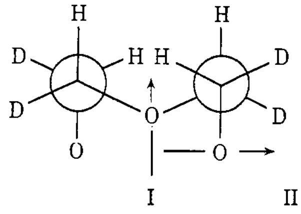
spectively.[6] Barlow confirmed this type of opening by X-ray analysis of poly(*trans*-2-butene oxide) which was found to be erythro diisotactic.[7] Present work on PEO shows that the conclusion about inversion ring opening may be extended to more general cases, that is, various types of polymerizations with cationic, anionic, and coordination catalysts.

Appendix

The internal coordinates and the numbering of the atoms are given in Table VII. The local symmetry coordinates for the *j*th monomeric unit, and the intermediate symmetry coordinates for the *p*th asymmetric unit (corresponding to eq 7 of ref 8) are given in Tables VIII and IX, respectively. In Table IX, the subscripts s and a represent symmetric and antisymmetric with respect to the twofold axes (on the midpoint of the C–C bond or the oxygen atom), respectively. The subscripts I and II for threo-disyndiotactic PEO-d_2 refer to the twofold rotation axes on the C–C bonds of the Newman projections I and II, respectively. The definition of the subscripts I and II for erythro-disyndiotactic PEO-d_2 are different from the threo-disyndiotactic case. These are associated with the twofold rotation axes on the oxygen atoms shown by the following Newman projection.



---

(6) E. J. Vandenberg, *J. Amer. Chem. Soc.*, **83**, 3538 (1961); *J. Polym. Sci., Part B*, **2**, 1085 (1964).

(7) M. Barlow, *J. Polym. Sci., Part A-2*, **4**, 121 (1966).

(8) H. Tadokoro, M. Kobayashi, Y. Kawaguchi, A. Kobayashi, and S. Murahashi, *J. Chem. Phys.*, **38**, 703 (1963).

Thermodynamics of Equilibrium Copolymerization in Solution. A General Expression and Its Application to Bulk Copolymerization

P. E. Harvey and J. Leonard*

Département de Chimie, Université Laval, Quebec 10, Canada.

Received June 16, 1972

ABSTRACT: Reversible addition of monomer A and monomer B to active copolymer chains leading to the formation of A–A, A–B, B–B, and B–A bonds is considered. P_{AA}, the probability that monomer A is added to a chain ending with A unit, is set equal to $K \exp(-\Delta G_{AAs}/RT)$, where K is a numerical constant found to be one and ΔG_{AAs} is the free energy change upon the addition in solution under conditions prevailing at equilibrium of 1 mol of monomer A to copolymer chains in order to form A–A bonds. All other probability terms P_{AB}, P_{BB}, and P_{BA} are defined analogously, and a simple general expression written in terms of free energy of polymerization in solution is obtained. This general expression is applied to equilibrium bulk copolymerization where monomers A and B are solvent for their copolymer. Making allowance for the nonideal behavior of the solution through the use of Flory's expression for the partial molar free energy of mixing of monomers and copolymer, an equation is written in terms of volume fractions of monomer A, ϕ_a, monomer B, ϕ_b, and copolymer, ϕ_p. Variations of ϕ_a and ϕ_b with ϕ_p and that of x_a with $\phi_a{}^0$ are computed for different values of free energy of polymerization and interaction parameters between monomer molecules, x_a being the mole fraction of monomer A in the copolymer and $\phi_a{}^0$ the volume fraction of the same monomer in the initial feed.

In recent years, copolymerization with depropagation with respect to both monomers has been treated by a number of authors. Solution to this complex problem has been considered through a kinetic[1-3] as well as thermodynamic approach.[4-6] Thermodynamic treatments by Theil[4] and Sawada[5] seem to refer to the formation of pure copolymer without any reference to the medium of copolymerization. More recently, Izu and O'Driscoll[6] have considered complete reversibility for copolymerization in an ideal solution and made use of a Monte Carlo technique for a numerical solution.[7] In the present paper, complete reversibility in equilibrium copolymerization in solution is considered, taking into account the nonideal behavior of the medium. Specific equations for equilibrium bulk copolymerization where monomers are solvent for their copolymer are derived.

The Model

In the case of equilibrium copolymerization in solution with complete reversibility, the overall equilibrium is established with respect to four reversible reactions

$$\sim\!A^* + A \rightleftharpoons \sim\!AA^* \qquad (I)$$

$$\sim\!B^* + A \rightleftharpoons \sim\!BA^* \qquad (II)$$

$$\sim\!B^* + B \rightleftharpoons \sim\!BB^* \qquad (III)$$

$$\sim\!A^* + B \rightleftharpoons \sim\!AB^* \qquad (IV)$$

These equations describe the reversible addition of monomers A and B to active chains ending with A* or B*; this set of reactions is known as the dyad model.[3]

In the present work, we consider the formation of 1 base mol of copolymer of infinite molecular weight and of composition

---

(1) A. A. Durgaryan, *Vysokomol. Soedin.*, **8**, 790 (1966).

(2) J. E. Hazell and K. J. Ivin, *Trans. Faraday Soc.*, **58**, 342 (1962); **61**, 2330 (1965).

(3) J. A. Howell, M. Izu, and K. F. O'Driscoll, *J. Polym. Sci., Part A-1*, **8**, 699 (1970).

(4) M. H. Theil, *Macromolecules*, **2**, 137 (1969).

(5) H. Sawada, *J. Polym. Sci., Part A-1*, **5**, 1383 (1967).

(6) M. Izu and K. F. O'Driscoll, *Polym. J.*, **1**, 27 (1970).

(7) M. Izu and K. F. O'Driscoll, *J. Polym. Sci., Part A-1*, **8**, 1675 (1970).

x_A and x_B, x_A and x_B being the mole fractions of monomer A and monomer B which are added to active chain ends under equilibrium conditions. The free energy of copolymerization is computed through the approach previously used in the cases of bulk[8] and solution[9] homopolymerizations. The free energy of copolymerization in an equilibrium mixture may be expressed as the sum of three terms

$$-(x_A\Delta\bar{G}_a + x_B\Delta\bar{G}_b) + \Delta G_{lc} + \Delta\bar{G}_p = 0 \qquad (1)$$

The first term in parentheses represents the free energy change associated with the removal of 1 mol of monomer from the equilibrium mixture without changing its concentration. $\Delta\bar{G}_a$ and $\Delta\bar{G}_b$ are the partial molar free energies of monomers A and B, respectively, multiplied by the appropriate quantities x_A and x_B. ΔG_{lc} is the free energy change for the conversion of 1 mol ($x_A + x_B$) of liquid monomer into 1 base mol of amorphous copolymer. $\Delta\bar{G}_p$ is the partial molar free energy of the copolymer, the free energy change associated with the addition of 1 base mol of copolymer to the equilibrium mixture.

ΔG_{lc} represents the sum of the free energy changes associated with reactions I–IV. ΔG_{AA} is the free energy change for the addition of 1 mol of liquid monomer A to amorphous copolymer chains ended by a monomer unit A. The contribution of this to ΔG_{lc} is given by $x_{AA}\Delta G_{AA}$, where x_{AA} is the fraction of monomer over a total of 1 mol of monomer that forms an A–A bond. ΔG_{BA}, ΔG_{BB}, ΔG_{AB} and x_{BA}, x_{BB}, x_{AB} are defined analogously for reactions II, III, and IV. The value of x_{AA} is equal to P_{AA}, the compound probability that monomer A is added to an active chain ending with A. Similarly, P_{BA} is the probability that monomer A is added to an active chain ending with B and is equal to x_{BA}. $P_{AA} + P_{BA}$ represents the probability that monomer A is added to an active chain end irrespectively of the nature of that chain end and this is equal to x_A. P_{BB} and P_{AB} being defined in a similar fashion, it follows from all these definitions that

$$x_A = x_{AA} + x_{BA} = P_{AA} + P_{BA} \qquad (2)$$

$$x_B = x_{BB} + x_{AB} = P_{BB} + P_{AB} \qquad (3)$$

$$x_A + x_B = P_{AA} + P_{BA} + P_{BB} + P_{AB} = 1 \qquad (4)$$

$$\Delta G_{lc} = P_{AA}\Delta G_{AA} + P_{BA}\Delta G_{BA} + P_{BB}\Delta G_{BB} + P_{AB}\Delta G_{AB} + \Delta G_D \qquad (5)$$

The introduction of the term ΔG_D is made necessary owing to the fact that in the course of monomer addition, two different monomers are distributed at the chain ends in order to form four types of bonds. ΔH for this process is negligible so that

$$\Delta G_D = -T\Delta S_D = -Tk \ln \Omega \qquad (6)$$

where k is the Boltzmann constant and Ω is the number of ways of arranging N_{AA}, N_{BA}, N_{BB}, and N_{AB} bonds among a total of N bonds, N being the Avogadro number. Using the law of permutations, one obtains

$$\Delta S_D = k \ln \Omega = k \ln \frac{N!}{N_{AA}!N_{BA}!N_{BB}!N_{AB}!} \qquad (7)$$

Using Stirling's approximation and with $N_{AA} = x_{AA}N = P_{AA}N$, $N_{BA} = x_{BA}N = P_{BA}N$, $N_{BB} = x_{BB}N = P_{BB}N$, and $N_{AB} = x_{AB}N = P_{AB}N$, eq 7 becomes

$$\Delta S_D = -Nk(P_{AA} \ln P_{AA} + P_{BA} \ln P_{BA} + P_{BB} \ln P_{BB} + P_{AB} \ln P_{AB}) \qquad (8)$$

ΔS_D is different from the entropy term included in ΔG_{AA}, ΔG_{BA}, ΔG_{BB}, and ΔG_{AB}. ΔS_{AA} is the change in entropy when one mol of liquid monomer A is transformed into polymer in order to form 1 mol of A–A bonds. In ΔS_{AA}, it is not taken into account that a mixture of four different types of bonds is formed, this contribution to the total entropy change being computed through ΔS_D.

A General Expression

In order to obtain a general expression in terms of measurable variables, one has to evaluate the above probability terms. The occurrence of reaction I, expressed by P_{AA}, is a function of ΔG_{AAs}, the free energy change when 1 mol of monomer is converted into 1 mol of A–A bonds in solution under overall equilibrium conditions. Accordingly, the probability that monomer A will add to a chain ending with a monomer unit A is set as $P_{AA} = K \exp[-\Delta G_{AAs}/RT]$. P_{BA}, P_{BB}, and P_{AB} are defined in the same manner, so that

$$\begin{aligned} P_{AA} &= K \exp[-\Delta G_{AAs}/RT] \equiv K \exp X \\ P_{BA} &= K \exp[-\Delta_{BAs}/RT] \equiv K \exp Z_a \\ P_{BB} &= K \exp[-\Delta G_{BBs}/RT] \equiv K \exp Y \\ P_{AB} &= K \exp[-\Delta G_{ABs}/RT] \equiv K \exp Z_b \end{aligned} \qquad (9)$$

where K is a proportionality constant. Assuming that, under equilibrium conditions, the proportions of chains ending with A and B remain constant and, since these proportions are not changed after reactions I and III, it necessarily follows that $P_{AB} = P_{BA}$ so that one can write

$$P_{AB} = P_{BA} = K \exp(Z_a + Z_b)/2 \qquad (10)$$

As has been stated in the case of eq 1, the free energy of polymerization of 1 mol of monomer in solution may be considered as the sum of three terms: the free energy change for the removal of 1 mol of monomer from the mixture ($-\Delta\bar{G}_a$ or $-\Delta\bar{G}_b$), the free energy change for the conversion of 1 mol of liquid monomer to 1 base mol of amorphous polymer (ΔG_{AA}, ΔG_{BA}, ΔG_{BB}, or ΔG_{AB}), and the free energy change for the addition of 1 base mol of copolymer to the mixture ($\Delta\bar{G}_p$). Consequently, the four free energy terms appearing in eq 9 may be written as

$$\begin{aligned} -\Delta G_{AAs}/RT &= (\Delta\bar{G}_a - \Delta\bar{G}_p - \Delta G_{AA})/RT = X \\ -\Delta G_{BAs}/RT &= (\Delta\bar{G}_a - \Delta\bar{G}_p - \Delta G_{BA})/RT = Z_a \\ -\Delta G_{BBs}/RT &= (\Delta\bar{G}_b - \Delta\bar{G}_p - \Delta G_{BB})/RT = Y \\ -\Delta G_{ABs}/RT &= (\Delta\bar{G}_b - \Delta\bar{G}_p - \Delta G_{AB})/RT = Z_b \end{aligned} \qquad (11)$$

Substituting eq 2, 3, 4, and 5 in eq 1, dividing by RT, rearranging the expression, and using definitions given in eq 11, one obtains

$$-P_{AA}X - P_{BA}Z_a - P_{BB}Y - P_{AB}Z_b + \Delta G_D/RT = 0 \qquad (12)$$

With $\Delta G_D/RT$ obtained from eq 6 and 8, and making use of eq 9 and 10, eq 12 becomes

$$(\ln K)(K \exp X + K \exp Y + 2K \exp\{(Z_a + Z_b)/2\}) = \qquad (13)$$

$$(\ln K)(P_{AA} + P_{BB} + P_{BA} + P_{AB}) = 0 \qquad (13a)$$

From eq 4, 9, and 10, it can be seen that the expression in parentheses in eq 13a is equal to unity and therefore K. From eq 13, one can write

$$\exp X + \exp Y + 2 \exp\{(Z_a + Z_b)/2\} = 1 \qquad (14)$$

---

(8) K. J. Ivin and J. Leonard, *Polymer*, **6**, 621 (1965).
(9) K. J. Ivin and J. Leonard, *Eur. Polym. J.*, **6**, 331 (1970).

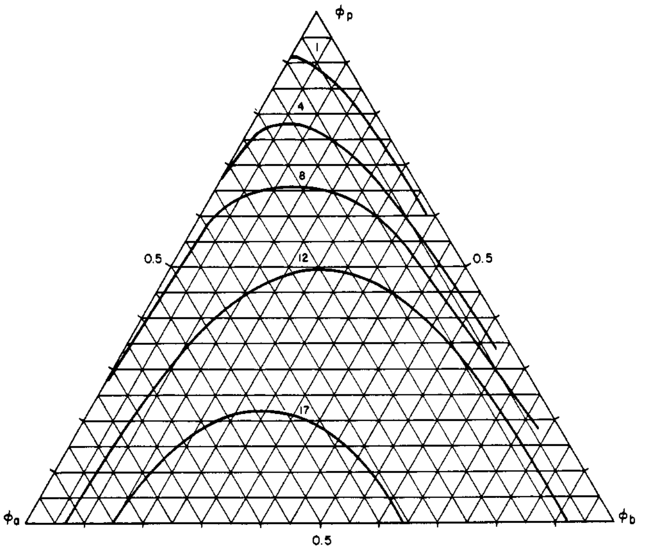


Figure 1. Equilibrium bulk copolymerization. Variation of volume fractions ϕ_a, ϕ_b, and ϕ_p for $\chi_{ab} = 0$, $\Delta G_{AA}/RT$, $\Delta G_{BB}/RT$, and $\Delta \bar{G}_{AB}/RT$ being respectively: (curve 1) -1.0, $+1.0$, 0; (curve 4) 0, $+1.0$, $+0.5$; (curve 8) $+0.5$, $+1.0$, $+0.75$; (curve 12) $+1.0$, $+1.0$, $+1.0$; (curve 17) $+1.0$, $+1.5$, $+1.25$.

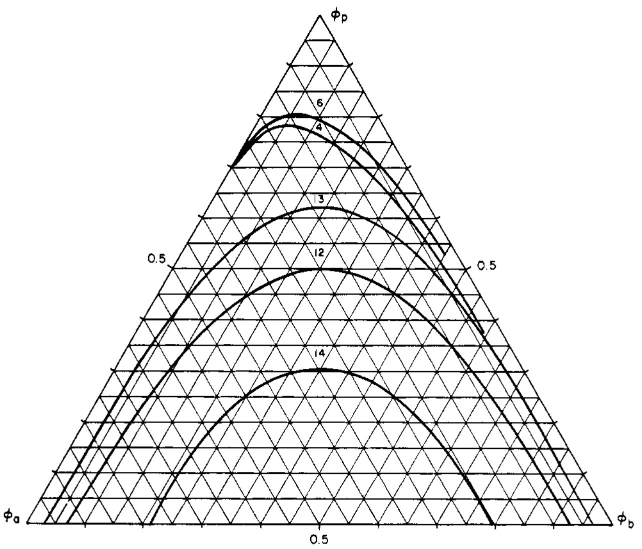


Figure 2. Equilibrium bulk copolymerization. Effect of χ_{ab} on the system-composition curve. With $\Delta G_{AA}/RT$, $\Delta G_{BB}/RT$, and $\Delta \bar{G}_{AB}/RT$ being equal to 0, $+1.0$, $+0.5$, respectively: (curve 4) $\chi_{ab} = 0$, (curve 6) $\chi_{ab} = +1.0$. With $\Delta G_{AA}/RT = \Delta G_{BB}/RT = \Delta \bar{G}_{AB}/RT = +1.0$, χ_{ab} is equal to: (curve 12) 0, (curve 13) $+1.0$, (curve 14) -0.5.

or more explicitly

$$\exp\{(\Delta\bar{G}_a - \Delta\bar{G}_p - \Delta G_{AA})/RT\} + \exp\{(\Delta\bar{G}_b - \Delta\bar{G}_p - \Delta G_{BB})/RT\} + 2\exp\{(\Delta\bar{G}_a + \Delta\bar{G}_b - 2\,\Delta\bar{G}_p - \Delta G_{AB} - \Delta G_{BA})/2RT\} = 1 \quad (15)$$

Equations 14 and 15 are simple general expressions which describe a complex situation. These equations are written solely in terms of free energy without any specific reference to probability terms as such. From eq 14 and 9, it follows that free energy changes associated with reactions I–IV in solution should be larger than zero in order to obtain every term smaller than one. In the case of homopolymerization, reactions II–IV do not take place and, under equilibrium conditions, ΔG_{AAs} is zero, which is consistent with eq 14.

Application to bulk copolymerization

Equation 15 is a general expression which should be applicable to any equilibrium copolymerization in solution. In the present study, this equation is applied to bulk copolymerization where the monomers are solvent for their copolymer. Then, the copolymerization mixture consists of a three-component system: two monomers and one copolymer.

Flory's thermodynamic treatment[10] of ternary systems consisting of a single polymer in a binary solvent mixture is applied to bulk copolymerization, so that for very high molecular weight copolymer, one can write

$$\Delta\bar{G}_a/RT = \ln\phi_a + (1 - \phi_a) - (V_a/V_b)\phi_b + (\chi_{ab}\phi_b + \chi_{ap}\phi_p)(\phi_b + \phi_p) - \chi_{bp}(V_a/V_b)\phi_b\phi_p \quad (16)$$

$$\Delta\bar{G}_b/RT = \ln\phi_b + (1 - \phi_b) - (V_b/V_a)\phi_a + (\chi_{ba}\phi_a + \chi_{bp}\phi_p)(\phi_a + \phi_p) - \chi_{ap}(V_b/V_a)\phi_a\phi_p \quad (17)$$

$$\Delta\bar{G}_p/RT = (1/n)[\ln\phi_p + (1 - \phi_p) - (nV_p/V_a)\phi_a - (nV_p/V_b)\phi_b + (\chi_{pa}\phi_a + \chi_{pb}\phi_b)(\phi_a + \phi_b) - \chi_{ab}(nV_p/V_a)\phi_a\phi_b] \quad (18)$$

Because $\Delta\bar{G}_p$ is referring to 1 base mol of copolymer, Flory's expression in eq 18 is divided by n, the average number of monomer units in a chain of copolymer. In these expressions, subscripts a, b, and p refer to monomer A, monomer B, and copolymer, respectively. ϕ is the volume fraction of any species under equilibrium conditions and χ is the interaction parameter between any two components of the system. V_a and V_b are the molar volumes of monomers A and B, respectively, and V_p is the average molar volume of a monomer unit in the copolymer.

With $\chi_{ji} = \chi_{ij}(V_j/V_i)$, assuming there is no preferential solvation of the copolymer so that $\chi_{ap} = \chi_{bp} = \chi$, taking $V_a = V_b = V_p$ and bearing in mind that n is large, eq 16, 17 and 18 become

$$\Delta\bar{G}_a/RT = \ln\phi_a + 1 - \phi_a - \phi_b + (\chi_{ab}\phi_b + \chi\phi_p)(\phi_b + \phi_p) - \chi\phi_b\phi_p \quad (19)$$

$$\Delta\bar{G}_b/RT = \ln\phi_b + 1 - \phi_b - \phi_a + (\chi_{ab}\phi_a + \chi\phi_p)(\phi_a + \phi_p) - \chi\phi_a\phi_p \quad (20)$$

$$\Delta\bar{G}_p/RT = -\phi_a - \phi_b + (\chi\phi_a + \chi\phi_b)(\phi_a + \phi_b) - \chi_{ab}\phi_a\phi_b \quad (21)$$

From eq 19, 20, and 21, with $\phi_a + \phi_b + \phi_p = 1$, it is readily found that

$$(\Delta\bar{G}_a - \Delta\bar{G}_p)/RT = \ln\phi_a + 1 + \chi_{ab}\phi_b + \chi - 2\chi(\phi_a + \phi_b) \quad (22)$$

$$(\Delta\bar{G}_b - \Delta\bar{G}_p)/RT = \ln\phi_b + 1 + \chi_{ab}\phi_a + \chi - 2\chi(\phi_a + \phi_b) \quad (23)$$

Substituting eq 22 and 23 in eq 15, one finally obtains

$$\exp\{1 + \chi - 2\chi(\phi_a + \phi_b)\}[\phi_a\exp\{\chi_{ab}\phi_b - \Delta G_{AA}/RT\} + \phi_b\exp\{\chi_{ab}\phi_a - \Delta G_{BB}/RT\} + 2\phi_a^{1/2}\,\phi_b^{1/2}\exp\{\chi_{ab}(\phi_a + \phi_b)/2 - (\Delta G_{AB} + \Delta G_{BA})/2RT\}] = 1 \quad (24)$$

---

(10) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 549.

TABLE I
THERMODYNAMIC PARAMETERS USED FOR THE COMPUTATION OF ϕ_a, ϕ_b, ϕ_p, and x_A with $\chi = 0.4$

Cases	$\Delta G_{AA}/RT$	$\Delta G_{BB}/RT$	$\Delta\bar{G}_{AB}/RT$	χ_{ab}	Remarks
1	−1.0	+1.0	0	0	Figure 1
2	−1.0	+1.0	0	+1.0	ϕ_p 1% higher than in case 1
3	−1.0	+1.0	0	−1.0	Identical with case 1
4	0	+1.0	+0.5	0	Figures 1 and 2
5	0	+1.0	+0.5	−1.0	Identical with case 4
6	0	+1.0	+0.5	+1.0	Figure 2
7	+0.5	+0.5	+0.5	0	Figure 4
8	+0.5	+1.0	+0.75	0	Figures 1 and 3
9	+0.5	+1.0	−0.25	0	Figure 3
10	+0.5	+1.0	+1.75	0	Figure 3
11	+0.5	+1.5	+1.0	+1.0	Figure 5
12	+1.0	+1.0	+1.0	0	Figures 1, 2, and 4
13	+1.0	+1.0	+1.0	+1.0	Figure 2
14	+1.0	+1.0	+1.0	−0.5	Figure 2
15	+1.0	+1.0	+1.0	−1.0	No polymeric material formed
16	+1.0	+1.0	−3.5	0	Figure 4
17	+1.0	+1.5	+1.25	0	Figure 1
18	+1.0	+1.5	+1.25	−0.5	No polymeric material formed
19	+1.5	+1.5	+1.5	0	No polymeric material formed
20	+1.5	+1.5	−2.0	0	Figure 4
21	+2.0	−1.0	+2.0	0	Figure 5

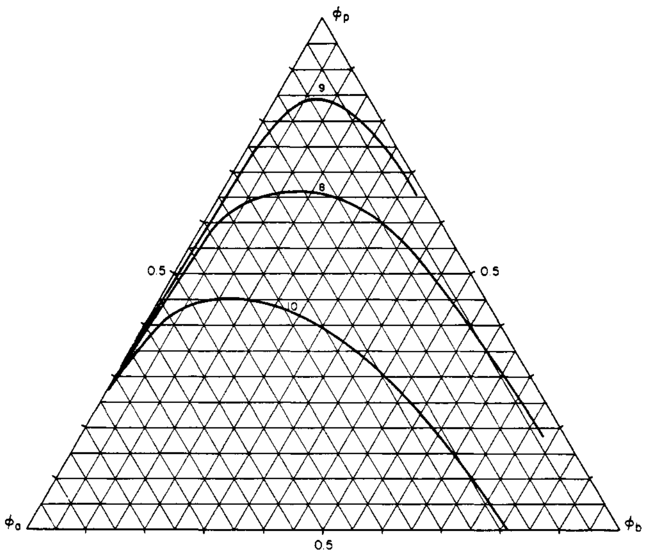


Figure 3. Equilibrium bulk copolymerization. Effect of $\Delta\bar{G}_{AB}/RT$ on the system–composition curve. With $\chi_{ab} = 0$, $\Delta G_{AA}/RT = +0.5$ and $\Delta G_{BB}/RT = +1.0$, $\Delta\bar{G}_{AB}/RT$ is equal to: (curve 8) +0.75, (curve 9) −0.25, (curve 10) +1.75.

If interaction parameters χ and χ_{ab} andΔG terms are known, eq 24 can be used for the computation of ϕ_a as a function of ϕ_b or ϕ_p. In the case where one of the monomers, say monomer B, is much more reactive than monomer A so that monomer B polymerizes completely and very rapidly, at equilibrium all active chains are ended by A units and are in equilibrium with monomer A. This situation is equivalent to an equilibrium homopolymerization. Under these conditions, ϕ_b is equal to zero and eq 24 is reduced to

$$1 + \chi - 2\chi\phi_a + \ln \phi_a - \Delta G_{AA}/RT = 0 \qquad (25)$$

which is the equation derived by Ivin and Leonard for equilibrium bulk polymerization.[8]

Calculations

Composition of a copolymerization system at equilibrium may be computed through the use of eq 24, values of $\Delta G_{AA}/RT$, $\Delta G_{BB}/RT$, $\Delta\bar{G}_{AB}/RT\,(=(\Delta G_{AB} + \Delta G_{BA})/2RT)$, χ_{ab}, and χ being known. Computations have been carried out for typical cases listed in Table I. A value of 0.4 has been ascribed to χ for all cases.

Figure 1 shows various system–composition curves for $\chi_{ab} = 0$ and $\Delta\bar{G}_{AB}/RT = {}^1/_2(\Delta G_{AA} + \Delta G_{BB})/RT$. As expected, curves are displaced toward the upper part of the diagram (high value of ϕ_p) with decreasing value of $\Delta G_{ij}/RT$. It can be seen from curve 1 that, due to the negative value of $\Delta G_{AA}/RT$, ϕ_a will be small compared to ϕ_b and ϕ_p. All free energies of polymerization being equal, curve 12 is symmetrical, since all possible additions of monomer molecules to the polymeric chains are equally favored. In this case, χ_{ab} being zero, monomer units A and B should be distributed at random in the polymeric chains. Curve 17 is typical of a system where both monomers have little tendency to polymerize or copolymerize. No high molecular weight material should be formed if all three $\Delta G_{ij}/RT$ values are equal to + 1.5.

The effect of interaction between the two monomers on the equilibrium position is observed by allowing χ_{ab} to vary. In general, a negative value of χ_{ab}, which may be related to strong attractions between monomer molecules, hinders the formation of copolymer, whereas a positive value enhances it. This effect is negligible when the degree of conversion is high, as in the cases 1–6 (see Table I and Figure 2). However, the effect becomes very important for high values of $\Delta G_{ij}/RT$. As can be seen from Figure 2 (cases 12–15), the maximum value of ϕ_p decreases from 0.62 for $\chi_{ab} = +1.0$ to 0.30 for $\chi_{ab} = -0.5$ and no high molecular weight material is formed with $\chi_{ab} = -1.0$.

All the curves given in Figures 1 and 2 are computed using $\Delta\bar{G}_{AB}/RT$ as the average of $\Delta G_{AA}/RT$ and $\Delta G_{BB}/RT$. However, this is often not the case, and the composition of the system at equilibrium may strongly depend on the value of $\Delta\bar{G}_{AB}/RT$. Curves with $\Delta\bar{G}_{AB}/RT$ equal to the average and differing by −1 and +1 from the average (cases 8, 9, and 10) are shown in Figure 3.

Composition of the copolymer is expressed by x_A, and from eq 9, 11, 22, and 23, one obtains

$$x_A = P_{AA} + P_{BA} = \exp\{1 + \chi - 2\chi(\phi_a + \phi_b)\} \times [\phi_a \exp(\chi_{ab}\phi_b - \Delta G_{AA}/RT) + \phi_a^{1/2}\phi_b^{1/2} \exp\{\chi_{ab}(\phi_b + \phi_a)/2 - \Delta\bar{G}_{AB}/RT\}] \qquad (26)$$

Recently[3] it has been shown that, in the case of a stationary system, there is equivalence between the conditional probability at chain end and that in the main chain. Izu and O'Driscoll[6] have expressed the copolymer composition F_A in terms of the conditional probabilities $1 - \eta$ and $1 - \epsilon$. With $1 - \eta = P_{AB}/x_B$ and $1 - \epsilon = P_{BA}/x_A$ and bearing in mind that $P_{BA} = P_{AB}$, it is found that F_A is identical with our function x_A, so that x_A may be considered as the copolymer composition. Computations of x_A as a function of ϕ_a^0, the volume fraction of monomer A in the initial feed, have been carried out for a number of cases and results are shown in Figures 4 and 5. Values of x_A are obtained from

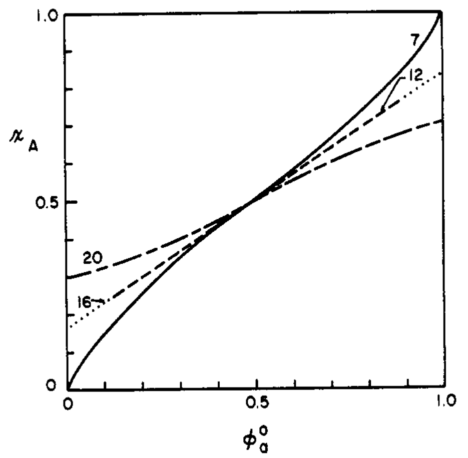


Figure 4. Variation of x_A, the mole fraction of monomer A in the copolymer, with ϕ_a^0, the volume fraction of monomer A in the initial feed with $\chi_{ab} = 0$ and $\Delta G_{AA}/RT$, $\Delta G_{BB}/RT$, and $\Delta \tilde{G}_{AB}/RT$ being respectively: (curve 7) +0.5, +0.5, +0.5; (curve 12) +1.0, +1.0, +1.0; (curve 16) +1.0, +1.0, −3.5; (curve 20) +1.5, +1.5, −2.0.

eq 26 and the corresponding value of ϕ_a^0 is obtained from $\phi_a^0 = \phi_a + x_A\phi_p$.

Figure 4 shows the curves obtained for cases 7 and 12 where all three values of $\Delta G_{ij}/RT$ are identical. With values of +0.5, the curve is slightly sigmoidal and linear with values of +1.0. In the latter case, the curve does not cover the full range of ϕ_a^0, since for ϕ_a^0 smaller than 0.1 and larger than 0.9, polymerization does not take place under those conditions. With $\Delta \tilde{G}_{AB}/RT = -3.5$ (case 16), the position of the curve is identical with that of case 12 but the full range of ϕ_a^0 is covered. Here, because of the low value of $\Delta \tilde{G}_{AB}/RT$, even at low concentration, the available monomer A will copolymerize to form A–B bonds. In case 20, both monomers have very little tendency to homopolymerize and a high proportion of A–B bonds is expected. This is reflected in the values of x_A that range between 0.3 and 0.7 for any initial feed.

Sets of dissimilar values of $\Delta G_{ij}/RT$ yield different types of curves, some of which are illustrated in Figure 5. In case 11, the value of x_A is always high, since the addition of monomer A is favored in comparison with that of monomer B. On the other hand, in case 21, because of the high values of $\Delta G_{AA}/RT$ and $\Delta \tilde{G}_{BA}/RT$, important addition of monomer A is prevented so that the A content in the copolymer is always low whatever the composition of the initial feed is.

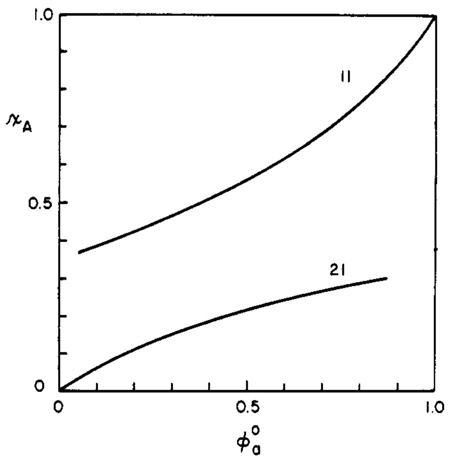


Figure 5. Variation of x_A, the mole fraction of monomer A in the copolymer, with ϕ_a^0, the volume fraction of monomer A in the initial feed with $\Delta G_{AA}/RT$, $\Delta G_{BB}/RT$, $\Delta \tilde{G}_{AB}/RT$, and χ_{ab} being respectively: (curve 11) +0.5, +1.5, +1.0, +1.0; (curve 21) +2.0, −1.0, +2.0, 0.

In general, the value of χ_{ab} has a negligible effect on the position of the copolymer–composition curve contrary to the system–composition curve (see Figure 2). However, the range of ϕ_a^0 where polymerization is possible is extended by an increase in the value of χ_{ab} if this increase is accompanied by a higher degree of conversion.

The curves presented in Figures 4 and 5 are similar to curves computed by Izu and O'Driscoll[7] through the use of the Monte Carlo method, although a direct comparison between the two sets of results is made difficult, since the reference states for the free energy terms are different.

Acknowledgments. The authors gratefully acknowledge financial support from the Defence Research Board of Canada, Grant No. DRB-9530-85 (UG). P. E. H. wishes to thank the Minister of Education, Province of Quebec, for the award of a fellowship.