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## Thermodynamic Theory of Equilibrium Copolymerization

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## Thermodynamic Theory of Equilibrium Copolymerization

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### ABSTRACT

General equations are derived for the thermodynamics of equilibrium copolymerization based on the diad model of copolymer. Physical interactions between components in solution are taken into consideration. Several special cases are treated in detail. When these physical interactions are absent, the relations obtained from the theory agree completely with those derived from the kinetics. Equilibrium monomer concentrations are illustrated as functions of excess free energy due to formation of heterodiad, equilibrium constants of homopolymerization, and initial monomer concentrations. It is shown that when the physical interactions are present, their effects cannot be ignored even in dilute solution. In bulk copolymerization, the physical interactions have a considerable effect on equilibrium, especially when the equilibrium monomer volume fractions are relatively small.

### INTRODUCTION

Izu and O' Driscoll [1] have recently formulated a theory of equilibrium copolymerization from a kinetical point of view based on the diad

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model. In the case of equilibrium homopolymerization, it is known that the thermodynamic treatment, which considers the interactions between components in solution, is more general than the kinetic treatment, and is a good explanation of the dependence of equilibrium monomer concentration on polymer concentration, initial monomer concentration, or solvent used [2-5]. Consequently, it is desirable to establish a thermodynamic theory of equilibrium copolymerization and compare it with that given by the above authors.

There exist several thermodynamic theories of equilibrium copolymerization, among which Sawada's [6] and Theil's [7] treat only the standard changes of thermodynamic functions and cannot be applied directly to the real equilibrium system. A more recent theory of Harvey and Leonard [8] gives a general relation of equilibrium in solution, and the bulk equilibrium copolymerization is treated in detail as a special case. But as will be shown later, their theory does not seem adequate and its extension to the ideal solution, i.e., the case in which no interactions exist between components, fails to agree with the equations derived by Izu and O'Driscoll.

In the present work we will present another thermodynamic theory of equilibrium copolymerization, the starting point of which is different from that of Harvey and Leonard.

### GENERAL TREATMENT

The modified form of the starting equation of Harvey and Leonard's theory can be expressed as

$$x_A \mu_A + x_B \mu_B = \mu_P \quad (1)$$

where  $\mu$  is the chemical potential,  $x$  the mole fraction of a component in the copolymer, and the suffixes A, B, and P refer to Monomer A, Monomer B and copolymer, respectively. The equation is analogous to the usual relation such as  $a\mu_A + b\mu_B = c\mu_C$  for an equilibrium of low molecular weight compounds given by  $aA + bB \rightleftharpoons cC$ . However, while the low molecular weight Compound C has a definite composition, the composition of a copolymer is considered as a variable which is affected by the equilibrium. In other words, Monomer A or B can go freely and independently into the copolymer or vice versa in the equilibrium copolymerization. Consequently, the partition of A and B in the monomer state and polymer state is the quantity to be governed by thermodynamics. The situation is similar to the equilibrium between two phases consisting of two components. Consequently, our starting point for equilibrium copolymerization is to equate the chemical potential of each component in the two states, i.e.,

$$\begin{aligned}\mu_A &= \mu_\alpha \\ \mu_B &= \mu_\beta\end{aligned}\quad (2)$$

The suffixes  $\alpha$  and  $\beta$  are used intentionally to denote the monomer units A and B in the copolymer.

The chemical potential of each component is obtained, as is well known, by the partial differentiation of the overall free energy of the equilibrated system. The latter is given for a system consisting of Monomer A, Monomer B, copolymer, and solvent (suffix: s) as

$$G = n_A G_A^\circ + n_B G_B^\circ + n_P G_P^\circ + n_S G_S^\circ + \Delta G_m \quad (3)$$

where  $G^\circ$  denotes the standard free energy,  $\Delta G_m$  the free energy of mixing of the components, and  $n$  the moles (or base moles) of each component. The chemical potentials of monomers are given simply as

$$\mu_A = G_A^\circ + \Delta\mu_A \quad (\text{similar equation for B}) \quad (4)$$

For the chemical potentials of monomer units in the copolymer, we have to know the free energy of 1 base mole of the amorphous copolymer  $G_P^\circ$ . According to the diad model, any copolymer can be specified by two properly selected parameters. In the following we use  $x_\alpha$  ( $= 1 - x_\beta$ ), the mole fraction of unit  $\alpha$  in the copolymer and  $\psi$ , the distribution parameter which is given by  $\psi = P_{\alpha\beta} + P_{\beta\alpha}$  where  $P_{\alpha\beta}$  (or  $P_{\beta\alpha}$ ) is the conditional probability of finding unit  $\beta$  (or  $\alpha$ ) succeeding unit  $\alpha$  (or  $\beta$ ). Theil [7] has calculated the free energy difference between 1 base mole of copolymer specified by  $x_\alpha$  and  $\psi$  and a mixture of homopolymers with the same composition. Rewriting his result by our notation, we obtain

$$\begin{aligned}G_P^\circ - (x_\alpha G_{\alpha\alpha}^\circ + x_\beta G_{\beta\beta}^\circ) &= \psi x_\alpha x_\beta \Gamma + RT \left\{ \psi x_\alpha x_\beta \ln \frac{\psi^2 x_\alpha x_\beta}{(1 - \psi x_\alpha)(1 - \psi x_\beta)} \right. \\ &\quad \left. + x_\alpha \ln(1 - \psi x_\beta) + x_\beta \ln(1 - \psi x_\alpha) \right\}\end{aligned}\quad (5)$$

Here,  $G_{\alpha\alpha}^\circ$  (or  $G_{\beta\beta}^\circ$ ) is the standard free energy associated with the diad  $\alpha\alpha$  (or  $\beta\beta$ ) or it represents the free energy of 1 base mole of

amorphous poly- $\alpha$  (or poly- $\beta$ ), and  $\Gamma$  is the standard free energy difference between hetero- and homodiads, i.e.,

$$\Gamma = G_{\alpha\beta}^{\circ} + G_{\beta\alpha}^{\circ} - G_{\alpha\alpha}^{\circ} - G_{\beta\beta}^{\circ} \quad (6)$$

This quantity is also regarded as a difference between the free energy changes of cross polymerizations and those of homopolymerizations:

$$\begin{aligned} \Gamma &= \Delta G_{\alpha\beta}^{\circ} + \Delta G_{\beta\alpha}^{\circ} - \Delta G_{\alpha\alpha}^{\circ} - \Delta G_{\beta\beta}^{\circ} \\ &= (\Delta H_{\alpha\beta}^{\circ} + \Delta H_{\beta\alpha}^{\circ} - \Delta H_{\alpha\alpha}^{\circ} - \Delta H_{\beta\beta}^{\circ}) - T(\Delta S_{\alpha\beta}^{\circ} + \Delta S_{\beta\alpha}^{\circ} \\ &\quad - \Delta S_{\alpha\alpha}^{\circ} - \Delta S_{\beta\beta}^{\circ}) \end{aligned} \quad (7)$$

The suffix  $\alpha\beta$  means that the Monomer B adds to the terminal unit  $\alpha$  in the copolymerization to form a diad  $\alpha\beta$ , and  $\Delta G_{\alpha\beta}^{\circ}$  the standard free energy change associated with this polymerization, and so on. Equation (7) is valid because  $G_{\alpha\beta}^{\circ} - G_{\alpha\alpha}^{\circ} = \Delta G_{\alpha\beta}^{\circ} - \Delta G_{\alpha\alpha}^{\circ}$  and  $G_{\beta\alpha}^{\circ} - G_{\beta\beta}^{\circ} = \Delta G_{\beta\alpha}^{\circ} - \Delta G_{\beta\beta}^{\circ}$ . When  $\Gamma$  is negative, copolymerization is easier than homopolymerization.

The first term of the right-hand side of Eq. (5) arises from the formation of heterodiads and the second term from the entropy of distribution of two monomer units in the copolymer. The entropy of distribution is calculated according to Mandelkern's formula [9] and differs from those obtained by Sawada [6] and Leonard [8] on a less rigorous basis.

In dynamic equilibrium the monomer units in the copolymer are distributed to attain the most stable structure. Consequently,  $\psi$  is not arbitrary but will have a value to minimize  $G_P^{\circ}$  for a definite composition. As has been done by Theil, the condition  $\partial G_P^{\circ} / \partial \psi = 0$  for Eq. (5) leads to the relation

$$\exp\left(-\frac{\Gamma}{RT}\right) = \frac{\psi^2 x_{\alpha} x_{\beta}}{(1 - \psi x_{\alpha})(1 - \psi x_{\beta})} \quad (8)$$

and  $\psi$  is calculated as a function of  $x_{\alpha}$  and  $\Gamma/RT$  by solving the above quadratic equation. From Eqs. (5) and (8),  $G_P^{\circ}$  at its minimum value is given by

$$G_P^{\circ} = x_{\alpha} G_{\alpha\alpha}^{\circ} + x_{\beta} G_{\beta\beta}^{\circ} + RT\{x_{\alpha} \ln(1 - \psi x_{\beta}) + x_{\beta} \ln(1 - \psi x_{\alpha})\} \quad (9)$$

Let us now calculate the chemical potential of monomer unit in the copolymer

$$\mu_{\alpha} = \frac{\partial (n_{\text{P}} G_{\text{P}}^{\circ})}{\partial n_{\alpha}} + \frac{\partial (\Delta G_{\text{m}})}{\partial n_{\alpha}} \quad (10)$$

where  $n_{\alpha}$  is the moles of unit  $\alpha$  in the copolymer and is equal to  $n_{\text{P}} x_{\alpha}$ . The implication of partial differentiation with respect to  $n_{\alpha}$  is that  $n_{\alpha}$  can be varied while  $n_{\beta}$  is kept constant, or in other word,  $\alpha$  and  $\beta$  behave independently as already mentioned. By the use of Eq. (9) the first term of Eq. (10) is calculated as

$$\frac{\partial (n_{\text{P}} G_{\text{P}}^{\circ})}{\partial n_{\alpha}} = G_{\alpha\alpha}^{\circ} + RT \ln(1 - \psi x_{\beta}) \quad (11)$$

Relations used in this calculation are

$$\partial x_{\alpha} / \partial n_{\alpha} = - \partial x_{\beta} / \partial n_{\alpha} = x_{\beta}$$

and

$$\partial \psi / \partial n_{\alpha} = \psi(1 - \psi)(x_{\alpha} - x_{\beta}) / n_{\text{P}} x_{\alpha} (2 - \psi)$$

The latter is obtained by partial differentiation of Eq. (8) with respect to  $n_{\alpha}$  followed by elimination of the term containing  $\psi$ , again using Eq. (8).

As for  $\Delta\mu_{\alpha}$ ,

$$\Delta\mu_{\alpha} = \frac{\partial (\Delta G_{\text{m}})}{\partial n_{\alpha}} = \frac{\partial n_{\text{P}}}{\partial n_{\alpha}} \frac{\partial (\Delta G_{\text{m}})}{\partial n_{\text{P}}} = \frac{\partial (n_{\alpha} + n_{\beta})}{\partial n_{\alpha}} \Delta\mu_{\text{P}} = \Delta\mu_{\text{P}} \quad (12)$$

where  $\Delta\mu_{\text{P}}$  is the excess chemical potential of the copolymer due to mixing. Consequently

$$\mu_{\alpha} = G_{\alpha\alpha}^{\circ} + RT \ln(1 - \psi x_{\beta}) + \Delta\mu_{\text{P}} \quad (13a)$$

and in a similar way

$$\mu_{\beta} = G_{\beta\beta}^{\circ} + RT \ln(1 - \psi x_{\alpha}) + \Delta\mu_{\text{P}} \quad (13b)$$

Then, using the basic Eqs. (2) for equilibrium, we obtain

$$-\ln(1 - \psi x_\beta) = \frac{1}{RT} (\Delta G_{\alpha A}^\circ + \Delta\mu_P - \Delta\mu_A) = Z_A \quad (14a)$$

$$-\ln(1 - \psi x_\alpha) = \frac{1}{RT} (\Delta G_{\beta B}^\circ + \Delta\mu_P - \Delta\mu_B) = Z_B \quad (14b)$$

where  $\Delta G_{\alpha A}^\circ = G_{\alpha\alpha}^\circ - G_A^\circ$  and  $\Delta G_{\beta B}^\circ = G_{\beta\beta}^\circ - G_B^\circ$  are the standard free energy changes of homopolymerization of A and B, and  $Z_A$  and  $Z_B$  are the simplifying notations for  $(\Delta G_{\alpha A}^\circ + \Delta\mu_P - \Delta\mu_A)/RT$  and  $(\Delta G_{\beta B}^\circ + \Delta\mu_P - \Delta\mu_B)/RT$ , respectively.

On substitution of  $\psi x_\alpha$  and  $\psi x_\beta$ , obtained from the above equations, into Eq. (8), we obtain

$$\exp\left(-\frac{\Gamma}{RT}\right) = [\exp(Z_A) - 1][\exp(Z_B) - 1] \quad (15)$$

This is the fundamental relation for the equilibrium copolymerization. Another important equation which defines the composition of the copolymer is obtained by elimination of  $\psi$  from Eqs. (14a) and (14b):

$$\frac{x_\beta}{x_\alpha} = \frac{1 - x_\alpha}{x_\alpha} = \frac{1 - \exp(-Z_A)}{1 - \exp(-Z_B)} \quad (16)$$

Now let us calculate the excess chemical potentials due to mixing,  $\Delta\mu_A$ ,  $\Delta\mu_B$ , and  $\Delta\mu_P$ . This is done by extending the lattice theory of solution by Flory [10] to a multicomponent system. The general expression obtained is given by

$$\begin{aligned} \frac{\Delta\mu_1}{RT} = & \ln \phi_1 + (1 - \phi_1) - \sum_{j \neq 1} \left(\frac{v_1}{v_j}\right) \phi_j + (1 - \phi_1) \left(\sum_{j \neq 1} \chi_{1j} \phi_j\right) \\ & - \sum_{\substack{k, l \neq 1 \\ k > l}} \chi_{kl} \left(\frac{v_1}{v_k}\right) \phi_k \phi_l \end{aligned} \quad (17)$$

where  $\phi_i$  and  $v_i$  are the volume fraction and molar volume of the  $i$ -th component, respectively, and  $\chi_{ij}$  is the usual interaction parameter

between the  $i$ -th and  $j$ -th components and has the relation  $\chi_{ji} = \chi_{ij}(v_j/v_i)$ . For simplicity we assume that all the molar volumes (and base molar volumes) of components are the same and that the degree of polymerization of the copolymer is very high. Then we obtain

$$Z_A = \frac{\Delta G_{\alpha A}^\circ + \Delta\mu_P - \Delta\mu_A}{RT} = \frac{\Delta G_{\alpha A}^\circ}{RT} - \ln \phi_A - 1 + \chi_{AP}(\phi_A - \phi_P) + (\chi_{BP} - \chi_{AB})\phi_B + (\chi_{SP} - \chi_{AS})\phi_S \quad (18a)$$

$$Z_B = \frac{\Delta G_{\beta B}^\circ + \Delta\mu_P - \Delta\mu_B}{RT} = \frac{\Delta G_{\beta B}^\circ}{RT} - \ln \phi_B - 1 + \chi_{BP}(\phi_B - \phi_P) + (\chi_{AP} - \chi_{AB})\phi_A + (\chi_{SP} - \chi_{BS})\phi_S \quad (18b)$$

Consequently, Eqs. (15) and (16) can be expressed in terms of  $\Delta G_{\alpha A}^\circ$ ,  $\Delta G_{\beta B}^\circ$ ,  $\phi_S$ , and  $\chi_S$ .

Besides the above two equations, another equation containing some other parameters is necessary for a complete description of the equilibrated system. We chose, as these parameters,  $\phi_{A0}$  and  $\phi_{B0}$ , the initial volume fractions of Monomer A and Monomer B before polymerization. More generally speaking,  $\phi_{A0}$  and  $\phi_{B0}$  are considered as the total volume fractions of the components A +  $\alpha$  and B +  $\beta$  in the system, respectively. They do not change during polymerization and it does not matter whether a certain amount of copolymer was present before polymerization, provided that the initial copolymer is living and can exchange its units freely. The above argument is based on the approximation that the volume is additive and all the molar volumes are the same. Then the following relations hold:

$$\phi_{A0} + \phi_{B0} = \phi_A + \phi_B + \phi_P = 1 - \phi_S \quad (19)$$

and

$$\frac{1 - x_\alpha}{x_\alpha} = \frac{\phi_{B0} - \phi_B}{\phi_{A0} - \phi_A} \quad (20)$$



Combination of Eq. (20) with Eq. (16) gives

$$\frac{\phi_{B0} - \phi_B}{\phi_{A0} - \phi_A} = \frac{1 - \exp(-Z_A)}{1 - \exp(-Z_B)} \quad (21)$$

Thus, in principle, three unknowns, i.e.,  $\phi_A$ ,  $\phi_B$ , and  $\phi_P$ , can be determined from the three Eqs. (15), (21) ( $Z_A$  and  $Z_B$  being given by Eqs. 18), and (19), provided that all the thermodynamic parameters ( $\Gamma/RT$ ,  $\Delta G_{\alpha A}^\circ$ ,  $\Delta G_{\beta B}^\circ$ , and  $\chi$ ) and initial conditions ( $\phi_{A0}$  and  $\phi_{B0}$ ) are known. Then the composition of the copolymer is given by Eq. (20).

In the following we will discuss some special cases. For this purpose it is convenient to mention the relation already known for equilibrium homopolymerization. This is given by [2, 5]

$$\frac{\Delta G_{\alpha A}^\circ}{RT} = \ln \phi_A^* + 1 - \chi_{A\alpha}(\phi_A^* - \phi_{\alpha}^*) - (\chi_{\alpha S} - \chi_{AS})\phi_S^* \quad (22)$$

(similar equation for B)

where the asterisk refers to the quantities in the equilibrium homopolymerization. This equation is also obtained by setting  $Z_A = 0$  and  $\phi_B = 0$  in Eq. (18a).  $Z_A = 0$  is the consequence of  $x_\beta = 0$  in Eq. (14a).

### CASE WITH NO INTERACTIONS

When there is no interaction between components, all the  $\chi$ 's are null. Then Eq. (15) with the aide of Eq. (18) becomes

$$\exp\left(-\frac{\Gamma}{RT}\right) = \left\{\frac{1}{\phi_A} \exp\left(\frac{\Delta G_{\alpha A}^\circ}{RT} - 1\right) - 1\right\} \left\{\frac{1}{\phi_B} \exp\left(\frac{\Delta G_{\beta B}^\circ}{RT} - 1\right) - 1\right\} \quad (23)$$

It is more convenient to use the equilibrium volume fractions in homopolymerization without interactions  $\phi_A^*$  and  $\phi_B^*$  instead of  $\Delta G_{\alpha A}^\circ$  and  $\Delta G_{\beta B}^\circ$ . From Eq. (22) they are given by

$$\ln \phi_A^* = \frac{\Delta G_{\alpha A}^\circ}{RT} - 1 \quad \text{and} \quad \ln \phi_B^* = \frac{\Delta G_{\beta B}^\circ}{RT} - 1 \quad (24)$$

Consequently

$$Z_A = \ln \frac{\phi_A^*}{\phi_A} \quad \text{and} \quad Z_B = \ln \frac{\phi_B^*}{\phi_B} \quad (25)$$

and

$$\exp\left(-\frac{\Gamma}{RT}\right) = \left(\frac{\phi_A^*}{\phi_A} - 1\right) \left(\frac{\phi_B^*}{\phi_B} - 1\right) = \left(\frac{[A]^*}{[A]} - 1\right) \left(\frac{[B]^*}{[B]} - 1\right) \quad (26)$$

The concentration of A, for example, is given by  $[A] = \phi_A / \phi_A^1$  where  $\phi_A^1$  is the volume fraction of A at 1 mole/liter. The validity of this relation and the constancy of  $\phi_A^1$  in any solution are based on the assumptions of the additivity of the volumes and the equality of the molar volumes. Thus, in the approximation used, it is permitted to equate the ratio of volume fractions to the ratio of concentrations.

In the same way, Eqs. (14) are reduced to

$$\frac{\phi_A}{\phi_A^*} = \frac{[A]}{[A]^*} = 1 - \psi x_\beta \quad (27a)$$

$$\frac{\phi_B}{\phi_B^*} = \frac{[B]}{[B]^*} = 1 - \psi x_\alpha \quad (27b)$$

In the diad model of copolymer,  $x_\beta = P_{\alpha\beta} / (P_{\alpha\beta} + P_{\beta\alpha}) = P_{\alpha\beta} / \psi$ . As a result,  $1 - \psi x_\beta = P_{\alpha\alpha}$  where  $P_{\alpha\alpha}$  is the conditional probability of finding unit  $\alpha$  succeeding unit  $\alpha$  in the copolymer. In the same way,  $1 - \psi x_\alpha = P_{\beta\beta}$ . If we remember that in homopolymerization without interaction,  $[A]^* = 1/K_{\alpha A}$  and  $[B]^* = 1/K_{\beta B}$ , where  $K_{\alpha A}$  and  $K_{\beta B}$  are the equilibrium constants for the homopolymerization of A and B in solution, it is obvious that Eqs. (26) and (27) are the same as those derived by Izu and O'Driscoll [1] on a kinetic basis. On the other hand, when Leonard's treatment [8] is extended in the same way, the following relation is obtained:

$$\exp\left(-\frac{\Gamma}{RT}\right) = \frac{1}{4} \frac{\phi_A^* \phi_B^*}{\phi_A \phi_B} \left(1 - \frac{\phi_A}{\phi_A^*} - \frac{\phi_B}{\phi_B^*}\right)^2 \left[ \neq \frac{\phi_A^* \phi_B^*}{\phi_A \phi_B} \left(1 - \frac{\phi_A}{\phi_A^*}\right) \left(1 - \frac{\phi_B}{\phi_B^*}\right) \right] \quad (28)$$

This resembles somewhat, but differs essentially from, Eq. (26), the modified form of which is given in brackets for comparison.

Equation (21) is also simplified by the use of Eq. (25) to

$$\frac{1 - \frac{\phi_A}{\phi_A^*}}{\frac{\phi_B}{\phi_B^*}} = \frac{\phi_{B0} - \phi_B}{\phi_{A0} - \phi_A} \quad (29)$$

or, expressed in terms of concentrations,

$$\frac{1 - \frac{[A]}{[A]^*}}{1 - \frac{[B]}{[B]^*}} = \frac{[B]_0 - [B]}{[A]_0 - [A]} = \frac{K_{\alpha A} \left( \frac{[B]_0}{[B]^*} - \frac{[B]}{[B]^*} \right)}{K_{\beta B} \left( \frac{[A]_0}{[A]^*} - \frac{[A]}{[A]^*} \right)} \quad (30)$$

The combination of Eqs. (26) and (30) gives the equilibrium monomer concentrations  $[A]$  and  $[B]$  as functions of the initial monomer concentrations ( $[A]_0$  and  $[B]_0$ ) and three thermodynamic parameters ( $\Gamma/RT$ ,  $[A]^* = 1/K_{\alpha A}$ , and  $[B]^* = 1/K_{\beta B}$ ).

In order to visualize the results obtained, we will show in the following some figures representing the equilibrium monomer concentrations. The normalized concentrations, i.e., the ratios  $[A]/[A]^*$  and  $[B]/[B]^*$ , are more convenient quantities than the concentrations themselves for representation. It is clear from Eqs. (27) that these ratios do not exceed unity or, in other words, the equilibrium concentration of each monomer is always equal or smaller than that in the corresponding homopolymerization. The relation given by Eq. (26) is illustrated in Fig. 1 (dotted lines) with various values of  $\exp(-\Gamma/RT)$ . It is seen that copolymerization is more favored with an increase of  $\exp(-\Gamma/RT)$  or with a decrease of  $\Gamma$  from positive to negative. Equation (30) shows that the normalized equilibrium monomer concentrations are not only functions of the ratio of the equilibrium constants of homopolymerization, but are also functions of the initial monomer concentrations. The full lines in Fig. 1 show the effect of the former on equilibrium for the case where the initial concentrations of A and B are kept at the equilibrium values in homopolymerization, i.e.,  $[A]_0 = [A]^*$  and  $[B]_0 = [B]^*$ . The cross

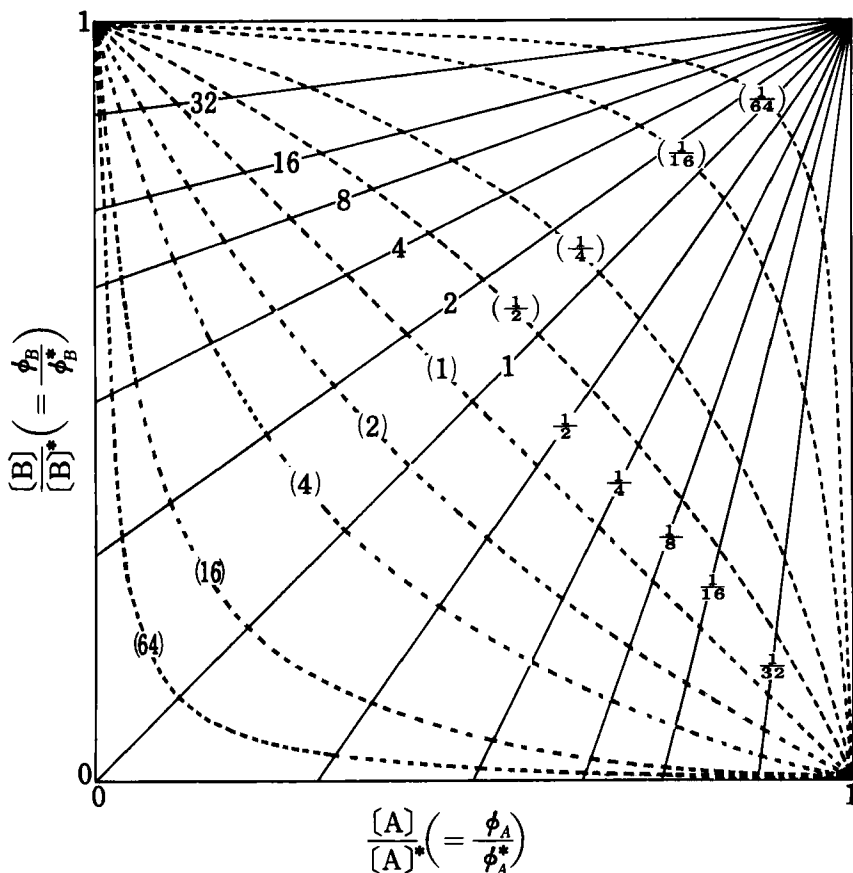


FIG. 1. Dependence of equilibrium monomer concentrations on  $\exp(-\Gamma/RT)$  and  $K_{\alpha A}/K_{\beta B}$  in solution without physical interactions.

Initial monomer concentrations are taken as  $[A]_0/[A]^* = [B]_0/[B]^* = 1$ . Full lines: Curves with constant  $K_{\alpha A}/K_{\beta B}$ . Dotted lines: Curves with constant  $\exp(-\Gamma/RT)$ . Values of  $K_{\alpha A}/K_{\beta B}$  and  $\exp(-\Gamma/RT)$  are given on the curves.

points of the full lines and the dotted lines determine the equilibrium concentrations of A and B for given sets of thermodynamic parameters  $\Gamma/RT$  and  $K_{\alpha A}/K_{\beta B}$  in the case of the initial conditions given above. It is seen from the figure that when one of the monomer is more susceptible to homopolymerization ( $K_{\alpha A}/K_{\beta B}$  is larger or less than unity), it

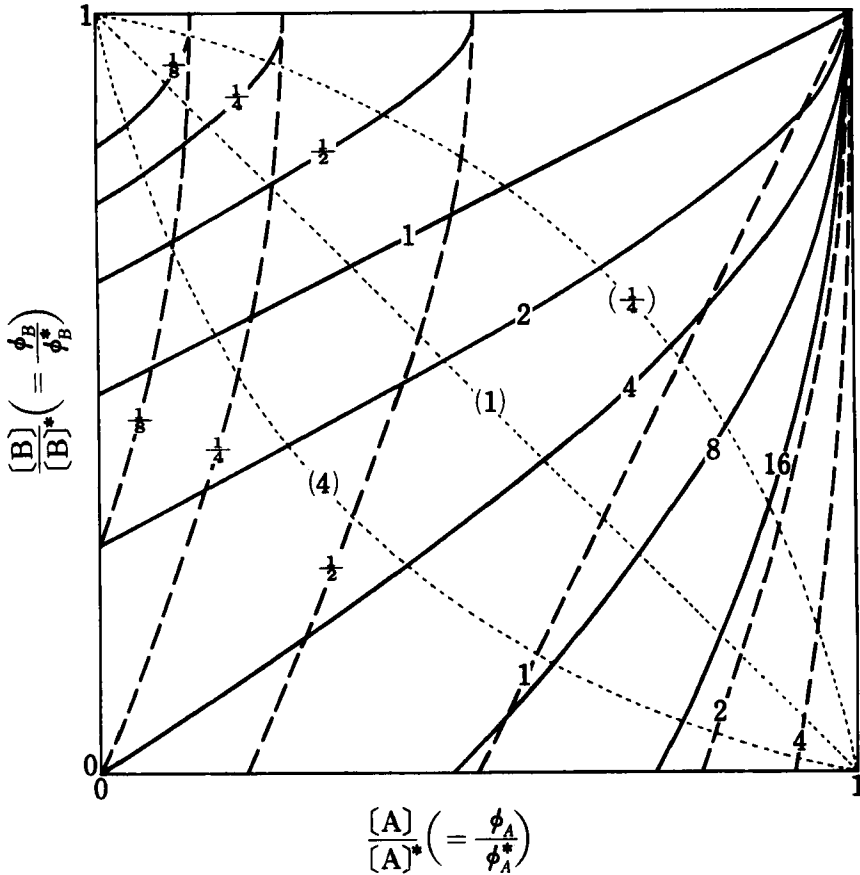


FIG. 2. Dependence of equilibrium monomer concentrations on initial monomer concentrations of A in solution without interactions. Initial monomer concentrations of B are taken as  $[B]_0/[B]^* = 1$ . Full lines and broken lines: Curves with constant  $[A]_0/[A]^*$  for  $K_{\alpha A}/K_{\beta B} = 4$  and  $1/4$ , respectively. Values of  $[A]_0/[A]^*$  are given on the curves. Dotted lines: Same as in Fig. 1.

copolymerizes more than the other as anticipated, and this unbalanced tendency is more pronounced as  $\exp(-\Gamma/RT)$  increases.

Now let us examine the effect of the initial monomer concentrations on the equilibrium. The full and broken lines in Fig. 2 show the relation given by Eq. (30) with  $K_{\alpha A}/K_{\beta B}$  equal to 4 and  $1/4$ , respectively,

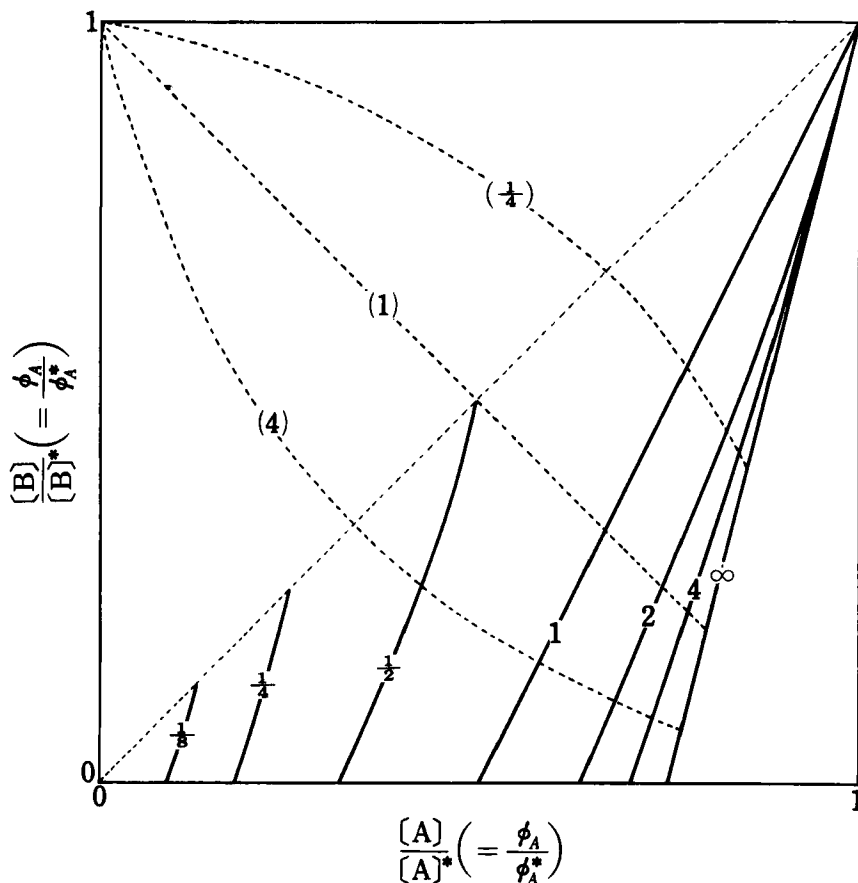


FIG. 3. Dependence of equilibrium monomer concentrations on initial monomer concentrations in solution without interactions.  $K_{\alpha A}/K_{\beta B}$  is taken as  $1/4$ . Initial monomer concentrations are so chosen as to keep their normalized values equal ( $[A]_0/[A]^* = [B]_0/[B]^*$ ). Full lines: Curves with constant initial monomer concentrations. Values of normalized initial monomer concentrations are given on the curves. Dotted lines: Same as in Fig. 1.

for the case where  $[B]_0$  is kept equal to  $[B]^*$  and  $[A]_0$  is varied. Some of the curves in Fig. 1 for Eq. (26) are reproduced again in Fig. 2 as dotted lines. When  $[A]_0$  increases, the equilibrium concentration of B decreases gradually and that of A increases. The decrease of  $[B]$  is more rapid when  $K_{\alpha A}/K_{\beta B}$  is smaller and  $\exp(-\Gamma/RT)$  is larger. At

very large value of  $[A]_0$ ,  $[B] \approx 0$  and  $[A] \approx [A]^*$ . It must be noted that even when  $[A]_0/[A]^*$  is less than unity, the equilibrium holds at any condition. But as is shown in Fig. 3, this is not the case when the initial monomer concentrations are chosen so as to keep the relation  $[A]_0/[B]_0 = [A]^*/[B]^*$  but the overall concentration is varied. For the equilibrium to hold, the equilibrium monomer concentrations must be less than the initial monomer concentrations. As a result, the curves corresponding to Eq. (30) are only segments in the region of lower initial concentrations and cannot cross some of the curves with low values of  $\exp(-\Gamma/RT)$ . Further, at very high initial monomer concentrations,  $[A]/[A]^*$  and  $[B]/[B]^*$  reach some limiting values. Thus the initial monomer concentrations are important variables in equilibrium copolymerization. Only in the very special case of  $\Gamma = 0$  and  $K_{\alpha A} = K_{\beta B}$  can it be shown that the equilibrium monomer concentrations are governed only by the composition of the feed as

$$\frac{[A]}{[A]^*} = \frac{[A]_0}{[A]_0 + [B]_0} \quad \text{and} \quad \frac{[B]}{[B]^*} = \frac{[B]_0}{[A]_0 + [B]_0} \quad (31)$$

and do not depend on the overall initial concentration which, however, must be larger than  $[A]^* (= [B]^*)$  for the equilibrium to hold.

#### CASE OF DILUTE SOLUTION

In dilute solution,  $\phi_S \approx 1$  and  $\phi_A$ ,  $\phi_B$ , and  $\phi_P$  are very small. Then, in Eqs. (18) and (22), all the terms containing the latter three except the logarithmic terms can be ignored and  $\phi_S$  can be put equal to unity. Consequently,  $\phi_A^*$  is, in this case also, a function of temperature only. Then Eqs. (18) are transformed with the aide of Eq. (22) to

$$Z_A = \frac{\Delta G_{\alpha A}^\circ}{RT} - 1 - \ln \phi_A + \chi_{SP} - \chi_{AS} = \ln \frac{\phi_A^*}{\phi_A} + \chi_{SP} - \chi_{S\alpha} \quad (32a)$$

$$Z_B = \ln \frac{\phi_B^*}{\phi_B} + \chi_{SP} - \chi_{S\beta} \quad (32b)$$

It follows that if  $\chi_{SP} = \chi_{S\alpha} = \chi_{S\beta}$ , the second and the third terms of the above equations disappear and all the argument given already for

equilibrium without interactions also holds in this case. Even when the above conditions are not fulfilled, if  $\phi_{SP}$  is constant and independent of the composition of the copolymer, it is possible to use the same equations in the case with no interactions by replacing  $\phi_A^*$  by  $\phi_A^* \exp(\chi_{SP} - \chi_{S\alpha})$  and  $\phi_B^*$  by  $\phi_B^* \exp(\chi_{SP} - \chi_{S\beta})$ . However, it is rather likely that the interaction parameter of the copolymer with solvent  $\phi_{SP}$  depends on the composition of the copolymer when  $\chi_{S\alpha}$  and  $\chi_{S\beta}$  differ appreciably. One of the possible variations of  $\chi_{SP}$  is the linear change with composition, i.e.,  $\chi_{SP} = x_\alpha \chi_{S\alpha} + x_\beta \chi_{S\beta}$ .

By solving Eqs. (15) and (16) for  $Z_A$  and  $Z_B$ , and introducing them into Eqs. (32), we can calculate  $\phi_A^*/\phi_A$  and  $\phi_B^*/\phi_B$  as functions of  $\Gamma/RT$ ,  $x_\alpha$ , and three  $\chi$ 's. Then the product  $\{(\phi_A^*/\phi_A) - 1\} \{(\phi_B^*/\phi_B) - 1\}$  is calculated too. This product is constant and equal to  $\exp(-\Gamma/RT)$  at any polymer composition at a constant temperature if the interactions are absent. But this does not hold when there are interactions between solvent and copolymer. Assuming the linear change of  $\chi_{SP}$  mentioned above and taking  $\chi_{S\alpha} - \chi_{S\beta} = 0.5$ , the ratio of this product to  $\exp(-\Gamma/RT)$  is calculated for the case of  $\exp(-\Gamma/RT)$  equal to 10, 1, and 1/10, and these are shown in Fig. 4. It is seen from the figure that when  $\exp(-\Gamma/RT)$  is larger than unity or  $\Gamma$  is zero or negative, the product is, as a very rough approximation, nearly constant to give an approximate value of  $\Gamma/RT$ . On the other hand, when  $\Gamma/RT$  is positive, the product is far from constant and differs appreciably from  $\exp(-\Gamma/RT)$ , especially near the middle of the composition axis.

The above example shows the importance of the interactions in solution even for the case of dilute solution in equilibrium copolymerization.

### CASE OF BULK COPOLYMERIZATION

When  $\phi_S$  is put equal to zero and  $\phi_P$  is eliminated by the use of the relation  $\phi_P = 1 - \phi_A - \phi_B$ ,  $Z_A$  and  $Z_B$  are expressed as

$$Z_A = \frac{\Delta G_{\alpha A}^\circ}{RT} - 1 - \ln \phi_A + \chi_{AP} (2\phi_A - 1) + (\chi_{AP} + \chi_{BP} - \chi_{AB}) \phi_B \quad (33a)$$

$$Z_B = \frac{\Delta G_{\beta B}^\circ}{RT} - 1 - \ln \phi_B + \chi_{BP} (2\phi_B - 1) + (\chi_{AP} + \chi_{BP} - \chi_{AB}) \phi_A \quad (33b)$$



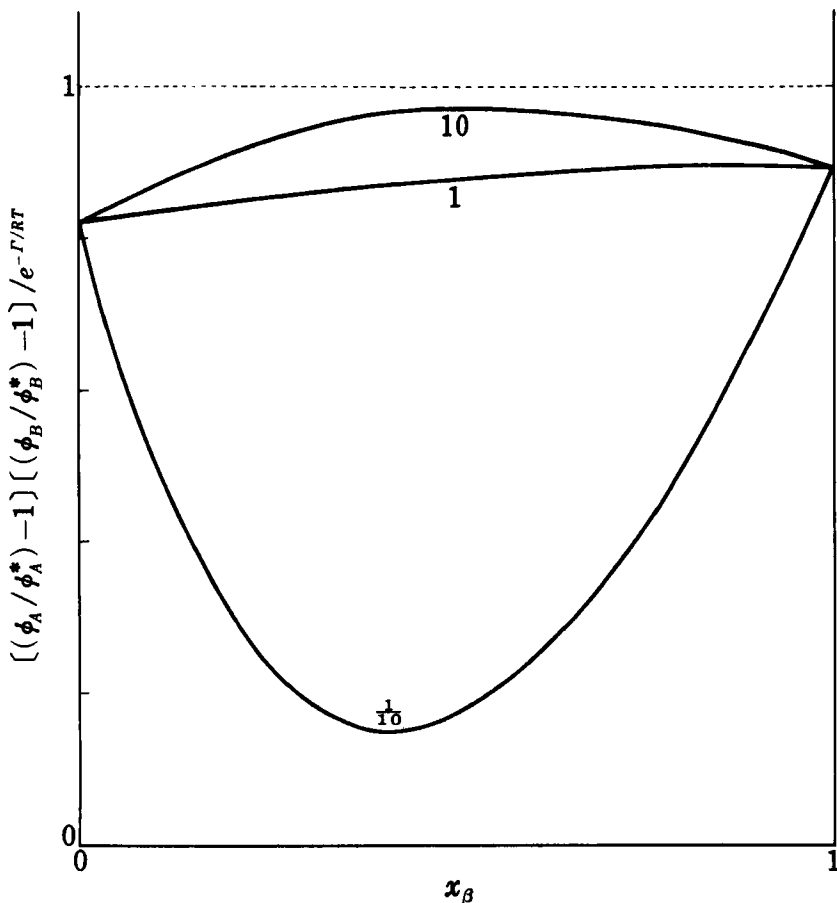


FIG. 4. Effects of polymer-solvent interactions on equilibrium in dilute solution.  $\chi_{S\alpha} - \chi_{S\beta}$  is taken as 0.5 and  $\chi_{SP}$  is assumed to change linearly with composition of copolymer. Values of  $\exp(-\Gamma/RT)$  are designated by numbers associated with the curves.

Substitution of the above two equations into Eqs. (15) and (21) affords two basic equations from which  $\phi_A$  and  $\phi_B$  can be calculated as functions of six thermodynamic parameters. Of the six parameters, three are chemical in nature ( $\Gamma/RT$ ,  $G_{\alpha A}^\circ/RT$ ,  $G_{\beta B}^\circ/RT$ ) and the other three are physical interaction parameters and have a secondary effect. The case where the latter are negligible was discussed

previously. It is noted, however, that there is a restriction on the initial conditions in this case, i.e.,

$$\phi_{A0} + \phi_{B0} = 1 \quad (34)$$

and Figs. 1 through 3 cannot be used because their initial conditions are not consistent with Eq. (34). Thus, we will show an example for the case with no physical interactions. In bulk copolymerization the triangle representation of the composition is convenient as has been done by Leonard [8].

Figure 5 shows the equilibrium composition in bulk copolymerization

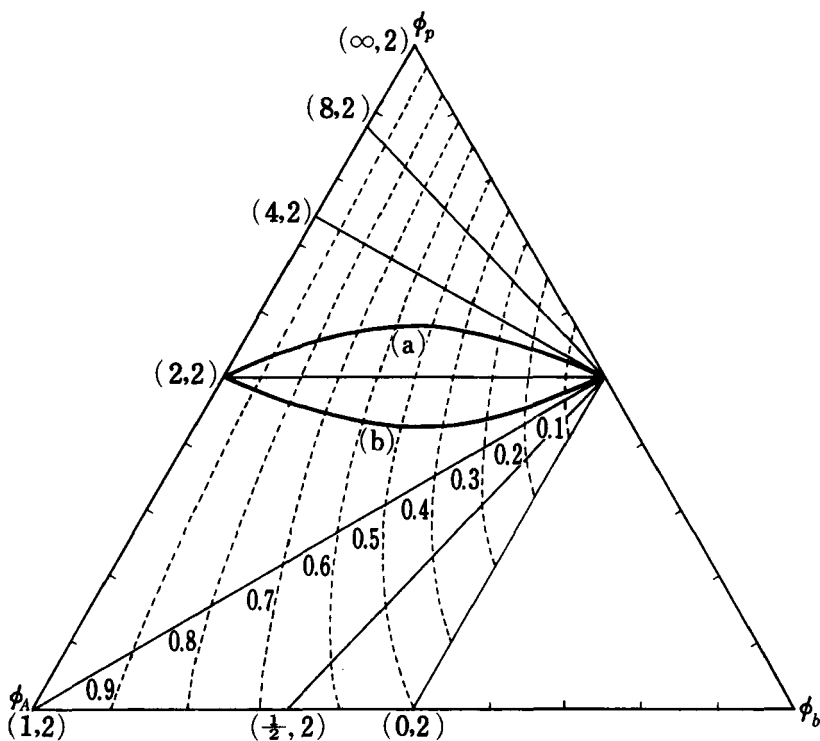


FIG. 5. Equilibrium composition in bulk copolymerization without physical interactions. Full lines: Curves with constant  $\Delta G_{\alpha A}^{\circ}/RT$  and  $\Delta G_{\beta B}^{\circ}/RT$ . Sets of values of  $\exp(-G_{\alpha A}^{\circ}/RT + 1)$  and  $\exp(-G_{\beta B}^{\circ}/RT + 1)$  are given in parentheses at the ends of curves. Linear lines,  $\Gamma = 0$ ; (a),  $\exp(-\Gamma/RT) = 2$  for (2,2); (b),  $\exp(-\Gamma/RT) = 1/2$  for (2,2). Dotted lines: Curves with constant initial volume fractions of A ( $\phi_{A0}$ ). Values of  $\phi_{A0}$  are given by numbers associated with the curves.

for the case without physical interactions. The full lines represent Eq. (15) with sets of constant values of  $\exp(-G_{\alpha A}^{\circ}/RT + 1)$  and  $\exp(-G_{\beta B}^{\circ}/RT + 1)$ . Here the values of the latter is kept as 2 and the sets of the values of two parameters are given in parentheses, e.g., as (2,2). The dotted lines represent curves with constant initial monomer volume fraction  $\phi_{A0}$ . The cross points give the equilibrium composition as before. When  $\Gamma = 0$ , the lines with constant chemical parameters are linear and the two ends of the linear lines at  $\phi_A = 0$  and  $\phi_B = 0$  correspond to the equilibrium values in homopolymerization. Even when  $\Gamma \neq 0$  these two points remain unchanged, but the lines are no longer linear. When  $\Gamma < 0$ , copolymerization is favored and the equilibrium shifts upward as is shown by Curve a which corresponds to the case with  $\exp(-\Gamma/RT) = 2$  for (2,2). When  $\Gamma > 0$ , the equilibrium shifts downward because of the instability of the copolymer. This is shown by Curve b for (2,2) [ $\exp(-\Gamma/RT) = 1/2$ ]. Similarly concaved curves can be drawn around each linear line, and the deviation from the linear lines depends on the value of  $\Gamma/RT$ . We have not shown them in detail but the essential feature may be understood by the two examples given above.

To examine the effect of physical interactions, several values of  $\chi_{AP}$ ,  $\chi_{BP}$ , and  $\chi_{AB}$  are chosen and the composition curves are constructed for two cases having, as the values of  $\exp(-\Delta G_{\alpha A}^{\circ}/RT + 1)$ , and  $\exp(-\Delta G_{\beta B}^{\circ}/RT + 1)$ , 1 and 2 in one case and 4 and 2 in the other case, respectively. They are represented as (1,2) and (4,2) in Fig. 6.  $\Gamma$  is taken as zero. The curves for the cases without interactions are reproduced from Fig. 5. For simplicity we used the case where  $\chi_{AP} = \chi_{BP}$ , and they are assumed to be independent of the composition of the copolymer.

The change in the equilibrium behavior due to physical interactions may be explained conveniently from the change in the chemical potentials. From the definition of  $Z_A$  and  $Z_B$  (Eqs. 14) and remembering that  $\mu_{\alpha} = \mu_{\beta} = \mu_P$  (Eq. 12), Eqs. (33) can be rewritten as

$$\frac{\Delta\mu_{\alpha} - \Delta\mu_A}{RT} (= Z_A - \frac{\Delta G_{\alpha A}^{\circ}}{RT}) = -1 - \ln \phi_A + 2\chi_P (\phi_A + \phi_B - \frac{1}{2}) - \chi_{AB}\phi_B \quad (35a)$$

$$\frac{\Delta\mu_{\beta} - \Delta\mu_B}{RT} (= Z_B - \frac{\Delta G_{\beta B}^{\circ}}{RT}) = -1 - \ln \phi_B + 2\chi_P (\phi_A + \phi_B - \frac{1}{2}) - \chi_{AB}\phi_A \quad (35b)$$

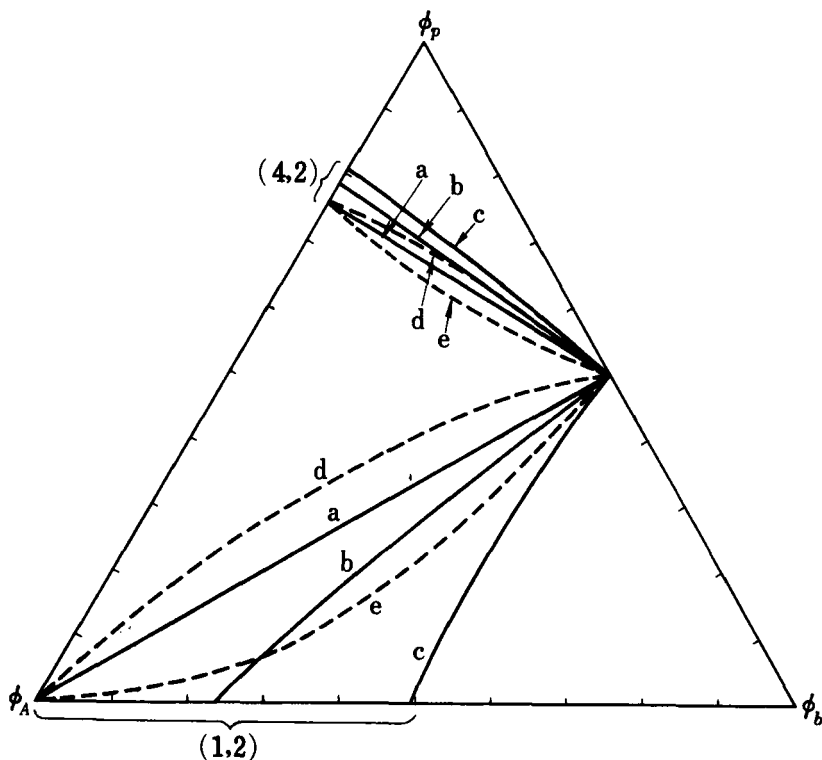


FIG. 6. Effects of physical interactions on equilibrium composition in bulk copolymerization.  $\Gamma$  is taken as 0. The curves with constant initial monomer volume fractions are not represented here. The two groups of curves correspond to the cases where  $\exp(-G_{\alpha A}^{\circ}/RT + 1)$  and  $\exp(-G_{\beta B}^{\circ}/RT + 1)$  are taken as (1 and 2) and (4 and 2), respectively. The interaction parameters are: (a),  $\chi_P = 0$ ,  $\chi_{AB} = 0$ ; (b),  $\chi_P = 0.2$ ,  $\chi_{AB} = 0$ ; (c),  $\chi_P = 0.4$ ,  $\chi_{AB} = 0$ ; (d),  $\chi_P = 0$ ,  $\chi_{AB} = 0.5$ ; and (e),  $\chi_P = 0$ ,  $\chi_{AB} = -0.5$ .

Because we are treating a special case of  $\chi_{AP} = \chi_{BP}$ , a new notation  $\chi_P$  is used. Without physical interactions,  $\ln \phi_A$  and  $\ln \phi_B$  or the differences in the excess chemical potential due to mixing have certain values governed by three chemical parameters and the initial

conditions. When physical interactions are introduced, the equilibrium will change according to the values of the last two terms in Eqs. (35). If they are positive, the chemical potential of the copolymer becomes larger than that of the monomers, and the equilibrium shifts to the side of the monomers by depolymerization. If they are negative, more polymer is formed.

The effect of  $\chi_P$  is reversed at  $\phi_A + \phi_B = 1/2$ . When  $\chi_P$  is positive, the volume fraction of the copolymer decreases in the region of  $\phi_A + \phi_B > 1/2$  as in the case of b and c for (1,2) in Fig. 6, and it increases in the region of  $\phi_A + \phi_B < 1/2$  as is seen in the case of b and c for (4.2). As  $\ln \phi_A$  tends to zero when  $\phi_A$  approaches unity, the term  $2\chi_P(\phi_A + \phi_B - 1/2)$  becomes relatively important and the deviation from the curves for no interactions will be larger. This is clearly seen in the case of (1,2). The coincidence of the curves at the other ends, i.e., at  $\phi_A = 0$ , is accidental because at this point  $\phi_A + \phi_B$  is just  $1/2$ . In general, the curves for the case with physical interactions do not coincide with those for no interactions, either at  $\phi_A = 0$  or at  $\phi_B = 0$ .

The effect of  $\chi_{AB}$  is different. When  $\chi_{AB}$  is positive, its introduction induces the shift of equilibrium toward the polymer side as in Curves d. Because  $\chi_{AB}\phi_B = 0$  at  $\phi_B = 0$ ,  $\ln \phi_A$  at this point is not affected. A similar relation holds at  $\phi_A = 0$ . Consequently, the values of  $\phi_A$  at  $\phi_B = 0$  and  $\phi_B$  at  $\phi_A = 0$  are the same as the equilibrium values without this monomer-monomer interaction (dotted lines).

The discussions given above hold for the general case where  $\Gamma$  has any arbitrary value. We believe, that it is not necessary to give other, more complicated examples because the behaviors are essentially similar in nature.

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