Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

General Method for Evaluation of Alternating Tendency in Copolymerization

George Stefanov Georgiev[a]
[a] Department of Chemistry, University of Sofia, Sofia, Bulgaria

To cite this Article Georgiev, George Stefanov(1978) 'General Method for Evaluation of Alternating Tendency in Copolymerization', Journal of Macromolecular Science, Part A, 12: 8, 1175 — 1195

To link to this Article: DOI: 10.1080/00222337808063182

URL: http://dx.doi.org/10.1080/00222337808063182

J. MACROMOL. SCI.–CHEM., A12(8), pp. 1175-1195 (1978)

General Method for Evaluation of Alternating Tendency in Copolymerization

GEORGE STEFANOV GEORGIEV

Department of Chemistry
University of Sofia
Sofia, Bulgaria

ABSTRACT

A new method for deriving expressions for the mole fractions of alternating n-ads and the average lengths of the alternating sequences of n-component copolymers ($n \geq 2$) was developed based on the apparatus of finite Markov chains. These characteristics are considered as indexes of alternating tendency for n-component copolymerization. A specific property of n-component copolymerization ($n \geq 3$) compared with binary copolymerization is the fact that alternating n-ads might be constructed by two, three, or more types of monomeric units. In order to express this specific property of three and multicomponent copolymers the term, alternating order, is introduced. The method developed in the paper permits the alternating indexes to be determined differentially in dependence of alternating order. Expressions for the average lengths and the compositions of all possible alternating sequences starting with a given monomer unit and ending with unit found only at that position, are derived as well. The alternating indexes for binary radical copolymerization of styrene and methyl methacrylate and for ternary radical copolymerization of styrene, methyl methacrylate, and acrylonitrile were determined.

INTRODUCTION

The product of polymerization constants r_1r_2 is the most frequently used index for evaluation of the alternating tendency in binary copolymerization. As the value of this product tends to zero, the alternating tendency increases [1, 2]. The value of the product r_1r_2 will be zero in two cases: when one of the constants is zero, or when both of them are zero. In the first case (for $r_1 = 0$) the copolymer chain is built of isolated units of one of the monomers (M_1 in this case), separated by sequences of units of the other monomer. The average length of these sequences is greater than unity. In the second case ($r_1 = r_2 = 0$) a strictly alternating copolymer, M_1M_2-. . .-M_1M_2-, is obtained. Therefore, the condition $r_1r_2 = 0$ does not guarantee in all cases a strictly alternating copolymer formation.

I consider that the arithmetical mean length of the homoblocks -M_iM_i-. . .-M_i-M_i- (ℓ_{ii}, i = 1,2) is more convenient as an alternating tendency index for binary copolymers [3]:

$$\ell_{11,22} = \sum_{i=1}^{2} \ell_{ii}/2 = \tfrac{1}{2} \sum_{i=1}^{2} 1/(1 - P_{ii}) \tag{1}$$

where p_{ii} are the conditional probabilities for an i-monomer joining the i-propagating radical.

$$P_{ii} = r_iu_i/(1 + r_iu_i) \qquad i = 1, 2 \tag{2}$$

$$u_i = [M_i]/[M_j] \qquad i, j = 1, 2 \tag{3}$$

The more the average length $\ell_{11,22}$ is greater than unity, the weaker the alternating tendency observed. For a strictly alternating copolymer $p_{ii} = 0$, and consequently $\ell_{11,22} = 1$. The advantage of this index compared with the product of copolymerization constants r_1r_2 is that it allows one to evaluate separately the ability of alternating chaining together in the macromolecule; when $\ell_{ii} = 1$ (i = 1, 2), then the i-monomer joins in isolated position in the macromolecule; the more ℓ_{ii} is greater than unity, the weaker the ability for alternating propagation.

Both the indexes for alternating tendency described above are inconvenient when treating ternary and multicomponent copolymerization processes. Actually for the ternary copolymerization six copolymerization constants exist: r_{12}, r_{13}, r_{21}, r_{23}, r_{31}, r_{32}; the probability their product has a value tending to zero when every multiplicand alone is different from zero is greater than that for binary copolymers. The average lengths of homoblocks ℓ_{ii} (i = 1, 2, . . ., n) in this case are better indexes for alternating tendency, as they give differential evaluation for the ability of the monomers for alternating joining in the macromolecule.

These lengths, however, and to a greater extent, the product of copolymerization constants, do not express the different possibilities for alternating propagation of the macromolecule for ternary and multicomponent copolymers. In fact, even for ternary copolymers, the alternating sequences may differ, for example, in the environment of every monomer part; whether it is surrounded by two identical $\ldots M_jM_iM_j\ldots$ (i, j = 1, 2, 3; i ≠ j) or by two different $\ldots M_jM_iM_k\ldots$ (i, j, k = 1, 2, 3; i ≠ j ≠ k) monomer parts. It is clear that for quaternary and multicomponent copolymers these possibilities are much more, and the indexes for alternating propagation of macromolecule described above give no information for their realization.

In this respect, the two new alternating tendency indexes for binary copolymerization suggested by Tada, Fueno, and Furukawa [4] seem to us more suitable: the mole fractions of the diads M_1M_2 (F_{12}), M_2M_1 (F_{21}), or of triads $M_1M_2M_1$ (F_{121}), $M_2M_1M_2$ (F_{212}) and the average lengths of the alternating sequences $-M_1M_2-\ldots-M_1M_2-$ ($\ell_{12,21}$). They are easily expressed by the copolymerization constants and the monomer feed composition.

$$F_{12} = F_{21} = P_{12}P_{21}/(P_{12} + P_{21}) \tag{4}$$

$$F_{iji} = [P_{12}P_{21}/(P_{12} + P_{21})]\,P_{ji} \qquad i, j = 1, 2;\ i \neq j \tag{5}$$

$$\ell_{12,21} \approx 2/(P_{11} + P_{22}) \tag{6}$$

where the conditional probabilities p_{ii} (i = 1, 2) are determined by Eq. (2), and p_{ij} (i, j = 1, 2; i ≠ j) are determined by Eq. (7):

$$P_{ij} = 1/(1 + r_iu_i) \qquad i, j = 1, 2;\ i \neq j \tag{7}$$

It is evident that if the conditions $r_1 \to 0$ and $r_2 \to 0$ are fulfilled, then it follows $F_{12} + F_{21} \rightarrow 1$, $F_{121} + F_{212} \rightarrow 1$ and $\ell_{12,21} \rightarrow \infty$. That corresponds to the composition of a strictly alternating copolymer. The closer mole fractions $F_{12} + F_{21}$ and $F_{121} + F_{212}$ are to zero, and the nearer length $\ell_{12,21}$ is to unity, the weaker the alternating tendency observed. The relation among these indexes and the monomer feed composition is discussed in detail in the work mentioned above [4].

The method used for deriving the above mentioned indexes [Eqs. (4)-(6)] is not applicable to determination of alternating indexes of n-component copolymerization when $n \geq 3$, especially for the average lengths of the alternating sequences ($\ell_{i,j,k,\ldots,m}$) for which even binary copolymerization Eq. (6) is only a conditional equality. In the present paper this limitation is overcome by using the Markov finite chains apparatus, and expressions are obtained for alternating tendency indexes for n-component copolymerization when $n \geq 3$.

RESULTS AND DISCUSSION

Simulating the copolymerization process using the Markov finite chains is an effective method for obtaining some important characteristics of this reaction [5-7]. At first the relations for alternating indexes for binary copolymerization will be discussed by means of such a model. The mole fraction expressions F_{ij} and F_{iji} [$i, j = 1, 2$; $i \neq j$; Eqs. (4) and (5)] are easily obtained if the propagating macromolecule is simulated with a second- or third-order regular Markov chain [5]. The elements of their transition matrixes (P_2 and P_3) are the corresponding probabilities for transition from a diad (i, j) in one or from a triad (i, j, k) in another, respectively.

$$P_2 = \begin{array}{c|cccc} & (11) & (22) & (12) & (21) \\ \hline (11) & P_{11} & 0 & P_{12} & 0 \\ (22) & 0 & P_{22} & 0 & P_{21} \\ (12) & 0 & P_{22} & 0 & P_{21} \\ (21) & P_{11} & 0 & P_{12} & 0 \end{array} \qquad (8)$$

The eigenvectors of these matrixes ($\bar{\alpha}_2$ and $\bar{\alpha}_3$): $\bar{\alpha}_2 = \bar{\alpha}_2 P_2$ and $\bar{\alpha}_3 = \bar{\alpha}_3 P_3$ [5], are of interest for our study. The elements of these vectors represent the mole fractions of the diads and triads (F_{ij} and F_{iji};

$$P_3 = \begin{array}{c|cccccccc} & (111) & (222) & (112) & (122) & (221) & (211) & (121) & (212) \\ \hline (111) & P_{11} & 0 & P_{12} & 0 & 0 & 0 & 0 & 0 \\ (222) & 0 & P_{22} & 0 & 0 & P_{21} & 0 & 0 & 0 \\ (112) & 0 & 0 & 0 & P_{22} & 0 & 0 & P_{21} & 0 \\ (122) & 0 & P_{22} & 0 & 0 & P_{21} & 0 & 0 & 0 \\ (221) & 0 & 0 & 0 & 0 & 0 & P_{11} & 0 & P_{12} \\ (211) & P_{11} & 0 & P_{12} & 0 & 0 & 0 & 0 & 0 \\ (121) & 0 & 0 & 0 & 0 & 0 & P_{11} & 0 & P_{12} \\ (212) & 0 & 0 & 0 & P_{22} & 0 & 0 & P_{21} & 0 \end{array} \tag{9}$$

i, j = 1, 2; i ≠ j) in binary copolymer, and the expressions coincide with the right-hand sides of Eqs. (4) and (5).

In order to calculate the average length of the alternating sequences $-M_1M_2-\ldots-M_1M_2-$, it is necessary for the Markov absorbing chains to be applied to the regular Markov chains studied [5]. For this purpose the states corresponding to the nonalternating diads (11) and (22) are assumed as absorbing. The transition matrix of the absorbing Markov chain results from the transformation of matrix P_2 [Eq. (8)].

$$P = \begin{array}{c|cccc} & (11) & (22) & (12) & (21) \\ \hline (11) & 1 & 0 & 0 & 0 \\ (22) & 0 & 1 & 0 & 0 \\ (12) & 0 & 0 & 0 & P_{21} \\ (21) & 0 & 0 & P_{12} & 0 \end{array} \tag{10}$$

From the latter, the fundamental matrix for these absorbing Markov chain is derived: $N = (I - Q)^{-1}$, where Q is a submatrix of the matrix P mentioned above, obtained after elimination of rows and columns corresponding to the absorbing states, and I is the single matrix.

$$N = \begin{array}{c|cc} & (12) & (21) \\ \hline (12) & 1/(1 - P_{12}P_{21}) & P_{21}/(1 - P_{12}P_{21}) \\ (21) & P_{12}/(1 - P_{12}P_{21}) & 1/(1 - P_{12}P_{21}) \end{array} \tag{11}$$

The elements of this matrix (n_{ij}) determine the average number of diads of the type shown above the corresponding (j-th) column of the matrix in the alternating chain, beginning with the diad shown in the left side of the corresponding (i-th) matrix row, and finishing with one of the nonalternating diads, (11) or (22). The sum of the matrix (N) elements by rows gives respectively the average lengths (numbers of diads) of the alternating sequences M_1M_2-. . .-M_1M_2- or -M_2M_1-. . .-M_2M_1- differing in the type of the initial diad. If the single vector is denoted by $\bar{\zeta}$ then the product $N\bar{\zeta}$ gives the vector $\bar{\tau}$ with elements equal to these average lengths.

$$\bar{\tau} = \begin{array}{c|c} (12) & \multirow{2}{*}{$\begin{pmatrix} (1 + P_{21})/(1 - P_{12}P_{21}) \\ \\ (1 + P_{12})/(1 - P_{12}P_{21}) \end{pmatrix}$} \\ & \\ (21) & \end{array} \qquad (12)$$

When $r_1 \rightarrow 0$ and $r_2 \rightarrow 0$, then $P_{12} \rightarrow 1$ and $P_{21} \rightarrow 1$, and it is clear that then the average lengths of the two alternating sequences tend to infinity. This corresponds to a strictly alternating copolymer.

It should be noted that the average lengths of the alternating sequences with different initial diads (elements of the vector $\bar{\tau}$) together with their composition (elements n_{ij} of matrix N) is a further new information for the alternating chains in the binary copolymer which have not been obtained till now.

In order to obtain the expression for the average length of the alternating sequence -M_1M_2-. . .-M_1M_2- ($i \neq j$; $i, j = 1, 2$) despite their starting, it is enough to summarize the elements of the vector $\bar{\tau}$, previously multiplied by the weights, equal to the mole fractions of the corresponding initial diads in the macromolecule. In fact, this means the vector $\bar{\tau}$ must be multiplied scalarly by the vector $\bar{\pi} = (F_{12}, F_{21})$, in this case the vector of the stationary distribution of the alternating diads (12) and (21). Obviously, the number of diads in a sequence is smaller by a unit than the number of monomer units in it. Hence, the average length mentioned above expressed by the number of the monomers units will be as follows:

$$\ell_{12,21} = \bar{\pi}\,\bar{\tau} = \frac{P_{12}P_{21}}{P_{12} + P_{21}} \left(\frac{2 + P_{12} + P_{21}}{1 + P_{12}P_{21}} \right) + 1 \qquad (13)$$

For a strictly alternating copolymer, as already shown above ($r_1 \rightarrow 0$) and $r_2 \rightarrow 0$) $\ell_{12,21} \rightarrow \infty$.

Consequently by using Markov finite chains, expressions were derived for the indexes suggested by Tada, Fueno, and Furukawa [4] for the alternating tendencies of binary copolymers. Moreover, by using this method, additional information for the average lengths and composition of alternating sequences, beginning with a given initial diad can be obtained. Only simple operations of matrix algebra are used, which is another advantage of the method.

However, the main advantage of the method developed is that it allows the expressions to be obtained for similar indexes of alternating tendency of n-component copolymerization when $n \geq 3$. In this case, the alternation can be realized among 2, 3, . . . , n monomer particles. In order to describe this feature of multicomponent copolymerization the term "alternating order" should be introduced. The alternating order for n-component copolymer is determined by the number of different type particles forming the n-ads. It is evident that the maximum alternating order is n-th (all particles in the alternating n-ads are different). The minimum value of alternating order is second (alternating n-ads are composed of two different types particles).

For example, for ternary copolymer, the alternating triads of third order are (123), (132), (213), (231), (312), and (321). The triads consisting of two different types of particles where there are no two identical adjoining particles are alternating of second order. These are the triads (121), (212), (131), (313), (232), and (323). The sum of the mole fractions of the triads, mentioned earlier, determines the first alternating index for the ternary copolymer from third order. The sum of the mole fractions of the triads of the second type determines the first alternating index for the ternary copolymer from the second order. The total sum gives the first index for the general alternating of the copolymer.

To calculate these mole fractions in the ternary copolymer it is necessary for the propagating chain of the copolymer to be compared with the regular Markov chain of third order. In the case when the first alternating index for n-component copolymerization is determined, it is necessary to operate with a Markov chain of n-th order. The transition matrix of this chain is given in Eq. (14). It is evident that for a ternary copolymer six triads possess third-order alternation and six others, second-order alternation. To determine their mole fractions it is necessary to find the components of the limiting vector $\bar{\alpha} = \bar{\alpha}P$. More specifically, the components $a_{22}, a_{23}, \ldots, a_{27}$ give the mole fractions F_{123}, F_{132}, F_{213}, F_{231}, F_{321}, and F_{312} and the components $a_{16}, \ldots, a_{21}$ give the mole fractions of the triads with alternating of second order: F_{121}, F_{131}, F_{212}, F_{232}, F_{313} and F_{323}. They are expressed by the transition probabilities p_{ij} (i, j = 1, 2, 3) as follows.

$$
P=\begin{array}{c|ccccccccccccccccccccccccccc}
 & (111) & (112) & (113) & (122) & (133) & (211) & (221) & (222) & (223) & (233) & (311) & (322) & (331) & (332) & (133) & (121) & (131) & (212) & (232) & (313) & (323) & (123) & (132) & (213) & (231) & (312) & (321) \\
\hline
(111) & P_{11} & P_{12} & P_{13} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
(112) & 0 & 0 & 0 & P_{22} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{21} & 0 & 0 & 0 & 0 & 0 & P_{23} & 0 & 0 & 0 & 0 & 0 \\
(113) & 0 & 0 & 0 & 0 & P_{33} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{31} & 0 & 0 & 0 & 0 & 0 & P_{32} & 0 & 0 & 0 & 0 \\
(122) & 0 & 0 & 0 & 0 & 0 & 0 & P_{21} & P_{22} & P_{23} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
(133) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{31} & P_{32} & P_{33} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
(211) & P_{11} & P_{12} & P_{13} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
(221) & 0 & 0 & 0 & 0 & 0 & P_{11} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{12} & 0 & 0 & 0 & 0 & 0 & P_{13} & 0 & 0 & 0 \\
(222) & 0 & 0 & 0 & 0 & 0 & 0 & P_{21} & P_{22} & P_{23} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
(223) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{33} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{32} & 0 & 0 & 0 & 0 & 0 & P_{31} & 0 & 0 \\
(233) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{31} & P_{32} & P_{33} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
(311) & P_{11} & P_{12} & P_{13} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
(312) & 0 & 0 & 0 & 0 & 0 & 0 & P_{21} & P_{22} & P_{23} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
(331) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{11} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{13} & 0 & 0 & 0 & 0 & 0 & P_{12} & 0 \\
(322) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{22} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{23} & 0 & 0 & 0 & 0 & 0 & P_{21} \\
(333) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{31} & P_{32} & P_{33} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
(121) & 0 & 0 & 0 & 0 & 0 & P_{11} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{12} & 0 & 0 & 0 & 0 & 0 & P_{13} & 0 & 0 & 0 \\
(131) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{11} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{13} & 0 & 0 & 0 & 0 & 0 & P_{12} & 0 \\
(212) & 0 & 0 & 0 & P_{22} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{21} & 0 & 0 & 0 & 0 & 0 & P_{23} & 0 & 0 & 0 & 0 & 0 \\
(232) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{22} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{23} & 0 & 0 & 0 & 0 & 0 & P_{21} \\
(313) & 0 & 0 & 0 & 0 & P_{33} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{31} & 0 & 0 & 0 & 0 & 0 & P_{32} & 0 & 0 & 0 & 0 \\
(323) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{33} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{32} & 0 & 0 & 0 & 0 & 0 & P_{31} & 0 & 0 \\
(123) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{33} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{32} & 0 & 0 & 0 & 0 & 0 & P_{31} & 0 & 0 \\
(132) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{22} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{23} & 0 & 0 & 0 & 0 & 0 & P_{21} \\
(213) & 0 & 0 & 0 & 0 & P_{33} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{31} & 0 & 0 & 0 & 0 & 0 & P_{32} & 0 & 0 & 0 & 0 \\
(231) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{11} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{13} & 0 & 0 & 0 & 0 & 0 & P_{12} & 0 \\
(312) & 0 & 0 & 0 & P_{22} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{21} & 0 & 0 & 0 & 0 & 0 & P_{23} & 0 & 0 & 0 & 0 & 0 \\
(321) & 0 & 0 & 0 & 0 & 0 & P_{11} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_{12} & 0 & 0 & 0 & 0 & 0 & P_{13} & 0 & 0 & 0
\end{array} \tag{14}
$$

For triads of third order alternation:

$$F_{1jk} = (P_{ij}P_{jk}/A) \{ P_{11} + P_{12}(P_{33} - P_{23}) + P_{13}(P_{22} - P_{32}) \}$$

$$j, k = 2, 3; j \neq k \qquad (15)$$

$$F_{2jk} = (P_{2j}P_{jk}/A) \{ P_{12}(1 + P_{13} + P_{33}) - P_{13}(P_{12} - P_{32}) \}$$

$$j, k = 1, 3; j \neq k \qquad (16)$$

$$F_{3jk} = (P_{3j}P_{jk}/A) \{ P_{13}(1 + P_{12} + P_{22}) - P_{12}(P_{13} - P_{23}) \}$$

$$j, k = 1, 2; j \neq k \qquad (17)$$

For triads of second-order alternation:

$$F_{1j1} = (P_{1j}P_{j1}/A) \{ P_{11} + P_{12}(P_{33} - P_{23}) + P_{13}(P_{22} - P_{32}) \}$$

$$j = 2, 3 \qquad (18)$$

$$F_{2j2} = (P_{2j}P_{j2}/A) \{ P_{12}(1 + P_{13} - P_{33}) - P_{13}(P_{12} - P_{32}) \}$$

$$j = 1, 3 \qquad (19)$$

$$F_{3j3} = (P_{3j}P_{j3}/A) \{ P_{13}(1 + P_{12} - P_{22}) - P_{12}(P_{13} - P_{23}) \}$$

$$j = 1, 2 \qquad (20)$$

In the above expressions, A stands for the following determinant:

$$A = \begin{vmatrix} 1 + P_{12} - P_{22} & P_{12} - P_{32} \\ P_{13} - P_{23} & 1 + P_{13} - P_{33} \end{vmatrix} \qquad (21)$$

The sum

$$\sum_{\substack{i,j,k=1 \\ i \neq k; \\ i \neq j \neq k}}^{3} F_{ijk}$$

defines copolymers of third-order alternation and the sum

$$\sum_{\substack{i,k=1;\\ i\neq k}}^{3} F_{iki}$$

describes second-order alternation. It is easily shown that when $r_{ij} \to 0$ (i, j = 1, 2, 3; $i \neq j$), the total alternation of copolymer determined by the sum of mole fractions of all possible triads tends to unity. In such a way the problem for determining the first index of alternation of a ternary copolymer is solved.

Obviously the method developed allows a differential calculation of this index as a function of the alternating order in the copolymer. That is one of its advantages.

In order to determine the average lengths of the sequences consisting of third-order alternating triads ℓ_{ijk} ($i \neq j \neq k$; $i \neq k$; i, j, k = 1, 2, 3) and second-order alternating triads ℓ_{iki} ($i \neq k$; i, k = 1, 2, 3) it is necessary to apply the Markov's absorbing chains to the regular chain studied. For example, if the average length of third-order alternating sequences should be determined ℓ_{ijk} (i, j, k = 1, 2, 3, $i \neq j \neq k$, $j \neq k$), it is necessary to transform into absorbing chains all states which do not correspond to third-order alternating triads. If the absorbing state to which the chain is converted after the ending of the alternating sequence of third order is of interest, the transition matrix P_3 (here and further the subscript will show the alternating order) will be [5] as shown in Eq. (22). The absorbing state which includes all the remaining 21 states of the starting regular Markov chain (corresponding to second-order alternating or nonalternating

$$P_3 = \begin{array}{c|ccccccc} & \Pi & (123) & (132) & (213) & (231) & (312) & (321) \\ \hline \Pi & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ (123) & 0 & 0 & 0 & 0 & P_{31} & 0 & 0 \\ (132) & 0 & 0 & 0 & 0 & 0 & 0 & P_{21} \\ (213) & 0 & 0 & P_{32} & 0 & 0 & 0 & 0 \\ (231) & 0 & 0 & 0 & 0 & 0 & P_{12} & 0 \\ (312) & 0 & P_{21} & 0 & 0 & 0 & 0 & 0 \\ (321) & 0 & 0 & 0 & P_{13} & 0 & 0 & 0 \end{array} \qquad (22)$$

$$N_3 = (I - Q_3)^{-1}$$

$$= \begin{array}{c|cccccc} & (123) & (132) & (213) & (231) & (312) & (321) \\ \hline (123) & (1 - f_{123})^{-1} & 0 & 0 & P_{31}(1 - f_{123})^{-1} & P_{31}P_{32}(1 - f_{123})^{-1} & 0 \\ (132) & 0 & (1 - f_{132})^{-1} & P_{21}P_{13}(1 - f_{132})^{-1} & 0 & 0 & P_{21}(1 - f_{132})^{-1} \\ (213) & 0 & P_{32}(1 - f_{132})^{-1} & (1 - f_{132})^{-1} & 0 & 0 & P_{21}P_{32}(1 - f_{132})^{-1} \\ (231) & P_{23}P_{12}(1 - f_{123})^{-1} & 0 & 0 & (1 - f_{123})^{-1} & P_{12}(1 - f_{123})^{-1} & 0 \\ (312) & P_{32}(1 - f_{123})^{-1} & 0 & 0 & P_{23}P_{13}(1 - f_{123})^{-1} & (1 - f_{123})^{-1} & 0 \\ (321) & 0 & P_{13}P_{32}(1 - f_{132})^{-1} & P_{13}(1 - f_{132})^{-1} & 0 & 0 & (1 - f_{132})^{-1} \end{array} \qquad (23)$$

where

$$f_{ijk} = P_{ij}P_{jk}Pki \qquad i, j, k = 1, 2, 3;\ i \neq j \neq k;\ j \neq k \qquad (24)$$

triads) is defined by the symbol Π. The fundamental matrix of the absorbing Markov chain so obtained (N_3) is to be found by the same method as it is for the binary copolymers.

The elements of this matrix [Eqs. (23) and (24)] have the same meaning as have the elements of the fundamental matrix of the absorbing Markov chain which simulates the binary copolymerization [Eq. (11)]. For example, the element $n_{44} = (1 - f_{123})^{-1}$ shows the average number of triads of the type (231) in the alternating sequences beginning with the triad (231) and ending with second order alternating triad or with nonalternating triad.

The zero elements of the matrix mentioned result from a cycle formation between the third-order alternating triads, for example, (123) → (231) → (312) → (123), which excludes the formation of some triads in sequences mentioned above [triads (132), (213), and (321) in the case discussed].

The vector $\overline{\tau_3} = \overline{N_3 \zeta}$ has the following components:

$$\overline{\tau}_3 = \begin{array}{c|c} (123) & \\ (132) & \\ (213) & \\ (231) & \\ (312) & \\ (321) & \end{array} \begin{pmatrix} (1 - f_{123})^{-1}(1 + P_{31} + P_{13}P_{12}) \\ (1 - f_{132})^{-1}(1 + P_{21} + P_{21}P_{13}) \\ (1 - f_{132})^{-1}(1 + P_{32} + P_{32}P_{21}) \\ (1 - f_{123})^{-1}(1 + P_{12} + P_{12}P_{23}) \\ (1 - f_{123})^{-1}(1 + P_{32} + P_{23}P_{13}) \\ (1 - f_{132})^{-1}(1 + P_{23} + P_{13}P_{32}) \end{pmatrix} \tag{25}$$

They determine the average lengths of the third-order alternating chains (the number of triads) which have as initial triads the triad shown at the left of the vector's $\overline{\tau}_3$ components. As in the two-dimensional case, the sum $2 + \overline{\tau}_3\overline{\pi}$ (where $\overline{\pi}$ is the vector with components equal to the mole fraction of the initial diads) gives the average length (ℓ_{ijk}) (number of units).

$$\ell_{ijk}^{(3)} = 2 + \tau_3^1 F_{123} + \tau_3^2 F_{132} + \tau_3^3 F_{213} + \tau_3^4 F_{231} + \tau_3^5 F_{312} + \tau_3^6 F_{321} \qquad i, j, k = 1, 2, 3;\ i \neq j \neq k;\ i \neq k \tag{26}$$

where the τ_3^i (i = 1,. . ., 6) are the components of the vector τ_3, and F_{ijk} are the mole fractions of the corresponding triads in copolymerization chain [Eqs. (15)-(17)]. The superscript of the sumbol $\ell_{ijk}^{(3)}$ shows the alternating order.

Analogously, the expression for the average length of the second-order alternating chain is obtained. In this case the transition and fundamental matrixes of the absorbing Markov chain, the vector, and the average lengths of the alternating sequences of second order ℓ_{iji} (i, j = 1, 2, 3; i ≠ j) are expressed as in Eqs. (27)-(30).

$$P_2 = \begin{array}{c|ccccccc} & \Pi & (121) & (131) & (212) & (232) & (313) & (323) \\ \hline \Pi & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ (121) & 0 & 0 & 0 & P_{12} & 0 & 0 & 0 \\ (131) & 0 & 0 & 0 & 0 & 0 & P_{13} & 0 \\ (212) & 0 & P_{21} & 0 & 0 & 0 & 0 & 0 \\ (232) & 0 & 0 & 0 & 0 & 0 & 0 & P_{23} \\ (313) & 0 & 0 & P_{31} & 0 & 0 & 0 & 0 \\ (323) & 0 & 0 & 0 & 0 & P_{32} & 0 & 0 \end{array} \qquad (27)$$

$$N_2 = (I - Q_2)^{-1}$$

$$N_2 = \begin{array}{c|cccccc} & (121) & (131) & (212) & (232) & (313) & (323) \\ \hline (121) & (1-f_{12})^{-1} & 0 & P_{12}(1-f_{12})^{1} & 0 & 0 & 0 \\ (131) & 0 & (1-f_{31})^{-1} & 0 & 0 & P_{13}(1-f_{31})^{-1} & 0 \\ (212) & P_{21}(1-f_{12})^{-1} & 0 & (1-f_{12})^{-1} & 0 & 0 & 0 \\ (232) & 0 & 0 & 0 & (1-f_{23})^{-1} & 0 & P_{23}(1-f_{23})^{-1} \\ (313) & 0 & P_{31}(1-f_{31})^{-1} & 0 & 0 & (1-f_{31})^{-1} & 0 \\ (323) & 0 & 0 & 0 & P_{32}(1-f_{23})^{-1} & 0 & (1-f_{23})^{-1} \end{array} \qquad (28)$$

$$\bar{\tau}_2 = \begin{array}{c|c} (121) & (1 - f_{12})^{-1}(1 + P_{12}) \\ (131) & (1 - f_{31})^{-1}(1 + P_{13}) \\ (212) & (1 - f_{12})^{-1}(1 + P_{21}) \\ (232) & (1 - f_{23})^{-1}(1 + P_{23}) \\ (313) & (1 - f_{31})^{-1}(1 + P_{31}) \\ (323) & (1 - f_{23})^{-1}(1 + P_{32}) \end{array} \qquad (29)$$

$$\ell_{iji}^{(2)} = \tau_2^{\ 1}F_{121} + \tau_2^{\ 2}F_{131} + \tau_2^{\ 3}F_{212} + \tau_2^{\ 4}F_{232} + \tau_2^{\ 5}F_{313} + \tau_2^{\ 6}F_{323} \qquad i, j = 1, 2, 3;\ j \neq i \tag{30}$$

where $\tau_2^{\ i}$ ($i = 1, \ldots, 6$) are the components of the vector $\bar{\tau}_2$, F_{ijk} are the mole fractions of the second-order alternating triad [Eqs. (18)-(20)], and $f_{ij} = f_{ji} = p_{ij}p_{ji}$. The elements of the matrix N_2 and the vector $\bar{\tau}_2$ have the same interpretation as the corresponding quantities characterizing the third-order alternating chains. The zero elements of the matrix N_2 result from cyclization in the formation of second-order alternating sequences, for example, (121) → (212) → (121) and therefore $n_{12} = n_{15} = n_{14} = n_{16} = 0$.

There are no difficulties, in principle, of determining the average lengths of sequences consisting of third- as well as second-order alternating triads. However, in this case the fundamental matrix $N_{2,3}$ is of 12 range (in this case all 12 alternating triads have to be considered). It is found according to the procedure already known starting from the transition matrix P_{23} of the absorbing Markov chain. The last matrix, Eq. (31), is derived from the matrix of Eq. (14) after transformation of all states corresponding to nonalternating triads into absorbing.

$$P_{2,3} = \begin{array}{c|ccccccc|cccccc}
 & \Pi & (121) & (131) & (212) & (232) & (313) & (323) & (123) & (132) & (213) & (231) & (312) & (321) \\
\hline
\Pi & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
(121) & 0 & 0 & 0 & p_{12} & 0 & 0 & 0 & 0 & 0 & p_{13} & 0 & 0 & 0 \\
(131) & 0 & 0 & 0 & 0 & 0 & p_{13} & 0 & 0 & 0 & 0 & 0 & p_{12} & 0 \\
(212) & 0 & p_{21} & 0 & 0 & 0 & 0 & 0 & p_{23} & 0 & 0 & 0 & 0 & 0 \\
(232) & 0 & 0 & 0 & 0 & 0 & 0 & p_{23} & 0 & 0 & 0 & 0 & 0 & p_{21} \\
(313) & 0 & 0 & p_{31} & 0 & 0 & 0 & 0 & 0 & p_{32} & 0 & 0 & 0 & 0 \\
(323) & 0 & 0 & 0 & 0 & p_{32} & 0 & 0 & 0 & 0 & 0 & p_{31} & 0 & 0 \\
\hline
(123) & 0 & 0 & 0 & 0 & p_{32} & 0 & 0 & 0 & 0 & 0 & p_{31} & 0 & 0 \\
(132) & 0 & 0 & 0 & 0 & 0 & 0 & p_{23} & 0 & 0 & 0 & 0 & 0 & p_{21} \\
(213) & 0 & 0 & p_{31} & 0 & 0 & 0 & 0 & 0 & p_{32} & 0 & 0 & 0 & 0 \\
(231) & 0 & 0 & 0 & 0 & 0 & p_{13} & 0 & 0 & 0 & 0 & 0 & p_{12} & 0 \\
(312) & 0 & p_{21} & 0 & 0 & 0 & 0 & 0 & p_{23} & 0 & 0 & 0 & 0 & 0 \\
(321) & 0 & 0 & 0 & p_{12} & 0 & 0 & 0 & 0 & 0 & p_{13} & 0 & 0 & 0
\end{array} \tag{31}$$

It is convenient that this matrix be expressed in block form [Eq. (32)]:

$$P_{2,3} = \begin{array}{c|ccc} & \Pi & (iji) & (ijk) \\ \hline \Pi & 1 & 0 & 0 \\ (iji) & 0 & Q_2 & B \\ (ijk) & 0 & C & Q_3 \end{array} \tag{32}$$

where (iji) denotes in this case all possible triads of second-order alternation and (ijk) denotes all possible triads with third-order alternation. According to the Frobenius formula [8], the fundamental matrix might be expressed as in Eq. (33)

$$N_{2,3} = (I - Q_{2,3})^{-1} = \begin{pmatrix} N_2 + N_2BH^{-1}CN_2 & N_2BH^{-1} \\ \\ H^{-1}CN_2 & H^{-1} \end{pmatrix} \tag{33}$$

where

$$H = (I - Q_3) - CN_2B \tag{34}$$

and N_2 and Q_3 are the matrixes determined by the expressions (28) and (22).

The vector $\bar{\tau}_{2,3}$ will possess the components:

$$\tau_{2,3}^{i} = \sum_{j=1}^{12} n_{ij} \qquad i, j = 1, \ldots, 12 \tag{35}$$

where n_{ij}(i, j = 1, . . ., 12) are the elements of the fundamental matrix $N_{2,3}$ [Eq. (33)]. These elements are interpreted too as average lengths of alternating sequences with alternation arbitrarily chosen on the condition that their construction starts with one of the twelve alternating triads. In order to determine the average length of all possible alternating sequences composed of second-order and third-order alternating triads (independently of the starting of the sequences) it is enough to multiply the elements of $\bar{\tau}_{2,3}$ by the corresponding mole fractions of the starting triads of these sequences and to summarize these products:

$$\ell_{ijk}^{(2,3)} = 2 + \sum_{j=1}^{12} (n_{ij}F_{123} + n_{2j}F_{131} + n_{3j}F_{212} + n_{4j}F_{232}$$

$$+ n_{5j}F_{313} + n_{6j}F_{323} + n_{7j}F_{123} + n_{8j}F_{132} + n_{9j}F_{213}$$

$$+ n_{10j}F_{231} + n_{11j}F_{312} + n_{12j}F_{321}) \qquad (36)$$

The expressions obtained for ℓ_{ijk} [Eq. (26)], ℓ_{iji} [Eq. (30)] and ℓ_{ijk} [Eq. (36)] determine the average lengths of all types alternating sequences of the ternary copolymer; alternating sequences of third, second, and mixed second and third order. This fact underlines once again the greater possibilities of the method proposed for characterizing the tendency to alternation of the multicomponent copolymers.

This method is easily applicable to 4-, 5- and multicomponent copolymers. For n-component copolymer it is necessary to take into account the different (their number is n^n) n-ads. From the definition of the alternating order it follows that the formation of n-ads of n-th, (n - 1)-th . . . and second alternating order is possible. For determination of their mole fractions ($F_{i,j,\ldots,n}$) the average lengths and compositions of alternating sequences built from the above shown n-ads, the procedure already used should be applied for determination of the limiting vector from the transition matrix of regular Markov chain of n-th order simulating the copolymerization process, then the elements of the fundamental matrix (N) of the absorbing Markov chain (the latter being obtained after transformation of the states corresponding to nonalternating n-ads into absorbing ones).

The indexes above shown for binary copolymerization are determined as an illustration. In Fig. 1 the relationship of the mole fractions of the diads F_{ij} (curves 1 and 3) and of the mole fractions of the triads F_{iji} (i, j = 1, 2; i ≠ j) (curves 2, 4, and 5) versus the product of copolymerization constants are shown. Two different cases are shown when the constants are equal ($r_1 = r_2$) (curves 1 and 2) on one hand, and on the other hand when they differ from one another under the condition that $r_1 = 1.0$ (curves 3, 4, and 5). As should be expected, with the increase of the product above the mole fractions of the alternating diads and triads decrease, and the alternating tendency decreases as well. It is evident too, that in the general case the mole fractions of the alternating diads and triads on copolymerization with equal constants are higher than those of copolymerization with different constants.

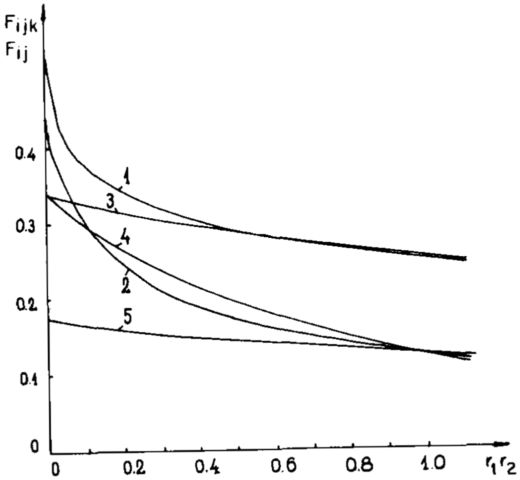

FIG. 1. Dependence of the mole fractions of the alternating diads ($F_{12} = F_{21}$) and triads (F_{121} and F_{212}) vs. the product of copolymerization constants (r_1r_2) for binary radical copolymerization of styrene (M_1) and methyl methacrylate (M_2): (1) $F_{12} = F_{21}$ (when $r_1 = r_2$); (2) $F_{121} = F_{212}$ (when $r_1 = r_2$); (3) $F_{12} = F_{21}$ (when $r_1 \neq r_2$, $r_1 =$ 1.0); (4) F_{121} (when $r_1 \neq r_2$, $r_1 = 1.0$); (5) F_{212} (when $r_1 \neq r_2$, $r_1 = 1.0$).

Figure 2 shows the relationship of the other alternating indexes (the average lengths of homoblocks and alternating sequences ℓ_{ii} and $\ell_{12,21}$; (i = 1, 2) and the copolymerization constants product. The average lengths of the homoblocks ℓ_{11} and ℓ_{22} (and consequently $\ell_{11,22}$ also) (curves 1, 3, and 4) increase, while the average lengths of alternating sequences $\ell_{12,21}$ (curves 2 and 5) decrease with increasing product of the copolymerization constants. This fact shows that these indexes are suitable for evaluation of the alternating tendency. In this case, too, for binary copolymerization with equal constants the length of the alternating sequences (curve 2) is greater than that for copolymerization with different constants (curve 5).

In Table 1 the relationships of the alternating tendency indexes (ℓ_{11}, ℓ_{22}, $\ell_{11,22}$, F_{12}, F_{21}, F_{121}, F_{212}, $\ell_{12,21}$) and the elements of the corresponding absorbing Markov chains (n_{ij}; i, j = 1, 2) versus the monomer feed composition are shown for radical copolymerization of styrene (M_1) and methyl methacrylate (M_2) at 60°C [9]. It is seen

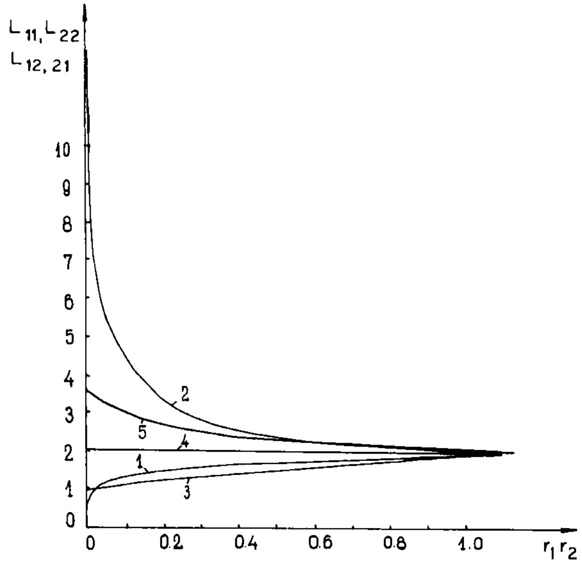

FIG. 2. Dependence of average lengths of homoblocks . . .M_iM_i. ... M_i. . . (ℓ_{ii}, i = 1, 2) and alternating sequences . . .M_1M_2. . .M_1M_2. . . ($\ell_{12,21}$) vs. product of copolymerization constants (r_1r_2) for binary radical copolymerization of styrene (M_1) and methyl methacrylate (M_2): (1) $\ell_{11} = \ell_{12}$ ($r_1 = r_2$); (2) $\ell_{12,21}$ ($r_1 = r_2$); (3) ℓ_{22}($r_1 \neq r_2$, $r_1 = 1.0$); (4) ℓ_{11} ($r_1 \neq r_2$, $r_1 = 1.0$); (5) $\ell_{12,21}$ ($r_1 = 1.0$, $r_2 \neq r_1$).

from Table 1 that the indexes $\ell_{11,22}$; $\ell_{12,21}$; $F_{12} = F_{21}$ show that the alternating tendency is most strongly expressed for equimolar monomer feed composition. The mole fractions of the alternating triads (F_{121} and F_{212}) do not give an unequivocal solution to this problem (F_{121} reaches its maximum value at $[M_1] = 0.6$ and F_{212} at $[M_1] = 0.4$). Therefore these mole fractions cannot serve as an adequate basis for evaluating the dependence of the alternating tendency on the monomer feed composition. Evidently, these data are important quantitative characteristics of the triad copolymer composition. The data for the homoblock lengths (ℓ_{11} and ℓ_{22}) have analogous meaning, while their arithmetic mean is an undeformed evaluation of alternating tendency.

TABLE 1. Changes of Average Lengths of Homoblocks . . .M_1M_1 M_1M_1. . .(l_{11}), . . .M_2M_2+. . .+M_2 . . .(l_{22}), of Their Arithmetic Means ($\ell_{11,22}$), of the Alternating Sequences . . .M_1M_2+. . .+M_1M_2. . . ($\ell_{12,21}$), of the Mole Fractions of the Alternating Diads . . .M_1M_2. . . ($F_{12} = F_{21}$), Triads . . .$M_1M_2M_1$. . . (F_{121}), . . .$M_2M_1M_2$. . .(F_{212}), and the Fundamental Matrix Elements of the Corresponding Absorbing Markov Chains (n_{ij}; i, j = 1, 2), Determining the Composition of the Alternating Sequences from the Monomer Feed Composition for Radical Copolymerization of Styrene (M_1) and Methyl Methacrylate (M_2)[a]

N	Mole fraction of M_1 in monomer feed	ℓ_{11}	ℓ_{22}	$\ell_{11,22}$	$F_{12} = F_{21}$	F_{121}	F_{212}	$\ell_{12,21}$	n_{11}	n_{12}	n_{21}	n_{22}
1	0.1	1.05	5.49	3.80	0.152	0.128	0.144	1.58	1.21	0.22	1.14	1.21
2	0.2	1.13	3.00	2.06	0.242	0.080	0.215	2.11	1.42	0.47	1.26	1.42
3	0.3	1.21	2.17	1.68	0.295	0.136	0.243	2.56	1.61	0.74	1.33	1.61
4	0.4	1.33	1.75	1.54	0.324	0.185	0.243	2.88	1.75	1.00	1.31	1.75
5	0.5	1.50	1.50	1.50	0.333	0.222	0.222	3.00	1.80	1.20	1.20	1.80
6	0.6	1.75	1.33	1.54	0.324	0.243	0.185	2.88	1.75	1.31	1.00	1.75
7	0.7	2.17	1.21	1.69	0.295	0.243	0.136	2.56	1.61	1.33	0.74	1.61
8	0.8	3.00	1.13	2.06	0.242	0.215	0.080	2.11	1.42	1.26	0.47	1.42
9	0.9	5.49	1.05	3.80	0.152	0.144	0.028	1.58	1.21	1.14	0.22	1.21

[a] Temperature T = 60°C, $r_1 = r_2 = 0.5 \pm 0.02$ [8].

The elements of the absorbing matrixes [Eq. (7)] summarized in Table 1 show the composition of different alternating sequences. For example, all elements n_{12} give the average number of diads (21) in the alternating sequences $-M_1M_2-...-M_1-M_2-$, starting with the diad (12). Evidently, the diagonal elements of this matrix read their maximum values at equimolecular feed composition, and thus they also provide undeformed evaluation for the alternating tendency.

As an example of ternary copolymerization, the above-mentioned indexes for alternation of the ternary radical copolymerization of styrene (M_1), methyl methacrylate (M_2), and acrylonitrile (M_3) at the following monomer feed compositions are calculated: $[M_1] = 0.359$; $[M_2] = 0.360$; $[M_3] = 0.281$; $r_{12} = 0.50 \pm 0.02$; $r_{13} = 0.41 \pm 0.08$; $r_{21} = 0.50 \pm 0.02$; $r_{23} = 1.20 \pm 0.14$; $r_{31} = 0.04 \pm 0.04$; $r_{32} = 0.15 \pm 0.07$ [9]. The results for the average lengths of the homoblock areas are $\ell_{11} = 1.25$; $\ell_{22} = 1.30$; $\ell_{33} = 1.02$. The greatest value for the average length of homoblocks of methyl methacrylate (ℓ_{22}) correspond to the following order of increasing products of copolymerization constants: $r_{21}r_{23} > r_{12}r_{13} > r_{31}r_{32}$.

By using Eqs. (15)-(21) the mole fractions of the third-order triads ($F_{213} = 0.071$, $F_{123} = 0.008$, $F_{132} = 0.009$, $F_{231} = 0.045$, $F_{312} = 0.119$, $F_{321} = 0.043$) and the second-order triads ($F_{212} = 0.075$, $F_{232} = 0.012$, $F_{121} = 0.025$, $F_{131} = 0.033$, $F_{313} = 0.113$, $F_{323} = 0.014$) were calculated. It is evident that the amount of triads starting from the diad (31); ($F_{312} = 0.119$, $F_{313} = 0.113$) is the highest, which may be explained by the fact that the copolymer constant $r_{31} = 0.04 \pm 0.04$ has the lowest value.

By using Eqs. (26), (30), and (36), the average lengths of alternation sequences from third ($\ell_{ijk}^{(3)} = 2.43$), second ($\ell_{iji}^{(2)} = 2.53$) and mixed second and third order ($\ell_{iji}^{(2,3)} = 2.97$) were determined. The fact that these values are smaller than 3.0 shows that a macromolecule exists which does not contain such triads. These indexes allow evaluation of the alternating tendency of various ternary copolymers from a comparison of the average lengths of alternating sequences from the corresponding order.

CONCLUSIONS

The term "alternating order" for n-component copolymer ($n \geq 3$) is proposed by means of which a more detailed evaluation of alternating tendency is reached.

By using the method of Markov finite chains, relations for alternating tendency for ternary and multicomponent copolymerization are obtained. The relation for similar indexes of binary copolymerization proved to be particular cases of the generalization stated above.

The elements of the fundamental matrixes of the corresponding absorbing Markov chains allow conclusions to be drawn for the composition of all possible alternating sequences in the copolymer.

REFERENCES

[1] T. Alfrey, J. J. Bohrer, and H. Mark, Copolymerization, Interscience, New York, 1952.

[2] G. E. Ham, Copolymerization, Interscience, New York, 1964.

[3] G. S. Georgiev, J. Macromol. Sci.–Chem., A10, 1081 (1976).

[4] K. Tada, T. Fueno, and J. Furukawa, J. Polym. Sci. A-1, 4, 2981 (1966).

[5] J. G. Kemeny and J. L. Snell, Finite Markov Chains, Princeton Univ. Press, Princeton, New Jersey, 1960.

[6] G. S. Georgiev, J. Macromol. Sci.–Chem., A10, 1063 (1976).

[7] F. P. Price, J. Chem. Phys., 36, 209 (1962).

[8] F. R. Gantmacher, Matrix Theory, Science, Moscow, 1966.

[9] F. M. Lewis, E. R. Mayo, and W. F. Hulse, J. Amer. Chem. Soc., 67, 1701 (1945).

Accepted by editor May 1, 1978
Received for publication June 6, 1978