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Use of Markov Chains in Treating Depropagation in Copolymerization. II. Distribution of Monomer Units in Copolymers

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Use of Markov Chains in Treating Depropagation in Copolymerization. II. Distribution of Monomer Units in Copolymers

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ABSTRACT

A regular Markov chain is set equivalent to n-component copolymerization ($n \geq 2$) with depropagation. It is shown that the elements of the matrix of the average times for first approach M (m_{ij}), represent the average number of units m_k ($k = 1, 2, \ldots, n; k \neq j$), occupying places between the units m_i and m_j in the macromolecules. These are the average lengths of the blocks, beginning with any monomer unit m_i and ending with any unit m_j, which however do not meet further in the block. For $n = 2$, the composition of these blocks is fully determined, because they are composed only of one type of units. When, however, $n \geq 3$, two or more types of monomer units are included in these blocks. By means of the absorbing Markov chains, expressions for the composition of these blocks when $n \geq 3$ are also obtained. In binary copolymerization the diagonal elements of the

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matrix M (m_{ij}) give the average lengths of the homoblocks $\sim m_i{-}m_i{-}\ldots{-}m_i \sim$ in the macromolecules. For the n-component copolymerization ($n \geq 3$), the elements m_{ii} do not give this information. Expressions for these lengths in this case may be obtained by additional probability analysis.

INTRODUCTION

The distribution of the monomer units in copolymers obtained in the binary copolymerization with depropagation is discussed in the works of Wittmer [1] and Mayo [2]. They have studied the copolymerization of α-methylstyrene and methyl methacrylate. The fractions of the bonds $m_i{-}m_j$ (f_{ij}) in the macromolecules are expressed by experimentally definable quantities. The probabilities for the formation of the possible sequences of units in the copolymers are determined by f_{ij}.

The use of the finite Markov chains [3] for simulation of the copolymerization with depropagation allows much more detailed information on the distribution of the monomer units in the binary copolymers to be obtained. It permits equations describing this distribution in n-component copolymers to be developed.

RESULTS AND DISCUSSION

The previous work [4] gave a solution for the fundamental matrix Z [3] for regular Markov chains, simulating an n-component ($n \geq 2$) copolymerization with depropagation. By means of the matrix Z the matrix of the average times (M) and the matrix of the dispersions ($\overline{M}$) for the first approach are determined.

For binary copolymerization with depropagation and the assumptions accepted for the previous work [4], the matrix M and $\overline{M}$ are of the type:

$$M = \begin{pmatrix} \dfrac{P_{12} + P_{21}}{P_{21}} & \dfrac{1}{P_{12}} \\ \dfrac{1}{P_{21}} & \dfrac{P_{12} + P_{21}}{P_{12}} \end{pmatrix} \qquad (1)$$

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$$\overline{M} = \begin{pmatrix} \dfrac{P_{12}(2 - P_{12} - P_{21})}{P_{21}^2} & \dfrac{1 - P_{12}}{P_{12}^2} \\ \dfrac{1 - P_{21}}{P_{21}^2} & \dfrac{P_{21}(2 - P_{12} - P_{21})}{P_{12}^2} \end{pmatrix} \qquad (2)$$

The elements of these matrix can be interpreted in the following way. The elements of the matrix M (m_{ij}) give the average number of monomer molecules that join to the growing chain of the type $\sim m_i$ until a molecule of monomer M_j is attached also. In other words, m_{ij} shows the average number of m_i units in the macromolecule after which the first m_j monomer unit is attached. The elements of the matrix $\overline{M}$ give the dispersions of these random variables.

Consequently, the mechanism used allows us not only to obtain an equation for the composition of the copolymers [4] but also gives information regarding the distribution of the monomer units in the macromolecules.

The diagonal elements of the matrix M (m_{ii}) express also increases in the unit average lengths of the blocks $\sim m_j - m_j - \ldots - m_j \sim$ in the macromolecules, provided the zero lengths of these blocks are considered in the definition. The real (without zero lengths) average lengths of these blocks can be obtained by means of the following probability analysis. Let ν_i be the probability for the formation of a sequence of i units of type m_j on the condition that such a unit is already attached to the end of the growing chain. Then:

$$\begin{aligned} \nu_1 &= 1 - P_{jj} \\ \nu_2 &= P_{jj}(1 - P_{jj}) \\ &\cdots\cdots\cdots\cdots \\ \nu_n &= P_{jj}^{n-1}(1 - P_{jj}) \end{aligned} \qquad (3)$$

In such a case, the average length of the block $\sim m_j - m_j - \ldots - m_j \sim$ $(\bar{L}_{mj})$ is equal to:

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TABLE 1. Average Lengths of Sequences $\sim m_i - m_k - \ldots - m_j \sim (j \neq i, k)$, (m_{ij}) and Their Dispersions $(\bar{m}_{ij})$ For Copolymers of α-Methylstyrene (M_1) and Methyl Methacrylate (M_2), Obtained in the Radical Polymerization at 60° C[a]

No.	M (mole %)		m_{11}	$\bar{m}_{11}$	m_{12}	$\bar{m}_{12}$	m_{21}	$\bar{m}_{21}$	m_{22}	$\bar{m}_{22}$
	In monomer mixture	In copolymer								
1	6	9.10	10.41	89.70	1.02	0.02	9.61	89.60	1.10	0.10
2	10	17.7	6.76	32.15	1.04	0.04	5.95	32.00	1.17	0.15
3	20	25.4	3.98	7.23	1.08	0.08	3.21	7.09	1.34	0.28
4	30	33.5	2.99	3.53	1.15	0.17	2.29	2.95	1.50	0.40
5	40	39.7	2.51	1.72	1.21	0.25	1.83	1.51	1.60	0.49
6	50	44.7	2.18	1.08	1.31	0.40	1.55	0.85	1.84	0.65
7	60	52.0	1.93	0.75	1.47	0.68	1.37	0.50	2.07	0.92
8	70	58.7	1.71	0.51	1.37	1.26	1.22	2.26	2.42	1.45
9	80	66.0	1.50	0.31	2.26	2.84	1.14	0.10	2.98	3.04

[a]Conditions: $r_1 = 0.30$, $r_2 = 0.55$; K = 0.14 liter/mole [1].

$$\overline{L}_{mj} = \sum_{n=1}^{\infty} nP_{jj}^{n-1}(1 - P_{jj}) = \frac{1}{1 - P_{jj}} \quad (4)$$

For the relations cited, the calculated average lengths of the possible sequences of the monomer units and their dispersions (for the copolymer of α-methylstyrene and methyl methacrylate [1]) are shown in Table 1.

It is seen from Table 1 that at 50% M_1 in the initial monomer mixture, the average length of the sequences $\sim m_2\text{–}m_2\text{–}\ldots\text{–}\underline{m_2} \sim (m_{21})$ is 1.55 units, while the dispersion of this random variable $(\overline{m}_{21})$ is 0.85.

From Eqs. (1) and (4) it is seen that in binary copolymerization the average lengths of the homoblocks $\sim m_i\text{–}m_i\text{–}\ldots\text{–}m_i \sim$ (i = 1.2) are just equal to the nondiagonal elements of the matrix M. Because of this, $\overline{L}_{m1} = m_{12}$ and $\overline{L}_{m2} = m_{21}$.

In ternary copolymerization with a possibility for depropagation of one of the monomers in conformity with assumptions in the previous work [4], the matrix M of the regular Markov chain is:

$$\overline{M} = \begin{pmatrix} \frac{1}{a_1} & \frac{A_{22} - A_{21}}{Ba_2} & \frac{A_{33} - A_{31}}{Ba_3} \\ \frac{A_{21} - A_{12}}{Ba_1} & \frac{1}{a_2} & \frac{A_{33} - A_{32}}{Ba_3} \\ \frac{A_{11} - A_{13}}{Ba_1} & \frac{A_{22} - A_{23}}{Ba_2} & \frac{1}{a_3} \end{pmatrix} \quad (5)$$

where A_{ij} and B are the cofactors and determinants of the matrix:

$$\begin{pmatrix} 1 + a_1 - P_{11} & a_2 - P_{12} & a_3 - P_{13} \\ a_1 - P_{21} & 1 + a_2 - P_{22} & a_3 - P_{23} \\ a_1 - P_{31} & a_2 - P_{32} & 1 + a_3 - P_{33} \end{pmatrix} \quad (6)$$

while a_i are the elements of the limit vector $\overline{\alpha} = (a_1, a_2, a_3)$.

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The matrix of the dispersions of times for the first approach ($\overline{M}$) cannot be presented in a general form; therefore we will try to find a numerical solution.

The interpretation of the elements of the matrix M is the same as in binary copolymerization. The difference is that units of the type m_i and m_k ($1 \leq i, j, k \leq 3$) are also included in the average number units, occupying places between m_i and m_j (equal to the element m_{ij}). With regard to this, the question arises as to the composition of these blocks, i.e., what part of the units occupying the place between m_i and m_j belong to monomer M_i and what part belong to monomer M_k? To solve this problem, the theory of the absorbing Markov chains is applied to the regular chain [3]. On considering the positions M_1, M_2, and M_3 as absorbing, three absorbing Markov chains are obtained. The other two positions in each of them are transitional. Theory [3] allows one to find the average number units of transition type in each of these chains until their transformation into the absorption position. After normalization of these numbers, the proportions of the different units in the blocks are obtained.

For example, let M_1 be the absorbing position. The composition of the statistic blocks beginning with m_2 or m_3, including only one unit m_1 in the end ($\sim m_2 m_3 m_2 \ldots m_3 m_1 \sim$ and $\sim m_3 m_2 m_3 \ldots m_2 m_1 \sim$), must be found. The transition matrix of the absorbing Markov chain thus obtained is:

$$P = \begin{array}{c} \\ M_1 \\ M_2 \\ M_3 \end{array} \begin{array}{|c} \begin{array}{ccc} M_1 & M_2 & M_3 \end{array} \\ \left(\begin{array}{ccc} 1 & 0 & 0 \\ P_{21} & P_{22} & P_{23} \\ P_{31} & P_{32} & P_{33} \end{array} \right) \end{array} \qquad (7)$$

The fundamental matrix N of the absorbing chain can be obtained on the basis of the equation, $N = (1 - Q)^{-1}$ [3], where Q is submatrix of P, obtained after the elimination of the first row and column in it, while 1 is the single matrix. In this case

$$N = \frac{1}{C} \begin{array}{|c} \begin{array}{cc} M_2 & M_3 \end{array} \\ \left(\begin{array}{cc} 1 - P_{33} & P_{23} \\ P_{32} & 1 - P_{22} \end{array} \right) \end{array} \begin{array}{l} \\ M_2 \\ M_3 \end{array} \qquad (8)$$

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where

$$C = (1 - P_{22})(1 - P_{33}) - P_{23}P_{32} \tag{9}$$

The elements of the fundamental matrix $N(n_{ij})$ represent just the average number of units of type J which would join to the growing chain of the type m_i till the attachment of the monomer M_i (i.e., until the system assumes an absorbing position). Consequently, the elements of every row are the average number of units of the type in the respective column in the statistic block beginning with that unit shown at the right of the row and ending with a unit m_1. After normalization of these elements, the desired fraction ($\bar{N}^{mi}_{mj}$) of the monomer units m_2 and m_3 in the examined blocks is obtained. The superscript in $\bar{N}^{mi}_{mj}$ denotes the initial monomer unit of the block, while the subscript shows which monomer unit is determined. In the case examined

$$\bar{N}^{m_2}_{m_2} = \frac{1 - P_{33}}{1 - P_{33} + P_{23}}$$

$$\bar{N}^{m_2}_{m_3} = \frac{P_{23}}{1 - P_{33} + P_{23}} \tag{10}$$

$$\bar{N}^{m_3}_{m_2} = \frac{P_{32}}{1 - P_{22} + P_{32}}$$

$$\bar{N}^{m_3}_{m_3} = \frac{1 - P_{22}}{1 - P_{22} + P_{32}}$$

These ratios can be written in a general form in the following way. If M_i is an absorbing position, then the fundamental matrix of the respective absorbing chain is:

$$N_i = \frac{1}{C_i} \begin{array}{c} \begin{array}{cc} M_j & M_k \end{array} \\ \left| \begin{array}{cc} 1 - P_{kk} & P_{jk} \\ P_{kj} & 1 - P_{jj} \end{array} \right| \begin{array}{l} M_j \\ M_k \end{array} \end{array} \qquad \begin{array}{l} i, j, k = 1, 2, 3 \\ j, k \neq i \end{array} \tag{11}$$

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and

$$\bar{N}_{mj}^{mj} = \frac{1 - P_{kk}}{1 - P_{kk} + P_{jk}} \qquad j, k = 1, 2, 3$$
$$\bar{N}_{mk}^{mj} = \frac{P_{jk}}{1 - P_{kk} + P_{jk}} \qquad j, k \neq i \qquad (12)$$

The dispersions of the random variable, expressing the number of monomer units in the studied statistic blocks can be found by means of the matrix of the dispersions $\bar{N}$ for the different absorbing chains [3]:

$$\bar{\bar{N}} = N\,(2N_{dg} - 1) - N_{sq}$$

The obtained results can be summarized from three aspects.

Distribution of the Monomer Units in n-Component Copolymers

From the fundamental matrix of the respective regular Markov chain [4], the following matrix M is obtained:

$$M = \begin{pmatrix} \frac{1}{a_1} & \frac{A_{22} - A_{21}}{B.a_2} & \cdots & \frac{A_{nn} - A_{n1}}{B.a_n} \\ \frac{A_{11} - A_{12}}{B.a_1} & \frac{1}{a_2} & & \frac{A_{nn} - A_{n2}}{B.a_n} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{A_{11} - A_{1n}}{B.a_1} & \frac{A_{22} - A_{2n}}{B.a_2} & \cdots & \frac{1}{a_n} \end{pmatrix} \qquad (13)$$

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Here B and A_{ij} are respectively the determinant and the cofactors of the n-dimensional matrix of the type (6). The elements of the matrix M (m_{ij}), as before, give the average length of blocks beginning with a unit m_i and ending with a unit m_j which occurs only at the end of the blocks (i, j = 1, 2, . . . , n). The composition of these blocks (the quantities $\overline{N}_{mj}^{mi}$) is determined by means of the absorbing Markov chain, as is shown for n = 3.

Case of Depropagation of n Monomer Units

The obtained results can be used also in the case when two, three, or n monomer units are able to split off the growing chain. In the previous paper [4] it was shown that in this case the forms of the transition (P) and the fundamental (Z) matrix are the same as in the case when only one type monomer unit depropagates. The difference is in the expressions for the probabilities of the transition P_{ij}, where for $n \geq 3$ two, three, or n equilibrium constants, respectively, will exist. This means that in this case the matrices M and $\overline{M}$ are obtained in the same way and give the same information as in the case when only one type of monomer unit depropagates.

Copolymerization without Depropagation

As previously mentioned, everything said for M and $\overline{M}$ can be used also when the copolymerization occurs without depropagation. In this case, the equilibrium constants K_i are eliminated in the expressions for the transition probabilities P_{ij}.

An example is the distribution of the monomer units in the tetrapolymer of styrene (M_1), methyl methacrylate (M_2), acrylonitrile (M_3), and vinylidene chloride (M_4), obtained by radical polymerization by Walling and Briggs [5]. In the previous paper [4] the transition matrix P of the regular Markov chain was calculated. The calculation of the matrix of the average times for first approach is based on Eq. (5) for n = 4. It gives information on the distribution of the monomer units in the macromolecules.

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$$M = \begin{array}{c} \\ M_1 \\ M_2 \\ M_3 \\ M_4 \end{array} \begin{array}{c} \begin{array}{cccc} M_1 & M_2 & M_3 & M_4 \end{array} \\ \begin{pmatrix} 2.43 & 3.30 & 3.67 & 13.02 \\ 1.92 & 3.64 & 4.42 & 13.33 \\ 1.41 & 3.73 & 4.10 & 14.56 \\ 1.75 & 3.66 & 4.69 & 14.29 \end{pmatrix} \end{array} \tag{14}$$

For example, the element m_{24} shows, that if we begin following the units in the macromolecule from the unit m_1, then after 13.33 monomer units for first time the unit m_4 can be met. A block containing about 13 units m_1, m_2, and m_3 is obtained. To determine this and the other 16 possible type blocks, the theory of the absorbing Markov chains is applied to the regular chain. If M_1, M_2, and M_3 are absorbing positions, then the fundamental matrices N_i of the obtained absorbing chains are:

$$N_1 = \begin{array}{c} \\ M_2 \\ M_3 \\ M_4 \end{array} \begin{array}{c} \begin{array}{ccc} M_2 & M_3 & M_4 \end{array} \\ \begin{pmatrix} 1.426 & 0.300 & 0.136 \\ 0.302 & 1.157 & 0.063 \\ 0.362 & 0.226 & 1.210 \end{pmatrix} \end{array}$$

$$N_2 = \begin{array}{c} \\ M_1 \\ M_2 \\ M_3 \end{array} \begin{array}{c} \begin{array}{ccc} M_1 & M_3 & M_4 \end{array} \\ \begin{pmatrix} 2.214 & 0.364 & 0.234 \\ 1.742 & 1.781 & 0.217 \\ 1.648 & 0.880 & 1.200 \end{pmatrix} \end{array}$$

$$N_3 = \begin{array}{c} \\ M_1 \\ M_2 \\ M_4 \end{array} \begin{array}{c} \begin{array}{ccc} M_1 & M_2 & M_4 \end{array} \\ \begin{pmatrix} 1.912 & 0.885 & 0.254 \\ 1.390 & 1.976 & 0.305 \\ 1.519 & 1.003 & 1.278 \end{pmatrix} \end{array}$$

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$$N_4 = \begin{array}{c|ccc} & M_1 & M_2 & M_3 \\ \hline M_1 & 4.823 & 2.728 & 2.608 \\ M_2 & 4.218 & 3.388 & 2.476 \\ M_3 & 4.544 & 2.776 & 3.252 \end{array} \qquad (15)$$

After normalization of the elements of these matrices on rows, the desired fractions of monomer units in the blocks $\bar{N}^{mj}_{imk}$ ($i \neq j, k$) ending with a monomer unit i while the indexes m_i and m_j are the same as previously obtained. The results obtained are given in matrix form:

$$\bar{N}_1 = \begin{array}{c|ccc} & m_2 & m_3 & m_4 \\ \hline m_2 & 0.764 & 0.162 & 0.073 \\ m_3 & 0.198 & 0.760 & 0.041 \\ m_4 & 0.201 & 0.126 & 0.673 \end{array}$$

$$\bar{N}_2 = \begin{array}{c|ccc} & m_1 & m_3 & m_4 \\ \hline m_1 & 0.787 & 0.129 & 0.083 \\ m_3 & 0.466 & 0.476 & 0.058 \\ m_4 & 0.442 & 0.236 & 0.322 \end{array}$$

$$\bar{N}_3 = \begin{array}{c|ccc} & m_1 & m_2 & m_4 \\ \hline m_1 & 0.627 & 0.280 & 0.093 \\ m_2 & 0.379 & 0.538 & 0.083 \\ m_4 & 0.400 & 0.264 & 0.336 \end{array}$$

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$$\bar{N}_4 = \begin{array}{c|ccc} & m_1 & m_2 & m_3 \\ \hline m_1 & 0.475 & 0.269 & 0.257 \\ m_2 & 0.418 & 0.336 & 0.246 \\ m_3 & 0.430 & 0.263 & 0.308 \end{array}$$

By using Eq. (4) the average lengths of the homoblocks $\sim m_i - m_i - \ldots - m_i \sim$ ($\bar{L}_{mi}$), ($1 \leq i \leq 4$) are calculated: $\bar{L}_{m1} = 1.30$; $\bar{L}_{m2} = 1.30$; $\bar{L}_{m3} = 1.03$; $\bar{L}_{m4} = 1.05$.

The studied examples show the great possibilities of using finite Markov chains for effective simulation of polymerization processes.

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