Polymer Bulletin 10, 527–532 (1983)

Polymer Bulletin

Other Determination Methods

Markov Chains Computational Method for Determination of the Copolymer Composition and Microstructure as a Function of the Conversion

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SUMMARY

A computational method is proposed for determination of the copolymer composition and microstructure dependence on the conversion on the basis of finite Markov's chains. The method is valuable because of its easy numeric realization and the possibility for a more profound characterization of the multi-component copolymers.

INTRODUCTION

Copolymer composition and microstructure dependence on the conversion is of great significance for the regulation of the copolymerization and synthesis of copolymers with desired properties. The integral relations (KOENIG 1980) employed for this aim are complex and difficult to use. In this aspect the proposed computational method (COLEMAN et al. 1982), based on the classical equations (MAYO, LEWIS 1944) is interesting. The employment of the finite Markov chains apparatus allows the development of an easy-realizable algorythm for numeric determination of the multi-component copolymer composition (dyad and tryad compositions), the lengths and compositions of the microblocks in their macromolecules, as well as the sequential homogeneity indexes for s-component (s 2) copolymers.

conversion is written on FORTRAN as well as on BASIC and a copy of it may be obtained upon request.

As an example the dependence between the composition and microstructure of N,N'-dimethylaminoethylmethacrylate (A) and vinylsulfonate (B) copolymer (GEORGIEV at al. 1983) and conversion is analysed. For binary copolymers

$$P_{AB} = [B] /(r_A[A] + [B]), \quad P_{BA} = [A] /(r_B[B] + [A]) \tag{7}$$

$$\alpha_1 = P_{BA}/(P_{AB} + P_{BA}), \quad \alpha_2 = 1 - \alpha_1 \tag{8}$$

$$M = \begin{matrix} & \begin{matrix} A & B \end{matrix} \\ \begin{matrix} A \\ B \end{matrix} & \left(\begin{matrix} (P_{AB}+P_{BA})/P_{BA}^2 & P_{AB}^{-1} \\ P_{BA}^{-1} & (P_{AB}+P_{BA})/P_{AB} \end{matrix} \right) \end{matrix} \tag{9}$$

$$M = \begin{matrix} & \begin{matrix} A & B \end{matrix} \\ \begin{matrix} A \\ B \end{matrix} & \left(\begin{matrix} P_{AB}(2-P_{AB}-P_{BA})/P_{BA}^2 & (1-P_{AB})/P_{AB}^2 \\ (1-P_{BA})/P_{BA}^2 & P_{BA}(2-P_{AB}-P_{BA})/P_{AB}^2 \end{matrix} \right) \end{matrix} \tag{10}$$

$$H = (P_{AB}P_{BA}(2-P_{AB}-P_{BA})/(P_{AB} + P_{BA})^3)^{0.5} \tag{11}$$

The parameter χ

$$\chi = \alpha_{AB}/(\alpha_A+\alpha_B) = P_{AB} + P_{BA} \tag{12}$$

which may be considered to be a measure of the deviation from randomness is introduced for these copolymers. α_{AB} is a mole fraction of the AB dyad in the copolymer chains and is determined by the relation $\bar{\alpha}P_2 = \bar{\alpha}$, $\sum_1^s \alpha_i = 1$ (P_2 -transition matrix of the second order Markov chain). For redoxinitiated copolymerization of the above mentioned monomers in water (pH = 7) $r_A = 1.00 \pm 0.05$, $r_B = 0.20 \pm 0.04$. The copolymer composition and microstructure dependence on conversion is illustrated in Table 1 and Table 2.

TABLE 1. Copolymer composition and microstructure dependence on conversion (q). $[A]_o = [B]_o = 0.5$

	mon. comp.	q	pol. comp.	χ	H	$\bar{L}_A$	$\bar{L}_B$	m_{AA}	$\bar{m}_{AA}$	m_{BB}	$\bar{m}_{BB}$
A	0.500	0.0	0.625	1.333	0.342	2.000	1.600	1.600	0.480	2.666	2.222
B	0.500		0.375								
A	0.469	0.2	0.605	1.346	0.340	1.883	1.227	1.651	0.523	2.534	1.890
B	0.531		0.395								
A	0.435	0.4	0.584	1.358	0.339	1.770	1.261	1.712	0.576	2.403	1.596
B	0.565		0.416								
A	0.398	0.6	0.561	1.370	0.336	1.661	1.302	1.784	0.643	1.783	1.336
B	0.602		0.439								
A	0.358	0.8	0.534	1.378	0.335	1.557	1.359	1.872	0.736	2.146	1.111
B	0.642		0.466								

TABLE 2. Number fractions of $(A)_n$ and $(B)_n$ sequences as a function of conversion (q)

	q	NUMBER FRACTION				
		n=1	n=2	n=3	n=4	n=5
A	0.0	0.500	0.250	0.125	0.062	0.031
B		0.833	0.139	0.023	0.004	0 0006
A	0.2	0.531	0.249	0.116	0.055	0.026
B		0.815	0.151	0.028	0.005	0.001
A	0.4	0.565	0.246	0.107	0.046	0.026
B		0.793	0.146	0.034	0.007	0.001
A	0.6	0.602	0.239	0.095	0.038	0.015
B		0.768	0.178	0.041	0.009	0.002
A	0.8	0.642	0.230	0.082	0.029	0.010
B		0.736	0.194	0.051	0.013	0.003

RESULTS AND DISCUSSION

The elements of the transition matrix (P)

$$P = \begin{array}{c} \\ A_1 \\ A_2 \\ \vdots \\ A_s \end{array} \begin{array}{c} \begin{array}{cccc} A_1 & A_2 & \cdots\cdots & A_s \end{array} \\ \begin{pmatrix} P_{A_1A_1} & P_{A_1A_2} & \cdots\cdots & P_{A_1A_s} \\ P_{A_2A_1} & P_{A_2A_2} & \cdots\cdots & P_{A_2A_s} \\ \cdots & \cdots & \cdots & \cdots \\ P_{A_sA_1} & P_{A_sA_2} & \cdots\cdots & P_{A_sA_s} \end{pmatrix} \end{array} \qquad (1)$$

of the Markov chain which simulates the propagating chain are expressed by the copolymerization constants and the molar fractions of the monomers in the monomer feed:

$$P_{A_iA_j} = [A_j] r_{ij}^{-1} / ([A_i] + \sum_{k=1}^{s} [A_k] r_{ik}^{-1}) \qquad (2)$$

The elements of the limiting vector ($\bar{\alpha}$) represent the molar fractions of the monomers in the copolymer (GEORGIEV 1976,A) and can be determined by the equations: $\bar{\alpha}P=\bar{\alpha}$ and $\sum_{1}^{s} \alpha_i = 1$. Then the algorythm for a determination of the copolymer composition dependence on the conversion (q) is reduced to a successive calculation of the iterative values of the transition probabilities $P_{A_iA_j}$ $(i,j = 1,\ldots,s)$ with the growth of the conversion by a step q. The change of these probabilities is a result of the change of $[A_i](i=1,\ldots,s)$

$$[A_i]_k = ([A_i]_o - \sum_{m=1}^{k-1} (\alpha_i)_m \Delta q)/(1 - (k-1)\Delta q) \qquad (3)$$

where k is the step number and $[A_i]_o$ is the mole fraction of the i monomer in the initial monomer feed. A similar approach is used for determination of the dyad and tryad copolymer composition dependence on the conversion. In this case second and

third order Markov chains are analyzed and the dimension of P is s^2 and s^3 respectively.

From the elements of the transition matrix, the average lengths of the homoblocks in the copolymer chain and the number and weight fractions of sequences of homoblocks with a different length are determined.

$$L_i = (1 - P_{A_iA_i})^{-1} \qquad (i = 1,\ldots,s) \qquad (4)$$

$$N_{A_i}(n) = (P_{A_iA_i})^{n-1}(1 - P_{A_iA_i}) \qquad (i = 1,\ldots,s) \qquad (5)$$

$$W_{A_i}(n) = nP_{A_iA_i}^{n-1}(1 - P_{A_iA_i})^2 \qquad (i = 1,\ldots,s) \qquad (6)$$

An advantage of the proposed method is the possibility for a more profound numeric information for the change of the microstructure from the conversion which is difficult to obtain with other methods. For example the elements of the matrix of the average times (m_{ij}) and dispersions ($\bar{m}_{ij}$) for the first approach give the lengths of the segments, located between A_i and A_j monomer units and the dispersions of these values (GEORGIEV 1976, B). The compositions of these segments when the number of the components is more than three are determined by an iterative calculation of the elements of the corresponding absorbing Markov chains (GEORGIEV 1976,B). In this way a full numeric description for the microstructure of the multi-component copolymers is obtained by means of cyclic matrix operations.

The sequential homogeneity index (H) is a general characteristic for the distribution of the monomer units. Its value is calculated by means of diagonal elements of the covariation matrix (C) of the Markov chain (GEORGIEV 1979).

The programme for calculation of the dependence of, the multi-component copolymer composition and microstructure on the

REFERENCES

J.L. KOENIG: Chemical microstructure of Polymer Chains, New York, John Wiley and Sons (1980)

M.M. COLEMAN, W.D.VARNELL: J. Chem. Ed., 59, 847 (1982)

F.R. MAYO, F.M. LEWIS: J. Americ. Chem. Soc., 66,1594 (1944)

G.S. GEORGIEV: J. Macromol. Sci.-Chem., A10(6),1063 (1976,A)

G.S.GEORGIEV: J. Macromol. Sci.-Chem., A10(6), 1081(1976,B)

G.S.GEORGIEV: Makromol. Chem., 180, 1277 (1979)

G.S.GEORGIEV, E.B.KOSEVA: To be published.

Accepted August 24, 1983