Thermodynamics and Crystallization of Random Copolymers

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ABSTRACT: Equations are developed for the bulk free energy of fusion, melting temperature, crystal thickness, and nucleation rate of copolymer crystals containing an arbitrary concentration of comonomer units. These equations which represent advances over earlier ones are shown to be consistent with experimental data for copolymers of L- and DL-lactides and *cis-* and *trans-*isoprenes. Analysis of the lactide data confirms an earlier prediction that the crystal thickness should increase linearly with increasing small concentrations of the comonomer units for crystallizations carried out at the same temperature. Further, this linear dependence is shown to extend to crystals containing both equilibrium and nonequilibrium concentrations of the comonomer units. The nucleation rate equation is in agreement with the observed linear dependence of the logarithm of the growth rate on the comonomer concentration in isoprene copolymers. The following are consistent with the experimental data for the lactides: 461°K, equilibrium melting temperature of the homopolymer; 403°K, equilibrium dissolution temperature in xylene; 1370 cal/mol of monomer (5730 J/mol) heat of fusion; 26.5 erg/cm^2 (2.65×10^{-2} J/m^2) surface free energy and 585 cal/mol (2447 J/mol) comonomer defect energy. Directions for future research are suggested.

I. Introduction

The crystalline state of a random copolymer must lie between two extremes which are illustrated schematically in Figure 1. In the first (lower figure), the crystalline phase is composed entirely of A units and is in metastable equilibrium with a mixed amorphous phase of A units and noncrystallizable B counits (comonomer exclusion). In the second (upper figure), the crystalline phase is a solid solution of A and B units; the B counits produce defects in the crystalline A lattice and both crystalline and amorphous phases have the same composition (uniform comonomer inclusion).

It has been shown that, for both of these extremes, the crystal thickness increases linearly with increasing small concentrations of the B counits for crystallizations carried out at the same temperature.[1] Further, it was proposed that this result which is a consequence of the crystallization kinetics is correct for intermediate concentrations of comonomer units in the crystal. It remained evident, however, that both experimental and analytical extensions of the basis for this prediction were needed.

Extensive measurement[2,3] on copolymers of L- and DL-lactides have provided data which permit further analysis and which exhibit the predicted effect for intermediate concentrations of comonomer units in the crystal. Thus, the data in Table I of ref 2 suggest (with interpolation) that, for crystallization temperatures of 85 and 90°, there is a linear dependence of thickness on comonomer concentration and that this dependence decreases with crystallization temperature until at 60° it is undetectable. We shall discuss this point in a more analytical manner in section IV where the linear dependence of crystal thickness on comonomer concentration is shown to apply to both equilibrium and kinetically determined concentrations of comonomer units in the crystal. To do this, it is necessary first to obtain in section II the expression for the bulk free energy of fusion of a crystal with an arbitrary concentration of comonomer units. In section III, this is used to determine the equation for the melting temperature of an infinitely large crystal with such a concentration of comonomer units. This equation is extended to lamellar crystals and fitted to experimental data to obtain thermodynamic parameters needed for the analysis of crystal thickness given in section IV. In section V, nucleation rate equations are developed and compared with experimental data[4] for polymers of *cis-* and *trans-*isoprene. The predicted linear dependence of the logarthim of the growth rate on comonomer concentration is confirmed.

II. Bulk Free Energy of Fusion

A real copolymer crystal is formed under kinetic conditions which determine the actual concentration (denoted by X_c) of B counits in the crystal. The bulk free energy difference between such a crystal and the melt with a concentration of B units equal to the overall composition, X (mole fraction), of the copolymer is given by

$$\Delta G = \Delta G^0 - RT\left\{\frac{\epsilon X_c}{RT} + (1 - X_c)\ln\left[\frac{1 - X_c}{1 - X}\right] + X_c \ln\left[\frac{X_c}{X}\right]\right\} \quad \text{(II.1)}$$

where $\Delta G^0 \simeq \Delta H^0\,(1 - T/T_m{}^0)$ is the bulk free energy difference and $T_m{}^0$ the equilibrium melting temperature for the homopolymer. (Superscripts of 0 refer to the homopolymer.) The excess free energy of the defect created by incorporating a B unit in the crystalline A lattice is ϵ. The derivation of eq II.1 follows that for the *equilibrium* free energy.[5] A binomial distribution of defects is assumed (see eq 2.4 in ref 5). A given term in the partition function is representative of a metastable state; the maximum term corresponds to the equilibrium state. Equation II.1 is the result obtained for the metastable states. Note that the first term within the braces is the enthalpic (energy) contribution while the remaining two terms are entropic. When X_c has the equilibrium value

$$X_{eq} = Xe^{-\epsilon/RT}/(1 - X + Xe^{-\epsilon/RT}) \quad \text{(II.2)}$$

eq II.1 reduces to the appropriate free energy of fusion for such a crystal.[5]

$$\Delta G = \Delta G^0 + RT\ln(1 - X + Xe^{-\epsilon/RT}) \quad \text{(II.3)}$$

Further, when X_c approaches zero, eq II.1 reduces to that for the exclusion model:[6]

$$\Delta G = \Delta G^0 + RT\ln(1 - X) \quad \text{(II.4)}$$

Finally, when X_c is equal to X, eq II.1 reduces to that for the uniform inclusion model[1,7]

$$\Delta G = \Delta G^0 - \epsilon X \quad \text{(II.5)}$$

III. Melting Temperature

Setting $\Delta G = 0$ in eq II.1 yields the melting temperature, T_m, of an infinitely large crystal of composition, X_c:

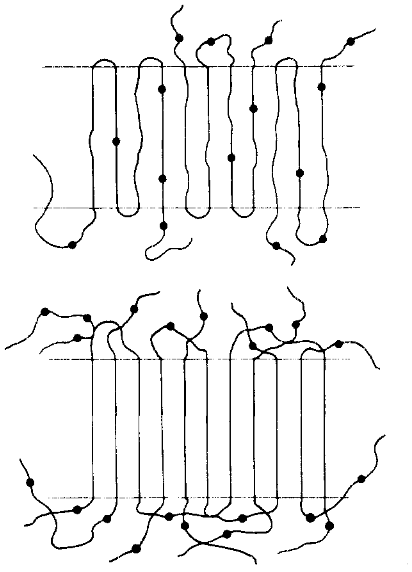

Figure 1. Schematic drawings showing the extreme states of crystalline random copolymers. That at the top represents uniform inclusion of the comonomer units in the crystal and that at the bottom represents complete exclusion.

$$\frac{1}{T_m{}^0} - \frac{1}{T_m} = -\frac{R}{\Delta H^0}\left\{\frac{\epsilon X_c}{RT_m} + (1 - X_c)\ln\left[\frac{1 - X_c}{1 - X}\right] + X_c \ln\left[\frac{X_c}{X}\right]\right\} \quad \text{(III.1)}$$

Since the expression for the free energy of fusion reduces properly to those for comonomer rejection, equilibrium inclusion, and uniform inclusion, eq III.1 also reduces correctly to the corresponding expressions for the melting temperature.[1,5-7]

Incorporation of eq II.1 into the expression $\Delta G - 2\sigma_e/l = 0$ yields the melting temperature, $T_m(l)$, of thin crystals:

$$T_m(l)\left\{1 + \frac{RT_m{}^0}{\Delta H^0} \times \left[(1 - X_c)\ln\left(\frac{1 - X_c}{1 - X}\right) + X_c \ln\left(\frac{X_c}{X}\right)\right]\right\} = T_m{}^0\left[1 - \frac{2\sigma_e}{\Delta H^0}(1/l) - \frac{\epsilon}{\Delta H^0}X_c\right] \quad \text{(III.2)}$$

In this equation, l is the thickness of the crystalline layer (not the long period) and σ_e is the fold surface free energy. As a test of eq III.2, experimental values[2,3] of $T_m(l)$, l, X, and X_c were used together with an assumed value of the ratio $T_m{}^0/\Delta H^0$ to adjust the values of $T_m{}^0$, σ_e, and ϵ to yield a least-squares fit in $T_m(l)$. The fit was found not to be very sensitive to the value of $T_m{}^0/\Delta H^0$ with a range of values of this parameter yielding a standard deviation of fit of 2.9°K. In view of the possible experimental errors associated with the four measured quantities, a deviation of 2.9°K is reasonable.[8] Further, it is significantly smaller at the 10% level of confidence than the deviation for the three-parameter equation which assumes uniform inclusion of the comonomer units ($X_c = X$).[1,7] Thus, eq III.2 is consistent with the experimental data and an improvement over the equation corresponding to uniform inclusion.

Because of the number of adjustable parameters, the range of the data, the experimental data scatter, and the form of eq III.2, the fit of the equation to the data varies little with the ratio $T_m{}^0/\Delta H^0$ as noted above. Consequently, the resultant values of $T_m{}^0$, ΔH^0, σ_e, and especially ϵ are subject to considerable uncertainty. On the other hand, both $T_m{}^0$ and ΔH^0 can be determined reasonably well from analysis of measurements on the homopolymer.[2,3] Therefore, these were used in conjunction, with eq III.2 and the experimental data to determine σ_e and ϵ. The resultant values are 585 cal/mol of comonomer units (~0.03 eV/defect) for ϵ and 26.5 erg/cm^2 (2.45 kcal/mol or 10.3 kJ/mol of folds) for σ_e corresponding to 461 ± 4°K for $T_m{}^0$ and 1370 cal/mol (5730 J/mol) of monomer units for ΔH^0. The value for σ_e seems reasonable in that it is comparable with the values for other polymers with C–O–C backone sequences: polyoxymethylene, 3; polyoxyethylene, 2.3; and polyoxypropylene, 3 kcal/mol of folds.[9] Similarly, ϵ is comparable with the only other available value: approximately 0.04 eV/defect for copolymers of tetrafluoroethylene and hexafluoropropylene.[1]

IV. Lamella Thickness vs. Comonomer Concentration

Previously it has been predicted[1] that the lamella thickness of a series of random copolymers should increase with increasing concentration of the noncrystallizable counit for crystallizations carried out at the same temperature. We briefly review and extend here the basis for this prediction. The kinetic theory of polymer crystallization predicts that the theoretical crystal thickness l^* is given by

$$l^* = l_c + \delta l \quad \text{(IV.1)}$$

where $l_c = 2\sigma_e/\Delta G$ and δl is a small additive term which is a weak function of temperature. The experimentally observed crystal thickness l_{obsd} will differ from l^* if the crystals thicken with time. In general

$$l_{obsd} = l_c + C(T) \quad \text{(IV.2)}$$

where $C(T)$ includes δl plus any thickening that may occur at the crystallization temperature, T. Of course, $C(T)$ is also a function of time, but it will be assumed that we are dealing with either a long time or an isochronal value of $C(T)$. For a copolymer, eq IV.2 can be rewritten as

$$l_{obsd} = \frac{2\sigma_e}{\Delta G^0}\left[\frac{\Delta G^0}{\Delta G}\right] + C(T) \quad \text{(IV.3)}$$

or

$$l_{obsd} = l_{obsd}{}^0 + l_c{}^0\left[\frac{\Delta G^0}{\Delta G} - 1\right] \equiv l_{obsd}{}^0 + l_c{}^0 f(X,T) \quad \text{(IV.4)}$$

Equation IV.4 follows from eq IV.3 under the assumption that σ_e and $C(T)$ are independent of X. (Under some conditions, the assumption for $C(T)$ can be relaxed.)[1] The isothermal concentration dependence of l_{obsd} is completely embodied in $f(X,T)$ in eq IV.4. Using eq II.2 yields for equilibrium inclusion:

$$f(X,T) = \frac{-RT\ln[1 - X + Xe^{-\epsilon/RT}]}{\Delta G^0 + RT\ln[1 - X + Xe^{-\epsilon/RT}]} \quad \text{(IV.5)}$$

Expansion of eq IV.5 in a power series in X yields

$$f(X,T) = \frac{RT}{\Delta G^0}(1 - e^{-\epsilon/RT}) \times X\left[1 + (1 - e^{-\epsilon/RT})\left(\frac{1}{2} + \frac{RT}{\Delta G^0}\right)X\right] \quad \text{(IV.6)}$$

which indicates that $f(X,T)$ is proportional to X for small X. This conclusion is valid whether ϵ/RT is large (exclusion favored) or small (inclusion favored), although the limitations on the values of X and $RT/\Delta G^0$ are slightly different in the two cases. These results further suggest that l_{obsd} might initially increase linearly with X for nonequilibrium concentrations. When eq II.1 is used instead of eq II.2 for ΔG in $f(X,T)$, it is not possible to expand $f(X,T)$ in a power series in X as above since X_c is an unknown function of X. However, it is possible to demonstrate linearity by numerical means for the lactide copolymers. All the quantities needed for this are available except the equilibrium dissolution temperature of the homopolymer, T_d^0.

The analysis in eq IV.1–IV.4 is valid for crystallization from solution if T_m^0 is replaced by T_d^0. Although the lactide copolymers of ref 2 and 3 were crystallized from solution at several temperatures, all the data can be analyzed simultaneously under the additional assumption that $C(T)$ in eq IV.3 is only weakly temperature dependent. Then eq IV.4 suggests that a plot of l_{obsd} vs. $(\Delta G^0/\Delta G)T_d^0/\Delta T = [1 + f(X,T)]T_d^0/\Delta T$ should be linear with a slope of $2\sigma_e/\Delta H^0$. Since all the parameters are known except T_d^0 in $f(X,T)$ and ΔT, fits of l_{obsd} vs. $[1 + f(X,T)]T_d^0/\Delta T$ were made for various values of T_d^0. The best linear fit which was obtained when T_d^0 is 130° is shown in Figure 2. The slope, $2\sigma_e/\Delta H^0$, equals 5.98 Å and the intercept which represents an average value of $C(T)$ is 39.8 Å. The standard deviation of the fit is 4.7 Å which is reasonable in view of the possible errors. The values of σ_e (26.5 ergs/cm^2) and ΔH^0 (1370 cal/mol) determined above from melting temperature and calorimetric data yield a $2\sigma_e/\Delta H^0$ ratio of 5.17 Å in pleasingly good agreement with the value obtained in the present analysis utilizing crystallization temperature and lamella thickness data from both homopolymers and copolymers.

All the quantities needed to demonstrate that $f(X,T)$ is linearly proportional to X for small X are now available. The linearity can be examined most clearly by graphical means. In Figure 3, the solid line gives $f(X,T)$ vs. X for the lactide copolymers crystallized from solution at 60° showing that $f(X,T)$ is indeed approximately proportional to X. Thus, this relationship applies not only to the extreme copolymer crystals with the comonomer units either rejected or uniformly included but also to crystals with intermediate concentrations. Therefore, $f(X,T)$ is given by:

$$f(X,T) \simeq AX \qquad \text{(IV.7)}$$

For rejection, $A \simeq RT/\Delta G^0$ for small X and, for uniform inclusion, $A \simeq \epsilon/\Delta G^0$.[1] The former is shown for comparison by the broken line on Figure 3.

V. Nucleation Rates

The nucleation rate, S, of a coherent surface nucleus is given by[1]

$$\ln S = \ln S_0 - \Delta G^*/RT - 2\sigma b_0 l_c^0\,[1 + f(X,T)]/RT \qquad \text{(V.1)}$$

where b_0 is the monomolecular thickness, σ is the lateral surface free energy of the crystal, and S_0 is a constant. The temperature dependence of the activation free energy ΔG^* for transport of a polymer segment across the melt–crystal interface is usually represented by

$$\frac{\Delta G^*}{RT} = \frac{2.303C_1C_2}{C_2 + T - T_g} \qquad \text{(V.2)}$$

where C_1 and C_2 are the WLF constants characteristic of a given polymer and T_g is the glass transition temperature. Proceeding as in the development of eq IV.4, we can express the nucleation rate of the copolymer in terms of the homopolymer nucleation rate plus a term that contains the comonomer concentration if we define the following function:

$$F(X,T) \equiv \frac{\Delta G^*}{\Delta G^{*0}} - 1 \qquad \text{(V.3)}$$

Thus, collecting the homopolymer terms yields:

$$\ln S = \ln S^0 - [\Delta G^{*0}F(X,T) + 2b_0\sigma l_c^0 f(X,T)]/RT \qquad \text{(V.4)}$$

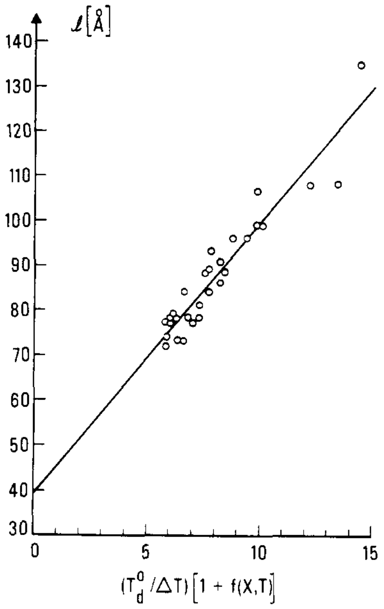

Figure 2. Illustration of the linear relationship between crystal thickness and $(T_d^0/\Delta T)[1 + f(X,T)]$.

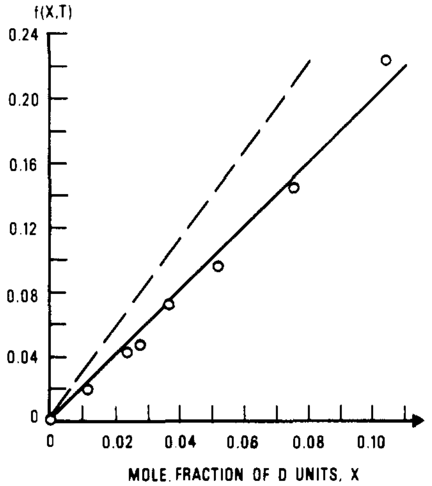

Figure 3. Plot illustrating the linear relationship between $f(X,T)$ and X. Data from ref 2 for the 60° crystallization temperature are used together with thermodynamic values given in the present text to yield the solid line. For comparison, the broken line shows $f(X,T)$ for the complete rejection mode of crystallization.

where S^0 is the nucleation rate of the homopolymer (not the preexponential factor S_0). We have assumed in deriving eq V.4 that S_0 is independent of X. Often $T_g \simeq T_g^0 + BX$ where B is a constant for small X and $F(X,T)$ can be approximated:[10]

$$F(X,T) \simeq \frac{BX}{C_2 + T - T_g} \equiv CX \qquad \text{(V.5)}$$

Then eq V.4 can be approximated as

$$\ln S \simeq \ln S^0 - [\Delta G^{*0}C + 2b_0\sigma l_c^0 A]X/RT \qquad \text{(V.6)}$$

From this equation it follows that the logarithm of the isothermal growth (nucleation) rate should be a linear function of comonomer concentration as has been observed for copolymers of *cis*- and *trans*-isoprene.[4] Assuming complete comonomer rejection and using the given values[4,11] for the parameters in eq V.6 yields a value for $\partial \ln S/\partial X$ which is comparable with that of Figure 10 in ref 4. A similar value obtains if one assumes uniform inclusion and a value of ϵ

comparable with RT. The effect of comonomer concentration on the temperature of maximum growth rate, $T_{\max}$, can also be estimated:

$$T_{\max} = T_{\max}{}^0 + \left(\frac{\partial T_{\max}}{\partial X}\right)_{X=0} X + \ldots \tag{V.7}$$

For either uniform comonomer inclusion or complete rejection a value of $(\partial T_{\max}/\partial X)_{X=0}$ of about −60° is obtained for the *cis*-isoprene–*trans*-isoprene copolymers. Thus, for a value of X of 0.024 only a small shift (about −1.5°) is expected in $T_{\max}$. This agrees with experimental observations.

For solution crystallization the second term in the square brackets of eq V.6 will dominate. Dividing the slope of ln S vs. X by the slope of l_{obsd} vs. X at the same crystallization temperature yields $-2b_0\sigma/RT$ and thus provides a method of determining σ. This also applies to melt crystallization if the temperature is well into the nucleation controlled range and thickening is not a strong function of copolymer composition.

VI. Conclusions

Equations have been developed for: the bulk free energy of fusion, melting temperature, and thickness of crystals containing an arbitrary concentration of comonomer units. These equations are consistent with experimental data for L- and DL-lactides[2,3] and confirm an earlier prediction[1] that the thickness of random copolymer crystals increases linearly with increasing small concentrations of the comonomer units for crystallizations carried out at the same temperature.

An equation has also been developed for the nucleation rate of crystals containing an arbitrary concentration of comonomer units. This equation is in agreement with the observed linear dependence of the logarithm of the growth rate on the trans concentration in *cis*-isoprene–*trans*-isoprene copolymers.[4] Furthermore, the observed weak dependence of the temperature of maximum growth rate on the trans concentration is also in agreement with this equation.

Further work is needed to understand the kinetically determined concentrations of the comonomer units in the crystal since these[2,3] do not agree with present theories.[5] One aspect of such work ought to be an investigation of the temperature dependence of the defect energy. Calculations with an elastic model show this energy to be proportional to the shear modulus of the matrix in which the defect is located.[12] Moreover, ultrasonic measurements show the modulus for longitudinal waves in polyethylene, for example, to increase by a factor of 3.8 in the 50° range below the melting temperature.[13] (The crystallization temperatures in ref 2 cover a 50° range.) Measurements of the shear modulus do not extend to the melting temperature but they show a factor of 10 increase between 130 and 80° in polyethylene.[14] While the source of these changes might be debated for a two-phase system near the melting temperature, they nevertheless do correspond to changes in the overall matrix in which the defect is located. Additionally, theoretical calculations for imperfect crystals of chain hydrocarbons yield changes of similar magnitude.[15] All these results suggest that the defect energy would increase and that the comonomer inclusion would therefore decrease from that otherwise predicted as the crystallization temperature is lowered. This is the trend observed in experimental data.[2,3] Thus, the consequences of a temperature dependent defect energy ought to be examined in more detail.

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