Thermochemical Aspects of Polymerization. Equilibrium Copolymerization

Michael H. Theil

Department of Textile Chemistry, North Carolina State University, Raleigh, North Carolina 27607. *Received September 4, 1968*

ABSTRACT: An expression is derived for the free energy of formation of an infinite molecular weight binary copolymer from the corresponding homopolymers where only nearest neighbor intrachain interactions are significant. Thermodynamic properties and the sequence length distribution of an equilibrium copolymer are then calculated. When there is no excess energy of interaction between unlike monomer units ($\Delta\epsilon_{AB}$) the randomness and the entropy of sequence length distribution (ΔS_D) are independent of temperature and, for a given composition, maximized. If $\Delta\epsilon_{AB}$ is negative and the copolymer contains unequal numbers of the two monomers there is a residual ΔS_D at 0°K. Positive values of $\Delta\epsilon_{AB}$ in this one-dimensional model never lead to the simultaneous generation of two independent sequence length distributions. The average sequence length of a unit increases as its mole fraction increases and as $\Delta\epsilon_{AB}$ becomes more positive; it tends toward randomness as the temperature increases. Two parameters, B and Q, which characterize copolymer randomness are compared. Both depend on $\Delta\epsilon_{AB}$ and the temperature; B also depends on composition. Q is analogous to the reactivity ratio product of kinetically controlled copolymerizations and is the reciprocal of the equilibrium constant for equilibrium copolymerization.

Equilibrium copolymerizations are characterized by reversible chain forming steps as well as by the involvement of more than one kind of monomer unit. Such a process normally occurs during melt condensation copolymerizations and near the ceiling temperature in addition copolymerizations.

It is desirable to be able to predict the detailed characteristics of the products of equilibrium copolymerizations. Tobolsky and Owen adopted a kinetically based approach to the process which provided estimates of total chain lengths that agreed well with experiment.[1] Complementary thermochemical approaches to equilibrium copolymerization have also been advanced.[2–4] This paper develops the theory from a simple thermochemical model to the point where quantitative aspects of the sequence length distribution and the thermodynamic state of the polymer may be calculated from a few parameters characteristic of the system.

Theoretical

Description of the Model and Notation. The present paper considers the formation of an infinite molecular weight binary copolymer against a reference state of two infinite molecular weight homopolymers. Configurational irregularities such as head-to-head, tail-to-tail enchainments or stereoirregular placements of monomers, while copolymeric in nature, are not specifically treated here. It is assumed that only interactions between nearest neighbors in the chain have any effect upon the copolymerization. The formation and possible effects of more than one phase is not considered. The reaction is assumed to take place at constant, moderate pressures with negligible change in volume. Therefore, the enthalpy and the internal energy of the copolymerization can be considered equivalent as can the Gibbs and Helmholtz free energies.

The system so outlined conforms to a one-dimensional Ising model, and it is, therefore, indicated that an exact solution may be obtained.[5–7] The present treatment is developed in terms of the sequence propagation probabilities which are of primary physical significance in understanding various thermodynamic properties of copolymers.[8,9]

Upper case A or B in subscripts will refer to the structural units so designated. It should be noted that the sequence propagation probabilities, P_{AA} and P_{BB}, and the sequence termination probabilities, P_{AB} and P_{BA}, as defined by Alfrey and Goldfinger[10] and as used here, are conditional rather than compound probabilities. For example, P_{AB} is the probability that a B unit follows a unit which has already been indentified as an A; that is, $P_{AB} \equiv P(B/A)$. In some instances in the recent literature such notation has been applied to compound probabilities.[11,12]

Other symbols are defined as follows: N_A, N_B = the number of sequences of a given counit in a molecule; N_0, N_{0A}, N_{0B} = the number of structural or repeating units; X_A, X_B = the mole fraction of a given structural unit.

The Entropy of Sequence Length Distribution. Orr[13]

---

(1) A. V. Tobolsky and G. D. T. Owen, *J. Polym. Sci.*, **59**, 329 (1962).

(2) T. Alfrey and A. V. Tobolsky, *ibid.*, **38**, 269 (1959); A. V. Tobolsky, "Properties and Structure of Polymers," John Wiley & Sons, Inc., New York, N. Y., 1960, pp 280–282.

(3) H. Sawada, *J. Polym. Sci., Part A*, **3**, 2483 (1965).

(4) H. Sawada, *ibid., Part A-1*, **5**, 1383 (1967).

(5) E. Ising, *Z. Physik*, **31**, 253 (1925).

(6) H. A. Kramers and G. H. Wannier, *Phys. Rev.*, **60**, 252 (1941).

(7) G. F. Newell and E. W. Montroll, *Rev. Mod. Phys.*, **25**, 353 (1953).

(8) P. J. Flory, *Trans. Faraday Soc.*, **51**, 848 (1955).

(9) C. H. Baker and L. Mandelkern, *Polymer*, **7**, 7 (1966).

(10) T. Alfrey and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

(11) H. Sawada, *J. Polym. Sci., Part A*, **2**, 3095 (1964).

(12) L. D. Maxim, C. H. Kuist, and M. E. Meyer, *Macromolecules*, **1**, 86 (1968).

(13) R. J. Orr, *Polymer*, **2**, 74 (1961).

first derived an expression for the entropy of distribution of a single monomer incorporated in a copolymer chain. Baker and Mandelkern expressed the number of distinguishable ways that both sequences of A and B could be arranged along a copolymer chain as[9]

$$\Omega = \frac{N_A!N_B!}{\prod_{J_A=1}^{\infty} N_{J_A}! \prod_{J_B=1}^{\infty} N_{J_B}!} \qquad (1)$$

where N_{J_A} and N_{J_B} are the number of sequences with J_A A units and J_B B units, respectively. $|N_A - N_B|$ must either be equal to zero or one. If it equals zero than eq 1 should be multiplied by two since the first sequence may be either of A or B units. However, the additional contribution to the entropy of sequence length distribution is negligible and will be ignored. From this expression and the procedure of Orr or Baker and Mandelkern it follows immediately that the entropy of sequence length distribution per mole of structural units in the copolymer is given by eq 2. This differs

$$\Delta S_D/N_0 = -R\{X_A[(1 - P_{AA}) + P_{AA} \ln P_{AA}] + X_B[(1 - P_{BB}) \ln (1 - P_{BB}) + P_{BB} \ln P_{BB}]\} \qquad (2)$$

from other expressions which do not recognize that the entropy of sequence length distribution includes the contributions of the separate arrangements of both the A and the B sequences.[3,13]

In order to assign values to ΔS_D it is necessary to define the interrelationship between the propagation probabilities P_{AA} and P_{BB}. One approach is to express the fraction of A–B junctions (which may also be viewed as B–A junctions) as

$$X_AP_{AB} = X_BP_{BA} \qquad (3)$$

Equation 3 is a special case of the more general relationships derived by Simha and Zimmerman which define systems containing up to four components and for which next nearest neighbor placements must be considered.[14] In the present case for an infinite molecular weight binary copolymer

$$P_{AA} + P_{AB} = 1 \qquad (4)$$

and

$$P_{BB} + P_{BA} = 1 \qquad (5)$$

The relationship

$$P_{BB} = (X_A/X_B)P_{AA} + 1 - (X_A/X_B) \qquad (6)$$

then follows immediately.

ΔS_D may now be expressed in terms of the copolymer composition and one of its homogeneous propagation probabilities P_{AA} as is shown in Figure 1. Conforming to intuitive expectation, when $P_{AA} = X_A$ each copolymeric composition considered achieves a state of maximum ΔS_D. For $0 < X_A < 0.5$ ΔS_D remains greater than zero when $P_{AA} = 0$. This residual ΔS_D derives from the multiplicity of distinguishable arrangements of different length B sequences along the polymer chain although only one distinguishable arrangement of A units exists when $P_{AA} = 0$.

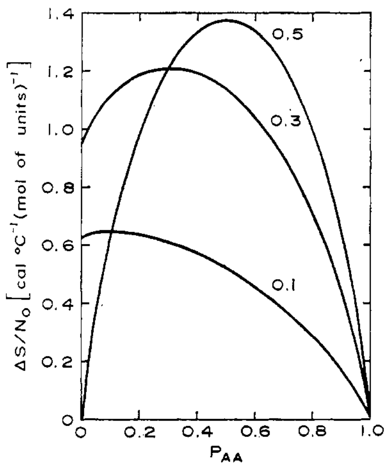

Figure 1. Entropy of sequence length distribution *vs.* propagation probability P_{AA} for copolymers with mole fraction of A units designated by numbers associated with curves.

The Energy of Copolymerization. The reactions which occur during the equilibrium copolymerization process may be symbolized by eq 7 in which the bonds

$$\sim\text{A–A}\sim + \sim\text{B–B}\sim \rightleftharpoons \sim\text{A–B}\sim + \sim\text{B–A}\sim \qquad (7)$$

on the left side of the equation, between like units, will be called homogeneous and those on the right side, heterogeneous. The distinction between bond types on the right side of the equation recognizes the differences between the head and tail of typical structural units such as occur in vinyl polymers. The energy corresponding to one of these bonds is given by an appropriately subscripted ϵ. Since, in this system, the formation or disappearance of an A–B bond is concomitant with the like process for a B–A bond, we may define an average energy content of a heterogeneous bond by

$$\epsilon_{\overline{AB}} = \tfrac{1}{2}(\epsilon_{AB} + \epsilon_{BA}) \qquad (8)$$

The energy of formation of an average heterogeneous bond may then be written as

$$\Delta\epsilon_{AB} = \epsilon_{\overline{AB}} - \tfrac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) \qquad (9)$$

The factor of $^1/_2$ signifies that two average heterogeneous bonds are formed for each pair of homogeneous bonds that disappear. For present purposes an expression is required for the total energy of reaction, $\Delta\epsilon_R$. This quantity is given by the product of $\Delta\epsilon_{AB}$ and the number of heterogeneous junctions in this system. The number of heterogeneous junctions is equal to the number of sequences contained in the system, $N_A + N_B$. Since $N_A = N_B$ in a binary infinite molecular weight copolymer we may write eq 10

$$\Delta\epsilon_R = 2N_A\Delta\epsilon_{AB} \qquad (10)$$

at the expense of concealing some of the symmetry present in this and subsequent equations. From the established relationship between the number of units and the number of sequences present eq 10 may be written as

$$\Delta\epsilon_R = 2N_{0A}(1 - P_{AA})\Delta\epsilon_{AB} \qquad (11)$$

The Free Energy of Copolymerization. The free energy of copolymerization may be stated as eq 12.

$$\Delta G = \Delta\epsilon_R - T\Delta S_D \qquad (12)$$

---

(14) R. Simha and J. M. Zimmerman, *J. Theoret. Biol.*, **2**, 87 (1962).

The term $\Delta\epsilon_R$ can be generalized to include an entropy contribution.[15] An entropy difference between a homogeneous and a heterogeneous bond pair might arise from steric or electrostatic nearest neighbor interactions. It would be expressed as a temperature coefficient of $\Delta\epsilon_{AB}$. $\Delta\epsilon_{AB}$ would then assume the character of a standard state free energy change which may be defined as eq 13, where ΔH_{AB} is the enthalpy

$$\Delta\epsilon_{AB} = \Delta H_{AB} - T\Delta S_{AB} \tag{13}$$

change in creating the average heterogeneous bond from homogeneous ones in analogy with eq 11. The standard state entropy of heterogeneous bond formation at constant pressure may be expressed as

$$\Delta S_{AB} = -\left(\frac{\partial\,\Delta\epsilon_{AB}}{\partial T}\right)_p \tag{14}$$

Then the total entropy of copolymerization is

$$\Delta S_T/N_0 = -R\{X_A[(1 - P_{AA})\ln(1 - P_{AA}) + P_{AA}\ln P_{AA}] + X_B[(1 - P_{BB})\ln(1 - P_{BB}) + P_{BB}\ln P_{BB}]\} + 2X_A(1 - P_{AA})\Delta S_{AB} \tag{15}$$

which may be written as

$$\Delta S_T = \Delta S_D + \Delta S_R \tag{16}$$

where ΔS_R is the entropy contributions described by the last term of eq 15. The enthalpy change in the copolymerization is then

$$\Delta H_R/N_0 = 2X_A(1 - P_{AA})\Delta H_{AB} \tag{17}$$

and

$$\Delta G = \Delta H_R - T\Delta S_T \tag{18}$$

The Equilibrium State. The equilibrium condition at a given temperature for this system is attained when the free energy as a function of the sequence length distribution attains a minimum value. Substituting eq 2 and 11 into 12, differentiating with respect to P_{AA}, and dividing by N_0

$$\frac{1}{N_0}\frac{\partial\Delta G}{\partial P_{AA}} = RT\left[X_A\ln\left(\frac{P_{AA}}{1 - P_{AA}}\right) + X_B\ln\left(\frac{P_{BB}}{1 - P_{BB}}\right)\frac{\partial P_{BB}}{\partial P_{AA}}\right] - 2X_A\Delta\epsilon_{AB} \tag{19}$$

is obtained. From eq 6, P_{BB} may be expressed in terms of P_{AA} and $\partial P_{BB}/\partial P_{AA}$ is evaluated as X_A/X_B. Letting the left side of eq 19 equal zero, making the implied substitutions, expressing the equation in exponential form, and rearranging terms, eq 20 is obtained

$$\left[\frac{X_A}{X_B}(1 - Q)\right]P_{AA}^2 + \left[1 - \frac{X_A}{X_B}(1 - 2Q)\right]P_{AA} - \frac{X_A}{X_B}Q = 0 \tag{20}$$

where $Q = \exp(2\Delta\epsilon_{AB}/RT)$. This quadratic equation may be solved for P_{AA}. That root which has a value between zero and one is the propagation probability for the composition, temperature and $\Delta\epsilon_{AB}$ given.

The equilibrium constant of the reaction may be extracted by again recasting the right side of eq 19 in exponential form after equating it to zero and substituting X_A/X_B for $\partial P_{BB}/\partial P_{AA}$. When $1 - P_{AA}$ is replaced by P_{AB} and $1 - P_{BB}$ by P_{BA} we obtain eq 21.

$$\frac{P_{AA}P_{BB}}{P_{AB}P_{BA}} = Q \tag{21}$$

The reciprocal of eq 21 is the equilibrium constant for the reaction as written in eq 7. That this is so is more readily apparent when eq 21 is rewritten as

$$\frac{(X_AP_{AB})(X_BP_{BA})}{(X_AP_{AA})(X_BP_{BB})} = Q^{-1} = K \tag{22}$$

since X_AP_{AB}, X_BP_{BA}, X_AP_{AA}, and X_BP_{BB} are, respectively, equal to the fractions of A–B, B–A, A–A, and B–B linkages present in the polymer. But for the lack of a configurational degeneracy in the model utilized, this expression would be equivalent to that deduced by Alfrey and Tobolsky.[2] With that exception, the vibrational partition functions in the latter expression are implicitly incorporated in the standard state free energy term, $\Delta\epsilon_{AB}$, employed in this development. The lack of configurational degeneracy between the A–B and the B–A junctions in this model implies a lack of symmetry with respect to the A–A and B–B junctions of the left side of eq 7. Thus, as a result of the "head–tail" nature of the structural units, symmetry factors are not included as preexponential factors in this equilibrium constant.

Analogous equilibrium constants have been derived by kinetic[16] as well as by thermodynamic treatments.[17]

Deductions Concerning Polymerizations and Polymer Structure

Thermodynamic Quantities. Once determined, the equilibrium value of P_{AA} may be applied to the calculation of the thermodynamic state of the equilibrium copolymer as well as to its sequence length distribution.

Calculations of the entropy of copolymerization as a function of temperature of reaction for this model are plotted in Figure 2. For a copolymerization in which $\Delta\epsilon_{AB} = 0$ the placement of a structural unit along the chain is independent of the nature of its nearest neighbors, and Bernoulli trial statistics are obeyed at all temperatures. The resulting sequence length distribution possesses the maximum randomness attainable for the composition given and is invariant with temperature. For $\Delta\epsilon_{AB} \neq 0$ the probability that a structural unit is in a given position in the chain is conditioned upon the nature of its nearest neighbors. The sequence length distributions attained in such cases are less random than that obtained when $\Delta\epsilon_{AB} = 0$ except in the limit of infinitely high temperature. Thus, when $\Delta\epsilon_{AB} = 0$, ΔS_D achieves a maximum value and is independent of temperature when $\Delta\epsilon_{AB} \neq 0$, ΔS_D assumes a lower value which increases with temperature.

Equations 2 and 15 show that the entropy associated with the copolymerization may be separated into two components—the entropy of sequence length distribution, ΔS_D, and that which arises from the contribution of the ΔS_{AB} term. In Figure 2, $\Delta S_T = \Delta S_D$ for those curves in which $\Delta S_{AB} = 0$ while in the case for which $\Delta S_{AB} = -1.0$ cal deg^{-1} mol^{-1}, ΔS_T and ΔS_D differ.

---

(15) E. A. Guggenheim, *Trans. Faraday Soc.*, 44, 1007 (1948).

(16) A. Silberberg and R. Simha, *Biopolymers*, 6, 479 (1968).

(17) T. L. Hill, "Introduction to Statistical Thermodynamics," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1960, pp 235–241.

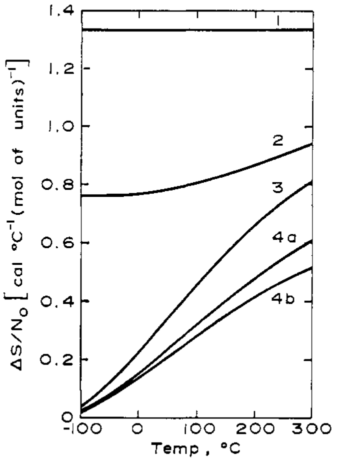

Figure 2. Entropy *vs.* reaction temperature for $X_A = 0.4$: (1) represents ΔS_D and ΔS_T where $\Delta H_{AB} = 0.0$ kcal/mol, $\Delta S_{AB} = 0.0$ kcal deg^{-1} mol^{-1} (eu); (2) represents ΔS_D and ΔS_T where $\Delta H_{AB} = -2.0$ kcal/mol, $\Delta S_{AB} = 0.0$ eu; (3) represents ΔS_D and ΔS_T where $\Delta H_{AB} = 2.0$ kcal/mol, $\Delta S_{AB} = 0.0$ eu; (4a) represents ΔS_D and (4b) represents ΔS_T where $\Delta H_{AB} = 2.0$ kcal/mol, $\Delta S_{AB} = -1.0$ eu.

Although each curve which corresponds to a nonzero value of $\Delta\epsilon_{AB}$ yields a ΔS_T that decreases with temperature only that case for which $\Delta\epsilon_{AB} > 0$ gives a ΔS_T which approaches zero as the reaction temperature approaches 0°K. When $\Delta\epsilon_{AB} < 0$ and $X_A \neq X_B \neq 0.5$ a temperature of 0°K produces a copolymer with a residual entropy of sequence length distribution of the kind illustrated in Figure 1 for $P_{AA} = 0$ and $X_A < 0.5$.

Calculated changes in free energy of the system as a function of temperature are illustrated in Figure 3. Those copolymerizations which proceed with a negative $\Delta\epsilon_{AB}$ produce consistently more negative ΔG values than those with positive $\Delta\epsilon_{AB}$ of the same magnitude. This may be attributed both to the negative enthalpy of reaction and to the residual entropy effect for the negative $\Delta\epsilon_{AB}$ case.

In addition to their dependence upon reaction temperature the calculated thermodynamic quantities vary as a function of the composition of the system as Figure 4 shows. These thermodynamic quantities as well as the entropy of reaction, which is not plotted, are symmetrical with respect to composition. The entropy of copolymerization was sufficiently positive in both cases considered to allow the reactions to take place even though their enthalpies were positive. Although the enthalpy of the reaction depends upon $\Delta\epsilon_{AB}$, its magnitude varies in an inverse manner to $\Delta\epsilon_{AB}$ when that parameter is positive. Thus it is seen that a decrease in the number of A–B junctions as the number of sequences in the copolymer decreases more than compensates for any increase in $\Delta\epsilon_{AB}$.

The smaller magnitudes of the free energy and the enthalpy of copolymerization which occur as the positive $\Delta\epsilon_{AB}$ increases in magnitude reflects the fact that the resulting copolymer has become increasingly like the homopolymers from which it derives, both with respect to enthalpy and in the arrangement of units along the chain, *i.e.*, it is becoming more blocklike.

In Figure 4 the plots ΔG *vs.* X_A for both moderately and highly positive values of $\Delta\epsilon_{AB}/RT$ pass through

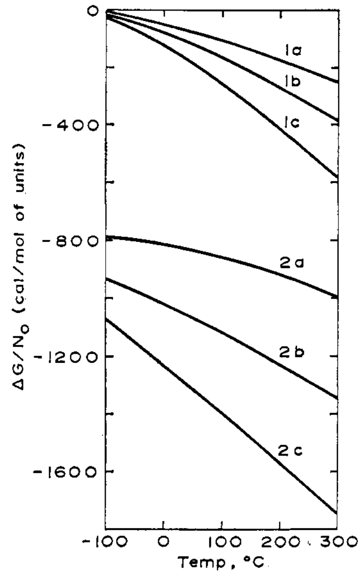

Figure 3. Free energy *vs.* reaction temperature for $X_A = 0.4$: (1) $\Delta H_{AB} = 1.0$ kcal/mol, (a) $\Delta S_{AB} = -1.0$ eu, (b) $\Delta S_{AB} = 0.0$ eu, (c) $\Delta S_{AB} = 1.0$ eu; (2) $\Delta H_{AB} = -1.0$ kcal/mol, (a) $\Delta S_{AB} = -1.0$ eu, (b) $\Delta S_{AB} = 0.0$ eu, (c) $\Delta S_{AB} = 1.0$ eu.

only one minimum. On the other hand, it has been predicted that for copolymerization systems where repulsive forces exist between unlike comonomers, *i.e.*, positive $\Delta\epsilon_{AB}$, the plot of free energy *vs.* composition may display two minima.[4] Under such circumstances certain initial compositions which are in the region between the two minima will gain in stability by the formation of two separate copolymers, each of distinct sequence length distribution and composition. Such a situation is completely analogous to phase separation in a binary mixture. In order to pass through two minima a curve must have inflections. Therefore, in the case considered $\partial^2(\Delta G)/\partial X_A^2$ should equal zero at these points. Alternatively for a copolymer in which a ΔG *vs.* X_A plot passes through two minima there should be certain initial compositions at which two separate sequence length distributions represent the lowest free energy. In that case certain plots of ΔG *vs.* P_{AA} at constant composition should have inflection points at which $\partial^2(\Delta G)/\partial P_{AA}^2 = 0$. This hypothesis can be tested by performing the appropriate differentiations upon eq 19. Inflection points are found at $P_{AA} = 1$ and $P_{AA} = 2X_A - 1$. In the latter case X_A must not be less than 0.5 for P_{AA} not to be negative, but if X_A exceeds 0.5, P_{BB} will be negative according to eq 6. Then the only physically significant value open to P_{AA} as defined by $2X_A - 1$ is $P_{AA} = P_{BB} = 0$ at $X_A = 0.5$. Since each of these P_{AA} values at which inflection points occur are at extremes of the possible values for this parameter neither of these points can lie between physically significant minima of the plot in question. Therefore, no ΔG *vs.* P_{AA} plot for these systems may have multiple minima, and no decomposition into two separate copolymers analogous to phase separation can occur. The reacting systems considered here are one-dimensional. It is not surprising that an analog of a phase transition is not observed for these systems in light of the well-known fact that first-order phase transitions are not predicted for ordinary

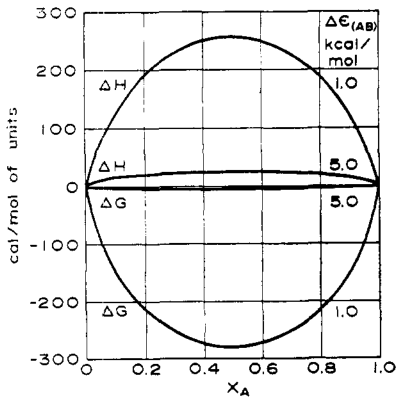

Figure 4. Enthalpy and free energy of reaction *vs.* composition for copolymerizations at 200° at designated values of $\Delta\epsilon_{AB}$.

one-dimensional systems which only involve nearest neighbor interactions. The derivative, $\partial^2(\Delta G)/\partial P_{AA}{}^2$, is positive at all other physically significant points. Therefore, every plot of ΔG *vs.* P_{AA} should pass through a single minimum. It may be concluded that the copolymer that may be formed will always be more stable and have a higher ceiling temperature than its parent homopolymers.

The Sequence Length Distribution. Details of the sequence length distribution of the copolymer may be calculated directly from the equilibrium propagation probabilities. For example, the number average sequence length of A units is given by the ratio of the probability of randomly selecting an A unit, X_A, to the probability of occurrence of an A–B junction, X_AP_{AB}. This may be expressed as

$$\bar{l}_{nA} = \frac{1}{1 - P_{AA}} \tag{23}$$

Similarly

$$\bar{l}_{nB} = \frac{1}{1 - P_{BB}} \tag{24}$$

The variation of the number average sequence lengths of the counits in a binary copolymer is shown as a function of temperature in Figure 5. It is seen that for positive $\Delta\epsilon_{AB}$ both $\bar{l}_{nA}$ and $\bar{l}_{nB}$ increase concomitantly as the temperature decreases. At any given temperature $\bar{l}_{nB} \neq \bar{l}_{nA}$ unless $X_A = X_B$. Figure 6 illustrates the effect of varying $\Delta\epsilon_{AB}$ on the relationships between temperature and sequence length. Positive values for $\Delta\epsilon_{AB}$ cause the sequence length in curves 1a and 1b to increase at low temperature and to remain consistently higher than that for random copolymer which is formed at all temperatures when $\Delta\epsilon_{AB} = 0$ kcal/mol (curve 2). Curve 1b when compared with 1a reflects the effect of the ΔS_{AB} component in the former curve. In curve 3, for which a negative value of $\Delta\epsilon_{AB}$ is given, the sequence length decreases with lower temperature until the A units are nearly isolated from one another at −100°.

Randomness parameters have been proposed as simple means of quantitatively describing the sequence length distributions in binary copolymers which obey either first-order Markoffian statistics or Bernoulli trial statistics. Two such parameters are compared here. One is Q, which was defined in eq 20 and 21. Q is the counterpart of $r_Ar_B = (k_{AA}k_{BB})/(k_{AB}k_{BA})$, the reactivity ratio product in a kinetically controlled addition co-

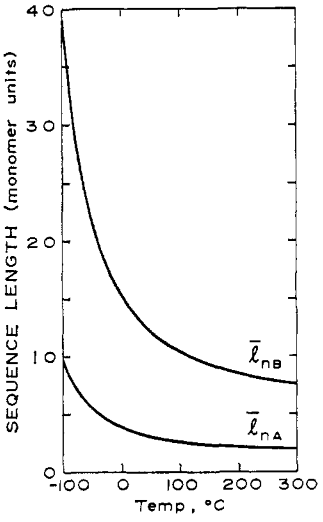

Figure 5. Number average sequence lengths *vs.* copolymerization temperature for a copolymer for which $X_A = 0.2$, $\Delta H_{AB} = 1.0$ kcal/mol, and $\Delta S_{AB} = 0.0$ eu.

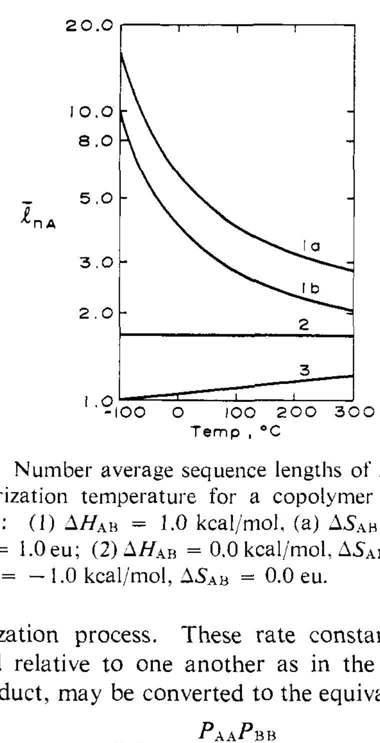

Figure 6. Number average sequence lengths of A units *vs.* copolymerization temperature for a copolymer for which $X_A = 0.4$: (1) $\Delta H_{AB} = 1.0$ kcal/mol, (a) $\Delta S_{AB} = 0.0$ eu, (b) $\Delta S_{AB} = 1.0$ eu; (2) $\Delta H_{AB} = 0.0$ kcal/mol, $\Delta S_{AB} = 0.0$ eu; (3) $\Delta H_{AB} = -1.0$ kcal/mol, $\Delta S_{AB} = 0.0$ eu.

polymerization process. These rate constants, when expressed relative to one another as in the reactivity ratio product, may be converted to the equivalent form

$$r_Ar_B = \frac{P_{AA}P_{BB}}{P_{AB}P_{BA}} \tag{25}$$

which is equal to Q (eq 21). Substitution of eq 4, 5, and 6 for terms in eq 21 gives eq 26. By eliminating

$$Q = \frac{P_{AA}[(1/X_A) - 2 + P_{AA}]}{(1 - P_{AA})^2} \tag{26}$$

the monomer feed composition from a version of the copolymer composition equation[18] and one of its associated propagation probabilities[10] r_Ar_B is found to equal the right side of eq 26. The complete analogy between Q and r_Ar_B as parameters which describe copolymer sequence length distribution is thereby confirmed. Q is equal to one for a random copolymer, approaches zero when the copolymer shows a strong tendency to alternate, and increases without limit as the copolymer becomes ordered in blocks. As shown in

---

(18) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 180.

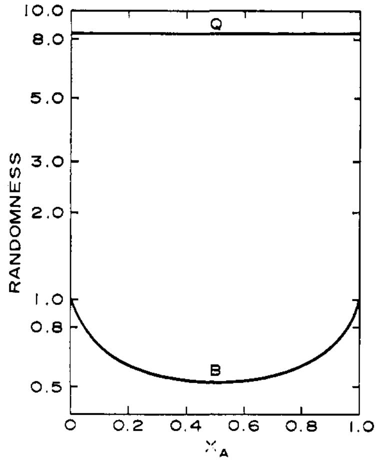

Figure 7. Randomness parameters Q and B *vs.* composition for copolymerizations at 200° for which $\Delta\epsilon_{AB} = 1.0$ kcal/mol.

eq 20 and in Figure 7, Q does not depend upon composition but is only a function of $\Delta\epsilon_{AB}/RT$.

The other parameter was defined by Yamadera and Murano[19] as

$$B = P_{AB} + P_{BA} \quad (27)$$

B, like Q, is equal to one for a random copolymer, but unlike Q, it is equal to two for a completely alternating copolymer and approaches zero for a block copolymer. It is affected by both changes in composition (Figure 7) and $\Delta\epsilon_{AB}/RT$ (Figure 8). Q is then the simpler of the two parameters, dependent on only one condition, besides temperature, which affects the sequence length distribution of the copolymer. The more complex parameter B reflects the composition dependent residual entropy of copolymerization as shown by curves 1–3 of Figure 8 not approaching two at low temperatures. It is suggested that the concurrent listing of both B and Q would more adequately describe the sequence length distribution of a copolymer than either used alone.

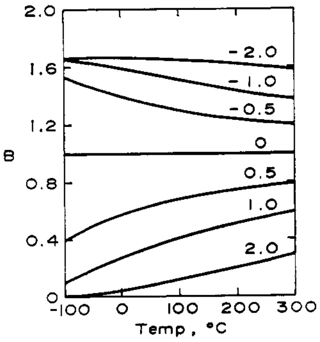

Figure 8. Randomness parameter B *vs.* copolymerization temperature for which $X_A = 0.4$ at ΔH_{AB} values designated by numbers associated with each curve, $\Delta S_{AB} = 0.0$ eu.

Acknowledgments. The author is grateful to Professor L. Mandelkern with whom he had helpful discussions at the inception of this study. The facilities of the Computing Center of North Carolina State University were utilized in this work.

---

(19) R. Yamadera and M. Murano, *J. Polym. Sci., Part A-1*, **5**, 2259 (1967).

Fractionation and Characterization of Larchwood Arabinogalactan Polymers A and B

Harold A. Swenson, Hilkka M. Kaustinen, John J. Bachhuber, and John A. Carlson

The Institute of Paper Chemistry, Appleton, Wisconsin 54911. Received October 30, 1968

ABSTRACT: Arabinogalactan, the extracellular water-soluble polysaccharide of larchwood, was separated by gpc to obtain fractions of the two polymers A (mol wt 37,000) and B (mol wt 7500) of which it is composed. The fractions were characterized by viscometry, osmometry, and sedimentation equilibrium analyses. The apparent Staudinger constant of polymer B is five times that of polymer A, evidence for its greater linearity. Plots of [η] *vs.* M also show that polymer B has fewer or shorter branches than does polymer A. The superiority of gpc over earlier fractionation methods was shown by the apparent monomolecularity of the fractions and by the ability of the method to separate cleanly the component polymers A and B.

Arabinogalactan is an extracellular, water-soluble polysaccharide which is particularly abundant in larchwood (genus *Larix*). It consists of a 1–3 linked backbone of galactose units to whose C-6 position side branches of arabinose and galactose are attached. The polysaccharide is similar to the gum exudates of which gum arabic from acacia is an example, although it has few acidic groups and little or no polyelectrolyte behavior. That it is a highly branched, approximately spherical molecule was first reported by Owens,[1] who found that the polymer had a constant partial specific volume in concentrations as high as 6.0% in water. Mosiman and Svedberg[2] later reported that the polysaccharide is made up of two polymers of approximately 100,000 and 16,000 molecular weight which were labelled A and B. The presence of two polymers was confirmed by Bouveng and Lindberg[3,4] and by Simson, Cote and Timell,[5] who showed that the two polymers were similar in composition and by Ettling and Adams,[6] who separated them by gel permeation chromatography.

In the present study the polysaccharide was obtained by successive extractions of larchwood with water.

---

(1) H. S. Owens, *J. Amer. Chem. Soc.*, **62**, 930 (1940).

(2) H. Mosiman and T. Svedberg, *Kolloid-Z.*, **100**, 99 (1942).

(3) H. O. Bouveng and B. Lindberg, *Acta. Chem. Scand.*, **12**, 1977 (1958).

(4) H. O. Bouveng, *Svensk Kem. Tidskr.*, **73** (3), 115 (1961).

(5) B. W. Simson, W. A. Cote, Jr., and T. E. Timell, *Tappi*, **51**, 33 (1968).

(6) B. V. Ettling and M. F. Adams, *ibid.*, **51**, 116 (1968).