation can be calculated from the measurements of refractive index increments in dialysis experiments. This experiment can be illustrated as in Figure 3.1.

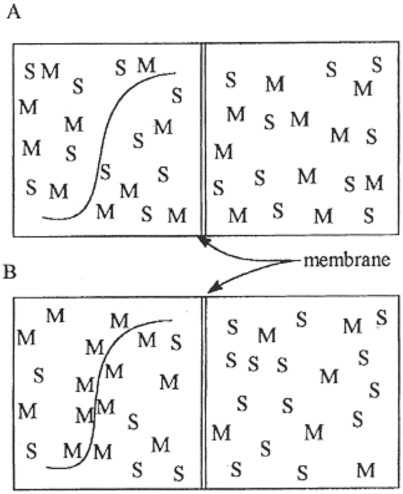


Figure 3.1. Schematic representation of preferential solvation. A - initial state; B - state after equilibrium.

Part A of the scheme represents the initial state. Two parts of the system are separated by semi-permeable membrane. Polymer (represented by ~) is surrounded by molecules of monomer, M, and molecules of solvent, S. Composition of mixed solvent (solvent and monomer) is initially uniform. If the interaction between monomer and polymer is stronger than that between polymer and solvent, the diffusion through the membrane takes place. Monomer molecules are associated with macromolecules while molecules of solvent are displaced to the right part of the vessel.

The state in which the system reached equilibrium is presented in part B of the diagram. The mixture of solvent, S, polymer, P, and monomer, M, has total volume V^0 before mixing and V after mixing. According to Aminabhavi and Munk[3] the value q can be calculated. This value expresses extra weight of monomer per gram of polymer in comparison with the amount in the surrounding solution. The equation below can be used for calculation:

$$q = \frac{V^0}{v_M^0 \Phi_S V} \times \frac{\nu - \nu_\mu}{dn/d\Phi_S} \qquad [3.1]$$

In this formula, ν and ν_μ are the increments of the refractive index for the polymer to the increments measured at constant molarity and at constant chemical potential, respectively. $(dn/d\Phi_S)$ is the refractive index increment of the monomer in pure solvent with volume fraction, Φ_S, and v_M is a volume of the monomer. Assuming that no change in volume occurs when monomer and solvent are mixed and expressing by α the extra volume (in mL) of monomer per gram of the polymer, we can use the simple formula:

$$\alpha = (\nu - \nu_{\mu}) / (dn / d\Phi_S) \qquad [3.2]$$

Interferometric measurements combined with equilibrium dialysis show that many monomers are selectively associated with polymers present in three-component solutions. For instance, for methacrylic acid in DMF in the presence of poly(2-vinylpyridine), it was found[4] that q = 0.4.

The template chain may be regarded as composed of two parts - the first - fully occupied by the monomer units (one monomer unit per one unit of the template) and the second part contains free sites. The friction of occupied sites is θ and that of free sites (1-θ).

Assuming that monomer can be bound by the template in a similar manner as in the adsorption process we can apply Langmuir`s theory to describe this process.

$$\theta = K_L [M_0] / (1 - K_L [M_0]) \qquad [3.3]$$

K_L can be calculated from dialysis experiments. However, it was demonstrated[5] that there is a large error in the calculation of K_L from the refractive index increments.

In the initial stage of template polymerization, one center of adsorption per one template unit can adsorb one monomer molecule. The dynamic equilibrium takes place between partially covered template and free monomer in the surrounding solution.

Equilibrium between monomer, M, and template units, T, can be described by equilibrium constant, K_M:

$$M + T \leftrightarrow MT, \quad K_M = [MT] / [M]\,[T] \qquad [3.4]$$

In solution, however, not only monomer but also some solvent, S, is present. The equilibrium in this case can be expressed by a set of equations:

$$M + T + S \leftrightarrow MT + S, \quad MT + S \leftrightarrow MS + T, \quad MS + T \leftrightarrow M + T + S \qquad [3.5]$$

There is also equilibrium between solvent and the template. The equilibrium constant for solvent K_S can be defined as:

$$S + T \leftrightarrow ST, \quad K_S = [ST] / [S]\,[T] \qquad [3.6]$$

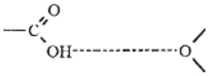
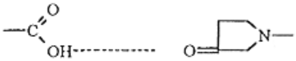
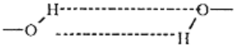
From the equations mentioned above, we have:

$$K_S / K_M = [TS]\,[M] / [MT]\,[S] \qquad [3.7]$$

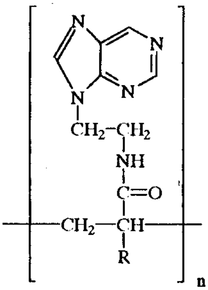
From this equation, it is clear that concentration of the solvent, S, influences a number of sites on the template which are occupied by the monomer, M. As the result of monomer units association with the template, the orientation of the substrate takes place and some special type of structure can be created. The structures, in which the monomer is aligned in a regular manner on the polymer template, were described by Chapiro[6] in the case of polymerization of acrylic acid and acrylonitrile and details are described below. The ordered structure increases concentration of monomer at the reaction site, affects distances between pre-oriented monomer molecules, and changes a steric hindrance. This change in structure leads to the change in the kinetics of the polymerization reaction and it is responsible for stereo-control of the propagation step.

A few examples illustrate the interaction between monomer and template groups and the nature of forces operating in the system template-monomer (Table 3.1).

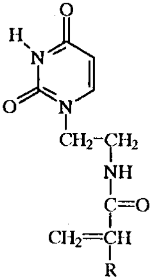
Table 3.1: Examples of interaction between monomer and template

Monomer	Template	Nature of forces
		**Hydrogen bonds**
		**Hydrogen bonds**
		**Hydrogen bonds**
		**Dipole-dipole**
		**Electrostatic**

More complex orientation of monomers on the template was described by Akashi *at al.*[6] in respect to polymerization of vinyl monomers containing nucleic acid bases. In polynucleotides, a specific type of interaction between pendant groups takes place. The interaction between such groups as thymine and adenine is very important in stabilization of double helix structure of polynucleotides such as DNA. A simple functional polymers containing nucleic acid bases can be used as templates for polymerization of monomers containing complementary pendant groups. Polymer containing adenine groups with following structure:



can be used as a template for monomer with pendant uracil groups:



The template polymerization was carried out at 60°C in dimethyl sulfoxide/ethylene glycol mixture using AIBN as radical initiator. It was found that under these conditions interaction between adenine and uracil groups is remarkable.

The template polymerization in the system mentioned was concluded to proceed according to the scheme 3.2, where U and A are uracil and adenine groups, respectively.

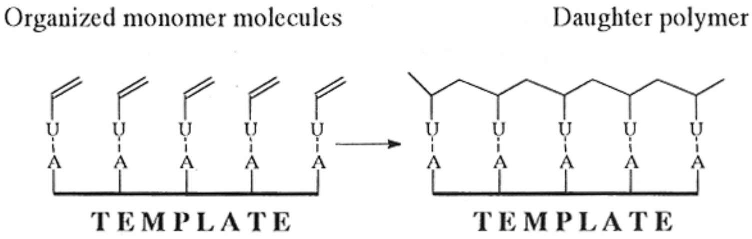


Figure 3.2 Template polymerization of monomer with uracil groups.

In this case, the monomer units were prearranged and prepared for polymerization on the template. Many other examples are described in the next chapters of this book.

Another possibility of prearranging monomer molecules on template is when monomer units are connected with the template by covalent bonds. Examples of such systems will be considered in the next chapters. Orientation of the reacting group (e.g., double bonds) is controlled by the distance of groups in the template connected with the reacting group. Not only local concentration but also orientation of reacting groups in the area of the reaction is controlled by the template. Depending on the spacer connecting the reacting groups with the template, we can expect difference in the abilities of these groups to polymerize. Long and flexible spacers cause steric hindrance, while short and stiff bonds have reacting groups fixed in position depending on the template structure. There is no experimental evidence how parameters such as distance between bonds, spacer length, and stereoregular structure of the template influence the rate of template polymerization and the structure of the daughter polymer.

The second important phenomenon controlling template polymerization is related to the cumulative interaction between template and polymeric product. Nature of the interaction between template groups and daughter polymer groups is the same as discussed previously. It can be based on the hydrogen bonding, electrostatic forces, dipole-dipole interaction, etc. In some systems, however, interactions template - monomer are very weak. Preferential solvation is not observed but, after polymerization, quite strong forces appear between template and daughter polymer, giving rise to complex formation.

It was observed that in some systems even oligomers are not able to complex but polymers with high molecular weight give insoluble, stable polymer-polymer complexes. The number of units in polymer chain sufficient for stable absorption is called critical length. Below the critical length, the growing chain can exist in solution, above the critical length the absorption takes place. The cumulative interaction leads to specific orientation of template polymerization products on the template.

As it was shown[7] based on the example of polymerization of urea with formaldehyde in the presence of poly(acrylic acid), the product obtained interacts so strongly that it is insoluble in the common solvents. Probability of intermolecular chemical reactions increases in such systems which leads to crosslinking of the polycomplex.

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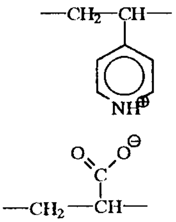
7. I. M. Papisov, O. E. Kuzovleva, S. V. Markov, and A. A. Litmanovich, *Eur. Polym. J.,* **20**, 195 (1984).

4

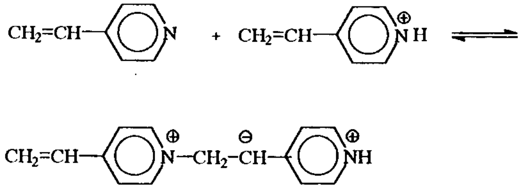
EXAMPLES OF TEMPLATE POLYMERIZATION

4.1 POLYACIDS AS TEMPLATES

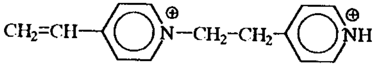
Spontaneous polymerization of 4-vinyl pyridine in the presence of polyacids was one of the earliest cases of template polymerization studied.[1,2,3] Vinyl pyridine polymerizes without an additional initiator in the presence of both low molecular weight acids and polyacids such as poly(acrylic acid), poly(methacrylic acid), poly(vinyl phosphonic acid), or poly(styrene sulfonic acid). The polyacids, in comparison with low molecular weight acids, support much higher initial rates of polymerization and lead to different kinetic equations. The authors suggested that the reaction was initiated by zwitterions. The chain reaction mechanism includes anion addition to activated double bonds of quaternary salt molecules of 4-vinylpyridine, then propagation in the activated center, and termination of the growing center by protonization. The proposed structure of the product, obtained in the case of poly(acrylic acid), used as a template is:



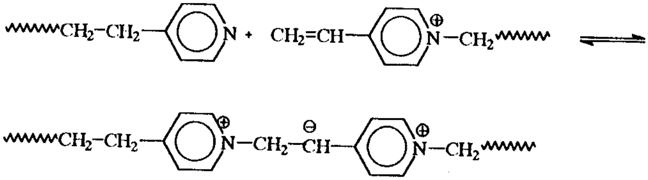
The study of template polymerization was preceded by examination of quaternary salts polymerization both in aqueous solution and in organic solvents. Examination of 4-vinylpyridine polymerization in water, induced by low molecular weight acids published by Salamone *at al.*[4] shows that in the first step, the following reaction occurs:



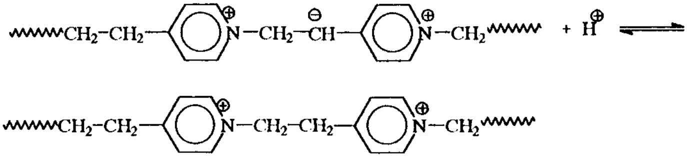
In the reaction environment, containing H^+; protonization occurs:



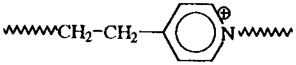
Then the reaction between products is also possible:



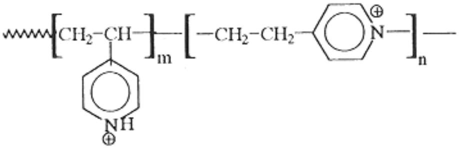
and after protonization



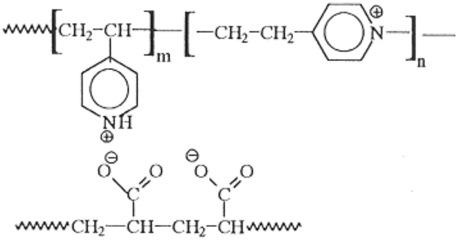
Accepting such a mechanism, it becomes evident that it is not a chain reaction but a stepwise reaction, and the product obtained is ionene with the following structure of the unit:



In the next paper, Russian authors[5] suggested the presence of ionene units in the reaction products, and postulated the following structure:



The ratio m/n depends on the reaction conditions. One cannot exclude the possibility of branched structure. As a consequence of such mechanism of the reaction in the presence of polyacids used as templates, two types of units can be expected in the product. For instance, if poly(acrylic acid) is used as a template, the structure is:



The mechanism of template polymerization in this case seems to be complex.[6] It involves both a stepwise and a chain reaction. However, experimental results show:

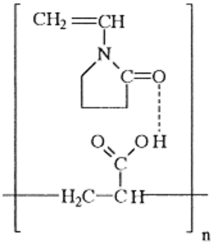
- an increase in the rate of reaction by one to two orders of magnitude in comparison with analogous low molecular weight compounds used instead of template
- change of reaction order with regard to monomer from 3 to 2 for analogous low molecular weight substances caused by template
- influence of organic salts on the initial rate of polymerization which differs when low molecular weight compound is used.

The authors thus concluded that the polymerization studied was affected by the template. The rules observed for polymerization of 4-vinylpyridine in the presence of low molecular weight acids and polyacids can be summarized as in the Table 4.1.[2]

Poly(methacrylic acid) was used as template for polymerization of N-vinylpyrrolidone.[7] Interaction between poly(methacrylic acid) and N-vinylpyrrolidone is based on the hydrogen bonding between COOH groups and carbonyl groups in the monomer:

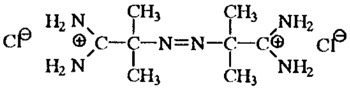
Table 4.1: Comparison of rules observed for polymerization of 4-vinylpyridine in the presence of low molecular weight acid and polyacids. [Reproduced from V. A. Kabanov, O. V. Kargina, V. A. Petrovskaya, Vysokomol. Soed., A13,348 (1971), with permission from Iz. Nauka]

Reaction in the presence of polyacids	Reaction in the presence of low molecular acids
Initial rate much higher than in the presence of monoacids	Initial rate much lower than in the presence of polyacids
Maximum initial rate at pH=5.6	Maximum initial rate at pH=5.3
Initial rate proportional to the second power of the monomer concentration (second order with respect to the monomer) in the absence of low molecular weight salts	Initial rate proportional to the third power of the monomer concentration (third order with respect to the monomer) in the absence of low molecular weight salts
Decrease of initial rate with addition of salts, such as LiCl, NaCl, KCl, CsCl, etc.	Increase of initial rate with addition of salts, such as LiCl, NaCl, KCl, CsCl, etc. Change of the order of the reaction with respect to the monomer from 3 to 2 with addition of excess salt

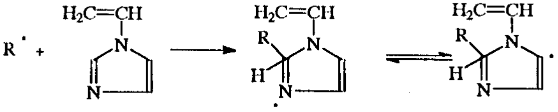


Because of acid-catalyzed hydrolysis of N-vinylpyrrolidone in water, polymerization was carried out in organic solvent - DMF. Three types of samples of poly(methacrylic acid) were used: syndiotactic - obtained by radiation polymerization, atactic - obtained by radical polymerization, and isotactic - obtained by hydrolysis of isotactic poly(methyl methacrylate). It was found that in all cases the rate enhancement appeared in comparison with the blank polymerization (without template). The rate enhancement became more pronounced with increasing chain length and syndiotacticity of the template. According to the authors, the rate enhancement is connected with the stronger complex formation between poly(vinyl pyrrolidone) and syndiotactic poly(methacrylic acid) then with isotactic template. This conclusion was supported by turbimetric titration in DMF/DMSO system and by model considerations. It is worth noting, however, that isotactic template, prepared by hydrolysis, contained 8% of non-hydrolyzed groups of methyl methacrylate, which can additionally influence the examined process.

A set of papers[8-12] was devoted to the polymerization of N- vinylimidazole in poly(methacrylic acid) matrix. Vinylimidazole is soluble in water and polymerization was carried out in aqueous system using 2,2`-azobis(2-amidopropane)2HCl as initiator:



Polymerization of N-vinylimidazole deviates from the polymerization of conventional vinyl polymers such as styrene or methyl methacrylate. The process leads usually to low molecular weight products, which is due to degradative addition. This process can be illustrated by the reaction:



In template polymerization this effect must also be taken into consideration. The authors[9] found that vinylimidazole adsorption occurs in the presence of poly(methacrylic acid). It was estimated that more than 40% of template groups are occupied by the monomer. On the basis of this finding and polymerization rate measurements, a propagation mechanism was proposed.[9] According to this mechanism, poly(methacrylic acid) reduced the monomer concentration in solution below a critical value, allowing for more rapid use of monomer in comparison with the conventional polymerization. Moreover, the template is able to reduce the number of inactive radicals in solution under conditions of degradative addition. Growth of template-associated radicals alongside the template with adsorbed monomer molecules impedes degradative addition.

Interesting conclusion was deduced from molecular weight measurements of polyvinylimidazole obtained by template polymerization.[11] It was found that molecular weights were up to 70 times higher than those of polymers produced in the absence of poly(methacrylic acid). Moreover, molecular weight of daughter polymer was up to 9 times higher then molecular weight of the template used. The authors explained this fact by assumption that radical hopping from the end of one template molecule to another takes place. Molecular weight of poly(vinylimidazole), obtained by template polymerization, depends on the ratio: template/monomer. This interesting relationship is illustrated in Figure 4.1.

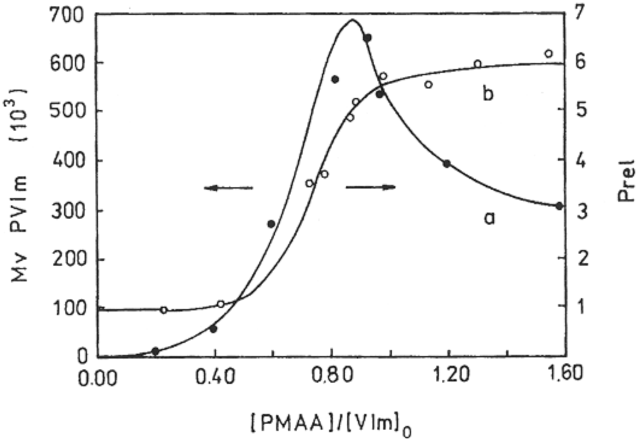


Figure 4.1. Influence of $[PMAA]/[VIm]_0$ on $M_{v,PVIm}$ (curve a •) and relative rate (curve b,o) $[VIm]_0 = 0.41$ M, $[AAP]_0 = 0.047$ M; $M_{v,PMM} = 89 \times 10^3$. Reprinted from H. T. van de Grampel, Y. Y. Tan, and G. Challa, *Macromolecules,* **24**, 3773 (1991), with kind permission from *ACS*.

The maximum of molecular weight appears when the ratio of template to monomer concentration is about 0.8. Molecular weight of polymer formed depends also on the initiator concentration as shown in the Figure 4.2.

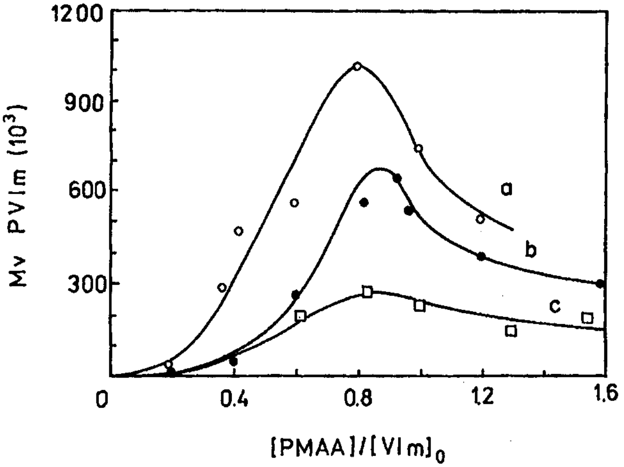
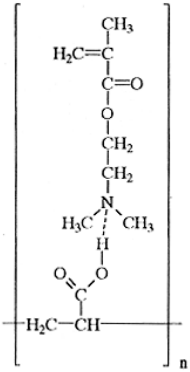


Figure 4.2. $M_{v,PVIm}$ versus $[PMAA]/VIm]_0$ for three initiator concentrations: $[AAP]_0$=0.024M (curve a, o), 0.047 M (curve b, •) and 0.072M (curve c, □) $[VIm]_0 = 0.41$M. Reprinted from H. T. van de Grampel, Y. Y. Tan, and G. Challa, *Macromolecules,* **24**, 3773 (1991), with kind permission from *ACS*.

The lower the initiator concentration the higher the molecular weight of polymer formed. Moreover, the effect of the ratio: template/monomer concentration is more pronounced for low initiator concentration. In addition, it was found that tacticity of the template does not influence the suppression of degradative addition nor the tacticity of the poly(vinyl imidazole) obtained by the template process.

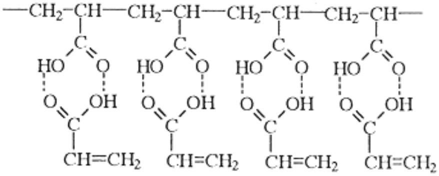
Polyacrylic acid was used as a template for the polymerization of dimethylaminoethylmethacrylate in acetone/water systems.[13] Interaction between monomer and the template is relatively strong.



The initial rate of polymerization versus base molar concentration ratio of template to monomer shows a sharp maximum in the range of [T]/[M] = 1.5. Polymerization was initiated by AIBN and UV light at 365 nm. Poly(dimethylaminoethyl methacrylate) with poly(acrylic acid) give a complex. During polymerization, precipitation takes place. From the product obtained, the daughter polymer and the template were isolated by dissolving the complex in 10% NaCl solution, addition of proper amount of NaOH, followed by dialysis.

Examining radiation-induced polymerization of acrylic acid in bulk and in a set of solvents, Chapiro and Dulieu[14] observed an unusual behavior of this monomer, with regard to the process kinetics.

It is well known that organic acids form dimeric complexes due to hydrogen bonding. The authors assumed that molecules of acrylic acid can take four forms: free monomer, cyclic dimer, linear oligomer, and monomer associated with polymeric template, depending on the nature of the solvent used, temperature and concentration. In pure acrylic acid and solutions in water, dioxane, and methanol (called by the authors the first group of solvents), linear oligomers are stabilized by selective hydrogen bonding. In toluene, chloroform, and CCl_4 (second group of solvents), the equilibrium of association is shifted from linear oligomers to cyclic dimers. Linear oligomer structure, appearing in a pure monomer and in solvents of the first group, facilitates organization of monomer molecules by polymer formed at very early stages of polymerization. It leads to a structure organized as follows:



The autoaccelerated character of acrylic acid polymerization is strictly correlated with such a form of monomer organization. The fast “zip-up” propagation takes place along oriented double bonds. Template mechanism of polymerization in these systems was also confirmed by examination of the tacticity of the polymer obtained.

Influence of temperature on the process of polymerization of acrylic acid in dioxane and toluene was examined.[15] It was found that in dioxane an increase in temperature destroys the oligomeric auto-associations of acrylic acid and gives rise to monomer-solvent association, making matrix effect less pronounced. In toluene, an increase in temperature converts the cyclodimeric autoassociations of the monomer into linear oligomers and the matrix effect appears.

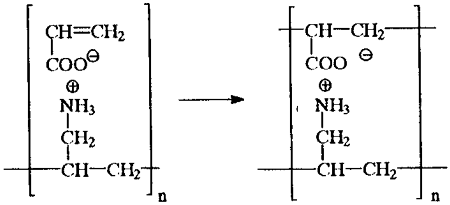
A very interesting phenomenon was observed[16] when a small amount of methanol was added to the solution of acrylic acid in n-hexane. In such system, the auto-acceleration of the polymerization is very high. It was suggested that the complex: (acrylic acid)$_2$ MeOH is formed. This complex associates very rapidly with the polymer formed at the early stages of the reaction to produce a structure in which ultrafast propagation occurs.

It was reported [14] that, in the contrast to acrylic acid, methacrylic acid does not exhibit any template effect under conditions described. However, template effect appears if a solvent such as water or methanol is added, and also at higher temperatures of polymerization.

4.2 POLYIMINES AND POLYAMINES AS TEMPLATES

As published by Ferguson and Shah[17] and independently by Bamford and Shiiki,[18] polyethylene imine can be used as template for polymerization of acrylic acid. It was found that polyethylene imine forms water insoluble complex with polyacrylic acid. Polymerization was carried out at 31°C, using potassium persulphate as an initiator. The polymerization was followed by turbimetry and bromometric titration. During polymerization, the precipitation takes place, however, at 60°C, degradation of the complex occurred and the precipitate rapidly disappeared. Rate of polymerization was found to go through a maximum for the system in which concentration of the template is much lower than the concentration of monomer. The authors suggested that such a large increase in the rate of polymerization is a result of template effect, the heterogeneity of the system and a change in the initiation due to the presence of a redox system (polyimine - persulphate). However, no graft or block copolymers were found in the reaction products which seems to suggests that template effect is dominant.

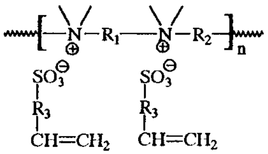
Recently, polymerization of sodium acrylate on polyallylamine hydrochloride template was described.[19] In aqueous solution, sodium acrylate molecules are adsorbed onto a template with ammonium cationic pendant groups. The complex was polymerized in water solution using AIBN or $K_2S_2O_8$ as initiators. Polymerization proceeds according to reaction:



The maximum rate of polymerization appears at the ratio of the template units to monomer units 1:1.

4.3 POLYBASE IONENES AS TEMPLATES

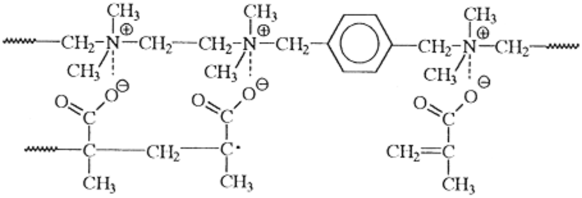
The system with very strong interaction between monomer and template was studied by Blumstein *at al.*[20,21] Polybase ionenes were used as templates. A set of ionenes such as poly(diazobiscycloocto-1butane), poly(diazobicycloocto-1-hexane), poly(diazobicycloocto-1-octane), poly(hexamino-1-hexane), and poly(hexamino-1-decane) were used. Molecular weight of ionenes was rather low and DP was estimated to be in the range of 5 to 12 units. Such polybase ionenes form complexes with p-styrene sulfonic acid or vinyl sulfonic acid applied as monomers. The general formula of complexes was:



where R_1 and R_2 : $-(CH_2)_x-$ with x = 4, 6, 8 or 10; $R_3 = 0$ for vinyl sulfonic acid or phenylene ring for p-styrene sulfonic acid.

The formation of complexes involved two steps. In the first step, the ionene bromide was converted to ionene hydroxide by replacing the Br^- ions with OH^- ions. In the second step, the equivalent quantities of acid and ionene were mixed together. Polymerizations were carried out mostly in water-isopropanol solution. AIBN or 4,4-azobis-4-cyanovaleric acid was used as initiator. Polymerization of p-styrene sulfonic acid onto various ionenes was studied as a function of the charge density of the template.[21] It was shown that a linear dependence of rate on charge density prevailed. From the results obtained, the authors concluded that the monomeric counterions possess mobility along the linear template. Poly(vinyl sulfonate) prepared on the template displays a different stereo-structure from poly(vinyl sulfonate) prepared in solution.

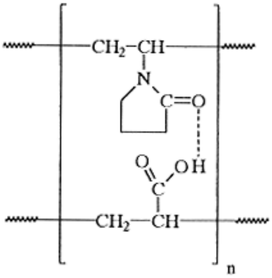
Tsuchida[22] described polymerization of methacrylic acid and acrylic acid in the presence of equimolar concentration of polycation. At high pH, the monomer molecules are fully adsorbed by the template. According to the authors the polymerizing system has the following structure:



According to this diagram the template can eliminate the electrostatic repulsion between negatively charged macroradical and the monomer. Such repulsion exists when polymerization proceeds without the template, especially at high pH. It leads to the increase in polymerization rate in the system in which template is present and at the high pH region. At very low pH (such as 3) the template does not have any significant influence on the polymerization rate. This effect seems related to interaction of poly(methacrylic acid) or poly(acrylic acid) with polycation only with the ionized carboxylic groups. It was found that around pH = 7 equimolar complex is formed between poly(methacrylic acid) and polycation.

4.4 POLY(ETHYLENE OXIDE), PEG, AND POLY(VINYL PYRROLIDONE), PVP, AS TEMPLATES

The most examined monomers for template polymerization have been either acrylic or methacrylic acids. This is probably because many polymers, such as poly(ethylene oxide), PEG, and poly(vinyl pyrrolidone), PVP, form complexes with poly(acrylic acid), PAA, or poly(methacrylic acid), PMA. The complexes of PAA or PMA with PEG were described long ago.[23,24] The fact that PVP forms strong, water insoluble complexes with PAA with the following structure:



was a starting point for Ferguson and Shah[17,25] in the examination of template polymerization of acrylic acid. A turbimetric technique was applied for kinetics measurement. It was found that the rate of AA polymerization in water, initiated by potassium persulphate at 74°C is strongly dependent on the concentration of PVP used as a template. The maximum point of this relationship corresponds to equimolar ratio of AA to PVP units. Equimolar complex composition was confirmed by gravimetric experiments. It was proven that template effect strongly depends on the complex formation. When AA was polymerized in the presence of PVP, but at pH=4.5 (when system was homogeneous), no increase in polymerization rate occurred. Also, no acceleration was observed when PVP was replaced by methyl pyrrolidone. The presence of polymeric, interacting compound was found essential for acceleration to take place.

A very interesting modification of the system was examined by Ferguson and McLeod.[26] The authors replaced poly(vinyl pyrrolidone) with copolymers vinyl pyrrolidone-styrene or vinyl pyrrolidone-acrylamide. It was found that the mechanism of polymerization is the same as in the presence of homopolymer (PVP). However, the rate of polymerization decreases rapidly when vinyl pyrrolidone concentration in copolymer decreases. The concentration of vinyl pyrrolidone residues was kept equimolar to the concentration of acrylic acid. It was stressed that structure of template and, in the case of copolymeric template, sequence distribution of units play an important role in template effect.

Polymerization of methacrylic acid, MA, in aqueous solutions, in the presence of PVP, was investigated by Shavit and Cohen.[27] Fractions of PVP of varying molecular weight were used as templates. The rate of polymerization increased with the increase in molecular weight of PVP. The change in tacticity of daughter polymer was observed as well as the change in kinetics in comparison with blank polymerization carried out under the same conditions but in the absence of PVP. The authors suggested that the polymerization process begun in solution with adsorption to template occurring only after a critical degree of polymerization was achieved. Dialysis experiments indicated that neither AA nor MA interact with PVP. The influence of molecular weight of PVP, used as template, on the degree of polymerization of polyacrylic acid obtained by template polymerization was examined in detail by Ferguson *et al.*[28] The degree of polymerization of PAA formed in template polymerization was found to be remarkably similar to the degree of polymerization of the PVP template as shown in Figure 4.3.

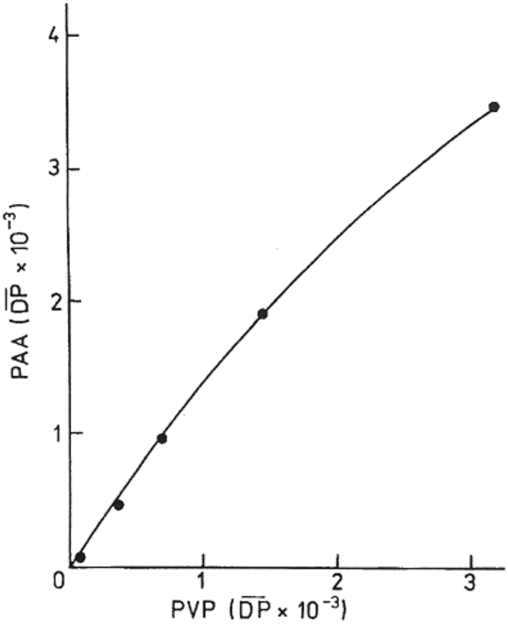


Figure 4.3. Variation of degree of polymerization of poly(acrylic acid) with degree of polymerization of template PVP. Reprinted from J. Ferguson, S. Al-Alawi, and R. Granmayeh, *Eur. Polym. J.*, **19**, 475 (1982) with kind permission from Elsevier Science Ltd.

The results are surprising since they apparently infer that monomer radical propagation starts at one end of the template and continues to the other end of the template when termination occurs. According to the authors[28] this needs not necessarily be the case. The explanation is illustrated in Figure 4.4.

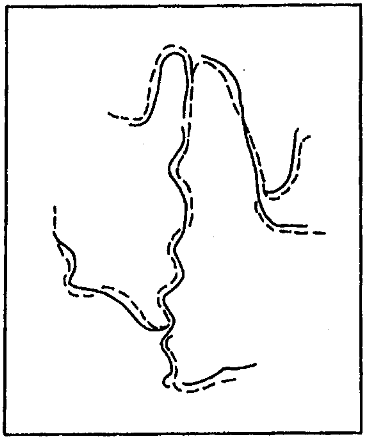
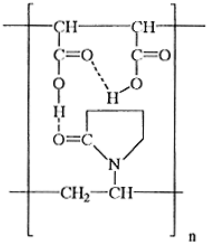


Figure 4.4. Schematic view of polymer-polymer interaction. Template ———: Daughter polymer - - - - -. Reprinted from J. Ferguson, S. Al-Alawi, and R. Granmayeh, *Eur. Polym. J.*, **19**, 475 (1982) with kind permission from Elsevier Science Ltd.

Continuous lines represent the template molecules, while dashed lines the growing daughter polymer molecules. Growing molecule can interact with two or more sites in the template molecule. If we only assume that growing molecule propagates longer in the presence of a higher molecular weight template, we can expect on average a degree of polymerization corresponding to the degree of polymerization of the template. For the same object of investigation, the content of isotactic sequences was found to be higher in the template polymerization product than in poly(acrylic acid) obtained in blank polymerization.

In a set of papers, template polymerization of methacrylic acid in an aqueous system, using PVP as template, was described.[29-33] The rate of the process was measured by the dilatometric technique and the results compared with either the polymerization of MA without template, or with the presence of low molecular weight analog. $Na_2S_2O_8$ or UO_2SO_4 were used as photoinitiators. It was found that template polymerization rate is higher than that for polymerization without template. The higher the molecular weight of the template used, the higher was the rate of polymerization. It was found, moreover, that in the case of template polymerization the process continues after switching off the light source. The examination of polymerization rate in post-effect leads to the conclusion that in template polymerization the lifetime of radicals is much longer than during polymerization in the absence of PVP.

Polyvinylpyrrolidone was also used[34] for polymerization of maleic acid. Maleic acid can be polymerized in water in the presence of polyvinylpyrrolidone while the same monomer is very difficult to polymerize in the conventional manner. It was suggested by the authors that a product of polymer-polymer complex is formed with the following structure:



The complex is insoluble in water. After methylation by diazomethane, and 50-60% polymerization, the product is an oligomer of poly(maleic acid methyl ester) with molecular weight, M = 400-500. Similar results were obtained for polymerization of citraconic acid in the presence of poly(vinyl pyrrolidone) with molecular weight 3.6x10^5. In this case, the complex obtained is soluble in cold water while precipitable in hot water. However, it seems that a substantial amount of graft copolymer is formed during the process of polymerization of both maleic and citraconic acids. It is connected with chain transfer to poly(vinyl pyrrolidone) in which abstraction of hydrogen from CH group is rather easy to achieve.

The published results concerning polymerization of acrylic acid or methacrylic acid in the presence of poly(ethylene oxide) in water are controversial. Ferguson and Shah[25] found that PEG with sufficiently high molecular weight increases the polymerization rate, while Kabanov *at al.*[35] found that in the presence of high molecular weight PEG the rate of polymerization of acrylic and methacrylic acids is lower than in blank reaction. Our results[36] show that in the case of methacrylic acid photopolymerization in the presence of PEG of mol. weight 20,000, the rate of the reaction increases. This differences can be explained by the conditions of polymerization as well as methods used to follow the process different in both studies.

Ferguson and Shah[25] described polymerization of AA in the presence of poly(ethylene oxide), PEG, having mol. weight of 1,500 and 6,000. Polymerizations were carried out in water at 55 and 74°C. Potassium persulphate was used as an initiator. Having examined the influence of template concentration on the rate of polymerization, it was found that the maximum rate appears not at equimolar ratio of monomer to template, but at much lower concentration of the template. Polymerization of AA in the presence of PEG in water at 74°C was treated by the authors as an example of the system in which the interaction between template and the monomer is rather weak. Indeed, only template with molecular weight of 6,000 or higher was effective. The influence of PEG with molecular weight of 6,000 leads to an increase in the polymerization rate by about seven times. The polymerization of AA and MA in the presence of PEG was a subject of work published by Papisov *et al*.[35] The influence of molecular weight of PEG on the rate of the reaction was examined. In the region of relatively low molecular weights (600-3,000 for MA and 1,000 to 6,000 for AA), the rate decreased rapidly but, even for molecular weights of 10^4 - 10^5 the change was not large. It is illustrated in the Figure 4.5 for methacrylic acid and in Figure 4.6 for acrylic acid.

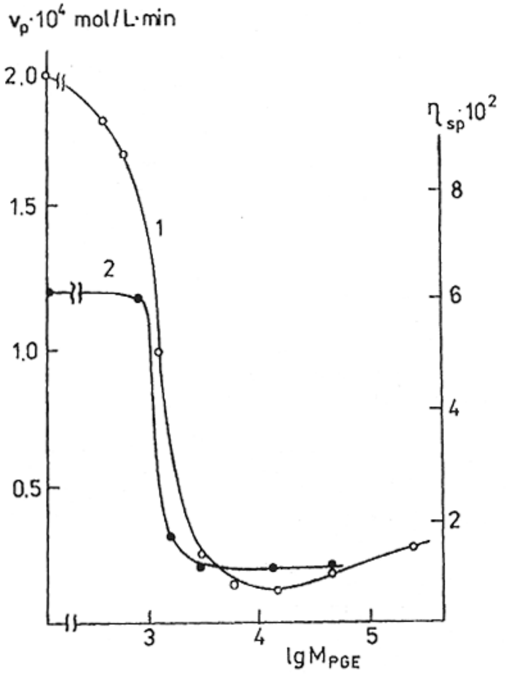


Figure 4.5. Dependence of polymerization rate of MA (1) and specific viscosity of solutions of equimolar mixtures of polyacid and PEG (2) on molecular weight of PEG. 1 - [MA]=[PEG]=3.5×10^{-2}; [$K_2S_2O_8$]=3.7×10^{-4} mol/L, 50°C. 2 - PMA M=170,000; c_{PMA}=0.1 g/dL, 45°C. Reprinted from I. M. Papisov, V. A. Kabanov, E. Osada, M. Leskano Brito, J. Reimont, and A. N. Gvozdeckii, *Vysokomol. Soed.*, **14**, 2462 (1972) with kind permission from *Iz. Nauka*.

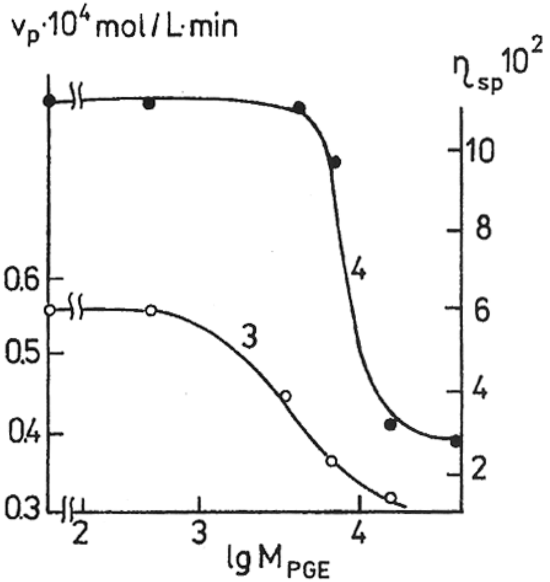


Figure 4.6. Dependence of polymerization rate of MA (1) and specific viscosity of solutions of equimolar mixtures of polyacid and PEG (2) on molecular weight of PEG. 1 - [MA]=[PEG]=3.5×10^{-2}; [$K_2S_2O_8$]=3.7×10^{-4} mol/L, 50°C. 2 - PMA M=120,000; c_{PMA}=0.1 g/dL, 45°C. Reprinted from I. M. Papisov, V. A. Kabanov, E. Osada, M. Leskano Brito, J. Reimont, and A. N. Gvozdeckii, *Vysokomol. Soed.*, **14**, 2462 (1972) with kind permission from *Iz. Nauka*.

The same figures show changes in viscosity. Both rates of reaction and viscosity decrease when molecular weight of PEG is higher than 1,000 for methacrylic acid and higher than 10^4 for acrylic acid. This range corresponds with the observations that for higher molecular weights the system PEG-poly(acrylic acid) becomes heterogeneous,[25] which explains dramatic decrease in viscosity. It was found that the initiation rate in systems examined is independent of the presence of PEG in the whole range of molecular weights as illustrated in Figure 4.7. As an inhibitor, 2,2,6,6-tetramethyl-4-hydroxy-piperidine-1-oxyl was used. Figure 4.7 shows that the addition of the inhibitor influences only the inhibition period (polymerization begins later) but does not influence the polymerization rate. The influence of solvent was also examined in detail. Polymerizations were carried out in pure water and in mixtures H_2O - methanol. For polymerization of MA without PEG the rate decreased very significantly as methanol content in the mixed solvent was increased. In contrast, for polymerization of AA or MA in the presence of PEG (in equimolar ratio), the rate of polymerization is independent of the content of methanol in the full range of mixture compositions. The

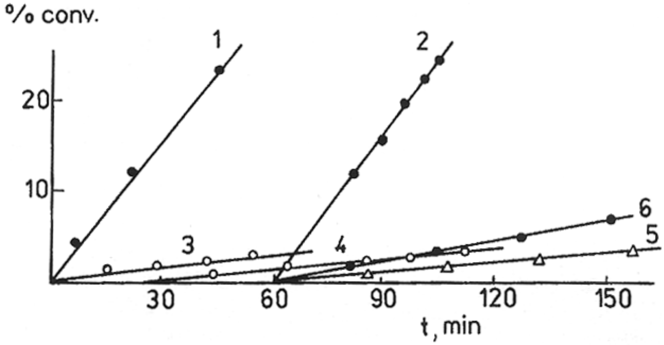


Figure 4.7. Dependence of conversion PMA on time of polymerization in absence (1,3) and presence of inhibitor (2,4-6); [MA]=3.5×10^{-2}; [$K_2S_2O_8$]= 3.7×10^{-4} [PEG]=3.5×10^{-2} mol/L. 1 - MA; 2 - MA+Inh. ($1.19\text{x}10^{-6}$ mol/L); 3 - MA+PEG; 4 - MA+PEG+Inh. (0.59×10^{-6} mol/L); 5 - MA+ PEG+Inh (1.19×10^{-6} mol/L); 6 - MA+CH_3OH 50% vol.+ Inh. (1.19’10^{-6} mol/L). Reprinted from I. M. Papisov, V. A. Kabanov, E. Osada, M. Leskano Brito, J. Reimont, and A. N. Gvozdeckii, *Vysokomol. Soed.*, **14**, 2462 (1972) with kind permission from *Iz. Nauka*.

change in tacticity of PMA obtained in the presence of PEG was rather small. An increase by about 6% in syndiotacticity was caused by PEG. The authors suggested that in the system examined the role of the template is limited to connecting the template macromolecules with growing chains and creating a surrounding for the growing center, similar to that for concentrated solutions of PEG or low molecular weight analog of the template.

Photopolymerization of MA onto PEG with molecular weight about 20,000 at low temperature (25°C) was reported.[36] In this case, no significant influence of the template on the rate of polymerization was found. The effect was slightly more pronounced if PEG with incorporated azo groups was used as template.

A very interesting case of template polymerization was described by Baranovski *et al.*[37] The authors used two templates with different strength of interaction with respect to the daughter polymer. The first template was poly(vinyl pyrrolidone) with molecular weight 9,000 or 4,000. Polyethylene glycol monolaurate with molecular weight of polyglycol part of 600 or 15,000 was used as the second template. Methacrylic acid was used as a monomer. Polymerization was carried out in water at 50^0C and was initiated by $K_2S_2O_8$. On the basis of kinetic measurements at various concentrations and ratios of both templates, the authors found that there are conditions in which poly(methacrylic acid) molecules, in the course of growing, move from the strong, but short poly(vinyl pyrrolidone) template to the weaker template - polyethylene glycol monolaurate micelles. The circumstances of such a substitution reaction (exchange reaction) are described by the equation:

$$c_1K_1^{\varepsilon 1} = c_2K_2^{\varepsilon^*}$$

where c_1 and c_2 are concentrations of template 1 (polyvinyl pyrrolidone) and 2 (polyethylene glycol monolaurate); K_1 and K_2 effective strength constants for template 1 and 2, ε_1 and ε^* are the corresponding degrees of polymerization.

4.5 POLY(METHYL METHACRYLATE) AS TEMPLATE

Many radical polymerization systems were examined by Challa *at al*.[38] A number of papers were devoted to polymerization of methyl methacrylate, MM, in the presence of poly(methyl methacrylate).[39-43] The role of tacticity of template was stressed. Isotactic PMM forms stereocomplex with syndiotactic PMM. Polymerizations of MM in the presence of isotactic PMM were carried out and the product (template + daughter polymer) was analyzed by ^{1}H NMR. When MM is polymerized in the polar solvent in the presence of isotactic PMM, the polymer formed is syndiotactic. For instance, if PMM with $M_v = 7.2 \times 10^5$ and with 90% of isotactic triads was used as a template, the polymer with $M_v = 7.5\times10^5$ and 95% of syndiotactic triads was obtained. Polymerization was carried out at low conversion (4%) in DMF solution at 25°C using bis(p-tert-butylcyclohexyl) dipercarbonate as an initiator. This very important observation was the evidence that the propagation mechanism had changed and it was very persuasive proof that polymerization of MM in the presence of stereoregular PMM occurs according to a template mechanism. Also, examination of the kinetics of this process offers evidence for the template influence on the mechanism. Dilatometric measurements of polymerization rate were carried out in DMF in the range of -11 to 60°C. The reaction was initiated by (p-tert-butylcyclohexyl) dipercarbonate. In most experiments, isotactic PMM was used as polymer template. An increase in the relative initial rate of template polymerization, $V_{R,}$ with respect to a blank polymerization (without template) was observed. It was shown that V_R depends on the template concentration. The increase was linear in the range of low concentrations. When the template concentration reaches a critical concentration (i.e., solution possesses a homogenous segmental distribution) a rapid increase in the polymerization rate occurs. On the basis of overall initial polymerization rate and using rotating sector technique, rate constants for blank and template polymerizations were calculated. It was reported that in the presence of the template, k_p value decreases about 5 times, and k_t almost 100 times.

Polymerization of MM in the presence of syndiotactic PMM was also reported.[40] In this case, PMM of mostly isotactic structure was produced. Interaction between growing chains and the template is rather weak. The template influence is not as pronounced as in the case of isotactic template. Matsuzaki *at al*.[42] used deuterated syndiotactic PMM as template for polymerization of MM. The measurements of tacticity by ^{1}H NMR were much easier than with undeuterated template and daughter polymer mixture, because separation of the product is not necessary. Simply, the template was “invisible” in ^{1}H NMR. Proton NMR gives only a spectrum of daughter polymer. The authors found that PMM formed in the presence of highly syndiotactic PMM has low isotacticity. Only a little decrease in syndiotacticity was observed at the early stages of polymerization in the presence of high molecular weight PMM.

According to Tan and Challa,[43] this result is caused by a template with too low a molecular weight and the influence of deuterium substitution. Critical length (minimum number of units necessary for template effect), estimated for isotactic PMM at 10-20 monomer units, is roughly 600 in the case of high molecular syndiotactic PMM.

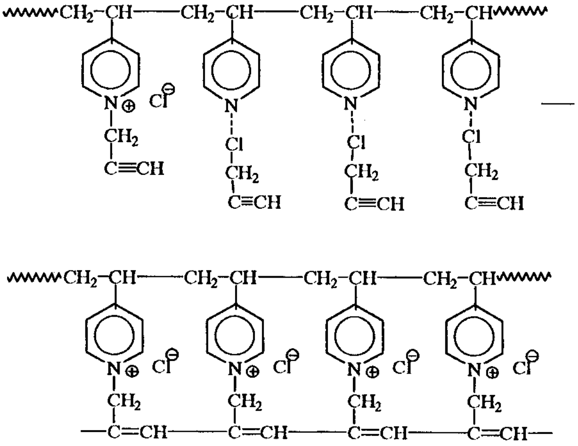
4.6 POLY(VINYLOPYRIDINES) AS TEMPLATES

An extensive literature is devoted to polymerization of methacrylic acid onto poly(2-vinylpyridine).[44-49] The influence of template concentration,[44] template tacticity,[47] initiator concentration,[45] monomer concentration,[46] and temperature[48] were studied in detail. The majority of findings deal with kinetics of the process which is considered in Chapter 8.

The influence of template concentration on polymerization of the system: methacrylic acid - atactic 2-vinylpyridine - DMF was examined.[44] Atactic poly(2-vinyl pyridine) with molecular weight M = 72,000 was used as a template and DMF as a solvent. Study of polymerization was followed by measurements of preferential solvation of methacrylic acid onto poly(2-vinylpyridine) in DMF in the range of concentration 0.2-0.6 of base M. Equilibrium dialysis by the interferometric technique was used. It was found that preferential adsorption is high in this system. The q value was 0.4 g of monomer per one gram of the template. Both dilatometric and calorimetric techniques were used for kinetic measurements. The reaction rate is a combination of the rates of three processes: polymerization in a free volume, polymerization according to the “zip-up mechanism”, and polymerization that depends on the transport of monomer molecules to the template (“pick-up mechanism”). The mechanism varied with the concentration of monomer. Below critical concentration of the template, polymerization proceeds mainly according to the zipping-up mechanism, whereas at higher concentrations the “pick-up” mechanism is dominant. The authors postulated that complexation between PMAA and the isotactic template is stronger than for atactic template.[47] Examination of template polymerization for the system mentioned, in the range of temperatures from 30°C to 60°C, allowed calculation of activation energy. The overall energy of activation for the template process both with atactic and isotactic template was found to be 40 kJ/mol while for the blank reaction the activation energy was twice as high. This large difference is caused by a high energy of activation of cross-termination reaction.

The influence of the solvent on the process is very important. Polymerization of methacrylic acid onto poly(2-vinylpyridine) template was studied by carrying out the process in solvents with different polarity, such as dimethylsulphoxide, DMSO, 1,4-dioxane and DMF.[49] The weak solvent-monomer interaction in the case of 1,4-dioxane leads to increasing polymerization rate, while in strong polar DMSO, polymerization proceeds as for a blank reaction (without template). It is consistent with the fact that poly(methacrylic acid) and poly(2-vinylopyridine) do not form complex in this strongly solvating medium.

A template mechanism was also proposed for spontaneous polymerization of propargyl chloride in the presence of poly(4-vinylpyridine).[50] The reaction consists of partial (6-8%) alkylation of P4VPy by propargyl chloride which leads to stable complex P4VPy with monomer and then to polymerization. The product obtained contains a conjugated bond system formed by opening triple bonds in the monomer according to reaction:



Poly(4-vinylpyridine) was used also as a template for polymerization of maleic anhydride.[51] Maleic anhydride is very difficult to polymerize by conventional radical polymerization, but in the presence of poly(4-vinylpyridine) in chloroform or in nitromethane, polymerization proceeds at room temperature just after mixing 0.5% solution of poly(4-vinylpyridine) with 1% solution of maleic anhydride. A yellow precipitate is obtained. The precipitate is a mixture of poly(maleic anhydride), poly(4-vinylpyridine), and unreacted maleic anhydride. In the absence of oxygen, polymerization is much slower. The reaction stops on the stage of donor-acceptor complex formation.

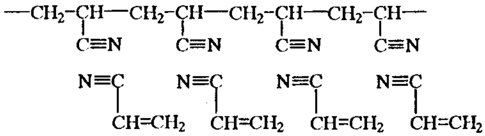
4.7 OTHER TEMPLATES

Tewari and Srivastava published the results on interaction between atactic poly(vinyl acetate)[52] and poly(acrylonitrile),[53] and poly(methyl methacrylate) and poly(methacrylic acid).[54] On the basis of viscometric measurements of DMF solutions of mixtures of the pair of polymers mentioned above, the authors concluded that for all the systems examined complex formation occurs. This observation explains the results published earlier by the authors about template polymerization of acrylonitrile, methacrylic acid, and methyl methacrylate carried out in the presence of poly(vinyl acetate). It was found that polymerization of acrylonitrile in DMF in the presence of atactic poly(vinyl acetate) (mol. weight 47,900) takes place much faster than without poly(vinyl acetate), especially, when concentration of the monomer is equimolar to the concentration of template repeat units. The overall energy of activation was found to be 55.76 kJ/mol for template polymerization and 77.01 kJ/mol for polymerization in the absence of the template.

The template polymerization of methacrylic acid at 60°C in DMF was studied[54] with atactic poly(vinyl acetate) M =66,400 used as a template. The effect of template, monomer, and initiator (AIBN) concentration on the kinetics of polymerization was studied dilatometrically. Viscometric measurements showed that complexation between poly(vinyl acetate) and poly(methacrylic acid) was maximized when the template to polymer ratio was 1:1, and for the same ratio of the monomer to the template, the rate of template polymerization also reached the maximum. The overall energy of activation was the same (115 kJ/mol) in the presence and absence of the template. The polymerization follows mechanism II ("pick up mechanism").

A similar set of experiments was carried out for the system poly(vinyl acetate) -methyl methacrylate.[52] Atactic poly(vinyl acetate) M =55,880 was used as a template and DMF as solvent. Polymerization was carried out at 60°C, and AIBN was used as an initiator. Also equimolar complex of daughter polymer and the template were suggested. As the concentration of the template increases, the relative rate of polymerization increases continuously, until a maximum rate is reached at 1:1 monomer to template. At higher concentrations, the relative rate of polymerization decreases. The overall energy of activation was 33.5 and 25.0 kJ/mol in the presence and absence of poly(vinyl acetate), respectively. A very interesting relationship was observed between molecular weight of the template and molecular weight of the daughter polymer. In the whole range of molecular weights studied (26,000-56,000), molecular weight of template was only slightly higher than that of poly(methyl methacrylate) extracted from the reaction products. The polymerization is a combination of three different mechanisms, the blank reaction and two template mechanisms (I and II).

Bulk polymerization of acrylonitrile initiated by gamma radiation was described by Chapiro *at al*.[55] The process is greatly complicated by other reactions. Occlusion of radicals during precipitation occurs especially at low temperatures. However, the template mechanism was suggested for polymerizations carried out above 60°C. Polyacrylonitrile, accumulated at the early stages of the reaction, acts as a template to which monomer associates by dipole-dipole interaction. It is illustrated by the formula:



In the associates, polymerization occurs according to the zip-propagation mechanism, and auto-acceleration takes place. In the range of temperatures from 10 to 60°C, the system gradually changes from the system dominated by occlusion to the system where template effect determines the kinetic behavior. In this range of temperatures, a significant post-effect occurs.[56]

A seemingly similar process of polymerization - the radiation induced polymerization of methyl acrylate in n-hexane - shows also auto-acceleration and post-polymerization.[57] Polymerization was carried out under precipitating conditions. Using the results of kinetics examination, the authors showed that all effects can be explained by the mechanism based on trapped radical reactions in particles of precipitated polymer. No influence of any template effect was detected in these systems.

Very interesting method of template polymerization was proposed by Japanese scientists.[58, 59] The method is based on the charge transfer interaction between template and monomer. In the course of the studies on the interaction of poly(maleic anhydride) with organic amines, the authors found strong charge transfer interaction of pyridines with poly(maleic anhydride). The polymer with pyridine gives brown-colored system with the absorption maximum at 480 nm.

The authors found[58] that 4- and 2-vinylpyridines and N,N-dimethylaminostyrene polymerize spontaneously at 50°C in DMF or acetone in the presence of poly(maleic anhydride). Product obtained consist of 1:1 mixture of poly(vinylpyridine) and the template. Moreover, degree of polymerization of daughter polymer was almost the same as degree of polymerization of the template used. After separation of the polymerization product, it was found that for PVP, $P_n = 14$, whereas for poly(maleic anhydride) used as a template, $P_n = 12$.

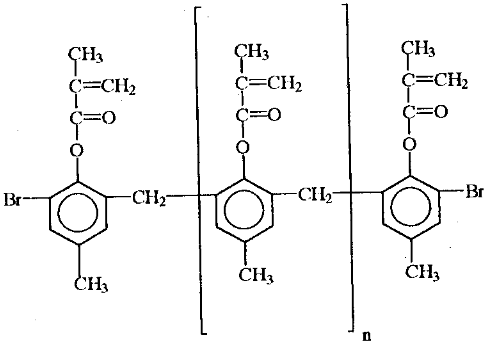
At temperature lower then 50°C, polymerization proceeds very slowly, whereas at 50°C, 4-vinylpyridine and 2-vinylpyridine polymerize very rapidly without any initiator. Using DMF as solvent, the system remains homogeneous through the polymerization time, whereas in acetone precipitates polymer mixture after a few minutes. It is also worth noticing that no polymerization was observed in the system - succinic anhydride/vinylpyridine/DMF or acetone.

Using copolymer maleic anhydride/styrene instead of poly(maleic anhydride) homopolymer as a template, the authors[59] found that polymerization of 4-vinyl pyridine proceeds also without any initiator, but with lower rate of reaction.

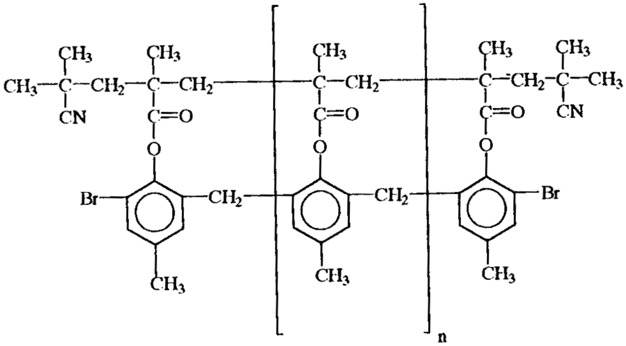
4.8 MULTIMONOMERS AS TEMPLATES

A special type of template polymerization takes place if monomer is connected with a template by covalent bonding. Initiation, propagation, and termination proceed in the close contact with the template. Many experimental examples of such reactions have been published in connection with the synthesis of ladder polymers.[60-67] One of the methods by which such polymers are obtained is “zipping up”. In general, the method involves making a linear polymer (template) containing appropriately located reactive functional groups and then linking these groups to form the second part of the ladder.

Kämmerer and colleagues were the pioneers in these investigations.[68-70] The p-cresyl-formaldehyde oligomers were used as a template. To assure linearity of the product obtained, an adequate method of synthesis was selected. End-groups of cresyl-formaldehyde resin were protected by bromine atoms, which made preparation of oligomers with predicted degree of polymerization possible. The template prepared was esterified by methacryloyl chloride or acryloyl chloride in order to obtain a multimonomer with the following structure:

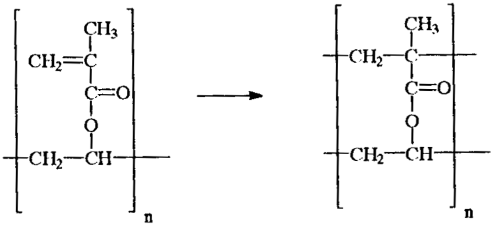


Polymerization of the multimonomers obtained was carried out in a very dilute benzene solution (about 1.4×10^{-2} base mol/L) for a long time (36 h) with a high concentration of AIBN used as an initiator. The initiator was added dropwise all the time during the reaction. Such procedure was used to minimize intermolecular reaction. The high concentration of the initiator leads to preferential reaction between primary radicals with growing chains. It was proven that every oligomeric molecule was terminated from both sides by cyanopropyl groups. The structure predicted by the authors was as follows:

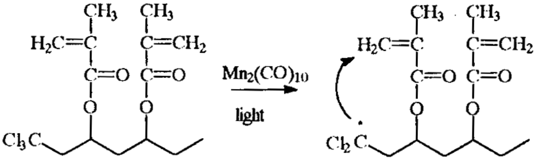


In order to prove the ladder structure of obtained products, hydrolysis was carried out. By hydrolysis, both ester and CN groups were converted to oligomeric polyacids with the number of units twice as high as the number of units in the template.

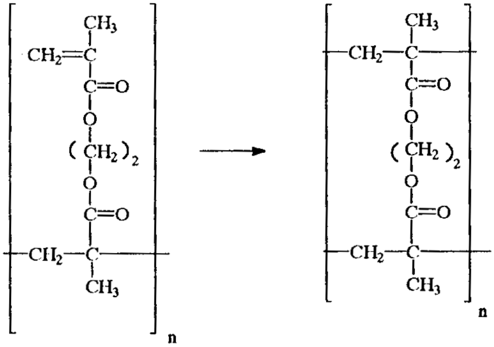
Another example is a synthesis of a ladder polymer suggested by Bamford[71] and examined afterwards by Jantas.[72] Poly(vinyl alcohol) esterified by methacrylic chloride was used as a template. Polymerization can be represented by the following reaction:



The polymerization can begin at any group present and may proceed in any direction. In other words, since the reactive groups are independent and initiation occurs randomly, polymerization (zipping) leads to isolated reactive groups which are both potential crosslinking sites and breaks in the ladder structure. Crosslinking, as an intermolecular reaction, can be minimized by conducting the reaction at an appropriate dilution. If, however, the initiation is not random, but starts at one end of the template, we might expect a very regular ladder structure. Such case was considered by Bamford.[71] Active radicals in multimonomer - poly(vinyl methacrylate) were created from -CCl_3 end-groups in the presence of manganese carbonyl $Mn_2(CO)_{10}$ by irradiation with light, $\lambda = 435.8$ nm. The radicals are expected to initiate selectively at one end of the template.



Another type of multimonomer has been synthesized and examined by Jantas.[73] Selecting an appropriate dilution, concentration of initiator, and temperature, even if initiation is random, the polymerization leads to the ladder-type structure of the product as shown in the example of template polymerization of multimethacrylates according to following reaction:



More examples of such " zipping up" reactions are reviewed in Table 4.2.

Polymerization of multimonomers can be discussed in terms of more general problems - polymerization of multifunctional monomers. Generally speaking, two types of reaction can take place when monomer has more than one double bond: intermolecular or intramolecular reaction as shown in Figure 4.8. The reaction proceeds according to the case A as "pure template" process, while the case B leads to the crosslinked structure. Moreover, in the last case, a part of double bonds is unreacted. From the amount of double bonds and end-groups analysis,[72-75] a percentage of template reaction (case A) can be estimated. This "percentage of template reaction" depends on the polymerization conditions and the structure of multimonomer. This value seems to be a good measure of "multimonomer ability" to template polymerization.

From the examples of template polymerization carried out under special conditions,[72-75] we can see that intermolecular polymerization can be neglected. Indeed, if the concentration of monomer used is very low, and concentration of initiating radicals is

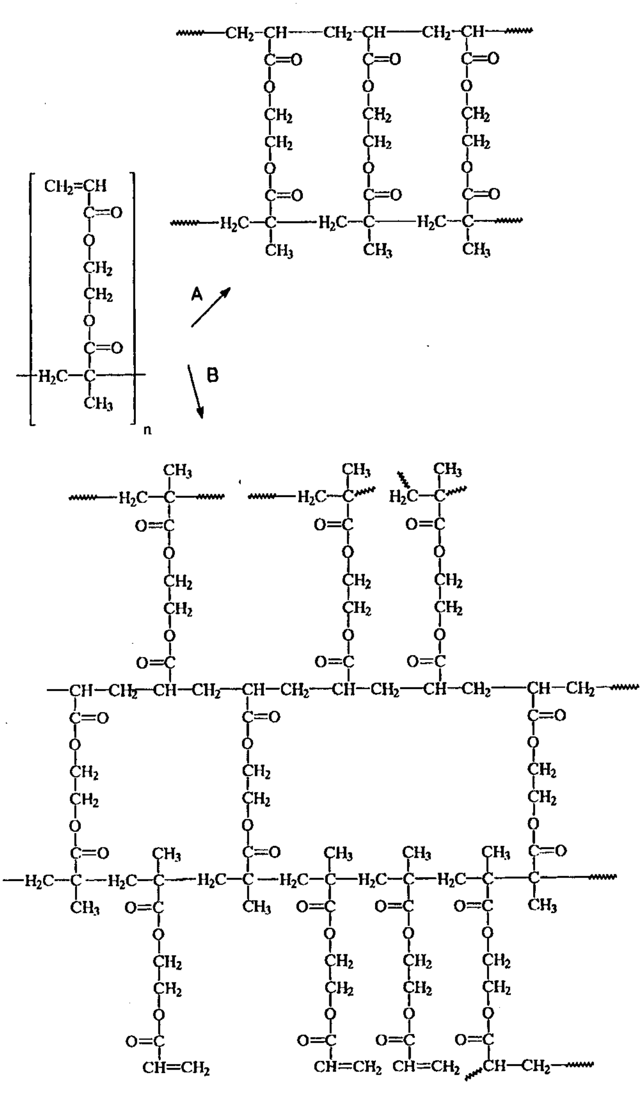


Figure 4.8. Schematic representation of multiacrylate polymerization. Template process (A), Intermolecular reaction (B). According to R. Jantas, J. Szumilewicz, G. Strobin, and S. Polowinski.[75]

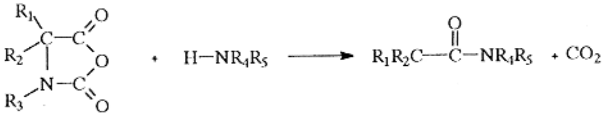
rather high, one can expect intramolecular polymerization leading to the product with ladder-type structure.

Table 4.2: Examples of multimonomers polymerization

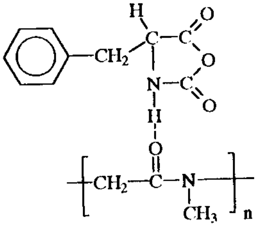
Initial polymer (multimonomer)	Initiation type	References
Poly(1,2-butadiene)	Cationic	60
Poly(3,4-isoprene)	Cationic	61
Poly(vinyl aldehyde)	Radical	62
Poly(methyl vinyl ketone)	Cationic+dehydratation	63-65
Poly(methyl vinyl ketone)	Phosphoric acid or HCl	63-65
Polyacrylonitrile	Thermal+oxidation	66
Poly(ethylene isocyanate)	γ radiation (radical)	67
Poly(vinyl methacrylate)	Radical	71,72
Poly(methacrylate p- cresyl resin)	Radical	68-70
Multimethacrylates	Radical	73
Multiallyl methacrylate	Radical	74
Multiacrylate	Radical	75

4.9 RING-OPENING POLYMERIZATION

A very interesting method of synthesis of polypeptides from N-carboxy-α-amino acid anhydrides was proposed by Ballard and Bamford.[76] Opening the ring of N-carboxy-α-amino acid anhydrides by primary or secondary amines can be illustrated by the following reaction:

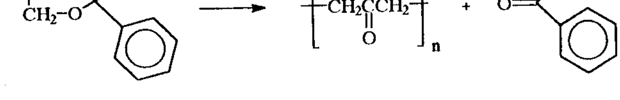


The R NH- group thus created can interact with the next molecule of the anhydride which leads to the addition of this molecule, decarboxylation, and restoration of the active center. Repetition of such a reaction gives the kinetic chain. Eventually, polypeptide with repeating units of -($NR_3CR_1R_2CO$)- was obtained. If a polypeptide containing a terminal secondary amine group is used as an initiator, a template effect can be expected. Ballard and Bamford reported[76] unusual features when polysacrosine dimethylamide was used to initiate polymerization of DL-phenylalanine NCA (N-carboxy-DL-phenylalanine anhydride), NCPA. Interaction between polysarcosine unit and molecule of phenylalanine NCA can be illustrated as follows:

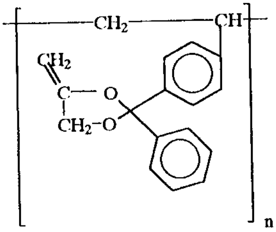


These types of interaction were confirmed by IR analysis by examination of N-H stretching vibrations in monomer and C=O stretching vibrations of the polysarcosine groups. At any step of the reaction, the monomer molecule was adsorbed onto polysacrosine. If the polysacrosine template contains at one end inactive $(CH_3)_2N$-group, and at the other end CH_3NH- group (active as an initiator), block copolymer polysacrosine/polyphenylalanine can be obtained. It was observed by the authors[76] that the rate of the reaction depends on the chain length of the template (chain effect) and also on the type of solvent used. The rate of polymerization was much higher in comparison with the polymerization in the presence of low molecular weight analogue. In nitrobenzene and chloroform, when polysacrosine with degree of polymerization 30 was used, the ratio of the rate of template polymerization to the rate of blank reaction was more then 10. It was also observed that the initial rate became independent of the concentration of monomer if concentration was sufficiently high for adsorption at all sites of the template.[77]

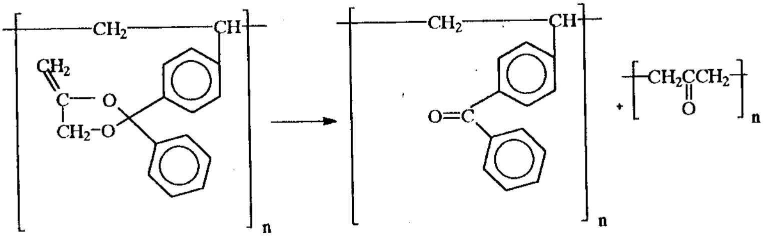
A very special type of template polymerization was presented by a group of Japanese scientists.[78,79] The method used was based on the observation that during radical polymerization of 2,2-diphenyl-4-methylene-1,3-dioxolane, elimination of benzophenone occurs according to reaction:



Similar groups can be arranged in template, or, in other words, connected with linear polymer, giving the following product:

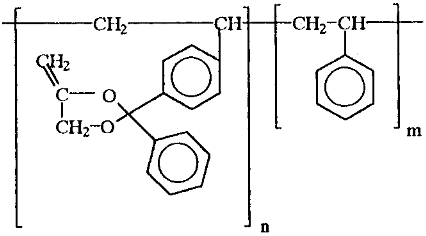


Such multimonomer can be polymerized according to reaction:



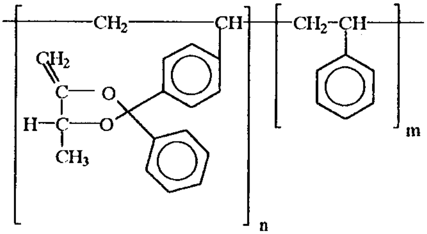
The described reaction is a very interesting case of template radical polymerization in which daughter polymer called by the authors of the article "newborn polymer" is not connected with the template by covalent bonds nor by hydrogen bridges. Separation the "newborn polymer" can be done without any operations such as hydrolysis or destruction of a polymeric complex. Examination of findings leads to the conclusion that in products of the described reaction, a small amount of graft copolymer exists.

Very interesting results were published[79] in respect of application of copolymers of 4-methylene-2-phenyl-2-(4-vinylphenyl)-1,3 dioxolane with styrene as a template:

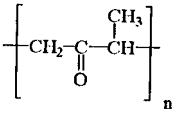


with random distribution of "n" and "m" sequences of units.

Statistical, not a block, copolymer was used. Methyl-substituted derivative was also used:



Polymerization of this compound leads to even better efficiency of “newborn polymer” with the structure:



$$-\!\left[CH_2-\underset{\underset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{CH}\right]_n\!-$$

Especially high efficiency (93%) was found when copolymer containing 60 mol% of styrene units was used. The efficiency was in this case much higher than obtained for polymerization of homopolymer-type prepolymer, both types - methylene substituted and unsubstituted. Improvement of solubility of the newborn polymer by the methyl substituent allowed to analyze the product by GPC method. It was found that molecular weight of the newborn polymer was lower then molecular weight of template polymer. It was the evidence that the newborn polymer is not connected with the template.

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5

EXAMPLES OF TEMPLATE COPOLYMERIZATION

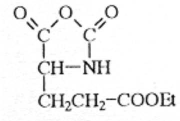
Copolymerization can be conducted stepwise (template copolycondensation), copolyaddition, radical or ionic copolymerization, ring-opening copolymerization, etc.

5.1 TEMPLATE COPOLYCONDENSATION

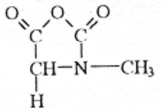
A good example of template copolycondensation has been described by Ogata *et al.*[1] Copolycondensation of 2,6-dimethyl pyridine dicarboxylate and dimethyl adipate with hexamethylene diamine was carried out in the presence of polysaccharide - Pullulane (mol. weight 30,000) used as a template. The reaction was carried out in DMSO at 60°C. It was found that the content of 2,6-dimethyl pyridine dicarboxylate units in the copolyamide, determined by NMR analysis, increased in the presence of Pullulane in comparison with the amount obtained in the absence of the template. This effect can be explained by preferential adsorption by the template of monomer having pyridine groups in comparison with the adsorption of dimethyl adipate. A set of experiments was carried out under the same conditions, but in the presence of poly(acrylonitrile) instead of Pullulane. The composition of copolyamides was the same as in copolycondensation without the template.

5.2 RING OPENING TEMPLATE COPOLYMERIZATION

Ring-opening copolymerization was simultaneously investigated with homopolymerization of N-carboxy-α-amino acid anhydrides, NCAs, by Bamford *at al.*[2,3] Polymerization of a mixture of NCAs of γ-ethyl-L-glutamate and sarcosine:



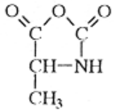
γ-Et-L-glutamate NCA



sarcosine NCA

was initiated by polysarcosine dimethylamide. Because sarcosine NCA cannot participate in the chain-effect reaction, the copolymer formed from the mixture of NCA`s has, the block structure: (sarcosine) (-ethyl-L-glutamate) (sarcosine).

Copolymerization of similar monomers was investigated by Volpe and Frisch.[4] The effect of poly(2-vinylpyridine) on the copolymerization of L-AlaNCA:



and Sarcosine NCA was determined. Since only L-AlaNCA is able to form hydrogen bonds with poly(2-vinyl pyridine), its local concentration along the template should be higher than in solution, resulting in a copolypeptide with a block structure of L-AlaNCA`s. Copolymerization was carried out in nitrobenzene solution at 25°C. Only the template with molecular weight higher than 20,000 affected the sequence of the copolypeptide. No template effect was visible when poly(2-vinylpyridine) with mol. weight of 3,100 was applied. The molecular weight of the template had a small effect on the apparent molecular weight of the resulting copolypeptides.

5.3 RADICAL TEMPLATE COPOLYMERIZATION

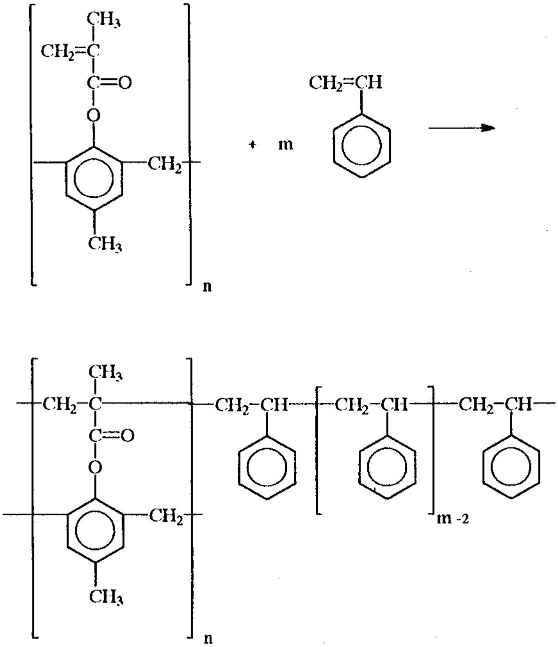
General mechanism of template radical copolymerization was described in Chapter 2. From general consideration, it is clear that two monomers in copolymerizing system can interact with the template in a different manner. Generally, we have two groups in the systems:

- at least one of the comonomers is a multimonomer (i.e., reacting units are connected with the template by covalent bonds)
- at least one of the comonomers is interacting with the template by electrostatic, dipole-dipole interactions, or hydrogen bonding.

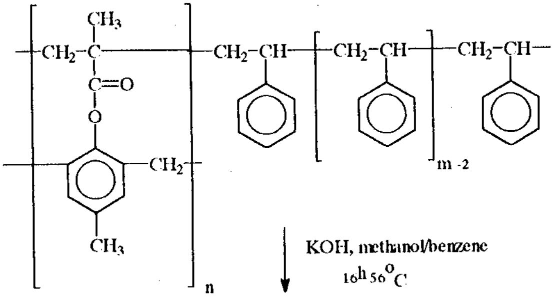
5.3.1 COPOLYMERIZATION WITH PARTICIPATION OF MULTIMONOMERS

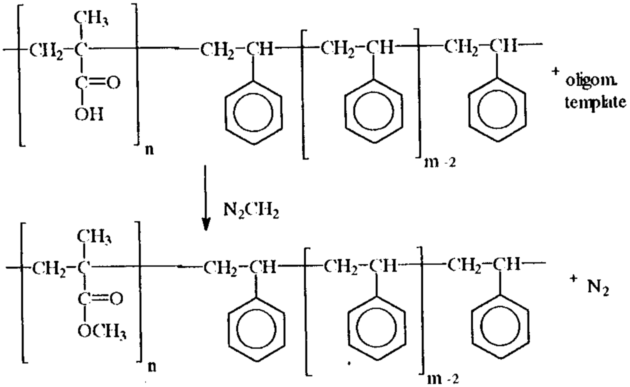
Synthesis of various multimonomers and their copolymerization with styrene, acrylonitrile or acrylic acid was described in a set of papers.[5-8] Most of the early work[5] on the copolymerization of multimonomers with vinyl monomers employed p-cresyl formaldehyde resins, esterified by methacryloyl chloride or acryloyl chloride, as one of the comonomers, and a simple vinyl monomer such as styrene or acrylonitrile as the other monomer.

In copolymerization of oligomonomers with 3, 6, and 8 units, polymerization in dilute solution in benzene initiated by AIBN or γ-rays leads to linear, or slightly branched, product with the following structure:



IR analysis shows[8] that double bonds were absent in the product within the range of an experimental error. The reaction product is composed of ladder blocks and the blocks of styrene units. In order to verify this structure, hydrolysis of the product was carried out in methanol-benzene and methanol solutions of KOH. After the hydrolysis, the product was esterified by diazomethane and styrene-methyl methacrylate copolymer was separated. The expected scheme of these reactions is as follows:



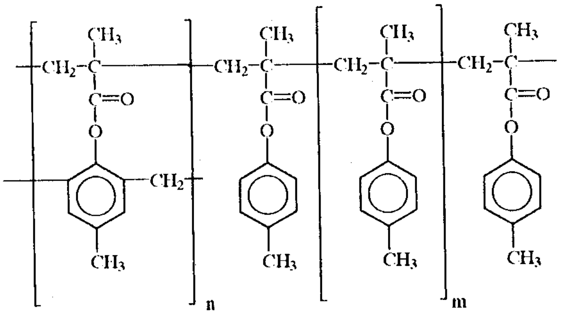


NMR study shows that the block copolymer of styrene-methyl methacrylate is present in the product of esterification. It confirms that the original copolymer consists of blocks of styrene units and the ladder type blocks. Analysis of a few fractions of the copolymer obtained from oligomeric multimonomer and styrene confirmed this type of structure. Data recalculated from publications[6,8] are presented in Table 5.1.
More than 90% double bonds react according to the template mechanism.

Table 5.1: Copolymerization of oligomeric multimonomer with styrene

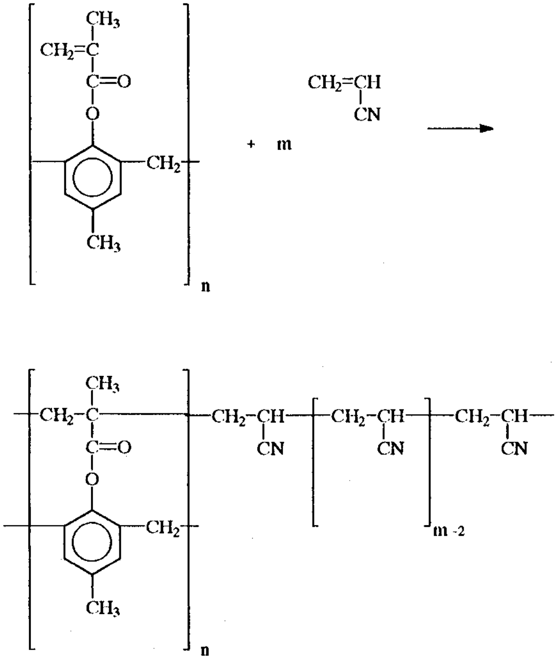
Fraction number	$M_w \times 10^{-5}$	Number of end-groups per molecule	Percentage template polymerization
2	2.50	24	97
3	2.01	20	96
4	1.07	16	93
6	0.47	12	92

Another example of copolymerization of multimonomers has been published.[7] p-Cresyl methacrylate was used as the second comonomer. It was expected that the copolymerization would occur in a similar way, and the product obtained would have the following structure:



In the product, there should be a ladder-type blocks linked by segments composed of p-cresyl methacrylate units. This type of structure was confirmed by IR and NMR spectrometry. However, by preparation of such copolymers with labeled ^{14}C end-groups (using radioactive AIBN), and by fractionating and radiometric analysis, it was shown[7] that copolymers obtained are slightly branched. There is slightly more branch points than in the case of copolymers with styrene. It could be an effect of chain transfer reaction.

Similar synthesis with acrylonitrile has been described by the following reaction scheme:[8]



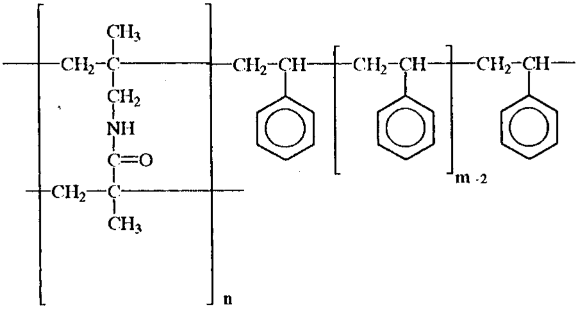
In order to determine the reactivity ratios, the relation between monomer feed and copolymers composition was examined. However, in this case the calculation of reactivity ratios is more complex than simple copolymerization of two vinyl monomers. The question arises - how can we calculate the molar ratio of comonomers? Should we use a mole concentration of both comonomers, or, for multimethacrylate concentration, should we apply a mole concentration of reactive groups (double bonds)? Both methods are used and discussed in the literature. The results of reactivity ratio computations are presented in Table 5.2

Table 5.2: Reactivity ratios for copolymerization of p-cresyl formaldehyde oligomers with methacrylic groups (10) and styrene (2). [Reproduced from S. Polowinski, Polimery, 39, 419 (1994), with kind permission from I. Ch. P.]

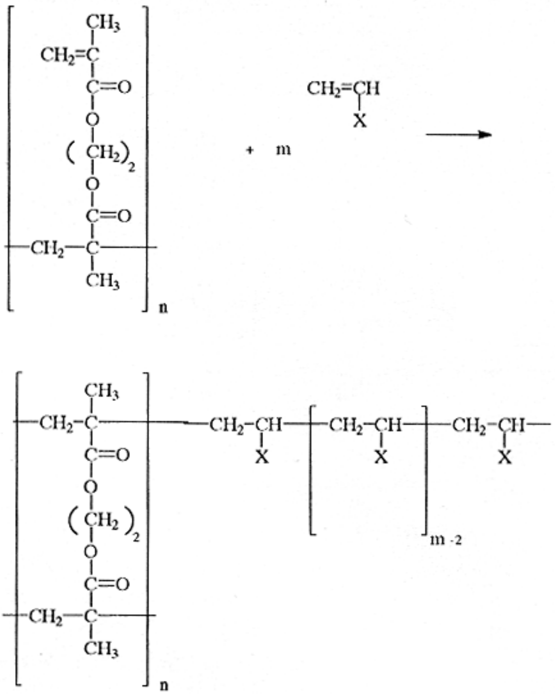
Number of units in template	Method I*		Method II**	
	r_1	r_2	r_1	r_2
9	0.066	10.3	0.012	2.36
7	0.070	8.9	0.015	2.55
5	0.089	8.0	0.015	2.85

*mole concentration of units with double bonds; **mole concentration of whole multimonomer

Another type of multimonomer was prepared from poly(methacryloyl chloride) and allilamine, and was used in order to examine copolymerization process with styrene.[10,11] The copolymerization was carried out in dioxane with AIBN as initiator. The basic reaction leads to the product with ladder-type blocks of allylmethacrylamide units, and blocks consist of styrene units:



The chain transfer reaction played an important role, particularly because of abstraction of the active hydrogen at α-carbon from the allyl group. Moreover, unreacted double bonds were present in the copolymer obtained. The influence of chain transfer reaction could be diminished by applying multimonomers which do not contain allyl groups. This was shown in the example of copolymerization of multimethacrylate prepared by esterification of poly(2-hydroxyethyl methacrylate) with methacryloyl chloride.[12-16] Copolymerization of the multimethacrylate with vinyl monomers such as styrene or acrylonitrile can be represented by the reaction:



where: x - benzene ring or CN.

The copolymerization within a wide range of initial compositions of the monomer mixtures was carried out in DMF solution in the presence of AIBN labeled with C.[14] The residual unsaturation (molar ratio of the unsaturated pendant methacrylate groups to the total methacrylate groups linked with the template chain in the copolymer) is rather low (from 0.01 to 0.08). Also, a number of branching points can be estimated at 1-2 per hundred repeating units. These results confirm the conclusion that propagation occurs along the template and leads to rather long ladder-type blocks linked with blocks consisting of styrene or acrylonitrile units.

The problem of the relationship between reaction conditions and structure of copolymers obtained from multimethacrylate and styrene as well as from multimethacrylate and acrylic acid has been discussed.[15] The method used was similar to the method described above. A description of the structure of these copolymers could be based on the following consideration. Because of random initiation and termination processes as well as a possibility of partial propagation "across" the template, we can expect that the product obtained contains unreacted double bonds and crosslinking points. The general structure of such macromolecule can be illustrated by Figure 5.1.

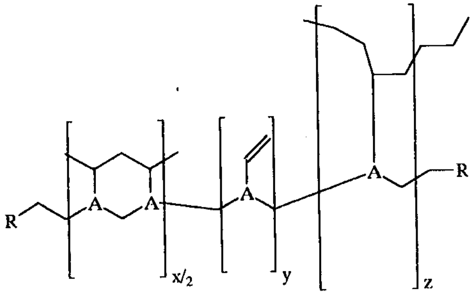


Figure 5.1. Schematic representation of copolymerization of multimonomer with vinyl monomer.

We can assume that on average for one macromolecule of product obtained, there are X units with ladder-type structure, Y unreacted groups with double bonds, and Z points of crosslinking. The scheme of copolymerization of multimethacrylate with acrylic acid and a possible structure of the product obtained are presented in Figure 5.2.

Using labeled ^{14}C initiator and radiometric analysis, the number of initiator fragments from the number of end-groups, R, can be evaluated and the number of crosslinking points can be calculated. The number of unreacted double bonds can be found by the bromometric method. On the basis of such analysis, we can find the percentage of units in the multimonomer which had reacted according to template mechanism. The results of the calculations for two examined systems are presented in Tables 5.3 and 5.4

Only a few percents of double bonds in multimonomer react "across" the template. A large majority of double bonds reacts along the template.

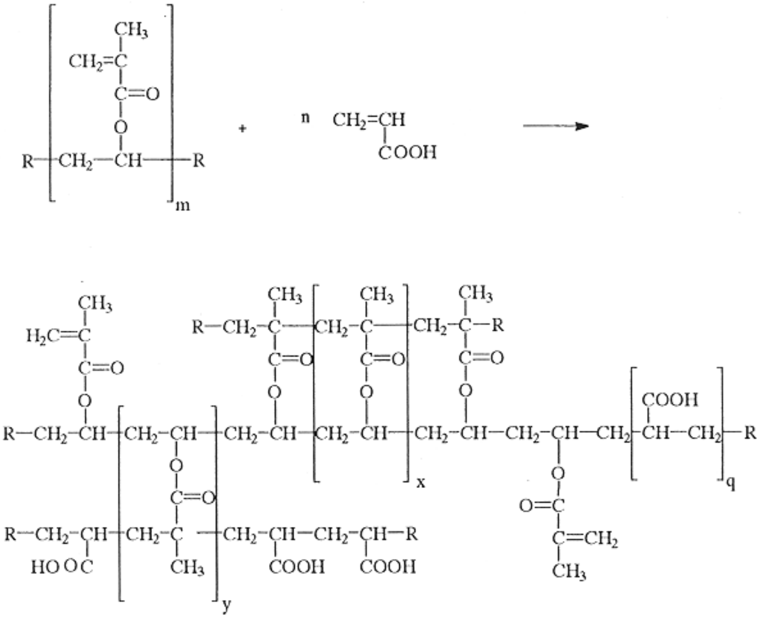


Figure 5.2. Copolymerization of multimethacrylate with acrylic acid.

Table 5.3: Copolymerization of poly(vinyl methacrylate) with acrylic acid

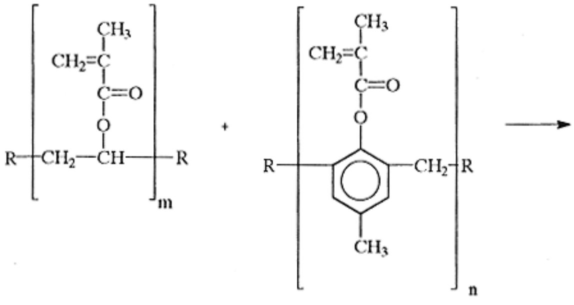
MM in monomer feed mol%	Unreacted double bonds %	Number of end-groups per molecule	Template reaction %
9.71	3	4.0	97
19.79	3	3.8	97
28.59	4	4.3	96
40.82	6	4.8	94

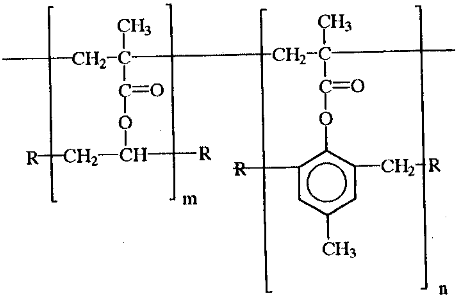
Table 5.4: Copolymerization of multimethacrylate with styrene

MM in monomer feed %	Unreacted double bonds %	Number of end-groups	Template reaction %
5.17	12	15.1	82
18.45	15	14.9	83
34.45	13	10.4	86
67.76	16	6.9	84
$[C^{14}\text{-AIBN}]\times10^{3}$			
0.89	19	7.0	81
4.31	15	16.2	83
8.07	-	26.4	-
15.95	6	41.0	84

5.3.2 COPOLYMERIZATION OF TWO DIFFERENT MULTIMONOMERS

Only one paper [15] has been published on copolymerization of two different multimonomers. One of them was poly(vinyl alcohol) esterified by methacrylyl chloride. The second was p-cresyl formaldehyde resin, with molecular weight corresponding to the tetramer, esterified by methacryloyl chloride. The predicted structure of both multimonomers was confirmed by IR spectrometry, H NMR spectrometry, and molecular weight determination by osmometric method. Copolymerization of these two multimonomers was carried out in DMF at 90°C using AIBN as an initiator. The predicted course of the reaction was as follows:





The copolymerization product was soluble in DMF and in chloroform. When the reaction was complete the product was precipitated with methanol, redissolved in chloroform, reprecipitated with methanol, and then dried. Hydrolysis of the copolymer followed by separation and analysis shows that one of the products of the hydrolysis is poly(vinyl alcohol) with molecular weight similar to that of the initial PVA. All these findings lead to the conclusion that by the copolymerization of two different multimonomers a copolymer with two ladder-type blocks can be obtained. However, the possibility that the copolymer is slightly branched cannot be excluded, and the assumption that mainly ladder-type, linear structure exists still needs confirmation.

There is no information in the literature up to now on polymerization of multimonomer in which two different types of groups are connected with one template by covalent bonds. In principle, such polymerization should lead to the ladder-type product, and, after hydrolysis, to the copolymer with composition controlled by the composition of the initial template.

5.3.3 COPOLYMERIZATION WITHOUT MULTIMONOMERS

The second case of template copolymerization deals with the systems in which at least one comonomer is interacting with the template by intermolecular forces, such as hydrogen bonding, dipole-dipole interaction, etc.

One of the examples[17] deals with the system in which one comonomer (A) forms a complex with the template, while the other comonomer (B) reveals a weak interaction or is not interacting with the template at all. The mechanism can be illustrated by Figure 5.3. Black circles represent comonomer molecules (A) which interact with the template, white - molecules of the second monomer (B) not interacting with the template. The first step of the copolymerization takes place without any interaction of the template until the sequence of A units of a proper length is created. Then, complexation occurs, and after complexation copolymerization proceeds along the template until a sequence of B units appears which is long enough to tear away the growing macroradical from the template. The copolymerization occurs again without the influence of the template until a proper sequence of A units appears.

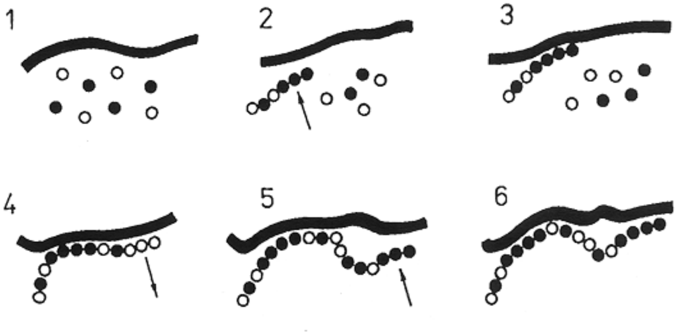


Figure 5.3. Schematic representation of the matrix copolymerization. Reprinted from S. Polowinski, *J. Polym. Sci., Polym. Chem.*, **22**, 2887 (1984).

As mentioned in Chapter 2, if two comonomers are not connected with the template by covalent bonds, reactivity ratios can be calculated on the basis similar to the conventional copolymerization. The only difference is that reactivity ratios r_1 and r_2 for both monomers depend on the concentration of the template. In order to compare experimental data with these considerations, copolymerization of methacrylic acid with styrene was carried out in the presence of PEG (mol. wt. 20,000) as the template. The reactivity ratios r_1` and $r_2$` can be calculated according to the Kellen-Tüdös method. The results are shown in the Figure 5.4. According to this method, a proper functions of monomer mixture composition, R, and copolymer composition, E, were plotted:

$$\eta = [R(E-1)]/(E+R^2); \quad \xi = R^2/(E+R^2); \quad \alpha = 0.8 \qquad [5.1]$$

Good agreement of experimental points with plotted straight line confirmed that the equation similar to the Mayo-Lewis relation can be used. Changing the concentration of the template, the reactivity ratio r` changes from 0.74 (copolymerization without the template) to 1.14 (for equimolar concentration of the template). Changes of r` for styrene were smaller (0.36 to 0.47). In copolymerization of methacrylic acid with methyl methacrylate, the presence of PGE (mol. wt. 20,000) significantly influences the reactivity ratios of both monomers. This is probably because both monomers are interacting with the template which confirms the presented theory.

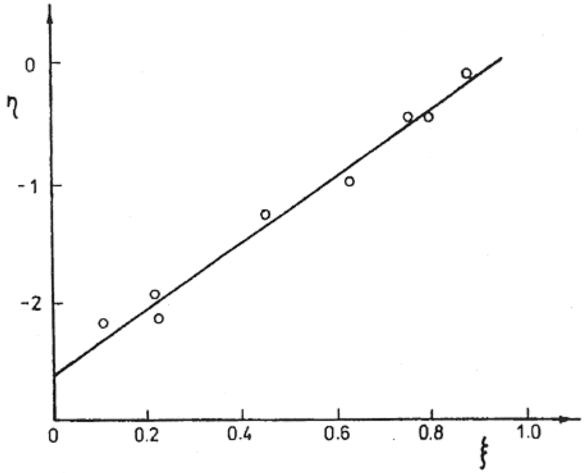


Figure 5.4. Kellen-Tüdös plot for calculation of reactivity ratios from composition of monomer mixture, R, and composition of copolymer, E; Copolymerization of methacrylic acid with methyl methacrylate in the presence of PEG 20,000. Reprinted from S. Polowinski, *Eur. Polym. J.*, **19**, 679 (1983) with kind permission from Elsevier Science Ltd.

Recently copolymerization of methacrylic acid with acrylic acid in the presence of the same template (PGE 20,00) was investigated.[19] Reaction was carried out in benzene or toluene solutions at 70°C using AIBN as initiator. A good correlation with the Mayo-Lewis equation was found, and r_1` (for methacrylic acid ) and $r_2$` (for acrylic acid) were computed. Also in this case the presence of template brings about a slight increase in r_1` and decrease in $r_2$` in comparison with the respective reactivity ratios for copolymerization without template. The same procedure was applied for template copolymerization in dioxane. However, in this case the results show considerable anomaly. A curvilinear course of the relationship predicted by the Kellen and Tüdös equation makes it impossible to find reactivity coefficients. Data obtained for the three pairs of monomers discussed here are presented in Table 5.5. The probability of addition of B-units to A-radical (P_{AB}) or A-unit to B (P_{BA}) depends on the corresponding reactivity ratios. More generally, change in reactivity ratios r_1 and r_2 leads to the change in any probability of unit sequence - for instance the probability of AAA triad formation.

From the composition equations described in the Chapter 2, the following relations between average length of units sequence and reactivity ratios can be derived:

$$\langle l_A \rangle = r_1 x + 1; \quad \langle l_B \rangle = (x + r_2)/x \qquad [5.2]$$

where x - composition of the monomers in feed, $<l_A>$ and $<l_B>$ are average length of units A and B, respectively. Table 5.6 illustrates the influence of the template on the sequence length for copolymerization of methacrylic acid (monomer A) with styrene, methyl methacrylate or acrylic acid (monomer B).[23]

Table 5.5: Template copolymerization of methacrylic acid, MA, with styrene (S), acrylic acid, AA, or methyl methacrylate, MM. Template: PEG 20,000. solvent:toluene

	r_1 (MA)	r_2	Second monomer
No template	0.74	0.36	S
With template	1.14	0.47	S
No template	2.12	0.42	AA
With template	2.77	0.29	AA
No template	1.50	0.55	MM
With template	2.10	0.10	MM

Table 5.6: Average length of sequence units for copolymerization of methacrylic acid with equimolar mixtures of comonomers. Template: PEG 20,000. [Reproduced from S. Polowinski, Polimery, 39, 417 (1994), with kind permission from I. Ch. P.]

Monomer B	Styrene		Methyl methacrylate		Acrylic acid	
	$<l_A>$	$<l_B>$	$<l_A>$	$<l_B>$	$<l_A>$	$<l_B>$
No template	1.74	1.36	2.50	1.55	3.12	1.42
With template	2.14	1.47	3.10	1.10	3.64	1.20

Copolymerization of methyl methacrylate with styrene in the presence of isotactic poly(methyl methacrylate) has been examined by O`Driscoll and Capek.[20] Copolymerization was carried out in acetone at 0^oC and redox system: benzoyl peroxide - dimethylaniline was used to initiate the polymerization process. Carrying out the process with various ratios of styrene to methyl methacrylate, it was found that the polymerization rate drops very quickly with the increase in styrene concentration. A very small amount of styrene destroys any template effect that it-poly(methyl methacrylate) exerts on the rate of the polymerization. Assuming, that the reactivity ratios are not changed by the template ($r_1 = r_2 = 0.5$), the critical length of the sequence of methacrylic units is 10- 20. Complexation occurs only if longer sequences, composed of methacrylic units, are present in the copolymer. This result is in accordance with the suggestion that the interaction between it-PMM and st-PMM is based on the stereocomplex formation.[21]

The influence of template on the sequence distribution was examined by Frisch and Qihua Xu.[22] Using direct methods (NMR both ^{1}H and ^{13}C), the authors have shown that copolymerization of methacrylic acid with styrene onto poly(2-vinyl pyridine) as a template, can be described by Markovian 1st order statistics. It was found that the presence of the template leads to copolymers with longer average sequences for both types of units. Both probabilities: P_{AA} and P_{BB} were found to be significantly larger than those in the non-template systems. Triad sequence for M centered triads measured by NMR are shown in Table 5.7.

Table 5.7: Observed triad sequence for copoly(St/MA). [Reprinted from H. L. Frisch and Qihua Xu, Macromolecules, 25, 5145 (1992), with kind permission from ACS.]

	St mol. fraction	MMM	SMM	SMS
No template	0.50	0.170	0.230	0.100
With template	0.54	0.240	0.170	0.050
No template	0.53	0.186	0.220	0.064
With template	0.41	0.403	0.159	0.029
No template	0.55	0.146	0.212	0.088
With template	0.47	0.345	0.158	0.030
No template	0.61	0.120	0.185	0.087
With template	0.63	0.249	0.104	0.020

In spite of the fact that the composition of copolymers for the template and non-template set of experiments is not exactly the same, one can see from the data presented in Table 5.7 that the fraction of MMM triads is much higher for the copolymers obtained in the template system. Assuming the first order Markovian statistics, the following set of equations can be applied:

$$[MMM] = F_1P_{11}^2$$

$$[MMS] = F_1P_{11}(1 - P_{11}) + F_2(1 - P_{22})P_{11}$$

$$[SMS] = F_2(1 - P_{22})(1 - P_{11}) \qquad [5.3]$$

$$F_1 = [MMM] + [MMS] + [SMS]$$

$$F_1(1 - P_{11}) = F_2(1 - P_{22})$$

where F_1 and F_2 are molar fractions of methacrylic and styrene units in copolymer, respectively, and P_{11} and P_{22} are probabilities of MM or SS diades in copolymer, or in other words probabilities of connection of monomer M to M macroradical (P_{11}) or monomer S to S macroradical (P_{22}) during copolymerization process. On the basis of this set of equations, P_{11} and P_{22} and average sequence lengths for both types of units (methyl methacrylate and styrene) were calculated.

Table 5.8: Statistical probabilities and average and sequence lengths for template, T, and non-template, N, systems. [Reprinted from H. L. Frisch and Qihua Xu, Macromolecules, 25, 5145 (1992), with kind permission from ACS]

System	Composition, mol. fraction		Probabilities		Average sequence length	
	MA	ST	P_{11}	P_{22}	$<l_{MA}>$	$<l_{ST}>$
N	0.50	0.50	0.59	0.59	2.44	2.44
T	0.46	0.54	0.72	0.76	3.57	4.17
N	0.47	0.53	0.63	0.67	2.70	3.03
T	0.59	0.41	0.83	0.75	5.88	4.00
N	0.45	0.55	0.57	0.65	2.33	2.86
T	0.54	0.47	0.80	0.77	5.00	4.35
N	0.39	0.61	0.55	0.71	2.22	3.45
T	0.37	0.63	0.82	0.89	5.56	9.09

Donor-acceptor interaction between monomer and polymer template offers an elegant methods of replication degree of polymerization. Similar system was described for copolymerization of vinylpyridine with p-chlorostyrene in the presence of poly(maleic anhydride) used as template.[24]

It was found that a mixture of 4-vinylpyridine with p-chlorostyrene copolymerizes without any initiator in the presence of poly(maleic anhydride) at 50°C in DMF. The fact that poly(maleic anhydride) cannot initiate the polymerization of styrene or phenyl vinyl ether shows that poly(maleic anhydride) does not act as a normal anionic or cationic initiator. The compositions of copolymers obtained with various initial compositions of comonomers were analyzed. The copolymer composition curve, which deviates greatly from the composition curve obtained from conventional radical copolymerization is attributed to a stronger interaction of poly(maleic anhydride) to 4-vinyl pyridine than to p-chlorostyrene.

On the basis of these examples, we can see that using templates connected by covalent bonds, we can produce a new class of copolymers - semi-ladder block copolymers - with blocks of ladder-type structure. By hydrolysis, the template can be removed and block copolymers with defined length of block can be obtained. Such synthesis by conventional copolymerization is very difficult and sometimes impossible.

Also copolymers with non-conventional structure can be obtained by copolymerization in the presence of templates interacting with comonomers. Average length of sequences of units is in such products higher. Changing the template concentration we can influence the reactivity ratios of monomers and the structure of the product.

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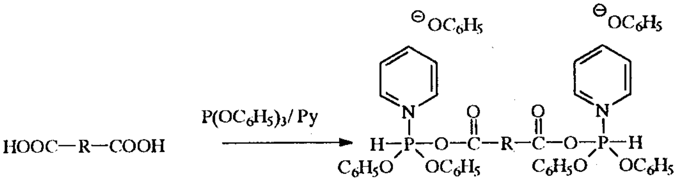
6

EXAMPLES OF TEMPLATE POLYCONDENSATION

Strong interactions between monomer and template are essential in template reactions. Extreme conditions of conventional high-temperature polycondensation or very high reactivity of substrates in low-temperature polycondensation make ordering of monomer molecules along the template difficult. Mild conditions are a prerequisite for the template polycondensation. One of the ways for polycondensation to occur under mild conditions is a direct polycondensation activated by triphenylphosphite in the presence of pyridine or N-methylpyrrolidone with LiCl. It is known that activated synthesis of polyamides or polyesters can involve the use of precursors or coreactants such as phosphorylating agents, which are able to produce activated intermediates *in situ* under mild conditions. These intermediates contain P-N and P-OCO bonds, which are very susceptible to acidolysis or alcoholysis reactions. The process is similar to the energy transfer in living cells with adenosine triphosphate, ATP. For instance, dicarboxylic acids are activated by $P(OC_6H_5)_3$/pyridine according to the reaction:



This type of reaction was a base for polycondensation reactions in the presence of preformed macromolecular compounds. It was found[2] that high molecular weight poly(terephtalamides) are obtained by use of poly(4-vinylpyridine), P4VP, in the place of pyridine. The results are presented in the Table 6.1

The lower the rate of pyridine association to the Py/P4VP template the higher the molecular weight (viscosity) of polymer formed. The molecular weight and amount of

P4VP added and also the type of solvent used affect the molecular weight of the resulting polyamides. In the reaction with P4VP, the template was assumed to be involved both in the increasing local concentration of acids through adsorption and in the activation, via the N-phosphonium salt of P4VP.

The addition of poly(ethylene oxide), PEO instead of P4VP also increases the inherent viscosity of the polymer produced.[2] The data obtained are presented in Table 6.2.

Table 6.1: Polycondensation of terephthalic acid, TPA, and 4,4'-diaminodiphenylmethane, MDA, in the presence of poly(4-vinylpyridine) in N-methylpyrrolidone-pyridine solvent. [Reprinted from N. Yamazaki and F. Higashi, Adv. Polym. Sci., 38, 1 (1981)]

Py ml	NMP ml	P4VP g	Py/P4VP mol/unit mol	η_{inh}*
5	45	1.0	6.5	1.13
10	40	1.0	13	1.04
10	40	0.5	26	1.17
20	30	1.0	26	0.67
20	30	0.0	-	0.33

*measured in H_2SO_4 at 30°C; TPA=MDA=0.01 mol; $P(OC_6H_5)_3$=0.022 mol; P4VP (MV)=1.0×10^5; LiCl=2.0 g; time=2 h; temperature=100°C

Table 6.2: Effect of the amount of poly(ethylene oxide), PEO, on the polymerization of terephthalic acid, TPA, and 4,4'-diaminodiphenylmethane, MDA, in the presence of triphenyl phosphite. [Reprinted from N. Yamazaki and F. Higashi, Adv. Polym. Sci., 38, 1 (1981)]

PEO amount g	PEO wt%	PEO unit mo/mol TPA	Polymer η_{inh}*
0	0	0	0.33
0.125	0.25	0.28	0.91
0.25	0.5	0.56	1.0
0.5	1.0	1.14	0.88
1.0	2.0	2.27	0.74
2.0	4.0	4.54	0.61

*measured in in H_2SO_4 at 30°C; TPA=MDA=0.01 mol; $P(OC_6H_5)_3$=0.022 mol; PEO (MW)=3-5×10^5; LiCl=2.0 g; Py/NMP=20/30 ml/ml; time= 2 h; temperature=100°C

When the ratio of template to acid is close to 0.5, the viscosity of the product is more than 3 times higher than the viscosity of the polymer obtained without the template. PEO participates in the change of local concentration by interaction with carbonyl groups, but not in the activation.[2] Solution of LiCl in N-methylpyrrolidone with $P(OC_6H_5)_3$ was found very effective system for synthesis of amides by the direct reaction of acids with amines in the presence of polymeric matrix.[4] High molecular weight poly(aminoacids) obtained by direct polycondensation reaction, promoted by triphenyl phosphite and LiCl in the presence of poly(vinylpyrrolidone), were synthesized by Higashi *et al*.[4] The results for polymerization of L-leucine in the presence of poly(vinyl pyrrolidone) are presented in the Table 6.3.

Table 6.3: Effect of the amount of poly(vinyl pyrrolidone), PVP, on the polymerization of L-leucine using triphenyl phosphite in NMP. [Reprinted from N. Yamazaki and F. Higashi, Adv. Polym. Sci., 38, 1 (1981)]

PVP amount g	PVP unit mol/mol of monomer	Yield %	Polymer η_{inh}*	M_n**
0	0	72	0.14	2,111
0.5	0.45	83	0.45	15,272
1.0	0.9	86	0.48	17,037
1.5	1.35	55	0.63	27,013

Table 6.4: Effect of the molecular weight of poly(vinyl pyrrolidone), PVP, on the polycondensation reaction of L-leucine. [Reprinted from N. Yamazaki and F. Higashi, Adv. Polym. Sci., 38, 1 (1981)]

PVP molecular weight	Polymer yield, %	η_{inh}	M_n
1×10^4	94	0.09	1,000
4×10^4	86	0.14	2,111
3.6×10^5	83	0.73	34,674

L-leucine=$P(OPh)_3$=0.01 mol; PVP=1 g; Li=1.0 g; NMP=30 ml; temperature=80°C; time=16 h

The presence of poly(vinylpyrrolidone) in the system increases substantially molecular weight of poly(L-leucine) obtained. If the ratio of template to monomer is 1.35, the molecular weight is more then 10 times higher than for the blank reaction. The influence of molecular weight of PVP template on the molecular weight of the daughter polymer was very significant as seen from the Table 6.4.

Polymerization of L-leucine in the presence of PVP with molecular weight $1x10^4$ gives polyleucine with M=1,000, while use of PVP with molecular weight $3.6x10^5$, leads to daughter polymer with M almost 35,000. Polycondensation of various amino acids by the synthesis with triphenyl phosphite in the presence of PVP is presented in Table 6.5.

Table 6.5: Polycondensation of various amino acids by means of triphenyl phosphite in the presence of PVP. [Reprinted from N. Yamazaki and F. Higashi, Adv. Polym. Sci., 38, 1 (1981)]

Amino acid	Yield, %	η_{inh}
L-leucine	83	0.73*
DL-leucine	75	0.62*
L-phenylalanine	66	0.65*
DL-phenylalanine	67	0.62*
L-methionine	55	0.78**
DL-methionine	53	1.09**
L-valine	19	0.34*
β-alanine	52	1.36***

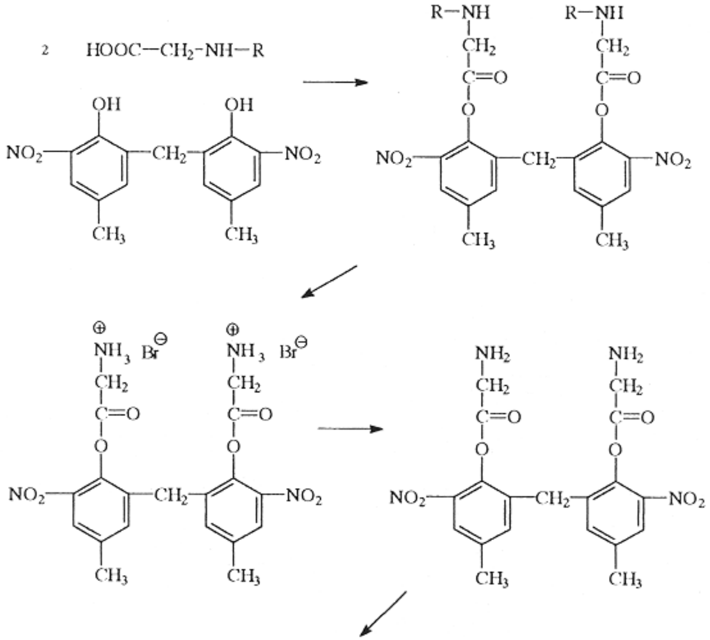
*measured at 0.5% concentration in dichloroacetic acid at 30°C; **measured at 0.5% concentration in m-cresol at 30°C; ***η_{sp}/c measured at 0.5% concentration in formic acid at 35°C; [monomer]=$[P(OPh)_3]$=0.01 mol; PVP (MW=3.6×10^5)= 1

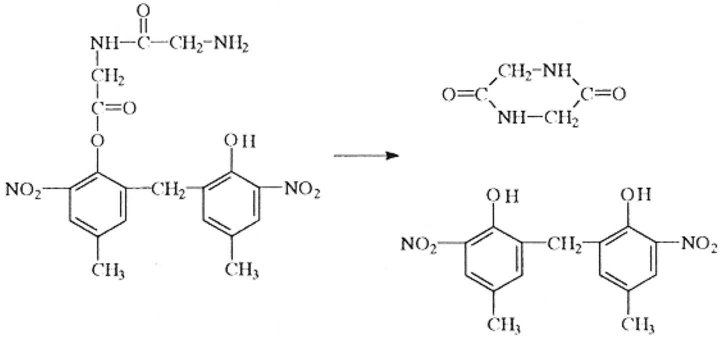
Template polycondensation through hydrogen bonding interaction was investigated by Ogata *at al*.[5,6] In the set of papers, the process of polycondensation of diethyl mucate, DEM, and dimethyl tartrate, DMT, with hexamethylenediamine, HMD, in the absence of the template was described and compared with the presence of the template. The reaction was carried out at 60°C in dimethylsulfoxide. The rate of polycondensation of DMT with HMD was rarely enhanced by the presence of the template. The rate of the polycondensation of DEM with HMD in the presence of P4VPy was slightly higher than in the absence of the template and in the presence of pyridine.

More pronounced is the influence of template on the molecular weight of the daughter polymer. The polycondensation of DEM with HMD in the presence of P4VPy yielded a polyamide with a much higher molecular weight than in the absence of P4VPy. The molecular weight of the resulting polyamide increased with increasing molecular weight of P4VPy. The chemical structure of template had a fundamental influence on the polycondensation of hydroxyl diesters with hexamethylenediamine.

It was found[7,8] that polycondensation in the presence of polysaccharides was greatly accelerated by the addition of Pullulan MW 30,000 and MW 10,000, saccharose, or cyclodextrine. Also, poly(vinyl alcohol), PVA, and poly(vinyl pyrrolidone) can play a role of template in this reaction. The rate of polycondensation in the presence of PVP was greater than in the presence of N-methyl pyrrolidone or in the absence of template. Polycondensation of DMT with HMD was slightly enhanced by the PVA template. The optimum molar ratio of monomer to PVA template (calculated as a repeating unit) to accelerate the polycondensation was 1/3 - 1/2.

Template oligomer synthesis was described by Böhmer and Kämmerer.[10] Using p-cresyl-formaldehyde oligomers as a frame of the template, esters of aminoacids were prepared. The reaction, which may be considered as a model of a template reaction, was studied in its simplest form, based on the synthesis of cyclic dimers. The process can be represented by the following set of reactions (R - carbobenzoxy group):





The generalization of the reaction described by Kämmerer and Böhmer,[9] using p-cresylformaldehyde polymers with higher molecular weight as templates, may lead to poly(amino acids) with higher molecular weight.

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7

SECONDARY REACTIONS IN TEMPLATE POLYMERIZATION

General question related to the template polymerization is how to distinguish between template and non-template reactions? The problem is mainly of definition. If template polymerization is defined as a process proceeding only on template, and replication of degree of polymerization is expected, one can classify most processes described in this book as "partially template-related". Any process can be divided to template polymerization and secondary reaction-polymerization in "free solution". This rigorous approach can be illustrated by the results published by Muramatsu and Shimidzu[1] which deal with polymerization of acrylic acid in the presence of poly(vinylpyrrolidone). The process is recognized by the majority of authors[2,3,4,5] as a template polymerization. However, Muramatsu and Simidzu[1] present arguments that the polymerization of acrylic acid in aqueous system initiated by $K_2S_2O_8$ in the presence of poly(vinylpyrrolidone) cannot be explained as a "replica polymerization". The authors found that mole ratio $[PVP]/[AA]_0$ at which the rate of the polymerization was at its maximum changed with the initial monomer concentration. Propionic acid (a low molecular weight analog of the monomer), added to the process, did not affect the rate of the polymerization. The composition of the polymer complex obtained in the polymerization varied with the complex-forming conditions. All these findings led the authors to the conclusion that polymerization proceeds not as template process. Two model mechanisms were considered by the authors:

- specific-site binding mechanism (replica polymerization of acrylic acid absorbed on poly(vinylpyrrolidone))
- polymer-atmosphere binding mechanism (the monomer drawn atmospherically by PVP)

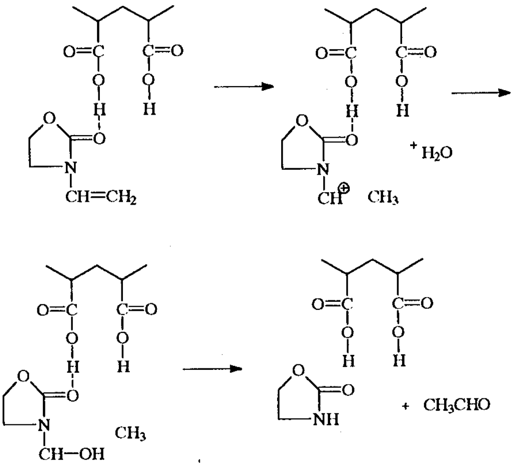
In fact, the first mechanism was accepted as a template polymerization by majority of authors[2,3,4,5,6] and, in principle, it is in a good agreement with the theory developed by Tan and Alberda van Ekenstein[7] presented in Chapter 3. However, according to Muramatsu and Shimidzu,[1] the experimental results did not agree with equations deduced from these assumptions. The authors concluded that polymer-atmosphere binding mechanism is more adequate to explain the experimental results. The overall polymerization rate, V_{ov}, depends on the volume fraction of polymer domain, f, in which concentration of monomer is M_p, and concentration of monomer, M_f in "free volume", i.e. in volume fraction (1-f). The relationship of parameters can be expressed, as follows:

$$V_{ov} = fk[M_p]^{1.5} + (1-f)k[M_f]^{1.5} \qquad [7.1]$$

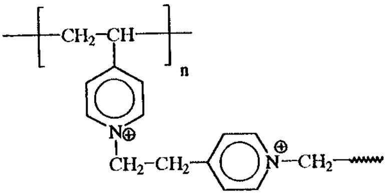
In both parts of the system the rate constant k is the same. Accepting, however that any reaction involving the polymer chain in proximity of template molecules, during at least part of its lifetime, may be called template or matrix polymerization. Polymerization proceeding outside the template is the secondary reaction. It is also convenient to generalize this definition to the step reactions, including in the template polymerization such cases in which polymerization proceeds only "partially" on the template.

Secondary reactions usually proceed in addition to template polymerization of the system: template-monomer-solvent. They influence both kinetics of the reaction and the structure of the reaction products. Depending on the basic mechanism of reaction, typical groups of secondary reactions can take place. For instance, in polycondensation, there are such well known reactions as: cyclization, decarboxylation, dehydratation, oxidation, hydrolysis, etc. In radical polymerization, usually, in addition to the main elementary processes (initiation, propagation and termination), we have the usual chain transfer to the monomer or to the solvent which change the molecular weight of the product obtained. Also, chain transfer to the polymer leads to the branched polymer.

In ring-opening polymerization many additional reactions can take place between monomer, solvent, and template depending on the chemical structure of the substrates. When the template or daughter polymer possesses a polyelectrolite character, dissociation takes place. The pH of the system is changed and leads to possibility of additional secondary reactions. A good example of the significance of the secondary reactions in radical template polymerization was described by Endo *et al.*[8] The authors examined polymerization of N-vinyl-2-oxazolidone in aqueous solutions using $K_2S_2O_8$ as an initiator. In solutions with pH=4, in addition to template polymerization, a large amount of acetaldehyde was formed. In some experiments, about 60% monomer was converted to 2-oxazolidone and acetaldehyde. It was suggested that the carboxylic group can activate absorbed molecules of N-vinyl-2-oxazoline according to reaction:



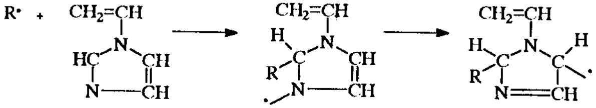
In radical template polymerization, when only weak interaction exists between monomer and template and pick-up mechanism is commonly accepted, the reaction partially proceeds outside the template. If macroradical terminates by recombination with another macroradical or primary radical, some macromolecules are produced without any contact with the template. In fact, such process can be treated as a secondary reaction. Another very common process - chain transfer - proceeds simultaneously with many template polymerizations. As a result of chain transfer to polymer (both daughter and template) branched polymers appear in the product. The existence of such secondary reactions is indicated by the difficulty in separating the daughter polymer from the template as described in many papers.[9] For instance, template polymerization of N-4-vinyl pyridine is followed, according to Kabanov *et al.*,[10] by the reaction of poly(4-vinylpyridine) with proper ions. The reaction leads to the branched structure of the product:



Ferguson and Shah[6] showed that, parallel to polymerization of acrylic acid in the presence of poly(vinylpyrrolidone), graft copolymer is formed. The reaction product was separated using paper electrophoresis. In contrast to the complex obtained by mixing of poly(acrylic acid) with poly(vinyl pyrrolidone), the product of template polymerization gives a distinct spot, identified as a graft copolymer. The existence of graft copolymers was confirmed in the next papers.[11,12]

In contrast, similar examination[13] of the product obtained by template polymerization of acrylic acid on poly(ethylene imine), using electrophoresis, leads to the conclusion that in this case graft copolymer is absent.

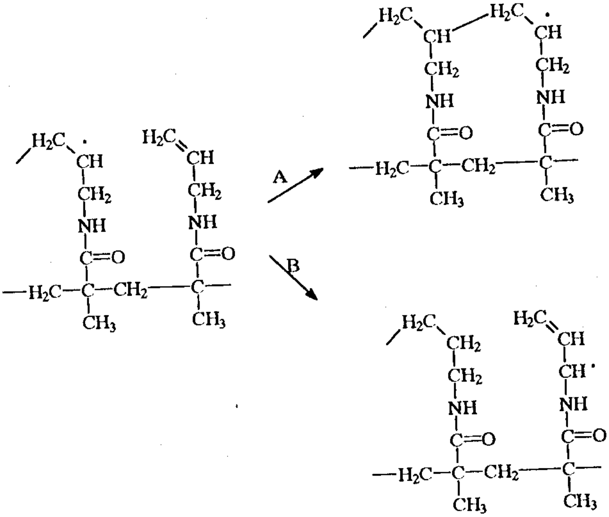
Chain transfer to the monomer is discussed by Van den Grampel in connection with polymerization of N-vinylimidazole in the presence of poly(methacrylic acid).[14] Degradative addition by a radical at the 2-position of the imidazole ring can be illustrated by the reaction:



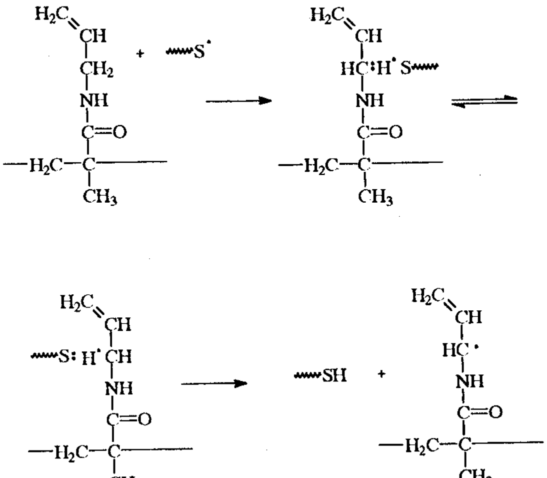
This reaction has been described for blank polymerization. It explains rates of polymerization and formation of low molecular weight of polymer. It is possible that a similar chain transfer reaction occurs during template polymerization. However, according to the authors,[14] degradative addition in the polymerization of N-vinylimidazole is suppressed by template polymerization as evidenced by the rate enhancement and the first order conversion plots. Only if concentration of the template is high enough (0.18 M) all radicals in solution will complex with the template chains after attaining the critical length. This implies that degradative addition in solution is either of minor importance or completely absent.

Chain transfer also takes place when monomer units are connected with the template by covalent bonds. Jantas and Polowinski[15] described the degradative chain transfer in the case of polymerization of multiallyl monomers. The active allyl center, formed as a result of initiation, may take part in further chain growth which is reproducible in an unchanged form. However, the radical may react with the adjacent allyl group extracting the active hydrogen atom. The process results in the formation of radical of a low activity at the alpha carbon. The radical is stabilized by resonance, and thus mostly incapable of further initiation, leading to kinetic chain breaking. It is illustrated by the following scheme:

In the diagram the main reaction is represented by A and degradative chain transfer by B.



A similar process takes place in the case of copolymerization of multiallyl monomers with styrene.[16] The mechanism proposed by the authors was as follows:



where ~~~ S• represents macroradical with styrene unit at the end. This mechanism of additional reaction was confirmed by the presence of a small amount of homopolystyrene in the product.

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8

KINETICS OF TEMPLATE POLYMERIZATION

The kinetics of template polymerization depends, in the first place, on the type of polyreaction involved in polymer formation. The polycondensation process description is based on the Flory's assumptions which lead to a simple (in most cases of the second order), classic equation. The kinetics of addition polymerization is based on a well known scheme, in which classical rate equations are applied to the elementary processes (initiation, propagation, and termination), according to the general concept of chain reactions.

8.1 TEMPLATE POLYCONDENSATION KINETICS

Investigation of template polycondensation kinetics has only been studied within a very narrow scope.[1-5] Polymerization of dimethyl tartrate with hexamethylene diamine was found to be enhanced by using as a template: poly(vinyl pyrrolidone),[1] poly(2-vinyl pyridine),[2] or polysaccharides and poly(vinyl alcohol),[3] poly(4-vinyl pyridine).[4] In this case, the template can be treated as a catalyst. No information exists on the influence of the template on the order of reaction. The increase in molecular weight of the polymerization product by the template can be induced by a shift of equilibrium or by an increase in the reaction rate. A similar increase in the reaction rate was observed when poly(4-vinyl pyridine) was used in the synthesis of poly(terephtalamides) activated by triphenyl phosphite.[4,5] The authors suggested that a high molecular weight template was involved in the increase of the local concentration of the substrate (terephthalic acid) by adsorption and activation via N-phosphonium salt of poly(4- vinyl pyridine).

8.2 TEMPLATE RING-OPENING POLYMERIZATION KINETICS

The only example of kinetic considerations dealing with the ring-opening polymerization was published by Ballard and Bamford.[6] The authors examined polymerization of N-carboxy-amino acid anhydrides proceeding onto polysacrosine. The authors assumed the equilibrium between adsorbed molecules of monomer, E, and free monomer, M, described by equilibrium constant, K, independent of the position in the template chain:

$$M + S \quad E \qquad [8.1]$$

The rate of reaction, measured by emission of CO_2, is proportional to the concentration of absorbed monomer molecules:

$$d[CO_2]/dt = k_{ev}[E] \qquad [8.2]$$

where k_{ev} - rate constant.

8.3 TEMPLATE RADICAL POLYMERIZATION KINETICS

In contrast to template polycondensation or ring-opening polymerization, template radical polymerization kinetics has been a subject of many papers. Tan and Challa[7] proposed to use the relationship between polymerization rate and concentration of monomer or template as a criterion for distinguishing between Type I and Type II template polymerization. The most popular method is to examine the initial rate or relative rate, R_r, as a function of base mole concentration of the template, [T], at a constant monomer concentration, [M]. For Type I, when strong interactions exist between the monomer and the template, R_r vs. [T] shows a maximum at $[T] = [M]_0$. For type II, R_r increases with [T] to the critical concentration of the template c* (the concentration in which template macromolecules start to overlap with each other), and then R_r is stable. c* (concentration in mols per volume) depends on the molecular weight of the template.

A kinetic model for template polymerization in dilute template systems has been published[7] by Tan and Challa. It is assumed that polymerization takes place in surrounding medium (free solution) and on the template. The presented scheme was as follows:

A. reaction steps in solution

1. initiator decomposition:

$$I \xrightarrow{k_d} 2R\bullet \qquad [8.3]$$

2. initiation:

$$R\bullet + M_f \xrightarrow{k_i} P\bullet_{B,1} \qquad [8.4]$$

3. blank propagation:

$$P\bullet_{B,n} + M_f \xrightarrow{k_{p,B}} P\bullet_{B,n+1} \qquad [8.5]$$

4. blank termination:

$$P\bullet_{B,n} + P\bullet_{B,n} \xrightarrow{k_{t,BB}} P_B \qquad [8.6]$$

B. complexation

1. monomer adsorption: $$\mathbf{M_f + T \overset{K_M}{\Leftrightarrow} M_T} \quad [8.7]$$

2. radical complexation: $$\mathbf{P{\bullet}_{B,n} + T \xrightarrow{k_c} P{\bullet}_{T,n}} \quad [8.8]$$

3. polymer complexation: $$\mathbf{P_B + T \xrightarrow{k_c} P_T} \quad [8.9]$$

C. Reaction steps on the template

1. template propagation: $$\mathbf{P{\bullet}_{T,n} + M \xrightarrow{k_{p,T}} P{\bullet}_{T,n}} \quad [8.10]$$

2. template-template termination: $$\mathbf{P{\bullet}_{T,n} + P{\bullet}_{T,m} \xrightarrow{k_{t,TT}} P_T} \quad [8.11]$$

3. cross-termination: $$\mathbf{P{\bullet}_{B,n} + P{\bullet}_{T,m} \xrightarrow{k_{t,BT}} P_B \quad (or\ P_T)} \quad [8.12]$$

Assuming termination of blank radicals, $P{\bullet}_B$, by recombination only at steady state of radicals $[R{\bullet}]$, i.e., $d[R{\bullet}]/dt = 0$, the authors deduced the following set of kinetic equations:

$$R_i = 2fk_d[I] \quad [8.13]$$

$$d[P{\bullet}]/dt = R_i - 2k_{t,BB}[P{\bullet}_B]^2 - k_{t,BT}[P{\bullet}_B][P{\bullet}_T] - k_c[P{\bullet}_B][T] \quad [8.14]$$

$$d[P{\bullet}_T]/dt = k_c[P{\bullet}_B][T] - k_{t,BT}[P{\bullet}_B][P{\bullet}_T] - 2k_{t,TT}[P{\bullet}_T]^2 \quad [8.15]$$

$$-d[M]/dt = R_P = R_{P,B} + R_{P,T} = (k_{P,B}[P{\bullet}_B] + k_{P,T}[P{\bullet}_T])[M_f] \quad [8.16]$$

$$d[P{\bullet}_B]/dt = k_{t,BB}[P{\bullet}_B]^2 - k_c[P{\bullet}_B][T] \quad [8.17]$$

$$-d[T]/dt = 2\nu_B k_c[P{\bullet}_B][T] + \nu_B k_c[P{\bullet}_B][T] + k_{P,T}[P{\bullet}_T][M_f] \quad [8.18]$$

The kinetic chain length of the blank radicals is

Table 8.1: Order of reaction with respect to initiator "n" and monomer "m".

Monomer	Template	Solvent	n	m	References
Acrylic acid	Poly(ethylene imine)	H_2O	1	1	8
N-vinyl pyrrolidone	Poly(acrylic acid)	DMF	0-0.3	1.5	9
p-Styrene sulfonic acid	Ionene	H_2O/i-pro	1	1	10
Methacrylic acid	Ionene	H_2O	0.8	0.3*	11
Methacrylic acid	Ionene	H_2O	0.8	0.9**	11
Methyl methacrylate	i-Poly(methyl methacrylate)	DMF	0.35-0.51	1	12
Acrylic acid	Poly(ethylene glycol)	H_2O	0.7	1.1	13
Methacrylic acid	Poly(ethylene glycol)	H_2O	0.7	1	13
Methacrylic acid	Poly(ethylene glycol)	H_2O	0.5	1	14
Methacrylic acid	Poly(2-vinyl pyridine)	DMF	0.23-0.26	1.5	15
Methacrylic acid	Poly(vinyl pyrrolidone)	H_2O	0.5	1	16
Acrylic acid	Poly(vinyl pyrrolidone-co-acrylamide)	H_2O	0.97	1.42	17

*for [monomer]/[template] > 1; **for [monomer]/[template] < 1

$$\nu_B = k_{P,B}[M_f]\tau_B \qquad [8.19]$$

with τ_B being the average lifetime of the blank radicals

$$\tau_B = [P\bullet_B]/R_i \qquad [8.20]$$

The composite rate constant, $k_{P,T}$, is given by

$$k_{P,T} = k_{P,I}k_{P,II}(1 + K_M[M_f])/(K_M k_{P,II}[M_f]^2 + k_{P,I}) \qquad [8.21]$$

where

$$[M_f] = \{-Q + (Q^2 + 4k_M[M])^{1/2}\}/2K_M \qquad [8.22]$$

$Q = K_M([T] - [M]) + 1$ and [M] is the sum of free and adsorbed monomer concentrations.

For pure Type I, the rate of template polymerization can be described by the simple equation:

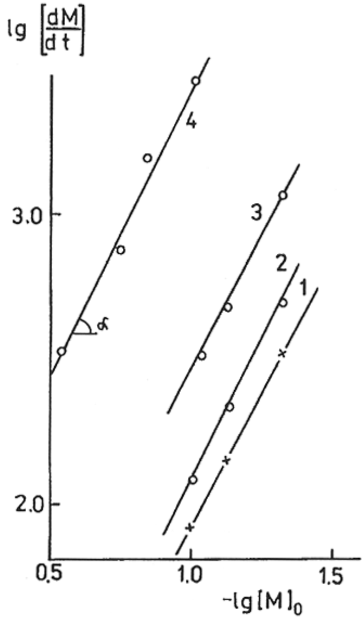


Figure 8.1. Dependence of initial polymerization rate in the presence of poly(methacrylic acid) (1), poly(acrylic acid) (2), poly(l-glutamic acid) (3), at pH=6 and polyphosphate (4) at pH=5.56 at 20°C; tgα =2. Reprinted from V. A. Kabanov, O. V. Kargina, and V. A. Petrovskaya, *Vysokomol. Soed.*, **A13**, 348 (1971), with kind permission from *Iz. Nauka*.

$$-d[M]/dt = k_{P,I}[P\bullet_T] \qquad [8.23]$$

where: $[P\bullet_T]$ is the concentration of radicals on the template.

For pure Type II, the rate of polymerization is:

$$-d[M]/dt = (k_{P,B}[P\bullet_B] + k_{P,II}[P_T\bullet])[M] \qquad [8.24]$$

where $[P_T\bullet]$ is a concentration of radicals outside the template. One can rearrange the equation to the form:

$$-d[M]/dt = k_{P,B}[P\bullet_B][M]\{1 + k_{P,II}/k_{P,B}([P\bullet_T]/P\bullet_B])\} \qquad [8.25]$$

If we assume that in some period of time $[P\bullet_T]/[P\bullet_B]$ is constant and equals β, we have:

$$-d[M]/dt = \varepsilon k_{P,B}[P\bullet_B][M] \qquad [8.26]$$

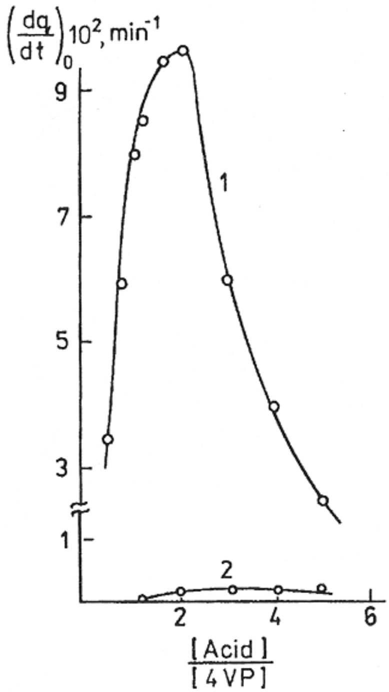


Figure 8.2. Dependence of) and acetic acid (2) on the molar ratio [Acid]/[4-VP] at 20°C; [4-VP] = 0.1 mol/L. Reprinted from V. A. Kabanov, O. V. Kargina, and V. A. Petrovskaya, *Vysokomol. Soed.*, A13, 348 (1971), with kind permission from *Iz. Nauka*.

where:

$$\varepsilon = 1 + \beta k_{P,II}/k_{P,B} \tag{8.27}$$

β is a partition coefficient for radicals between two parts of the system - template and surrounding medium. The kinetic scheme of template polymerization is more complicated than that for simple radical polymerization. For many systems (monomer-template-solvent) general kinetic equation was applied:

$$-d[M]/dt = [I]^n[M]^m \tag{8.28}$$

The template influenced not only the rate constant but also exponents n and m. For many systems, n and m was found to be different for template polymerization than blank polymerization (usually n=0.5; m=1). Examples of experimental results accumulated in the literature are presented in Table 8. 1.

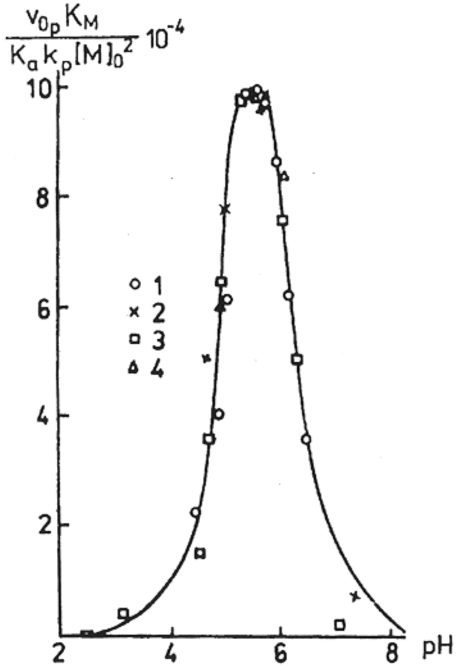


Figure 8.3. Dependence of calculated from $v_{0p}K_M/K_ak_p[M]^2$ initial polymerization rate in presence of various polyacids at 20°C with pH: (1) - pH adjusted by the ratio [PAA]/[4-VP]; [4-VP] = 0.1 mol/L; (2) - pH adjusted by addition HCl or NaOH at [PAA]=[4-VP] = 0.1 mol/L; (3) - pH adjusted by addition o polyphosphate - poly(ethylenephosphoric acid) at [4VP] = 0.1 mol/L. Reprinted from V. A. Kabanov, O. V. Kargina, and V. A. Petrovskaya, *Vysokomol. Soed.*, A13, 348 (1971), with kind permission from *Iz. Nauka*.

Application of classical type of kinetic equations to the template polymerization was demonstrated by Kabanov *at al.*[18] It was shown that 4-vinylpyridine, in the presence of poly(methacrylic acid), poly(acrylic acid), poly(l-glutamic acid), and polyphosphate, polymerizes according to the classical equation and the order of reaction with respect to the monomer is 2 as demonstrated in the Figure 8.1. In log-log coordinates, for the all sets of polymerizations, experimental points fit straight lines. In the same paper dependence of the initial rate on the molar ratio of acid to monomer was examined. This relationship is shown on the Figure 8.2. The rate of polymerization in the presence of the poly(acrylic acid) is much higher than that for the low molecular analogue (acetic acid). The polymerization rate riches its maximum for the molar ratio [acid]/[monomer]′2. The authors found kinetic equation for template polymerization of 4-vinylpyridine in the presence of different polyacids in the form:

$$V_{op} = \frac{k_p K_a [M]_0^2}{K_M} \times \frac{[H^+]}{(K_a + [H^+])^2} \qquad [8.29]$$

where: K_M and K_a are equilibrium constants for protonization of the monomer and creating the ionic pairs, respectively, k_p - propagation rate constant. In order to check this equation for many examined systems, Figure 8.3 was constructed. The reaction rate depends on the pH for all examined systems in accordance to proposed equation.

In order to estimate kinetic constants for elementary processes in template polymerization two general approaches can be applied. The first is based on the generalized kinetic model for radical-initiated template polymerizations published by Tan and Alberda van Ekenstein.[19] The second is based on the direct measurement of the polymerization rate in a non-stationary state by rotating sector procedure or by post-effect in photopolymerization. The first approach involves partial absorption of the monomer on the template. Polymerization proceeds according to “zip” mechanism (with propagation rate constant $k_{p,I}$) in the sequences filled with the monomer, and according to “pick up” mechanism (with rate constant $k_{p,II}$) at the sites in which monomer is outside the template and can be connected by the macroradical placed onto template. This mechanism can be illustrated by the following scheme:

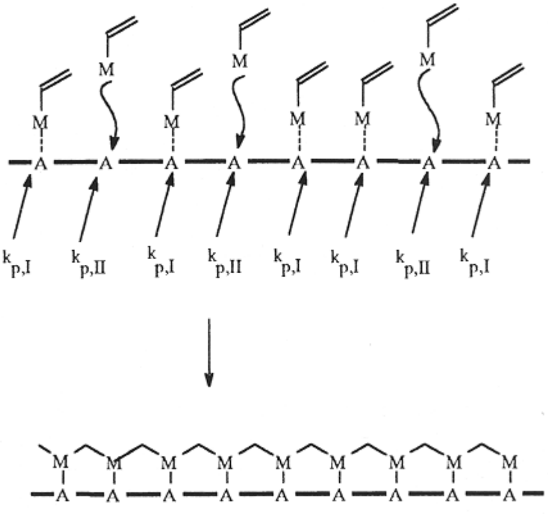


Table 8.2: Rate constants* for template polymerization of methacrylic acid.

Template	Temp., ^oC	Solvent	k_{pI}	k_{pII}	k_{BT}	k_{TT}	Refs.
P2VP atactic	30	DMF	800	50	2400	1100	7
P4VP isotactic	30	DMF	150	50	-	480	7
P4VP	60	MeOH	$5x10^3$	$22.5x10^3$	$6x10^4$	$3x10^4$	21
P2VP isotactic	30	Dioxane	85	200	-	450	7
P2VP atactic	30	Dioxane	85	200	-	1000	7
PVPy**	25	H_2O		29.2	$2.4x10^2$		22
PVPy (low MW)	25	H_2O		18.8	$1.4x10^2$		22
PDAM***	25	H_2O	76		$1.4x10^2$		23
PDAM (low MW)	25	H_2O	52.5		$2.2x10^3$		22
None	25	H_2O	2260		$3.2x10^6$		22

*k_{pI} and k_{pII} rate constants for propagation of Type I and Type II mechanisms, respectively; k_{BT} and k_{TT} terminations constants for blank-template reaction and template-template reaction, respectively; **PVPy - polyvinylpyrrolidone; ***PDAM - poly(N,N-dimethyloaminoethylenemethacrylate)

Table 8.3: Rate constants for template polymerization of acrylic acid.

Template	Temp., ^oC	Solvent	k_{pI}	k_{pII}	k_{BT}	k_{TT}	Refs.
P4VP	60	MeOH	$20x10^3$	$10x10^3$	$1000x10^4$	$500x10^4$	19
Polyethyl eneimine	25	Acetone/H_2O	30	750	1500	750	19
PVPyrr	74	H_2O	$1x10^4$	$5x10^4$	$10x10^4$	$5x10^4$	19
PVPyrr	74	H_2O	$1x10^4$	$5x10^4$	$2x10^4$	$1x10^4$	19

explanation of symbols given in Table 8.2.

where: M is the monomer molecule, A template unit, and the arrow shows the place where reaction is proceeding at the corresponding rate constant. On the basis of the "generalized model", $k_{p,I}$, $k_{p,II}$ can be estimated, as well as termination constants: $k_{t,TB}$ for cross-termination (termination between a radical on the template with a radical from surrounding solution) and $k_{t,TT}$ (for termination of macroradicals bound to the template). Experimental data from the literature recalculated according to the theory, using computer simulations, are shown in Table 8.2.

In order to verify the theory, Tan and Alberda van Ekenstein[19] recalculated also data for acrylic acid polymerization (Table 8.3).

Bamford and Shiiki found[24] that initial rate of acrylic acid polymerization in the presence of polyethyleneimine is a function of the ratio: template concentration to monomer concentration. The following equation was proposed to describe the rate of polymerization:[24]

$$-d[M]/dt = C \exp(-\alpha Z^{\beta}/kT)[X] \qquad [8.30]$$

where α and β are curve fitting constants, [X] - concentration of monomer adsorbed onto template, Z - [T]/[X] ratio.

Using these experimental data, Tan and Alberda van Ekenstein [19] calculated corresponding rate constants and predicted the curve presented in Figure 8.4 which fits very well the experimental points.

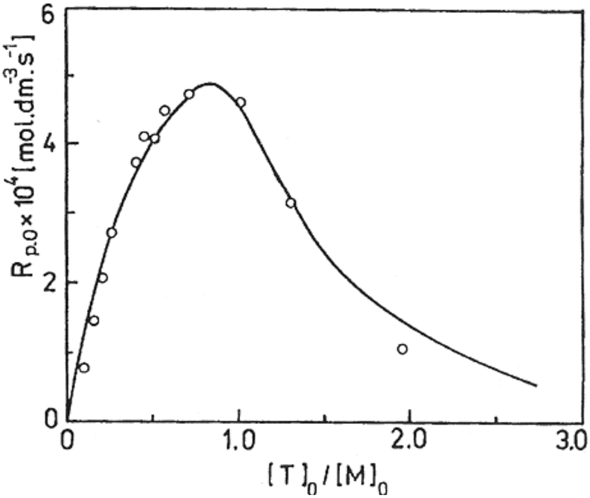


Figure 8.4. Template polymerization of AA along polyimine as a function of $[T]_0/[M]_0$ at constant $[M]_0$ in acetone/water (2/1 v/v) at 25°C. (o) Data from Bamford and Shiiki.[24] The curve is derived from the computed rates using the constants calculated by Tan and Alberda van Ekenstein.[19] Reprinted from Y. Y. Tan and O. R. Alberda van Ekenstein, *Macromolecules*, 24, 1641 (1991) with kind permission from *ACS*.

The next example deals with polymerization of acrylic acid along with poly(N-vinyl pyrrolidone) as reported by Ferguson and Shah.[32] Similar calculations[19] lead to a curve which fits well experimental points. The results are presented in Figure 8.5. The maximum polymerization rate appears very close to [T]/[M] ratio equal one. However, it is not a rule. Recalculated data obtained by Fujimori *et al*.[21] for polymerization of acrylic acid are presented in Figure 8.6 and for methacrylic acid Figure 8.7. The data give maximum rate of polymerization at much lower value of [T]/[M]. In all cases presented, the results

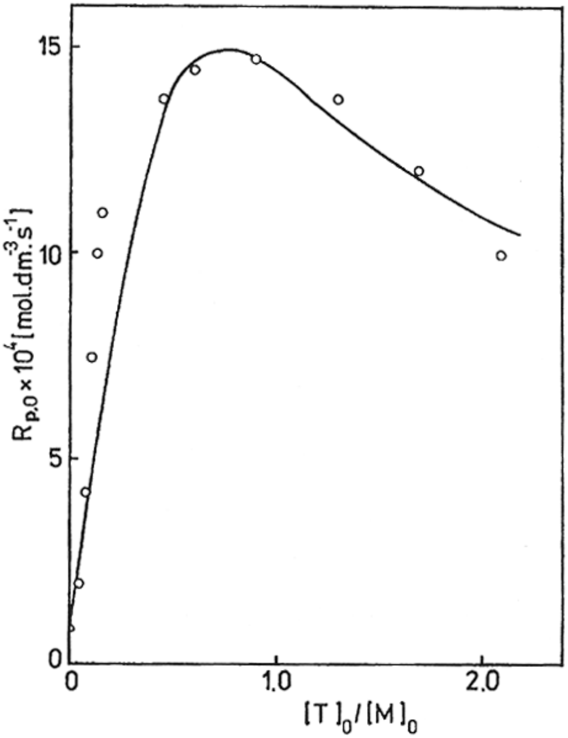


Figure 8.5. Template polymerization of AA along poly(N-vinylpyrrolidone) as a function of $[T]_0/[M]_0$ in water with $K_2S_2O_8$ as initiator at 74°C. (o) Data from Ferguson and Shah.[8] $[AA]_0 = 0.02$ mol.dm^{-3}. The curve is derived from computed rates using the constants calculated by Tan and Alberda van Ekenstein.[19] Reprinted from Y. Y. Tan and O. R. Alberda van Ekenstein, *Macromolecules*, 24, 1641 (1991) with kind permission from *ACS*.

were calculated applying the rate constants from the same experimental points. Thus, the results presented in the Figures 8.6 and 8.7 are only a very rough estimation. Table 8.2 contains k_p and k_t values obtained by direct measurements using rotating sector method or applying "post effect" in photopolymerization. This effect deals with the observations[16] that polymerization initiated by UV light is still running after switching off the light source. It confirms assumptions that life-time of radicals in template polymerization is much longer than in conventional polymerization. Examples of such runs for polymerization in "post effect" for methacrylic acid template polymerization are shown in the Figures 8.8 and 8.9. In this case the rate constants k_t and k_p are calculated according to the equations:

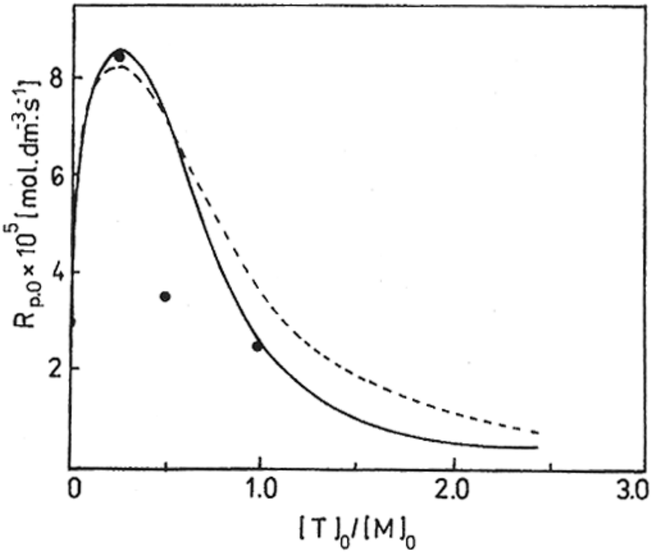


Figure 8.6. Template polymerization of AA along poly(N-vinylpyridine) as a function of $[T]_0/[M]_0$ at constant $[M]_0 = 0.06$ mol.dcm^{-3} in methanol at 60°C. (o) Data from Fujimori *et al.*[21] The curves are derived from computed rates using two sets of constants calculated by Tan and Alberda van Ekenstein.[19] Reprinted from Y. Y. Tan and O. R. Alberda van Ekenstein, *Macromolecules*, 24, 1641 (1991) with kind permission from *ACS*.

$$k_p^2 / k_t = 2R_p^2 / R_i [M]^2 \quad [8.31]$$

$$(1 - \alpha)/(d\alpha / dt) = (k_t / k_p) \times t + \text{const} \quad [8.32]$$

where R_p - overall rate of polymerization, R_i - rate of initiation, α - ratio of conversion in post-effect, t - time of polymerization, [M] - monomer concentration. k_t for template polymerization is often lower by a few orders of magnitude than k_t for a blank reaction. Also, k_p decreases in the presence of the template. However, k_p^2/k_t is usually higher for the template process, and this is the reason for enhancement of the overall rate of template polymerization.

Data presented in Table 8.2 for templates having low molecular weight (PVP and PDAMA with degree of polymerization of about 50) are an interesting exemption from this rule. The presence of both types of template - PVP or PDAMA - changes the rate constants, k_p and k_t, of elementary processes. In comparison with polymerization without template, k_t for template polymerization is lower by a few orders of magnitude. Also, k_p

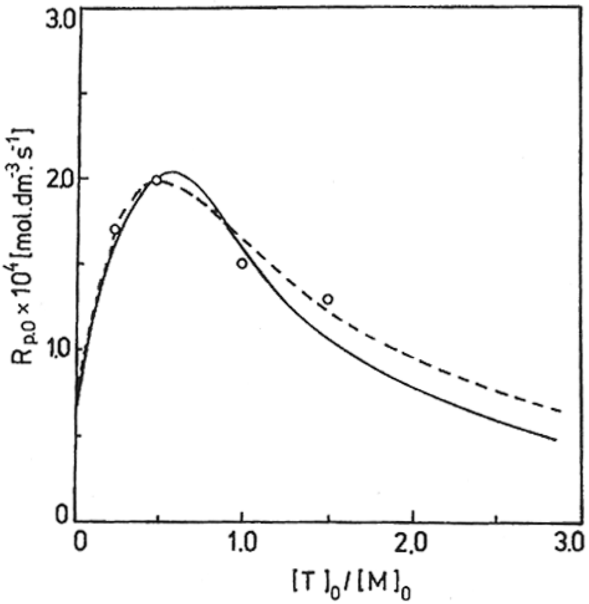


Figure 8.7. Template polymerization of MA along poly(N-vinylpyridine) as a function of $[T]_0/[M]_0$ at constant $[M]_0 = 0.06$ mol.dcm^{-3} in methanol at 60°C. (o) Data from Fujimori *et al.*[21] The curves are derived from computed rates using two sets of constants calculated by Tan and Alberda van Ekenstein.[19] Reprinted from Y. Y. Tan and O. R. Alberda van Ekenstein, *Macromolecules*, 24, 1641 (1991) with kind permission from *ACS*.

is lower but in the systems examined k_p^2/k_t is just the same as for the polymerization without template. This leads to conclusion that the overall rate of the polymerization with and without template is the same. The change in the propagation rate constants is clear evidence that the template influences the propagation. It leads to the conclusion that propagation takes place in the immediate neighborhood of the template which is confirmed by strong interactions between the monomer and such templates as PVP and PDAMA.

In order to find the initiation rate, a set of polymerizations, in the presence of inhibitor (2,2,6,6-tetramethyl-4-hydroxy-piperidine-1-oxy), was carried out.[22] Inhibition period was measured for polymerization with poly(dimethylmethacrylate), polyethylene glycol, or without any template. The results are presented on the Figure 8.10. The plot of concentration vs. inhibition time is a straight line — the same for all experimental points. It means that initiation rate is the same, independent of the presence of tem-

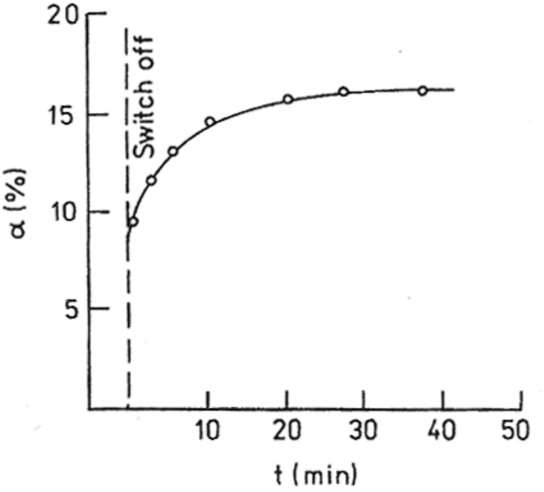


Figure 8.8. Conversion during the post-effect for MAA with PDAMA template. Reprinted from J. Matuszewska-Czerwik and S. Polowinski, *Eur. Polym. J.*, 28,1482, (1992) with kind permission from *Elsevier Science Ltd*.

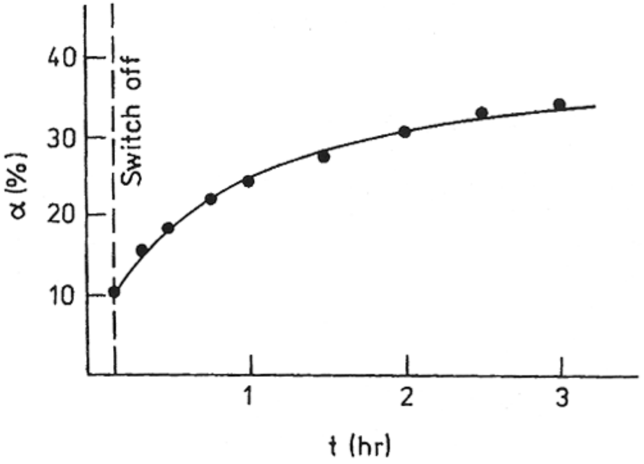


Figure 8.9. Conversion during the post-effect for MAA with PVP template. Reprinted from J. Matuszewska-Czerwik and S. Polowinski, *Eur. Polym. J.*, **28**,1482, (1992) with kind permission from *Elsevier Science Ltd*.

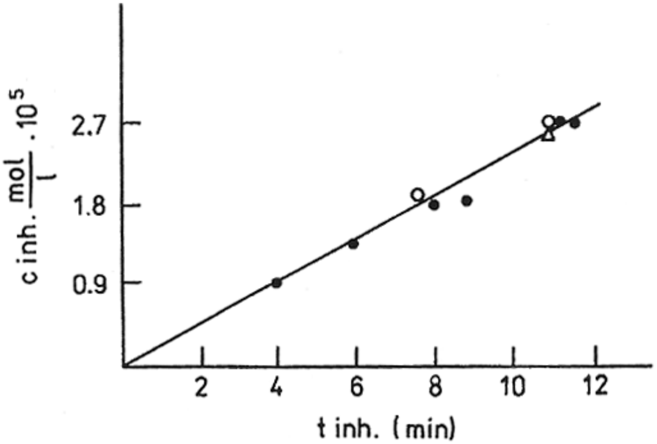


Figure 8.10. Inhibitor concentration vs inhibition time. • without template, o with PDAMA (DP=54), Δ with PVP (DP=52). Reprinted from J. Matuszewska-Czerwik and S. Polowinski, *Eur. Polym. J.*, **28**, 1482, (1992) with kind permission from *Elsevier Science Ltd.*

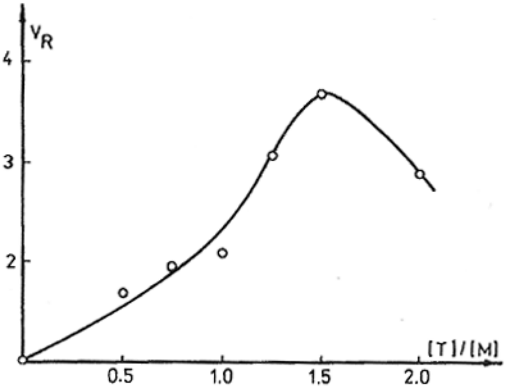


Figure 8.11. Template polymerization of methacrylic acid along with poly(N-vinylpyrrolidone).[23] Overall rate as a function of $[T]_0/[M]_0$.

plate. From data in Table 8.2, it is evident that k_p calculated for low molecular weight PVP has almost the same value as the k_p value for high molecular weight template. In the last case, the rate enhancement is quite significant. It seems that in the case of both low and high molecular weight template, the propagation step proceeds with the same rate constant depending only on the geometry of interacting centers.

The results obtained lead to the conclusion that even if the overall rate enhancement does not appear (the relative rate is unity), template mechanism of reaction can still be accepted. Moreover, from the data accumulated in the literature, we can see that in all systems investigated the propagation rate constant for template process is lower than the corresponding constant for blank reaction. In other words $k_{p,II}/k_{p,B}$ is lower than 1. All presented results corresponds to the equimolar ratio template-monomer. It seems interesting to examine the rate constants for non-equimolar ratios. Our last results[22] for polymerization of methacrylic acid in the presence of poly(vinyl pyrrolidone), having high molecular weight, are presented in Figures 8.11 to 8.13. Figure 8.11 shows dependence of overall rate V_R on the [T]/[M]. As we can see the curve possess a maximum for [T]/[M] = 1.5. Very similar shape was predicted by Tan and Alberda van Ekenstein [19] for polymerization of acrylic acid, only the maximum was for [T]/[M]. It was found[23] that not only V_R, but also the curve of k_p vs. [T]/[M] has a maximum as shown in Figure 8.12.

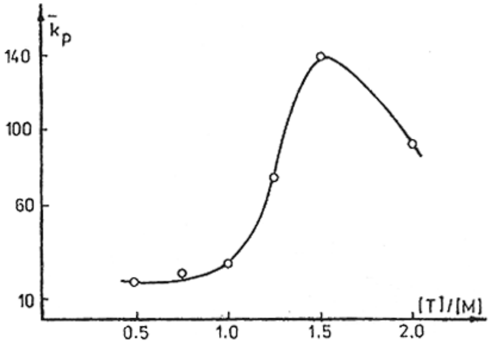
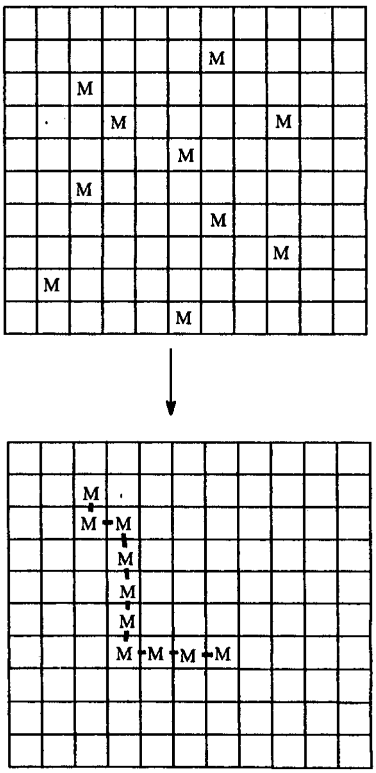


Figure 8.12. Template polymerization of methacrylic acid along with poly(N-vinylpyrrolidone).[23] Propagation rate constant as a function of $[T]_0/[M]_0$.

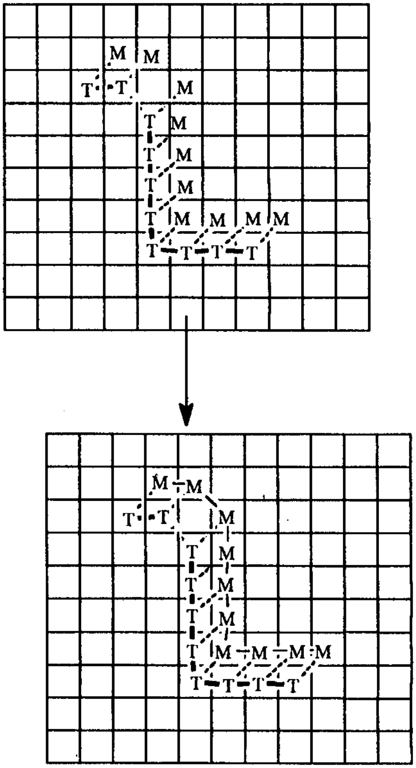
Further understanding of the kinetic of template polymerization needs consideration of the process entropy. Applying a well known lattice model, it is easy to see that entropy changes, ΔS, in “free” polymerization and the template polymerization, differs considerably. According to the principles of statistical thermodynamics, the entropy of mixing is given by the equation:

$$S = k_B \ln\Phi \qquad [8.33]$$

in which k_B is Boltzmann’s constant and Φ the number of different ways of placing the units. For “free” polymerization schematic representation of the polymerization process can be as follows:



The initial state (entropy S_0) can be realized by various ways of placing the monomer units then the final state (entropy S_1). In this case, $S_0 > S_1$ and for the process $\Delta S < 0$. With template unit denoted by T, and monomer unit, M, connected with the template by covalent bonding or by strong interactions denoted by "/", the system template- monomer can be represented as follows:



The number of ways of placing the units for initial position (corresponds to the initial entropy, $S_{0,T}$) and for final position (corresponds to entropy $S_{1,T}$) is almost the same because, in both cases, the monomer units cannot be located far from the template. It means that the volume accessible for a monomer molecule is reduced to the nearest neighborhood. In this case, $S_{0,T} \approx S_{1,T}$ and $\Delta S \approx 0$. The change of entropy concerns the propagation step of the template reaction. There is very little information in the literature about experimental results of entropy changes during template polymerization.

The overall change in entropy ΔS_{ov} is an algebraic sum of the partial components of elementary processes - propagation (ΔS_p), decomposition of the initiator (ΔS_d) and termination (ΔS_t). Assuming typical kinetic equation, the following equation is valid:

$$\Delta S_{ov} = \Delta S_p + 1/2\,\Delta S_d - 1/2\,\Delta S_t \qquad [8.34]$$

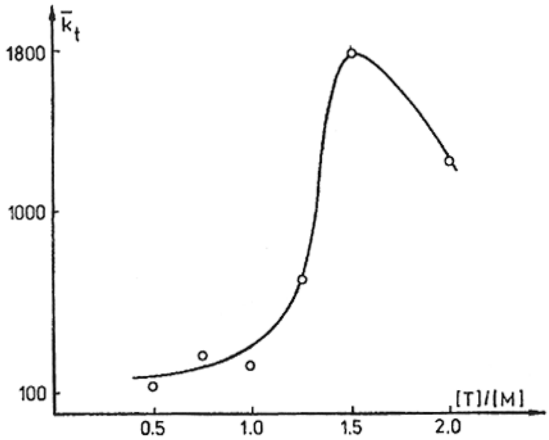


Figure 8.13. Template polymerization of methacrylic acid along with poly(N-vinylpyrrolidone).[23] Termination rate constant as a function of $[T]_0/[M]_0$.

Indeed, it was observed[12] that ΔS_{ov} is lower for template polymerization ($\Delta S_{ov,T}$) than for blank reaction ($\Delta S_{ov,B}$). Investigating polymerization of methyl methacrylate, in the presence of isotactic poly(methyl methacrylate), Gons *et al.*[12] found that there is a difference in entropy of about 84 J mol^{-1} K^{-1} between template polymerization and the blank reaction. A similar value (90-100 J mol^{-1} K^{-1}) was found by Lohmeyer *et al.*[25] It is more likely that the decrease of ΔS originates predominantly in the propagation process.

In contrast, polymerization of N- vinylpyrrolidone onto poly(methacrylic acid) used as a template gives[26] ΔS almost the same as for blank polymerization. Decrease in ΔS was found to be 19 J mol^{-1} K^{-1} despite weaker interactions between the template and the daughter polymer. Blumstein and Kakivaya,[10] investigating polymerization of p-styrene-sulfonic acid and using cationic ionenes as a template, found a decrease in overall energy of activation from 22.8 to 16.9 kcal/mol. Such large decrease in activation energy can be attributed to the decrease in activation energy of propagation and increase of energy of termination process. In polymerization without template, distances between monomer molecules depend (at random) on the concentration. In the Type I template process, the distances between two reacting monomer units are fixed, depending on the distance of interacting groups in the template.

Let us consider the case in which monomer is strongly bound to template. Initiation proceeds in a different way below and above the critical concentration of the template used. If concentration of the template is small and coils of the template are separated, primary radicals appear mainly outside the coils and then migrate to the surface of coils in which monomer is present. Then monomer growing centers are created inside the coil and propagation occurs. The mechanism is similar to the mechanism proceeding in emulsion polymerization or suspension polymerization. Monomer concentration in coils does not change only if [T]/[M] ratio does not change. By dilution of the system, concentration of the monomer inside the coil does not change and the rate of polymerization for [I] = const should be constant. In other words, the order of the reaction in respect to monomer concentration should be zero.

In type II template polymerization, critical chain length plays an important role in description of the process. It is connected with the cooperative interactions between monomer and template complementary groups. When interactions are weak, only oligoradicals with higher than critical chain length can be complexed by the template. After such complexation, the propagation can proceed on the template. The rate of template polymerization should be compared not only with the polymerization rate of the same monomer in the same solvent, but also with the system in which the low molecular weight compound, template analog, is present. It is well known that the presence of such groups as tertiary amines, sulfonic groups, etc. has catalytic influence on the decomposition of peroxides changing the rate of initiation.

Change in chemical composition of the solvent used can also change the velocity of polymerization. Viscosity of the examined system is another very important parameter which should be taken into account. Templates, as any macromolecular compounds, change viscosity in comparison with the viscosity of polymerizing system in a pure solvent. It is well known that the increase in viscosity can change the rate constant of termination and eventually the rate of polymerization. In many systems, an insoluble complex is formed as a product of template polymerization. It is obvious that the character of polymerization and its kinetics change.

Description of polymerization kinetics in heterogeneous systems is complicated, even more so given that the structure of complex formed is not very well defined. In template polymerization we can expect that local concentration of the monomer (and/or initiator) can be different when compared with polymerization in the blank system. Specific sorption of the monomer by macromolecular coil leads to the increase in the concentration of the monomer inside the coil, changing the rate of polymerization. It is a problem of definition as to whether we can call such a polymerization a template reaction, if monomer is randomly distributed in the coil on the molecular level but not "ordered" by the template.

Let us divide the overall volume of the reacting system, V, into two parts: first V_1 filled up with template coils being in contact with each other (possesses the critical concentration c* in g/L) and the second part V_2 "free" from the template. Monomer is divided into these two parts in such a way that concentrations are $[M]_1$ and $[M]_2$, respectively. The overall rate of the polymerization R_{ov} is a sum of the rate in the first part, R_1, and in the second part, R_2, multiplied by the corresponding volume fractions $\phi_1 = V_1/V$ and the following equations are valid:

$$\phi_2 = V_2 / V \qquad [8.35]$$

$$R_{ov} = R_1\phi_1 + R_2\phi_2 \qquad [8.36]$$

or

$$R_{ov} = k_T\,[I]^{1/2}\,[M]_1\,\phi_1 + k_B\,[I]^{1/2}\,[M]_2\,\phi_2 \qquad [8.37]$$

where k_T and k_B are overall rate constants for template and blank reaction, respectively.

For c* (in g/L), we have $m_T/V_1 = c^*$ where m_T is the number of grams of the template. If [T] is the concentration of the template (in base moles per L) and M_x is the molecular weight of template unit, we have

$$m_T = [T]M_xV \qquad [8.38]$$

and then ϕ_1 is $[T]M_x/c^*$. From this we have:

$$R_{ov} = k_T[I]^{1/2}[M]_1[T]M_xc^{*-1} + k_B[I]^{1/2}[M]_2(1 - [T]M_xc^{*-1}) \qquad [8.39]$$

because $c^{*-1} = [\eta]$ where $[\eta]$ is intrinsic viscosity of the template.

$$R_{ov} = k_T[I]^{1/2}[M]_1[T]M_x[\eta] + k_B[I]^{1/2}[M]_2(1 - [T]M_x[\eta]) \qquad [8.40]$$

In the critical concentration of the template, $[T]M_x[\eta] = 1$ and $R_{ov} = k[I]^{1/2}[M]$. The same is valid when $[M]_2 = 0$ that is if all the monomer is adsorbed (or bound) onto the template. These conditions are optimal for the template polymerization to proceed. If template process leads to the rate enhancement, R* is the maximal value of the rate.

Above the critical concentration of the template, the monomer-template contacts are replaced in part by mutual contacts between template units, but description of this case seems to be more complicated. The considerations mentioned above do not pre-judge that polymerization proceeds inside the coils of “the template” according to template mechanism. It shows only that local concentration of the monomer in the reaction place is different from the overall concentration.

The same considerations can be applied in regard to the initiator concentration. In the extreme case, the initiator can be adsorbed by the template coils or can be a part of the template. Bamford[27] has suggested initiation of polymerization by the end-groups of the polyvinyl alcohol template. Also, polyethylene glycol with azo-groups has been used for initiation of template polymerization of methacrylic acid.[28] Initiation was possible

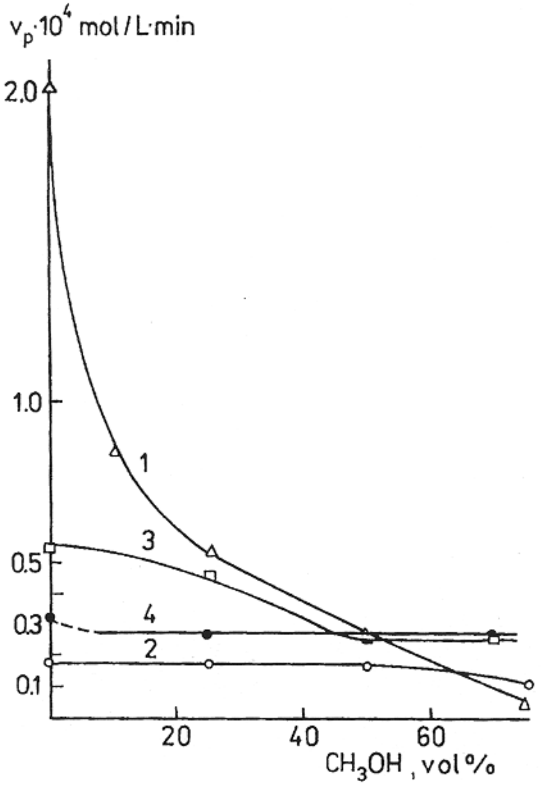


Figure 8.14. Dependence of initial polymerization rate on the methanol concentration in the reaction mixture. 50°C, $[K_2S_2O_8] = 3.7\times10^{-4}$ mol/L, mol. weight PEG =15,000, 1-[MA]= 3.5×10^{-2}, 2-[MA]=[PEG]= 3.5×10^{-2}, 3-[AA]=4.17×10^{-2}, 4-[AA]=[PEG]=4.17×10^{-2} mol/L. Reprinted from I. M. Papisov, V. A. Kabanov, E. Osada, M. Leskano Brito, J. Reimont, and A. N. Gvozdeckii, *Vysokomol. Soed.*, **14**, 2462 (1972) with kind permission from *Iz. Nauka*.

only by radicals formed at the ends of the template. On the other hand, initiator can be deactivated by the template as shown by Ferguson and Eboatu.[29]

The solvent used can change interaction between template and monomer. For instance polymerization of methacrylic or acrylic acid in water and in water-methanol mixtures proceeds with different rates which depend on the composition of the solvents mixture as pertaining from the results in Figure 8.14.

Rates of polymerization of methacrylic acid or acrylic acid in water in the absence of template, PEG, was much higher than that for template polymerization. However, the rate decreases with methanol concentration increasing, while the rate of template polymerization does not substantially change with methanol content. It can be connected with complicated equilibria between various forms of acrylic or methacrylic acids as well as with interaction of monomer-template.

All these observations lead to the conclusion that it is very difficult to judge whether the examined case is template polymerization or not on the basis of kinetic effects alone. It is especially true if the form of kinetic equation (exponents n and m) is different for template and blank polymerization since more complicated mechanism of reaction can be expected.

Many methods were applied to investigation of the kinetics of template polymerization and are discussed in detail in Chapter 11. The most common method is the dilatometric method. The method is based, for blank reactions, on a change in volume of the reacting system. The method usually neglects the change in volume connected with complexation. The turbidimetric method was used by Ferguson and Shah[8] to follow extent of polymerization. Insoluble complex was formed during polymerization of polyacrylic acid in the presence of poly(vinyl pyrrolidone), poly(vinyl imine), or poly(ethylene glycol). In fact, in this method, the rate of polycomplex formation, rather than the rate of polymerization, is determined. However, the method was compared with bromometric titration and comparable results were obtained.

Application of calorimetric method to determine the rate of template polymerization was elaborated by Smid.[30] The method is based on heat determination in microcalorimeter, followed by determination of the heat of blank polymerization as well as the heat of complexation.

Quite recently,[31] GPC method was applied for investigation of both template homopolymerization and copolymerization. In this method, the disappearance of the monomer or both comonomers can be determined and also the disappearance of "free" template can be measured. In some cases, molecular weight of the product and its molecular weight distribution can also be determined.

8.4 KINETICS OF MULTIMONOMER POLYMERIZATION

Only a few publications appeared on the polymerization in the systems with covalent bonding of monomer.[32,33,34] The process can be examined by bromometric titration, IR spectrometry,[32] or by dilatometric techniques.[34] In the last case, it is necessary to calculate density of the reaction product. The peculiarity of the process lies in the fact that monomer (multimonomer) and the product are both polymers frequently having the same molecular weight. Separation of the product by methods used in the conventional polymerization (e.g., by precipitation) is not practical. There are also difficulties with purification. Density measurements for dilatometric method require calibration and some indirect methods can be applied.[34] The kinetics of multiacrylate was examined carrying out the process in DMF and using AIBN and UV light as initiator.

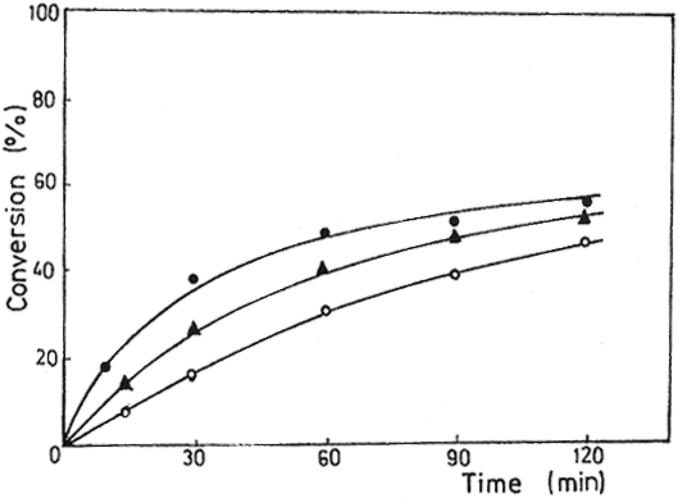


Figure 8.15. Time-conversion curves for the polymerization of MM with M_n=46,500 and various multimonomer concentrations: (o) [MM] = 6.30×10^{-2} mol/L; (Δ) [MM]=25.20×10^{-2} mol/L; (•) [MM]=37.85×10^{-2} mol/L. According to R. Jantas, S. Polowinski, and G. Strobin, *Polym. Int.*, **37**, 315

It was found[34] that conventional equation can be applied for description of the process. The process is the first order with respect to monomer and the order with respect to initiator is 0.25. The energy of activation was estimated at 43 kJ/mol. Moreover, it was found that without initiator, photopolymerization also occurs when the system is illuminated by UV light.

Kinetics of multimethacrylate polymerization was examined only with limited interest.[33] Conversion in this case was measured by IR spectroscopy. The kinetic curves for three concentrations of multimonomer are presented in Figure 8.15.

Polymerization was carried out in dioxane solution at 75°C. For kinetics examination multimonomer with molecular weight M_n = 46,500 was selected. It was found that polymerization proceeds according "pure template" mechanism - without changes in molecular weight and molecular weight distribution up to more than 60% conversion. More experimental data is needed in order to determine the order of reaction with respect to monomer and initiator, as well as energy of activation.

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9

PRODUCTS OF TEMPLATE POLYMERIZATION

Two types of polymer materials can be obtained as a result of template polymerization:

- polymers or copolymers with at least partially ladder-type structure
- polycomplexes with a structure of a more ordered form than obtained by mixing two polymer components.

9.1 POLYMERS WITH LADDER-TYPE STRUCTURE

Zipping-up reaction is a well known method for ladder polymer production.[1-5] The most important from the practical point of view is cyclization and carbonization of polyacrylonitrile.[1-4] The mechanism of the thermal conversion of polyacrylonitrile to carbonized product has been intensively studied and it is extremely complex.[2-4] The reaction can be partially treated as a template polymerization proceeding according to the reaction:

The details of so-called Black Orlon production have been given in many papers.[1-4] Also, the properties of carbonized polyacrylonitrile are well known because of which it is in demand especially as a component of composites, mainly because of its strength and high thermal resistance.

Zipping-up reaction very seldom leads to polymers with full ladder structure. Very often the reaction proceeds with a break in the ladder, and isolated reactive groups are present in the product.[5] Moreover, structure investigations are very difficult because ladder polymers are mostly insoluble. Decrease in transmission made IR spectra unintelligible as in the case of cyclization and aromatization of polybutadiene. NMR analysis by simple techniques is also impossible.

Covalent bonding of acrylic or methacrylic monomer to the template leads to multifunctional monomers (multimonomers).[6-8] If monomer units are connected by covalent bonds within the frame of the template and polymerization proceeds according to the "zip mechanism", a product with ladder-type structure can be expected. The structure of products obtained depends on the competition between the reactions proceeding on the template and the reaction between groups belonging to different macromolecules (templates).[7] Template homopolymerization in this case can be represented by the scheme given in Figure 9.1.

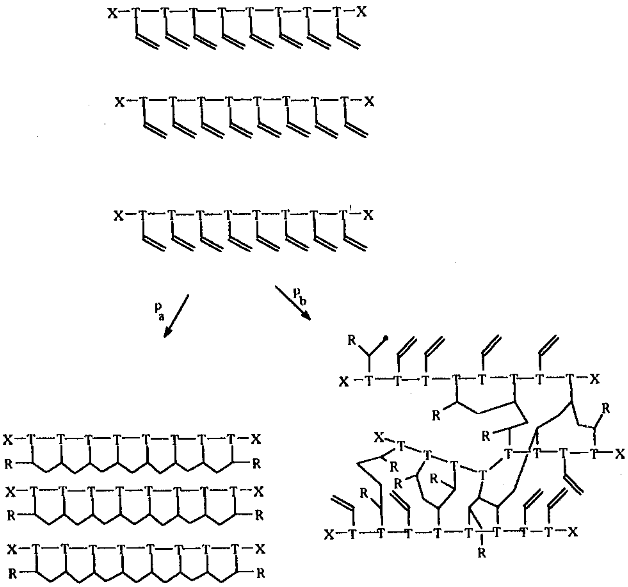


Figure 9.1. Schematic representation of multimonomer polymerization, where: X- end group in the template; R- end group of initiator; p_a - a probability that the radical will be reacting along the template; p_b - a probability that the radical will be reacting with a group located on the neighbor template.

Depending on the "template activity", the ratio p_a/p_b is different. If the template is selected properly, distances between groups are such that tensions in a ladder structure are as small as possible (for instance for 6 member ring), and bonds are flexible (e.g, ether bonds). In this case, the ratio p_a/p_b is high. In the opposite case, if the substrate molecules are stiff and distances between reacting groups are too large (or too small), we can expect that template makes polymerization more difficult ($p_a/p_b < 1$) or eventually can make it impossible $p_a = 0$. A competition between these two reactions leads to the differences in the structure of the products obtained. From the point of view of the product structure, p_a is a fraction of rings (ladder units), assuming full conversion. The p_b value is connected with the degree of crosslinking. The number of branching points per 100 monomeric units is 100 pb. Because side reactions take place, depending on polymerization conditions, such polymers can be crosslinked or branched. They can also contain unreacted double bonds. In some cases, however, almost linear, soluble ladder polymers can be obtained.[7,8,9]

If polymerization proceeds only as a template process ($p_a = 1$), and template-template termination can be neglected, molecular weight and molecular weight distribution does not change in the course of the process. Proper conditions can be selected for polymerization of multiacrylates[7] in order to produce ladder polymers with the same molecular weight distribution as in the substrate. The examples of GPC study of multiacrylate polymerizing are given in Figure 9.2.

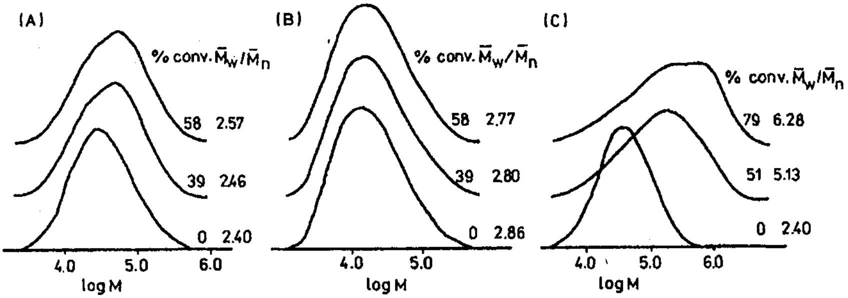


Figure 9.2. MWD of the reaction mixture. Samples taken during the polymerization of multiacrylate (A) at 75°C, eluent DMAc; (B) at 75°C, eluent THF; and (C) at 85°C, eluent DMAc. According to R. Jantas, J. Szumilewicz, G. Strobin, and S. Polowinski, *J. Polym. Sci., Polym. Chem.*, **32**, 295 (1994).

At 75°C, molecular weight distribution does not changes up to 58% of conversion. At 85°C, the increase in molecular weight takes place. It can be connected with template-template termination or with crosslinking (p_b). From these findings one can conclude that by template polymerization, polymeric materials with ladder type structure and with predicted molecular weight distribution can be produced. Similar results were found for polymerization of multimethacrylate.[8] The influence of molecular weight of the template on the structure of products obtained is illustrated in the Figure 9.3. If molecular weight is high enough (46,500) polymerization proceeds to more than 50% of conversion according to "pure template process" as illustrated in the Figure 9.4.

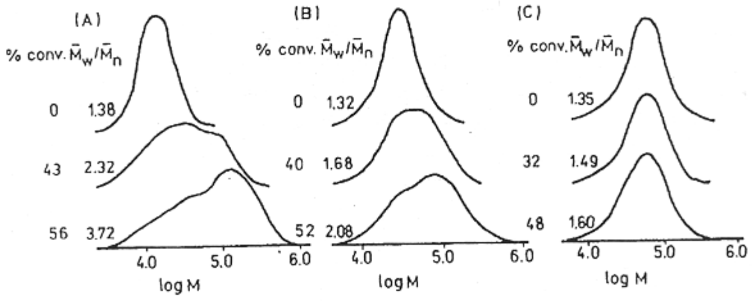


Figure 9.3. MWD of the reaction mixtures. Samples taken during the polymerization of multimethacrylate with various molecular weights: A M_n=13,500; B M_n=26,900, and C M_n=46,500. According to R. Jantas, S. Polowinski, and G. Strobin, *Polym. Int.*, **37**, 315 (1995).

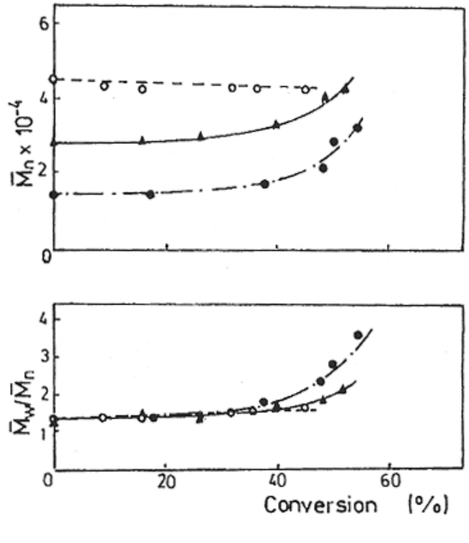
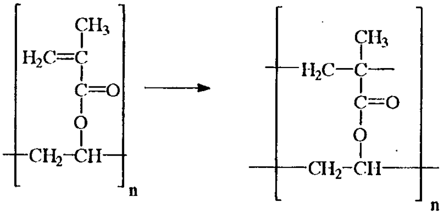


Figure 9.4. Dependence of the conversion of M_n and M_w/M_n of the reaction mixture samples taken during polymerization of MM with various molecular weights: (•) M_n=13,500, (Δ) M_n=26,900, (o) M_n=46,500. According to R. Jantas, S. Polowinski, and G. Strobin, *Polym. Int.*, **37**, 315 (1995).

For high molecular weight, M_n and M_w/M_n do not change in the course of polymerization up to about 60% conversion. These results confirm that under proper conditions (polymerization at moderate temperature, template of high enough molecular weight, moderate concentration of substrates) ladder-type polymers can be obtained by template polymerization of multiacrylates or methacrylates.

Polymerization of multimethacrylate from poly(vinyl alcohol) leads to polymers with long ladder-type blocks according to the reaction:[9]



This regular structure is obtained when polymerization proceeds at 70°C and at rather low concentration of monomer. The material obtained in more concentrated solutions has more complex structure composed of ladder-type blocks, branchings, and unreacted groups. It can be illustrated by the scheme represented in the Figure 9.5.

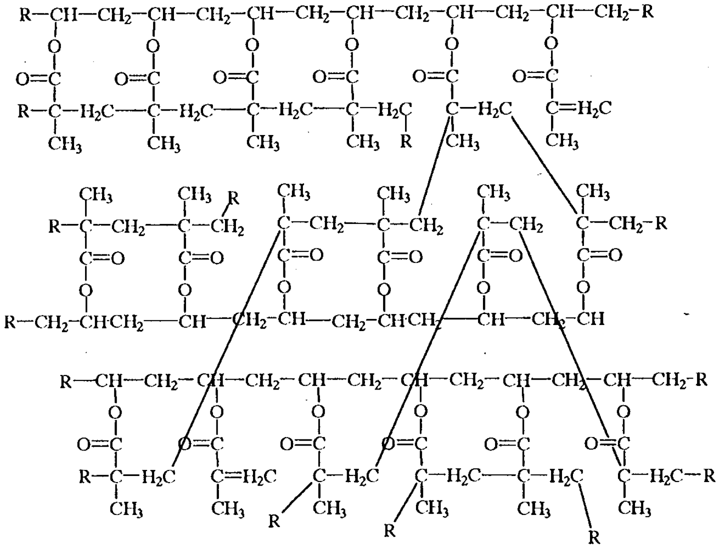
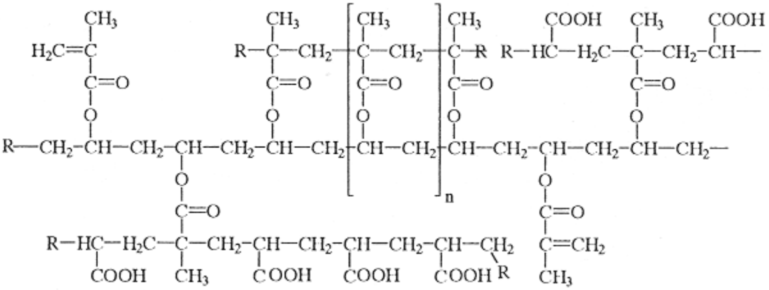


Figure 9.5. Schematic representation of crosslinked molecule obtained by polymerization of multimethacrylate from poly(vinyl alcohol).

Such branched or slightly crosslinked materials possess unreacted groups and ladder blocks. The products after drying are usually insoluble in common solvents, therefore precise structure investigation is difficult.

The copolymerization of multimonomers with vinyl monomers such as acrylic acid, styrene, or acrylonitrile results in semi-ladder copolymers soluble in many common solvents.[9,10,11] Such products consist of ladder-type blocks created from multimonomer molecules and blocks of repeated units formed from vinyl monomer, both connected with branching points and fastened together by fragments of the molecule with ladder structure. Semi-ladder copolymer (multimethacrylate-acrylic acid, partially crosslinked) has the following structure:



Styrene-multimethacrylate ladder copolymers, varying in molecular weight and composition, were also synthesized from styrene and methacryloyl ester of p-cresyl-formaldehyde oligomers.[11,12] The samples were examined by IR spectrometry and GPC.[12,13] The copolymers have a unimodal molecular weight distribution but rather high heterogeneity. Investigation of the set of copolymers by thermogravimetric analysis and inverse gas chromatography shows that the ladder-type copolymers are, in solid state, double phase systems since they have two glass transition temperatures. One of them is very close to the glass transition temperature of polystyrene and indicates that this phase consists of the blocks of polystyrene. The second glass transition temperature depends on the copolymer composition and is close to the value for multimethacrylate homopolymer (in the range of 120 - 140°C). Figure 9.6 shows DSC thermogram for polystyrene and homopolymer obtained by polymerization of multimonomer. Figure 9.7 gives DSC thermograms for copolymers of varying composition. The second phase can be regarded as a homogeneous system, in which blocks of multimethacrylate and polystyrene co-exist. Such thermal properties are connected with the stiffness of ladder blocks. Other properties of such copolymers were only investigated within a limited scope.

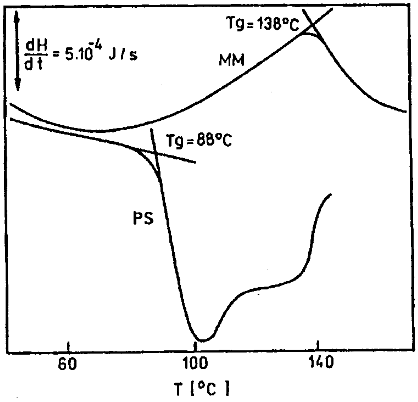


Figure 9.6. DSC thermogram of homopolymers: PS- polystyrene; MM- polymerized multimonomer. Reprinted from S. Rabiej and A. Wlochowicz, *Eur. Polym. J.*, 24, 183 (1992) with kind permission from *Elsevier Science, Ltd.*

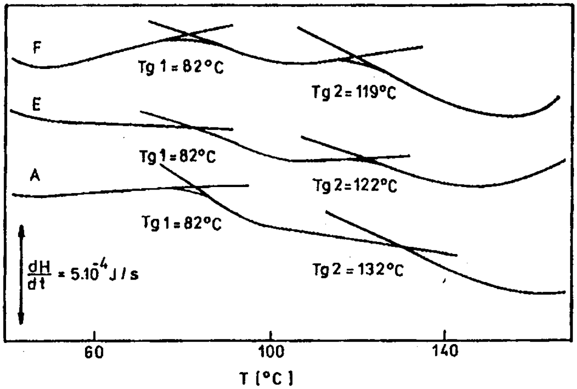


Figure 9.7. DSC thermogram of copolymers: sample F - 41% MM; sample E - 53% MM; sample A - 74% MM. Reprinted from S. Rabiej and A. Wlochowicz, *Eur. Polym. J.*, **24**, 183 (1992) with kind permission from *Elsevier Science, Ltd.*

9.2 POLYMER COMPLEXES

Polymerization of monomers interacting with template by ionic or charge transfer interactions or by hydrogen bonding leads to polycomplexes. Formation of polymeric complexes from two mutually interacting polymers is well known.[14,15] By mixing two solutions of polyelectrolytes having opposite charges, one can obtain the polymeric complex usually in the form of precipitate or liquid phase containing a high concentration of the two polymeric components and a second liquid phase containing much lower concentration of the polymers. Methods of synthesis, properties, and characteristics of polyelectrolyte complexes have been described in many papers.[14,15] A structure of typical polycomplexes is illustrated in Figures 9.8 and 9.9.

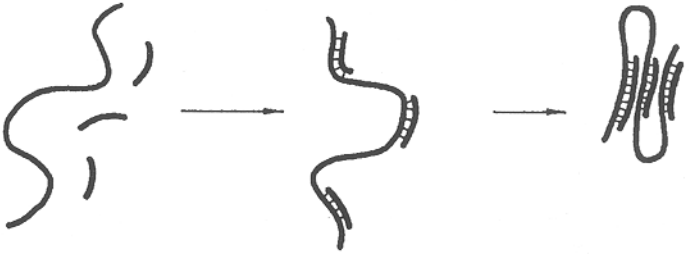


Figure 9.8. Polycomplex creation from high molecular weight polymer and oligomeric molecules. "Host-guest" model.

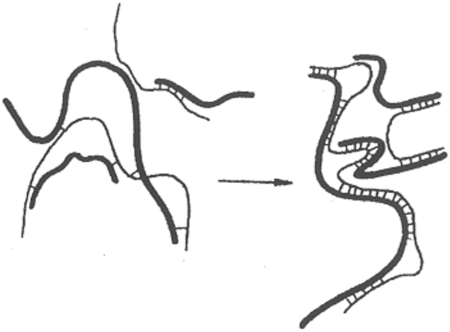


Figure 9.9. Polycomplex formation from two high molecular weight polymers. "Scrambled eggs" model.

If one polymer has much higher molecular weight than the other, a model "host-guest" is commonly applied (Figure 9.8). Smaller "guest" molecules are absorbed on the "host" molecule. Because hydrophobic interactions take place between created blocks, the molecule of the complex becomes more compact. Similar intermolecular interactions can lead to precipitation. It seems probable that similar process takes place at the very beginning of the template polymerization proceeding according to "pick-up" mechanism. The case in which two macromolecular components have high molecular weight is presented in Figure 9.9. Interacting molecules are bonded at random. Short "ladder" parts of the polycomplex as well as "loops" created from unconnected parts of the components are present in the product. Such structure is sometimes called "scrambled eggs" model. Similar polycomplexes can be obtained by template polymerization of complementary monomer on the proper template. The template and the daughter polymer in this case form polymer complexes. The structure of such polycomplexes is in many cases different from the analogous complexes obtained by mixing two complementary polymers. For instance, template polymerization of 4-vinylpyridine in water in the presence of poly(sodium phosphate) leads to highly ordered crystallizable polymer complex.[16] Also, polymerization of 4-vinylpyrridine using poly(oxyphosphinatooxytri-methylene) as a template gives crystallizable complexes with structure that differs from the structure of complexes obtained from mixtures.[17]

Template polymerization of urea and formaldehyde onto poly(acrylic acid) gives polycomplexes with fibrillized structure.[18] The polycomplexes are glasses characterized by a high compressive strength and susceptibility to forced elastic deformation. It was found[19] that polycomplexes prepared by template polymerization of acrylic acid in the presence of poly(vinylpyrrolidone) have different moisture regain properties in comparison with complexes prepared by mixing. The moisture regain of the complex depends on the tacticity of the poly(acrylic acid).[20] Polycomplex prepared from atactic poly(acrylic acid) has the highest value, and from isotactic the lowest. The polycomplex prepared by template polymerization of acrylic acid in the presence of template polyvinyl pyrrolidone has an intermediate value. This shows that a considerable degree of isotacticity has been induced to poly(acrylic acid) by template polymerization. Eboatu and Ferguson [20] found that in polycomplexes poly(acrylic acid)/poly(vinyl pyrrolidone) there is much higher water absorption than by a similar complex formed by mixing of the components and by pure poly(vinyl pyrrolidone). The authors conclude that the complex obtained by template polymerization has a high number of active centers for water absorption. Some differences in morphology and thermal properties of films obtained from complexes prepared in these two ways were also observed.

Aleksina *et al.*[21] investigating polymerization of methacrylic acid in the presence of poly-L-lysine found that the complex obtained by template polymerization has a 1:1 stoichiometry, while the same components obtained by separation of the complex and repeated mixing gave a complex in which the ratio of polylysine units to polyacid units is 2:3. The stable conformation of polylysine macromolecule in the complex obtained by template polymerization is the conformation of α-helix.

The polycomplex obtained by template polymerization of polyacrylamide with uracil groups onto template, from polyacrylamide with adenine groups, was found to be very stable compared with the polymer complex which was formed by mixing both polymers in solution.[22] The ratio of monomer to template in the complex, when the template has rather high molecular weight and growing radical is short, can be very different from the final product ratio.

At the very beginning of the reaction, strong hydrophobic interactions can substantially change the conformation of the template. It is shown by Kharenko *et al*.[23] that when using long macromolecule (host) and many short chains (guests), a special equilibrium and special kind of stoichiometry is established. The equilibrium is illustrated by the Figures 9.10 and 9.11.

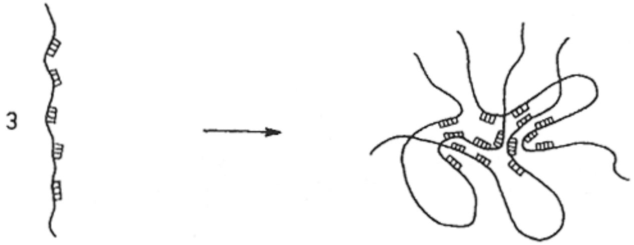


Figure 9.10. Schematic representation of complex molecules association. Reprinted from O. A. Kharenko, V. A. Izumirudov, A. V. Kharenko, V. A. Kasaikin, A. B. Zezin, and V. A. Kabanov, *Vysokomol. Soed.,* **22**, 218 (1980), with kind permission from *Iz. Nauka*.

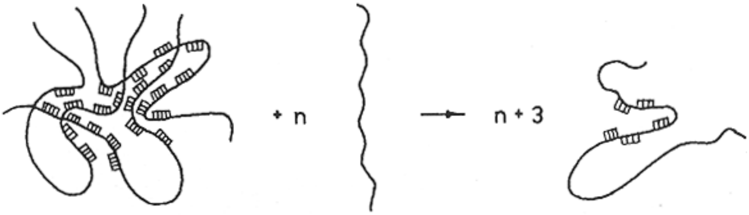


Figure 9.11. Schematic representation of complex molecules dissociation. Reprinted from O. A. Kharenko, V. A. Izumirudov, A. V. Kharenko, V. A. Kasaikin, A. B. Zezin, and V. A. Kabanov, *Vysokomol. Soed.,* **22**, 218 (1980), with kind permission from *Iz. Nauka.*

Three molecules of the "host-guest" complex can associate in three-molecular associate (Figure 9.10). This structure was confirmed by light scattering measurements. When "free matrix" was added to the associated system, dissociation occurs (Figure 9.11).

Stereocomplexes are a special group of compounds which can be obtained as a result of template polymerization and stereocomplex formation, described many years ago. The best known is the stereocomplex formed from isotactic and syndiotactic polymethylmethacrylate. Liquori *at al.*[24] described the first complex. Mixtures of isotactic and syndiotactic poly(methyl methacrylate) crystallize, forming stereocomplexes. By interpreting the results of x-ray diffraction measurements, Liquori *et al.*[24] proposed a model for stereocomplex which is based on a stoichiometric ratio of iso- and syndio-PMMA 1:2. The structure of the stereocomplex was confirmed by Vorenkamp *et al.*[25] and by Schomaker[26] who employed a variety of techniques applied to varying conditions of complex preparation. The details of the stereocomplex structure are still not completely clear. The general concept is based on the model in which an isotactic molecule is surrounded by a syndiotactic molecule in a helix form. There is evidence that stereocomplexes have a similarly sophisticated structure. The diagram of such a structure is shown in Figure 9.12.

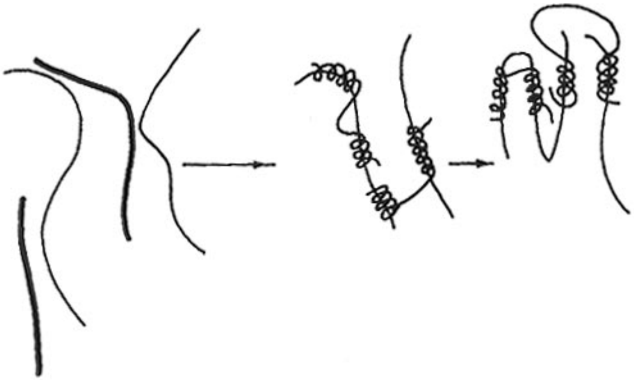


Figure 9.12. Schematic representation of stereocomplex formation.

As a result of specific interactions, molecules of one component are surrounded by molecules of the second component in the segments of helix form. On the basis of these findings it is possible to assume that similar structures are formed during polymerization of methyl methacrylate in the presence of the isotactic template, or polymerization of methacrylic acid in the presence of poly(L-lysine). However, more experimental results are still needed.

Special type of template polycondensation product was obtained by Papisov *at al.*[14] Polycondensation of urea with formaldehyde in the presence of poly(acrylic acid) gives polycomplexes or polycomplex composites with various structures and properties. The

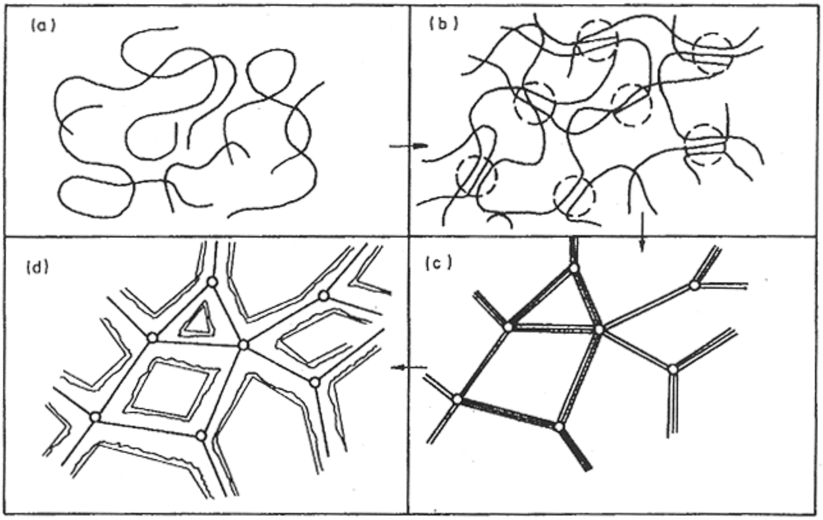


Figure 9.13. Schematic representation of matrix polymerization of urea and formaldehyde in the presence of PAA: (a) moderately concentrated solution of PAA and monomers (monomer molecules are not indicated), (b) 1st step of the process - gel formation (composite polycomplex + excess of PAA), (c) polycomplex PAA-PFU =1:1, (d) composite polycomplex + excess of PFU. Reprinted from I. M. Papisov, O. E. Kuzovleva, S. V. Markov and A. A. Litmanovich, *Eur. Polym. J.*, **20**, 195 (1984),

synthesis of polycomplexes or polycomplex composites proceeds in a few steps. Schematic representation of the process is presented in Figure 9.13.

First step (a) represents the initial system - solution of the poly(acrylic acid) (urea and formaldehyde are not shown). Then, growing macromolecules of urea-formaldehyde polymer recognize matrix molecules and associate with them forming polycomplex. This process leads to physical network formation and gelation of the system (step b). Further process is accompanied by polycomplex formation to the total saturation of the template molecules by the urea-formaldehyde polymer (step c). Chemical crosslinking makes the polycomplex insoluble and non-separable into the components. In the final step (c), fibrilar structure can be formed by further polycondensation of excess of urea and formaldehyde.

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10

POTENTIAL APPLICATIONS

Production of materials in which the daughter polymer and the template together form a final product seems to be the most promising application of template polymerization because the template synthesis of polymers requiring further separation of the product from the template is not acceptable for industry at the present stage. Possible method of production of commonly known polymers by template polymerization can be based on a template covalently bonded to a support and used as a stationary phase in columns. Preparation of such columns with isotactic poly(methyl methacrylate) covalently bonded to the microparticulate silica was suggested by Schomaker.[1] The template process can be applied in order to produce a set of new materials having ladder-type structure, properties of which are not yet well known. A similar method can be applied to synthesis of copolymers with unconventional structure.

Template polymerization is the only way to produce polycomplexes and polycomplex composites in which one of the polymer components is insoluble and the polycomplex cannot be obtained by mixing solutions of polymers previously prepared. In this way, interpenetrating networks were obtained.

Properties of composites obtained by template polycondensation of urea and formaldehyde in the presence of poly(acrylic acid) were described by Papisov *et al*.[2] Products of template polycondensation obtained for 1:1 ratio of template to monomers are typical glasses, but elastic deformation up to 50% at 90°C is quite remarkable. This behavior is quite different from composites: polyacrylic acid-urea-formaldehyde polymer obtained by conventional methods. Introduction of polyacrylic acid to the reacting system of urea-formaldehyde, even in a very small quantity (2-5%) leads to fibrilization of the product structure. Materials obtained have a high compressive strength (30-100 kg/cm^3). Further polycondensation of the excess of urea and formaldehyde results in fibrillar structure composites. Structure and properties of such composites can be widely varied by changes in initial composition and reaction conditions.

In situ polycondensation leads to aromatic polyamides or polyesters dispersed within the matrix of polyarylate. Mechanical and thermal properties of the films formed from these systems were investigated. It was found that, especially at high temperatures (100-150°C), tensile modulus of these films is much higher than that for unmodified polyarylate.

Many polymer-polymer complexes can be obtained by template polymerization. Applications of polyelectrolyte complexes are in membranes, battery separators, biomedical materials, etc. It can be predicted that the potential application of template polymerization products is in obtaining membranes with a better ordered structure than it is possible to obtain by mixing the components. The examples of such membranes from crosslinked poly(ethylene glycol) and poly(acrylic acid) were described by Nishi and Kotaka.[4] The membranes can be used as so-called chemical valves for medical applications. The membranes are permeable or impermeable for bioactive substances, depending on pH.

The polycomplexes obtained by template polymerization of methacrylic acid or acrylic acid in the presence of poly(N,N,N`,N` - tetramethyl-N-p-xylene-ethylenediammonium dichloride) were used for spinning of fine fibers 5 to 50 μm in diameter.[5] The fibers are soluble in water but become stable after thermal treatment at about 80°C. The polycomplex with regular structure, obtained by template polymerization, is expected to be of considerable interest for textile industry.

Rätzsch[6] reported an application of template polymerization similar in technique to photolitography. Plates, covered by a thin layer of the mixture containing monomer (acrylic acid) are exposed through a mask to UV light. Polymerization is initiated in the places exposed to light. In exposed places, an insoluble complex is formed. By dissolving a soluble unreacted part and treating the plates with a proper dye or colored metal ions an image appears.

Template polymerization can be used for production of polymers with much higher molecular weights in comparison with those obtained by conventional process (in the last case a degradative addition frequently takes place). It was shown based on the example of N-vinylimidazole polymerization.[7] By the template process, polymers with up to 70 times higher molecular weight than in conventional polymerization were obtained.

As reported,[8] by polycondensation of dicarboxylic acids with diamines or by polycondensation of aminoacids in the presence of polyvinylpyrrolidone, polymers with very high molecular weight were obtained. The viscosities of poly(terephthalamides) prepared by template polymerization in the presence of polyvinylpyrrolidone from p-phenylenediamine and 4,4`-diaminodiphenylosulfone and of poly(m-benzamid) are very high. Also, polypeptides with molecular weight of 20-30 thousands were obtained by template polymerization in the presence of polyvinylpyrrolidone.[8]

Chapiro reported[9] that semi-permeable membranes containing carboxylic groups and pyridine groups can be obtained by polymerization of 4-vinylpyridine onto polyterefluoroethylene films previously grafted by acrylic acid. The films after grafting were neutralized by KOH in order to convert grafted polymer to poly(potassium acrylate). The films were then subjected to polymerization of 4-vinylpyridine initiated by γ-rays. In order to reach 100% grafting, the films without poly(acrylic acid) were irradiated with total dose of 138,000 rads and process was carried out for 48 hrs. Films with grafted 35% poly(acrylic acid) were polymerized only 6 min and with total dose 300 rads. It is most probable that polymerization in the last case proceeds according to template mechanism.

Template copolymerization seems to be applied to the synthesis of copolymers with unconventional sequences of units. As it was shown, by copolymerization of styrene with oligomers prepared from p-cresyl-formaldehyde resin esterified by methacrylic or acrylic acid - short ladder-type blocks can be introduced to the macromolecule. After hydrolysis, copolymer with blocks of acrylic or methacrylic acid groups can be obtained. Number of groups in the block corresponds to the number of units in oligomeric multimonomer. Such copolymers cannot be obtained by the conventional copolymerization.

Short block copolymers with well defined number of units in the blocks could be applied as selective absorbents, compatibilizers for polymer blends, components for polymeric membranes, etc.

As discussed in Chapter 5, copolymers with unconventional distribution of units can be obtained by copolymerization in the presence of proper template. Synthesis of polymers with defined tacticity can be realized by template polymerization or copolymerization. In spite of the fact that many interesting potential applications seems to be possible neither template polymerization as a method of synthesis nor the products obtained in this process have been applied on an industrial scale until now.

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11

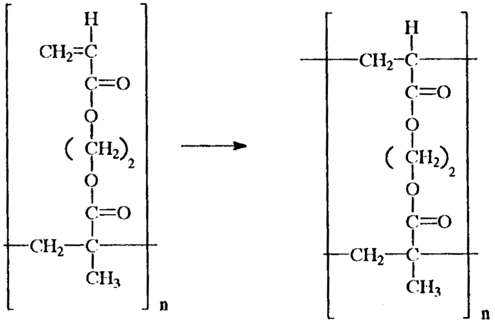
EXPERIMENTAL TECHNIQUES USED IN THE STUDY OF TEMPLATE POLYMERIZATION

11.1 METHODS OF EXAMINATION OF POLYMERIZATION PROCESS

Many experimental techniques were used to examine polymerization kinetics and products of template polymerization. In kinetic measurements, many conventional methods of determination of monomer concentration were applied, very often UV spectrometry[1] or bromometric titration.[2,3] For many systems examined, bromometric titration gives results comparable with the results obtained by other methods. However, systems were found in which the method successful for blank reaction gives results incomparable with another analytical methods. Perhaps some specific reaction with the complex formed affects the analytical procedure.[4]

A simple gravimetric method based on the precipitation and weighting of the dried product in the case of template polymerization is more complicated than in the case of common polymerization. Usually polymeric template precipitates with the daughter polymer and separation is difficult. For these reasons this method is not very often used.

IR spectrometry is a convenient method of examination of template copolymerization[5] and polymerization kinetics. For instance, IR spectroscopy was applied[6] in order to examine kinetics of template polymerization of multiacrylate according to the reaction:



In the initial multimonomer, absorption band of CH_2=CH- groups appears at 1630 cm^{-1}.[6,7] The extent of polymerization of this multiacrylate was determined from the change in the ratio of absorption at 1630 cm^{-1} to the absorption of C=O group at 1720 cm^{-1}. Selected spectra are shown in Figure 11.1.

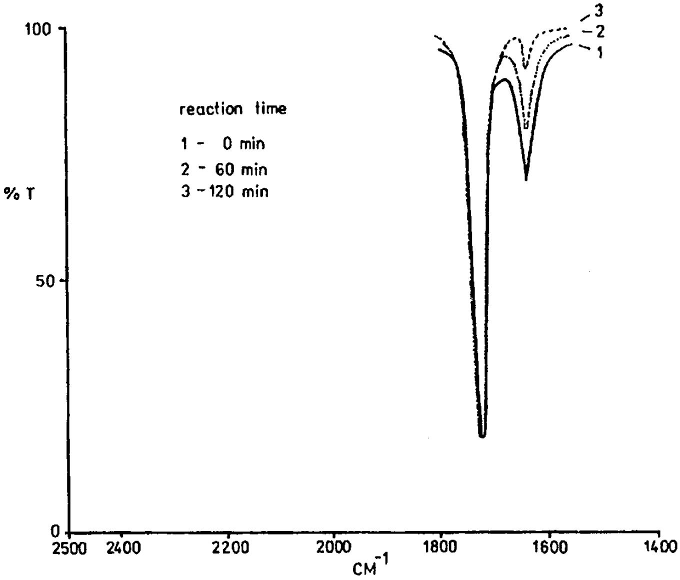


Figure 11.1. Polymerization of multiacrylate by UV light (from the author's laboratory).

The peak of double bonds disappears while intensity of the carbonyl group peak is independent of reaction time. Using this method, the conversion of double bonds vs. time was calculated[6] to monitor polymerization of multiacrylate at two different temperatures (Figure 11.2).

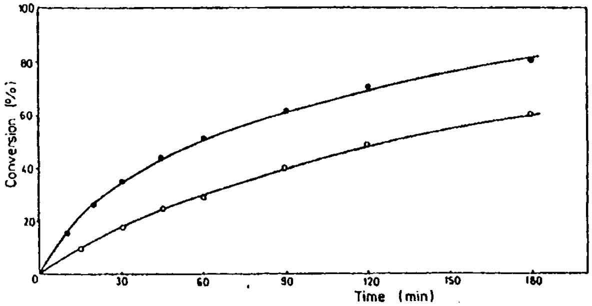


Figure 11.2. Time-conversion curve for polymerization of multiacrylate in dioxane (o) at 75°C, and (•) at 85°C. Reprinted from R. Jantas, J. Szumilewicz, G. Strobin, and S. Polowinski, *J. Polym. Sci., Polym. Chem.*, **32**, 295 (1994).

Dilatometry is a convenient method for measuring polymerization rate. The method is based on a decreasing volume of the examined system along with conversion of monomer to polymer. For simple polymerization, usually carried out in solution in capillary dilatometer, the decrease in volume, Δv, is calculated from measurements of the decrease in the level of reacting mixture $h_0 - h = \Delta h$ in capillary with radius, r. Using equation:

$$\Delta v = \pi r^2 \Delta h \qquad [11.1]$$

percent of conversion can be calculated according to the following equation:

$$\alpha = \frac{\pi r^2 \Delta h 100}{(1/d_p - 1/d_M)m} \qquad [11.2]$$

where: d_p and d_M are densities of polymer and monomer, respectively, and m - the weight of the monomer in sample. The polymer density, d_p, is usually determined from pycnometric measurements of polymeric solutions, and calculated from the formula:

$$d_p = \frac{1}{V}\,\frac{m_p}{1-(m-m_p)/m_0} \qquad [11.3]$$

where: m_p and m are respectively weight of polymer, and solution in pycnometer of the volume V; and m_0 is the weight of pure solvent in the same volume, V. The dilatometric method is very convenient for examination of photopolymerization, especially for rotating sector technique[8] or, more generally, for examination of polymerization in a non-stationary state. In this way, reactivity rate constants of elementary processes can be calculated. In a set of our papers,[8-10] propagation and termination rate constants were calculated for template polymerization of methacrylic acid. Also, the rotating sector technique was applied for template polymerization of methyl methacrylate[11] and methacrylic acid.[12]

Dilatometric technique can also be used for determination of polymerization rate in the case of multimonomer polymerization. However, in this case calibration of the dilatometric method is more complex. The substrates and products are both polymers with similar molecular weights. Difference in density during the course of polymerization is connected only with the conversion of double bonds to the single bonds. It is difficult to obtain a macromolecular product in which double bonds are fully converted to single bonds. Calibration must be based on simultaneous measurements of Δh and independent method (e.g., IR spectroscopy) and calculation of $(1/d_p \setminus 1/d_M)$.

Determination of the reaction rate from calorimetric measurements, using DSC technique, is very useful and was applied with success for many template polymerization systems[13] and for blank polymerizations.[14,15,16] Two types of calorimetric measurements were described: isothermal and scanning experiments. The heat of polymerization can be measured by DSC method, measuring thermal effect of polymerization and ignoring the heat produced from decomposition of the initiator and heat of termination. In isothermal experiments sample is placed at a chosen temperature and thermogram is recorded versus time. Assuming typical relationship

$$-d[M]/dt = k[M][I]^{1/2} \qquad [11.4]$$

and constant concentration of the initiator, the following formula can be applied:

$$\ln\{[M]_0]/[M]\} = k[I]^{1/2}t \qquad [11.5]$$

The total area under thermogram A corresponds to the complete monomer conversion and is proportional to $[M_0]$. The area “a” of the thermogram up to the time t, corresponds to the reacted part of the monomer, thus (A-a) corresponds to the residual part of the monomer. From this:

$$\ln\{A/(A - a)\} = k[I]^{1/2}t \qquad [11.6]$$

In scanning experiments, results were recorded as usual for DSC measurements as a function of temperature, T, with a proper scan speed

$$\beta = dT/dt \qquad [11.7]$$

The equation for rate constant was formulated:[15]

$$k = \frac{dH/dt}{\left\{(\Delta H_{p,o}/\Delta H_p)H_{tot} - H\right\}[I]^{1/2}} \qquad [11.8]$$

where: H_{tot} is the total reaction heat derived from the area under the total DSC curve, H is the reaction heat up to time t, or temperature T, dH/dt is the rate of heat evolution related to the scan speed, β. ΔH_{po} and ΔH_p are actual and apparent heats of polymerization, respectively. The former value can be obtained by taking a sufficient amount of initiator and extrapolating the reaction heat to zero scan speed. [I] is the instantaneous initiator concentration which can be calculated from the activation parameters for decomposition of the initiator E_d and A_d according to the formula:

$$\ln[I]_0/[I] = A_d/\beta \times \int_{T_0}^{T} \exp(-E_d/RT)dT \qquad [11.9]$$

Activation parameters for template polymerization were computed from Arrhenius relationship:

$$k = A\exp(-E_a/RT) \qquad [11.10]$$

The method was applied for examination of the polymerization of N-vinylpyrrolidone in DMF,[14] methacrylic acid in DMF,[15] and 2-vinylpyridine in DMF.[16]

Another technique which is used to follow the extent of template polymerization vs. time is turbidimetry. Two types of measurements can be used here. The first is based on the determination of passed light intensity, the second on the determination of scattered light intensity. The former was used in many papers by Ferguson and co-workers for studies on polymerization of acrylic acid in aqueous solution in the presence of many homopolymers used as templates[17,18] as well as for application of copolymers with interacting and non-interacting groups.[19] This measurement was also used for studying complex formation between poly(vinyl pyrrolidone) and poly(acrylic acid).[20] The total light scattered in all directions from the incident beam, as it traverses a suspension, is measured as turbidity, τ.

The intensity, I_0, of an incident beam is reduced to I on the passage through distance x in the medium. The expression similar to the expression for absorption of light is:

$$I/I_0 = \exp(-\tau x) \tag{11.11}$$

The total concentration of complex formed during the complexation is proportional to τ. During template polymerization of acrylic acid, a stable colloidal precipitate resulted in the systems under investigation, and turbidity measurements could be used, assuming that direct reading from the turbidimeter (in logarithmic scale) is proportional to the amount of polymeric product. The assumption was checked by calibration procedure. The light absorption (%) is proportional to the concentration of poly(acrylic acid)-poly(vinyl pyrrolidone) mixture.[17] 100% conversion was assumed when no increase in turbidity was detected by the recorder. In the case when copolymers were used as templates,[18] the apparatus was calibrated for each copolymers separately.

GPC is a promising method for examination of template polymerization, especially copolymerization. Copolymerization of methacrylic acid with methyl methacrylate in the presence of poly(dimethylaminoethyl methacrylate) can be selected as an example of GPC application for examination of template processes.[21] The process was carried out in tetrahydrofurane as solvent at 65°C. After proper time of polymerization, the samples were cooled, diluted by THF, filtered, and injected to GPC columns. Two detectors on line: UV and differential refractometer, DRI, were applied. UV detector was used to measure concentration of two monomers, while the template was recorded by DRI detector (Figure 11.3) The decrease in concentration of both monomers can be measured separately. It was found that a big difference in the rate of polymerization between template process and blank polymerization exists. The rate measured separately for methacrylic acid (decrease of concentration of methacrylic acid in monomers mixture) was much higher in the template process. Furthermore, the ratio of both monomers changes in a different manner. Reactivity ratios for both monomers can be computed. Decrease in concentration during the process is shown in Figure 11.4.

The molecular weight distribution shows a small change in template molecular weight, but the average molecular weight decreases during the process. Changes in molecular weight of the poly(dimethylaminoethyl methacrylate) used as template in copolymerization of methyl methacrylate with acrylic acid[21] are presented in Figure 11.5.

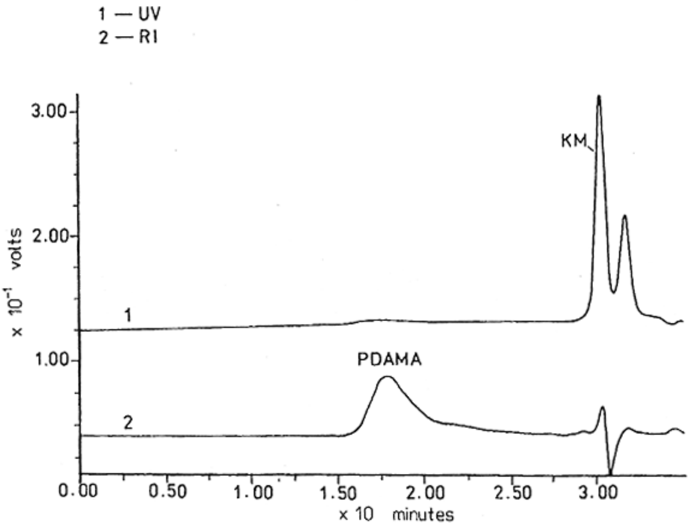


Figure 11.3. Chromatogram of the reacting mixture: methylmethacrylate-meth-acrylic acid poly(dimethylaminoethyl methacrylate). Initial state. [PDAMA]=[KM]=[MM]=0.2 mol/L. According to ref. 21.

The decrease in molecular weight probably occurs because template molecules with high molecular weight are engaged by the first portions of the complex formed. They are then removed from a polydisperse mixture with precipitated product. Observation of this phenomenon is possible only by GPC method. The complex formed was removed by filtration. The concentration of template existing in the system was compared with the concentration of the monomers during reaction. The change in complex composition as a function of time can be computed. Figure 11.6 shows composition of polycomplex formed during template copolymerization calculated from chromatography data.[21]

The GPC method allows to measure:

- rates of reaction for both monomers separately
- the rate of complex formation
- composition of the complex
- changes in molecular weight distribution of soluble parts of the system.

The method proposed by Blumstein *at al.*[22] is based on the conductivity measurements. It is suitable for the systems in which shift of ionization equilibrium during polymerization takes place. This method was successfully applied to follow template polymerization of p-styrene sulfonic acid in the presence of polycationic ionenes used as template. The results confirm data obtained for the same system by another methods.

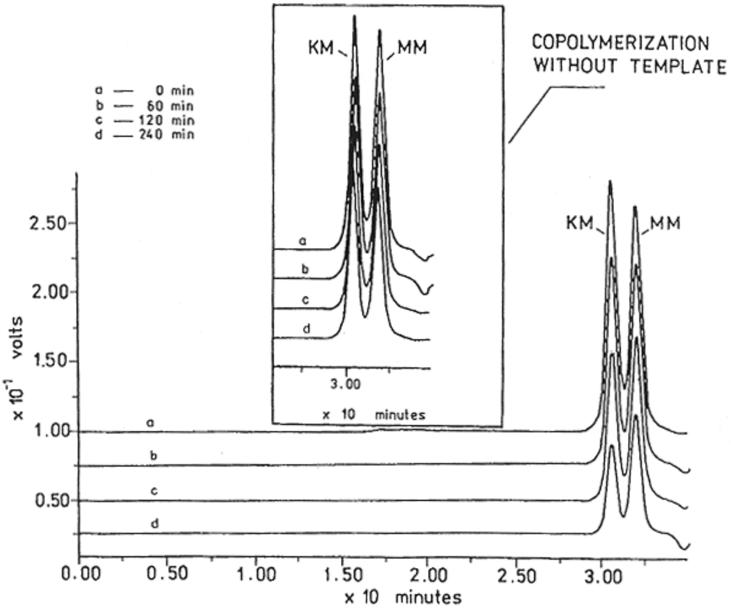


Figure 11.4. Chromatogram of the reacting mixture: methylmethacrylate- methacrylic acid poly(dimethylaminoethyl methacrylate). [PDAMA]=[KM]=[MM]=0.2 mol/L. According to ref. 21.

11.2 METHODS OF EXAMINATION OF TEMPLATE POLYMERIZATION PRODUCTS

Polymerization products are different for polymer complexes and for ladder-type polymers.

11.2.1 POLYMERIC COMPLEXES

If a product of template polymerization is composed of a daughter polymer and a template involved in polymer complex, the first step of analysis is separation of these two parts. Separation of two polymers forming a complex is sometimes difficult and depends on interactions between the components. Very often polymeric complexes are insoluble in water and also in organic solvents. In order to dissolve such compounds, aqueous or non-aqueous solutions of inorganic salts such as LiBr, LiCl, NH_4CNS are used. Dimethylformamide or dimethylacetamide are commonly used as non-aqueous solvents. If one of the components is a polyacid, alkali solutions are used as solvent. Ferguson and Shah[17] reported that the complex obtained by polymerization of acrylic acid in

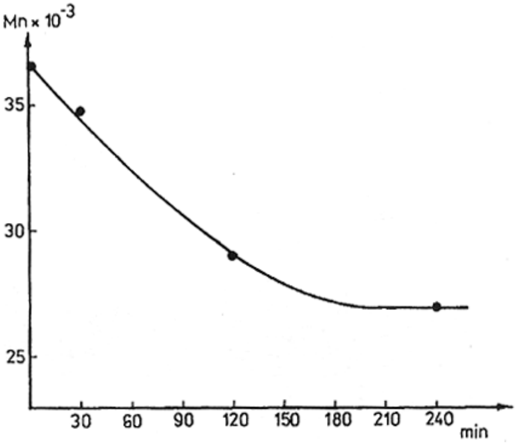


Figure 11.5. Changes in molecular weight of the template during copolymerization of methyl methacrylate with methacrylic acid. Template: poly(dimethyl aminoethyl methacrylate) PDAMA. Initial concentrations: [PDAMA]=[MM]= [MA]=0.2 mol/L. Solvent THF. Temperature 65°C. According to ref. 21.

the presence of poly(vinyl pyrrolidone) was soluble in 0.5N NaOH and 1N NH_4OH. The later solvent was used for electrophoresis in order to separate components of the template polymerization product. The complexes were applied as 1 per cent solutions in 1N NH_4OH on a Whatman No. 1 paper strip and subjected to electrophoresis for up to 6 h at 500 V. The chromatogram was dried and developed by bromocresol green (yellow spots indicate polyacid presence). In a separate step, iodine in potassium iodide solution gave brown spots in the areas containing poly(vinyl pyrrolidone). The complex formed as a result of template polymerization gave three spots: one identified as poly(vinyl pyrrolidone) and two others (slightly overlapping) as poly(acrylic acid) and graft copolymer. The last compound, located in the region in between the two main components, gave yellow spot when tested with bromocresol green and brown spot when tested with iodine. Using the same method, the complex obtained by mixing poly(vinyl pyrrolidone) with poly(acrylic acid) was separated into only two distinct spots corresponding to the initial components.

Paper chromatography was also used to separate the complex obtained by polymerization of acrylic acid in the presence of poly(ethylene imine).[18] In this case, both the complex obtained by mixing of two polymers and the complex obtained in template polymerization gave two distinct spots. No trace was found of any graft copolymer.

Another method of analysis of polymeric complexes is based on the separation of components by chemical reaction. Isolation of daughter polymer from polymeric complex obtained by template polymerization of methacrylic acid in the presence of poly(vi-

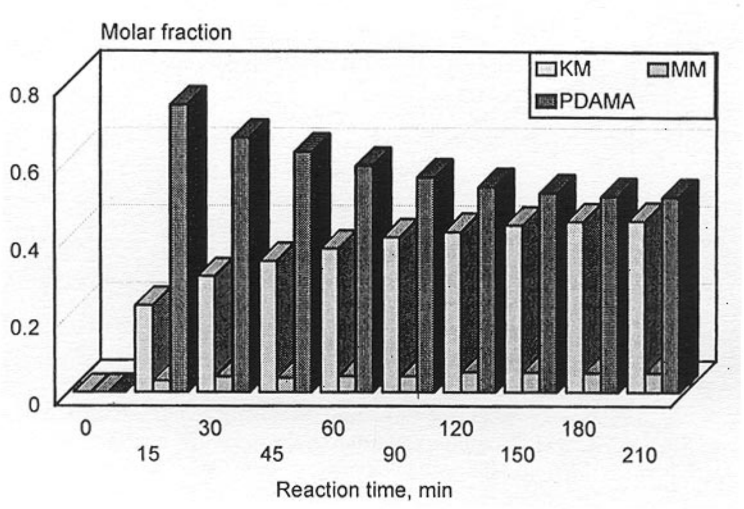


Figure 11.6. Composition of polycomplex as a function of time. According to ref. 21.

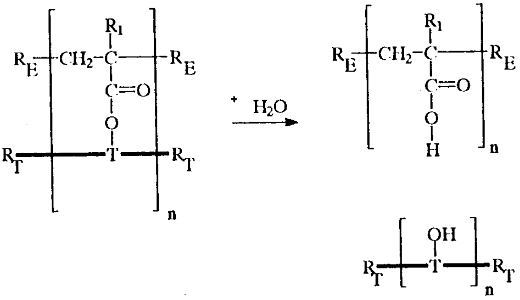
nyl pyrrolidone) was achieved by treating the complex suspended in benzene with diazomethane.[2] Poly(methyl methacrylate) was soluble in benzene. After filtration the polymer was precipitated from the benzene solution and dried. The insoluble part of the complex was not an object of analysis. For poly(methyl methacrylate) separated in this manner, molecular weight was determined by viscosity measurements in chloroform solution. Also NMR spectrometry was applied in order to determine tacticity of the polymer.

A similar procedure was described by Eboatu and Ferguson.[23] An object of analysis was the complex obtained by template polymerization of acrylic acid in the presence of poly(vinyl pyrrolidone). The polycomplex was dispersed in dry benzene and treated with diazomethane. The insoluble portion was filtered. The filtrate containing poly(methyl acrylate) was concentrated and finally dried. The insoluble fraction was scrubbed with methanol to extract poly(vinyl pyrrolidone). The residue was further washed with methanol and then dried. These three portions were characterized by IR spectroscopy. It was found that only about 70% separation of the complex is achieved. The occurrence of inseparable portion is attributed to a graft copolymer formation. For the separated poly(methyl acrylate), molecular weight was determined using viscometric method. NMR triad analysis of the polymer shows that about 40% of isotactic triades is present in poly(methyl acrylate) examined.

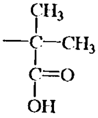
Another complex obtained by template polymerization of dimethylaminoethyl methacrylate in the presence of poly(acrylic acid) was synthesized and analyzed by Abd-Ellatif.[24] The procedure of separation was as follows: to the complex dissolved in 10% NaCl solution, 10% NaOH solution was added dropwise and white gel was precipitated. Addition of sodium hydroxide was continued until no more precipitate was separated. The soluble polymer after dialysis was dried and identified as poly(acrylic acid). The insoluble polymer fraction was found to be insoluble in toluene, benzene, tetrahydrofurane, but soluble in acetone/water (2:1 v/v). Elemental analysis and IR spectra lead to the conclusion that this fraction consists of pure poly(dimethyl aminoethyl methacrylate) which was expected as a daughter polymer.

11.2.2 LADDER POLYMERS

In the case of template polymerization, when reacting units are connected with the template by covalent bonds, analysis of the products can also be based on the separation of daughter polymer from the template. However, the covalent bonds should be broken for instance by hydrolysis of ester groups. This method was applied by Kämmerer and Jung[25] in order to prove that daughter polymer has the same number of units (plus end-groups) as the template. The scheme of the reaction can be represented as follows:

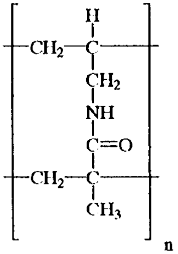


where R_1 is H or CH_3; R_E is end-group from initiator decomposition; R_T is end-group in the template. In the case described by Kämmerer,[25] "T" was a unit of p-cresyl-formaldehyde oligomer, R_T was Br and R_E was $-C(CN)(CH_3)_2$ - from AIBN decomposition. These groups were converted during alkaline hydrolysis to:



$$\begin{array}{c} CH_3 \\ | \\ -C-CH_3 \\ | \\ C=O \\ | \\ OH \end{array}$$

A similar method of hydrolysis was described[7] for poly(vinyl alcohol) used as a template. In this case, “T” was -CH_2-CH- and, after hydrolysis, poly(vinyl alcohol) and polyacrylic or polymethacrylic acid were obtained. The hydrolyzed product gives the color reaction with I_2 in the presence of H_3BO_3 - specific to poly(vinyl alcohol). The second product of hydrolysis, after esterification by diazomethane, was identified as poly(methyl methacrylate) by NMR and IR spectrometry. Hydrolysis was also applied in the case of ladder-type polymers obtained by polymerization of mutliallyl monomers.[26] The polymerization should result in polymer consisting, at least partly, ladder-type blocks:



After hydrolysis by 2N methanol solution of H_2SO_4, the product was neutralized with KOH to pH=5 and methanol evaporated. The dry residue was expected to be poly(allilamine), polymethacrylic acid, and K_2SO_4. Indeed, after extraction with anhydrous methanol and acetone, poly(allilamine) was identified by NMR and IR spectrometries. After evaporation, solvent from the methanol part of the extract insoluble in chloroform part was obtained. After esterification by diazomethane the product was identified as poly(methyl methacrylate) on the basis of IR and ^{1}H-NMR spectroscopy. IR spectroscopy was applied in order to examine the copolymerization of multimethacrylate (p-cresyl-formaldehyde oligomers with methacrylic groups) with styrene.[5] It was found that double bond peak at 1650 cm^{-1} disappeared during the process and it was absent in the product of polymerization. Polymerization and

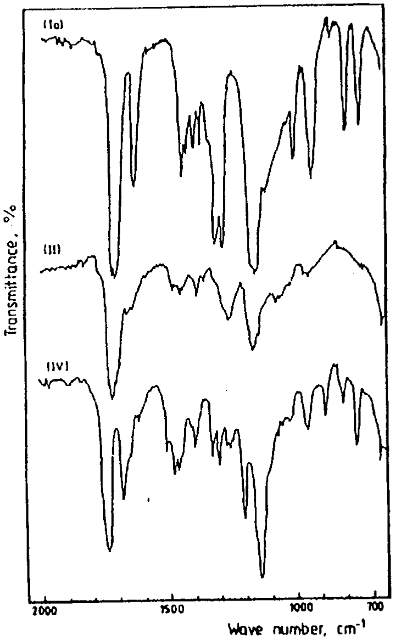
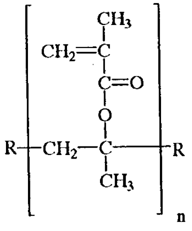


Figure 11.7. IR spectra of multimethacrylate (Ia), homopolymer (II), and copolymer (IV). Reprinted from: R. Jantas and S. Polowinski, *J. Polym. Sci., Polym. Chem.*, **24**, 1819 (1986).

copolymerization of multimethacrylate obtained by reacting poly(vinyl alcohol) with methacryloyl chloride were also examined by IR spectroscopy.[7] Change in the intensity at 1630 $\mathrm{cm^{-1}}$ is illustrated in Figure 11.7.[7]

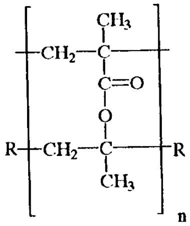
Disappearance of absorption band at 1630 $\mathrm{cm^{-1}}$ was found for the multimethacrylate homopolymer (II) and copolymer (IV) of these two different multimonomers. IR spectra, NMR spectra and hydrolysis experiments lead to the following structures:

for multimethacrylate Ia:

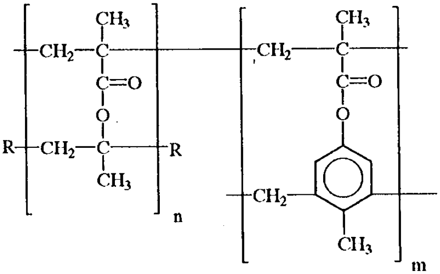


$$\mathrm{R}-\left[\mathrm{CH_2}-\underset{\displaystyle \mathrm{CH_3}}{\overset{\displaystyle \mathrm{CH_2{=}C(CH_3)-C(=O)-O}}{\mathrm{C}}}\right]_n-\mathrm{R}$$

for homopolymer II:



and for copolymer:



Application of typical methods such as X-ray diffraction for examination of this class of materials is still to be assessed.

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