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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 parafines, cycloparafines and polyethylene, acid and base hydrolysis of polymethyl methacrylate and polydiphenylmethyl 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 reactions of the macromolecule–macromolecule type are reviewed in the case when the intermacromolecular interaction leads to form polycomplexes and new polymeric products of ladder-type structure and the possibility to simulate this interaction with the aid of display attachment to the computer is demonstrated.

Chemical modification of polymers today is a field closely related with the problems of the reactivity of units and functional groups in the chains. The synthesis of special type polymeric materials and a great number of various organic reactions in which polymers are now involved as macromolecular reagents are impossible without a precise analysis of the particularities of chemical behaviour of their functional groups.

The reactivity of functional groups of macromolecules may be different from that of low molecular analogs.[1] These variations are connected with stereochemical influences, with the neighbouring groups effect and with conformational and supermolecular characteristics of polymeric reagents.[2,3] The review was made by the author at the International Symposium on Macromolecular Chemistry in Boston in 1971[4] and at the NATO Conference on Chemical Transformations of Polymers in Troy in 1973[5] 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 k_0, k_1, k_2 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[9] and on some new approaches developed in our laboratory at the University of Moscow and the Institute of Petrochemical Synthesis.[4–8]

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 $k_0 : k_1 : k_2$ for units, having 0, 1 and 2 of the already reacted neighbours.[8]

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[8] 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.[10]

In Table 1 the experimental data on the individual rate constants of chlorination of linear parafines, cycloparafines and polyethylene are shown.[11,12] 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 ($-CH_2-CH_2-CH_2-$) is changed. But the ratio of these constants for the methylene groups reaction in the center of such

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

	$k_0 \times 10^3$ l$^{1/2}$mol$^{1/2}$sec $CCl_4^{50°}$ or C_6H_5Cl	$k_0:k_1:k_2$
Cyclooctane	0·70	1:0·43:0·18
 C_8H_{16}		
Cyclododecane	0·82	1:0·43:0·17
 CH_2 $C_{12}H_{24}$		
Cyclooctacosane $C_{28}H_{56}$	1·0	1:0·43:0·18
Cetane $C_{16}H_{34}$	0·7	1:0·35:0·08
Polyethylene $(-CH_2-)_n$	1·85	1:0·38:0·11

triads and in the center of triads (–CH_2–CH_2–CHCl–) and (–CHCl–CH_2–CHCl–) remains practically constant. This means that conformational peculiarities of various cycles and linear parafine molecules do not play any essential role in the reactivity of the CH_2-groups in the chlorination. Moreover, these compounds starting with 8-membered parafinic ring can be used for the simulation of the reaction with polyethylene. The polymeric chain of parafinic type behaves in such reactions according to the well-known scheme of the inductive influence of substituents (chloromethylene groups) on the kinetics of the chlorination, which results in the autoretardation in the course of the reaction. Chemical behaviour of polyethylene in this case apparently is not infiuenced by the conformational and as well as other effects provided by the macrochain. So it looks like chlorination of polyethylene is an example of such reaction where extrapolation can be done to the polymer level of all available information about the reactions with small molecules.

The role of stereochemical and conformational factors in autoacceleration and autoretardation of the reactions with the macromolecular functional groups can be demonstrated on the example of the polymethacrylic esters hydrolysis. Here if the system under study can be kinetically described in the frame of the only set of the individual rate constants with the neighbouring group effect, and experimental data on the units distribution confirm the parameters calculated from the same set of rate constants a strong argument arises that states that a given macromolecular reaction can be treated in the light of the simple model for the practical usage to get the product of given structure and the given set of properties. The deviations in calculated and experimental parameters 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.

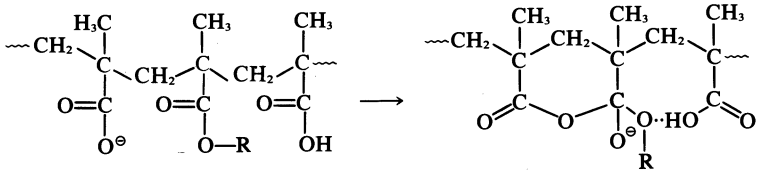
Klesper published some results in this field earlier[13] but they concerned only polymethyl methacrylate. To exclude the stereochemical influence on the kinetics the stereoregular samples and kinetical method of polymeric models was employed by us. To study the neighbouring group effect the stereoregular copolymers of MMA and MAA with the known and proved statistical bernullian, distribution of reacted and nonreacted groups were subjected to hydrolysis.[6,14]

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 carboxylate 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 carboxylate 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 syndiotactic one. At the same time the retardation effect for iso-models is not so markedly pronounced (1:0·4:0·4) as for syndiotactic ones (1:0·2:0·05). Passing to more dilute alkali solution the retardation effect in the hydrolysis of syndiotactic PMMA is not so pronounced as in the concentrated alkali solution.

Thus the results can already give some useful information about the mechanism and kinetics of the complicated process of polymeranalogous reaction with the reactivity of the units changing with conversion.

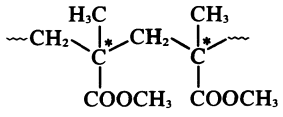
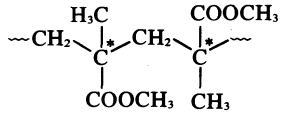
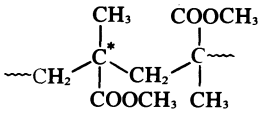
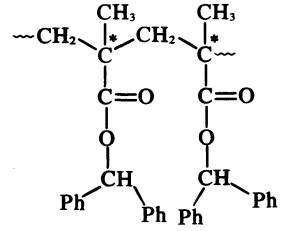
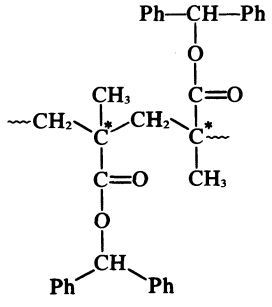
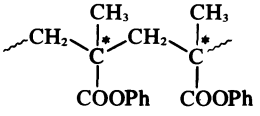
The hydrolysis of stereoregular methacrylic polymers in the pyridine–water medium is taking place with acceleration provided by neighbouring groups. Tenfold increase in the rate when the carboxyl groups appear in the neighbourhood of the esters groups can be explained by the anchimeric action according 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 simultaneous interaction of one dissociated and one nondissociated 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 comparison 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°

Polymer	Stereoregularity	Medium	$k \times 10^4$ min k_0	k_1	k_2	$k_0:k_1:k_2$
Polymethyl methacrylate 	isotactic	0·2 M KOH	90	35	35	1:0·4:0·4
Polymethyl methacrylate 	syndiotactic	0·2 M KOH (0·05 M KOH)	5·8 (1·9)	1·2 (1·3)	0·3 (1·3)	1:0·2:0·05 1:0·7:0·7
Polymethyl methacrylate 	isotactic	pyridine–water 95:5	5·3	42	530	1:8:100
Polydiphenyl-methyl methacrylate 	isotactic	pyridine–water 95:5	0·3	7	33	1:20:100
Polydiphenyl-methyl methacrylate 	syndiotactic	pyridine–water 95:5	0·5	0·5	0·5	1:1:1
Polyphenyl methacrylate 	isotactic	pyridine–water	6	240	6000	1:40:1000

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 polydiphenyl-methyl 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 can not be described with the same one set of constants.[14] As can be seen from Fig. 2 the samples form two different

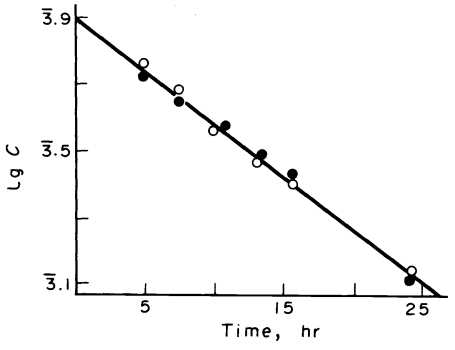


Fig. 1. Kinetics of acidic hydrolysis of polydiphenylmethyl methacrylate at 66°; ●—syndiotactic; ○—isotactic polymer.

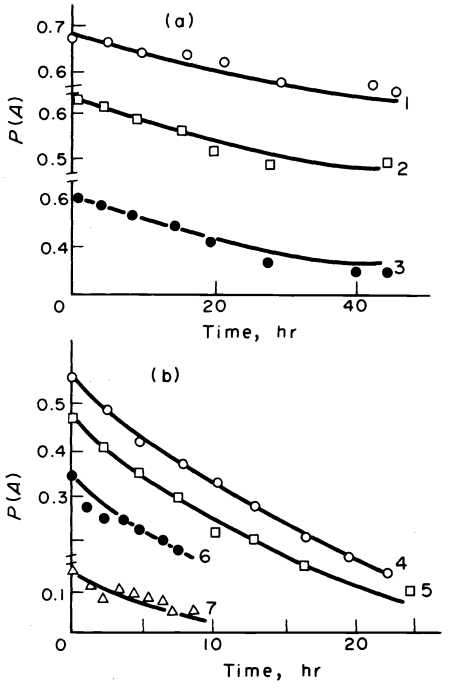


Fig. 2. Kinetics of hydrolysis of isotactic copolymers of diphenylmethyl methacrylate and methacrylic acid with the initial content of ester groups 68(1), 63(2), 60(3), 55(4), 48(5), 38(6) and 13(7) molar % at 145° in pyridine–water (95:5 in volume). Points—experimental data, curves—calculated for $k_2:k_1:k_0$ ratios 1:0·1:0·01(a) and 1:0·2:0·01(b) when $k_2 = 20 \times 10^{-4}$ min^{-1}(a) and 33×10^{-4} min^{-1}(b).

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 $P(A) \geq 0{\cdot}06$ to the models of composition $P(A) \leq 0{\cdot}55$ 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 $P(A) = 0{\cdot}5$–$0{\cdot}6$ 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[4,7,8] 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.[4–6] Using just this approach the chlorination rate constants and polymethacrylic esters hydrolysis rate constants were obtained. The stereochemical influences could be estimated using radiotracer technics 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.

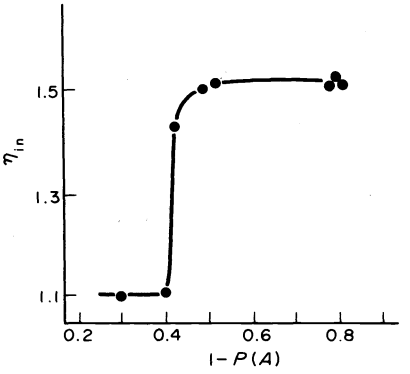


Fig. 3. Intrinsic viscosity data for 1% solutions of isotactic copolymers of DPhMMA–MAA in pyridine–water (95:5) at 60° vs composition.

Below are some results obtained in our laboratory which demonstrate quantitatively these possibilities. Six signals in the α-methyl region of PMAA spectrum correspond to six possible triads of monomeric *A* and *B* units,[17] 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

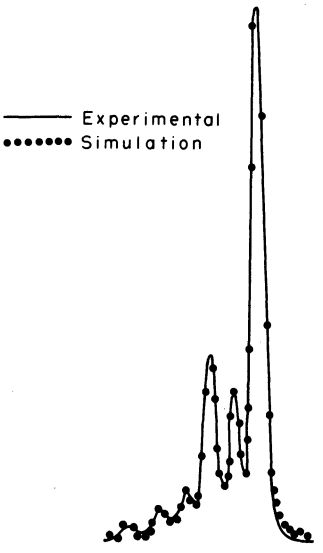


Fig. 4. Experimental and simulated NMR-spectrum of α-methyl protons of the product of partial hydrolysis of syndiotactic PMMA having 75% MMA units.

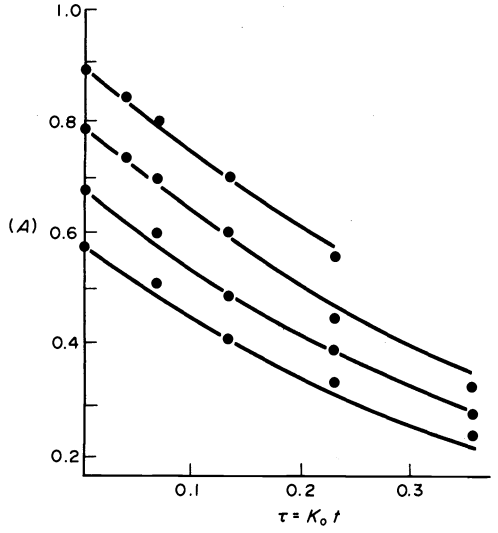


Fig. 5. Dependence of the unreacted units (A) fraction in hydrolysis product of syndiotactic PMMA vs time. Points—experimental data, curves—calculation for $k_0 = 1{\cdot}1 \times 10^{-4}$ min^{-1}, $k_1 = 2{\cdot}8 \times 10^{-4}$ min^{-1}, $k_2 = 3{\cdot}7 \times 10^{-4}$ min^{-1}.

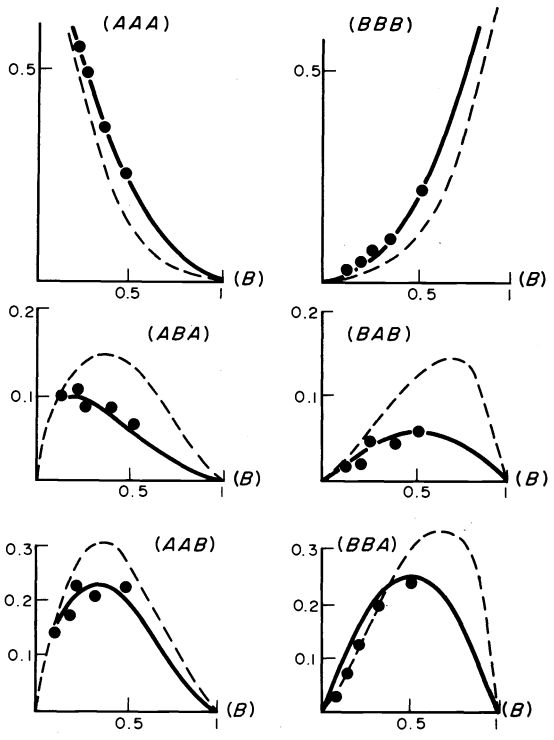


Fig. 6. Dependence of the various triads of the A and B units in the product of hydrolysis of syndiotactic PMMA containing 89% of the ester groups, vs conversion. Points—experimental data, curves—calculation for $k_0 : k_1 : k_2 = 1:3:5$ and $k_0 = k_1 = k_2$ (dotted curves).

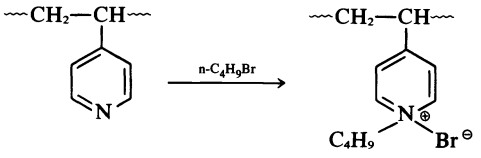
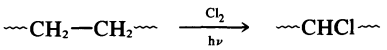
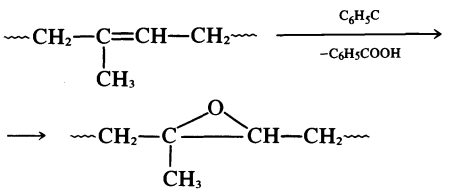
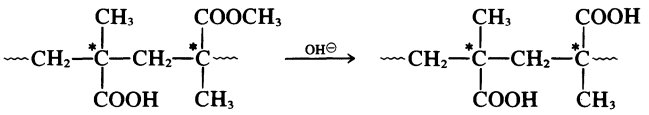
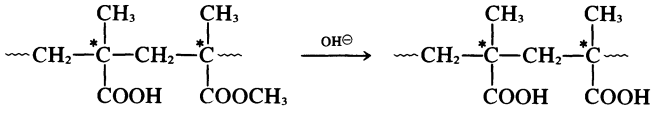
evaluated by a special computer program.[18–19] Figure 6 shows the obtained data. A good coincidence can be seen of rate constants ratio found by NMR-technics and by kinetical approach. Both of them show a slight autoacceleration effect of hydrolysis influenced by neighbouring reacted groups. So, the 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.[6]

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 stereochemical 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.[4,20–22] The degree of this nonhomogeneity is sharply increased when the autoaccel-

Table 3

Reaction	Conditions	Rate constants
Quaternization of polyvinyl pyridine 	25° tetramethylene sulphone	$k_0 = k_1 = 6{\cdot}54 \times 10^{-4}$ l mol^{-1} min^{-1} $k_2 = 2{\cdot}10 \times 10^{-4}$ $k_0 : k_1 : k_2 = 1 : 1 : 0{\cdot}32$ R. Fuoss
Chlorination of polyethylene 	50° u.v.-radiation (230 lux) C_6H_5Cl	$k_0 = 6{\cdot}1 \times 10^{-4}$ l mol^{-1} sec^{-1} $k_1 = 2{\cdot}1 \times 10^{-4}$; $k_2 = 0{\cdot}48 \times 10^{-4}$ $k_0 : k_1 : k_2 = 1 : 0{\cdot}35 : 0{\cdot}08$ A. D. Litmanovich
Epoxidation of natural rubber 	25° benzene	$k_0 = -0{\cdot}61$ l mol^{-1} min^{-1} $k_1 = 6{\cdot}4$; $k_2 = 4{\cdot}0$ $k_0 : k_1 : k_2 = 1 : 0{\cdot}67 : 0{\cdot}42$ J. Tutorski J. Chodjaeva
Hydrolysis of syndiotactic copolymer MMA with MAA 	145° 5 mmol KOH in 12 ml H_2O (250 mg of polymer)	$k_0 : k_1 : k_2 = 0 : 0{\cdot}5 : 0{\cdot}25$ E. Klesper
Hydrolysis of isotactic copolymer MMA with MAA 	145° pyridine–water (95:5)	$k_0 = 5{\cdot}3 \times 10^{-4}$ min^{-1} $k_1 = 4{\cdot}2 \times 10^{-4}$; $k_2 = 530 \times 10^{-4}$ $k_0 : k_1 : k_2 = 1 : 8 : 100$ N. Platé A. Litmanovich

eration of 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[23] and Figs. 7 and 8 show corresponding curves which goes 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, tenfold excess of alkylating agent).[23-24] 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).

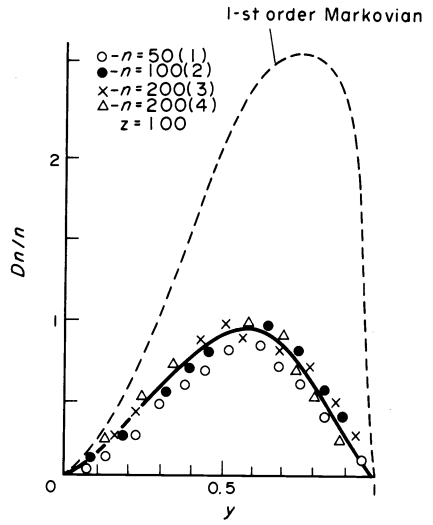
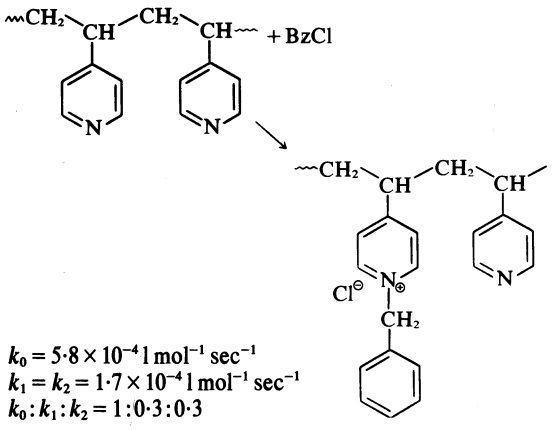


Fig. 7. Ratio of dispersion of composition distribution to chain length (Dn/n) vs degree of conversion $y = 1 - P(A)$ for $k_0 : k_1 : k_2 = 1 : 5 : 100$; broken curve—first-order Markovian approximation, solid curve—modified first-order Markovian approximation; points—Monte Carlo calculation at chain 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:



$k_0 = 5{\cdot}8 \times 10^{-4}$ l mol^{-1} sec^{-1}
$k_1 = k_2 = 1{\cdot}7 \times 10^{-4}$ l mol^{-1} sec^{-1}
$k_0 : k_1 : k_2 = 1 : 0{\cdot}3 : 0{\cdot}3$

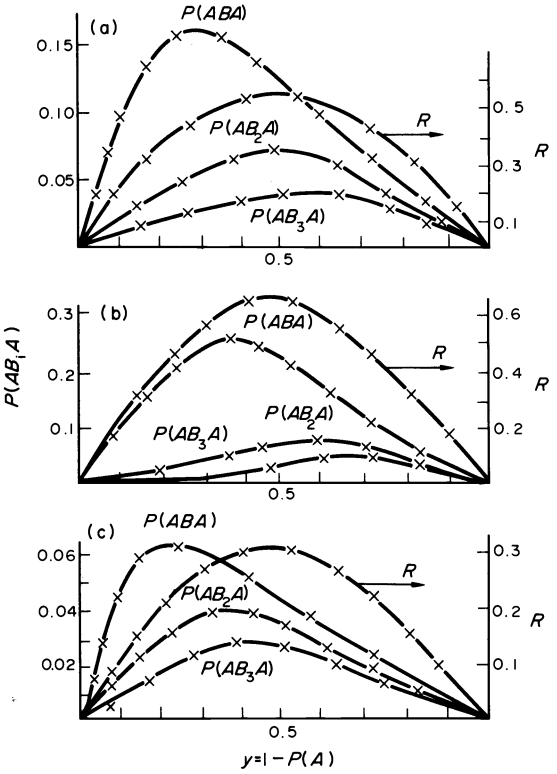


Fig. 9. Characteristics of the sequence length distribution vs $y = 1 - P(A)$; points—Monte Carlo calculation; curves—the exact solution for $k_0 : k_1 : k_2 = 1 : 1 : 1$(a), $1 : 0{\cdot}3 : 0{\cdot}3$(b) and $1 : 5 : 5$(c).

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% 85·5 and 92·5% of quaternized units. A certain deviation of experimental results toward a more narrow distribution for the sample having 92·5% degree of conversion shows that apparently

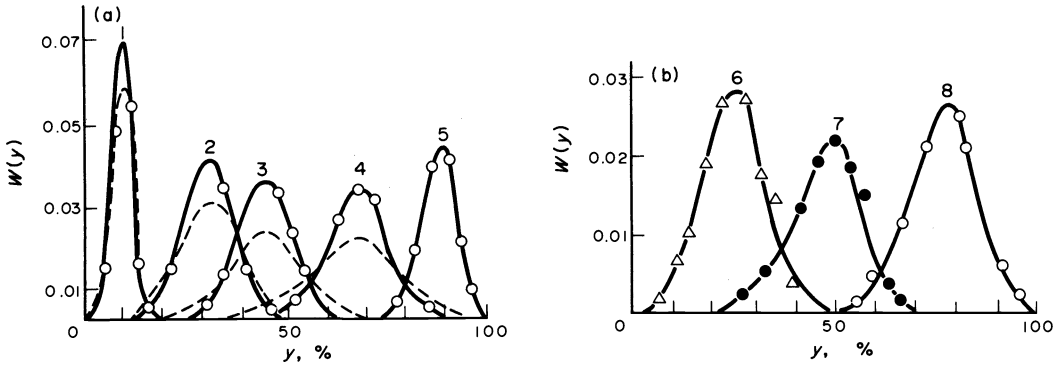


Fig. 8. Composition distribution functions $W(y)$ at y = 10% (1), 30% (2), 46% (3), 71% (4), 89% (5), 25% (6), 50% (7), 77% (8) for $k_0 : k_1 : k_2 = 1 : 5 : 100$ (a) and 1:50:99 (b); broken curves—first-order Markovian approximation; solid curves—modified first-order Markovian approximation; points—the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

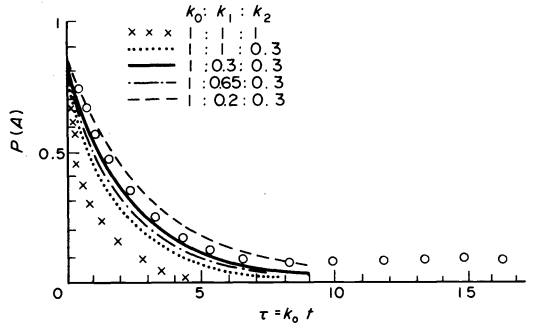


Fig. 10. Kinetics of the quaternization of poly-4-vinylpyridine; $P(A)$, fraction of unreacted groups vs $\tau = k_0 t$; points—experimental data; curves—calculation for $k_0 : k_1 : k_2 = 1:1:1(1)$, $1:1:0{\cdot}3(2)$, $1:0{\cdot}3:0{\cdot}3(3)$, $1:0{\cdot}65:0{\cdot}3(4)$, $1:0{\cdot}2:0{\cdot}3(5)$.

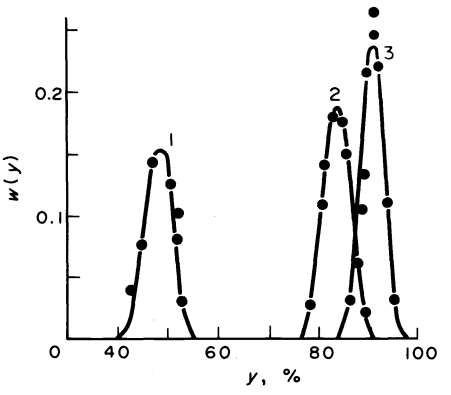


Fig. 11. Composition distribution for products of reaction of quaternization of poly-4-vinylpyridine at average degree of conversion $y = 48(1)$, $85{\cdot}5(2)$ and $92{\cdot}5\%(3)$; points—experimental data; curves—calculation for $k_0 : k_1 : k_2 = 1:0{\cdot}3:0{\cdot}3$.

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.

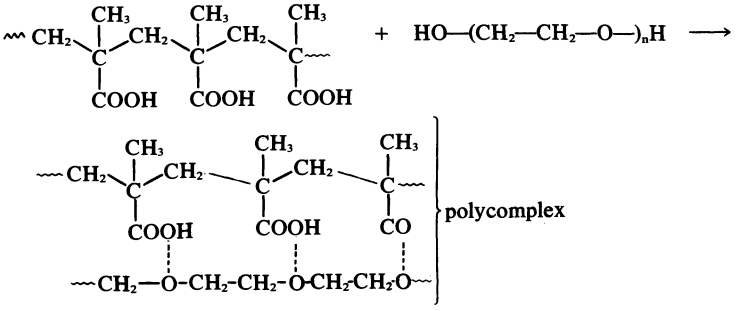
To predict the composition heterogeneity one can use the diagrams in the way shown in Fig. 12, where knowing the constants ratio one can estimate the dispersion of composition heterogeneity for the product of any intermediate degree of conversion.

The further steps in the theory of polymeranalogous reactions should include the quantitative evaluation of the stereochemical contribution to the reaction rate and transition to more concentrated solutions of polymeric reagents where intermolecular forces can change the conformation of coil as well as its reactivity.

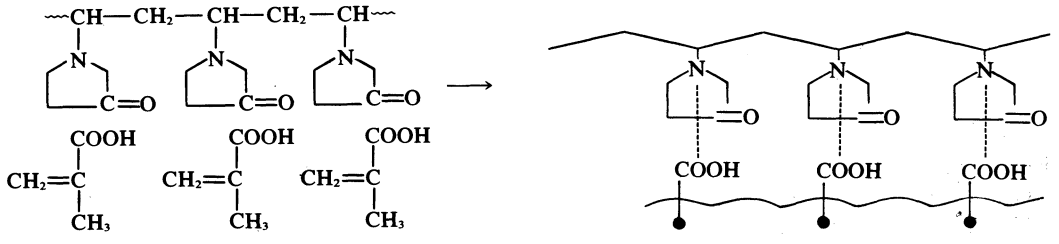
Of special interest is the field of intermacromolecular reactions—in fact a new chapter in the chemical transformations and modification of polymers. Here I would like to point out some new possibilities.

On studying the reaction between two macromolecules it is important to understand and to know if there is any "polymeric" effect and if so then how big it is. One of the examples of intermacromolecular reactions is the polymer 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 polymethacrylic acids when they form a complex with polyethylene glycol.

Figure 13 shows that when one mixes the water solutions 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 parameters takes place. Such critical effects unanimously show the cooperative character of macromolecule–macromolecule interaction[25]



Several experiments made by Papisov, Kabanov and others[25] have shown that the stability of polycomplexes depends on the fact whether or not condition of critical length chain formation is fullfilled. 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



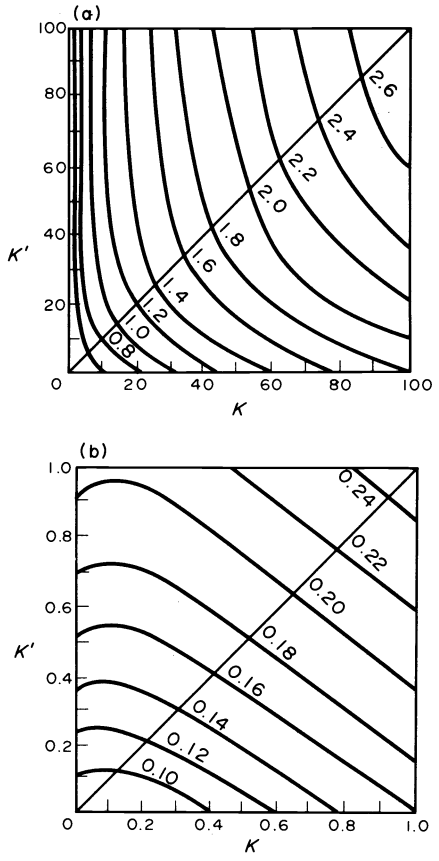


Fig. 12. Dn/n dependence on $k_0 : k_1 : k_2$ for the accelerating effect (a) $k_1 \geq k_0$, $k_2 \geq k_0$, and for the retarding effect (b) $k_1 \leq k_0$, $k_2 \leq k_0$, at 50% conversion ($k = k_1/k_0$, $k' = k_2/k_0$).

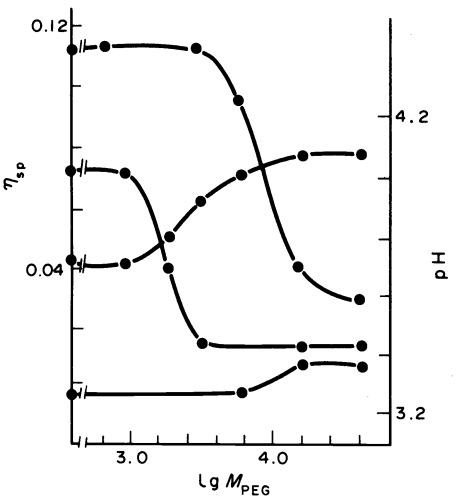


Fig. 13. Specific viscosity (1,2) and pH (1′,2′) for solutions of equimol mixtures PMAA–PEG (1,1′) and PAA–PEG (2,2′) vs molecular weight of PEG. Concentration of polyacids, 0·1 g/dl, mol.weight of PMAA–10^5 PAA–$1{\cdot}2 \times 10^5$.

presence of two types of macromolecules—polyvinylpyrrolidone and polyethylene glycol with which the formation of polycomplex (Fig. 14) is possible.

If there is a very small amount of polyvinylpyrrolidone in the reaction system together with polyethylene glycol, for instance, the amount sufficient to bind only 10% of 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 polyvinylpyrolidone–isobutyric 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_1 with one of the chains P_2, P_3 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.[26] 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_ν on the oligomer length—ν; $k_\nu = k_1^\nu$ where k_1 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.[27]

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.[28] 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.[28] This approach appears to give an opportunity for a new look onto simulation of various chemical and physical processes with macromolecules as participants

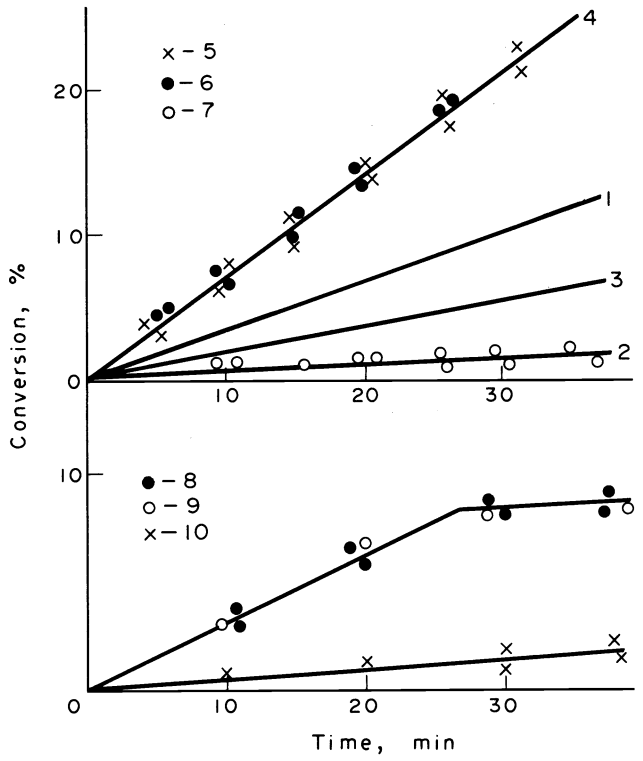


Fig. 14. (a) Kinetic curves of methacrylic acid polymerization without matrix (1) and with matrix; PEG (2), PVA (3), Polyvinyl pyrrolidone (4) and with two matrixes together, PEG and PVPD (5,8–10), PVA and PVPD (6), PVA and PEG (7) 50°, concentrations of MAA, PEG, PVPD and PVA $3{\cdot}5 \times 10^{-2}$ mol/l, $K_2S_2O_8 = 1{\cdot}85 \times 10^{-4}$ mol/l; mol.weights of PVPD–40,000; PVA–75,000. PMMA–3×10^5. 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.

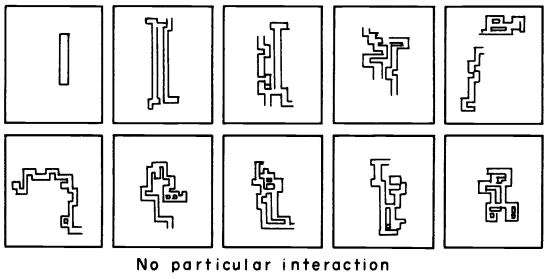


Fig. 15. Order–disorder transition in the system of the two interacting chains T–O (a), 100(b), 500(c), 1000(d), 2000(e), 5000(f), 10,000(g), 20,000(h), 30,000(i), 50,000(j).

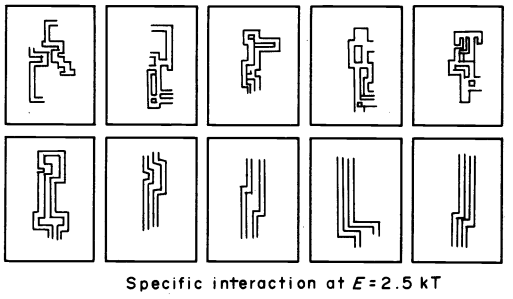
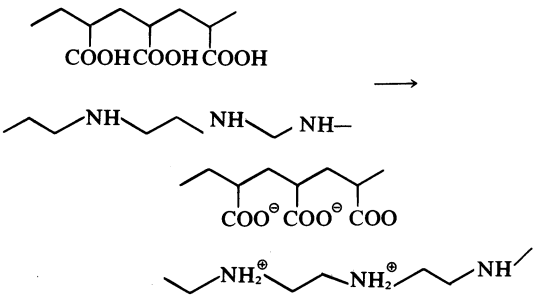


Fig. 16. Ordering of the two specifically interacting chains at $E = 2{\cdot}5kt$. T = 0(a), 800(b), 10,000(c), 20,000(d), 40,000(e), 45,000(f), 50,000(g), 55,000(h), 60,000(i).

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

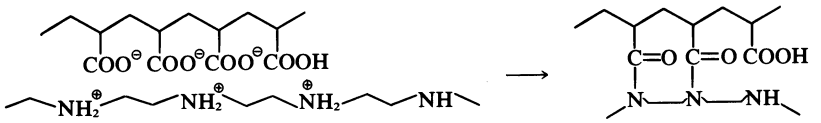
The neighbouring group effect plays a certain part in the reactions macromolecule–macromolecule too as was demonstrated above with the reaction of polyacid with polyethylene glycol. If both types of the particles are changed macromolecules some peculiar reactions can be observed. Thus, on studying the 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:



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.

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