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## EQUILIBRIUM COPOLYMERIZATION. III. SEQUENCE DISTRIBUTION IN EQUILIBRIUM COPOLYMER

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### ABSTRACT

The sequence distributions for the copolymers generated in three cases of binary equilibrium copolymerization, including the effect of the ultimate unit, are studied theoretically. From the equilibrium sequence distribution functions, the copolymer sequence structure, the number- and weight-average sequence lengths of monomer units, the run number, the randomness parameter, and the fractions of different diads in the copolymer are derived. According to the relation between the parametric variables introduced in the formulas and the equilibrium copolymerization conditions, all of the structural sequence parameters of the resulting copolymers can be predicted from the comonomer feed composition and the equilibrium constants for initiation and propagation. Finally, the relation between the reaction temperature and the structural sequence parameters is given.

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## INTRODUCTION

In previous papers [1, 2] we derived two-dimensional molecular weight distributions and other molecular parameters of copolymers formed in three cases of binary equilibrium copolymerization with or without the effect of ultimate unit. Recently, Szwarc and Perrin [3] also presented a general treatment of equilibrium copolymerization of two or more comonomers deduced from the initial state of the system. Their treatment leads to the determination of the equilibrium concentrations of the comonomers, the molecular weight distribution of the resulting copolymers, the average composition of  $n$ -mers as a function of  $n$ , the probability of having a specified comonomer in the  $m$ th segments of  $n$ -mers, etc. It is important to determine their sequence distribution and other structural sequence parameters for the copolymers, since many of their physical properties depend profoundly on these parameters.

Alfrey and Tobolsky [4] first treated the case of an infinitely long copolymer molecule with the aid of statistics to determine the sequence distribution along the chain. Frensdorff and Pariser [5, 6] derived the compositional distribution and block-frequency distribution of copolymers containing any number of monomers by a Markov-chain approach. Sawada [7], Theil [8], Izu and O'Driscoll et al. [9, 10] studied the relation between reaction temperature and number-average sequence lengths of monomer units in a binary copolymer, and drew some important conclusions. However, the authors could not solve the problem for a general case of equilibrium copolymerization involving different mechanisms and equilibrium constants of initiation. They are also not quite clear about the relation between the copolymerization conditions and the sequence distribution and other structural sequence parameters of the resulting copolymers, and it is difficult to predict these parameters directly from the reaction conditions by the relations derived by the early authors. Thus, the problem needs to be studied more carefully.

If a clear relation between the equilibrium copolymerization conditions and the chemical microstructure of the resulting copolymers is derived, we can predict the structure of the copolymer chains formed under any given reaction conditions, and know what reaction parameters are important or negligible in the copolymerization process. Furthermore, it will make it easy for us to regulate and control the copolymerization process to optimize the structure of the resulting copolymers with desired physical properties.

In this work we rigorously derive the sequence distribution functions from the two-dimensional molecular weight distributions for three cases of binary equilibrium copolymerization with different mechanisms of initiation. On the

basis of the sequence distribution functions, we obtain several important structural sequence parameters, such as the average sequence lengths of the monomer units, the run number, the randomness parameter, the fractions of different diads in copolymer, etc. This work makes it possible for us to predict the structural sequence parameters of the equilibrium copolymer from the given reaction conditions, such as the comonomer feed composition and equilibrium constants of initiation and propagation or reaction temperature.

### I. SEQUENCE DISTRIBUTION FUNCTION OF EQUILIBRIUM COPOLYMER

There are three general cases of binary equilibrium copolymerization which are distinguished as cases I-III and were listed in Table 1 of our previous paper [1]. We shall first study the equilibrium sequence distribution of the copolymer formed in Case I. In the equilibrium copolymerization system for Case I, all the copolymers are generated from Initiator I, and there are four types of copolymer chains with different initial and final monomer units:



We designate the equilibrium concentrations of the above chains as  $N_{m,n}^1$ ,  $N_{m,n}^2$ ,  $N_{m,n}^3$ , and  $N_{m,n}^4$ , respectively, all of which contain  $m$  monomeric units of A and  $n$  of B. In a previous paper [2], when deriving the equilibrium concentrations of the copolymer chains with ultimate unit A and with B, i.e.,  $N_{m,n}^A$  and  $N_{m,n}^B$ , we obtained the following expressions for the four equilibrium concentrations,

$$N_{m,n}^1 = aI\alpha^m\beta^n \sum_{i=0}^{\min(m-1,n)} \binom{m-1}{i} \binom{n-1}{i-1} R^i, \quad (1)$$

$$N_{m,n}^2 = e_1 I\alpha^m\beta^n \sum_{i=1}^{\min(m,n)} \binom{m-1}{i-1} \binom{n-1}{i-1} R^i, \quad (2)$$

$$N_{m,n}^3 = e_2 I \alpha^m \beta^n \sum_{i=1}^{\min(m,n)} \binom{m-1}{i-1} \binom{n-1}{i-1} R^i, \quad (3)$$

$$N_{m,n}^4 = b I \alpha^m \beta^n \sum_{i=0}^{\min(m,n-1)} \binom{m-1}{i-1} \binom{n-1}{i} R^i. \quad (4)$$

All the nomenclature adopted in this paper is the same as that of the previous paper [2], namely,  $\alpha = K_{AAA}$ ,  $\beta = K_{BBB}$ ,  $a = K_A/K_{AA}$ ,  $b = K_B/K_{BB}$ ,  $e_1 = K_B/K_{AB}$ ,  $e_2 = K_A/K_{BA}$ , and  $R = K_{AB}K_{BA}/(K_{AA}K_{BB})$ . In Eqs. (1) and (4), we defined

$$\left. \binom{m-1}{i-1} \binom{n-1}{i} \right|_{\substack{m=0 \\ i=0}} = \left. \binom{m-1}{i} \binom{n-1}{i-1} \right|_{\substack{n=0 \\ i=0}} = 1. \quad (5)$$

The values of the parametric variables  $\alpha$  and  $\beta$  can be calculated from the comonomer feed composition and equilibrium constants of initiation and propagation by the method given before.

Now, we analyze the sequence distribution of the first type of copolymer chain I-A $\cdots$ A\*. In Eq. (1), index  $i$  is the number of block B in the copolymer chain. Obviously, the number of block A is  $i+1$ . Here, we define  $A_{m,n}^{i,j,k}$  as the concentration of blocks of A sequences of length  $j$  in the  $k$ th type of copolymer chain which possesses  $i$  blocks of B sequences,  $m$  monomeric units of A, and  $n$  of B. Then, it is easy to obtain the following equations,

$$A_{m,0}^{0,m,1} = a I \alpha^m, \quad (6)$$

$$A_{m,n}^{1,j,1} = 2 a I R \alpha^m \beta^n, \quad j = 1, 2, \dots, m-1, \quad (7)$$

$$A_{m,n}^{2,j,1} = 3 a I \alpha^m \beta^n R^2 \binom{m-1-j}{1} \binom{n-1}{1}, \quad j = 1, 2, \dots, m-2, \quad (8)$$

$$A_{m,n}^{3,j,1} = 4 a I \alpha^m \beta^n R^3 \binom{m-1-j}{2} \binom{n-1}{2}, \quad j = 1, 2, \dots, m-3, \quad (9)$$

The explicit expression for  $A_{m,n}^{i,j,1}$  is deduced by induction:

$$A_{m,n}^{i,j,1} = (i+1) \binom{m-1-j}{i-1} \binom{n-1}{i-1} a I \alpha^m \beta^n R^i, \quad j = 1, 2, \dots, m-i \quad (10)$$

In a similar way, we can obtain the following functions from Eqs. (2)-(4),

$$A_{m,n}^{i,j,2} = i \binom{m-1-j}{i-2} \binom{n-1}{i-1} e_1 I \alpha^m \beta^n R^i, \quad (11)$$

$$A_{m,n}^{i,j,3} = i \binom{m-1-j}{i-2} \binom{n-1}{i-1} e_2 I \alpha^m \beta^n R^i, \quad (12)$$

$$A_{m,n}^{i,j,4} = i \binom{m-1-j}{i-2} \binom{n-1}{i-1} b I \alpha^m \beta^n R^i, \quad (13)$$

where  $j = 1, 2, \dots, m-i+1$ . The concentrations of B sequences of length  $j$  in the  $k$ th type of copolymer chain that possesses  $i$  blocks of A sequences,  $m$  monomeric units of A, and  $n$  of B,  $B_{m,n}^{i,j,k}$  ( $k = 1, 2, 3, 4$ ), are deduced symmetrically,

$$B_{m,n}^{i,j,1} = i \binom{n-1-j}{i-2} \binom{m-1}{i} a I \alpha^m \beta^n R^i, \quad (14)$$

$$B_{m,n}^{i,j,2} = i \binom{n-1-j}{i-2} \binom{m-1}{i-1} e_1 I \alpha^m \beta^n R^i, \quad (15)$$

$$B_{m,n}^{i,j,3} = i \binom{n-1-j}{i-2} \binom{m-1}{i-1} e_2 I \alpha^m \beta^n R^i. \quad (16)$$

In the above three equations,  $j = 1, 2, \dots, n-i-1$ .

$$B_{m,n}^{i,j,4} = (i+1) \binom{n-1-j}{i-1} \binom{m-1}{i-1} b I \alpha^m \beta^n R^i, \quad j = 1, 2, \dots, n-i \quad (17)$$

From Eqs. (10)-(13), we can obtain the expression for the number of A sequence of length  $j$  in the resulting copolymer chain,

$$\begin{aligned} A_j &= \sum_{m,n} \sum_i \sum_{k=1}^4 A_{m,n}^{i,j,k} \\ &= F(a, b, \alpha, \beta) \cdot \alpha^{j-1} (1-\alpha)^2, \end{aligned} \quad (18)$$

where

$$F(a, b, \alpha, \beta) = \frac{I \alpha [a(1-\beta)^2 + bR\beta^2 + eR\beta(1-\beta)]}{[1-\alpha-\beta+\alpha\beta(1-R)]^2} \quad (19)$$

and  $e = e_1 + e_2$ . Equation (18) is the equilibrium distribution function of sequence **A** in the copolymer chain generated under the equilibrium copolymerization condition for Case I. The equilibrium distribution function of sequence **B** is obtained similarly:

$$B_j = \sum_{m,n} \sum_i \sum_{k=1}^4 B_{m,n}^{i,j,k} \\ = F(b, a, \beta, \alpha) \cdot \beta^{j-1} (1 - \beta)^2. \quad (20)$$

The differential distribution functions of sequences **A** and **B** result from Eqs. (18), (20), (27), and (30),

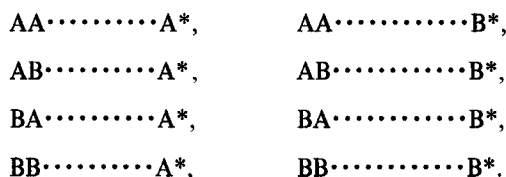
$$W_A(j) = jA_j / \sum_j jA_j = j(1 - \alpha)^2 \alpha^{j-1}, \quad (21)$$

$$W_B(j) = jB_j / \sum_j jB_j = j(1 - \beta)^2 \beta^{j-1} \quad (22)$$

Figures 1 and 2 are the differential distribution curves of sequences **A** of the copolymer chains formed under different reaction conditions. From the above distribution functions and Figs. 1 and 2, it is obvious that sequences **A** or **B** in a equilibrium copolymer chain follows the Schulz-Flory distribution, which is the same as the polymer chain formed in equilibrium homopolymerization [9, 10].

If we let  $I = 1$  in Eqs. (18) and (20), the distributions of sequence lengths of the copolymer chains formed in Case II are obtained. Equations (21) and (22) apply directly to Case II.

For Case III, there are eight types of chains, i.e.,



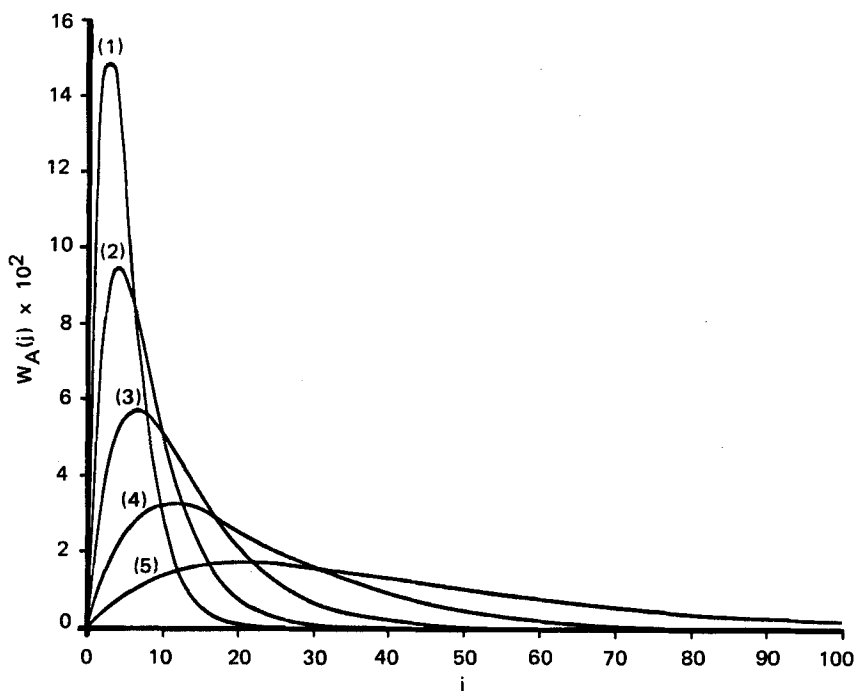


FIG. 1. Differential distribution of sequences A in the equilibrium copolymer chain formed in Case II:  $K_A = 10^{-7}$ ,  $K_B = 10^{-7}$ ,  $K_{AA} = 0.95$ ,  $K_{AB} = 0.25$ ,  $K_{BA} = 0.15$ ,  $K_{BB} = 0.15$ . (1):  $A_0 = 4$  mol/L,  $B_0 = 6$  mol/L. (2)  $A_0 = 5$  mol/L,  $B_0 = 5$  mol/L. (3):  $A_0 = 6$  mol/L,  $B_0 = 4$  mol/L. (4):  $A_0 = 7$  mol/L,  $B_0 = 3$  mol/L. (5)  $A_0 = 8$  mol/L,  $B_0 = 2$  mol/L.

Though the derivation of the distributions of sequence lengths for such a case is much more complicated, we can still obtain a comparatively simple result,

$$A_j = F(a_1, b_1, a_2, b_2, a_3, b_3, \alpha, \beta) \cdot (1 - \alpha)^2 \alpha^{j-1}, \quad (23)$$

$$B_j = F(b_1, a_1, b_2, a_2, b_3, a_3, \beta, \alpha) \cdot (1 - \beta)^2 \beta^{j-1}, \quad (24)$$

where



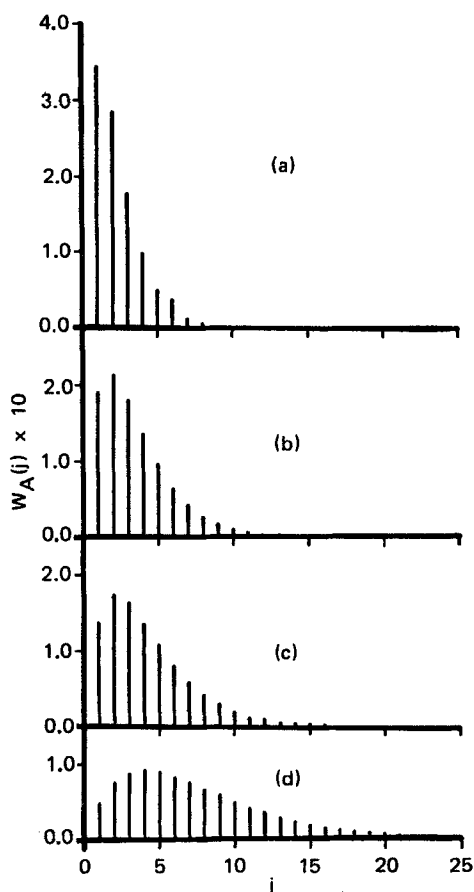


FIG. 2. Differential distribution of sequence A in the equilibrium copolymer chain formed in Case II;  $A_0 = 7.5$  mol/L,  $B_0 = 2.5$  mol/L,  $K_A = 10^{-7}$ ,  $K_B = 10^{-7}$ . (a):  $K_{AA} = 0.075$ ,  $K_{AB} = 1.5$ ,  $K_{BA} = 0.075$ ,  $K_{BB} = 1$ . (b):  $K_{AA} = 1$ ,  $K_{AB} = 2$ ,  $K_{BA} = 2$ ,  $K_{BB} = 1$ . (c):  $K_{AA} = 0.15$ ,  $K_{AB} = 0.45$ ,  $K_{BA} = 0.15$ ,  $K_{BB} = 0.35$ . (d):  $K_{AA} = 1$ ,  $K_{AB} = 5$ ,  $K_{BA} = 0.05$ ,  $K_{BB} = 0.05$ .

$$\begin{aligned}
 F(a_1, b_1, a_2, b_2, a_3, b_3, \alpha, \beta) = & \frac{\alpha}{(1-E)^2} \left\{ \alpha(2-E) \left( a_1 + \frac{a_2 R \beta}{1-\beta} \right) \right. \\
 & \left. + \frac{R \beta^2}{1-\beta} \left( b_2 + \frac{b_1 \beta}{1-\beta} \right) + \frac{a_3 R \beta}{1-\beta} \left[ (1-E)^2 + \frac{R \alpha \beta (2-E)}{1-\beta} \right] + b_3 R \beta \right\}.
 \end{aligned}
 \tag{25}$$

The definitions of  $a_1$ ,  $b_1$ ,  $a_2$ ,  $b_2$ ,  $a_3$ ,  $b_3$ , and  $E$  are identical with those given in a previous paper [2]. The differential distribution functions of sequences A and B for Case III are the same as those for Cases I and II.

## II. SOME IMPORTANT STRUCTURAL SEQUENCE PARAMETERS FOR EQUILIBRIUM COPOLYMER

In the above section we have obtained the sequence distribution functions for three cases of equilibrium copolymerization. On the basis of this, we can derive several important structural sequence parameters of the resulting copolymer. For Case I, Eq. (18) yields

$$\sum_j A_j = (1 - \alpha) F(a, b, \alpha, \beta), \tag{26}$$

$$\sum_j j A_j = F(a, b, \alpha, \beta), \tag{27}$$

$$\sum_j j^2 A_j = (1 + \alpha) F(a, b, \alpha, \beta), \tag{28}$$

and Eq. (20) results in

$$\sum_j B_j = (1 - \beta) F(b, a, \beta, \alpha), \tag{29}$$

$$\sum_j j B_j = F(b, a, \beta, \alpha), \tag{30}$$

$$\sum_j j^2 B_j = (1 + \beta) F(b, a, \beta, \alpha). \tag{31}$$

Comparing Eqs. (27) and (30) with Eqs. (13), (17), and (18) in a previous paper [2], it is easy to find the following relations,

$$\sum_j jA_j = \sum_{m,n} mN_{m,n}, \quad (32)$$

$$\sum_j jB_j = \sum_{m,n} nN_{m,n}, \quad (33)$$

which demonstrate that the results obtained here are correct. The number and weight-average sequence lengths of monomeric units **A** are derived from Eqs. (26)-(28):

$$\bar{A}_n = \frac{1}{1 - \alpha}, \quad (34)$$

$$\bar{A}_w = \frac{1 + \alpha}{1 - \alpha}. \quad (35)$$

Similarly, those of monomeric units **B** are

$$\bar{B}_n = \frac{1}{1 - \beta}, \quad (36)$$

$$\bar{B}_w = \frac{1 + \beta}{1 - \beta}. \quad (37)$$

For equilibrium homopolymerization with a multifunctional initiator [11, 12],  $1/(1 - \alpha)$  is the average number of monomers present in each arm of the star-shaped polymer, which is identical with the number-average degree of polymerization for monofunctional initiation. For binary equilibrium copolymerization, the above results demonstrate that  $1/(1 - \alpha)$  represents the average number of monomer **A** present in block **A** of copolymer chain and  $1/(1 - \beta)$  represents that of monomer **B** present in block **B**. These results are quite reasonable and reveal the physical meaning of parametric variables  $\alpha$  and  $\beta$ . Figure 3 shows the relation between the number-average sequence lengths of monomeric unit **A** and the comonomer feed composition  $f_A$  for Case II with different equilibrium constants for propagation. It is clear that increasing the initial concentration of monomer **A** causes the sequence length of monomeric unit **A** to increase.

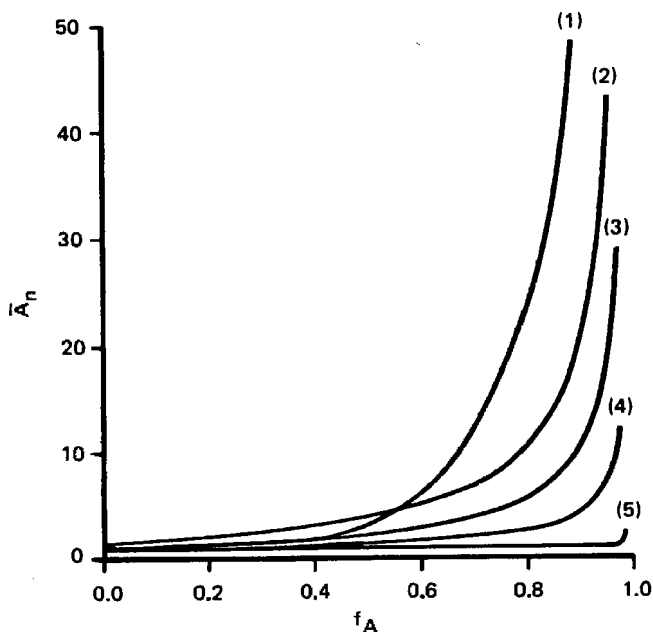


FIG. 3. Number-average sequence lengths of monomeric unit A,  $\bar{A}_n$ , versus comonomer feed composition  $f_A$  in Case II;  $(A_0 + B_0) = 10$  mol/L,  $K_A = 10^{-7}$ ,  $K_B = 10^{-7}$ . (1):  $K_{AA} = 0.2$ ,  $K_{AB} = 0.15$ ,  $K_{BA} = 0.05$ ,  $K_{BB} = 0.3$ . (2):  $K_{AA} = 1$ ,  $K_{AB} = 0.05$ ,  $K_{BA} = 1.5$ ,  $K_{BB} = 0.05$ . (3):  $K_{AA} = 1$ ,  $K_{AB} = 5$ ,  $K_{BA} = 0.05$ ,  $K_{BB} = 0.05$ . (4):  $K_{AA} = 1$ ,  $K_{AB} = 2$ ,  $K_{BA} = 2$ ,  $K_{BB} = 1$ . (5):  $K_{AA} = 0.05$ ,  $K_{AB} = 50$ ,  $K_{BA} = 50$ ,  $K_{BB} = 0.05$ .

From Eqs. (27) and (30), the mole fraction of monomer A in copolymer is obtained,

$$F_A = \frac{\sum_j jA_j}{\sum_j j(A_j + B_j)}$$

$$= \frac{\alpha[a(1-\beta)^2 + bR\beta^2 + eR\beta(1-\beta)]}{\alpha[a(1-\beta)^2 + bR\beta^2 + eR\beta(1-\beta)] + \beta[b(1-\alpha)^2 + aR\alpha^2 + eR\alpha(1-\alpha)]}, \quad (38)$$

which was derived in a different way [2]. Let (AB) represent both diads AB and BA in copolymer chains. Since it can be seen that the number of diads (AB) in a copolymer chain is the total number of blocks A and B minus one, the concentration of the diad (AB) can be expressed as

$$\begin{aligned} \sum_j j(\text{AB})_j &= \sum_j (A_j + B_j) - \sum_{m,n} N_{m,n} \\ &= \frac{IR\alpha\beta \{2a\alpha(1-\beta) + 2b\beta(1-\alpha) + e[1-\alpha-\beta + \alpha\beta \cdot (1+R)]\}}{[1-\alpha-\beta + \alpha\beta(1-R)]^2}. \end{aligned} \quad (39)$$

It is obvious that, for diad (AA),

$$\sum_j j(\text{AA})_j = \sum_j (j-1)A_j = \alpha \cdot F(a, b, \alpha, \beta), \quad (40)$$

and for diad (BB),

$$\sum_j j(\text{BB})_j = \sum_j (j-1)B_j = \beta \cdot F(b, a, \beta, \alpha). \quad (41)$$

From Eqs. (39)-(41), the mole fractions of different diads in the copolymer chain are deduced:

$$\begin{aligned} F_{(\text{AA})} &= \frac{\sum_j j(\text{AA})_j}{\sum_j j[(\text{AA})_j + (\text{BB})_j + (\text{AB})_j]} \\ &= G\alpha^2 [a(1-\beta)^2 + bR\beta^2 + eR\beta(1-\beta)], \end{aligned} \quad (42)$$

$$\begin{aligned} F_{(\text{BB})} &= \frac{\sum_j j(\text{BB})_j}{\sum_j j[(\text{AA})_j + (\text{BB})_j + (\text{AB})_j]} \\ &= G\beta^2 [b(1-\alpha)^2 + aR\alpha^2 + eR\alpha(1-\alpha)], \end{aligned} \quad (43)$$

$$F_{(AB)} = \frac{\sum_j j(AB)_j}{\sum_j j[(AA)_j + (BB)_j + (AB)_j]}$$

$$= RG\alpha\beta \{2a\alpha(1-\beta) + 2b\beta(1-\alpha) + e[1-\alpha-\beta+\alpha\beta(1+R)]\}, \quad (44)$$

where

$$G^{-1} = a\alpha^2 [R + (1-R)(1-\beta)^2] + b\beta^2 [R + (1-R)(1-\alpha)^2]$$

$$+ eR\alpha\beta [1 + \alpha\beta(R-1)]. \quad (45)$$

From the above three equations we can clearly see the sequence structure of the resulting copolymer. Figures 4-7 demonstrate the dependence of the mole fractions of different diads in copolymer,  $F_{(AA)}$ ,  $F_{(BB)}$ , and  $F_{(AB)}$ , on the comonomer feed composition  $f_A$  for Case II with different equilibrium constants of propagation.

From Eqs. (1)-(4), we can get the concentrations of four different copolymer chains in the reaction system,

$$\sum_{m,n} N_{m,n}^1 = IZa\alpha(1-\beta), \quad (46)$$

$$\sum_{m,n} N_{m,n}^2 = IZe_1R\alpha\beta, \quad (47)$$

$$\sum_{m,n} N_{m,n}^3 = IZe_2R\alpha\beta, \quad (48)$$

$$\sum_{m,n} N_{m,n}^4 = IZb\beta(1-\alpha), \quad (49)$$

where  $Z = [1 - \alpha - \beta + \alpha\beta(1 - R)]^{-1}$ . Therefore, the mole fractions for these four chains are given by

$$C_{AA} = \frac{\sum_{m,n} N_{m,n}^1}{\sum_{m,n} N_{m,n}} = aC\alpha(1-\beta), \quad (50)$$

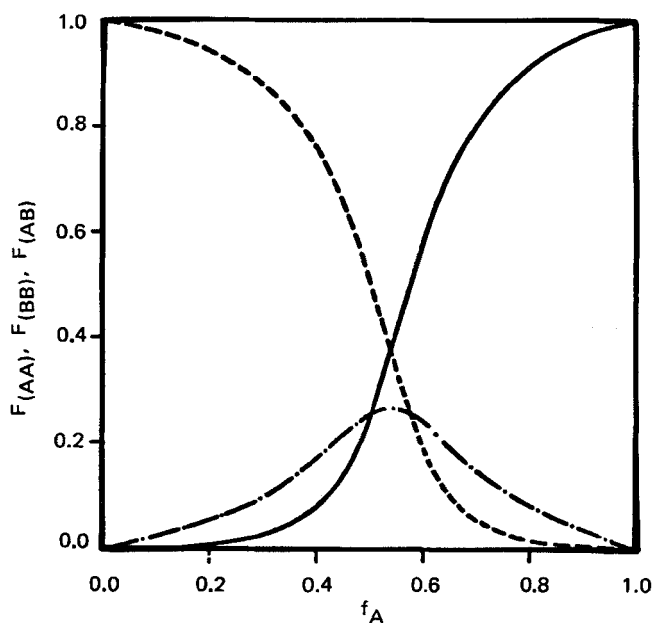


FIG. 4. Mole fractions of different diads in the equilibrium copolymer,  $F_{(AA)}$ ,  $F_{(BB)}$ , and  $F_{(AB)}$ , versus comonomer feed composition  $f_A$ ; Case II:  $K_A = 10^{-7}$ ,  $K_B = 10^{-7}$ ,  $K_{AA} = 0.2$ ,  $K_{AB} = 0.15$ ,  $K_{BA} = 0.05$ ,  $K_{BB} = 0.3$ .  $F_{(AA)}$ : (—).  $F_{(BB)}$ : (---).  $F_{(AB)}$ : (-·-).

$$C_{BA} = \frac{\sum_{m,n} N_{m,n}^2}{\sum_{m,n} N_{m,n}} = e_1 C R \alpha \beta, \quad (51)$$

$$C_{AB} = \frac{\sum_{m,n} N_{m,n}^3}{\sum_{m,n} N_{m,n}} = e_2 C R \alpha \beta, \quad (52)$$

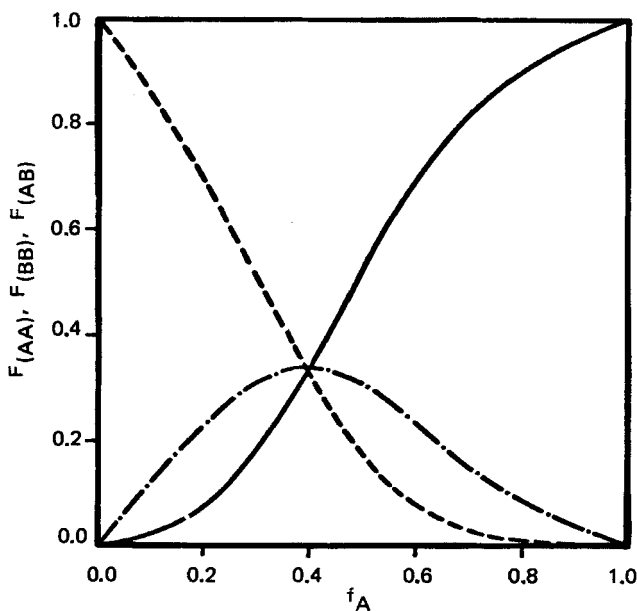


FIG. 5. Mole fractions of different diads in the equilibrium copolymer,  $F_{(AA)}$ ,  $F_{(BB)}$ , and  $F_{(AB)}$ , versus comonomer feed composition  $f_A$ ; Case II:  $K_{AA} = 0.95$ ,  $K_{AB} = 0.25$ ,  $K_{BA} = 0.15$ ,  $K_{BB} = 0.15$ ; other conditions as in Fig. 4.

$$C_{BB} = \frac{\sum_{m,n} N_{m,n}^4}{\sum_{m,n} N_{m,n}} = bC\beta(1 - \alpha), \quad (53)$$

where  $C = [a\alpha(1 - \beta) + b\beta(1 - \alpha) + eR\alpha\beta]^{-1}$ . From Eq. (19) in the previous paper [2] and Eqs. (34) and (36), we can obtain the average numbers of blocks A and B in the equilibrium copolymer:

$$\bar{N}_A = \frac{\bar{P}_A}{\bar{A}_n} = ZC\alpha(1 - \alpha) \cdot [a(1 - \beta)^2 + bR\beta^2 + eR\beta(1 - \beta)], \quad (54)$$



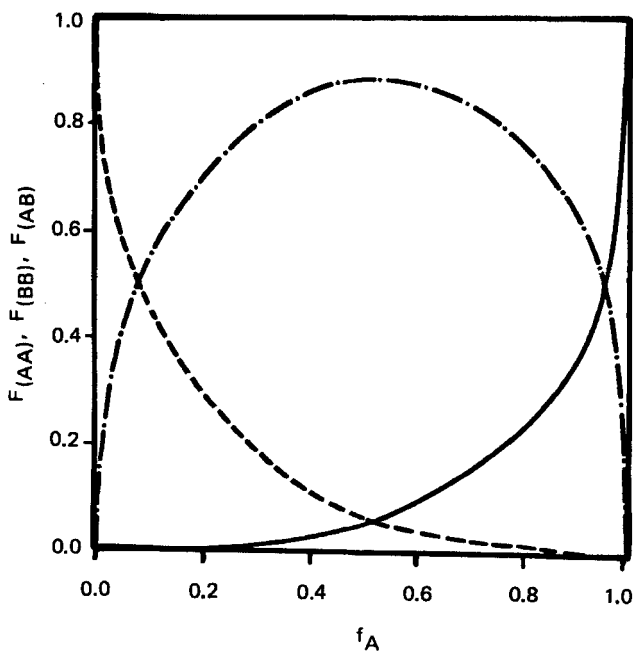


FIG. 6. Mole fractions of different diads in the equilibrium copolymer,  $F_{(AA)}$ ,  $F_{(BB)}$ , and  $F_{(AB)}$ , versus comonomer feed composition  $f_A$ ; Case II:  $K_{AA} = 0.1$ ,  $K_{AB} = 9.25$ ,  $K_{BA} = 0.1$ ,  $K_{BB} = 0.15$ ; other conditions as in Fig. 4.

$$\bar{N}_B = \frac{\bar{P}_B}{\bar{B}_n} = ZC\beta(1 - \beta) \cdot [b(1 - \alpha)^2 + aR\alpha^2 + eR\alpha(1 - \alpha)]. \quad (55)$$

Figure 8 shows the curves of  $\bar{N}_A$  versus  $f_A$  for Case II with different equilibrium constants of propagation. The relation between  $\bar{N}_A$  and  $\bar{N}_B$  is determined by

$$\bar{N}_A = \bar{N}_B + \delta, \quad |\delta| \leq 1. \quad (56)$$

The run number of the copolymer is defined as the number of blocks A and B in every 100 monomeric units along the copolymer chain, and it can be calculated by

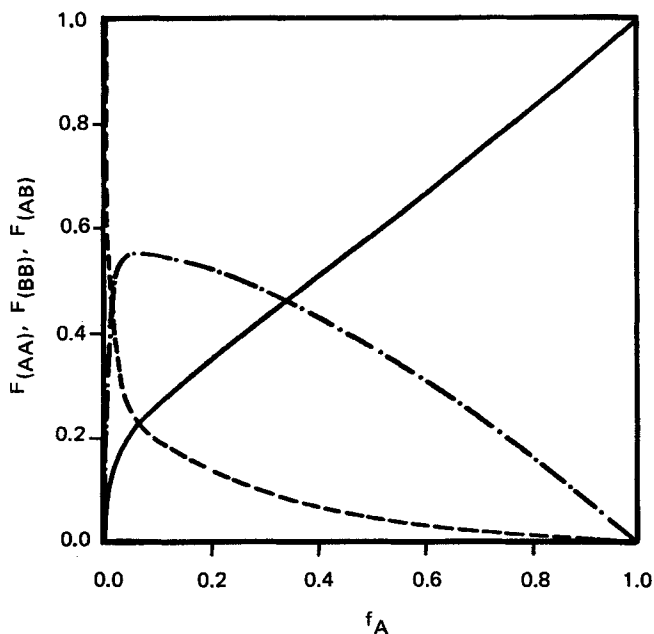


FIG. 7. Mole fractions of different diads in the equilibrium copolymer,  $F_{(AA)}$ ,  $F_{(BB)}$ , and  $F_{(AB)}$ , versus comonomer feed composition  $f_A$ ; Case II:  $K_{AA} = 2$ ,  $K_{AB} = 0.05$ ,  $K_{BA} = 3$ ,  $K_{BB} = 0.05$ ; other conditions as in Fig. 4.

$$N_R = \frac{\bar{N}_A + \bar{N}_B}{\bar{P}} \cdot 100, \quad (57)$$

where  $\bar{P}$  is the number-average degree of copolymerization of the copolymer, which was derived in the previous paper [2].

The randomness parameter,  $\Psi$ , is also an important sequence parameter of the copolymer. For an equilibrium copolymer, its value can be calculated by

$$\Psi = \frac{1}{\bar{A}_n F_B} = \frac{1 - \alpha}{CZ [b\beta(1 - \alpha)^2 + aR\alpha^2\beta + eR\alpha\beta(1 - \alpha)]}. \quad (58)$$

From the value of  $\Psi$ , one can know what type of copolymer is formed under equilibrium conditions (see Table 1).

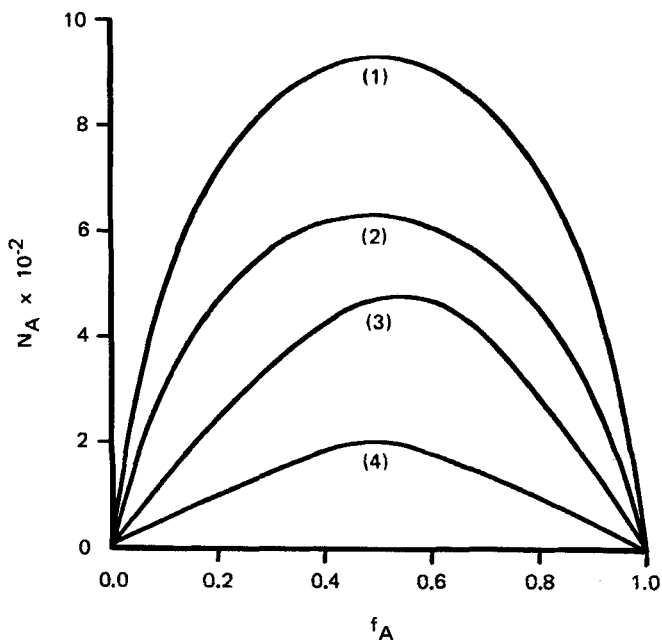


FIG. 8. Average number of blocks A in the equilibrium copolymer,  $\bar{N}_A$ , versus comonomer feed composition  $f_A$ ; Case II:  $K_A = 10^{-7}$ ,  $K_B = 10^{-7}$ . (1):  $K_{AA} = 1$ ,  $K_{AB} = 5$ ,  $K_{BA} = 0.05$ ,  $K_{BB} = 0.05$ . (2):  $K_{AA} = 1$ ,  $K_{AB} = 0.05$ ,  $K_{BA} = 1.5$ ,  $K_{BB} = 0.05$ . (3):  $K_{AA} = 0.95$ ,  $K_{AB} = 0.25$ ,  $K_{BA} = 0.15$ ,  $K_{BB} = 0.15$ . (4):  $K_{AA} = 0.2$ ,  $K_{AB} = 0.15$ ,  $K_{BA} = 0.05$ ,  $K_{BB} = 0.3$ .

TABLE 1. Relation between the Randomness Parameter  $\Psi$  and the Type of Equilibrium Copolymer

$\Psi$	Type of copolymer
1	Random copolymer
>1	Alternating copolymer
<1	Block copolymer
2	Completely alternating copolymer
0	Completely block copolymer

All of the formulas, though derived from Case I, are suitable for Case II if we let  $I$  in these formulas be unity (i.e.,  $I = 1$ ). For Case III, the sequence parameters of the resulting copolymer are listed in Table 2.

For Cases I and II, not all six equilibrium constants are necessary for solving the equations; the sufficient values are  $K_A$ ,  $K_B$ ,  $K_{AA}$ ,  $K_{BB}$ , and  $R$  ( $= K_{AB}K_{BA}/(K_{AA}K_{BB})$ ), which can be expressed in terms of the standard free energy changes of the elementary steps,

$$K_A = \exp(-\Delta G_A^\circ / RT), \quad (59)$$

$$K_B = \exp(-\Delta G_B^\circ / RT), \quad (60)$$

$$K_{AA} = \exp(-\Delta G_{AA}^\circ / RT), \quad (61)$$

$$K_{BB} = \exp(-\Delta G_{BB}^\circ / RT), \quad (62)$$

$$R = \exp(-2\omega / RT), \quad (63)$$

$$\omega = \frac{1}{2}(\Delta G_{AB}^\circ + \Delta G_{BA}^\circ - \Delta G_{AA}^\circ - \Delta G_{BB}^\circ), \quad (64)$$

where  $R$  is the gas constant, and  $\Delta G_A^\circ$ ,  $\Delta G_B^\circ$ ,  $\Delta G_{AA}^\circ$ ,  $\Delta G_{BB}^\circ$ ,  $\Delta G_{AB}^\circ$ , and  $\Delta G_{BA}^\circ$  are the standard free energy changes of the corresponding elementary steps. They can be expressed by the corresponding standard enthalpy and entropy changes, i.e.,

$$\begin{aligned} \Delta G_A^\circ &= \Delta H_A^\circ - T\Delta S_A^\circ, \\ \Delta G_B^\circ &= \Delta H_B^\circ - T\Delta S_B^\circ, \\ \Delta G_{AA}^\circ &= \Delta H_{AA}^\circ - T\Delta S_{AA}^\circ, \\ \Delta G_{BB}^\circ &= \Delta H_{BB}^\circ - T\Delta S_{BB}^\circ, \\ \Delta G_{AB}^\circ &= \Delta H_{AB}^\circ - T\Delta S_{AB}^\circ, \\ \Delta G_{BA}^\circ &= \Delta H_{BA}^\circ - T\Delta S_{BA}^\circ. \end{aligned} \quad (65)$$

From experiment or from references, we can obtain the values of  $\Delta G_A^\circ$ ,  $\Delta G_B^\circ$ ,  $\Delta G_{AA}^\circ$ ,  $\Delta G_{BB}^\circ$ ,  $(\Delta G_{AB}^\circ + \Delta G_{BA}^\circ)$ , or  $\Delta H_A^\circ$ ,  $\Delta H_B^\circ$ ,  $\Delta H_{AA}^\circ$ ,  $\Delta H_{BB}^\circ$ ,  $(\Delta H_{AB}^\circ + \Delta H_{BA}^\circ)$ , and  $\Delta S_A^\circ$ ,  $\Delta S_B^\circ$ ,  $\Delta S_{AA}^\circ$ ,  $\Delta S_{BB}^\circ$ ,  $(\Delta S_{AB}^\circ + \Delta S_{BA}^\circ)$ . If we substitute Eqs. (59)-(65) into the equations given in this

TABLE 2. Sequence Parameters of the Copolymers Formed by Equilibrium Copolymerization for Case III (for explanation of the symbols, see text)

Parameters	Expressions
$A_j$	$F(a_1, b_1, a_2, b_2, a_3, b_3, \alpha, \beta) \cdot (1 - \alpha)^2 \alpha^{j-1}$
$B_j$	$F(b_1, a_1, b_2, a_2, b_3, a_3, \beta, \alpha) \cdot (1 - \beta)^2 \beta^{j-1}$
$W_A(j)$	$j(1 - \alpha)^2 \alpha^{j-1}$
$W_B(j)$	$j(1 - \beta)^2 \beta^{j-1}$
$\bar{A}_n$	$1/(1 - \alpha)$
$\bar{A}_w$	$(1 + \alpha)/(1 - \alpha)$
$\bar{B}_n$	$a/(1 - \beta)$
$\bar{B}_w$	$(1 + \beta)/(1 - \beta)$
$\sum_j j(\text{AA})_j$	$\alpha \cdot F(a_1, b_1, a_2, b_2, a_3, b_3, \alpha, \beta)$
$\sum_j j(\text{BB})_j$	$\beta \cdot F(b_1, a_1, b_2, a_2, b_3, a_3, \beta, \alpha)$
$\sum_j j(\text{AB})_j; (\Gamma)$	$(1 - \alpha) \cdot F(a_1, b_1, a_2, b_2, a_3, b_3, \alpha, \beta) + (1 - \beta) \cdot F(b_1, a_1, b_2, a_2, b_3, a_3, \beta, \alpha) - F_0$
$F_0$	$F(a_1, a_2, a_3, \alpha, \beta) + F(b_1, b_2, b_3, \beta, \alpha)$
$F(a_1, a_2, a_3, \alpha, \beta)$	$Z \{ a_1 \alpha^2 (1 - \beta) + R \alpha \beta [a_2 \alpha + a_3 (1 - \alpha)] \}$
$\Omega$	$\sum_j j [(\text{AA})_j + (\text{BB})_j + (\text{AB})_j]$
$F_{(\text{AA})}$	$\alpha \cdot F(a_1, b_1, a_2, b_2, a_3, b_3, \alpha, \beta) / \Omega$
$F_{(\text{BB})}$	$\beta \cdot F(b_1, a_1, b_2, a_2, b_3, a_3, \beta, \alpha) / \Omega$
$F_{(\text{AB})}$	$\Gamma / \Omega$
$\bar{N}_A$	$\frac{(1 - \alpha)^3}{\alpha \cdot F_0} \cdot F(a_1, b_1, a_2, b_2, a_3, b_3, \alpha, \beta)$

TABLE 2 (continued)

Parameters	Expressions
$\bar{N}_B$	$\frac{(1 - \beta)^3}{\beta \cdot F_0} \cdot F(b_1, a_1, b_2, a_2, b_3, a_3, \beta, \alpha)$
$N_R$	$100 \cdot \alpha \beta \cdot F_0 \cdot (\bar{N}_A + \bar{N}_B) / [\beta(1 - \alpha)^2 \cdot F(a_1, b_1, a_2, b_2, a_3, b_3, \alpha, \beta) + \alpha(1 - \beta)^2 \cdot F(b_1, a_1, b_2, a_2, b_3, a_3, \beta, \alpha)]$
$\Psi$	$(1 - \alpha)[\beta(1 - \alpha)^2 \cdot F(a_1, b_1, a_2, b_2, a_3, b_3, \alpha, \beta) + \alpha(1 - \beta)^2 \cdot F(b_1, a_1, b_2, a_2, b_3, a_3, \beta, \alpha)] / [\alpha(1 - \beta)^2 \cdot F(b_1, a_1, b_2, a_2, b_3, a_3, \beta, \alpha)]$

paper and in a previous paper [2], we can relate all the molecular and structural sequence parameters of the equilibrium copolymer to the reaction temperature  $T$ . Therefore, if the standard free energy changes or the standard enthalpy and entropy changes of the elementary reaction steps, as well as the comonomer feed composition are given, one can predict the molecular and structural sequence parameters of the equilibrium copolymer formed at different reaction temperatures. A similar result can also be obtained for Case III.

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