PROBLEMS OF POLYMER MODIFICATION AND THE REACTIVITY OF FUNCTIONAL GROUPS OF MACROMOLECULES

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Abstract—General approach to the study of kinetics and mechanism of macromolecular reactions in comparison with the reactions with low molecular substances is developed. The neighbouring group effect in the transformation of functional groups of macromolecules is considered on the experimental basis of chlorination reaction with paraffines, cycloparafines and polyethylene, acid and base hydrolysis of polymethyl methacrylate and polydiphenylmethyly methacrylate of different microstructure and of quaternization of polyvinyl pyridine. The effect of microtacticity and of conformational peculiarity on kinetical behaviour of various polymeric samples in polymeranalogous reaction is considered. A new computer technique to calculate the individual rate constants for macromolecular reactions is described and the theoretical approach to estimate the units distribution sequences and the composition heterogeneity of the products is developed.

The reactivity of functional groups of macromolecules may be different from that of low molecular analogs. These variations are connected with stereochimical influences, with the neighbouring groups effect and with conformational and supermolecular characteristics of polymeric reagents. The review was made by the author at the International Symposium on Macromolecular Chemistry in Boston in 1971 and at the NATO Conference on Chemical Transformations of Polymers in Troy in 1973 concerning theoretical study on units distribution sequences as a result of polymeranalogous reaction with neighbouring groups effects. The quantitative approach to calculating the composition heterogeneity of the products was also presented.

In this lecture some new results in the field of the theory of macromolecular reactivity as well as in the experimental study of this problem will be discussed.

If the reaction between functional groups of macromolecular reagent and low molecular substance takes place and its rate depends on the fact whether the units neighbouring with the given group have already reacted or not one should bear in mind that there is a theoretical and mathematical methods now to describe quantitatively the kinetics of the reaction with three individual rate constants and the distribution sequences of units along the chain that have reacted and those that have not.

These calculations are based on the utilization of McQuarrie's kinetic equations and on some new approaches developed in our laboratory at the University of Moscow and the Institute of Petrochemical Synthesis. The various reactions of polyacrylates and polyvinyl esters hydrolysis, acetylation of polyvinyl alcohol and cellulose, halogenation of polyolefines, alkylation of polymeric quaternary nitrogen bases are of that type.

It was found that to calculate the sequences distribution of reacted and unreacted units in the chains at intermediate conversions, the noncomplicated mathematical approximation of the type of 2nd and 3rd Marcov's chains can be successfully used. The final results of the probabilities of appearance of these or other triads, tetrads and other sequences of A and B units coincide with the results of the exact analytical solution of the corresponding equations in the computer, also being obtained in a simpler way than the last ones. These probabilities depend on the individual rate constants ratio for units, having 0, 1 and 2 of the already reacted neighbours.

And here we ask ourselves how different are the values of these rate constants and the ratio in the case of macromolecules if it is compared with the corresponding low molecular analogs? The right answer to this question is important from the viewpoint utilizing the existing information on the chemical behaviour of the groups belonging to these small molecules for chemical transformations of polymers and for building models for these processes. The complexity of the experimental analysis of the distribution of the various sequences of even two types A and B units often does not give the chance to check the distribution. Meanwhile the character of the units distribution in the chain of polymers of the same average composition controls not only the melting point, glass point transition and mechanical properties of the chemically modified product but also, for instance, the important biological side effect as it was shown for solutions of polyvinyl alcohol containing the residual acetyl groups which were distributed along the chain in a different manner.

In Table 1 the experimental data on the individual rate constants of chlorination of linear parafines, cycloparafines and polyethylene are shown. This is an example of the reaction widely used for the chemical modification of polyethylene.

Passing from the cycloparafines to linear polyethylene the only absolute value of the rate constants of chlorination of methylene groups in the center of triads (–CH₂–CH₂–CH₂–) is changed. But the ratio of these constants for the methylene groups reaction in the center of such
triads and in the center of triads (-CH2-CH2-CHCl-) and
(-CHCl-CH2-CHCl-) remains practically constant. This
means that conformational peculiarities of various cycles
and linear parafinic molecules do not play any essential
role in the reactivity of the CH2-groups in the chlorina-
tion. Moreover, these compounds starting with 8-
membered parafinic ring can be used for the simulation of
the reaction with polyethylene. The polymeric chain of
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and linear parafine molecules do not play any essential
effects in the reactivity of the CH2-groups in the chlorina-
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the reaction with polyethylene. The polymeric chain of

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_0 \times 10^3$</th>
<th>$k_0/k_1/k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclooctane</td>
<td>0.70</td>
<td>1:0.43:0.18</td>
</tr>
<tr>
<td>Cyclooctacosane</td>
<td>1.0</td>
<td>1:0.43:0.18</td>
</tr>
<tr>
<td>C8H18</td>
<td>0.7</td>
<td>1:0.35:0.08</td>
</tr>
<tr>
<td>Polyethylene (-CH2-)a</td>
<td>1.85</td>
<td>1:0.38:0.11</td>
</tr>
</tbody>
</table>

Table 1. Individual rate constants of chlorination of polyethylene
and its analogs

will testify to the fact that a more complicated mechanism
of the process is at work and one should try to find other
explanations besides the neighbouring group effect.

The experimental data on the individual rate constants
of hydrolysis of various polymethacrylic esters are given
in the Table 2.

Klesper published some results in this field earlier13 but
they concerned only polymethyl methacrylate. To
exclude the stereochemical influence on the kinetics the
stereoregular samples and kinetical method of polymeric
models was employed by us. To study the neighbouring
group effect the stereoregular copolymers of MMA and
MAA with the known and proved statistical bernullian,
distribution of reacted and nonreacted groups were sub-
jected to hydrolysis.6,7,8

The evident influence of the reacted groups, i.e. units of
methacrylic acid onto the rate of hydrolysis can be seen
from Table 2. The reason for the retardation in the case of
syndio and isotactic polymers could be the electrostatic
repulsion of OH- ions governing the alkali hydrolysis by
the carboxylic anions. Taking into consideration the fact
that the total kinetics can be described with equations
based only on the effect of immediate neighbours it can be
stated that the interaction of OH- ions with the carboxy-
late groups neighbouring with ester group takes place
under given conditions rather than the interaction with the
macromolecular coil as a whole.

The value of $k_0$ for isotactic PMMA is one order higher
than for the syndiactic one. At the same time the
retardation effect for iso-models is not so markedly
pronounced (1:0:4:0:4) as for syndiactic ones
(1:0:2:0:05). Passing to more dilute alkali solution the
retardation effect in the hydrolysis of syndiactic PMMA
is not so pronounced as in the concentrated alkali solu-
tion.

Thus the results can already give some useful informa-
tion about the mechanism and kinetics of the complicated
process of polymeranalogous reaction with the reactiv-
ity of the units changing with conversion.

The hydrolysis of stereoregular methacrylic polymers
in the pyridine–water medium is taking place with accelera-
tion provided by neighbouring groups. Tenfold increase
in the rate when the carboxyl groups appear in the
neighbourhood of the esters groups can be explained by
the anchimeric action according to the nucleophilic
mechanism. But the interesting phenomenon is that $k_2$
value is not two times higher than $k_1$ value as could be
expected, but is ten times higher (compare $k_2$: $k_1$ for
isotactic samples). This can be related to the bifunctional
electrophilic–nucleophilic catalysis when the simultane-
ous interaction of one dissociated and one non-dissociated
carboxyl groups takes place in the presence of weak alkali
base:

Such mechanism is apparently realized in the enzymatic
reactions of ester bond hydrolysis.

The data summarized in Table 2 also enables compari-
son of the reactivity of ester bonds toward hydrolysis in the
dependence of the type and size of the substituent in the
Table 2. The rate constants of hydrolysis of polymethacrylic esters at 145°

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Stereoregularity</th>
<th>Medium</th>
<th>$k \times 10^4$ min</th>
<th>$k_0$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_0:k_1:k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymethyl methacrylate</td>
<td>isotactic</td>
<td>0.2 M KOH</td>
<td>90</td>
<td>35</td>
<td>35</td>
<td></td>
<td>1:0:4:0:4</td>
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<tr>
<td><img src="image1" alt="Polymethyl methacrylate" /></td>
<td></td>
<td>(0.05 M KOH)</td>
<td>(1.9)</td>
<td>(1.3)</td>
<td>(1.3)</td>
<td></td>
<td>1:0:7:0:7</td>
</tr>
<tr>
<td>Polymethyl methacrylate</td>
<td>syndiotactic</td>
<td>pyridine—water</td>
<td>5.3</td>
<td>42</td>
<td>530</td>
<td></td>
<td>1:8:100</td>
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<tr>
<td><img src="image2" alt="Polymethyl methacrylate" /></td>
<td></td>
<td>95:5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polydiphenyl-methyl methacrylate</td>
<td>isotactic</td>
<td>pyridine—water</td>
<td>0.3</td>
<td>7</td>
<td>33</td>
<td></td>
<td>1:20:100</td>
</tr>
<tr>
<td><img src="image3" alt="Polydiphenyl-methyl methacrylate" /></td>
<td></td>
<td>95:5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polydiphenyl-methyl methacrylate</td>
<td>syndiotactic</td>
<td>pyridine—water</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td>1:1:1</td>
</tr>
<tr>
<td><img src="image4" alt="Polydiphenyl-methyl methacrylate" /></td>
<td></td>
<td>95:5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyphenyl methacrylate</td>
<td>isotactic</td>
<td>pyridine—water</td>
<td>6</td>
<td>240</td>
<td>6000</td>
<td></td>
<td>1:40:1000</td>
</tr>
<tr>
<td><img src="image5" alt="Polyphenyl methacrylate" /></td>
<td></td>
<td></td>
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<td></td>
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</table>

ester series. Thus, in particular, in spite of the same acceleration character of the reaction of the isotactic polymers in the pyridine—water medium, the presence of bulky diphenylmethyl groups brings about the decrease of absolute rate constant value in comparison with polymethyl methacrylate. Syndiotactic polydiphenylmethyl methacrylate does not show the neighbouring group effect at all in the weak alkali medium and the
whole process can be easily described in the frame of the same reactivity of the ester group and of one rate constant.

This polymer shows a surprising “nonsensitivity” of its stereochemical configuration to the hydrolysis rate. Figure 1 demonstrates the kinetic curves for acidic hydrolysis in the presence of external hydrolysing agent (i.e. in conditions of suppression of chains carboxylic groups dissociation) for syndiotactic and isotactic samples.

It can be seen that entire process is realized as classical first order reaction with the same rate constant.

On the other hand the hydrolysis of isotactic copolymers of diphenylmethyl methacrylate with methacrylic acid of various composition in the pyridine–water medium cannot be described with the same one set of constants. As can be seen from Fig. 2 the samples form two different groups, not coinciding with each other according to the set of constants by which the kinetics of the process is described. From models of composition $P(A) > 0.06$ to the models of composition $P(A) \leq 0.55$ the reactivity of ester groups increases. One of the possible explanations is the change of the conformation of these polymeric reagents exactly in this range of composition. The viscosity measurements may confirm this supposition. It can be seen (Fig. 3) that in the range of $P(A) = 0.5-0.6$ the sharp increase of viscosity takes place, which evidently is related to the increase of coil dimensions due to electrostatic repulsion of hydrolysed groups in copolymer. In this less dense coil the availability of ester groups to be attacked by hydrolysing agents and anchimeric action of neighbouring units are favoured. All together it shows a very probable role of conformational effects in the reaction and provides the ground for the understanding of the mechanism of the process and of the chemical structure of the reaction product which is most important for the problems of chemical modification of polymers.

As has been mentioned above the existing theory permits us to predict the microstructure of the chain and the composition heterogeneity of products if one knows the rate constants $k_0$, $k_1$, $k_2$. The relationships obtained in$^4$ are realized as computer programs and the only thing one must know is the rate constants ratio.

Without going into a detailed analysis of the existing methods of evaluation of rate constants we shall point out that up to now one practical real method is an experimental study of the reaction's kinetics, simulation of it in computer with the aid of algorithm $A(t/k_0, k_1, k_2)$ and a search of $k_0, k_1, k_2$ set which is in the best agreement with the experimental kinetic curves. Using just this approach the chlorination rate constants and polymethacrylic esters hydrolysis rate constants were obtained. The stereochemical influences could be estimated using radiotracer techniques proposed by Harwood.$^{15}$ But there exists another approach which includes the microstructure analysis of the chain by NMR-spectroscopy, the simulation on the computer the concentration dependence of all possible triads of A and B units from product of the given composition and a search of such a ratio of these constants which is in the best agreement with the experiment. Firstly, these techniques for qualitative evaluation of rate constants based on the microstructure of the chain was made by Klesper,$^{16}$ but all the possibilities of this method have not been demonstrated.
Below are some results obtained in our laboratory which demonstrate quantitatively these possibilities. Six signals in the a-methyl region of PMAA spectra correspond to six possible triads of monomeric A and B units, which permits to determine experimentally the concentrations of all triads (Fig. 4). To calculate the individual rate constants according to the method of polymeric models the kinetics of syndiotactic PMMA hydrolysis were studied (Fig. 5). At the same time with the aid of the algorithm $T(A/k_0, k_1, k_2)$ the dependences of triad concentrations $AAA$, $AAB$, $BAB$, $BBA$, $ABA$, $BBB$ on the content of A units in the polymer for different ratios of constants were calculated. These calculated relationships were compared with the experimental data obtained from NMR-spectra. To get maximum information from NMR experiment the spectrum was simulated in computer as a sum of six Lorentz components, whose parameters were evaluated by a special computer program. Figure 6 shows the obtained data. A good coincidence can be seen of rate constants ratio found by NMR-technics and by kinetical approach. Both of them show a slight autoacceleration effect of hydrolysis influenced by neighbouring reacted groups. So, the developed technics of analysis of the usually poorly resolved NMR-spectra of polymeric samples permitted to fulfill the complete triad analysis of the microstructure of partially hydrolysed products and to get information about the mechanism of process.

Experimental data existing in literature about the individual rate constants of other polymeranalogous and intramolecular reactions with the neighbouring groups effect are given in Table 3. It is clearly seen that together with already discussed data in Table 2 this list comprises a score of systems and is the basis which is now built for developing of theory of macromolecular reactions. If one adds the information about the stereochimical configurational contribution to the reactivity of iso-, hetero- and syndio-units published in the works of Harwood, Sakurada, Smets, Morawetz, one should consider that today we have an essential volume of information which can be used to calculate the kinetics of the complicated process and the distribution of the different units along the chain.

No less important is the problem of composition heterogeneity of products at intermediate conversions. Using Monte Carlo simulation method we have shown earlier that even if the polymeranalogous or intramolecular reaction is proceeding without the influence of the reacted units the products are very heterogeneous from the viewpoint of composition. The degree of this nonhomogeneity is sharply increased when the autoaccel-
### Table 3

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Conditions</th>
<th>Rate constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quaternization of polyvinyl pyridine</td>
<td>25° tetramethylene sulphone</td>
<td>$k_0 = k_1 = 6.54 \times 10^{-4}$ mol$^{-1}$ min$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_2 = 2.10 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_0 : k_1 : k_2 = 1:1.0:32$ R. Fuoss</td>
</tr>
<tr>
<td>Chlorination of polyethylene</td>
<td>50° u.v.-radiation (230 lux) C$_6$H$_5$Cl</td>
<td>$k_0 = 6.1 \times 10^{-4}$ mol$^{-1}$ sec$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_1 = 2.1 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_2 = 0.48 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_0 : k_1 : k_2 = 1:0.35:0.08$ A. D. Litmanovich</td>
</tr>
<tr>
<td>Epoxidation of natural rubber</td>
<td>25° benzene kC$_6$H$_5$</td>
<td>$k_0 = 0.61$ mol$^{-1}$ min$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_1 = 6.6; k_2 = 4.0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_0 : k_1 : k_2 = 1:0.67:0.42$ J. Tutorski, J. Chodjaeva</td>
</tr>
<tr>
<td>Hydrolysis of syndiotactic copolymer MMA with MAA</td>
<td>145° 5 mmol KOH in 12 ml H$_2$O (250 mg of polymer)</td>
<td>$k_0 : k_1 : k_2 = 0.05:0.25$ E. Klesper</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrolysis of isotactic copolymer MMA with MAA</td>
<td>145° pyridine-water (95:5)</td>
<td>$k_0 = 5.3 \times 10^{-4}$ min$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_1 = 4.2 \times 10^{-4}$; $k_2 = 530 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_0 : k_1 : k_2 = 1:8:100$ N. Platé, A. Litmanovich</td>
</tr>
</tbody>
</table>

The reaction takes place and passes through maximum at intermediate (40–60%) degrees of conversion. To simplify the entire procedure we have developed a method to calculate the composition heterogeneity using relatively simple modified approximation of the 1st order Markov chain. The details of such approach are published and Figs. 7 and 8 show corresponding curves which go to say that they are practically identical with the results obtained by Monte Carlo simulation technics. It should be noted that an attempt to describe the composition heterogeneity with the normal nonmodified Markovian approximation of first order results in the sharp discrepancy with the data obtained by Monte Carlo method.

How correct is the Monte Carlo method itself? Rather good coincidence of results of the calculation of units distribution sequences obtained by Monte Carlo technics and by solution of exact but cumbersome kinetical equations (Fig. 9) shows that Monte Carlo method can be taken as an analog of exact solution not only to evaluate the distribution of units but the composition heterogeneity as well. It can be also seen that to put the length chain equal to 200 units and the number of such chains equal to 100 into computer is quite sufficient to get all the picture of the phenomena that can be extrapolated for longer chains and greater amounts of them thus being closer to reality.

A mathematically very simple modified first order Markovian approximation, the results of which do not differ from the results of Monte Carlo method can be recommended to calculate the composition heterogeneity of the system; this will also consume a very short computer time.

The validity of all these theoretical contraptions could be demonstrated by the comparison with the experiments on the quaternization of poly-4-vinylpyridine with benzyl chloride (60°, solvent-nitromethane : methanol 6:1, ten-fold excess of alkylating agent). First of all, the values of individual rate constants were found by kinetical method. This reaction proceeds with autoretardation as a result of the influence of alkylated pyridine units (Fig. 10).
Fig. 7. Ratio of dispersion of composition distribution to chain length \( (Dn/n) \) vs degree of conversion \( y = 1 - P(A) \) for \( k_0 : k_1 : k_2 = 1:5:100 \); broken curve—first-order Markovian approximation, solid curve—modified first-order Markovian approximation; points—Monte Carlo calculation at chain length 50(1), 100(2,4) and 200(3) units for 100(1—3) and 200(4) chains.

The values of constants were found as follows:

\[
\begin{align*}
-k_0 &= 5.8 \times 10^{-4} \text{ mol}^{-1} \text{ sec}^{-1} \\
k_1 &= 1.7 \times 10^{-4} \text{ mol}^{-1} \text{ sec}^{-1} \\
k_0 : k_1 : k_2 &= 1:3:3
\end{align*}
\]

Fig. 8. Composition distribution functions \( W(y) \) at \( y = 10\% \) (1), 30\% (2), 46\% (3), 71\% (4), 89\% (5), 25\% (6), 50\% (7), 77\% (8) for \( k_0 : k_1 : k_2 = 1:5:100 \) (a) and 1:50:99 (b); broken curves—first-order Markovian approximation; solid curves—modified first-order Markovian approximation; points—the Monte Carlo calculation.

Fig. 9. Characteristics of the sequence length distribution vs \( y = 1 - P(A) \); points—Monte Carlo calculation; curves—the exact solution for \( k_0 : k_1 : k_2 = 1:1:1 \) (a), 1:3:0.3 (b) and 1:5:0.3 (c).

Then, using the constants ratio obtained the composition heterogeneity of the products of partial quaternization of polyvinyl pyridine was calculated according to the above mentioned method. These results were compared with experimentally obtained data with fractionation by GP-chromatography. From the Fig. 11 it is seen that a good coincidence of the experimental and calculated data is observed for samples containing 48\% 85\% and 92\% of quaternized units. A certain deviation of experimental results toward a more narrow distribution for the sample having 92\% degree of conversion shows that apparently
some additional factors of retardation of the reaction start
to play some part in this range of conversion.

The interest for that kind of calculation is supported by
the fact that information can be received about the
composition heterogeneity and distribution of units in
cases where experimentally this information is not or
hardly available.

To predict the composition heterogeneity one can use
the diagrams in the way shown in Fig. 12, where knowing
the constants ratio one can estimate the dispersion of
composition heterogeneity for the product of any inter-
mediate degree of conversion.

The further steps in the theory of polymer-analogous
reactions should include the quantitative evaluation of the
stereochemical contribution to the reaction rate and trans-
ition to more concentrated solutions of polymeric reag-
ents where intermolecular forces can change the confor-
mation of coil as well as its reactivity.

Of special interest is the field of intermacromolecular
complex formation when one of the reagents is polyacid
and the other—polybase. There can be a situation when
one of the reagents is the donor and the other is the
acceptor as in the case for instance, of polyacrylic or
poly(meth)acrylic acids when they form a complex with
polyethylene glycol.

Figure 13 shows that when one mixes the water solu-
tions of high molecular samples of polyacids with
ethylene glycol oligomers the polycomplex is formed. The
viscosity and pH of the solution of the equimolar mixture
of polyacid and oligomer remain the same with the
increase of oligomer chain length up to the moment until
the oligomer chains reach a certain critical length; beyond
that point a sharp change in the above mentioned parame-
ters takes place. Such critical effects unanimously show
the cooperative character of macromolecule—
macromolecule interaction25

Several experiments made by Papisov, Kabanov and
others25 have shown that the stability of polycomplexes
depends on the fact whether or not condition of critical
length chain formation is fulfilled. The high selectivity of
the complex formation reaction when there is a choice
between several types of complexes can be illustrated by
kinetical curves of methacrylic acid polymerization in the
Problems of polymer modification

K

K

(a)

I

4.0

t.g MPEG

Fig. 13. Specific viscosity (1,2) and pH (1,2') for solutions of equimol mixtures PMAA—PEG (1,1') and PAA—PEG (2,2') vs molecular weight of PEG. Concentration of polyacids, 0.1 g/dl, mol.weight of PMAA—10^5 PAA—12 x 10.

presence of two types of macromolecules—polymethacrylic acid, the kinetical curve of methacrylic acid polymerization has a bend and at first a more stable complex with polyvinylpyrrolidone is formed. Only after that a weaker partner—polyethylene glycol enters into the reaction. It should be noted that these are the examples of the reactions which on the macromolecule—low molecular substance level do not show any interaction between reagents, as in the case of polyvinylpyrrolidone—isobutyrinic acid.

Thus the intermacromolecular reactions are highly selective and specific in the sense that even very small differences in the bonds' energy between complementary chains results in the selective bonding of given macromolecule \( P_i \) with one of the chains \( P_1, P_2, \) etc, which are present in the system at the same time. Such selectivity also results in the substitution of one macromolecule with another in polycomplex. This selectivity is related to the cooperative character of the bounding between macromolecules and it is proceeding very quickly with increase in the chain length. An analysis of the simple model of polycomplex formation reaction predicts a very strong dependence of oligomer bonding constant \( k \) on the oligomer length—\( \nu; k = k_i \) where \( k_i \) is the effective bonding constant of monomeric substance with polymer molecule matrix.

Another important peculiarity of polyreactions is the realization of nonrandom distribution of the components following the principle of "either everything or nothing". It means that when one mixes the components under homogeneous conditions only one part of macromolecules is totally involved in complex formation with oligomers while the other part is practically free. The reason for such disproportionation and such composition heterogeneity of the reaction products could be the conformational transitions of macromolecules in the course of polycomplex formation.

It is well known that this principle is widely observed in the reactions with biopolymers and their synthetic models.

The systems described above are in a certain sense examples of ladder-type polymers and the reactions macromolecule—macromolecule are the illustrations of a new method of synthesis of such polymers. It is possible to produce films and fibers using rather simple technology mixing of two macromolecular reagents in common solution when the polycomplex formed is not soluble in it. To explore further this new prominent field it is important to develop the theory of such equilibria and interactions which is not yet studied well. In connection with this I will say a few words about one more approach to the simulation of the process of interaction between two macromolecules using the TV-screen in combination with computer. We have realized the visual picture of two macromolecule interactions in the frame of mobility in planar cubic lattice model of the chains visible with the aid of display attachment to the computer. The dynamics of such a model can be easily algorithmized and one can observe and follow the conformational transitions of coil-globula type or of order-disorder type, the complex formation, the cross-linking and curing processes etc.

Figures 15 and 16 give some idea what it looks like, demonstrating stop-cadres for certain moments of such motion. The details of computer program and principal scheme of such simulation have been published recently. This approach appears to give an opportunity for a new look onto simulation of various chemical and physical processes with macromolecules as participants,
Fig. 14. (a) Kinetic curves of methacrylic acid polymerization without matrix (1) and with matrix; PEG (2), PVA (3), Polyvinyl pyrrolidone (4) and with two matrices together, PEG and PVPD (5, 8–10), PVA and PVPD (6), PVA and PEG (7) 50°; concentrations of MAA, PEG, PVPD and PVA 3.5 × 10⁻² mol/l, K₂S₂O₈ = 1.85 × 10⁻² mol/l; mol. weights of PVPD—40,000; PVA—75,000. PMMA—3 × 10⁴ g. PVPD: PEG : MAA = 0.1:0.1:1 (8), 0.1:2:1 (9), 0.1:0.5:1 (10), but in the presence of presynthesized PMAA in amount sufficient to involve all the PVPD in the complex.

and to get new information on the dynamics and structural aspects of these processes.

The neighbouring group effect plays a certain part in the reactions macromolecule–macromolecule too as was demonstrated above with the reaction of polyacid with polyethylene glycol. If both types of the particles are changed macromolecules some peculiar reactions can be observed. Thus, on studying the interaction of polyacrylic and polymethacrylic acid with polyethylene imine it was found that a polyelectrolyte complex with salt-like bounds is formed:²²

The fraction of salt-like bounds i.r.-spectroscopically estimated is 70% for polyacrylic acid and 60% for polymethacrylic acid.

If the complex is further thermotreated in films the interchain amide bounds are formed which lead to a ladder-type polymer. It is essential that only those functional groups participate in amide groups formation which
were earlier involved in the salt-like groups:

\[
\begin{align*}
\text{COOH}^+ & \quad \text{COO}^- \\
\text{NH}_3^+ & \quad \text{NH}_2^- \quad \text{NH}_2^- \\
\end{align*}
\]

The analysis shows that nonionized COOH and NH- groups in the chain are the places of structural defects. In the case of more rigid polymethacrylic acid chain the formation of one amide bond results in the abstinence of 3–4 neighbouring units at least from such reaction and this ladder polymer will have a lot of chemical defects. In the case of much more structurally complementary molecules of polyacrylic acid and polyethylene imine the long uniform sequences of amide bounds could be realized along the chains independently of the microstructure of the chains.

REFERENCES