

## Copolymerization with Depropagation

### VI.\*\* Equilibrium between Copolymer and Monomer

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**ABSTRACT:** Equations are derived based on the previously developed diad model to describe the composition and sequence distribution in a copolymer formed in an equilibrium state in the presence of the two monomers. Applications of these equations to typical models reveal the analogies between monomer-copolymer equilibria and binary liquid-vapor equilibria.

**KEY WORDS** Equilibrium Copolymerization / Depropagation / Sequence Distribution / Ceiling Temperature /

The theory of equilibrium copolymerization was first treated by Alfrey and Tobolsky.<sup>1</sup> They specifically treated the problem of sequence distribution in the equilibrium state. The problems of equilibrium composition and of degree of copolymerization were later treated by Tobolsky and Owen for some special models,<sup>2</sup> in which they neglected the interaction between monomer units in the polymer chain, so that the equilibrium sequence distribution of these models should be always random.

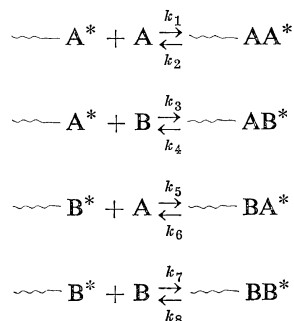
Sawada, on the other hand, discussed this subject from a thermodynamic point of view,<sup>3-4</sup> and has derived an equation which expresses the free energy change for a copolymerization which we have termed the diad model<sup>5</sup> and which is probably applicable to most addition copolymerization systems. Recently, Theil has treated this subject in detail from a statistical thermodynamic point of view and obtained an equation which describes the equilibrium sequence distribution.<sup>6</sup>

The theories mentioned above are directly applicable to the determination of the equilibrium state of a system where only polymer is present. Since, from a pragmatic point of view, the equilibrium state will occur near the ceiling temperature in the case of addition copolymerization, it is desirable to develop a theory giving an equation for the equilibrium monomer concentrations.

We will treat here the equilibrium system where the monomers and the copolymer coexist. We use the kinetic method with the probability parameters introduced in the previous paper of this series.<sup>5</sup>

#### THEORY

The model of the copolymerization which we will treat in this paper is the previously described diad model:<sup>5</sup>



The following probability parameters were defined<sup>5</sup> to express the relative amount of various chain ends:

$$(A)_t = a \quad (1)$$

$$(A_{n-1}|A_n)_t = \varepsilon \quad (2)$$

$$(B_{n-1}|B_n)_t = \eta \quad (3)$$

$(A)_t$  is the probability of finding A unit at the chain end:

$(A_{n-1}|A_n)_t$  is the conditional probability of

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\*\* Part V is Reference 5.

finding A unit at the penultimate unit given that the chain end is occupied by A unit:

$(B_{n-1}|B_n)_t$  is the conditional probability defined analogously.

The following relationships are obtained.

$$(B)_t = 1 - a \quad (4)$$

$$(B_{n-1}|A_n)_t = 1 - \varepsilon \quad (5)$$

$$(A_{n-1}|B_n)_t = 1 - \eta \quad (6)$$

It is assumed that the propagation and depropagation reactions are in equilibrium. This assumption implies that the chain ends are living. According to the principle of detailed balancing at equilibrium, we have for a chain of infinite length:

$$k_1[A]_e a - k_2 a \varepsilon = 0 \quad (7)$$

$$k_3[B]_e a - k_4(1-a)(1-\eta) = 0 \quad (8)$$

$$k_5[A]_e(1-a) - k_6 a(1-\varepsilon) = 0 \quad (9)$$

$$k_7[B]_e(1-a) - k_8(1-a)\eta = 0 \quad (10)$$

$[A]_e$ ,  $[B]_e$  are the monomer concentrations at equilibrium.

Supposing that the values of the rate constants are known, we have five variables ( $a$ ,  $\varepsilon$ ,  $\eta$ ,  $[A]_e$ , and  $[B]_e$ ). Since we have four independent equations, we can determine all the variables if a condition which gives another equation between variables is specified.

From Eqs. 7-10, we have

$$[A]_e = \frac{\varepsilon}{K_1}; [B]_e = \frac{\eta}{K_4} \quad (11)$$

$$K_2 K_3 = \left( \frac{1}{[A]_e} - K_1 \right) \left( \frac{1}{[B]_e} - K_4 \right) \quad (12)$$

$$\frac{K_2 K_3}{K_1 K_4} = \left( \frac{1-\varepsilon}{\varepsilon} \right) \left( \frac{1-\eta}{\eta} \right) \quad (13)$$

Where the equilibrium constants are  $K_1 = k_1/k_2$ ;  $K_2 = k_3/k_4$ ;  $K_3 = k_5/k_6$ ;  $K_4 = k_7/k_8$ .

Eq. 12 expresses the relation between the equilibrium monomer concentrations, while Eq. 13 expresses the relation between the conditional probability parameters which describe the terminal diad. It should be noted that Eq. 13 would be identical to the equation recently derived by Theil<sup>6</sup> (Eq. 21 in his paper), provided that the conditional probability parameters at the chain end are equal to those on the main chain.

This equation is analogous to the equation derived by Alfrey and Tobolsky<sup>1</sup>, as was pointed out by Theil.

The suggested equivalency between the conditional probability at the chain end and that in the main chain:

$$(A|A) = (A_{n-1}|A_n)_t = \varepsilon$$

$$(B|B) = (B_{n-1}|B_n)_t = \eta$$

*etc.*

(where  $(A|A)$  and  $(B|B)$  are the conditional probabilities in the main chain) has already been discussed and proved for the case of a stationary system in the previous paper of this series.<sup>5</sup> That proof should be valid in this case also, since the equilibrium state is a special case of the stationary state. This consideration leads to the satisfying conclusion that the sequence distribution of copolymer in its equilibrium state, imaginarily attained only by the occurrence of the propagation and depropagation reactions, corresponds to that having the minimum free energy among all the possible sequence distributions.

Thus, it is possible to express the copolymer composition and diad fractions in terms of  $\varepsilon$  and  $\eta$ :

$$F_A = \frac{1-\eta}{2-\varepsilon-\eta} \quad (14)$$

$$F_B = \frac{1-\varepsilon}{2-\varepsilon-\eta} \quad (15)$$

$$F_{AA} = \frac{\varepsilon(1-\eta)}{2-\varepsilon-\eta} \quad (16)$$

$$F_{AB} = F_{BA} = \frac{(1-\varepsilon)(1-\eta)}{2-\varepsilon-\eta} \quad (17)$$

$$F_{BB} = \frac{\eta(1-\varepsilon)}{2-\varepsilon-\eta} \quad (18)$$

where  $F_A$  and  $F_B$  are the mole fractions of A and B units in the copolymer and  $F_{AA}$ ,  $F_{AB}$ ,  $F_{BA}$ , and  $F_{BB}$  are diad fractions.

Assuming that there is no side-reaction in the system, we obtain the following constraint which states that the monomer structure is conserved in the system.

$$[A]_e + F_A\{[M]_0 - ([A]_e + [B]_e)\} = f_A[M]_0 \quad (19a)$$

$$[B]_e + F_B\{[M]_0 - ([A]_e + [B]_e)\} = f_B[M]_0 \quad (19b)$$

$$\text{The Monomer State} + \text{The Polymer State} = \text{The Total} \quad (20)$$

$[M]_0$  is the total concentration of both monomer units including both the monomer and polymer states;  $f_A$  and  $f_B$  are the mole fractions of A and B monomer units.

Since  $F_A$  and  $F_B$  are expressed in terms of  $\eta$  and  $\varepsilon$ , either of these equations gives the last relation necessary to determine the values of all the variables.

It should be noticed that the rate constants appear in the term  $(K_2K_3)/(K_1K_4)$  in Eq. 13 and in the terms  $K_1$  and  $K_4$  in Eq. 19; these two equations are necessary and sufficient to determine  $\varepsilon$  and  $\eta$ . Accordingly, all eight rate constants are not necessary for solving the equations; the sufficient values are  $K_1$ ,  $K_4$  and  $(K_2K_3)/(K_1K_4)$  which are expressed in terms of the standard free energy changes of the elementary steps:

$$K_1 = \exp(-\Delta G^\circ_{AA}/RT) \quad (21)$$

$$K_4 = \exp(-\Delta G^\circ_{BB}/RT) \quad (22)$$

$$\frac{K_2K_3}{K_1K_4} = \exp(-2\omega/RT) \quad (23)$$

$$\omega \equiv \frac{1}{2}(\Delta G^\circ_{AB} + \Delta G^\circ_{BA} - \Delta G^\circ_{AA} - \Delta G^\circ_{BB}) \quad (24)$$

$\Delta G^\circ_{AA}$ ,  $\Delta G^\circ_{AB}$ ,  $\Delta G^\circ_{BA}$ , and  $\Delta G^\circ_{BB}$  are the standard free energy changes of the corresponding elementary steps.

$\omega$  as defined here is equivalent to the standard free energy of formation of a heterogeneous bond from homogeneous bonds.

Therefore, we are able to predict theoretically the equilibrium state of an addition copolymerization which obeys the diad model if  $[M]_0$ ,  $f_A$ ,  $K_1$ ,  $K_4$ , and  $\omega$  are given.

#### APPLICATIONS OF THEORY

We apply here the theory developed above to predict the critical condition beyond which the monomer mixture fails to be polymerized.

At the critical condition, the following equation should hold:

$$[A]_e + [B]_e = [M]_0 \quad (25)$$

Therefore, if we specify the value of  $[M]_0$ , the values of  $[A]_e$  and  $[B]_e$  at the critical condition can be calculated from Eqs. 12 and 25. The results

of calculations for some hypothetical cases are shown in Figures 1, 2 and 3. The dependence of  $\Delta H^\circ$  or  $\Delta S^\circ$  on temperature was neglected. Three cases demonstrated here correspond to the cases where there is 1) no interaction 2) positive interaction and 3) negative interaction between dissimilar monomer units. The monomer curves represent the condition above which the monomer state is more stable. The polymer curves represent the copolymer composition which is expected to be formed reversibly at the critical condition; these curves are calculated using the Eqs. 11, 14, and 15 from the values of  $[A]_e$  and  $[B]_e$ . It is

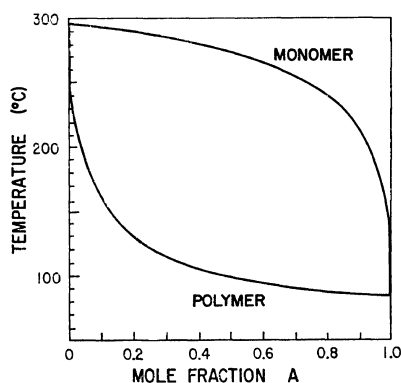


Figure 1. Equilibrium copolymer and comonomer compositions computed as a function of temperature for  $[M]_0 = 1.0$ ,  $\Delta S^\circ_{AA} = \Delta S^\circ_{BB} = -28$  e.u.,  $\Delta H^\circ_{AA} = -10$  kcal/mol,  $\Delta H^\circ_{BB} = -16$  kcal/mol,  $\omega = 0$ .

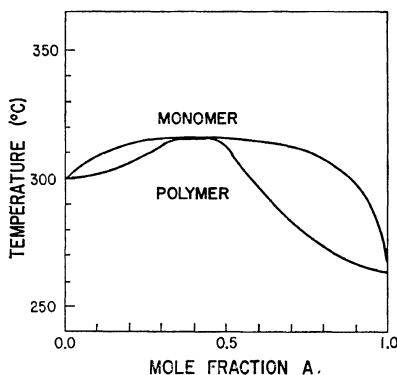
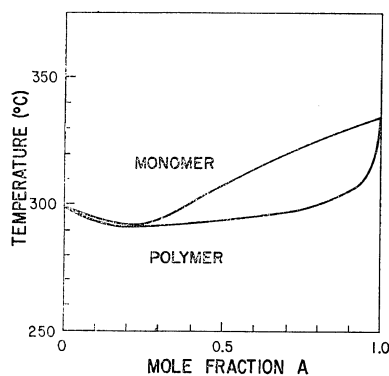


Figure 2. Equilibrium copolymer and comonomer compositions computed as a function of temperature for  $[M]_0 = 1.0$ ,  $\Delta S^\circ_{AA} = \Delta S^\circ_{BB} = -28$  e.u.,  $\Delta H^\circ_{AA} = -15$  kcal/mol,  $\Delta H^\circ_{BB} = -16$  kcal/mol,  $\omega = -1.5$  kcal/mol.



**Figure 3.** Equilibrium copolymer and comonomer compositions computed as a function of temperature for  $[M]_0 = 1.0$ ,  $\Delta S^\circ_{AA} = \Delta S^\circ_{BB} = -28$  e.u.,  $\Delta H^\circ_{AA} = -17$  kcal/mol,  $\Delta H^\circ_{BB} = -16$  kcal/mol,  $\omega = +1.5$  kcal/mol.

seen in Figures 2 and 3 that either maximum or minimum critical temperature for the monomer mixture is observed when there is a positive or negative interaction, respectively.

The analogies of these figures to liquid-vapor (or liquid-solid) phase transition diagrams of binary systems are obvious. But it should be noted that the analogy in a rigorous sense will be valid only when the system is bulk and separation of monomer and polymer phases occurs. This

can readily be discerned from the Gibbs Phase Rule for constant pressure:

$$F = C - P + 1$$

Where there is one degree of freedom ( $F$ ) and two components ( $C$ ), the number of phases must be 2. That there are two phases is implicit in our model. Since it postulates only chain growth, it therefore implies an infinite polymer chain, which would necessarily be insoluble.

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