General Model of the Complex-Dissociation Radical Copolymerization

Ventsislava Toncheva GEORGIEVA and George Stefanov GEORGIEV

Department of Chemistry, University of Sofia, 1126 Sofia, Bulgaria

(Received October 7, 1996)

ABSTRACT: General model of complex radical copolymerization included the previous complex-participation and complex-dissociation models as partial cases is developed. Relationships for copolymer compositions, average lengths and dispersions of the different composition sequences, number fraction of the monomer units included into the copolymer chain as complex components are derived and applied for maleic anhydride–styrene copolymerization. Another advantage of this model is that it could be easily expanded to multicomponent complex copolymerization with any number of monomers and complexes.

KEY WORDS Regular Markov Chain / Transition Matrix / Probability of Complex Dissociation / Complex-Participation Mechanism / Complex-Dissociation Mechanism /

The complex mechanism (CM) of radical copolymerization is established for a number of monomer pairs with differences in polarity, polarisability and electron-donor ability of the comonomers.^{1–3} At first, it was supposed that both the complex components are added to the propagating radicals in one propagation step.^{4,5} This supposition is the basis of the complex-participation mechanism (CPM). In 1971 Tsuchida and Tomono⁶ assumed that the comonomer complex dissociates during the propagation step with only one of the two complex components inclusion into the propagation chain. This was the beginning of a new branching of CM, termed complex-dissociation mechanism (CDM). The latter is of special importance for weak complexes.⁷ Hill *et al.*⁸ proposed a statistical model for this mechanism. However, according to their model, there is a unity probability ($\Omega = 1$) that one of the complex components does not become incorporated into the propagating chain. Therefore, this model is opposite to the model of CPM where there is a zero value of Ω . A general model for CM with Ω -values at any point in $[0, 1]$ interval is developed in the present work. The regular Markov chain apparatus is used to this goal. Additional Markov chain states are also introduced. They corresponds to the propagating ends obtained after the incorporation of only one complex component to the growth chain. In fact, the model developed simulates a common real situation, when the complex dissociates with probability Ω ($0 \leq \Omega \leq 1$) and with a probability $1 - \Omega$ that the second complex component is also added to the propagating chain. Therefore, this model is more common than proposed previous models describing CM, and includes CPM and CDM as partial cases. This model allows a more detailed description of the complex to the propagating chain than by CPM and CDM accounting for the influence of both the second complex component and the nature of the propagating end on Ω value. Another advantage of the proposed model is that it could be expanded very easily to the multicomponent complex copolymerization with any number of monomers and complexes.

THEORETICAL BACKGROUND

The base approach of the model developed is the

simulation of the propagating copolymer chain by a regular Markov chain⁹ with the states corresponding to the different macromolecular propagating ends obtained after each step of macromolecular elongation with one monomer unit only. It means that the complex addition should be simulated by the transition to two different Markov chain states. This approach was used in our previous work concerning with the triad composition determination in the copolymers prepared by a copolymerization with complex participation.¹⁰ If 0, 1 and 0–1 (or 1–0) denote the comonomers and the complex between them, the following kinetic equations describe the propagation of the copolymer chain:

where $k_{i,j}$ are the rate constants of 0, 1, and 0–1 additions to the propagation ends of the type $\sim 0^*$ and $\sim 1^*$. However, the first steps of the complex additions (reactions 3, 4, 7, 8) yield new kinds of chain end radicals ($\sim 0^*-1$ and $\sim 1^*-0$) coupled by noncovalent bond with the second complex components. According to the model developed, these radicals dissociate with probability Ω

or incorporate the second complex component with probability $1 - \Omega$:

From a chain elongation point of view, however, the transitions ((9), (10)) are not equivalent to the transitions ((11), (12)). Transitions ((11), (12)) cause the chain to elongate by one monomer unit, while transitions ((9), (10)) do not cause such elongation. One possibility to make these two types of transitions equivalent is to associate the nonproductive transitions ((9), (10)) with the neighboring transitions: ((1)–(4)) for the transition (9),

and (5–8) for the transition (10):

Similar to Hill *et al.*⁸ the transition probabilities p_{ij} in these equations can be expressed by the comonomer and complex concentrations and the reactivity ratios:

$$p_{00} = r_0 C_0 / \Sigma 0; \quad p_{01} = C_1 / \Sigma 0; \quad (21)$$

$$p_{01^*} = s_0 C_{01} / \Sigma 0; \quad p_{00^*} q_0 C_{01} / \Sigma 0;$$

$$p_{10} = C_0 / \Sigma 1; \quad p_{11} = r_1 C_1 / \Sigma 1; \quad (22)$$

$$p_{11^*} = q_1 C_{01} / \Sigma 1; \quad p_{10^*} S_1 C_{01} / \Sigma 1;$$

where C_0 , C_1 , C_{01} (C_{10}) are 0, 1, 01(10) concentrations, respectively, denominators

$$\Sigma 0 = r_0 C_0 + C_1 + s_0 C_{01} + q_0 C_{01} \quad (23)$$

$$\Sigma 1 = C_0 + r_1 C_1 + S_1 C_{01} + q_1 C_{01}, \quad (24)$$

and reactivity ratios

$$r_0 = k_{0,0} / k_{0,1}; \quad q_0 = k_{0,01} / k_{0,1}; \quad s_0 = k_{0,10} / k_{0,1}; \quad (25)$$

$$r_1 = k_{1,1} / k_{1,0}; \quad q_1 = k_{1,10} / k_{1,0}; \quad s_1 = k_{1,01} / k_{1,0}. \quad (26)$$

The complex concentration C_{01} ($= C_{10}$) can be expressed

in terms of the equilibrium constant K and the total monomer concentrations according to the equilibrium

Let us consider the propagation chain ends $\sim 0^*$, $\sim 1^*$, $\sim 0^* - 1$ and $1^* - 0$ as states of the regular Markov chain 0, 1, 0^* , and 1^* , respectively. The associated transitions introduced above (eq 13–16 for 0^* and eq 17–20 for 1^*) allow us to describe the macromolecular propagation by a regular Markov chain¹⁰ with the following transition matrix

$$P = \begin{matrix} & \begin{matrix} 0 & 0^* & 1 & 1^* \end{matrix} \\ \begin{matrix} 0 \\ 0^* \\ 1 \\ 1^* \end{matrix} & \begin{bmatrix} p_{00} & p_{00^*} & p_{01} & p_{01^*} \\ \Omega p_{00} & \Omega p_{00^*} & 1 - \Omega + \Omega p_{01} & \Omega p_{01^*} \\ p_{10} & p_{10^*} & p_{11} & p_{11^*} \\ 1 - \Omega + \Omega p_{10} & \Omega p_{10^*} & \Omega p_{11} & \Omega p_{11^*} \end{bmatrix} \end{matrix} \quad (28)$$

The second and the fourth rows of this matrix include the association transitions introduced above from the specified states 0^* and 1^* to the other states forming the probability vectors. The components of the eigen vector of $P(\bar{\alpha}P = \bar{\alpha}; \bar{\alpha} = (\alpha_0, \alpha_{0^*}, \alpha_1, \alpha_{1^*}))$ give the mole fractions of the different types of propagating ends produced during the copolymerization. Therefore, the copolymer composition equation as a ratio of the two types of monomer units is

$$m_1 / m_0 = (\alpha_1 + \alpha_{1^*}) / (\alpha_0 + \alpha_{0^*}) = \Delta / (\Delta_0 + \Delta_{0^*}) - 1 \quad (29)$$

where:

determinants

$$\Delta = |\bar{\beta}_0, \bar{\beta}_{0^*}, \bar{\beta}_1|, \quad \Delta_0 = |\bar{\beta}, \bar{\beta}_{0^*}, \bar{\beta}_1|, \quad (30)$$

$$\Delta_{0^*} = |\bar{\beta}_0, \bar{\beta}, \bar{\beta}_1|,$$

are expressed by the transition probabilities through the column vectors

$$\bar{\beta} = ((1 - p_{10})\Omega - 1, -\Omega p_{10^*}, -\Omega p_{11})^T \quad (31)$$

$$\bar{\beta}_0 = ((1 - p_{10})\Omega + p_{00} - 2, p_{00^*} - \Omega p_{10^*}, p_{01} - \Omega p_{11})^T \quad (32)$$

$$\bar{\beta}_{0^*} = ((1 - p_{10} + p_{00})\Omega - 1, (p_{00^*} - p_{10^*})\Omega - 1, (p_{01} - p_{11} - 1)\Omega + 1)^T \quad (33)$$

$$\bar{\beta}_1 = ((1 - p_{10})\Omega + p_{10} - 1, p_{10^*}(1 - \Omega), p_{11}(1 - \Omega) - 1)^T \quad (34)$$

As could be expected, if $\Omega = 1$ eq 29 describes the copolymer chain propagation through CDM and transforms to the composition equation deduced by Hill *et al.*⁸

$$m_1 / m_0 = (p_{01} + p_{01^*}) / (p_{10} + p_{10^*}) \quad (35)$$

The CPM copolymer composition equation proposed for the first time by Seiner and Litt¹¹

$$m_1 / m_0 = [(1 - p_{00})(p_{10} - p_{11^*}) + (1 - p_{10})(p_{01} + p_{00^*})] / [(1 - p_{01})(p_{10} + p_{11^*}) + (1 - p_{11})(p_{01} + p_{00^*})] \quad (36)$$

is the other partial case (when $\Omega = 0$) of eq 29. It is

noteworthy that at the same conditions these eq 35 and 36 could be deduced directly, using the corresponding modifications of the transition matrix $\mathbf{P}$ (eq 28) and the method used. In the case when $\Omega=1$, the couples of states 0, 0* and 1, 1* become equivalent, so eq 35 can be deduced after the association of these states. This association is the precursor of the general idea used in this work.

RESULTS AND DISCUSSION

To test the Ω influence on the complex copolymerization the reactivity ratio and equilibrium constant values are necessary. They are calculated for the maleic anhydride (0)–styrene (1) bulk copolymerization at 60°C; $r_0=0.028$; $q_0=5.10-6$, $s_0=2.9$, $r_1=0.31$, $q_1=9.2$, $s_1=16.5$, and $K=2.2 \text{ dm}^3 \text{ mol}^{-1}$.⁸ Using these parameter values⁸ however, the calculated copolymer compositions at the both terminal Ω values ($\Omega=1$ for CDM and $\Omega=0$ for CPM) are very close to the experimental obtained. This is a result of the specific set of the calculated reactivity ratio values providing the dominant monomer unit alternation at $\Omega=1$, as well as at $\Omega=0$. Therefore, the copolymer composition is not Ω -sensitive. However, it appears that the sequence distribution of 1 or 0 monomer units in the initial copolymers shows such sensitivity. The number fractions of the unit 1 sequences of length 1 and 2 at $\Omega=1$ and $\Omega=0$ are quite different.⁸ The calculated number fractions of the unit 1 sequences of length 2 ($N(1^2)$) at $\Omega=0.0, 0.2, 0.5, 0.8$, and 1.0 as a function of the monomer feed composition are included in Table I. New more general relationships than that deduced by Hill *et al.*⁸ are used in this case.

$$N(1^n) = [(p_{11} + \Omega p_{11*})^{n-1}] / [(1 - \Omega)p_{10*} / (p_{01} + p_{01*})(p_{10} + p_{10*}) + (1 - p_{11} - \Omega p_{11*})], \quad n \geq 2 \quad (37)$$

$$N(1^1) = [(p_{01} + \Omega p_{01*})(p_{10} + p_{10*}) + (1 - \Omega)p_{10*}] / [(1 - \Omega)p_{10*} + (p_{01} + \Omega p_{01*})(p_{10} + p_{10*}) \times (1 - p_{11} - \Omega p_{11*})^{-1}] \quad (38)$$

They turn to the Hill's equations⁸ if $\Omega=1$

$$N(1^n) = (p_{10} + p_{10*})(p_{11} + p_{11*})^{n-1}, \quad (39)$$

while if $\Omega=0$, the relationships obtained

Table I. Number fraction of the 0110 sequences in the maleic anhydride (0)–styrene (1) copolymers produced by a bulk radical copolymerization at 60°C as a function of the 1 mol fraction in the monomer feed (M_1) and the complex dissociation probability (Ω) values

M_1	0110 number fraction				
	$\Omega=1.0$	$\Omega=0.8$	$\Omega=0.5$	$\Omega=0.2$	$\Omega=0.0$
0.1	0.179	0.139	0.073	0.021	0.001
0.2	0.208	0.159	0.083	0.022	0.001
0.4	0.224	0.171	0.091	0.028	0.003
0.5	0.227	0.176	0.096	0.031	0.005
0.6	0.230	0.180	0.113	0.036	0.007
0.8	0.238	0.192	0.120	0.058	0.025
0.9	0.246	0.210	0.181	0.094	0.061

$$N(1^n) = p_{11}^{n-1} / [(1 - p_{11})^{-1} + p_{10*} / p_{01}(p_{10} + p_{10*})] \quad n \geq 2 \quad (40)$$

$$N(1^1) = [p_{01}(p_{10} + p_{10*}) + p_{10*}] / [p_{10*} + p_{01}(p_{10} + p_{10*})(1 - p_{11})^{-1}] \quad n = 1 \quad (41)$$

give the values of these sequences for CPM—the other partial case of eq 37 and 38.

Another advantage of the model developed here is that it offers a basically new information about the complex copolymerization and the produced copolymers. For an example the number fraction ($P(c)$) of the copolymer monomer units which resource are the complex (01) components could be expressed through the eigen vector (α) components α_{0*} and α_{1*} mentioned above. In the most simple case when $\Omega=1$ (CDM)

$$P(c) = \alpha_{0*} + \alpha_{1*} \quad (42)$$

since the first linked to the propagating chain complex components are included into the copolymer macromolecule only ad hoc. If $\Omega \neq 1$ the second complex components are included into the copolymer chain also with a probability $1 - \Omega$. So, the general relationship for $P(c)$ is

$$P(c) = (2 - \Omega)(\alpha_{0*} + \alpha_{1*}) \quad (43)$$

It includes the both eq 42 and the relationship for CPM ($\Omega=0$) as partial cases. If $\Omega=0$ any realization of the states 0* or 1* yields an incorporation of the both complex components into the copolymer chain. The calculated through this equation $P(c)$ values at different monomer feed composition and Ω values are presented in Table II. It is clear that high $P(c)$ values depending on the both Ω values and monomer feed composition characterizes this copolymerization. A similar information is of a primary importance for the complex copolymerization control.

The composition triad formation depends on the type of the propagation chain end whether it belongs to the specified (0*, 1*) or to the nonspecified (0, 1) states. The propagating chain passes through with these two kinds of states. To account this peculiarity the frequency ratios of the specified states (σ_{0*} and σ_{1*} for 0* and 1*, respectively) are introduced. By definition σ_{0*} is the relative frequency of the realization of the 0* state among the states 0* and 1* and so, $\sigma_{0*} = 1 - \sigma_0$ (σ_0 is the frequency ratio for the nonspecified state 0). The similar ratios are introduced for the states 1* and 1 (σ_{1*} and σ_1 , respectively) also. They could be expressed by the com-

Table II. Number fraction of the monomer units included in the copolymer chains as complex components ($P(c)$) in dependence of 1 mol fraction into the monomer feed (M_1) and the complex dissociation probability Ω

Ω	$P(c)$		
	$M_1=0.2$	$M_1=0.5$	$M_1=0.8$
0.0	0.882	0.877	0.812
0.5	0.854	0.858	0.780
1.0	0.799	0.786	0.736

Table III. Number fractions of the 1-centered triads ($F_{(111)}$, $F_{(010)}$, $F_{(110+011)}$) the maleic anhydride (0)–styrene (1) copolymers as a function of the 1 mol fraction in the monomer feed (M_1) and the probability for a complex dissociation Ω

M_1	$\Omega=0.0$			$\Omega=0.5$			$\Omega=1.0$		
	$F_{(111)}$	$F_{(010)}$	$F_{(011+110)}$	$F_{(111)}$	$F_{(010)}$	$F_{(011+110)}$	$F_{(111)}$	$F_{(010)}$	$F_{(011+110)}$
0.2	0.027	0.848	0.125	0.057	0.495	0.448	0.090	0.491	0.419
0.5	0.059	0.722	0.219	0.086	0.446	0.468	0.122	0.424	0.454
0.8	0.094	0.609	0.297	0.121	0.399	0.480	0.151	0.373	0.476

ponents of the vector $\bar{\alpha}$ again: $\sigma_{0*} = \alpha_{0*}/(\alpha_{0*} + \alpha_0) = 1 - \sigma_0$ and $\sigma_{1*} = \alpha_{1*}/(\alpha_{1*} + \alpha_1) = 1 - \sigma_1$. At the same time, they allow to use the classical approach for the determination of the compositional triad number fractions.⁸ For an example, the relationships for the 1-centered composition triad number fractions are:

$$F_{(111)} = (p_{11} + p_{11*})^2 (\sigma_1 + \Omega \sigma_{1*}) \quad (44)$$

$$F_{(011+110)} = 2(p_{11} + p_{11*})(p_{10} + p_{10*})(\sigma_1 + \Omega \sigma_{1*}) + (1 - \Omega)\Omega \sigma_{1*} \quad (45)$$

$$F_{(010)} = (p_{10} + p_{10*})^2 (\sigma_1 + \Omega \sigma_{1*}) + \sigma_{1*}(1 - \Omega)^2 \quad (46)$$

The similar equations could be written also for the 0-centered triads by the substitution of the 0 index with 1 and 1 index with 0. These relationships are used for the calculation of the triad number fractions of 01 copolymers produced by the copolymerization discussed (Table III). The fraction of the alternating 010 triad increases with the decrease of the Ω value and 1 mol fraction in the monomer feed. The other two kinds of triads (111 and 110+011) are changed in an opposite direction. It is noteworthy that eq 44–46 could be derived by the simulation of the copolymer macromolecule propagation by the third order Markov chain

$$P' = \begin{matrix} & 0' & 1' \\ \begin{matrix} 0' \\ 1' \end{matrix} & \begin{bmatrix} \sigma_0(p_{00} + p_{00*}) + \sigma_{0*}\Omega(p_{00} + p_{00*}) & \sigma_0(p_{01} + p_{01*}) + \sigma_{0*}\Omega(p_{01*} + p_{01} - 1) + \sigma_{0*} \\ \sigma_1(p_{10} + p_{10*}) + \sigma_{1*}\Omega(p_{10*} + p_{10} - 1)\Omega + \sigma_{1*} & \sigma_1(p_{11} + p_{11*}) + \sigma_{1*}\Omega(p_{11} + p_{11*}) \end{bmatrix} \end{matrix} \quad (47)$$

where $0'$ and $1'$ denote the new associate states. It is clear that the P' elements are expressed through the elements of P (eq 28) and the frequency ratios σ_0 and σ_1 introduced above. The matrix M for this new consolidate Markov chain is¹¹

$$M = \begin{matrix} & 0' & 1' \\ \begin{matrix} 0' \\ 1' \end{matrix} & \begin{bmatrix} (g+h)/h & 1/g' \\ 1/h & (g+h)/g \end{bmatrix} \end{matrix} \quad (48)$$

Even so, according to the Markov chain theory¹¹ the dispersions of the sequential lengths mentioned above could be calculated as elements of the matrix

$$M^D = \begin{matrix} & 0' & 1' \\ \begin{matrix} 0' \\ 1' \end{matrix} & \begin{bmatrix} g(2-g-h)/h^2 & (1-g)/g^2 \\ (1-h)/h^2 & h(2-g-h)/g^2 \end{bmatrix} \end{matrix} \quad (49)$$

The calculated M and M^D element values are presented in Table 4. As could be expected m_{01} values are very close to unity because of the limitation of 0 homo-

also, accounting the transitions from and to any terminal composition macromolecule triad.

An unique information about the average lengths of the different kind monomer unit sequences in the copolymer chain offers the matrix of the first attainment (M)¹¹ determined on the base of the transition matrix P (eq 28). The M elements (m_{ij} ; $i, j=0, 1$) give the average number of the propagation steps for the formation of the sequences with a arbitrary initial monomer unit and terminal one added to this sequence for the first time after its start: $01^{n-1}0$ (m_{00}), $10^{n-1}1$ (m_{11}), $00^{n-1}1$ (m_{01}), and $11^{n-1}0$ (m_{10}). For the copolymer, as an end product, it is not important the history of 0 and 1 monomer units; whether they belonged to the specified (0^* , 1^*) or to non-specified (0, 1) states. To express this unification of 0 with 0^* and 1 with 1^* these states should be associated and the 4×4 transition matrix P (eq 28) transform to the following (P') 2×2 consolidated one

polymerization in this case.

CONCLUSIONS

The model developed here includes CDM and CPM as partial cases when the probability for dissociation of the complex during its addition to the propagation chain $\Omega=1$ or 0, respectively. Besides the ability to derive copolymer composition equations for complex copolymerization with all other possible Ω values, this model allows to determine also the number fraction of the monomer units included in the copolymer chain as complex components, different kinds of the composition triads, tetrads, etc., as well as the average lengths and their dispersions of the sequences with arbitrary initial and terminal monomer unit met in the sequence end for the first time after the sequence start.

The possibility to expand the application of this model in two directions is another model advantage. The first one is the model ability to offer the mentioned above information about the complex copolymerization and

Table IV. Average lengths of the $01^{n-1}0$ (m_{00}), 00^{n-1} (m_{01}), $11^{n-1}0$ (m_{10}), and $11^{n-1}1$ (m_{11}) monomer unit sequences in the macromolecule of the maleic anhydride (0)-styrene (1) copolymers produced by a bulk radical copolymerization at 60°C

M_1	Ω	m_{00}	m_{01}	m_{10}	m_{11}
0.2	0.0	1.96 ± 0.19	1.04 ± 0.04	1.00 ± 0.01	2.03 ± 0.04
	0.5	2.01 ± 0.71	1.03 ± 0.09	1.34 ± 0.46	1.77 ± 0.23
	1.0	2.36 ± 0.66	1.04 ± 0.06	1.42 ± 0.05	1.73 ± 0.26
0.5	0.0	2.20 ± 0.25	1.01 ± 0.05	1.20 ± 0.24	1.84 ± 0.15
	0.5	2.34 ± 0.41	1.01 ± 0.01	1.33 ± 0.43	1.78 ± 0.18
	1.0	2.52 ± 0.91	1.01 ± 0.09	1.54 ± 0.91	1.66 ± 0.49
1.0	0.0	2.32 ± 0.42	1.00 ± 0.01	1.32 ± 0.42	1.76 ± 0.18
	0.5	2.44 ± 0.65	1.00 ± 0.01	1.45 ± 0.65	1.69 ± 0.22
	1.0	2.63 ± 1.04	1.00 ± 0.01	1.64 ± 0.52	1.61 ± 0.21

produced copolymers in more common case, when the complex dissociation probability Ω depends on the nature of both the extracted second complex component during the complex dissociation and the chain terminal monomer unit to which the first complex component is

added. There are four different probabilities Ω_{ij} ($i, j = 0, 1$) in this case (i denotes the kind of the terminal monomer unit of the propagating chain and j denotes the kind of the extracted complex component). The Markov chain transition matrix in this, the most complex case

$$P'' = \begin{matrix} & \begin{matrix} 00 & 00^* & 10^* & 11 & 11^* & 01^* \end{matrix} \\ \begin{matrix} 00 \\ 00^* \\ 10^* \\ 11 \\ 11^* \\ 01^* \end{matrix} & \begin{bmatrix} p_{00} & p_{00^*} & 0 & p_{01} & 0 & p_{01^*} \\ \Omega_{10}p_{00} & \Omega_{10}p_{00^*} & 0 & 1 + \Omega_{10}(p_{01} - 1) & 0 & \Omega_{10}p_{01^*} \\ \Omega_{11}p_{00} & \Omega_{11}p_{00^*} & 0 & 1 + \Omega_{11}(p_{01} - 1) & 0 & \Omega_{11}p_{01^*} \\ p_{10} & 0 & p_{10^*} & p_{11} & p_{11^*} & 0 \\ 1 + \Omega_{01}(p_{10} - 1) & 0 & \Omega_{01}p_{10^*} & \Omega_{01}p_{11} & \Omega_{01}p_{11^*} & 0 \\ 1 + \Omega_{00}(p_{10} - 1) & 0 & \Omega_{00}p_{10^*} & \Omega_{00}p_{11} & \Omega_{00}p_{11^*} & 0 \end{bmatrix} \end{matrix} \quad (50)$$

where 00, 00*, 10*, 11, 11*, and 01* denotes the Markov chain states corresponding to the terminal propagation chain diads. Through the procedure described already the following copolymer composition equation is derived

$$m_1/m_0 = (\alpha_{11} + \alpha_{11^*} + \alpha_{01^*})/(\alpha_{00} + \alpha_{00^*} + \alpha_{10^*}) \\ = (\Delta_{11} + \Delta_{11^*} + \Delta_{01^*})/(\Delta - \Delta_{11} - \Delta_{11^*} - \Delta_{01^*}) \quad (51)$$

where

$$\alpha_{ij} = \Delta_{ij}/\Delta; \quad i, j = 0, 1, 0^*, 1^* \quad (52)$$

$$\Delta_{11} = |\bar{\beta}_{00}, \bar{\beta}_{00^*}, \bar{\beta}, \bar{\beta}_{11^*}, \bar{\beta}_{01^*}| \quad (53)$$

$$\Delta_{11^*} = |\bar{\beta}_{00}, \bar{\beta}_{00^*}, \bar{\beta}_{11}, \bar{\beta}, \bar{\beta}_{01^*}| \quad (54)$$

$$\Delta_{01^*} = |\bar{\beta}_{00}, \bar{\beta}_{00^*}, \bar{\beta}_{11}, \bar{\beta}_{11^*}, \bar{\beta}| \quad (55)$$

$$\Delta = |\bar{\beta}_{00}, \bar{\beta}_{00^*}, \bar{\beta}_{11}, \bar{\beta}_{11^*}, \bar{\beta}_{01^*}| \quad (56)$$

$$\bar{\beta}_{00} = (p_{00}(1 - \Omega_{11}) - 1, p_{00^*}(1 - \Omega_{11}), 1, 0, \\ p_{01^*}(1 - \Omega_{11}))^T \quad (57)$$

$$\bar{\beta}_{00^*} = (p_{00}(\Omega_{10} - \Omega_{11}) - 1, p_{00^*}(\Omega_{10} - \Omega_{11}), 1, 0, \\ p_{01^*}(\Omega_{10} - \Omega_{11}))^T \quad (58)$$

$$\bar{\beta}_{11} = (p_{10} - \Omega_{11}p_{00}, -\Omega_{11}p_{00^*}, p_{10^*} + 1, p_{11^*}, \\ -\Omega_{11}p_{01^*})^T \quad (59)$$

$$\bar{\beta}_{11^*} = (1 + \Omega_{01}(p_{01} - 1) - \Omega_{11}p_{00}, -\Omega_{11}p_{00^*}, \\ \Omega_{01}p_{10^*} + 1, \Omega_{01}p_{11^*} - 1, -\Omega_{11}p_{01^*})^T \quad (60)$$

$$\bar{\beta}_{01^*} = (1 + \Omega_{00}(p_{10} - 1) - \Omega_{11}p_{00}, -\Omega_{11}p_{00^*}, \\ \Omega_{00}p_{10^*} + 1, \Omega_{00}p_{11^*}, 1 - \Omega_{11}p_{01^*})^T \quad (61)$$

$$\bar{\beta} = (-\Omega_{11}p_{00}, -\Omega_{11}p_{00^*}, 1, 0, -\Omega_{11}p_{01^*})^T \quad (62)$$

The used in the previous section copolymer composition

eq 29 is a partial case of eq 51 when $\Omega_{00} = \Omega_{01} = \Omega_{11} = \Omega_{10} = \Omega$. By the same manner as from P (eq 28), the more general relationships for $P(c)$, number fractions of the composition triads, average lengths of the different kinds of monomer unit sequences and their dispersions could be deduced also using matrix P'' (eq 50).

The second direction for the more general application of the method developed in this work is the simulation of the multicomponent complex copolymerization with the formation of two and more complexes between the comonomers. There are not limitations. The P and P'' ranges and the calculation work will increase only.

Acknowledgment. This work was supported by the Bulgarian National Scientific Fund (Grant No. MY-XP-11/94).

REFERENCES

1. J. M. G. Cowie, "Alternating Copolymers," Plenum Press, New York, N.Y., 1985.
2. H.-J. Bae, T. Miyashita, M. Tino, and M. Matsuda, *Macromolecules*, **26**, 21 (1988).
3. P. G. Brown and K. Fujimori, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 2971 (1990).
4. J. A. Seiner and M. Litt, *Macromolecules*, **4**, 308 (1971).
5. C. U. Pittman and T. D. Rounsefell, *Macromolecules*, **8**, 46 (1975).
6. E. Tsuchida and T. Tomono, *J. Makromol. Chem.*, **141**, 265 (1971).
7. P. Karad and C. Schnider, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1137 (1978).
8. D. J. T. Hill, J. H. O'Donnell, and P. W. O'Sullivan, *Macromolecules*, **16**, 1295 (1983).
9. G. S. Georgiev, *J. Macromol. Sci.-Chem.*, **A10**(6), 1063 (1976).
10. G. S. Georgiev, *Macromolecules*, **28**, 6883 (1995).
11. J. G. Kemeny and L. Snell, "Finite Markov Chains," Princeton University Press, Princeton, New Jersey, 1960.