Determination of the Participation of Comonomer Complexes in the Macromolecule Propagation by Copolymer Composition Triads

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ABSTRACT: A new method for the determination of the participation of comonomer complexes, participation in the formation of the copolymer molecule and the reactivities of comonomers before and after their incorporation in the complex, is developed. Its essence consists of the simulation of copolymer chain propagation by the regular Markov chain with three types of states reflecting the addition of the comonomer molecules and the first or second components of the complex to the propagating chain. The problem is in the determination of the transition probabilities of the Markov chain. An algorithm using the experimental information for the composition of the triad fractions is proposed to this end. The triads for radical-synthesized styrene–methyl methacrylate copolymers calculated by this method are much closer to the experimental ones than those calculated by a terminal model which neglects comonomer complex participation in the copolymer chain formation.

Introduction

As a result of donor–acceptor, ionic, Van der Waals, and hydrophobic interactions and of hydrogen bond formation, complexes between comonomer molecules are formed fairly often. The participation of these comonomer complexes in the macromolecule propagation influences considerably the copolymerization velocity, the copolymer composition and microstructure, and the physicochemical properties of the copolymers.[1] Therefore a number of different methods for the quantitative estimation of this participation are developed. Some of them are based on the deviation of the experimentally determined copolymer composition from that calculated by the Mayo–Lewis equation or by its derivatives.[2] Others are based on the extreme dependence of the copolymerization rate on the monomer feed[3–5] and the third group of methods—on the shift of the configurational copolymer composition from that calculated using the Bernoullian and Markov statistics.[6] A method taking into account the deviation of the copolymer composition triads calculated by the Bovey and Markov statistics[7] from those determined experimentally by ^{13}C NMR is developed in this work. This deviation is attributed to comonomer complex participation in the propagation reaction. This participation is considered by the suggested method while it is ignored by the above mentioned statistics. Good agreement between the experimentally determined and calculated copolymer composition triad fractions is achieved by this method. The total probability of macromolecule formation by the addition of comonomer complexes to the propagating ends can be estimated by this method. Moreover, it allows a comparison of the comonomer reactivities before and after their incorporation in complexes or tetramethylene intermediates at both propagating ends. The method is applicable when only comonomer complexes or tetramethylene intermediates[8] take part in the propagation reaction.

Theoretical Background

The general assumption of our method is the division of the bimolecular comonomer complex addition to the propagating chain into two individual steps. If the possibility of addition of single monomer molecules is also taken into account, the kinetic scheme of the copolymer macromolecule propagation should be

$$\sim A^* + A \xrightarrow{k_{A,A}} \sim A^* \quad (1)$$

$$\sim A^* + B \xrightarrow{k_{A,B}} \sim B^* \quad (2)$$

$$\sim A^* + AB \xrightarrow{k_{A,CA}} \sim \hat{A}...B \quad (3)$$

$$\sim A^* + BA \xrightarrow{k_{A,CB}} \sim \hat{B}...A \quad (4)$$

$$\sim B^* + A \xrightarrow{k_{B,A}} \sim A^* \quad (5)$$

$$\sim B^* + B \xrightarrow{k_{B,B}} \sim B^* \quad (6)$$

$$\sim B^* + AB \xrightarrow{k_{B,CA}} \sim \hat{A}...B \quad (7)$$

$$\sim B^* + BA \xrightarrow{k_{B,CB}} \sim \hat{B}...A \quad (8)$$

The propagating chains with active ends ~Â...B and ~B̂...A are intermediates formed after the first step of the complex (C ≡ AB) addition to ~A* or ~B*. Since the complex components (A and B) are fixed together, the probability that the propagating ends obtained from the intermediates ~B̂...A and ~Â...B will be ~A* and ~B*, respectively, is unity. However, the introduction of an intermediate is particularly useful for the determination of the complex participation in the formation of copolymer macromolecules and of the reactivities both of the comonomers (A and B) and of the two sides of complex AB.

$$r_{A,B} = \frac{k_{A,A}}{k_{A,B}} \qquad r_{A,CA} = \frac{k_{A,A}}{k_{A,CA}} \qquad r_{A,CB} = \frac{k_{A,A}}{k_{A,CB}} \quad (9)$$

$$r_{B,A} = \frac{k_{B,B}}{k_{B,A}} \qquad r_{B,CA} = \frac{k_{B,B}}{k_{B,CA}} \qquad r_{B,CB} = \frac{k_{B,B}}{k_{B,CB}} \quad (10)$$

First of all it is necessary to evaluate the average time during which the propagating chain remains in the special states ~Â...B and ~B̂...A ($\hat{F}_A$,$\hat{F}_B$) and in states ~A* and ~B* (F_A,F_B). This is achieved using the

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regular Markov chain[9] with four transition states, corresponding to the above discussed active ends of the propagating macromolecule. The transition matrix (**P**) of this Markov chain is

$$\mathbf{P} = \begin{array}{c} \\ A \\ \hat{A} \\ B \\ \hat{B} \end{array} \begin{array}{c} \begin{array}{cccc} A & \hat{A} & B & \hat{B} \end{array} \\ \begin{pmatrix} P_{AA} & \hat{P}_{AA} & P_{AB} & \hat{P}_{AB} \\ 0 & 0 & 1 & 0 \\ P_{BA} & \hat{P}_{BA} & P_{BB} & \hat{P}_{BB} \\ 1 & 0 & 0 & 0 \end{pmatrix} \end{array} \tag{11}$$

The above mentioned average times of chain residence (ATCR) form a vector $\bar{F}$ and can be determined by the equation[10] $\bar{F}\mathbf{P} = \bar{F}$ and the rate-setting one $F_A + F_B + \hat{F}_A + \hat{F}_B = 1$.

$$F_A = \frac{P_{BA} + \hat{P}_{BB}}{D} \tag{12}$$

$$F_B = \frac{P_{AB} + \hat{P}_{AA}}{D} \tag{13}$$

$$\hat{F}_A = \frac{(P_{AB} + \hat{P}_{AA})\hat{P}_{BA} + (P_{BA} + \hat{P}_{BB})\hat{P}_{AA}}{D} \tag{14}$$

$$\hat{F}_B = \frac{(P_{AB} + \hat{P}_{AA})\hat{P}_{BB} + (P_{BA} + \hat{P}_{BB})\hat{P}_{AB}}{D} \tag{15}$$

where

$$D = (P_{BA} + \hat{P}_{BB})(1 + \hat{P}_{AA} + \hat{P}_{AB}) + (P_{AB} + \hat{P}_{AA})(1 + \hat{P}_{BA} + \hat{P}_{BB}) \tag{16}$$

As the mole fractions of A and B (m_A and m_B) in the copolymers are

$$m_A = F_A + \hat{F}_A \quad \text{and} \quad m_B = F_B + \hat{F}_B \tag{17}$$

respectively, the following composition equation can be deduced for the obtained copolymers:

$$\frac{m_A}{m_B} = \frac{(P_{AB} + \hat{P}_{AA})\hat{P}_{BA} + (P_{BA} + \hat{P}_{BB})(1 + \hat{P}_{AA})}{(P_{BA} + \hat{P}_{BB})\hat{P}_{AB} + (P_{AB} + \hat{P}_{AA})(1 + \hat{P}_{BB})} \tag{18}$$

This equation is easily expressed by the monomer concentrations and by the copolymerization ratios (eqs 9 and 10) if the transition probabilities are substituted by the expression considering the competition among the addition rates of the reactive particles to the propagating ends ~A* and ~B*.

$$P_{AA} = \frac{[A]}{\gamma_A} \tag{19}$$

$$P_{AB} = \frac{[B]r_{A,B}^{-1}}{\gamma_A} \tag{20}$$

$$\hat{P}_{AA} = \frac{[C]r_{A,CA}^{-1}}{\gamma_A} \tag{21}$$

$$\hat{P}_{AB} = \frac{[C]r_{A,CB}^{-1}}{\gamma_A} \tag{22}$$

$$P_{BB} = \frac{[B]}{\gamma_B} \tag{23}$$

$$P_{BA} = \frac{[A]r_{B,A}^{-1}}{\gamma_B} \tag{24}$$

$$\hat{P}_{BB} = \frac{[C]r_{B,CB}^{-1}}{\gamma_B} \tag{25}$$

$$\hat{P}_{BA} = \frac{[C]r_{B,CA}^{-1}}{\gamma_B} \tag{26}$$

$$\gamma_A = [A] + [B]r_{A,B}^{-1} + [C](r_{A,CA}^{-1} + r_{A,CB}^{-1}) \tag{27}$$

$$\gamma_B = [B] + [A]r_{B,A}^{-1} + [C](r_{B,CA}^{-1} + r_{B,CB}^{-1}) \tag{28}$$

It is clear that the copolymerization values can be easily calculated from eqs 19–28 if the transition probability values are known:

$$r_{A,B} = \frac{[B]}{[A]}\frac{P_{AA}}{P_{AB}} \tag{29}$$

$$r_{A,CA} = \frac{[C]}{[A]}\frac{P_{AA}}{\hat{P}_{AA}} \tag{30}$$

$$r_{A,CB} = \frac{[C]}{[A]}\frac{P_{AA}}{\hat{P}_{AB}} \tag{31}$$

$$r_{B,A} = \frac{[A]}{[B]}\frac{P_{BB}}{P_{BA}} \tag{32}$$

$$r_{B,CA} = \frac{[C]}{[B]}\frac{P_{BB}}{\hat{P}_{BA}} \tag{33}$$

$$r_{B,CB} = \frac{[C]}{[B]}\frac{P_{BB}}{\hat{P}_{BB}} \tag{34}$$

Moreover, it is evident from eqs 12–17 that ATCR in the intermediate states Â ($\hat{F}_A$) and B̂ ($\hat{F}_B$) can be calculated after the determination of the transition probability values. These average times determine directly the total probability of macromolecule formation by the addition of the complex to the propagating ends (P(C)) as

$$P(C) = \hat{F}_A + \hat{F}_B \tag{35}$$

Obviously, the problem thus formulated could be solved when the transition probability values (the matrix **P** elements) are calculated. The number of the unknown probabilities is 6 since the events with probabilities forming a row of **P** represent a full set and hence $P_{AA} + \hat{P}_{AA} + P_{AB} + \hat{P}_{AB} = 1$ and $P_{BB} + \hat{P}_{BB} + P_{BA} + \hat{P}_{BA} = 1$. The determination of these six probabilities cannot be achieved by the single independent equation for the monad copolymer composition (eq 17 or 18). The number of linear independent relationships for the diad copolymer composition (they are two) is also insufficient.

$$m_{AA} = F_{AA} + \hat{F}_{AA} = \frac{(P_{BA} + \hat{P}_{BB})(P_{AA} + \hat{P}_{AA})}{D} \tag{36}$$

$$m_{BB} = F_{BB} + \hat{F}_{BB} = \frac{(P_{AB} + \hat{P}_{AA})(P_{BB} + \hat{P}_{BB})}{D} \quad (37)$$

$$m_{AB} = F_{AB} + F_{BA} + \hat{F}_{AB} + \hat{F}_{BA} = 1 - m_{AA} - m_{BB} \quad (38)$$

where $\hat{F}_{AA}$ and $\hat{F}_{BB}$ are ATCR in the intermediate states ~AÂ...B and ~BB̂...A. The average times $\hat{F}_{AB}$ and $\hat{F}_{BA}$ are defined in the same way for the states ~AB̂...A and ~BÂ...B. Their expressions can be deduced either by the second-order Markov chain with eight states (AA, ÂA, AB, ÂB, BB, B̂B, BA, B̂A) or by the Bovey scheme:[7]

$$F_{AA} = F_A P_{AA} \qquad F_{AB} = F_A P_{AB} + \hat{F}_A$$
$$\hat{F}_{AA} = F_A \hat{P}_{AA} \qquad \hat{F}_{AB} = F_A P_{AB} \quad (39)$$

$$F_{BB} = F_B P_{BB} \qquad \hat{F}_{BB} = F_B \hat{P}_{BB}$$
$$F_{BA} = F_B P_{BA} + \hat{F}_B \qquad \hat{F}_{BA} = F_B \hat{P}_{BA} \quad (40)$$

Identical expressions for ATCR are obtained by both methods. They can be used to express the mole fractions m_{AA}, m_{AB}, and m_{BB} by the transition probabilities (eqs 36–38).

Expressions for the experimentally determined mole fractions of the compositional triads in copolymer macromolecules can be deduced by the same procedure:

$$m_{AAA} = \frac{(1 - \beta_2)\alpha_1 P_{AA}}{D} \quad (41)$$

$$m_{BBB} = \frac{(1 - \alpha_2)\beta_1 P_{BB}}{D} \quad (42)$$

$$m_{ABA} = \frac{(1 - \alpha_2)(1 - \beta_1)(1 - P_{BB}) + (1 - \beta_2)(\alpha_2 - P_{AA})}{D} \quad (43)$$

$$m_{BAB} = \frac{(1 - \beta_2)(1 - \alpha_1)(1 - P_{AA}) + (1 - \alpha_2)(\beta_2 - P_{BB})}{D} \quad (44)$$

$$m_{AAB} = \frac{2(1 - \beta_2)(1 - P_{AA})\alpha_1}{D} \quad (45)$$

$$m_{BBA} = \frac{2(1 - \alpha_2)(1 - P_{BB})\beta_1}{D} \quad (46)$$

where

$$\alpha_1 = P_{AA} + \hat{P}_{AA} \quad (47)$$

$$\alpha_2 = P_{AA} + \hat{P}_{AB} \quad (48)$$

$$\beta_1 = P_{BB} + \hat{P}_{BB} \quad (49)$$

$$\beta_2 = P_{BB} + \hat{P}_{BA} \quad (50)$$

are four compound probabilities with values in the ranges of

$$P_{AA} \le \alpha_i \le 1 \qquad i = 1, 2 \quad (51)$$

$$P_{BB} \le \beta_i \le 1 \qquad i = 1, 2 \quad (52)$$

The denominator D can be expressed by these compound probabilities

$$D = (1 - \alpha_2)(1 - 2P_{BB} + \beta_1 + \beta_2) + (1 - \beta_2)(1 - 2P_{AA} + \alpha_1 + \alpha_2) \quad (53)$$

These substitutions are more convenient for the determination of the transition probabilities from the experimental mole fractions of the compositional triads. The method we suggest uses the ratios between the compositional triad equations (eqs 41–46). The probabilities P_{AA} and P_{BB} are deduced directly from the relations m_{AAA}/m_{AAB} and m_{BBB}/m_{BBA}

$$P_{AA} = \frac{2m_{AAA}}{2m_{AAA} + m_{AAB}} \quad (54)$$

$$P_{BB} = \frac{2m_{BBB}}{2m_{BBB} + m_{BBA}} \quad (55)$$

Four of the thirteen remaining ratios of the mole fractions of the compositional triads define transformational relationships between $(1 - \beta_2)/(1 - \alpha_2)$ and β_1/α_1

$$\frac{1 - \beta_2}{1 - \alpha_2} = \frac{m_{AAA}P_{BB}}{m_{BBB}P_{AA}}\frac{\beta_1}{\alpha_1} = \frac{m_{AAB}(1 - P_{BB})}{m_{BBA}(1 - P_{AA})}\frac{\beta_1}{\alpha_1}$$
$$= \frac{2m_{AAA}(1 - P_{AA})}{m_{BBA}P_{AA}}\frac{\beta_1}{\alpha_1} = \frac{m_{AAB}P_{BB}}{2m_{BBB}(1 - P_{AA})}\frac{\beta_1}{\alpha_1} \quad (56)$$

It is worth noting that only the mole parts of compositional triads with at least two identical adjacent units (AA or BB) take part in the six ratios. All the other nine ratios include mole fractions of the alternating triads m_{ABA} and m_{BAB}. On the other hand they are subdivided into three different subclasses. The first one includes four ratios between m_{ABA} and the nonalternating mole fractions, and the second one, the other four ratios between m_{BAB} and the same nonalternating triad mole fractions. The third subclass involves only the m_{ABA}/m_{BAB} ratio. It is easy to show that when combining each ratio from the first subclass with one of the expressions for $(1 - \beta_2)/(1 - \alpha_2)$ (56) four different but equivalent dependences of α_2 on α_1 and β_1 can be deduced. For example, if the ratio $(1 - \beta_2)/(1 - \alpha_2)$ in the expression for m_{ABA}/m_{BBB}, obtained by division of eqs 43 and 42, is substituted with $2m_{AAA}(1 - P_{AA})\beta_1/m_{BBA}P_{AA}\alpha_1$ (56)

$$\alpha_2 = P_{AA} + \left[\frac{m_{ABA}}{m_{BBB}} - \frac{1 - P_{BB}}{P_{BB}}\frac{1 - \beta_1}{\beta_1}\right]\frac{m_{BBA}P_{AA}P_{BB}\alpha_1}{2m_{AAA}(1 - P_{BB})} \quad (57)$$

Analogously, 16 equivalent dependences of β_2 on α_1 and β_1 can be derived from the second subclass ratios. When for example, in the expression for m_{BAB}/m_{AAA} (eqs 41 and 44) the ratio $(1 - \beta_2)/(1 - \alpha_2)$ is substituted with its equivalent $m_{AAB}P_{BB}\beta_1/2m_{BBB}(1 - P_{AA})\alpha_1$ (56)

$$\beta_2 = P_{BB} + \left[\frac{m_{BAB}}{m_{AAA}} - \frac{1 - P_{AA}}{P_{AA}}\frac{1 - \alpha_1}{\alpha_1}\right]\frac{m_{AAB}P_{BB}P_{AA}\beta_1}{2m_{BBB}(1 - P_{AA})} \quad (58)$$

It is evident that the last two expressions are symmetrical and can be derived from each other by the substitutions A → B, B → A, $\alpha_1 \rightarrow \beta_1$, and $\alpha_2 \rightarrow \beta_2$. The symmetry is valid also for the other possible expressions for α_2 and β_2.

Table 1. Experimental Data and Calculated Values by the Terminal and Suggested Models of the Mole Fractions of the Compositional Triads for S–M Copolymers, Obtained at Different Monomer Feeds [Δ (%) = $(m_{ijk}^{exp} - m_{ijk}^{calc}) \times 10^2/m_{ijk}^{exp}$ (i, j, k = S, M)]

no.	mole fraction of S in monomer feed	triads	mole fraction of the compositional triads				
			exp[11]	calc by terminal model[7]	Δ (%)	calc by suggested model	Δ (%)
1	0.40	MMM		0.08_2			
		MMS		0.26_4			
		SMS		0.20_4			
		SSS	0.10_8	0.03_1	71.3	0.09_0	16.7
		SSM	0.24_2	0.17_1	29.3	0.24_0	0.8
		MSM	0.10_0	0.24_8	−148.0	0.12_0	−20.0
2	0.45	MMM	0.14_0	0.06_0	58.0	0.14_0	0.0
		MMS	0.24_0	0.23_0	4.2	0.24_0	0.0
		SMS	0.13_0	0.22_0	−73.2	0.13_0	0.0
		SSS	0.11_0	0.04_9	54.6	0.11_0	0.0
		SSM	0.26_0	0.21_1	18.8	0.26_0	0.0
		MSM	0.12_0	0.23_0	−88.5	0.12_0	0.0
3	0.50	MMM	0.08_3	0.04_2	49.4	0.11_0	−33.7
		MMS	0.22_5	0.19_3	14.2	0.22_2	1.3
		SMS	0.15_2	0.22_5	−48.0	0.13_8	9.2
		SSS	0.14_0	0.06_5	53.6	0.13_5	−3.6
		SSM	0.27_6	0.23_2	15.9	0.27_7	0.4
		MSM	0.12_4	0.24_3	−96.0	0.11_8	0.6
4	0.60	MMM		0.02_1			
		MMS		0.14_3			
		SMS		0.25_6			
		SSS	0.16_8	0.11_6	16.5	0.18_9	−12.5
		SSM	0.31_9	0.28_4	9.3	0.30_4	4.7
		MSM	0.09_3	0.18_0	−40.6	0.09_7	−4.3

Only two linear-independent relationships between experimentally determined mole fractions of the compositional triads are used when the probabilities P_{AA} (54) and P_{BB} (55) are determined. The other three relationships are (56)–(58). It is clear that they define a correspondence between planes (α_1, β_1) and (α_2, β_2). Therefore each point (α_1, β_1) of the rectangle ($P_{AA} \le \alpha_1 \le 1$, $P_{BB} \le \beta_1 \le 1$) corresponds to one set of values for α_1 and β_1, i.e., for unknown probabilities $\hat{P}_{AB}$ and $\hat{P}_{BA}$. Here it is necessary to establish a criterion for the optimum choice of the basic probability (α_1 or β_1) value. The minimum of the residual sum of squares (SS) is proposed as such a criterion.

$$\min SS = \min \sum_{M_A} \sum_{1}^{6} (m_{igk}^{exp} - m_{igk}^{calc})^2 \qquad i, g, k = A, B \tag{59}$$

where m_{igk}^{exp} and m_{igk}^{calc} are the experimental and calculated mole fractions of the compositional triads. The sum is double in order to account for the differences between the experimental and the calculated compositional triad values in copolymers, obtained for all compositions of the monomer feed (M_A is the mole fraction of monomer A in the monomer feed). It is clear that the above discussed algorithm could be achieved if the compositional triad values of at least two copolymers, obtained at different monomer feeds are determined. The P_{AA} and P_{BB} values for one of the copolymers (denoted as the "basic" one) are calculated by relations 54 and 55. The relationships $\alpha_2(\alpha_1,\beta_1)$, and $\beta_2(\alpha_1,\beta_1)$ for basic experiments are determined by eqs 57 and 58. Then a series of α_1 and β_1 values in the ranges of eqs 51 and 52 are set with a fixed step. For each point (α_1, β_1) the values of α_2 and β_2 are obtained. They are used in the calculation of the transitional probabilities (eqs 20–22 and 24–26) by applying the already determined P_{AA}, P_{BB}, the definition equations (47)–(50), and the following relationships:

$$P_{AB} = 1 + P_{AA} - \alpha_1 - \alpha_2 \tag{60}$$

$$P_{BA} = 1 + P_{BB} - \beta_1 - \beta_2 \tag{61}$$

Then the copolymerization reactivity ratios can be calculated after eqs 29–34. The fact that these ratios are the same for all monomer feeds allows their use in calculating the compositional triads for all copolymers. The inverse problem is solved in this case: the transitional probabilities (eqs 19–26) and then the mole fractions of the copolymer compositional triads (eqs 41–46) are calculated using the already determined reactivity ratios of the comonomers and their complexes. These calculated values are compared to those obtained experimentally. The procedure is run for each set α_1 and β_1. Criterion 59 allows one to choose the optimum point (α_1, β_1) and hence the optimum copolymerization reactivity ratio values. The algorithm described can be easily realized with this program.

Experimental Check of the Method

In order to check the suggested model, data for the compositional triad composition of styrene (S) and methyl methacrylate (M) copolymers[11] are used. M and S are two monomers with fairly different values of the e parameters[12] ($e_S = -0.80$, $e_M = 0.40$). These copolymers are obtained by radical bulk copolymerization with AIBN as initiator at a temperature of 60 °C.[11] The experimentally determined (by ^{13}C NMR spectroscopy) mole fractions of the compositional triads of four compositions obtained at different monomer feeds are compared to the mole fractions calculated by the terminal[11] and by the suggested models (Table 1). The basis for calculations by the suggested method is experiment no. 2 ($M_S = 0.45$). It is evident that the copolymer obtained in this case is one of the two copolymers with all experimentally determined mole fractions of the compositional triads. This is a necessary condition for the application of the method. P_{SS} and P_{MM} values for the basic experiment calculated by eqs 54 and 55 are 0.458 and 0.538, respectively. The double sum SS is minimized at the optimum α_1 and β_1 values: $\alpha_{1,opt} = 0.605$, $\beta_{1,opt} = 0.715$. α_2 and β_2 calculated by eqs 57 and 58 amount to 0.695 and 0.606, respectively. They are used for the determination of the copolymerization reactivity ratios by eqs 29–34:

$$r_{MS} = 1.81 \qquad r_{SM} = 4.09$$

$$\frac{r_{M,CM}}{K} = 3.91 \qquad \frac{r_{S,CS}}{K} = 0.98 \qquad (62)$$

$$\frac{r_{M,CS}}{K} = 1.54 \qquad \frac{r_{S,CM}}{K} = 1.70$$

It is clear that the copolymerization constants of the copolymer complex SM are determined as ratios of these constants with an unknown equilibrium complexing constant K. This is a result of the assumption that the K value is small enough to satisfy the equation [C] = K[S][M]. The reactivity ratios (62) are used for the determination of the transitional probabilities (eqs 19–26) and through them the mole fractions of the compositional triads (eqs 41–46) of the copolymers, obtained at other monomer feeds. It is evident from the data in Table 1 that the mole fractions thus calculated are closer to the experimental ones than those calculated by the terminal model. Comparison of the SS values (59), calculated from the deviation of experimentally determined mole fractions of the compositional triads with those calculated by the above mentioned methods (Table 2) leads to the same conclusion. As could be expected, there is no deviation of the experimentally obtained values from those calculated by the methods discussed for the basic experiment (Table 1, no. 2); hence, this experiment should not be taken into account when the statistical confidence of the results obtained by both methods is estimated. This statistical confidence is estimated by Hill's F-test:[13-15]

$$F_{calc} = \frac{[(SS)_{term} - (SS)_{com}]/(N_{com} - N_{term})}{(SS)_{term}/(n - N_{term})} \qquad (63)$$

where $(SS)_{term}$ and $(SS)_{com}$ are the residual sum of squares calculated by the terminal and the suggested (complex) methods, respectively, N_{term} and N_{com} are the corresponding numbers of the variable parameters in both models (N_{term} = 0, N_{com} = 2), and n is the total number of data points. If the basic experiment (no. 2) is excluded, n = 12 and $(SS)_{term}$ = 74.128; $(SS)_{com}$ = 2.336 (Table 2). Thus, according to eq 63, F_{calc} = 5.811. This value is greater than the values from the statistical tables[16] for the significance levels 0.95 ($F_{0.95}(2.12)$ = 3.88); since $F_{0.95} < F_{calc}$, the values of the compositional triads calculated by the suggested method are statistically more significant than those calculated by the terminal model for this significance level. This result proves the necessity to account for the possibility of chain propagation by comonomer complex addition to the active ends in the cases when the comonomer polarities differ from each other and especially when the differences between the values found experimentally and calculated by the terminal model compositional triad mole fractions are considerable.

The considerable statistical confidence of the mole fractions of the compositional triads calculated by the method suggested also proves the reliability of the copolymerization constants r_{MS}, $r_{M,CM}/K$, $r_{M,CS}/K$; r_{SM}, $r_{S,CM}/K$, and $r_{S,CS}/K$. The last values allow us to calculate the transition probabilities P_{AA}, $\hat{P}_{AA}$, P_{AB}, $\hat{P}_{AB}$, P_{BB}, $\hat{P}_{BB}$, P_{BA}, and $\hat{P}_{BA}$ for the copolymerization of S and M at different monomer feeds (Table 3). Using these probability values, it is possible to calculate the dependence of P(C) on the monomer feed (Table 4) by eqs 14–16 and 35. Table 3 shows the significant difference between the dependences of the comonomer addition probabilities (P_{SS}, P_{MM}, P_{MS}, P_{SM}) and the complex addition probabilities ($\hat{P}_{SS}$, $\hat{P}_{MM}$, $\hat{P}_{MS}$, $\hat{P}_{SM}$) to the propagating ends on the monomer feed. The dependences of the first type are monotonous, while those of the second type are extremal with a maximum close to the equimole comonomer composition. The same differences can be observed between the dependences of F_S and F_M on the one hand and $\hat{F}_S$ and $\hat{F}_M$ and P(C) on the other hand on the monomer feed composition.

Although the maximum value of P(C) is only 0.234, the participation of complexes in the chain propagation is responsible for the observed alternating tendency. The comonomer addition in the noncomplexed state does not contribute to the alternating sequence formation, as both r_{MS} and r_{SM} are greater than 1 (62). Since $K \ll 1$, the copolymerization constants $r_{M,CM}$, $r_{M,CS}$, $r_{S,CM}$, and $r_{S,CS}$ are smaller than 1, too. This result proves that the complex reactivities are much greater than those of the free monomers. For this reason the alternating tendency appears at much smaller complex concentrations.

The experimental data on the composition and triad fractions of the methyl acrylate (A)–1,1-diphenylethylene (D) copolymer obtained by Ito and Yamashita in a block radical copolymerization[17] provide a partial possibility for an ad-

Table 2. Residual Sum of Squares of the Differences between the Experimental and Calculated Mole Fractions of the Compositional Triads

no.	mole fraction of S in monomer feed	triads	SS × 10^3: calc by terminal model	SS × 10^3: calc by suggested model
1	0.40	MMM		
		MMS		
		SMS		
		SSS	5.929	0.324
		SSM	5.041	0.004
		MSM	21.904	0.400
2	0.45	MMM		0
		MMS		0
		SMS		0
		SSS		0
		SSM		0
		MSM		0
3	0.50	MMM	1.681	0.729
		MMS	1.024	0.009
		SMS	5.329	0.126
		SSS	5.625	0.025
		SSM	1.936	0.001
		MSM	14.161	0.036
4	0.60	MMM		
		MMS		
		SMS		
		SSS	2.704	0.441
		SSM	1.225	0.225
		MSM	7.569	0.016
			74.128[a]	2.336[a]

[a] Total sum SS.

Table 3. Calculated Transition Probabilities of S–M Copolymerization at Different Monomer Feeds

no.	M_S	P_{SS}	P_{SM}	$\hat{P}_{SS}$	$\hat{P}_{SM}$	P_{MM}	P_{MS}	$\hat{P}_{MM}$	$\hat{P}_{MS}$
1	0.1	0.21_5	0.47_3	0.19_8	0.11_4	0.86_8	0.05_3	0.02_2	0.05_7
2	0.2	0.30_6	0.30_0	0.25_0	0.14_4	0.75_8	0.10_5	0.03_9	0.09_8
3	0.3	0.37_2	0.21_2	0.26_1	0.15_5	0.66_3	0.15_7	0.05_1	0.12_9
4	0.4	0.42_9	0.15_7	0.26_3	0.15_1	0.57_8	0.21_3	0.05_9	0.15_0
5	0.5	0.48_8	0.11_9	0.24_9	0.14_4	0.49_9	0.27_5	0.06_4	0.16_2
6	0.6	0.55_4	0.09_0	0.22_6	0.13_0	0.42_2	0.34_9	0.06_5	0.16_4
7	0.7	0.63_0	0.06_6	0.19_3	0.11_1	0.34_2	0.44_1	0.06_1	0.15_6
8	0.8	0.72_3	0.04_4	0.14_8	0.08_5	0.25_4	0.56_2	0.05_2	0.13_2
9	0.9	0.84_2	0.02_3	0.08_6	0.04_9	0.14_7	0.73_3	0.03_4	0.08_6

Table 4. Dependence of the ATCR in All S, M, Ŝ, and M̂ States and of the Total Probability for the Copolymer Macromolecule Formation by the Complex Addition to the Propagating Ends (P(C)) on the Mole Fraction of S in the Monomer Feed

no.	M_S	F_S	F_M	$\hat{F}_S$	$\hat{F}_M$	P(C)
1	0.1	0.09_2	0.81_6	0.06_4	0.02_8	0.09_2
2	0.2	0.17_2	0.66_1	0.12_3	0.04_4	0.16_7
3	0.3	0.23_7	0.54_6	0.15_4	0.06_3	0.21_7
4	0.4	0.30_2	0.46_9	0.15_8	0.07_1	0.22_9
5	0.5	0.36_7	0.39_9	0.15_6	0.07_8	0.23_4
6	0.6	0.43_6	0.33_3	0.15_3	0.07_8	0.23_1
7	0.7	0.51_8	0.26_7	0.14_1	0.07_4	0.21_5
8	0.8	0.62_4	0.19_5	0.11_8	0.06_3	0.18_1
9	0.9	0.77_2	0.11_0	0.07_6	0.04_2	0.11_8

Table 5. Experimental[17] and Calculated, by Cais et al.[13] (CM) and by Suggested (SM) Models, Copolymer Composition, Triad Fractions, and Total Probability for the Copolymer Macromolecule Formation by the Complex Addition to the Propagating Ends (P(C)) for the Methyl Acrylate (A)−1,1-Diphenylethylene (D) System

		m_A			m_{AAA}			m_{AAD}			m_{ADA}			
no.	M_A	exp[17]	calc (CM)[13]	calc (SM)	exp[17]	calc (CM)[13]	calc (SM)	exp[17]	calc (CM)[13]	calc (SM)	exp[17]	calc (CM)[13]	calc (SM)	P(C)
1	0.700	0.56	0.56	0.55	0.09	0.05	0.05	0.35	0.34	0.33	0.56	0.62	0.62	0.014
2	0.854	0.61	0.61	0.61	0.16	0.13	0.14	0.44	0.46	0.46	0.40	0.41	0.40	0.013
3	0.900	0.65	0.65	0.65	0.20	0.20	0.21	0.48	0.50	0.50	0.32	0.30	0.29	0.012
4	0.930	0.68	0.68	0.69	0.28	0.29	0.30	0.52	0.50	0.51	0.20	0.22	0.20	0.011
5	0.960	0.74	0.75	0.76	0.48	0.44	0.48	0.42	0.45	0.43	0.10	0.11	0.09	0.009
6	0.984	0.85	0.85	0.87	0.70	0.69	0.72	0.23	0.28	0.25	0.07	0.03	0.03	0.005

ditional check of the model. These authors consider their data in terms of the terminal and penultimate models, the former one being preferred. Litt and Seiner[18] prove the better description of the same data by the complex participation model. This model is confirmed also by Cais et al.[13] using the direct search method for the determination of the "best-fit" reactivity ratio values ($r_i = k_{ii}/k_{ij}$, $p_i = k_{ici}/k_{icj}$, $s_i = k_{icj}/k_{ij}$; $i,j \equiv$ A, D) from the available experimental information. Their calculated $r_{A,D}$ value (9.7×10^{-2}) is smaller than that ($r_{A,D} = 28$) determined by Litt and Seiner.[18] Comparison of the copolymer composition and triad fractions (only A-centered triads) calculated by Cais et al.[13] and by the method developed in this work is shown in Table 5. The direct application of the suggested method for the calculation of the $r_{A,D}$, $r_{A,CA}$, $r_{A,CD}$, $r_{D,A}$, $r_{D,CA}$, and $r_{D,CD}$ values in this case is impossible, as experimental information is available only for A-centered triads. However, these values can be expressed by the above mentioned "best-fit" parameters: $r_{A,D} = r_A = 9.7 \times 10^{-2}$; $r_{A,CA} = r_A/P_AS_A = 5.565 \times 10^{-2}$; $r_{A,CD} = r_A/S_A = 4.62 \times 10^{-2}$; $r_{D,A} = r_D$; $r_{D,CD} = r_D/P_DS_D$; $r_{D,CA} = r_D/S_D$. Since Cais et al.[13] set $r_D = P_D = 0$, here also the very small value of 10^{-6} is assumed for $r_{D,A}$, $r_{D,CD}$, and $r_{D,CA}$. Comparison of the results included in Table 5 clearly indicates that the copolymer composition and triad fractions calculated by both methods are very close one to another and to the experimenal ones. This fact proves the reliability of eqs 18−28 and 41−50 used in the calculation by the suggested method. The advantages of the proposed model are the smaller number of parameters (two against seven) of the optimization procedure, the possibility for direct calculation of P(C) (eq 35), and last but not least, the possibility for simple expansion of the applicability of the method to three-component and multicomponent copolymerization.

Conclusion

The advantages of the proposed method reside in the direct determination of r_{AB}, r_{BA}, $r_{A,AB}/K$, $r_{A,BA}/K$, $r_{B,AB}/K$, $r_{B,BA}/K$, and P(C), the simple calculation procedure, and the more reliable initial experimental information in comparison to the dependences of copolymerization rate on monomer feed used in the other above mentioned methods.[3−5] Its application is possible if the copolymer compositional triad composition is determined. The Hill F-test used in this work is an objective criterion for the discrimination of the terminal, penultimate, and complex copolymerization models. The method offers an interesting evaluation under the assumption that the probability of the second complex component addition to the propagating end differs from unity.

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