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Template polymerisation and co-polymerisation

Stefan Połowiński*

Technical University of Łódź, 90-924 Lodz, Poland

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Abstract

The general characteristics of template polymerisation were discussed on the basis of examples of template radical polymerisation, template co-polymerisation, poly condensation or addition. The formation of interpolymer complexes and ladder-type polymers was presented. Kinetic effects as well as the mechanism of the template reactions were considered.

Products of template polymerisation and possible applications were briefly described. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Template polymerisation; Template co-polymerisation; Multimonomers; Ladder polymers; Kinetics

Contents

1. Introduction

The term ‘replica’ polymerisation was first used by Szwarc [1] in 1954 and then displaced by ‘matrix’

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* Fax: +48-42-636-5767.
E-mail address: stepol@ck-sg.p.lodz.pl (S. Połowiński).

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or 'template' polymerisation. Since this time, many articles, reviews and chapters of encyclopaedias have been published [2–12]. The great interest of template polymerisation is connected to an analogy between the synthesis of simple polymers onto simple matrices and the synthesis of biopolymers onto matrices such as DNA or RNA or certain enzymatic reactions. In spite of the fact that the analogy is somewhat stretched, template polymerisation can be treated as a simple model for this type of reaction.

Template or matrix polymerisation is usually defined as a process in which the monomer units are organised by a preformed macromolecule (template) and refers to one face systems in which the monomer and template are soluble in the same solvent or are present in a form of a swollen gel.

The organization of a monomer unit can be realized in many ways, by hydrogen bonds, electrostatic forces or by covalent bonds.

Template polymerisation can be classified as template polycondensation, radical or ionic polymerisation, polyaddition or ring opening polymerisation, depending on the mechanism of the reaction.

The criteria by which a process can be recognized as a template process are not very clearly defined. Usually, the experimental criterion is a 'template effect', which can be expressed as a change in kinetics (kinetic effect), a change in molecular weight and its distribution ('molecular effect'), a change in tacticity or sequence distribution of units in the case of co-polymerisation.

2. Radical template polymerisation

2.1. Examples of radical template polymerisation

Most information and experimental data has been published about radical template polymerisation.

It is generally accepted [3–12] that template polymerisation can proceed according to two different mechanisms: type I ('zip' mechanism) or type II ('pick-up' mechanism). In the first case, monomer units are connected with a matrix by strong forces (electrostatic, hydrogen bridges); in the second, the monomer at the beginning of the reaction is 'free' and polymerisation starts outside the template. When oligoradicals reach a critical length, the complexation with the template occurs and propagation proceeds along the template by addition of monomer molecules from the surrounding solution. These two types of reactions can be illustrated by the following schemes presented in Figs. 1 and 2.

It seems that the difference between these two types of mechanisms is not very distinct. If the length of oligomer units, which can be adsorbed by the template (critical length), is small, then mechanism II is close to mechanism I.

However, if the critical length is long, mechanism II operates purely. Two values can be applied in order to describe the interaction between the monomer and the template: (a) the preferential adsorption coefficient, which is a measure of adsorption of the monomer onto the template, and (b) the complexation constant, which describes the equilibrium between the growing oligomer and the template. However, this value increases together with the increase of the growing oligomer due to the co-operative effect.

From preferential adsorption coefficient measurements, which in many cases were classified as 'mechanism I', it was found that adsorption is not 'full', and the template is not fully covered by the monomer in the condition of polymerisation.

To be absolutely certain that the system fulfils mechanism I assumptions, the monomer can be attached to the template by covalent bonds or a stoichiometric complex, formed for instance by strong electrostatic forces.

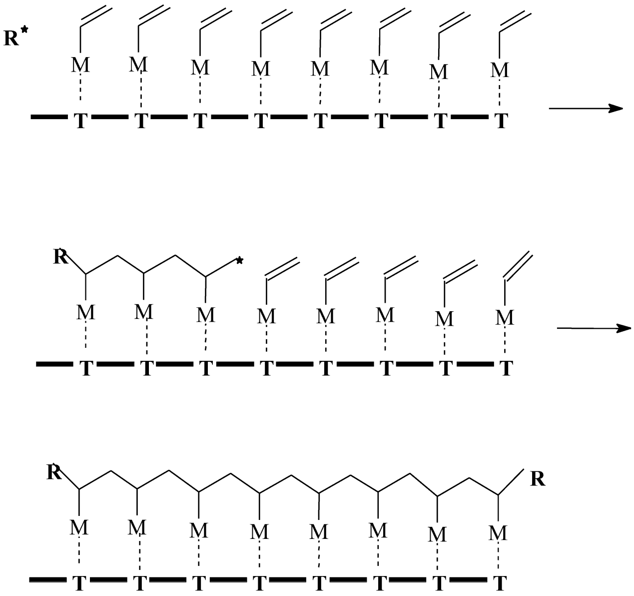


Fig. 1. Schematic representation of chain template polymerisation type I. (Zip mechanism).

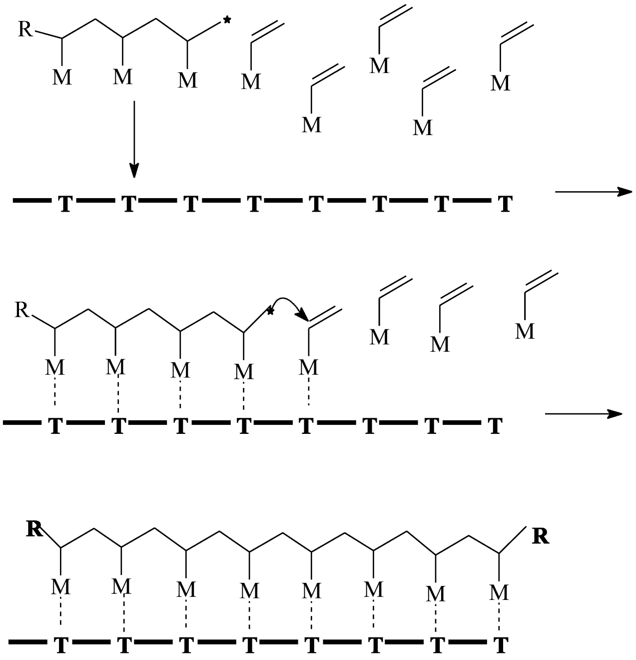
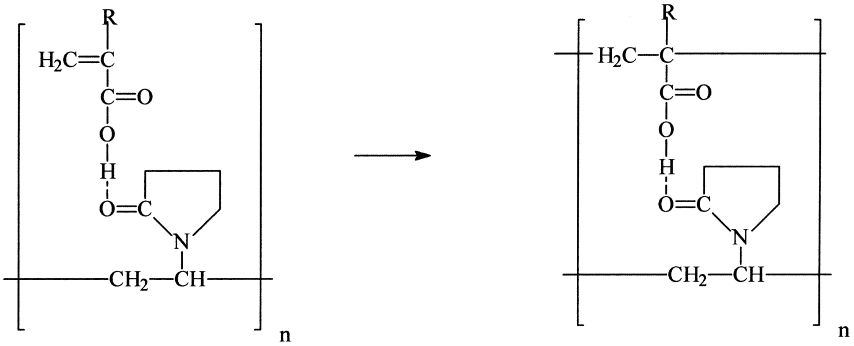


Fig. 2. Schematic representation of chain template polymerisation 'type II'. (Pick-up mechanism).

The type of mechanism is usually deduced from kinetic studies in which the rate of polymerisation is determined as a function of template concentration [T] at constant monomer concentration $[M]_0$. The model of the kinetics and mechanism of the process will be described in the next point in detail. Usually, the rate is compared with the rate of blank reaction — measured for the same conditions but without the template and represented by relative rate R_{rel}.

In the proposed scheme, the maximum of relative rate vs. [T]/[M] is 1 for type I mechanism and then R_{rel} decreases, while for type II mechanism, after reaching maximum for a critical concentration of the template $[T]^*$, the rate is stable.

The most elaborated example of template radical polymerisation is a polymerisation of acrylic acid or methacrylic acid in the presence of different templates. This system was the subject of many publication [10,32] since Ferguson and Shah in 1968 [13] up to Rainaldi et al. [32] in 2000. Although experimental results obtained by different methods are similar, more data are needed in order to obtain a complete picture of the polymerisation mechanism and kinetics. Originally [13], zip-up mechanism was proposed for the polymerisation of acrylic acid onto poly(vinyl pyrrolidone) template. According to the authors, strong hydrogen bonds exist in this system, and the template effect (increase of the reaction rate) depends on pH.



where R is $-H$ or $-CH_3$

Studies on the polymerisation of acrylic [13,16] or methacrylic acid [15], in dilute aqueous systems in the presence of poly(vinyl pyrrolidone) have yielded much experimental data which can be generalized and applied to other similar systems. In all cases, an increase in the reaction rate with concentration of the template is observed, despite the fact that experiments were carried out in different temperatures and ranges of concentrations. The maximum of the relative rate is close to the equivalence of acid and PVP unit concentration. It was found that the higher the molecular weight of the template, the greater is the increase in the relative rate and higher is the molecular weight of daughter polymer. Some peculiarities were found when Fenton's reagent was used as an initiator [14]

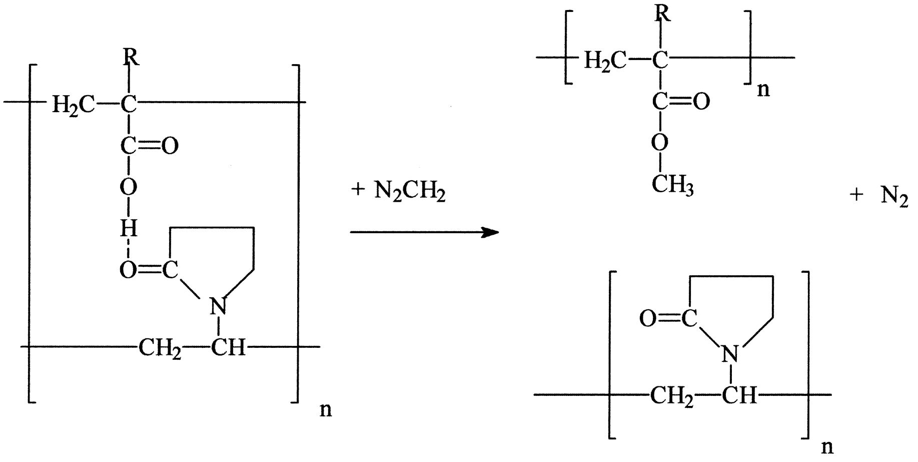
A similar system, the polymerisation of methacrylic acid in the presence of poly(vinyl pyrrolidone) was examined by Shavit and Cohen [17]. Using fractions of PVP, the authors found that the increase in polymerisation rate depends on the molecular weight of the template. This fact was explained by the authors in terms of equilibrium between polyacid and poly(vinyl pyrrolidone). It was assumed that the equilibrium constantly increases with increasing molecular weight of the template. Later, molecular recognition in radical template polymerisation was studied experimentally by Szumilewicz [18] applying GPC method. For polymerisation of methacrylic acid onto poly(vinyl pyrrolidone) in methanol or tetrahydrofuran, it was found that complexation occurs first for molecules of the template with a higher molecular weight. Both the molecular weight and the polydispersity of the uncomplexed template became lower during the course of the reaction. The same phenomenon was found for other systems under examination.

Template photopolymerisation of methacrylic acid onto poly(vinyl pyrrolidone) in aqueous systems was reported in a set of papers [19–23].

It was confirmed that the rate of polymerisation depends on the degree of polymerisation (DP) of the template. Moreover, it was found that polymerisation in the presence of the template proceeds even after switching off the initiating light. The rate of this polymerisation 'in post-effect' is also dependent on the DP of the template. The higher molecular weight of the template is the higher is the rate of polymerisation. The observed course of polymerisation in post-effect indicates unusually long life of the radicals. Calculations of the termination and propagation rate constants based on the post-effect experiments will be discussed in the chapter devoted, kinetics of template polymerisation.

Ferguson [16] found that the DP of poly(acrylic acid) obtained during template polymerisation onto poly(vinyl pyrrolidone) is remarkably similar to the DP of the template. These results were surprising even for the authors since they suggest that monomer radical propagation starts at one end of the template and continue to the other end of the template when termination occurs. This was explained by the authors [16] in terms of possibility of longer propagation of the growing molecule in the presence of higher molecular weight of the template and the interaction of the growing molecule with two or more template molecules.

The case described was rather exceptional, induced by the advantageous selection of initiator concentration. The dependence of the DP of the template on the DP of the daughter polymer was examined [24] for polymerisation of methacrylic acid onto poly(vinyl pyrrolidone) in ethyl alcohol. In these experiments, fractions of poly(vinyl pyrrolidone) were used. After polymerisation, the complex obtained was treated with azomethane in order to convert polyacid to poly(methyl methacrylate).



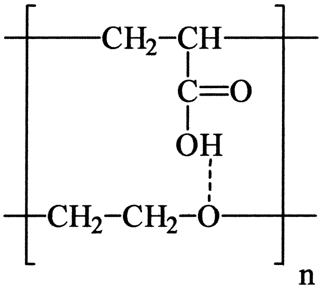
The molecular weight of the PMM was then determined by the GPC method. The results were recalculated and the DP the template DP(PVPy) and degree polymerisation of the product DP(PMM) were compared for two series of experiments carried out with different concentrations of initiator.

As we can see from the results presented in Table 1, the molecular weight of the daughter polymer can differ substantially from the molecular weight of the template.

Table 1
Dependence of polymerisation degree of daughter polymer DP(PMM) on the degree of polymerisation of the template DP(PVPy)

DP(PVPy)	DP(PMM) [I] = 5.56×10^{-3} mol/l	DP(PMM) [I] = 7.93×10^{-3} mol/l
2300	277	–
1750	254	165
1550	260	171
1230	218	154
1046	180	88

The polymerisation of acrylic or methacrylic acid in the presence of poly(ethylene glycols) is a good example of the system in which rather weak interactions operate. However, it is known that PAA/PEG and PMA/PEG complexes were obtained and were an object of quantitative analysis [25,26]. The complex of poly(methacrylic acid) or poly(acrylic acid) with poly(ethylene glycol) was chosen as a model for quantitative studies of interaction between complementary polymers and oligomers in solution. [25–29]. The structure of the complexes was found to be



Studying the polymerisation of methacrylic acid and acrylic acid in the presence of poly(ethylene glycols) of different molecular weight, Papisov et al. [27] found that the rate of polymerisation is lower than that for a blank reaction. Polymerisation was carried out in water, initiated by $K_2S_2O_8$ at 50°C. For a similar system, Ferguson and Shah [28] found that the presence of poly(ethylene glycol) increases the reaction rate. In contrast with the published data for polymerisation involving thermal initiators, in the temperature range of 5–40°C, no effect of PGE on the rate was found for photopolymerisation [29]. The difference in these findings was explained in part by the Russian authors [27], taking into consideration the fact that the increase in the reaction rate in the range over 10% of conversion is connected with the precipitation of the complex. In addition, the method of the rate examination was different. Bromometric titration was applied in Ref. [27], turbidimetry and partially bromometric titration in Ref. [28] and dilatometry in Ref. [29]. All the methods in the case of an inhomogenic system can give a systematic but different error. In addition, an influence of the type of initiator on the rate constant observed in Ref. [14] suggests that specific sorption or occlusion of radicals may take place, which can influence the termination process. However, all the authors agree that specific interactions between PEG and monomer (or at least growing oligomers) exist, and that polymerisation proceeds as a template process. Eventually, an insoluble complex precipitates. It seems that the polymerisation proceeds according to a pick-up mechanism, despite the fact that the rate of the reaction was found to be independent of the ratio of template-to-monomer concentration.

The differences can be also connected to the polydispersity of the template used.

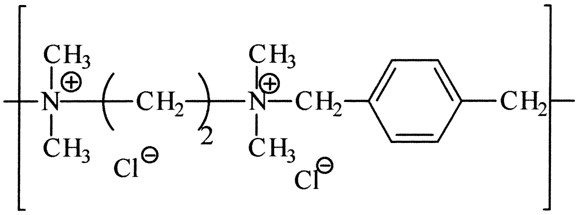
Quantitative studies concerning the interaction between complementary polymers and oligomers, and especially the interaction between polyacids and PEG, have been published and discussed in Refs. [25,26]. Equilibrium between the oligomer and the template was considered, as there was an influence of this equilibrium on template polymerisation. Selective sorption leads to the phenomenon which the authors call 'recognition effect'. In the successive paper [18], molecular recognition in radical template polymerisation was discussed based on the GPC measurements.

In a set of papers [30–32], Smid et al. described the template polymerisation of methacrylic acid using poly(2-vinylpyridine) (P2VP) as a template. Most of these experiments was carried out in DMF, but some experiments were also done in DMSO and 1,4 dioxane. In these solvents, it was found that preferential adsorption occurs, determined by equilibrium dialysis and interferometric measurements. The complexation tendency was find to be stronger in 1,4 dioxane than in DMF. The rate of template polymerisation was measured by DSC technique mainly in 30°C, but also in different temperatures in order to calculate the energy of activation. *T*-butylcyclohexylperoxydicarbonate was used as an initiator. Influence of the tacticity of the template was not found very significant.

Kinetics analysis based on the model presented by the authors will be discussed later.

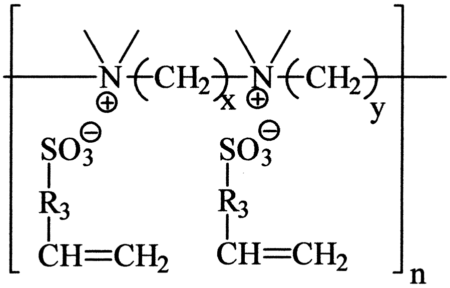
Extensive studies of the template polymerisation of acrylic and methacrylic acid onto poly(4-vinyl pyrridine) were carried out by Fujimori et al. [33]. On the basis of a simple model system, it was demonstrated that two types of complexes exist in the system acid–pyridine, with a ratio of acid units to pyridine units of 2:1 (in bulk or high concentration) and 1:1 (for diluted solutions). This finding was confirmed by refractometry and IR spectrometry. A similar type of interaction was found in the system template (poly(vinyl pyrridine)) and the monomer (acrylic or methacrylic acid) in methanol. However, the amount of the monomer complexed in the polymerisation conditions, as was shown, is only a few percent of the amount of the monomer in the final, interpolymer complex. The authors suggest that the polymerisation cannot proceed according to a zip-up mechanism, but a growing polymer chain forms a complex with the template. In conclusion, the authors suggest a mechanism based on the domain formation model.

Template polymerisation of methacrylic and acrylic acid in the presence of positively charged template was studied by Tsuchida and Osada [34]. As a template poly(*N*,*N*,*N*′,*N*′-tetramethyl-*N*-*p*-xylylene-ethylenediammonium dichloride):



In the presence of the template, the rates of polymerisation were remarkably increased especially in high pH. Under these conditions, as it is known, the blank reaction is difficult because of electrostatic repulsion between the macroradicals and the monomer. The authors suggested that the template could eliminate the electrostatic repulsion between these negatively charged reaction species very effectively by adsorption on its positive charges through coulombic force.

Similar phenomenon was observed by Blumstein and Kakivaya [35] concerning the template polymerisation of *p*-styrenesulfonic acid onto ionenes with different charge densities. The authors used ionenes with different number of methylene groups *x* and *y*.



The authors defined the charge density as the number of charges per 10 Å length of the ionene template. It was found that the rate of polymerisation decreases with the decrease in charge density i.e. when increasing the distance between two charged groups. This means that the distance between two reacting groups (double bonds) is much higher then 4 Å, but polymerisation steel occurs. The authors explain this phenomenon by assuming that the monomeric counterions possess considerable mobility along the template.

Moreover, the authors found a rapid decline in the polymerisation rate after a certain conversion (50–70%) was reached. The authors explains this fact as an "impaired supply of monomer to polymerisation sites and a reaction which is controlled by diffusion in the case of the long distance between the growing radical and the next monomeric site".

However, these two interesting observations can also be explained by assuming conformational movements of the methylene groups in template during polymerisation, statistical initiation and absence of termination between radicals located on two separate templates.

Recently, a set of papers dealing with template polymerisation onto poly(allylamine hydrochloride) or chitosane was published by scientists from Pisa [36–42].

Template polymerisation of sodium acrylate onto poly(allylamine hydrochloride) was described [36]. The reaction was carried out in water using AIBN (1×10^{-2} M) at 80°C or at 50°C using $K_2S_2O_8$ as an initiator. The product obtained was compared with a polymer complex of the same composition obtained by mixing the components in solution.

Interesting results were obtained by the authors in examination of the kinetics of the process.

These were examined at 50°C using $K_2S_2O_8$ 1×10^{-2} M in water. The polymerisation rate was determined by dilatometry. It was found that the reaction order with respect to the monomer depends on the template to monomer ratio. For low [T]/[M] up to 0.5, the order was 0.9–1.2. For higher [T], the reaction order decreases to 0.5–0.6.

Because the experiments were carried out at only one initiator concentration, the order of the reaction with respect to the initiator concentration was not determined. It is also worth mentioning that all kinetic calculations were done for initial rate of the reaction.

Analysing the relative rate of polymerisation versus $[T]/[M]_0$, it was found that the plot is typical of the zip mechanism.

The product obtained as a result of template polymerisation was studied by differential scanning calorimetry. It was found that a certain amount of water was still present in the complex. Between

200–300°C, an intense endothermic peak present in the thermogram was explained by the authors as a result of formation of amide bonds between carboxylate and ammonium groups.

After heating to 300°C, the complex is stable up to 450°C. In the heated complex, amide bonds were also detected by FT-IR spectrometry. This result suggests that the structure of the complex is similar to the 'ladder-type' model.

The next system under investigation deals with vinyl sulphonate sodium salt as a monomer and poly(allylamine) hydrochloride as a template [37]. Polymerisation was carried out in water and potassium persulphate was used as an initiator.

Both the monomer and the template are ionised in water. The reaction rate was studied by the dilatometric technique for different ratios [T]/[M]. It was found that the order of polymerisation with respect to the monomer concentration for both template and blank reaction is 1.3.

Investigation of the reaction in conditions when the template to monomer ratio was 0.25 shows many peculiarities. Neither temperature nor monomer concentration have any qualitative effect on the trend of kinetic curves. Conversion versus time curves have a deflection point; in other words, the reaction rate slows down, increases after reaching minimum and then decreases again. Moreover, the blank reaction is faster then polymerisation in the presence of the template. Such unusual behaviour was explained by the authors by the assumption that the template polymerisation takes place according to pick-up mechanism, in spite of the fact that strong interactions take place between SO_3^- and NH_3^+ groups, and termination event is more probable for template associated radicals than for free radicals and propagation rate for template reaction is slower than for blank polymerisation. The second assumption seems to be more probable, taking into account that if termination is 'more probable', it means that the termination rate constant is higher, and overall rate could be higher and not lower. The authors also draw attention to the reduced freedom of the macroradicals connected with the template.

It must be stressed that the system was heterogeneous, and that precipitation of the complex occurs during the process.

In a later paper [38], acrylic acid and sodium 4-styrenesulfonate were polymerised onto chitosan as the template. The degree of acetylation for chitosan under investigation was 0.24. The reaction was carried out in water, initiated by $K_2S_2O_8$ at 50°C. In all cases, insoluble interpolymer complex was obtained as a product of the reaction.

Chitosan for polymerisation of sodium 4-styrenesulphonate was transformed to hydrochloride in order to cause strong ionic interactions between monomer and the template. By the dilatometric technique, it was found that the reaction rate increases with increasing [T]/[M] ratio within the range 0–0.25 up to about 2.5, and then is stable. On the basis of this observation, the authors assumed a pick-up mechanism for this process.

The polymerisation of acrylic acid in the presence of chitosan does not demonstrate any enhancement of the reaction rate. An examination of the structure and the thermal behaviour of the complexes obtained in this case showed differences in comparison with the structure of the same complex obtained by mixing the components. In template polymerisation, more 'ordered' complex can be obtained. However, because the molecular weights of poly(acrylic acid) — both those obtained in template polymerisation and those used for mixing — were not known, the differences can be also linked with these differences.

A new method for investigation of template polymerisation rate based on conductivity measurements was proposed and compared with the dilatometric technique for polymerisation of sodium acrylate and methacrylate [39,40]. It was assumed that the conductivity changes were only due to the disappearance of the monomer. Changes in pH, initiator decomposition and change in polymer concentration were neglected.

The method was applied for a kinetics study of template polymerisation of acrylic acid in the presence of poly(*N*-vinylpyrrolidone) [41].

Co-polymerisation of acrylic acid and 2-hydroxyethyl methacrylate onto poly(*N*-vinylpyrrolidone) [42] will be discussed in the chapter 'template co-polymerisation'

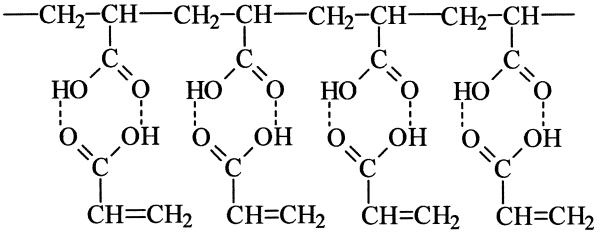
In his thesis [43] and related publications [44–50], van de Grampel described an interesting case of template polymerisation: polymerisation of *N*-vinyl imidazole along poly(methacrylic acid) in water. It was proved that a strong complex formation takes place with 1:1 basemolar ratio. Polymerisation was carried out at 50°C using 2,2′-azobis(2-aminopropane)·HCl as an initiator. Conventional polymerisation of *N*-vinyl imidazole, without template leads to rather low molecular weight, because of degradative protonation and chain transfer. However, poly(*N*-vinyl imidazole) obtained in template polymerisation has a high molecular weight depending on the molecular weight of the template used [46]. Moreover, molecular weight of daughter polymer was 5–9 times higher then the molecular weight of the template. This interesting phenomenon was discussed by the authors in terms of a possibility of hopping of a radical to a neighbouring template after reaching the end of a template macromolecule. Molecular weight of the polymer formed also depends on the initiator concentration and on the template to monomer ratio.

A specific type of template polymerisation was elaborated by Buter, Tan, Challa and Gons in Groningen [52–59]. These authors found that polymerisation of methyl methacrylate in the presence of isotactic poly(methyl methacrylate) proceeds as a template reaction. It was known before [51] that isotactic poly(methyl methacrylate) forms a stereocomplex with syndiotactic PMM. Extensive examination of the template polymerisation process led the authors to general and important conclusions about the influence of molecular weight, the tacticity of the template, and the temperature and nature of the solvent; namely, the higher molecular weight of the template, the higher increase in reaction rate.

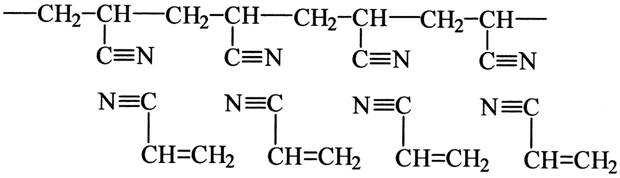
The template effect strongly depends on the nature of the solvent. In the case under investigation, the effect is quite pronounced in DMF, very weak in toluene and completely disappears in chloroform. This is in agreement with the strength of complex formation in these solvents. The relative initial rate, which was taken as a measure of the template effect, decreases with temperature. Even in DMF, the effect was present below 35°C. At higher temperatures, polymerisation proceeds at the same rate as in the system without template (blank reaction).

Polymerisation of acrylic acid in bulk and in different solvents initiated by γ-rays was the subject of an extensive study carried out by Chapiro and co-workers [60–63]. Based on IR spectrometry it was found that in solutions of acrylic acid, two types of associates exists, cyclic dimers and linear oligomers. The equilibrium between these two forms depends on the nature of the solvents. Water, methanol and dioxane stabilize the linear oligomers while in hydrocarbons and chlorinated derivatives, the equilibrium is shifted to cyclic dimers [61]. This finding leads to assumption that poly(acrylic acid) formed in the reaction medium in the course of polymerisation act as a template. Linear oligomers associate with the polyacid template and polymerisation proceeds as a template process. An examination of radiation initiated polymerisation in different solvents [62] and at different temperatures [63] leads to the conclusion that 'matrix effect' is closely correlated with the existence of the linear oligomers. It was found that a small amount of methanol added to dilute solution of acrylic acid in hexane give rise to a very high increase in polymerisation rate.

The authors suggest a zip-up mechanism of aggregated monomer units:

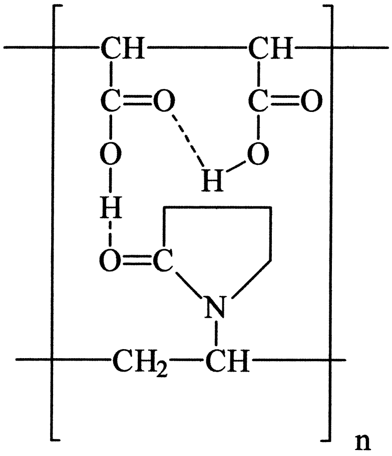


While examining the co-polymerisation of acrylic and methacrylic acids, it was found [63] that the matrix effect appears only if more then 80% of acrylic acid is present in a monomers feed. A matrix effect similar to that described above was also found for the polymerisation of acrylonitrile in block [65] and in solution in DMSO [66]. In this case also the authors assumed that matrix effect is connected to the existence of oriented aggregates from the monomer and polymer present in the reaction medium.



In this case, post-polymerisation was observed, indicating the existence of stable radicals. The authors takes into account the influence of precipitating conditions on the post-effect.

The polymerisation of maleic acid and citronic acid was described by Sato [67]. The process was carried out in water, in the presence of poly(vinyl pyrrolidone) as a template and potassium persulphate as an initiator. The polymerisation proceeded easily at 50–80°C and a polymer complex formation was observed. The product was analysed by methylation of the resulting complex by diazomethane. The poly(maleic acid) methyl ester was separated, identified by IR spectroscopy, and the molecular weight measured by GPC. The product was found to be an oligomer with a molecular weight of 400–500. The composition of the complex obtained was found to be equimolar. The authors suggest the following structure of the complex:

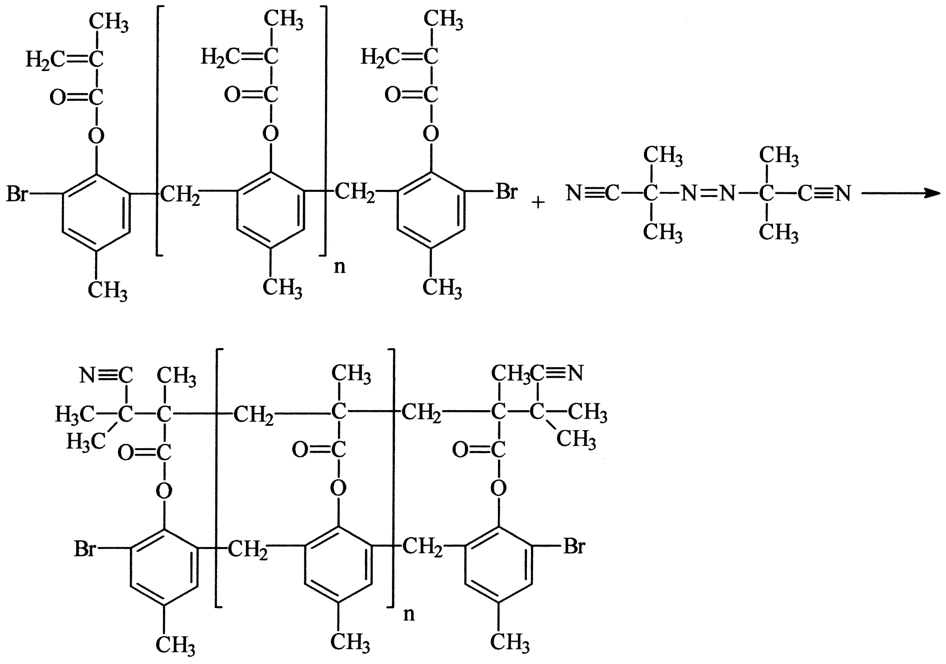


Similar results were obtained by the authors for polymerisation of citraconic acid.

A special group of monomers containing nucleic acid bases were selected for examination of template polymerisation with specific interactions [68]. Such groups as adenine, uracil, thymine and theophyline were connected with the methacrylyl group by an ethylene spacer. The complementary pairs of substituents in the template and in the monomer were selected in order to study the influence of the selective interaction on the rate of the reaction. For instance, the polymerisation of *N*-β-methacryloyloxyethyl-adenine (MAOA) onto atactic poly(methacryloyloxyethyl thymine) (PMAOT) [69] in pyridine has been studied. The rate of the polymerisation was about four times greater than that for the blank reaction (without PMAOT). On the contrary, the polymerisation of *N*-β-methacryloyloxyethyl-thymine in the presence of PMAOT proceeds even slower then the blank reaction. The authors explain the matrix effect by an interaction between the growing chain and the template. The increase in the reaction rate does not appear in chloroform or in DMSO.

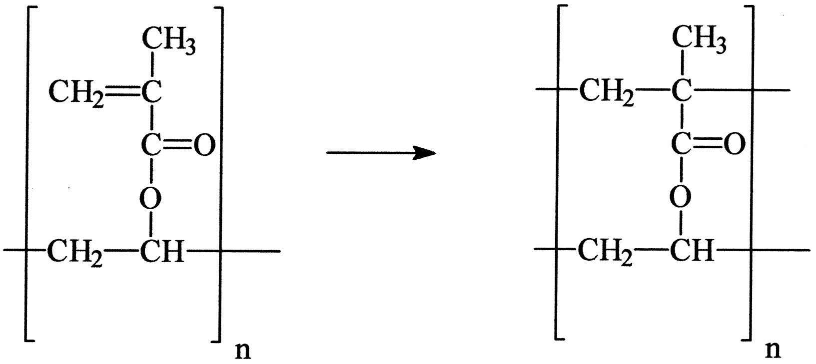
2.2. Polymerisation of multimonomers

It seems that a good model for examining the 'type I' mechanism is a polymerisation of multimonomer compounds in which monomer units are connected by covalent bonds with the matrix. The synthesis and polymerisation of such compounds was studied by Kämmerer [70–72] and in a set of our own papers [73–81]. The peculiar characteristic of the phenomenon lies in the fact that the substrate and the product of the reaction is a polymer with the same molecular weight, and the structure of the product is 'fixed', in contrast to the case when a polymeric complex is formed. The reproduction of the polymerisation degree in the template process is sometimes called a 'replication'. This means that the daughter polymer has the same DP as the template. Indeed for the polymerisation of multimonomers, Kämmerer found [70] that for the oligomeric template, with an excess of AIBN, the reaction takes place according to a scheme which can be called a replication:

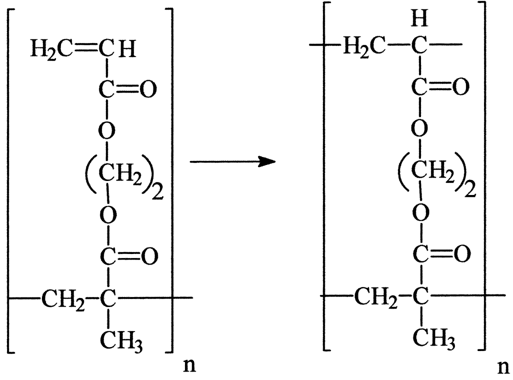


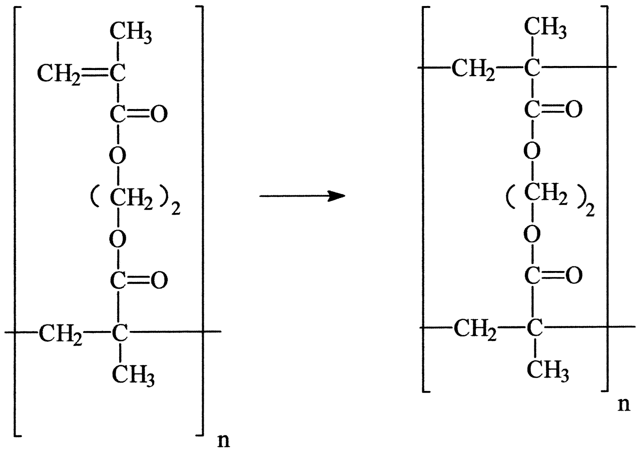
The template in this case was rather stiff, and excess of an initiator leads to termination by primary radicals.

Another example is a synthesis of a ladder polymer suggested by Bamford [2] and examined afterwards by Jantas [75]. Poly(vinyl alcohol) esterified by methacrylic chloride was used as a template. Polymerisation can be represented by the following reaction:



In our papers [74–80], template polymerisation of multiacrylate and multimethacrylate have been studied. The reaction proceeds according to the scheme:





It was found that neither the average molecular weight nor the distribution of molecular weights changes during polymerisation, provided the molecular weight is high enough and the concentration is low [79]. For multiacrylates, it was found that distribution of molecular weights is the same up to more than 50% of the conversion of double bonds. This means that under correct conditions, intermolecular reaction can be neglected and the polymerisation proceeds as a template process. However, for high conversion and high monomer concentration, an increase in molecular weight takes place and eventually the product becomes insoluble and cross-linked. A very similar behaviour was observed for the photopolymerisation of multimethacrylate [80]. The kinetics of template polymerisation of multimethacrylates, poly(2-methacryloyloxyethyl methacrylate) and poly(2-acryloyloxyethyl methacrylate), were studied.. Experiments were carried out in dioxane solution, and the rate of reaction was measured by the dilatometric method. The possibility of describing the process in terms of conventional kinetic equations was considered. It has been found that the order of the reaction with respect to the monomer is 1, while the order of reaction with respect to the initiator is 0.25. The kinetics of polymeric radicals disappearing in the system with the EPR method has been examined, and it was found that the radicals connected with the template are very stable. It has been found that for the description of the process, dispersive kinetics [81,82,83] should be used.

2.3. Kinetics of template radical polymerisation

The first problem connected with the description of template polymerisation kinetics deals with the definition of the process. As was mentioned in Section 1, the definition of template polymerisation is not precise. Many factors which can influence the kinetics of the polymerisation can lead to effects similar to the template effect. The increase in the reaction rate is known as the ‘Tromsdorff effect’ or ‘gel effect’. The polymerisation classified as the ‘template process’ often proceeds in a non-homogenous system similar to polymerisation in suspension. Some authors explain the template effect in systems like methacrylic or acrylic acid–poly(4-vinylpyridine) [33] or acrylic acid–poly(vinyl pyrrolidone) [15] by a change in ‘local concentration’. As was demonstrated [84], if the monomer is distributed into two parts — inside template coils and in a free volume — the kinetic equation can be transformed into the conventional form, provided the concentration of the template is lower than the critical concentration. The presence of an ‘additional’ substance (such as a template) in the polymerising system can influence many processes as a chain transfer to polymer, which leads to grafting, selective sorption of initiating system, or changing an equilibrium monomer–dimer in the case of monomeric acids. It seems necessary to apply other methods than kinetics to ensure that the template influences the polymerisation process on the ‘molecular level’, to compare the process with the low molecular weight analogue and analyse all additional effects. Quite a different polymerisation mechanism may exist in a given template system above and below the critical template polymer concentration. In the latter case, polymerisation can proceed inside the template coil and in a free solution. Nevertheless, an enhancement of the reaction rate is, in fact, the most pronounced effect of template polymerisation. For many systems, a conventional kinetic equation has been applied:

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = K_{\mathrm{ov}}[\mathrm{I}]^n[\mathrm{M}]^n$$

It has been found that sometimes the template influences not only the rate constant but also the exponents *n* and *m*. This is illustrated by Table 2.

Table 2
Examples of conventional kinetic equation application to template polymerisation of acrylic or methacrylic acid

Monomer	Template	Solvent	Initiator	*n*	*m*	Activation energy kJ/mol	Ref.
Acrylic acid	Poly(ethylene glycol)	H_2O	$K_2S_2O_8$	0.7	1.1	83.7	[27]
Acrylic acid	Poly(ethylene glycol)	H_2O + 50% methanol	$K_2S_2O_8$	0.7	–	–	[27]
Acrylic acid	Poly(vinyl pyrrolidone)	H_2O	$K_2S_2O_8$	1	1.5	95	[13]
Acrylic acid	Poly(vinyl pyrrolidone)	H_2O	$K_2S_2O_8$			71.2–73.6	[41]
Acrylic acid	Poly(vinyl pyrrolidone)	H_2O	$K_2S_2O_8$	0.5	1.9		[15]
Acrylic acid	Poly(ethylene imine)	H_2O	$K_2S_2O_8$	1	1	45.2	[28]
Methacrylic acid	Poly(ethylene glycol)	H_2O	$K_2S_2O_8$	0.7	1	71.1	[27]
Methacrylic acid	Poly(ethylene glycol)	H_2O + 50% methanol	$K_2S_2O_8$			71.1	[27]
Methacrylic acid	Poly(ethylene glycol)	H_2O	$Na_2S_2O_8$[a]	0.5	1	17.2	[29]
Methacrylic acid	Poly(vinyl pyrrolidone)	H_2O	UO_2SO_4[a]	0.5	1		[19]
Methacrylic acid	Poly(vinyl pyrrolidone)	H_2O	$K_2S_2O_8$	0–0.5	1.5		[17]
Methacrylic acid	Ionene	H_2O	$K_2S_2O_8$	0.8	0.3–0.9[b]		[34]
p-styrene sulfonic acid	Ionene	H_2O + isopropanol	AIBN	1	1	70.8	[35]

[a] P — photoinitiation.

[b] C — dependent on the concentration.

The mechanism of a template polymerisation influences the kinetics of the reaction. Different approaches can be applied for type I (zip-up) and type II (pick-up) mechanisms.

The most complete model of chain template polymerisation was published by Tan and Alberda van Ekenstein [85]. Assuming that the polymerisation goes outside the template (blank reaction — symbols without subscript), and onto the template (symbols with '*'), the process can be described by a set of equations:

1. Blank reaction
   Initiator decomposition

   $$I \rightarrow 2R\cdot \quad \text{with rate constant } k_d$$

   Initiation

   $$R\cdot + M \rightarrow P_n\cdot \quad \text{with rate constant } k_i$$

   Propagation

   $$P_n\cdot + M \rightarrow P_{n+1}\cdot \quad \text{with rate constant } k_p$$

   Termination

   $$P_n\cdot + P_m\cdot \rightarrow P \quad \text{with rate constant } k_t$$

2. Complexation
   Monomer adsorption

   $$M + T \Leftrightarrow M^* \quad \text{with equilibrium constant } K_M$$

   Radical complexation

   $$P_n\cdot + T \rightarrow P_n\cdot^* \quad \text{with rate constant } k_c$$

   Polymer complexation

   $$P + T \rightarrow P^* \quad \text{with rate constant } k_c$$

   Reaction onto the template
   Propagation

   $$P_n\cdot^* + M \rightarrow P_{n+1}\cdot^* \quad \text{with rate constant } k_p^*$$

Template–template termination

$$\mathrm{P}_n\cdot^* + \mathrm{P}_m\cdot^* \quad \text{with rate constant } k_\mathrm{t}^*$$

Cross-termination

$$\mathrm{P}\cdot + \mathrm{P}\cdot^* \rightarrow \mathrm{P}(\text{or } \mathrm{P}^*) \quad \text{with rate constant } k_\mathrm{t}^{\prime *}$$

This set of equations leads to the expression on the composite rate constant $\overline{k_{\mathrm{p,T}}}$

$$\overline{k_{\mathrm{p,T}}} = \frac{k_{\mathrm{p,I}}k_{\mathrm{p,II}}(1 + K_\mathrm{M}[\mathrm{M_f}])}{K_\mathrm{M}k_{\mathrm{p,II}}[\mathrm{M_f}]^2 + k_{\mathrm{p,I}}}$$

where

$$[\mathrm{M_f}] = \frac{-Q + (Q^2 + 4K_\mathrm{M}[\mathrm{M}])^{1/2}}{2K_\mathrm{M}}$$

and $Q = K_\mathrm{M}([\mathrm{T}] - [\mathrm{M}]) + 1$, where [M] is the sum of free and adsorbed monomer.

If K_M is very small, the equation leads to expression $\overline{k_{\mathrm{p,T}}} = k_{\mathrm{p,II}}$.

If K_M is very large, it leads to a rather unusual relation $\overline{k_{\mathrm{p,T}}} = k_{\mathrm{p,I}}/[\mathrm{M_f}]$. However, according to the authors, in this case, the overall rate of polymerisation $R_\mathrm{p} = R_{\mathrm{p,I}} = k_{\mathrm{p,I}}[\mathrm{P}\cdot_\mathrm{T}]$.

On the basis of this kinetic scheme, the results of extensive study concerning the polymerisation of methacrylic acid onto poly(vinyl pyridine) were calculated.

The discussion of the results obtained was based on the model, originally drawn by the authors and later called 'Generalized model' [85]. According to this model, one can calculate rate constants for elementary processes for the type I (zip-up) and type II (pick-up) mechanism: $k_{\mathrm{p,I}}$, $k_{\mathrm{p,II}}$, respectively and the rate constant for termination proceeding onto the template k_{TT} and for cross-termination k_{TB}. These values can be compared with the corresponding values for blank reaction: propagation rate constant $k_{\mathrm{p,B}}$ and termination rate constant $k_{\mathrm{t,B}}$. The recalculated data from [9] are listed in Table 3.

As we can see, apart from $k_{\mathrm{p,I}}$ for polymerisation in DMF, in all other cases the rate constants for template polymerisation are lower. The change in propagation rate constant is not so great, but the termination rate constants for template process are lower by 10^3–10^4 times.

This means that radicals connected with template are much more stable then growing radicals in blank reaction.

A set of papers [19–23] was devoted to the kinetic study of template photopolymerisation of

Table 3
The ratios of blank to template rates constants

Template	Solvent	$k_{\mathrm{p,B}}/k_{\mathrm{p,I}}$	$k_{\mathrm{p,B}}/k_{\mathrm{p,II}}$	$k_{\mathrm{t,B}}/k_{\mathrm{TT}}$	$k_{\mathrm{t,B}}/k_{\mathrm{TB}}$
at-P2VP	DMF	0.087	1.4	5×10^3	2.1×10^3
it-P2VP	DMF	0.5	1.4	1.04×10^4	
at-P2VP	1,4 dioxane	2.94	1.25	2×10^4	
it-P2VP	1,4 dioxane	2.94	1.25	4.4×10^4	

methactylic acid in aqueous systems. The dilatometric method was applied to determine the polymerisation rate. Poly(vinyl pyrrolidone) (PVPy), poly(ethylene glycol) (PEG) with different molecular weight, poly(ethylene glycol) with azo groups (PEGN) and poly(dimethyl aminoethyl methacrylate) (PDAMA) were used as templates. Using UO_2SO_4 as a photo-initiator, it was found that template polymerisation proceeds for some considerable time after switching off the light, in contrary to the reaction without template. Assuming a second order of termination reaction the 'post-effect' allows calculation of the rate constants of elementary processes: $k_{p,T}$ for propagation and $k_{t,T}$ for termination. For determination of the corresponding values for blank reaction $k_{p,B}$ and $k_{t,B}$, the rotation sector technique was applied. It was found [22] that in comparison with corresponding values for blank reaction, $k_{p,T}$ is lower by about two orders of magnitude, while $k_{t,T}$ lower by 3–4 orders of magnitude. The corresponding values recalculated from [22] are presented in Table 4.

Moreover, it was found [23] that both $k_{p,T}$ and $k_{t,T}$ depend on the template-to-monomer ratio, with a pronounced maximum for [T]/[M] equal to about 1.5.

The most extreme case of zip-up polymerisation is when a monomer is connected with the template by covalent bonds and polymerisation proceeds as an intermolecular reaction. However, for a typical type I mechanism, for instance multimonomer polymerisation, this set of equations should be revised. From point 1 (blank reactions), only decomposition of the initiator takes place.

$$I \longrightarrow 2R\cdot \quad \text{with rate constant } k_d$$

The initiation reaction should be modified, taking into account that 'M' monomer units are connected with the template by covalent bonds:

$$R\cdot + M \longrightarrow P*\cdot \quad \text{with rate constant } k_i$$

Assuming that this reaction is much slower than initiator decomposition, and that termination of primary radicals proceeds with the rate

$$V_{t,R} = k_{t,R}[R\cdot]^2$$

one can state that $[R\cdot]$ is proportional to $[I]^{0.5}$.

Propagation reaction onto the template proceeds according to the equation

$$P_n\cdot^* + M \longrightarrow P_{n+1}\cdot^* \quad \text{with rate constant } k_p^*$$

Provided that M is a neighbouring unit in relation to $P_n\cdot{}^*$, the rate of propagation is:

$$V_p = k_p[P\cdot^*]$$

which is in accordance to the discussion in the General Kinetic Model section.

Table 4
The ratios of blank to template rates constants for photopolymerisation of methacrylic acid

Template	DP	$k_{p,B}/k_{p,T}$	$k_{t,T}/k_{t,T}$
PVP	52	91.5	7.44×10^3
PVP	8860	77.4	1.33×10^4
PDAMA	50	43	1.45×10^3

Template-to-template termination proceeds according to the reaction:

$$P_n\cdot^* + P_m\cdot^* \rightarrow P$$

with rate constant k_t^*, but cross-termination is not present because of the absence of P·.

However, termination by primary radicals can take place

$$R\cdot + P\cdot^* \rightarrow P(\text{or } P^*) \quad \text{with rate constant } k_t'^*$$

Assuming that template–template termination predominates, we can state:

$$k_i[R\cdot][M^*] = k_{t,TT}[P\cdot^*]^2$$

This leads to the result that the concentration of the radicals connected with the template is proportional to $[I]^{0.25}$, and then the overall rate of polymerisation is also proportional to $[I]^{0.25}$, which is in accordance with the literature [9].

In a set of our papers [79–81], the template polymerisation kinetics of multiacrylate and multimethacrylate have been studied. A typical polymerisation was carried out in dioxane in a quartz dilatometer. The monomer concentration was low (0.15 basic mol per dm^3). AIBN was used as a photoinitiator. The monomer solution was saturated by helium and illuminated by an XBO 150 lamp. The light intensity as measured under the same conditions using a ferric dosimeter (in water) was 7×10^{14} quants/ml. In some experiments, samples were taken from the dilatometer and analysed by IR or by ^1H NMR in order to determine the conversion of double bonds.

For a set of such experiments, GPC measurements were carried out. The results show that the molecular weight does not change during polymerisation of up to 10–40% of conversion for the polymerisation of multiacrylates and multiacrylates, respectively. The results obtained confirm that polymerisation proceeds according to the template mechanism, and under this condition, cross-linking can be neglected.

The reaction proceeds according the scheme shown in the previous chapter.

Most of the kinetics measurements were carried out by the dilatometric technique for a low conversion, changing the concentration of monomers and concentration of the initiator. For a description of the data obtained, a classical type of kinetic equation $V = k_{gl}[I]^n[M]^m$ was applied, where V is a initial rate of reaction and k_{gl} the global rate constant. The results of calculations n and m are presented in Table 5 for polymerisation of multimethacrylates (MM) and multiacrylates (MA).

However, it was found that polymerisation takes place after the light was switched off. This post-effect was examined both by dilatometry and by EPR techniques. It was found that the reaction could be described as second-order for only a very low conversion. It seems that in this case, the Brownian motion, which operates in conventional polymerisation is replaced by conformational changes in the

Table 5
Coefficients *n* and *m* in classical kinetic equation for polymerisation of multimethacrylates (MM) and multiacrylates (MA)

Type of multimonomer	*n*	*m*	Ref.
MA	0.25	1.07	[80]
MM	0.25	1.0	[81]

template molecules. Such considerations are related only to dilute solutions below a critical concentration of the template. This consideration particularly concerns propagation, which could be dependent on the flexibility of the template. In addition, in this case termination can be much more difficult then in the case of conventional polymerisation. The apparent second-order rate constant for termination (disappearance of radicals) in the polymerisation of multimethacrylates in dioxane measured by the EPR technique was 11.8 l/mol s, in comparison to a termination rate constant for free methylmethacrylate of 66×10^6 l/mol s. Moreover, it was found that the termination rate does not agree with the conventional second-order equation, but a description of the process by dispersive kinetics should be used. It confirms the assumption that the process is in fact controlled by conformational movements, and classic kinetic equations should not be applied to describe the process. It is noteworthy that all presented schemes of the template polymerisation are based on the steady state. In the light of the above findings, it is difficult to accept this assumption.

3. Template radical co-polymerisation

Co-polymerisation of two monomers can proceed in the presence of a template according to different schema. First, a template can be a homopolymer or a co-polymer. In the first case, one or both monomers can interact with the template. At least these interactions can be strong (mechanism type I) or less strong, but still sufficient to form a complex with a polymer of proper length (mechanism type II).

A strong intermolecular interaction (type I) with monomer A, and weak or no interactions with monomer B, can be illustrated by the following schematic representation (Fig. 3).

In this case, the distribution of monomer A units is fixed but stochastic. The amount of monomer A on the template is dependent on the [A]/[T] ratio. Polymerisation of monomer B is independent of the template's existence.

The particular instance of this mechanism takes place if the template is short and connected by covalent bounds with monomer A (Fig. 4).

The co-polymerisation of multimonomers with the 'simple' monomers was described in papers [73,75,86–88].

As an example of this type of reaction oligomeric multimonomers with 3, 6 or 8 units were co-polymerised with styrene, [86] acrylonitrile, [73] acrylic acid or *p*-cresyl methacrylate [86].

NMR and IR spectrometry as well as the end group analysis using labelled ^{14}C initiator confirmed the structure predicted. It was found that the product is a 'semi-ladder' co-polymer and more then 90% of double bonds in multimonomer reacts according to the template mechanism. However, because chain

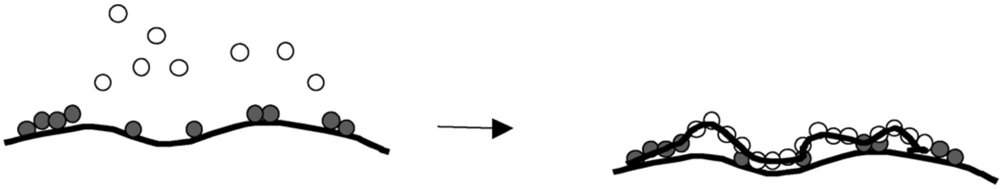
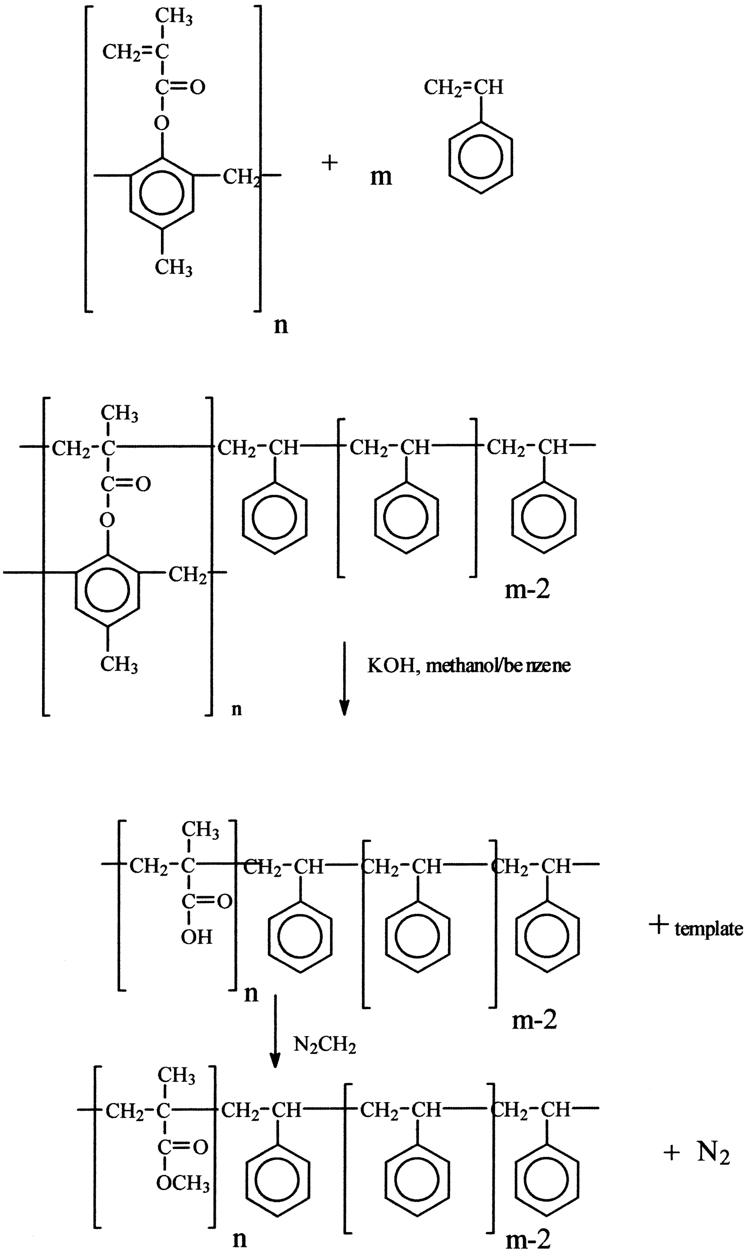


Fig. 3. Schematic representation of template co-polymerisation: strong interaction with monomer A (●) and weak interaction with monomer B (○).

transfer to the polymer the product is slightly branched (1–2 branching points per hundred of repeating units). Only in the case of allyl-type multimonomers, degradative chain transfer leads to the more complicated structure [89]. It was shown that, based on this type of synthesis short-block co-polymers can be obtained. The synthesis of styrene–methyl methacrylate co-polymers with oligoblocks controlled by the template used are shown in the following scheme:



In addition, the co-polymerisation of multimethacrylate with styrene or acrylonitrile in dilute

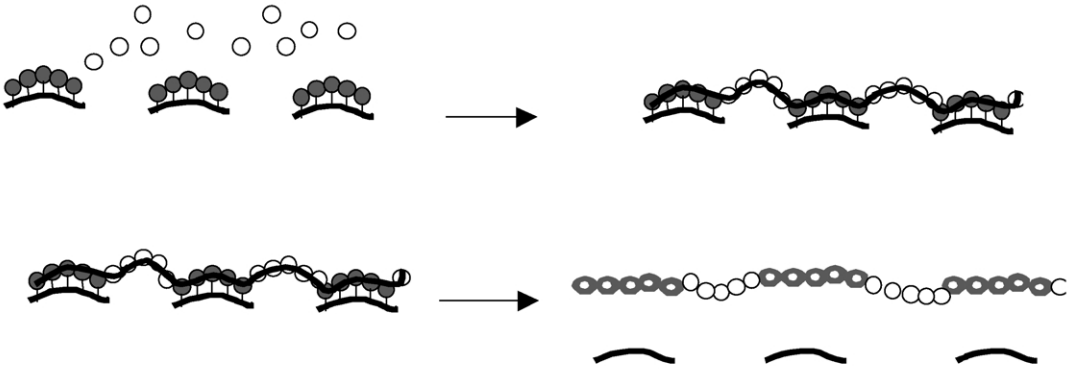


Fig. 4. Schematic representation of template co-polymerisation: multimonomer with free monomer B- o.

DMF solutions has been investigated [90]. The examination of the co-polymerisation initiated by AIBN labelled with ^{14}C allowed us to determined the number of branching points in co-polymer molecules. It was found that for co-polymerisation of multimethacrylate with acrylonitrile, less than 6 end groups are present in the co-polymer molecule with the molecular weight about 50,000. It means that only four branching points per molecule are present. The result shows that the co-polymerisation process results in co-polymer composed mainly of ladder-type blocks and blocks of vinyl monomer units. For co-polymer with styrene with number average molecular weight almost 1,00,000 the 16 number of branching was found.

In the previous point, monomer A was connected by strong interaction with a template. If monomer A can polymerise according to mechanism II, a sufficiently long sequence of A units can form a complex with the template. The system in which one co-monomer (A) forms a complex according to the mechanism II with the template, while the other (B) reveals a weak interaction or is not interacting with the template at all, has been described [91].

The mechanism of such co-polymerisation can be illustrated by the following schematic representation (Fig. 5).

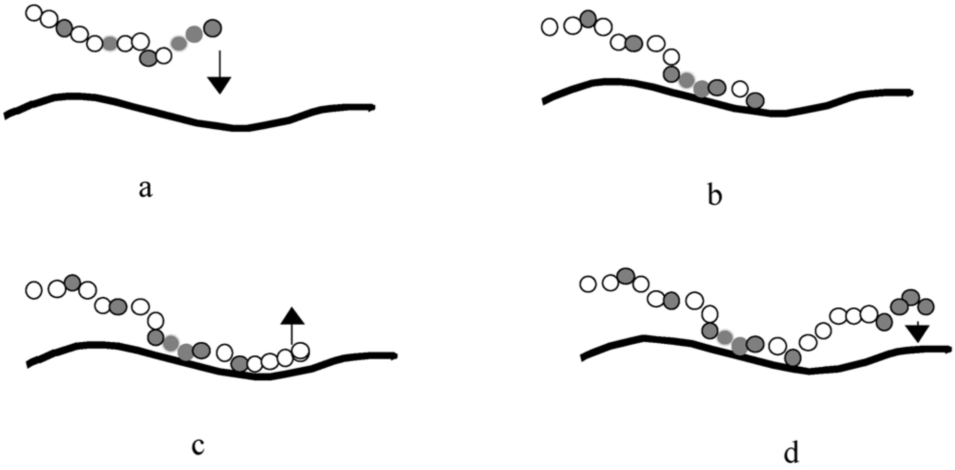


Fig. 5. Schematic representation of template co-polymerisation proceeding according to pick-up mechanism.

A few described systems seem to be close to this mechanism. A series of co-polymerisations of methacrylic acid and styrene were carried out using various compositions of initial monomer mixtures [91]. The process was carried out in benzene in the presence of PEG. The system styrene–methacrylic acid and poly(2-vinyl pyridine) used as a template was studied by Frish and Xu [92]. Rainaldi et al. [42] reported the template co-polymerisation of acrylic acid and 2-hydroxyethyl methacrylate onto poly(*N*-vinylpyrrolidone).

The gamma-ray initiated co-polymerisation of acrylic or methacrylic acid with methyl acrylate and acrylonitrile was reported by Chapiro [64], who found a substantial difference between the reactivity ratios of the monomers for co-polymerisation in bulk and in different solvents. The author explains this phenomenon in terms of the association of acid monomers leading to linear plurimolecular aggregates of the monomer. The association of the monomer via hydrogen bonds affects the bulk reactivity and sometimes the microstructure of the resulting co-polymer, while in other solvents association is much lower. Similar results were found for co-polymerisation of acrylamide. Interesting results were published in the next paper by Chapiro [93]. The authors found a pronounced matrix effect for the gamma- ray initiated co-polymerisation of acrylic acid with methacrylic acid. The co-polymerisation was carried out in bulk, hexane or methanol solutions. In all cases, when acrylic acid concentration was at least 80%, auto-acceleration appears.

The reactivity ratios calculated for methacrylic acid (r_1) and acrylic acid (r_2) depend on the solvent and concentration of the mixture of the monomers. For co-polymerisation carried out in bulk, $r_1 = 2.7$ and $r_2 = 0.24$.

For solutions containing 25, 50 and 75% of methanol, r_1 changes from 2.2 to 6 while r_2 was 0.18; 0.30 and 0.02, respectively. It is noteworthy that excluding co-polymerisation in the 75% methanol solution, all the systems under investigation were heterogeneous. In the course of the reaction, precipitation of the product occurs. It was also found [94] that in co-polymerisation of acrylic acid with acrylamide, reactivity ratios are very sensitive to the solvent. The results were discussed by the authors in terms of a possibility of a template effect.

For the case when co-monomers polymerise according to the pick-up mechanism, composition equation for template co-polymerisation was formulated [91].

The composition and the distribution of units in co-polymerisation is controlled mainly by the propagation process. Denoting by *, radicals connected with the template we can write the following set of reactions and corresponding kinetic equations [91]

$$\mathrm{A}\cdot + \mathrm{A} \rightarrow \mathrm{A}\cdot \qquad v_{\mathrm{AA}} = k_{\mathrm{AA}}[\mathrm{A}\cdot][\mathrm{A}]$$

$$\mathrm{A}\cdot^* + \mathrm{A} \rightarrow \mathrm{A}\cdot^* \qquad v_{\mathrm{A^*A}} = k_{\mathrm{A^*A}}[\mathrm{A}\cdot^*][\mathrm{A}]$$

$$\mathrm{A}\cdot + \mathrm{B} \rightarrow \mathrm{B}\cdot \qquad v_{\mathrm{AB}} = k_{\mathrm{AB}}[\mathrm{A}\cdot][\mathrm{B}]$$

$$\mathrm{A}\cdot^* + \mathrm{B} \rightarrow \mathrm{B}\cdot^* \qquad {}_{\mathrm{A^*B}} = k_{\mathrm{A^*B}}[\mathrm{A}\cdot^*][\mathrm{B}]$$

$$\mathrm{B}\cdot + \mathrm{A} \rightarrow \mathrm{A}\cdot \qquad v_{\mathrm{BA}} = k_{\mathrm{BA}}[\mathrm{B}\cdot][\mathrm{A}]$$

$$\mathrm{B}\cdot^* + \mathrm{A} \rightarrow \mathrm{A}\cdot^* \qquad v_{\mathrm{B^*A}} = k_{\mathrm{B^*A}}[\mathrm{B}\cdot^*][\mathrm{A}]$$

$$\mathrm{B}\cdot + \mathrm{B} \rightarrow \mathrm{B}\cdot \qquad v_{\mathrm{BB}} = k_{\mathrm{BB}}[\mathrm{B}\cdot][\mathrm{B}]$$

$$\mathrm{B}\cdot^{*} + \mathrm{B} \rightarrow \mathrm{B}\cdot^{*} \qquad v_{\mathrm{B^*B}} = k_{\mathrm{B^*B}}[\mathrm{B}\cdot^{*}][\mathrm{B}]$$

It was reported [91] that similar to the Mayo–Lewis equation, composite reactivity ratios can be defined as

$$r'_{\mathrm{A}} = \frac{k_{\mathrm{AA}}[\mathrm{A}\cdot] + k_{\mathrm{A^*B}}[\mathrm{A}\cdot^{*}]}{k_{\mathrm{AB}}[\mathrm{A}\cdot] + k_{\mathrm{A^*B}}[\mathrm{A}\cdot^{*}]}$$

and

$$r'_{\mathrm{B}} = \frac{k_{\mathrm{BB}}[\mathrm{B}\cdot] + k_{\mathrm{B^*B}}[\mathrm{B}\cdot^{*}]}{k_{\mathrm{BA}}[\mathrm{B}\cdot] + k_{\mathrm{B^*A}}[\mathrm{B}\cdot^{*}]}$$

The initial composition of co-polymer S ($-\mathrm{d}[\mathrm{A}]/-\mathrm{d}[\mathrm{B}]$) can be expressed by

$$S = x\frac{xr'_{\mathrm{A}} + 1}{x + r'_{\mathrm{B}}}$$

where x is the composition of monomers feed [A]/[B].

In contrast to the conventional Mayo–Lewis equation, the reactivity ratios are dependent on the template concentration [T] and equilibrium constant (K_{A}) of the reaction:

$$\mathrm{A}\cdot + \mathrm{T} \Leftrightarrow \mathrm{A}\cdot^{*}$$

Equation for r'_{A} can be written as

$$r'_{\mathrm{A}} = \frac{k_{\mathrm{AA}} + k_{\mathrm{A^*A}}K_{\mathrm{A}}[\mathrm{T}]}{k_{\mathrm{AB}} + k_{\mathrm{A^*B}}K_{\mathrm{A}}[\mathrm{T}]}$$

It is easy to see that if $K_{\mathrm{A}} = 0$ (i.e. radicals are not present onto the template), $r'_{\mathrm{A}} = k_{\mathrm{AA}}/k_{\mathrm{AB}}$ as in conventional co-polymerisation. If interaction between radicals and the template is strong, $K_{\mathrm{A}}[\mathrm{T}] \gg k_{\mathrm{AA}}$ and k_{AB}, and the co-polymerisation proceeds only onto the template and

$$r'_{\mathrm{A}} = k_{\mathrm{A^*A}}/k_{\mathrm{A^*B}}.$$

From the general rules concerning radical co-polymerisation, it is possible to find a relation between reactivity ratios and the average numbers of A-type units in a sequence $\overline{l_{\mathrm{A}}}$, and B units in a sequence $\overline{l_{\mathrm{B}}}$.

$$\overline{l_A} = r_{\mathrm{A}}x + 1 \text{ and } \overline{l_{\mathrm{B}}} = \frac{x + r_{\mathrm{B}}}{x}$$

where $x = [\mathrm{A}]/[\mathrm{B}]$.

In many papers [91,92,95], it has been found that the template co-polymerisation can be described by Markovian first-order statistics. For instance, Frish and Xu [92] determined the average length of sequences in co-polymer styrene-*co*-methacrylic acid obtained by the template polymerisation onto poly(2-vinyl pyridine) using ^{1}H and ^{13}C NMR.

The results were compared with corresponding data for co-polymerisation without the template. For a different composition of co-monomers in the initial feed, the length of sequences for both methacrylic acid and styrene units was higher when co-polymerisation was carried out in the presence of the template.

Similar results were found [91] for template polymerisation of methacrylic acid and styrene onto PEG 20,000 in toluene. In this case, in the presence of the template, the average length for both monomers increases in comparison to blank co-polymerisation. However, for co-polymerisation of methacrylic acid with methyl methacrylate in the same solvent, only the average length for acid units increases. The same effect was observed for co-polymerisation of methacrylic acid with acrylic acid. The recalculated data from [42] for template co-polymerisation of HEMA with acrylic acid leads to the conclusion that in this case, the average length for HEMA sequences decreases, while the length of acrylic acid units is the same as for the blank reaction.

The free radical co-polymerisation of methacrylic acid with methyl methacrylate in the presence of poly(*N*,*N*′-dimethyl-2aminoethyl methacrylate) was initiated by AIBN in THF [95]. As a method of examination, the exclusion chromatography technique was applied. By this technique, not only the concentration decreased for both co-monomers measured in the course of the process, but also the change in the macromolecular part of the system; that is, the change in molecular weight of the template and the complex formed. From the results, reactivity ratios for monomers were calculated and compared with the similar values for co-polymerisation without the template. Significant differences were found in these values. Moreover, it was observed that the molecular weight distribution of the template changes in the course of the reaction. This phenomenon was explained by the author on the basis of the molecular recognition effect. The template molecules with the higher molecular weight react first, forming a complex, while lower molecular weight templates remain in the solution. This phenomenon should be taken into account when polydispersed template is used.

All these results show that the template influences the reactivity ratios and the sequence distribution of monomeric units in co-polymerisation. This is illustrated in Table 5, denoting relative reactivity ratios by $R_1 = r'_1/r_1$ and $R_2 = r'_2/r_2$ (Table 6).

Slightly different phenomenon was observed by O'Driscoll and Capek [98] when template co-polymerisation leads to the stereocomplex. In the case of co-polymerisation of methyl methacrylate and styrene in the presence of it-poly(methyl methacrylate), it was found that a very small amount of styrene

Table 6
Relative reactivities for template co-polymerisation

Template	Solvent	Monomer 1	Monomer 2	R_1	R_2	Ref.
PEG 20,000	Toluene	Metacrylic acid	Styrene	1.54	1.30	[91]
PEG 20,000	Toluene–benzene	Methacrylic acid	Acrylic acid	1.25	0.4	[96]
				1.26	0.66	
PEG 20,000	Toluene	Methacrylic acid	Methyl methacrylate	1.40	0.18	[97]
P2VP	Toluene–acetone 4:1	Methacrylic acid	Styrene	1.9	2.8	Recalc. from [92]
PVP[a]	Water	Acrylic acid	HEMA	1.06	0.40	Recalc. from [42]
PDAMA[b]	THF	Methacrylic acid	Methyl methacrylate	2.13	0.82	Recalc. from [95]

[a] Poly(vinyl pyrrolidone).

[b] Poly(*N*,*N*′-dimethyl-2-aminoethyl methacrylate.

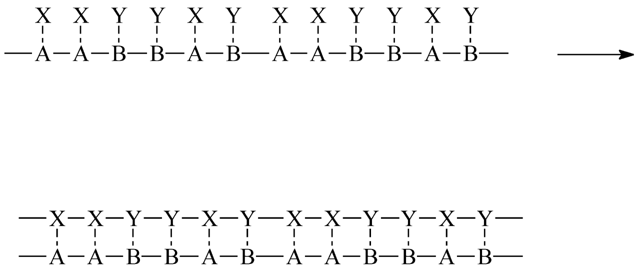


Fig. 6. Co-polymerisation onto co-polymer template (strong interactions).

destroys any template effect. Complexation occurs only if longer than 10–20 units sequences of methacrylate are present in the co-polymer.

An interesting case of template co-polymerisation was described by Kakui et al. [99]. Poly(maleic anhydride) used as a template interacts with one of co-monomers (vinyl pyridine) by strong charge transfer forces while the second (*p*-chlorostyrene) was not interacting. The co-polymer obtained in the course of the co-polymerisation was much more rich in vinyl pyridine units than that obtained in the course of conventional co-polymerisation.

Another example of a template co-polymerisation occurs if a co-polymer is used as a template. We can distinguish the following cases:

When strong interactions are present between both monomers and corresponding groups in the co-polymer template, the reaction proceeds according to mechanism I. Let us assume that monomer X interacts with A unit of the template, and monomer Y — with B unit. This case can be illustrated by the following schematic representation (Fig. 6).

If only one monomer is interacting by strong intermolecular forces (for instance monomer X with A units) and the second (Y) is not interacting with the template, the co-polymerisation proceeds partially onto the template (Fig. 7).

In principle, such co-polymerisation should lead to the co-polymer with composition controlled by the composition of the template.

Only one paper deals with a case when a co-polymer was used as a template in radical polymerisation [100]. Acrylic acid was polymerised in the presence of co-polymers: vinyl pyrrolidone–acrylamide

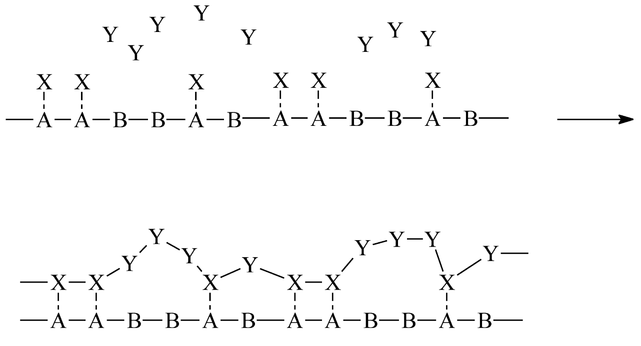
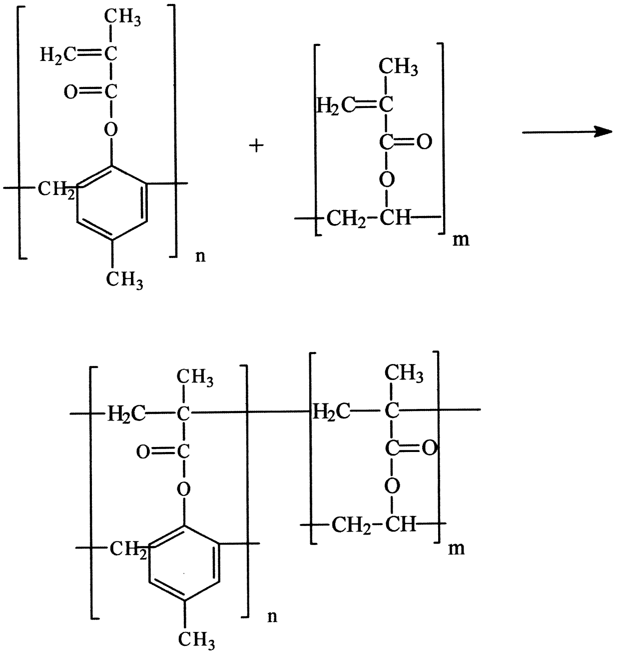


Fig. 7. Co-polymerisation onto co-polymer template (strong interactions A–X only).

or vinyl pyrrolidone–styrene with a different composition. It was found that the rate of polymerisation decreases with a decrease in the vinyl pyrrolidone contents in the co-polymer. The order of the reaction rate with respect to the monomer concentration was found to be 1. The same order of reaction with respect to initiator concentration was found. When the co-polymer styrene–vinyl pyrrolidone was used as a template, the order with respect to monomer and initiator concentration was 1.42 and 0.97, respectively. The examination of complex composition obtained by template polymerisation leads to the conclusion that the ratio of vinyl pyrrolidone units to acrylic acid units was close to 1, and independent of the composition of co-polymer used, while the complexes obtained by mixing dilute solutions of the components (polyacid and co-polymer) were richer in the acid component. In contrast, when co-polymer styrene–vinyl pyrrolidone was used as a template, it was found that both types of complexes contained fewer acrylic acid units than would be expected on the basis of a 1:1 molar ratio.

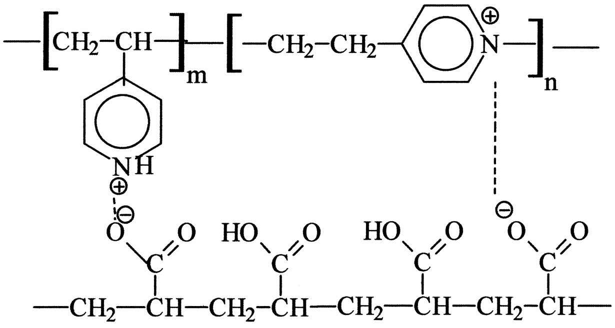
Another case occurs if there are two different templates connected by covalent bonds with monomeric units. In other words, it is a co-polymerisation of two different multimonomers.

This case was described in the example of the multimonomer prepared from poly(vinyl alcohol) and the multimonomer from cresyl–formaldehyde resin [75].



4. Spontaneous and ring-opening polymerisation

Spontaneous template polymerisation of vinyl pyridine in the presence of poly(acrylic acid) was first observed by Kargin and Kabanov [101–103]. In initial papers, it was assumed that polymerisation of vinyl pyridine proceeds similar to conventional polymerisation of vinyl monomers by vinyl group. However, Salamone [104] and the Russian authors [105] drew the conclusion that, at least partially, 1-6 addition occurs, which leads to the daughter polymer structure of



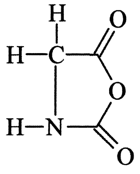
connected with the template. Furthermore, spontaneous polymerisation was observed in the case of polymerisation of maleic anhydride in the presence of poly(vinyl pyridine) [106]. The authors find that polymerisation proceeds without any initiator in chloroform or nitromethane, although oxygen from air must be present. The authors explain the spontaneous polymerisation by charge transfer interaction between the template and the monomer; however, the mechanism of the reaction is not fully clear.

The reverse system was the object of investigation by Shima et al. [107]. The polymerisation of 2-vinyl pyridine, 4-vinyl pyridine and dimethylaminostyrene was carried out in the presence of poly(maleic anhydride). The polymerisation proceeds spontaneously without any initiator at 50°C in DMF or acetone. In order to separate the poly(vinyl pyridine) from the template, the reaction product was passed through a column packed with Dowex, and analysed by IR spectrometry. The molecular weight of daughter polymer was low (DP = 14) but the DP of template used was also low and almost same(DP = 12). It suggests that because strong-change transfer-interaction monomer is fully adsorbed, polymerisation proceeds as type I reaction.

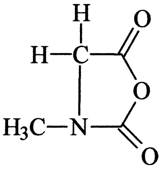
Polymerisation of 4-vinyl pyridine onto alternating co-polymer maleic anhydride–styrene leads to similar results. Very low molecular weight (500) was found for poly vinyl pyridine obtained onto template with molecular weight 4640. The authors explain the results in terms of unfavourable location of the monomer units on the co-polymer template.

It was found that the composition of the complex obtained was equimolar in the case of both 2-vinylpyridine and 4-vinylpyridine, while in the case of dimethylaminostyrene there is 0.4 unit the later for every one unit of the template. The polymerisation mechanism suggested by the authors assumed adsorption of monomer units onto the template, while the initiation mechanism was not clear.

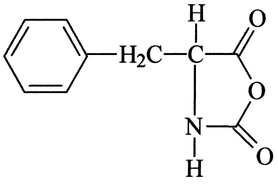
One of the earliest example of the application of template polymerisation for polypeptide synthesis was reported by Ballard and Bamford [108]. The substrate for the synthesis was *N*-carboxy-α-amino acid anhydrides (NCA):



Glicyne NCA

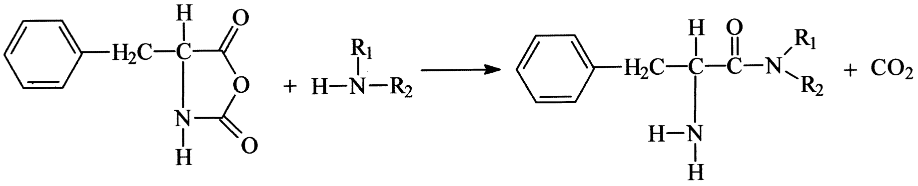


Sarcosine NCA



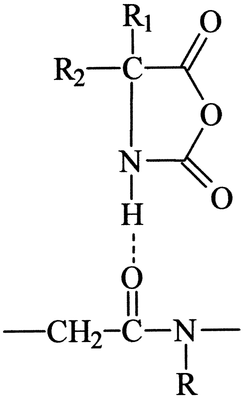
phenylalanine NCA

The first step consists of the reaction of NCA with secondary amine. In the course of the reaction, decarboxylation occurs:

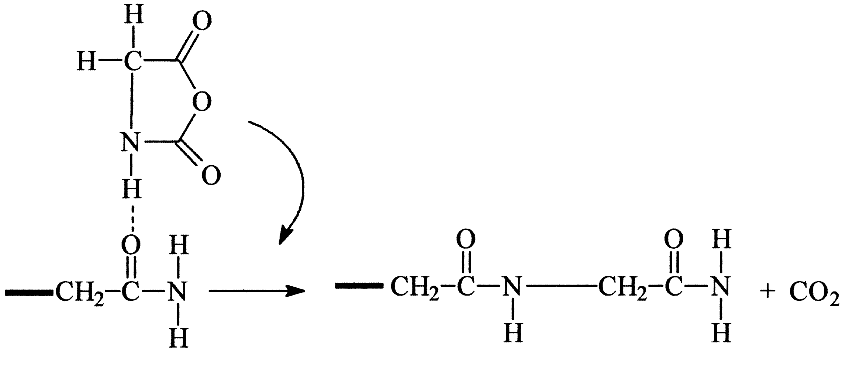


The product containing the amine group is an initiator for the next NCA molecule. The ring-opening process and the elimination of CO_2 proceeds as a chain reaction. Examination of the kinetics of the process leads to the conclusion that the NCA has been adsorbed on the polypeptide chain serving as a template, and then polymerisation occurs.

The 'chain effect' appears only when the NCA contains a >N–H group. The existence of hydrogen bonds between a carbonyl group in the polypeptide and the >N–H group was confirmed by IR spectroscopy.



For instance, in the course of polymerisation of phenylalanine NCA absorbed onto a polyglycine template, a ring-opening reaction and decarboxylation occurs with a restoration of the growing centre.

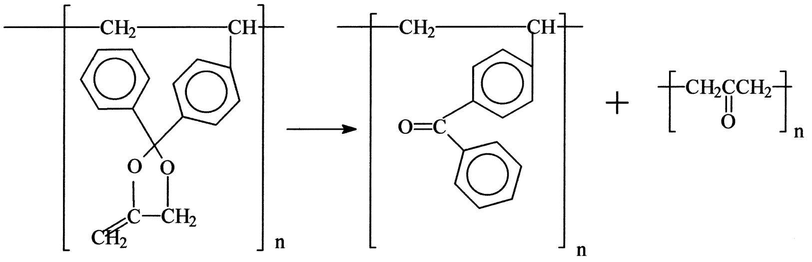


Valuable experimental material about polymerisation of many different *N*-carboxyanhydrides initiated by many different polypeptides [109–111] as well as by poly(vinyl pyridine) [112,113] was accumulated by Imanishi et al.

Using polysarcosine with a different DP as an initiator of polymerisation of DL-phenylalanine NCA, the authors found that the rate of reaction depends on the DP of polysarcosine, and on the solvent used.

Sugiyama et al. [114,115] report a template process by the ring-opening polymerisation induced by radicals. The polyethylene template was connected with 2,2-diphenyl-4-methylene-1,3-dioxolane groups by covalent bonds.

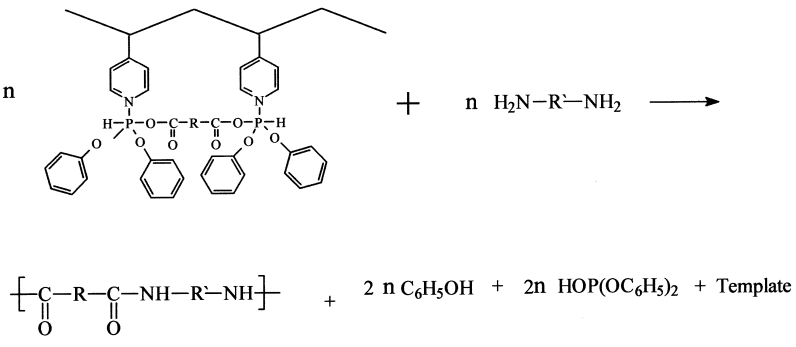
In the course of the polymerisation, elimination of the benzophenone group occurs as does an opening of the dioxolane ring. As the result of these reactions, benzophenone groups remain connected with the main chain, while a new polymer is formed. The process can be illustrated by the reaction:



On contrary to the template processes described below, the daughter polymer is not up to that point connected with the template either by hydrogen or covalent bonds. The authors have also noted an interesting phenomenon, namely that when using styrene co-polymer and the same monomer, the polymerisation efficiency is even higher than for the homopolymer.

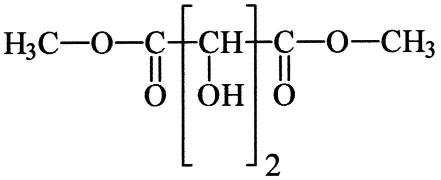
5. Template polycondensation

Extensive studies on template polycondensation were carried out by Higashi and Yamazaki [116–118]. The direct polycondensation method was applied. Activation of carboxyl groups in dicarboxylic acid by triphenylphosphite and pyridine groups leads to the reaction with diamines proceeding in mild conditions and giving products with high molecular weight. The presence of templates like poly(4-vinylpyridine), poly(vinyl pyrrolidone) or poly(ethylene oxide) substantially increases the molecular weight of the polyamides obtained. A good example is the polycondensation of terephthalic acid with hexamethylene diamine in *N*-methyl pyrrolidone with LiCl activated by triphenylphosphite. As a template, poly(4-vinylpyridine) was used [116]. Activated terephthalic acid connected with the template reacts with diamine according to the reaction



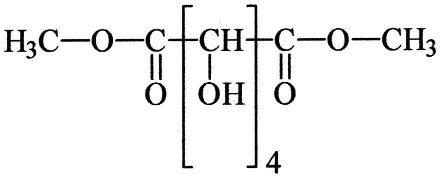
A similar reaction with poly(ethylene oxide) as a template was described in the next paper. In this case, poly(ethylene oxide) interacts with carbonyl groups by hydrogen bonds, but does not participate in the activation. Polyterephthalamides of high molecular weight were obtained using different diamines like *p*-phenylenodiamine, 4,4′-diaminodiphenyl methane, 4,4′-diaminodiphenylether and many others.

Another example of template polycondensation was described by Ogata et al. [119–122]. Polycondensation of dimethyl tartrate



$$H_3C-O-\underset{\displaystyle O}{\underset{\|}{C}}-\left[\underset{\displaystyle OH}{\underset{|}{CH}}\right]_2-\underset{\displaystyle O}{\underset{\|}{C}}-O-CH_3$$

or dimethyl muconate

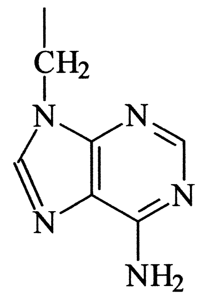


$$H_3C-O-\underset{\displaystyle O}{\underset{\|}{C}}-\left[\underset{\displaystyle OH}{\underset{|}{CH}}\right]_4-\underset{\displaystyle O}{\underset{\|}{C}}-O-CH_3$$

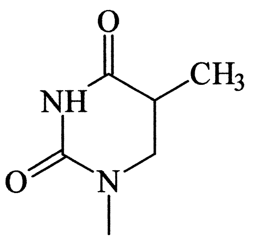
with hexamethylenediamine was increased by the presence of poly(vinyl pyrrolidone) and poly(vinyl alcohol). It was also found that polysaccharides increase the polycondensation rate. It seems that hydroxyl groups play a substantial role in absorption of monomers onto the template.

A very interesting method of polycondensation was described by Hattori et al. [123]. Di-*p*-nitrophenyl methylsuccinate with thymine or theophylline was condensed with piperazine.

The strong interaction between complementary groups: adenine A in the template and thymine B in the monomer was confirmed by IR and the NMR techniques.

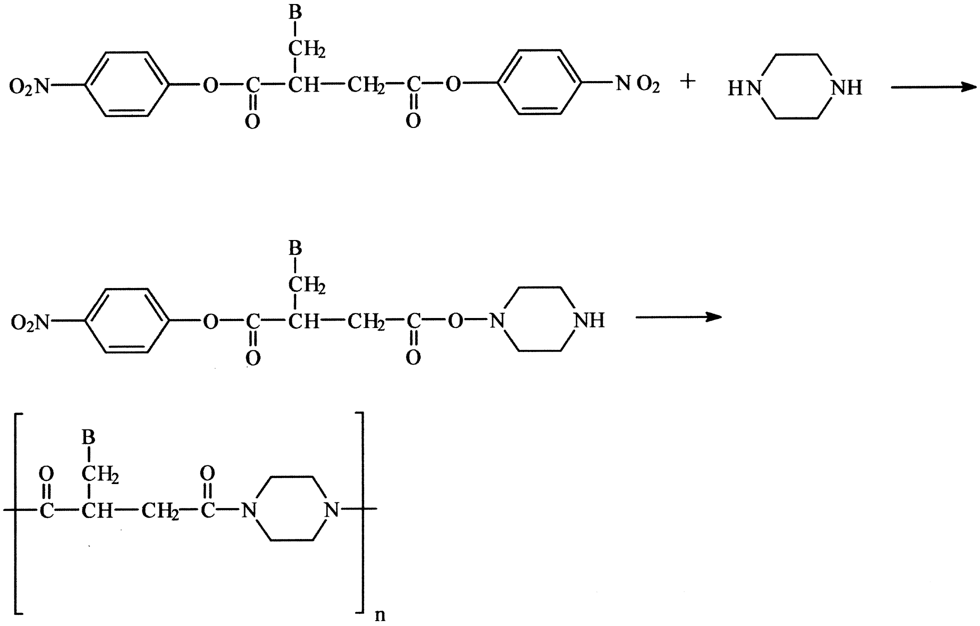


A

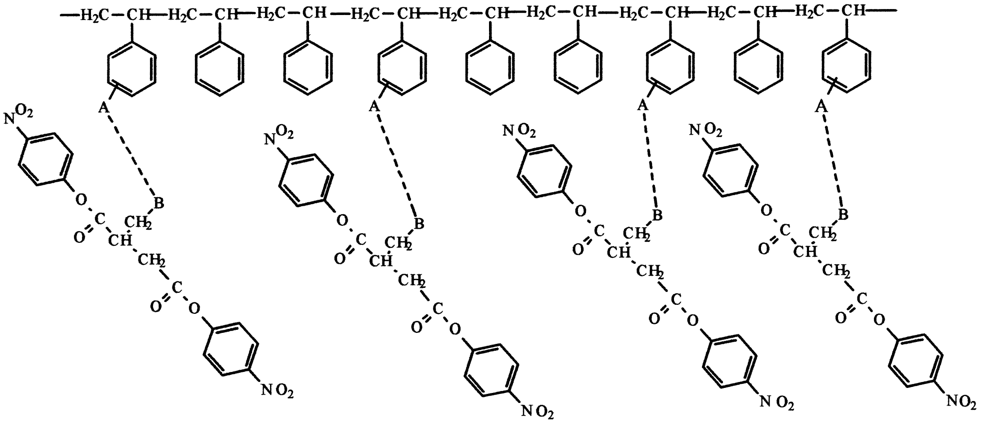


B

The reaction proceeds according to the scheme:

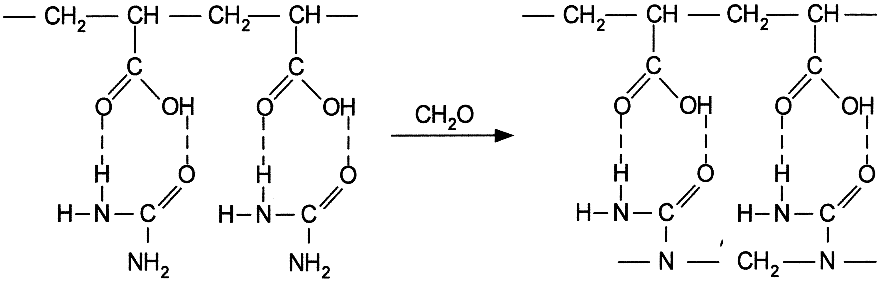


The reaction was carried out in a pyridine/methylene chloride mixture or DMF in the presence of co-polymer of styrene and styrene derivatives with adenine groups as a template. The following structure of the complex can be suggested:

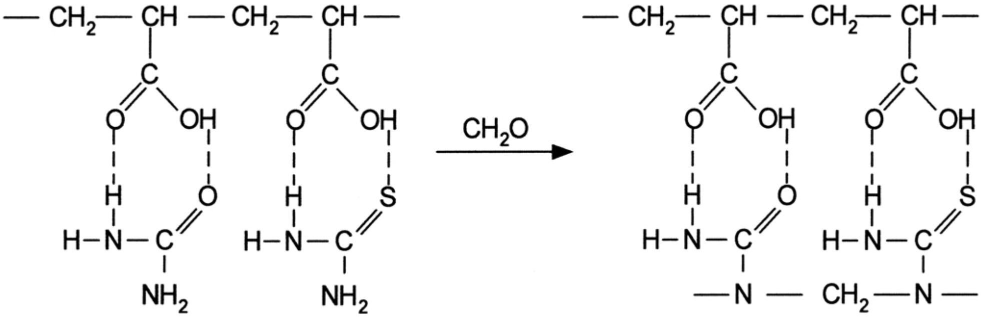


It was found that depending on the percentage of adenine groups in the co-polymer, the rate of reaction was different. For instance, for a monomer with thymine groups the maximum of acceleration appears in about 50% of adenine groups in the template co-polymer and the ratio of 1:1 monomer to the template.

A template polycondensation of urea with formaldehyde in the presence of acrylic acid was published by Papisov et al. [124–127, 129]. The authors suggest that a complex with polyacid is formed during the reaction. The complex has a different structure than urea–formaldehyde resin mixed with poly(acrylic acid). If during the reaction the pH is kept below 3.7, NH_2 groups are present in the obtained polycomplex. The presence of NH_2 groups was confirmed by the presence of 3440 cm^{-1} in the IR spectrum. In the absence of poly(acrylic acid), polycondensation leads to the structure $–CH_2–NH–CO–NH–$. The authors explain the mechanism of the template reaction by assuming an interaction between carboxylic groups and urea. Indeed, it is known that hydrogen bonds are formed in such a system, and the following reaction can be written:



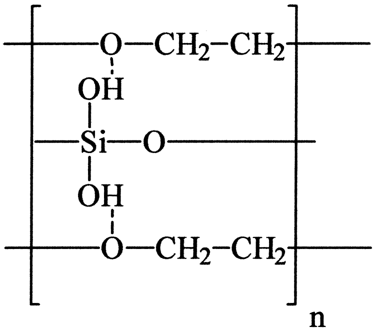
In our work [128], the process of template co-polycondensation was an object of investigation using urea and tiourea as co-reagents. It was expected that, similar to the reaction described by Papisov, co-polycondensation in the presence of poly(acrylic acid) would proceed according to the scheme:



A set of experiments was carried out at 25°C. The reacting mixture after stirring for 4 h, was kept for 7 days. The precipitated complex was centrifuged, washed a few times with water and dried under vacuum. From the results of the elemental analysis, the percent of tiourea in the product was calculated. As can be seen from the results, the percentage of tiourea in the product is similar to the percentage of tiourea in the monomer mixture. It seems that if the reaction time is long enough, all urea and tiourea is built up into the product.

A second set of experiments was carried out at 50°C. The procedure was the same as in the first set; however, the reaction proceeded for about 150 min. The complex was then washed with water, centrifuged and dried. From the elemental analysis and IR spectrometry, it was proved that the tiourea is incorporated into the product; however, the tiourea percentage in the product is slightly lower than in the monomer mixture.

In the last few years, progress has been made in understanding template polycondensation. The theoretical considerations [12] have been enriched by new concepts [126] and new experiments. The earlier publication deals with heteropolycondensation. This means that two monomers with two different groups were used as substrates. For instance, in papers published by Ogata et al. [119,120], it was found that polycondensation of diethylmucate or dimethyltartrate with hexamethylenediamine is enhanced by poly(vinyl pyrrolidone) or poly(vinyl alcohol). The optimum of this template effect was for the molecular ratio monomer to template equal about 1/2. This means that two molecules of the template were involved in formation of the active complex. This fact was not interpreted in such terms. However, results published on the polycondensation of tetraacetoxysilane in the presence of poly(ethylene glycol) [125,126] can, according to the authors, lead to the structure:



This means that the polycondensation — in this case a homopolycondensation — takes place between two template molecules. This is of course still quite far from biological processes, such as for instance DNA replication, but one can find some analogy with the process proceeding in replication origin. It fulfils a postulate of three-dimensional centre of reaction.

The scheme proposed by the authors [12] is also interesting, taking into account the influence of the length of oligomers capable of recognising the template. This is dependent on the interaction between the monomer or the oligomers and the template. The stronger the intermolecular interaction is the higher is the level of matrix control of the daughter polymer structure.

We may apply to template polycondensation a similar approach as in the case of template polymerisation. If the interaction between a monomer and the template is strong, and the monomer is adsorbed onto the template, polycondensation proceeds only onto the template. It is illustrated by the following scheme (Fig. 8).

In the case of weak binding of a monomer, polycondensation proceeds outside the template up to the step in which oligomers of a proper length appear. Adsorption then takes place and polycondensation is carried out onto the template. The template controls the process only in this step. The process can be illustrated by the following scheme (Fig. 9).

It was emphasised [12] that the structure of the daughter chain may depend on the length of oligomers capable of 'recognising' the template.

The theoretical consideration and models for kinetics description of template reaction in biological systems was published by Simha et al. [130]. The model was constructed on the basis of addition reaction in order to apply to the synthesis of biological molecules, for instance DNA replication.

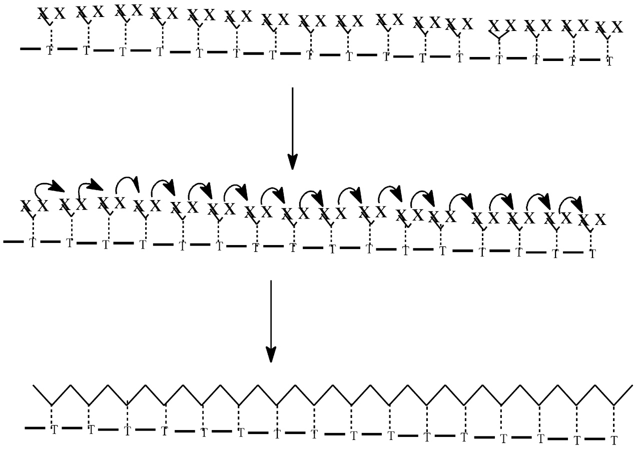


Fig. 8. Polycondensation onto template with strong interactions template–monomer.

6. Products of template polymerisation and potential applications

Products of template polymerisation can find a potential application as polymers with a structure that is difficult to obtain by other methods. However, an isolation of the daughter polymer from the product of the synthesis is usually difficult and not acceptable for industry. The synthesis of styrene–methyl methacrylate short block co-polymers described in the chapter devoted to co-polymerisation is a good example. Such co-polymers with regular 3, 6 or 8 methacrylic units in the chain very difficult can be obtained by other methods. In addition, polyesters or polyamides obtained by template polycondensation must be separated from the substantial amount of by-product.

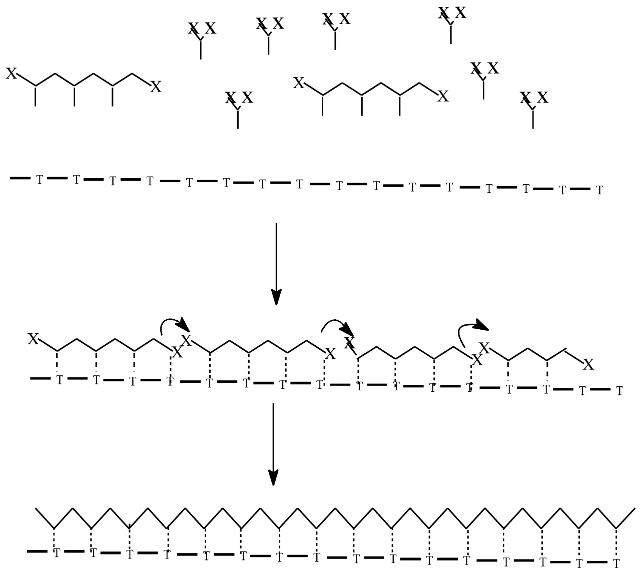


Fig. 9. Polycondensation onto template with weak interactions template–monomer.

More promising is an application of the template polymerisation products without separation. Sometimes the products have a unique structure and properties.

Template polymerisation leads to the formation of two type of products: interpolymer complexes and ladder-type polymers. The former are formed if the monomer or growing polymer chains interact with the template by intermolecular forces, while the latter are formed when the monomer units are connected by covalent bonds with the template, or when that type of bond is formed in an interpolymer complex, for instance by thermal treating. The structure of polycomplexes formed in the course of the template process is frequently different from the structure of complexes obtained by mixing component solutions.

Such complexes can be used as high efficient or selective absorbents.

Ferguson et al. [131] found that sorption of water by complexes obtained by polymerisation of acrylic acid in the presence of poly(vinyl pyrrolidone) is different from that for complexes of the same composition but which were obtained by mixing the components. Al-Alawi [132], examining the same type of complexes, also found a difference in properties between mixtures and template polymerisation products. It is known [133,134,135] that interpolymer complexes with ladder-type sequences of bonds and 'loops' can exist. In extreme cases, the ladder-type model or 'scrambled-eggs' model can be applied to the description of the structure. Depending on the fraction of the bonds engaged, the ladder structure is connected with the thermal properties of the complexes. Thermochemical reactions in polycomplexes have been described [136]. It was found that polycomplexes obtained by template polymerisation have a more regular structure, and the fraction of groups unbounded in polycomplex is lower than in similar complexes obtained by mixing. For instance, polymeric complexes with free carboxylic groups in loops can be determined by the thermal dehydratation reaction with formation of cyclic anhydride groups [12]. The new family of crystallisable polyelectrolyte complexes was obtained by template polymerisation of 4-vinylpyridine onto poly(sodium phosphate) [137]. The composition and crystallinity of the complexes was different from similar complexes obtained by mixing. The radical template polymerisation of sodium acrylate onto poly(allyl amine) hydrochloride leads to polycomplexes with a more ordered structure than that obtained by mixing. It was demonstrated [36] by transforming the complexes to cross-linked, insoluble compounds that the template products have a structure similar to ladder macromolecules.

Mohammadi et al. [138] reported that electrically conducting polymer composite films can be synthesized by template polymerisation of pyrrole in the system poly(4-vinylpyridine) cupric ion.

Ratzsch [139] presents an application of template polymerisation to the acquisition of images by a technique similar to photolithography. A thin film of the monomer (for instance acrylic acid) and the template placed onto a plate was exposed through a mask to UV light. In exposed places, an insoluble complex was formed, and then the unreacted monomer was dissolved. By treating the plate with appropriate dyes or metal ions, an image appears. The picture definition was very high, and application in microlithography was suggested.

Semi-permeable membranes containing carboxylic and vinyl pyridine groups were obtained by polymerisation of 4-vinylpyridine onto fluoroethylene films previously grafted by acrylic acid.

Extensive studies of the structure and transformations of template polymerisation products obtained from urea and formaldehyde on polyacrylic acid were reported [140]. The authors show that not only for template polycondensation is it possible to obtain a complex with a unique chemical structure, but also (depending on condition of the reaction) a different secondary structure of the product can be reached. Tsuchida and Osada [34] found that spinning of fibres is possible from complexes obtained as a result of template polymerisation of acrylic or methacrylic acid onto poly(N,N,N',N' tetramethyl N-p-xylilene ethylenediammonium dichloride). Template polymerisation is sometimes the only method for obtaining linear polycomplexes, for instance composites obtained by the hydrolysis of Tetraacetoxysilane or titanium (IV) hydroxide in the presence of polyethylene glycol [141].

Template polymerisation of multimonomers is another example of obtaining materials which cannot be obtained in the conventional way. The template effect leads to materials with a ladder or semi-ladder structure. As it was mentioned, Kämmerer et al. [70–72] succeeded in obtaining oligomers with a ladder-type structure from esterificated cresyl-formaldehyde resin. A ladder-type polymer can be obtained as a result of template polymerisation of poly(vinyl methacrylate) and other multimonomers. It is interesting that the polymers are soluble in common solvents like DMF, DMSO, chloroform or toluene.

Soluble in chloroform co-polymers containing two different ladder-type blocks were also reported.

Co-polymers with one block of ladder-type and another of conventional structure were investigated. Especially styrene-multioligomers with different numbers of units (from 4 to 10) in multioligomer from *p*-cresyl-formadehyde resin and esterificated by methacrylic groups were the object of structural investigation [142–144]. Thermal properties and supermolecular structure were investigated by DSC, SAXS and WAXS methods, and a model of the supermolecular structure of the co-polymers was proposed [141]. It was further proved [142,143] that hydrolysis of such co-polymers leads to short block co-polymers of styrene–methacrylic acid, which are difficult to obtain in another way.

Thermal properties of ladder-type polymers obtained from multimonomers were described [145]. The results obtained shows that ladder polymer obtained with poly(2-acryloxyethyl methacrylate), has a considerably higher thermal stability than that of their linear analogue.

As was mentioned above, template polymerisation of multimonomers (or co-polymerisation) in dilute solutions leads to products with a ladder-type structure. However, polymerisation in a concentrated state leads to cross-linking. We found [146] that co-polymerisation of methylmethacrylate with multimonomers carried out in concentrated solution or in bulk leads to networks, which have different properties in comparison with the networks obtained by using a classical cross-linker like 1,4-butandiol diethacrylate (DMBD). Swelling, which is a good measure of cross-linking density, makes a good example. Let us assume for a moment that the cross-linking points are distributed at random, and we can thus calculate cross-linking density ν from the Flory–Rehner equation [147].

$$\nu = -\left[\nu_2 + \nu_2^2\chi + \ln(1-\nu_2)\right]/V_1\left(\nu_2^{1/3} - 0.5\nu_2\right)$$

where ν_2 is the volume fraction of polymer in the swollen network, χ the Flory–Huggins interaction parameter between solvent and polymer, V_1 the molar volume of the solvent.

Results for the networks obtained by polymerisation of methyl methacrylate with 1,4-butandiol dimethacrylate and multimethacrylate with different degrees of polymerisation (DP) are compared in Table 7.

As we can see, the higher the molecular weight of the cross-linker, the lower the cross-linking density. We can assume that the ratio $\nu_{\mathrm{DM}}/\nu_{\mathrm{MM}}$ is a measure of this ‘multiplicity’, that is, the deflection from random distribution. We can see from the table that the higher the molecular weight of the multimonomer is the higher is the deflection from random distribution. This leads to the conclusion that unconventional networks can be obtained by template polymerisation.

The new type of reactions called by Papisov [12] ‘pseudomatrix processes’ leads to formation of solid particles or micelles. Eventually, polymer–inorganic composites or small particles of metals can be

Table 7
Relative cross-linking density of poly(methacrylate) cross-linked with multimethacrylates

DP	$\overline{M_n}$	ν_{DM}/ν_{MM}	ν_{MM}
2[a]	212	1	39.80
79	14,700	1.60	24.80
144	26,500	2.30	17.37
148	27,200	3.79	10.51

[a] Poly(*N*,*N*′-dimethyl-2-aminoethyl methacrylate [146].

obtained. Litmanovich et al. [148] described the pseudomatrix processes of the reduction of bivalent copper. The copper particles with a diameter 7–10 nm in this process were obtained. Similar nickel particles reduced in an aqueous poly(vinyl pyrrolidone) solution were presented on electron micrograph [12]. It was shown that the process allows directional variation of the size of the particles. The author suggests that various nanostructured materials can be used, for example, as highly efficient absorbents and catalysts.

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