

Configurational statistics of copolymers prepared by complex-radical polymerization

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Radical copolymerization is considered theoretically taking into account the effect of complexing on the configurational statistics of macromolecules formed. A kinetic model has been developed that considers, apart from the ordinary addition of single monomer units to a propagating chain, the possible addition of monomer unit pairs along with a complexing agent in the form of a ternary complex. Within the framework of this model, the problem of calculating the probabilities of formation of any sequences of monomer units (taking into account their microtacticity) in a macromolecule has been rigorously solved as well as the problem of finding the composition distribution of the copolymer formed. It has been shown that this distribution is described by a conventional Gauss law and the appropriate parameters are given. Possible generalizations of the suggested approach are indicated.

Keywords Copolymer; complex-radical mechanism of polymerization; monomer units distribution; composition distribution; Markov chains; stereoconfigurations

INTRODUCTION

The problem of the participation of molecular complexes of monomers in the propagation reaction during radical polymerization is of principal importance for understanding the mechanism of the reactions involved. The use of the effects induced by complexing agents in many cases permits control of the rates of polymerization and the structure of the resulting polymers^{1,2}. In particular, interesting possibilities are found in copolymerization, when, by varying the concentrations of the complexing agents, one can obtain regular alternating copolymers instead of statistical ones.

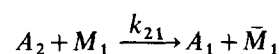
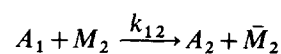
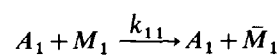
Until recently, the participation of molecular complexes in radical copolymerization was either postulated from their presence in the reaction mixture³⁻⁵, or at best it was determined by analysis of the kinetic features of the polymerization^{6,7} or of the average composition of the copolymer^{8,9}. It is believed that the participation of molecular complexes in a polymerization affects the configurational structure of the resulting macromolecules, including the distribution of monomer units and the stereochemical structure of copolymer chains. If the appropriate quantitative theory describing the relation between the parameters of the polymer configurational structure and the kinetic mechanism of the chain propagation reaction is available, fine details of the mechanism and the kinetics of chain propagation can be found using data on chain microstructure (e.g. obtained by n.m.r.).

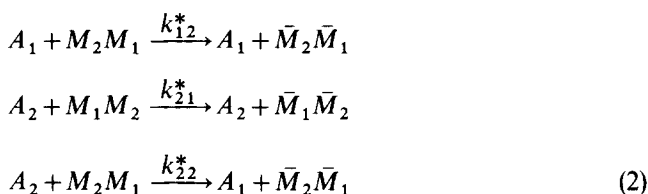
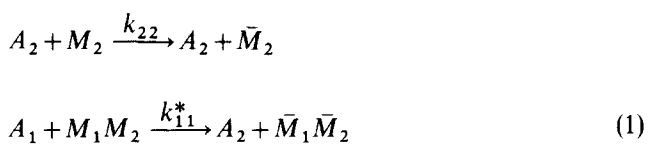
In addition, such a theory could be useful in choosing the conditions of synthesis of copolymers with certain optimal properties. It has been shown, for example⁹, that glass transition temperatures of equimolar statistical and alternating copolymers of a given pair of monomers can differ considerably. On the other hand, a simple correlation has been found experimentally¹⁰, permitting the determination of the glass transition temperature, T_g , of a random copolymer from the known glass transition

temperatures T_{11} and T_{22} of the homopolymers M_1 and M_2 , that of the alternating copolymer T_{12} , and the fractions of diads $P(\bar{M}_1\bar{M}_1)$, $P(\bar{M}_2\bar{M}_2)$ and $P(\bar{M}_1\bar{M}_2)$. If there were a theory for calculation of the fractions of diads, it would be possible to relate the conditions of copolymer synthesis to its T_g .

A theory of this kind has been developed, rigorously substantiated and reliably supported by experiments for a variety of classical radical copolymerization systems, when, in the course of propagation, monomer units add to macromolecules only one-by-one. It has been shown that any statistical characteristics of the resulting copolymers can be calculated in a routine way by means of a well developed mathematical procedure based on Markov chain theory^{11,12}. Here, the fraction of macromolecules with a given sequence of units in a copolymer equals the probability of formation of the appropriate Markov chain. The parameters of the latter are simply connected with the relative activities and with the composition of a monomer mixture. The above-mentioned Markov chain statistics will be of the first, second, etc., order depending on the kinetic model (ultimate, penultimate, etc.) describing a given system.

The purpose of the first section of this paper is a similar statistical description of the products of complex-radical copolymerization, when as well as the single addition of monomers to the chain, their addition to its end in pairs is possible in the form of a molecular complex M_1M_2 . In this case the kinetic scheme of a propagation reaction can be represented as:





where A_i is an active centre corresponding to a free valence of the polymer radical terminating with a monomer unit M_i . The dependence of the instantaneous composition of the copolymer^{13,14} and of the fractions of different triads and blocks of monomer units in macromolecules¹⁵ on the concentrations of monomers in the system has already been calculated within the framework of the kinetic scheme of reactions (1) and (2). The probability approaches¹⁵ for calculations of the above-mentioned statistical characteristics have a limited importance compared to the general statistical method suggested in this paper. Using this method, complete calculations of the sequence and compositional inhomogeneities of the copolymer have been performed. The second section of the paper gives a detailed description of the configurational statistics of monomer units in the copolymer taking into account their mutual stereoconfigurations, i.e. tacticity of the polymer chain.

The analysis of the kinetic equations of the 'classical' copolymerization, described by reactions (1), has shown¹² that the distribution of the units \bar{M}_1 and \bar{M}_2 in the products is characterized by Markov statistics. A similar analysis of a copolymerization with simultaneous reactions (1) and (2) leads to the conclusion that the distribution of the units \bar{M}_1 and \bar{M}_2 in the polymer chains cannot be described by means of a Markov chain of any finite order. Hence, we are dealing with a non-Markovian copolymer. The general theory for this case does not exist except for various simple relations between probabilities of some selected sequences, following from the conditions of statistical stability of a random walk along the copolymer chains¹⁶. These conditions practically always hold, except for oligomers, and therefore are also used here.

CALCULATION OF UNIT DISTRIBUTION AND COMPOSITION INHOMOGENEITY OF THE COPOLYMER

The general problem of the calculation of sequence distributions in a copolymer is reduced to the construction of an algorithm for calculating the probability of a random selected sequence U_k , consisting of any number, k , of monomer units. For non-Markovian copolymers, this problem has been solved only for the products of polymer-analogue reactions^{17,12}. Here we give its solution for copolymers obtained by a complex-radical mechanism by means of some auxiliary Markov chain with four states S_1, S_2, S_3 and S_4 . To introduce these states, we distinguish monomer units as 'coloured' black and white. This conditional colouring is a demonstrative

procedure permitting us, while considering sequences of monomer units, to distinguish besides their type the manner of their adding to a polymer chain. The unit \bar{M}_i is black if the corresponding monomer M_i is added to the radical as the first monomer of the complex. In other cases when the corresponding monomer M_i is either added alone or as the second monomer of the complex, the monomer unit \bar{M}_i is white. Now the states of the monomer unit are characterized by two features: its type ($i=1,2$) and its colour (white or black). For example, we consider that the unit is in the state S_1 if it is of the first type and white, i.e. \bar{M}_1^w . All other states S_i are defined similarly:

$$S_1 \sim \bar{M}_1^w, \quad S_2 \sim \bar{M}_1^b, \quad S_3 \sim \bar{M}_2^w, \quad S_4 \sim \bar{M}_2^b \quad (3)$$

In a real polymer chain, each monomer unit has no memory about the manner of its adding to a macromolecule. It is characterized only by its type, and from this point of view is uncoloured. Therefore, experimentally determined characteristics of the copolymer microstructure are described by a sequence of uncoloured units. Hence, it is clear that each state \bar{M}_i of the sequence of 'uncoloured' units is a combination of the corresponding pair of states of the sequence of the 'coloured' units, i.e. $\bar{M}_1 = S_1 + S_2, \bar{M}_2 = S_3 + S_4$.

If a method similar to that of Kuchanov¹² is applied to prove the Markovian character of the statistics of the classical copolymerization products, it is possible, proceeding from the kinetic equations of the scheme (1)–(2), to prove rigorously that a sequence of 'coloured' units in macromolecules forms a Markov chain with the states S_1, S_2, S_3, S_4 and a transition matrix:

$$Q = \begin{pmatrix} v_{11} & v_{12} & v_{13} & v_{14} \\ 0 & 0 & 1 & 0 \\ v_{31} & v_{32} & v_{33} & v_{34} \\ 1 & 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} Q_{11} & Q_{12} \\ Q_{21} & Q_{22} \end{pmatrix} \quad (4)$$

The non-zero and non-unit elements of this matrix:

$$\begin{aligned} v_{11} &= M_1 k_{11} \Delta_1^{-1}, & v_{12} &= M_{12} k_{11}^* \Delta_1^{-1}, & v_{13} &= M_2 k_{12} \Delta_1^{-1}, \\ v_{14} &= M_{12} k_{12}^* \Delta_1^{-1}, & v_{31} &= M_1 k_{21} \Delta_2^{-1}, & v_{32} &= M_{12} k_{21}^* \Delta_2^{-1}, \\ v_{33} &= M_2 k_{22} \Delta_2^{-1}, & v_{34} &= M_{12} k_{22}^* \Delta_2^{-1}, \\ \Delta_1 &= M_1 k_{11} + M_2 k_{12} + M_{12} (k_{11}^* + k_{12}^*), \\ \Delta_2 &= M_1 k_{21} + M_2 k_{22} + M_{12} (k_{21}^* + k_{22}^*) \end{aligned} \quad (5)$$

are functions of two dimensionless variables characterizing the composition of a ternary mixture (two monomers and their complex with concentrations M_1, M_2 and M_{12} , respectively). These functions depend on six dimensionless kinetic parameters of relative reactivities. They can be the following:

$$\begin{aligned} r_{12} &= \frac{k_{11}}{k_{12}}, & r_{21} &= \frac{k_{22}}{k_{21}}, & r_{11}^* &= \frac{k_{11}}{k_{11}^*}, \\ r_{12}^* &= \frac{k_{11}}{k_{12}^*}, & r_{21}^* &= \frac{k_{22}}{k_{21}^*}, & r_{22}^* &= \frac{k_{22}}{k_{22}^*} \end{aligned} \quad (6)$$

It should be emphasized once more that a sequence of 'uncoloured' units \bar{M}_1 and \bar{M}_2 is not a Markovian

random process, but its statistical characteristics can be expressed in terms of transition probabilities (5) of an auxiliary Markov chain. For example, the components π_i ($i=1, 2$) (equal to molar fractions of the i th type units in a copolymer formed just at a given instant) of the vector π of instantaneous copolymer composition, according to (3), are simply connected with the components $\tilde{\pi}_i$ ($i=1, 2, 3, 4$) of the limiting vector of this chain:

$$\pi_1 = \tilde{\pi}_1 + \tilde{\pi}_2, \quad \pi_2 = \tilde{\pi}_3 + \tilde{\pi}_4 \quad (7)$$

The routine calculation^{11,12,18} of the vector π of the matrix (4) gives the values of its components:

$$\tilde{\pi}_1 = (v_{31} + v_{34})\Delta^{-1}, \quad \tilde{\pi}_2 = [v_{13}v_{32} + v_{12}(1 - v_{33})]\Delta^{-1},$$

$$\tilde{\pi}_3 = (v_{12} + v_{13})\Delta^{-1}, \quad \tilde{\pi}_4 = [v_{31}v_{14} + v_{34}(1 - v_{11})]\Delta^{-1},$$

$$\Delta = v_{13}(1 + v_{32}) + v_{31}(1 + v_{14}) + v_{12}(2 - v_{33}) + v_{34}(2 - v_{11}) \quad (8)$$

Substitution of the latter into (7), taking into account (5) and (6), leads to a known expression^{13,14} relating the instantaneous copolymer composition to the concentrations of the monomers and of the complex. The latter can be expressed in terms of M_i and the equilibrium constant k by

$$M_{12} = kM_1M_2 \quad (9)$$

Substitution of (9) into (5) leads to expressions for v_{ij} . The latter are determined not only by the relative content of monomers in the mixture, $\theta = M_2/M_1$, but also by their absolute concentrations. Therefore, for the complex-radical copolymerization, in contrast to the classical one, the copolymer composition depends also on the values of these absolute concentrations. The probabilities $P\{\bar{M}_i\bar{M}_j\}$ of all diads $\bar{M}_i\bar{M}_j$ can be written with the known values of $\tilde{\pi}_i$ (see equation (8)):

$$P\{\bar{M}_1\bar{M}_1\} = \tilde{\pi}_1(v_{11} + v_{12}),$$

$$P\{\bar{M}_1\bar{M}_2\} = \tilde{\pi}_1(v_{13} + v_{14}) + \tilde{\pi}_2,$$

$$P\{\bar{M}_2\bar{M}_1\} = \tilde{\pi}_3(v_{31} + v_{32}) + \tilde{\pi}_4,$$

$$P\{\bar{M}_2\bar{M}_2\} = \tilde{\pi}_3(v_{33} + v_{34}) \quad (10)$$

It is easy to verify that $P\{\bar{M}_1\bar{M}_2\} = P\{\bar{M}_2\bar{M}_1\}$ as it should be due to the statistical stationarity of a random process. Formulae (10) are derived from simple statistical considerations. Thus, the diad $\bar{M}_1\bar{M}_1$ is obtained if, in the process of an imaginary movement along the copolymer chain, the first unit is in the state S_1 (with probability $\tilde{\pi}_1$) and at the next step a transition from S_1 to the states S_1 or S_2 occurs (with probabilities v_{11} and v_{12} , respectively). The diad $\bar{M}_1\bar{M}_2$ can be obtained in three ways: either when the first unit is in state S_1 and the transition proceeds into S_3 or S_4 , or when the first unit is in state S_2 , when the next unit for certain is \bar{M}_2 . The other two relations (10) are derived in a similar way.

Let us now give the general algorithm for the calculation of the probability, $P\{U_n\}$, of any given kind of sequence:

$$U_n = \bar{M}_{i_1}\bar{M}_{i_2} \dots \bar{M}_{i_n}$$

consisting of n monomer units. This sequence is unambiguously defined by the n -dimensional vector i , its components being integers 1 or 2. The sequence of states

$$V_n = S_{j_1}S_{j_2} \dots S_{j_n}$$

can be defined similarly by means of the vector j , with the integer components from 1 to 4. The sequence of 'uncoloured' units can be obtained from a set of sequences of 'coloured' units by their combination, according to conditions (3). Thus, $P\{U_n\}$ is, evidently, equal to the sum of the probabilities of all sequences V_n having S_1 and S_2 instead of \bar{M}_1 in the appropriate places and S_3 and S_4 instead of \bar{M}_2 . Hence

$$P\{\bar{M}_{i_1}\bar{M}_{i_2} \dots \bar{M}_{i_n}\} = \sum P\{S_{j_1}S_{j_2} \dots S_{j_n}\} \quad (11)$$

where the summation is carried out using the vectors j with each k th component being 1 and 2 in the case $i_k = 1$ or 3 and 4 in the case $i_k = 2$. Since the sequence of coloured units forms a Markov chain we have:

$$P\{S_{j_1}S_{j_2} \dots S_{j_n}\} = \tilde{\pi}_{j_1}v_{j_1j_2}v_{j_2j_3} \dots v_{j_{n-1}j_n} \quad (12)$$

and therefore formula (11) can be written in the matrix form

$$P\{\bar{M}_{i_1}\bar{M}_{i_2} \dots \bar{M}_{i_n}\} = \tilde{\pi}^{(i_1)}\mathbf{Q}_{i_1i_2}\mathbf{Q}_{i_2i_3} \dots \mathbf{Q}_{i_{n-1}i_n}\mathbf{1}^T \quad (13)$$

where

$$\tilde{\pi}^{(1)} = \{\tilde{\pi}_1, \tilde{\pi}_2\}, \quad \tilde{\pi}^{(2)} = \{\tilde{\pi}_3, \tilde{\pi}_4\}, \quad \mathbf{1} = \{1, 1\}$$

are two-element row vectors, $\mathbf{1}^T$ is the transpose of $\mathbf{1}$, and \mathbf{Q}_{ij} are second-order matrices:

$$\mathbf{Q}_{11} = \begin{pmatrix} v_{11} & v_{12} \\ 0 & 0 \end{pmatrix}, \quad \mathbf{Q}_{12} = \begin{pmatrix} v_{13} & v_{14} \\ 1 & 0 \end{pmatrix},$$

$$\mathbf{Q}_{21} = \begin{pmatrix} v_{31} & v_{32} \\ 1 & 0 \end{pmatrix}, \quad \mathbf{Q}_{22} = \begin{pmatrix} v_{33} & v_{34} \\ 0 & 0 \end{pmatrix} \quad (14)$$

It is interesting to note that formula (13) resembles (12) in its structure, but in contrast to (12) contains matrix factors (14) (instead of scalar factors) which are submatrices for the matrix \mathbf{Q} (equation (4)).

Relation (13), taking into account (8) and (14), permits calculation of the probability of a given sequence, U_n , of monomer units and thus completely describes their distribution in the copolymer obtained by the complex-radical mechanism. As an example of use of formula (13), we give expressions for fractions of all triads of \bar{M}_i units, obtained using this formula:

$$P\{\bar{M}_1\bar{M}_1\bar{M}_1\} = \tilde{\pi}_1v_{11}(v_{11} + v_{12}),$$

$$P\{\bar{M}_1\bar{M}_1\bar{M}_2\} = P\{\bar{M}_2\bar{M}_1\bar{M}_1\} = (\tilde{\pi}_3v_{31} + \tilde{\pi}_4)(v_{11} + v_{12}),$$

$$P\{\bar{M}_1\bar{M}_2\bar{M}_1\} = (\tilde{\pi}_1v_{13} + \tilde{\pi}_2)(v_{31} + v_{32}) + \tilde{\pi}_1v_{14},$$

$$P\{\bar{M}_2\bar{M}_1\bar{M}_2\} = (\tilde{\pi}_3v_{31} + \tilde{\pi}_4)(v_{13} + v_{14}) + \tilde{\pi}_3v_{32},$$

$$P\{\bar{M}_1\bar{M}_2\bar{M}_2\} = P\{\bar{M}_2\bar{M}_2\bar{M}_1\} = (\tilde{\pi}_1v_{13} + \tilde{\pi}_2)(v_{33} + v_{34}),$$

$$P\{\bar{M}_2\bar{M}_2\bar{M}_2\} = \tilde{\pi}_3v_{33}(v_{33} + v_{34}) \quad (15)$$

Experimental measurements of triads, for example by high-resolution n.m.r. with different concentrations of initial monomers and of complexing agent allow, pro-

ceeding from formulae (15) and taking into account (5), (8) and (9), assessment of the adequacy of the kinetic model (1) and (2) and evaluation of its parameters (6).

As an example of the applicability of the general algorithm for calculations of probabilities of any sequence, one can give formulae obtained on the basis of (13) and (14):

$$\begin{aligned}
 f_N^{(1)}(n) &= \frac{P\{\bar{M}_2 \bar{M}_1^n \bar{M}_2\}}{P\{\bar{M}_2 \bar{M}_1\}} \\
 &= \frac{(\bar{\pi}_3 v_{31} + \bar{\pi}_4)(v_{11} + v_{12})(1 - v_{11})}{\bar{\pi}_3(v_{31} + v_{32}) + \bar{\pi}_4} v_{11}^{n-2} \\
 f_N^{(2)}(n) &= \frac{P\{M_1 M_2^n M_1\}}{P\{M_1 M_2\}} \\
 &= \frac{(\bar{\pi}_1 v_{13} + \bar{\pi}_2)(v_{33} + v_{34})(1 - v_{33})}{\bar{\pi}_1(v_{13} + v_{14}) + \bar{\pi}_2} v_{33}^{n-2} \quad (16)
 \end{aligned}$$

for the function of the number distribution $f_N^{(i)}$ according to lengths of the i type monomer unit blocks.

One of the main problems of the statistical description of copolymers is the calculation of their compositional inhomogeneity. In our case this is determined by the fraction ζ_1 of monomer units \bar{M}_1 . Since the chain length (l) of the copolymer in question is sufficiently high, the variable ζ_1 can be continuously varied from 0 to 1. It is expressed in a simple way $\zeta_1 = \xi_1 + \xi_2$ by fractions ξ_i of 'coloured' monomer units S_i . Since a sequence of these units forms a Markov chain with a transition matrix (4), the variable ζ_1 at large l being asymptotic normally distributed, similar to that describing inhomogeneity of the products of the classical copolymerization^{12,17}. However, in the case considered here, the parameters describing this inhomogeneity, i.e. the average composition π and the homogeneity index of sequences (D), are calculated in a different way. The former is found by formula (7) and the latter by the following formula:

$$D = \bar{D}_{11} + \bar{D}_{12} + \bar{D}_{21} + \bar{D}_{22} \quad (17)$$

where \bar{D}_{ij} are indices of homogeneity of sequences in the chain of coloured units. The quantities \bar{D}_{ij} are calculated in a routine way^{12,18} as this sequence is a Markovian one.

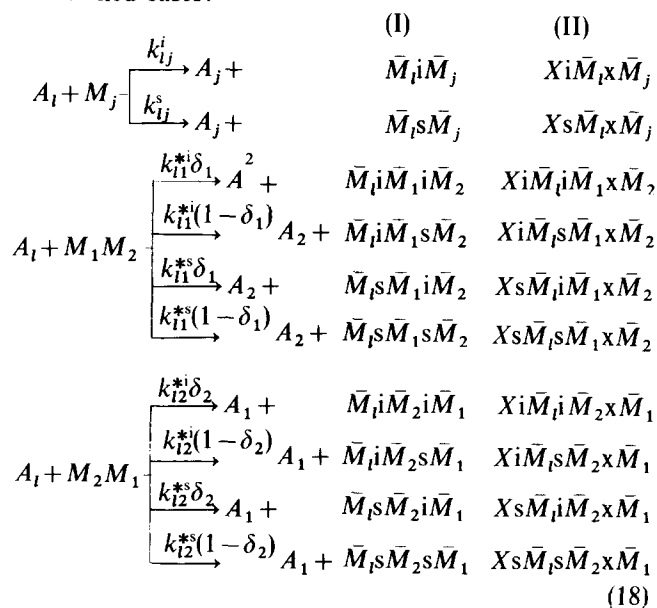
The kinetic model (1)–(2) considered in this paper has six independent parameters (6) and is a generalization of the two-parameter model of the classical copolymerization (1). For the determination of r_1 and r_2 in the latter model, it suffices to measure only the dependence of the original composition of the copolymer on the monomer feed, whereas more experimental information is required for the evaluation of the six parameters (6). This information can be obtained by studying the copolymer microstructure, e.g. by n.m.r. The treatment of experimental data on the proportions of different triads of monomer units in copolymers permits, in accord with formulae (15), evaluation of the set of relative activities (6). To verify the adequacy of the model (1)–(2), it is necessary to measure the microstructure of copolymers obtained at different ratios of monomers in the initial mixture and at different values of their absolute concentrations.

COMPLETE DESCRIPTION OF THE COPOLYMER CONFIGURATIONAL STATISTICS WITH CONSIDERATION OF ITS TACTICITY

Let us now consider a more detailed description of the microstructure of a copolymer (taking into account its tacticity). While choosing a kinetic scheme generalizing (1) and (2), it is assumed (similar to the description of the tacticity of homopolymers¹⁹) that the probability of a certain mutual configuration of substituents of a pair of adjacent units does not depend on the configurations of other units. The probability δ_j (or $1 - \delta_j$) that the second of a pair of configurations after addition of a complex will be isotactic (i) (or syndiotactic (s)) is determined only by the type of monomer M_j in the complex which is the first to add to the polymer chain.

Since each pair of adjacent monomer units in a macromolecule is characterized by a certain type of i or s of its mutual configuration, a fragment of the copolymer chain can be presented schematically in the form $\bar{M}_1 i \bar{M}_2 s \bar{M}_1 i \bar{M}_1$. For a complete statistical description of the configurational structure of such a copolymer, it is necessary to construct an algorithm for the calculation of the probabilities $P\{U_n\}$ of arbitrary sequences U_n of monomer units with respect to way of alternation of units and their stereoconfigurations. Two cases (I) and (II) will be considered within the framework of the kinetic model. In (I), the mutual stereoconfiguration of substituents of terminal and preterminal units in a macroradical is assumed to be fixed, while in (II) free rotation of the propagating radical end around a carbon-carbon bond occurs. In (II), probably realized more frequently²⁰ in radical copolymerization, the configuration of the terminal pair of monomer units remains uncertain until the addition of the next monomer or complex. However, in the polymerization of some monomers (for example, methyl methacrylate²¹) it is possible that the end of the propagating radical cannot rotate freely due to the height of the corresponding energy barrier. Evidently such systems belong to case (I).

Taking into account the assumption concerning the mechanism of the chain propagation reaction, one can derive the kinetic scheme involving both of the above-mentioned cases:



where X is any of the units \bar{M}_1 or \bar{M}_2 and x is any of their

stereoconfigurations *i* or *s*. The M_i units in the polymer chain are 'coloured' as above. Then an auxiliary Markov chain with the states S_i ($i=1,2,\dots,8$) is constructed, the latter are chosen in different ways for the cases (I) and (II) of the equations (18):

$$(I) \quad \begin{aligned} S_1 &\sim Xi\bar{M}_1^w, & S_2 &\sim Xs\bar{M}_1^w, & S_3 &\sim Xi\bar{M}_1^b, & S_4 &\sim Xs\bar{M}_1^b, \\ S_5 &\sim Xi\bar{M}_2^w, & S_6 &\sim Xs\bar{M}_2^w, & S_7 &\sim Xi\bar{M}_2^b, & S_8 &\sim Xs\bar{M}_2^b; \end{aligned} \quad (19)$$

$$(II) \quad \begin{aligned} S_1 &\sim XiXx\bar{M}_1^w, & S_2 &\sim XsXx\bar{M}_1^w, & S_3 &\sim XiXx\bar{M}_1^b, & S_4 &\sim XsXx\bar{M}_1^b, \\ S_5 &\sim XiXx\bar{M}_2^w, & S_6 &\sim XsXx\bar{M}_2^w, & S_7 &\sim XiXx\bar{M}_2^b, & S_8 &\sim XsXx\bar{M}_2^b \end{aligned} \quad (20)$$

Proceeding from a system of kinetic equations corresponding to the equations (18), one can rigorously show that a sequence of the S_i states actually forms a Markov chain. Note that the probabilities of this random process are similar for both cases (I) and (II). The difference between them is exhibited in the expressions for the probabilities of actually observed sequences of the monomer units \bar{M}_i , taking into account the stereoconfigurations of their substituents *via* the probabilities of the corresponding sequences of the S_i states of the Markov chain with a transition matrix:

$$Q = \begin{bmatrix} v_{11} & v_{12} & v_{13} & v_{14} & v_{15} & v_{16} & v_{17} & v_{18} \\ v_{21} & v_{22} & v_{23} & v_{24} & v_{25} & v_{26} & v_{27} & v_{28} \\ 0 & 0 & 0 & 0 & v_{35} & v_{36} & 0 & 0 \\ 0 & 0 & 0 & 0 & v_{45} & v_{46} & 0 & 0 \\ v_{51} & v_{52} & v_{53} & v_{54} & v_{55} & v_{56} & v_{57} & v_{58} \\ v_{61} & v_{62} & v_{63} & v_{64} & v_{65} & v_{66} & v_{67} & v_{68} \\ v_{71} & v_{72} & 0 & 0 & 0 & 0 & 0 & 0 \\ v_{81} & v_{82} & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (21)$$

obtained from the matrix (4), replacing each element of (5) by a square matrix of the second order with similar rows:

$$\begin{aligned} M_i k_{ji} \Delta_j^{-1} &\rightarrow \begin{pmatrix} M_i k_{ji}^i \Delta_j^{-1} & M_i k_{ji}^s \Delta_j^{-1} \\ M_i k_{ji}^i \Delta_j^{-1} & M_i k_{ji}^s \Delta_j^{-1} \end{pmatrix}, \\ M_{12} k_{ji}^* \Delta_j^{-1} &\rightarrow \begin{pmatrix} M_{12} k_{ji}^{*i} \Delta_j^{-1} & M_{12} k_{ji}^{*s} \Delta_j^{-1} \\ M_{12} k_{ji}^{*i} \Delta_j^{-1} & M_{12} k_{ji}^{*s} \Delta_j^{-1} \end{pmatrix} \end{aligned} \quad (22)$$

where Δ_j are the same as in (5) if one designates $k_{ji} = k_{ji}^i + k_{ji}^s$, $k_{ji}^* = k_{ji}^{*i} + k_{ji}^{*s}$. Null elements of the matrix (4) are transformed into null matrices, while the unit elements corresponding to the transitions from \bar{M}_1^b to \bar{M}_2^w and from \bar{M}_2^b to \bar{M}_1^w are transformed into:

$$\begin{aligned} 1 &\rightarrow \begin{pmatrix} \delta_1 & 1-\delta_1 \\ \delta_1 & 1-\delta_1 \end{pmatrix} = \begin{pmatrix} v_{35} & v_{36} \\ v_{45} & v_{46} \end{pmatrix}, \\ 1 &\rightarrow \begin{pmatrix} \delta_2 & 1-\delta_2 \\ \delta_2 & 1-\delta_2 \end{pmatrix} = \begin{pmatrix} v_{71} & v_{72} \\ v_{81} & v_{82} \end{pmatrix} \end{aligned} \quad (23)$$

respectively.

The fixed probability vector $\bar{\pi}'$ of the matrix (21) is calculated as (8) in a routine way. Its components $\bar{\pi}'_i$ ($i=1,2,\dots,8$) due to relations (22) and (23) can be expressed by the corresponding components $\bar{\pi}_i$ of the fixed probability vector of the matrix (4) and the components of the matrix (21):

$$\begin{aligned} \bar{\pi}'_1 &= \bar{\pi}_1 v_{11} + \bar{\pi}_3 v_{51} + \bar{\pi}_4 \delta_2, \\ \bar{\pi}'_2 &= \bar{\pi}_1 v_{12} + \bar{\pi}_3 v_{52} + \bar{\pi}_4 (1 - \delta_2), \\ \bar{\pi}'_3 &= \bar{\pi}_1 v_{13} + \bar{\pi}_3 v_{53}, \\ \bar{\pi}'_4 &= \bar{\pi}_1 v_{14} + \bar{\pi}_3 v_{54}, \\ \bar{\pi}'_5 &= \bar{\pi}_1 v_{15} + \bar{\pi}_2 \delta_1 + \bar{\pi}_3 v_{55}, \\ \bar{\pi}'_6 &= \bar{\pi}_1 v_{16} + \bar{\pi}_2 (1 - \delta_1) + \bar{\pi}_3 v_{56}, \\ \bar{\pi}'_7 &= \bar{\pi}_1 v_{17} + \bar{\pi}_3 v_{57}, \\ \bar{\pi}'_8 &= \bar{\pi}_1 v_{18} + \bar{\pi}_3 v_{58} \end{aligned} \quad (24)$$

Here, naturally the following relations hold:

$$\bar{\pi}_1 = \bar{\pi}'_1 + \bar{\pi}'_2, \quad \bar{\pi}_2 = \bar{\pi}'_3 + \bar{\pi}'_4, \quad \bar{\pi}_3 = \bar{\pi}'_5 + \bar{\pi}'_6, \quad \bar{\pi}_4 = \bar{\pi}'_7 + \bar{\pi}'_8 \quad (25)$$

The values $\bar{\pi}_i$ allow, for example, one to find the fraction of monomer units entering a macromolecule via addition of complex. This fraction is $2(\bar{\pi}'_3 + \bar{\pi}'_4 + \bar{\pi}'_7 + \bar{\pi}'_8)$.

The Markov chain with the matrix (21) is always lumpable with respect to a partition $\bar{M}_1^w = S_1 + S_2$, $\bar{M}_1^b = S_3 + S_4$, $\bar{M}_2^w = S_5 + S_6$, $\bar{M}_2^b = S_7 + S_8$, introduced in the first section of this paper. The transition matrix of the lumped chain, naturally, coincides with (4), i.e. all formulae given above describing the statistics of the sequence distribution, irrespective of their mutual configurations, remain valid. Hence, this fundamental property, previously known in the theory of the classical copolymerization, has been generalized for the scheme (18).

General formulae permitting calculation of the probability of an arbitrary sequence of units with given stereoconfigurations are derived from the same considerations as for (13). However, now they have a different form depending on which case (I) or (II) of the scheme (18) is realized in the polymerization. For demonstration, we give a derivation of expressions for the probabilities of diads. The stereoconfiguration of units in a diad will be designated with t_1 corresponding to iso- and t_2 to syndio-configuration. Then in the case (I) we obtain

$$P\{\bar{M}_j t_\alpha \bar{M}_k\} = \sum \bar{\pi}_i v_{im} \quad (26)$$

where summation is carried over indices l and m with $l=1,2,3,4$ or $l=5,6,7,8$ when $j=1$ or $j=2$, respectively, and the index m has the values $m=1,3$; $m=2,4$; $m=5,7$; $m=6,8$, when $\alpha=1, k=1$; $\alpha=2, k=1$; $\alpha=1, k=2$; $\alpha=2, k=2$, respectively. In the case (II) we similarly obtain from the scheme (18)

$$P\{\bar{M}_j t_\alpha \bar{M}_k\} = \sum \bar{\pi}_i v_{lm} v_{mn} \quad (27)$$

where l runs over the values 1,2,3,4 when $j=1$ and

5, 6, 7, 8 when $j=2$; m runs over the values 1, 2, 3, 4 when $k=1$ and 5, 6, 7, 8 when $k=2$; while $n=1, 3, 5, 7$ or $n=2, 4, 6, 8$ when $\alpha=1$ or $\alpha=2$, respectively. Since the functional dependences of $\bar{\pi}_i$ and v_{im} on monomer concentrations are similar for both cases (I) and (II), there is a possibility of distinguishing between these cases in experiment (due to the difference between formulae (26) and (27)) by studying dependences of fractions of different diads on the concentrations M_1 and M_2 .

The case of an alternating regular polymer, formed at a sufficient concentration of complexing agent in the system, is of special interest, since the distribution of the units \bar{M}_1 and \bar{M}_2 in all macromolecules of such a copolymer has the form $\sim \bar{M}_1 \bar{M}_2 \bar{M}_1 \bar{M}_2 \bar{M}_1 \sim$. Here, as in the case of homopolymer, macromolecules, in addition to the degree of polymerization, differ only in the sequence of stereoconfigurations of monomer units. However, while describing tacticity of alternating copolymers, one finds considerable differences in comparison to homopolymers, because of the necessity of distinguishing sequences U_n of configurations by the types of the initial and terminating monomer units bordering U_n . Thus, the diads $\bar{M}_1 i \bar{M}_2$ and $\bar{M}_2 i \bar{M}_1$ have different probabilities, although they are indistinguishable in experiment. The same concerns $\bar{M}_1 s \bar{M}_2$ and $\bar{M}_2 s \bar{M}_1$ and also the pairs of triads $\bar{M}_1 i \bar{M}_2 s \bar{M}_1$ and $\bar{M}_1 s \bar{M}_2 i \bar{M}_1$, $\bar{M}_2 i \bar{M}_1 s \bar{M}_2$ and $\bar{M}_2 s \bar{M}_1 i \bar{M}_2$. Spectroscopic measurements permit determination of only $P(i) = P\{\bar{M}_1 i \bar{M}_2\} + P\{\bar{M}_2 i \bar{M}_1\}$ and also the quantities $P(\bar{M}_1 i \bar{M}_2 s \bar{M}_1) = P\{\bar{M}_1 i \bar{M}_2 s \bar{M}_1\} + P\{\bar{M}_1 s \bar{M}_2 i \bar{M}_1\}$ and $P(\bar{M}_2 i \bar{M}_1 s \bar{M}_2) = P\{\bar{M}_2 i \bar{M}_1 s \bar{M}_2\} + P\{\bar{M}_2 s \bar{M}_1 i \bar{M}_2\}$ separately. A sum of the last two quantities $P(is)$ gives together with $P(i) = 1 - P(s)$, the coefficient of microheterogeneity

$$K_M = P(is)/2P(i)P(s) \quad (28)$$

The equality of the latter to unity is a necessary condition for the description of the tacticity of an alternating copolymer by Bernoullian statistics.

It is interesting to find the relations between kinetic constants which independently of monomer concentrations give $K_M=1$. As the analysis has shown, these relations are:

$$k_{jk}^i/k_{jk} = k_{jk}^{*i}/k_{jk}^* = \delta_1 = \delta_2 = \sigma \quad (j=1, 2; k=1, 2) \quad (29)$$

In the framework of the considered kinetic scheme (18), the latter are found to be sufficient conditions for a description of copolymer tacticity by a Bernoullian scheme with parameter σ . It is of interest that when (29) does not hold the copolymer tacticity cannot be described by a Markov chain. However, at some ratios between the kinetic parameters, 'pseudo-Bernoullian' statistics are possible with two parameters of alternation of stereoconfigurations σ_{12} and σ_{21} , when the probabilities σ_{ij} of the isotactic arrangement of substituents in adjacent units $\bar{M}_i \bar{M}_j$ do not depend on their environment along the chain. These relations are

$$\delta_1 = k_{12}^i/k_{12} = k_{12}^{*i}/k_{12}^*, \quad \delta_2 = k_{21}^i/k_{21} = k_{21}^{*i}/k_{21}^* \quad (30)$$

The parameters $\sigma_{12} = \delta_1$, $\sigma_{21} = \delta_2$ in the case (I) and $\sigma_{12} = \delta_2$, $\sigma_{21} = \delta_1$ in the case (II).

DISCUSSION AND POSSIBLE GENERALIZATIONS OF THE MODEL

Hirai *et al.*²² have shown the non-Bernoullian statistics of stereoconfigurations using n.m.r. studies of the tacticity of alternating copolymers of methyl methacrylate (M_1) and styrene (M_2) obtained in the presence of different complexing agents. To explain this fact, they suggested a mechanism of polymer chain propagation based on two assumptions:

(1) Only one radical type (A_1) is present in the system and hence monomers are added only in the form of a complex.

(2) The fixing of a pair of stereoconfigurations, as a result of complex addition, occurs one after the other, the probabilities $\sigma_2^{(i)}$ and $\sigma_2^{(s)}$ of iso-diad appearance with the second bond will vary depending on the first bond's stereoconfiguration (i or s), and the probability σ_1 of the latter does not depend on the tacticity of the radical terminal pair of units.

Stereocontrol in the framework of such a model is attributed by the authors²² to Markovian statistics of the first order, although, rigorously, the sequence of stereoconfigurations is a superposition of these statistics and Bernoullian statistics. However, the interpretation of experimental data obtained²² on the basis of this model is not unique. We shall show that these data do not contradict the results obtained proceeding from the present kinetic model (18).

The values of probabilities (fractions) of different triads were found²² by n.m.r. with a high accuracy (better than 1-2%):

$$f_{x1} = 2P\{\bar{M}_2 s \bar{M}_1 s \bar{M}_2\}, \quad f_{z1} = 2P\{\bar{M}_2 i \bar{M}_1 i \bar{M}_2\}, \\ f_{y1} = 1 - f_{x1} - f_{z1}, \quad (31)$$

$$f_{x2} = 2P\{\bar{M}_1 s \bar{M}_2 s \bar{M}_1\}, \quad f_{z2} = 2P\{M_1 i M_2 i M_1\}, \\ f_{y2} = 1 - f_{x2} - f_{z2}$$

and the values of the parameters

$$D_i = f_{yi}^2 - 4f_{xi}f_{zi} \quad (i=1, 2) \quad (32)$$

are calculated using them. In particular, it was found in the system where EtBCl_2 was taken as a complexing agent and at the temperature -20°C

$$f_{x1} = 0.36, \quad f_{z1} = 0.18, \quad f_{y1} = 0.46, \quad D_1 = -0.048, \\ f_{x2} = 0.29, \quad f_{z2} = 0.11, \quad f_{y2} = 0.60, \quad D_2 = 0.232 \quad (33)$$

In addition, it was found²² for different systems where an alternating regular copolymer is formed that the probabilities of triads satisfy the condition

$$f_{x1} - f_{x2} = f_{z1} - f_{z2} \quad (34)$$

The data of²² convincingly show the inapplicability of not only the routine Bernoullian single-parameter statistics, but also of two parameter 'pseudo-Bernoullian' statistics, since in both cases it follows that $D_1 = D_2 = D \geq 0$ with the equality corresponding to the first case. As it is seen from (33), D_1 and D_2 even have different signs. For explanation of their experimental data, Hirai *et al.*²² suggested a more general three-parameter kinetic model, the main assumptions of which

were given above. As one of the main arguments in favour of the adequacy of this model, they state that the relation (34) follows from it. However, as the theoretical analysis developed by us has shown, this relation holds for any alternating regular copolymer independently of its mechanism of formation. At the same time, experimental values of triad probabilities (31) for the corresponding choice of the kinetic parameters can also be calculated within the framework of models differing from that suggested. In particular, a kinetic model corresponding to case (I) of the scheme (18) gives an alternating copolymer with the triad probabilities (33) for the values of the matrix parameters (21):

$$\begin{aligned} v_{15} = v_{25} = 0.232, & \quad v_{16} = v_{26} = 0.084, & \quad v_{17} = v_{27} = 0.006, \\ v_{18} = v_{28} = 0.678, & \quad v_{51} = v_{61} = 0.032, & \quad v_{52} = v_{62} = 0.551, \\ v_{53} = v_{63} = 0.305, & \quad v_{54} = v_{64} = 0.112, & \quad v_{35} = v_{45} = 0.695, \\ v_{36} = v_{46} = 0.305, & \quad v_{71} = v_{81} = 0.625, & \quad v_{72} = v_{82} = 0.375 \end{aligned} \quad (35)$$

and the other $v_{ij} = 0$.

Note that our model (18), similar to the model proposed, leads to essentially non-Bernoullian statistics of stereoconfigurations. However, the reasons causing it are quite different in both models. According to the latter model, the reason is the mutual dependence of a pair of stereoconfigurations, formed during the addition of the complex, and in the second one the reason is a mixed mechanism of adding single monomers and pairs of monomers to a polymer chain with the condition that all stereoconfigurations, formed during the addition of the complex, and in the former the reason is a mixed as a complex according to model (18) with the values of the parameters in (35) is 0.742, while in the proposed model²² it is unity. Since both models explain equally well the stereochemical data obtained in ref. 22, their adequacy in describing the true mechanism of the propagation reactions at alternating radical copolymerization can be settled only after additional experimental studies.

A general kinetic scheme can be considered, which involves both above-mentioned models as particular cases. For this the constants k_{ij}^{*ii} , k_{ij}^{*is} , k_{ij}^{*si} , k_{ij}^{*ss} must be introduced into scheme (18) instead of the reaction rate constants k_{ij}^{*i} , k_{ij}^{*s} and the probabilities δ_1 , δ_2 independent of k_{ij}^{*i} and k_{ij}^{*s} . For example k_{11}^{*is} is the rate constant of the fourth reaction of scheme (18) when the complex is added to the radical by the monomer M_1 with the first and second bonds, respectively, fixed in iso- and syndio-

configurations. One may show that with an appropriate choice of a larger number of states S_i some Markov chain for their sequence is again obtained. The model²² follows from this general kinetic model if one assumes that all constants are zero except k_{12}^{*ii} , k_{12}^{*is} , k_{12}^{*si} , k_{12}^{*ss} which are related to the parameters of the model²² by the simple relations:

$$\begin{aligned} \frac{k_{12}^{*ii}}{k_{12}^{*i}} &= \sigma_1 \sigma_2^{(i)}, & \frac{k_{12}^{*is}}{k_{12}^{*i}} &= \sigma_1 (1 - \sigma_2^{(i)}), \\ \frac{k_{12}^{*si}}{k_{12}^{*i}} &= (1 - \sigma_1) \sigma_2^{(s)}, & \frac{k_{12}^{*ss}}{k_{12}^{*i}} &= (1 - \sigma_1) (1 - \sigma_2^{(s)}), \end{aligned} \quad (36)$$

where $k_{12}^{*i} = k_{12}^{*ii} + k_{12}^{*is} + k_{12}^{*si} + k_{12}^{*ss}$

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