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Thermodynamic Study on Fusion, in Crystalline Polymer and Its Mixture with Diluent, based on Folded Chain Crystalline Model

By

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In accordance with the regular folded chain crystallite model, an expression for the melting point depression of crystalline polymer in diluent was derived by extending the treatment given by Flory. The equation obtained is

$$\frac{1}{T_m(l)}-\frac{1}{T_m^0}=\left(\frac{R}{\Delta H_u}\right)\left[\left(\frac{V_u}{V_1}\right)v_1+\frac{v_2}{x}-\frac{1}{\zeta}\ln v_2-\frac{1}{\zeta}\ln\frac{x-\zeta+1}{x}-\left(\frac{V_u}{V_1}\right)\chi_1 v_1^2\right]$$
$$+\frac{2\sigma_e}{T_m(l)\cdot\Delta h_f\cdot l}$$

which reduces for very large x and considerably large ζ to

$$\frac{1}{T_m(l)}-\frac{1}{T_m^0(l)}=\left(\frac{R}{\Delta H_u}\right)\left(\frac{V_u}{V_1}\right)(v_1-\chi_1 v_1^2)$$

where T_m^0 is the melting point of the pure polymer of infinite fold length and chain length, $T_m^0(l)$ is the melting point of the pure polymer of fold length l, $T_m(l)$ is the melting point for the polymer of fold length l in the presence of diluent, ΔH_u is the heat of fusion per mole of repeating unit, V_u and V_1 are the molar volumes of the polymer repeating unit and the diluent, respectively, x is the degree of polymerization, v_1 and v_2 are the volume fractions of the diluent and the polymer, respectively, ζ is the fold length in number of repeating units, σ_e is the end surface free energy per unit volume, Δh_f is the heat of fusion per unit volume, and χ_1 is the diluent-polymer interaction parameter. The model used here was discussed in relation to the fringed micelle model.

Introduction

In our preceding papers of this series, the melting point depressions in polypropylene-n-alkane systems[1] and polyethylene-n-alkane systems[2] were determined for the purpose of evaluating the interaction parameter between n-alkanes and polymer by using the Flory's theory on the melting of crystalline polymer in diluent[3]. In these papers, the Flory's theory was discussed from various points of view. The present discussion refers to the statistical thermodynamic theory of fusion in an ideal crystalline polymer, whose crystal-

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lites are all composed of regular folded chain structure[4], and in its mixtures with diluents.

Flory[3] has shown, according to the fringed micelle crystallite model, that the equilibrium melting temperature of a crystalline polymer may be depressed by a diluent incorporated in the polymer. According to his statistical-thermodynamic treatment of the melting of crystalline polymer (uniform chain length) in diluent,

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \left(\frac{R}{\Delta H_u}\right)\left[\left(\frac{V_u}{V_1}\right)v_1 + \left(\frac{1}{x}\right)\left\{v_2 + \frac{x}{x - \zeta_e + 1}\right\} - \left(\frac{V_u}{V_1}\right)\chi_1 v_1^2\right] \qquad (1)$$

where T_m^0 is the melting point for the pure polymer of infinite chain length, T_m is the depressed melting temperature, R is the gas constant, ΔH_u is the heat of fusion per mole of repeating unit, V_u and V_1 are the molar volumes of the polymer repeating unit and the diluent, respectively, x is the degree of polymerization, v_1 and v_2 are the volume fractions of the diluent and the polymer, respectively, ζ_e is the equilibrium crystallite length in number of repeating unit, and χ_1 is the interaction parameter. If x is very large, the influence of the chain length vanishes and Eq. (1) reduces to

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \left(\frac{R}{\Delta H_u}\right)\left(\frac{V_u}{V_1}\right)(v_1 - \chi_1 v_1^2) \qquad (2)$$

assuming $\chi_1 = BV_1/RT_m$, where B represents the interaction energy density characteristic of the solvent-solute pair. By dividing both sides of Eq. (2) by v_1, we obtain

$$\left(\frac{1}{T_m} - \frac{1}{T_m^0}\right)\Big/ v_1 = \left(\frac{R}{\Delta H_u}\right)\left(\frac{V_u}{V_1}\right)\left(1 - \frac{BV_1}{R}\cdot\frac{v_1}{T_m}\right) \qquad (3)$$

According to Eq. (3), a plot of the quantity $(1/T_m - 1/T_m^0)/v_1$ against v_1/T_m should be a straight line, whose intercept is related to ΔH_u and slope is related to the quantity of B.

The second term of the right hand side in Eq. (1) includes an equilibrium crystallite length ζ_e. The value of ζ_e can be computed using the nucleation constant D, but the numerical value of the constant D can not explicitly be obtained from the theory. Thus in the Flory's paper, ζ_e is computed assuming a appropriate value for D. Therefore, the Flory's theory does not definitely answer the questions on the relation between the degree of crystallinity and the size of crystallites, as well as the solvent concentration. Moreover, in the Flory's theory the fringed micelle structure is assumed as crystallite model and also the effect of swelling in amorphous region is not considered.

Now we will refer briefly studies on the melting and the degree of crys-

tallinity of crystalline polymers. Tung et al.[5] investigated the effect of molecular weight on the degree of crystallinity of polyethylene assuming the fringed micelle structure as a model of crystallite and they elucidated the facts that the lower the molecular weight is, the higher the degree of crystallinity becomes. Krigbaum et al.[6] evaluated the equilibrium degree of crystallinity based on both the "single pass" (fringed micelle) crystallite model and the folded chain crystallite model. According to their theory, the limit in crystallinity arises from the deformation produced in the intervening amorphous chain as crystallization proceeds. They computed thermodynamically the free energy change for the crystallization for both models and discussed the relation between the equilibrium degree of crystallinity and temperature. Thus they succeeded in elucidating quantitatively the experimental results on the relation between the degree of crystallinity and temperature in a temperature range except the vicinity of melting point. However, the surface free energy of crystal was neglected and also the crystallite length was not taken into consideration in their paper.

Relation between the fold length of single crystal, crystallized from dilute solution, and the crystallization temperature was investigated by Lauritzen and Hoffman[7]. According to their theory

$$\bar{l} = \frac{2\sigma_e T_m}{\Delta h_f \cdot (T_m - T_c)} + \frac{kT}{h\sigma_s} \tag{4}$$

where $\bar{l}$ is the average fold length of single crystal, σ_e and σ_s the surface free energies per unit area of crystal end and side surfaces, respectively, T_m the melting point of the crystal in the presence of solvent, T_c the crystallization temperature, and Δh_f the heat of fusion per unit volume, and h the effective width of a chain. Thus it follows that the fold length of single crystal is dependent on the crystallization temperature only. Moreover, it was shown that the distribution of the fold length of single crystal is very sharp. Hoffman and Weeks[8] also deduced the equilibrium melting point of single crystal, $T_m^0(l)$, as a function of fold length l by a simple thermodynamic calculation :

$$T_m^0(l) = T_m^0 \left\{ 1 - \frac{2\sigma_e}{\Delta h_f \cdot l} \right\} \tag{5}$$

where T_m^0 is the equilibrium melting point, in the absence of diluent, of single crystal of infinite fold length, for which the effect of end surface free energy may be neglected. The numerical value of the limiting melting point, T_m^0 of polyethylene, for example, is 416.2°K as shown by Brown and Edy[9].

Deduction of Fusion Function Based on "Folded Chain" Crystallite Model

The "fringed micelle" crystallite model assumed in the Flory's theory was compared schematically with the regular "folded chain" crystallite model in Fig. 1. Let us discuss the Flory's theory from the standpoint of the regular

(a) Fringed micelle   (b) Folded chain
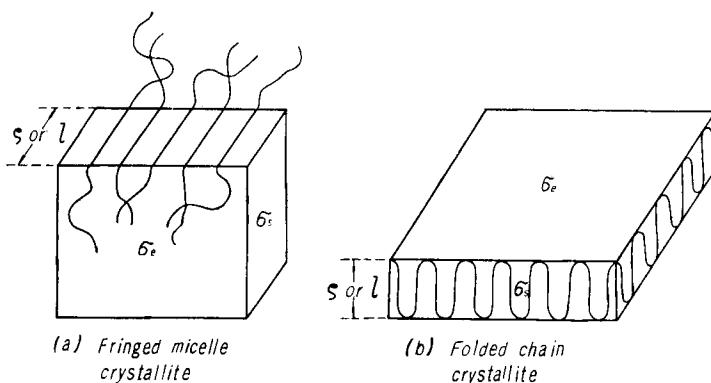crystallite   crystallite

Fig. 1. Models of polymer crystals.

folded chain crystallite model. (a) In the Flory's theory it is considered that the equilibrium crystallite length ζ_e is distributed broadly from zero to x, the degree of polymerization. However, we assumed that the equilibrium crystallite length of the single crystal of polyethylene crystallized from dilute solution or crystallized very slowly from melt at a temperature near the melting point has a definite value. Further it may be assumed that the crystallite length (fold length of crystal) is decided by crystallization temperature only, and that the distribution of the fold length of crystal is homogeneous. Moreover, in the case of the determination of the melting point of polyethylene crystallized very slowly at a temperature near the melting point, it may be assumed that the fold length of crystal is almost constant during the fusion process unless the heating rate is extremely slow. Recently, Iida et al.[10] investigated fusion process by depolarization method. According to their paper, recrystallization did not occur in fusion process for polyethylene crystallized very slowly at 130°C, while in the case of polyethylene crystallized at 123°C recrystallization undoubtedly occured in fusion process. Considering these facts, our assumption seems to be reasonable. (b) In the Flory's theory, the melting point of pure polymer increases with the increasing degree of polymerization x and becomes constant at large value of x. Thus in Flory's equation (1) for melting point depression, T_m^0 is defined

as the melting point of pure polymer of infinite chain length. Indeed, melting point depends on the value of x, but it depends rather strongly on the fold length of crystal. Therefore, in the present paper, T_m^0 is defined as the melting point of pure polymer of infinite chain length and of infinite fold length. (c) In the fringed micelle model, the amorphous regions are interspersed with the crystallites and are not mechanically separable from crystal regions. So, the phase relationship for such polymer in diluent may be represented[11,12] by $L+[L(a)+S(c)]$, where L represents a free liquid or solution, $L(a)$ a liquid phase in the form of amorphous regions of "solid" polymer which surround the crystallites, represented by $S(c)$, and square brackets indicate that the pair of phases are not mechanically separable. On the other hand, for the regular folded chain model, the phase relationship may be given by $L+S(c)$. (d) In the Flory's theory, the contribution of the surface free energy of crystal to the free energy of fusion was not explicitly taken into account. However, the surface free energy of crystal is very important when the size of crystallites is small. Therefore, in our following treatment the surface free energy was taken into account.

Now the entropy and free energy changes of fusion are derived in the same manner as the lattice treatment of polymer solution by Flory. The definitions and assumptions used in the Flory's paper except the four items mentioned above were used for the treatment on the regular folded chain crystallite model in the present paper. Let us examine a mixture of N homogeneous polymer molecules, consisting of x repeating units each, and n solvent molecules. The number of segments per repeating unit is expressed by z and the ratio of the molar volume of the solvent to the molar volume of the segment (or lattice cell) is expressed by z_s. Further definitions are as follows:

m = total number of crystalline sequences

l = length (average) of crystallite in cm

ζ = length (average) of crystallite in number of units

v_1 = volume fraction of solvent

v_2 = volume fraction of polymer

λ = $(xN-\zeta m)/xN$ = fraction of the polymer in the amorphous, or liquid, state.

The entropy of fusion per repeating unit is Δs_u written as[13]

$$\Delta s_u = kz \ln \frac{\zeta-1}{e} \tag{6}$$

where γ is the lattice coordination number. On redefining n, N, m, and ΔS_u to represent the molar quantities, the entropy of fusion per mole of unit was expressed[3] by the following equation:

$$\frac{\Delta S_f'}{xN} = (1-\lambda)\Delta S_u - R\left\{\left(\frac{z}{z_s}\right)\frac{v_1}{v_2} + \frac{1}{x}\right\} \ln\{1 - v_2(1-\lambda)\}$$

$$-R\left(\frac{1-\lambda}{\zeta}\right)\left\{\ln\frac{v_2(\gamma-1)}{zed} + \ln\frac{x-\zeta+1}{x}\right\} \qquad (7)$$

$(x-\zeta+1)/x$ in Eq. (7) expresses the principal consequence of the requirement that the ends of molecules shall be excluded from the crystallites, and is strictly valid only when the degree of crystallinity is small. In the folded chain crystallite model, all ends of the molecules are not necessarily to be excluded from the crystallites. On account of the difficulty to introducing this effect in calculation, however, this term was obliged to be use as it is for the present model. In addition, the correction, d, for the sharpness of the change of internal order near the end of a crystallite was neglected ($d=1$) on account of assumption (c) for the present model.

Now let us consider the effect of the end surface free energy of crystal. Letting Σ_e, H_e, and S_e express the surface free energy, surface energy, and surface entropy of the end surface in molar quantity, respectively,

$$\Sigma_e = H_e - TS_e \qquad (8)$$

The entropy change of fusion ΔS_f, taking into consideration the surface free energy, is represented by

$$\Delta S_f = \Delta S_f' - 2mS_e \qquad (9)$$

Therefore, substituting Eq. (7) in Eq. (9), we obtain

$$\frac{\Delta S_f}{xN} = (1-\lambda)\Delta S_u - R\left\{\left(\frac{z}{z_s}\right)\frac{v_1}{v_2} + \frac{1}{x}\right\} \ln\{1 - v_2(1-\lambda)\}$$

$$-R\left(\frac{1-\lambda}{\zeta}\right)\left\{\ln\frac{v_2(\gamma-1)}{ze} + \ln\frac{x-\zeta+1}{x} + \frac{2S_e}{R}\right\} \qquad (10)$$

The heat change accompanying disappearance of crystallites in the mixture of semi-crystalline polymer and solvent is divided into two parts: the heat of fusion proper, $\Delta H_f'$, referring solely to the heat of fusion of the crystallites, and the heat of mixing, ΔH_m, of the previously crystalline polymer segment with the surrounding polymer solution. The heat of fusion can be expressed, by taking into account the surface free energy, as follows:

$$\Delta H_f' = \zeta m\Delta H_u - 2mH_e \qquad (11)$$

If the heat of dilution of the liquid polymer with solvent can be expressed

by van Laar's formula,

$$\frac{\Delta H_f}{xN} = \frac{\Delta H_f' + \Delta H_m}{xN} = (1-\lambda)\left(\Delta H_u - \frac{2H_e}{\zeta}\right) + BV_u v_1^2 \frac{1-\lambda}{1-v_2+v_2\lambda} \tag{12}$$

Thus, the free energy change accompanying the fusion process ΔF_f $(= \Delta H_f - T\Delta S_f)$ is obtained by using Eqs. (10) and (12).

$$\begin{aligned}
\frac{\Delta F_f}{xN} = {}& (1-\lambda)(\Delta H_u - T\Delta S_u) + RT\left[\left(\frac{z}{z_s}\cdot\frac{v_1}{v_2}+\frac{1}{x}\right)\ln\{1-v_2(1-\lambda)\}\right. \\
& + \frac{(1-\lambda)}{\zeta}\left\{\ln\frac{v_2(r-1)}{ze}-\left(\frac{2H_e}{RT}\right)\right\}+\ln\frac{x-\zeta+1}{x}+\frac{2S_e}{R} \\
& \left. + \left(\frac{z}{z_s}\right)v_1^2\left(\frac{1-\lambda}{1-v_2+v_2\lambda}\right)\chi_1\right]
\end{aligned} \tag{13}$$

where
$$\chi_1 = BV_1/RT \tag{14}$$

By definition, z/z_s equals to V_u/V_1. Further, T_m^0, the melting point for the pure polymer of infinite chain length and infinite crystallite length in the absence of diluent, is given by

$$\Delta H_u/\Delta S_u = T_m^0. \tag{15}$$

Assuming $z=1$ for simplicity, and by differentiating Eq. (13) with respect to λ (ζ=constant) and equating the result to zero, we obtain

$$\begin{aligned}
\frac{1}{T} - \frac{1}{T_m^0}\left(1-\frac{1}{\zeta}\right) = {}& \frac{R}{\Delta H_u}\left[\frac{(V_u/V_1)v_1+(v_2/x)}{1-v_2(1-\lambda)}-\frac{1}{\zeta}\ln v_2+\frac{2}{\zeta}\left(\frac{H_e-TS_e}{RT}\right)\right. \\
& \left. -\left(\frac{1}{\zeta}\right)\ln\frac{x-\zeta+1}{x}-\left(\frac{V_u}{V_1}\right)\left\{\frac{v_1}{1-v_2(1-\lambda)}\right\}^2\chi_1\right]
\end{aligned} \tag{16}$$

The third term of the right hand side of Eq. (16) is written in terms of the fold length of crystallite l, the heat of fusion per unit volume Δh_f, and the surface free energy per unit area of crystal end surface σ_e.

$$\frac{R}{\Delta H_u}\cdot\frac{2}{\zeta}\left(\frac{H_e-TS_e}{RT}\right) = \frac{2\sigma_e}{T\cdot\Delta h_f\cdot l} \tag{17}$$

Substituting Eq. (17) into Eq. (16), we obtain the following equation, under the condition of $1-(1/\zeta)\cong1$.

$$\begin{aligned}
\frac{1}{T} - \frac{1}{T_m^0} = {}& \frac{R}{\Delta H_u}\left[\frac{(V_u/V_1)v_1+(v_2/x)}{1-v_2(1-\lambda)}-\frac{1}{\zeta}\ln v_2-\frac{1}{\zeta}\ln\frac{x-\zeta+1}{x}\right. \\
& \left. -\left(\frac{V_u}{V_1}\right)\left\{\frac{v_1}{1-v_2(1-\lambda)}\right\}^2\chi_1\right]+\frac{2\sigma_e}{T\cdot\Delta h_f\cdot l}
\end{aligned} \tag{18}$$

At the melting point, setting $\lambda=1$ in Eq. (18), we have

$$\frac{1}{T_m(l)} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\left[\frac{V_u}{V_1}v_1 + \frac{v_2}{x} - \frac{1}{\zeta}\ln v_2 - \left(\frac{1}{\zeta}\right)\ln\left(\frac{x-\zeta+1}{x}\right) - \left(\frac{V_u}{V_1}\right)\chi_1 v_1^2\right]$$
$$+ \frac{2\sigma_e}{T_m(l)\cdot\Delta h_f\cdot l} \tag{19}$$

where $T_m(l)$ represents the melting point of polymer when pure polymer of fold length l is mixed with diluent at a concentration of volume fraction v_2. The last term of the right hand side of Eq. (19) is written[14] as:

$$\frac{2\sigma_e}{T_m(l)\cdot\Delta h_f\cdot l} = \frac{1}{T_m(l)} - \frac{1}{T_m(l=\infty)} \tag{20}$$

where $T_m(l=\infty)$ represents the melting point of pure polymer, of infinite fold length and chain length, in the presence of diluent. Substituting Eq. (20) into (19), we have

$$\frac{1}{T_m(l=\infty)} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\left[\left(\frac{V_u}{V_1}\right)v_1 + \frac{v_2}{x} - \frac{1}{\zeta}\ln v_2 - \frac{1}{\zeta}\ln\frac{x-\zeta+1}{x} - \left(\frac{V_u}{V_1}\right)\chi_1 v_1^2\right] \tag{21}$$

If x is very large and ζ is considerably large, Eq. (21) reduces to

$$\frac{1}{T_m(l=\infty)} - \frac{1}{T_m^0} = \left(\frac{R}{\Delta H_u}\right)\left(\frac{V_u}{V_1}\right)(v_1 - \chi_1 v_1^2) \tag{22}$$

This equation is formally identical with the Flory's equation (Eq. (2)), but it includes the melting point of polymer of infinite fold length in the presence of diluent in place of T_m.

We proceed further in the case of pure polymer in the absence of diluent. Setting $v_2=1$, we have the following equations:

$$\frac{1}{T} - \frac{1}{T_m^0} = \left(\frac{R}{\Delta H_u}\right)\left[\frac{1}{x\lambda} - \frac{1}{\zeta}\ln\frac{x-\zeta+1}{x}\right] + \frac{2\sigma_e}{T\cdot\Delta h_f\cdot l} \tag{23}$$

and at the melting point,

$$\frac{1}{T_m^0(l)} - \frac{1}{T_m^0} = \left(\frac{R}{\Delta H_u}\right)\left[\frac{1}{x} - \frac{1}{\zeta}\ln\frac{x-\zeta+1}{x}\right] + \frac{2\sigma_e}{T_m^0(l)\Delta h_f\cdot l} \tag{24}$$

or

$$\frac{T_m^0(l)}{T_m^0} + T_m^0(l)\left(\frac{R}{\Delta H_u}\right)\left[\frac{1}{x} - \frac{1}{\zeta}\ln\frac{x-\zeta+1}{x}\right] = 1 - \frac{2\sigma_e}{\Delta h_f\cdot l} \tag{25}$$

If x is very large, Eq. (25) becomes:

$$T_m^0(l) = T_m^0\left(1 - \frac{2\sigma_e}{\Delta h_f\cdot l}\right) \tag{26}$$

This equation expresses the relation between the melting point of pure polymer and the fold length l, and is identical with the equations derived by Hoffman and Weeks[8], and Hirai et al.[15].

Sudtracting Eq. (24) from Eq. (19) and combining the result with Eq. (25), we get

$$\left[\frac{1}{T_m(l)}-\frac{1}{T_m^0(l)}\right]\left[\frac{T_m^0(l)}{T_m^0}+T_m^0(l)\left(\frac{R}{\varDelta H_u}\right)\left\{\frac{1}{x}-\frac{1}{\zeta}\ln\frac{x-\zeta+1}{x}\right\}\right]$$
$$=\left(\frac{R}{\varDelta H_u}\right)\left[\left(\frac{V_u}{V_1}\right)v_1-\frac{v_1}{x}-\frac{1}{\zeta}\ln v_2-\left(\frac{V_u}{V_1}\right)\chi_1 v_1^2\right] \tag{27}$$

If $T_m^0(l)/T_m^0$ is assumed to be equal to unity, and if x is very large and ζ is considerably large, Eq. (27) is reduced to

$$\frac{1}{T_m(l)}-\frac{1}{T_m^0(l)}=\left(\frac{R}{\varDelta H_u}\right)\left(\frac{V_u}{V_1}\right)(v_1-\chi_1 v_1^2) \tag{28}$$

This equation also is formally identical with Eq. (2). In this case, the quantities $T_m(l)$ and $T_m^0(l)$ are easily determined.

In Figs. 2, 3 and 4 were shown calculated curves for the relation between the equilibrium degree of crystallinity and the temperature, according to Eqs. (18) and (23) with the numerical values[9,10], $\sigma_e=100$ erg./cm.[2] and $T_m^0=416.2°$K.

Discussion

In the treatment mentioned above, assumed model of crystallite is regular folding. Now some discussions will be presented on the applicability of such ideal model to the real polymer crystals. Single crystal of polyethylene seems to be almost perfectly crystalline, because its density[16] is close to the crystallographic density of 1.00. On the other hand, the density of polyethylene, crystallized very slowly from the melt at a temperature near the melting point, also approaches to the crystallographic density, as was reported by Mandelkern et al.[17]. Thus, the regular folded chain crystallite model may be reasonably available to some extent for the solution-crystallized single crystal and also for the melt-crystallized polymer crystallized very slowly in the vicinity of melting point.

Effects of the fold length l and the degree of polymerization x on the degree of crystallinity-temperature relationship are shown in Figs. 2, 3 and 4 by the use of Eqs. (18) and (23). With these equations, the calculated degree of crystallinity amounts to unity at a temperature slightly below the melting point. Fig 5 shows the experimental result[18] on linear polyethylene annealed for about 40 days. The shape of the curve is quite similar to those shown in Figs. 2, 3 and 4. But in this case the degree of crystallinity in the low temperature range is lower than unity. If a sample which has the crystallographic density as mentioned above is used for experiment, then the degree of crystallinity should be equal to unity. Further, the degree of crystallinity
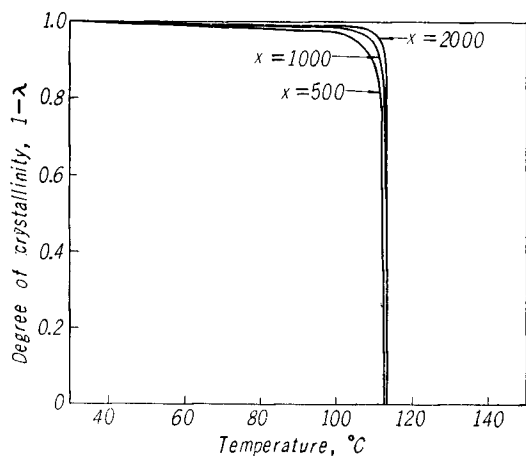
Fig. 2. Degree of crystallinity as a function of temperature for various degrees of polymerization x. Curves calculated from Eq. (23) for $l=$ 100Å, $\sigma_e=100$ ergs/cm², and $T_m^\circ=416.2°K$.
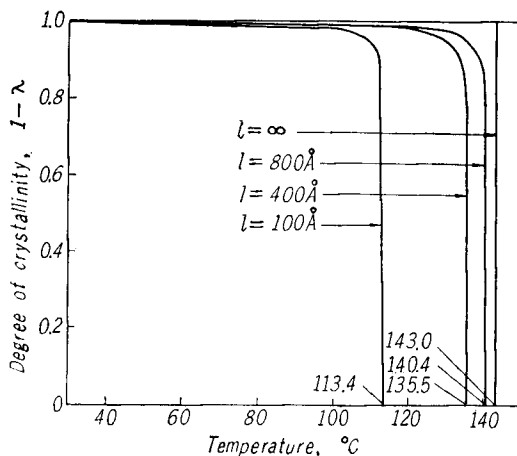
Fig. 3. Degree of crystallinity as a fucction of temperature for various fold lengths l. Curves calculated from Eq. (23) for $x=1000$, $\sigma_e=100$ ergs/cm², and $T_m^\circ=416.2°K$.
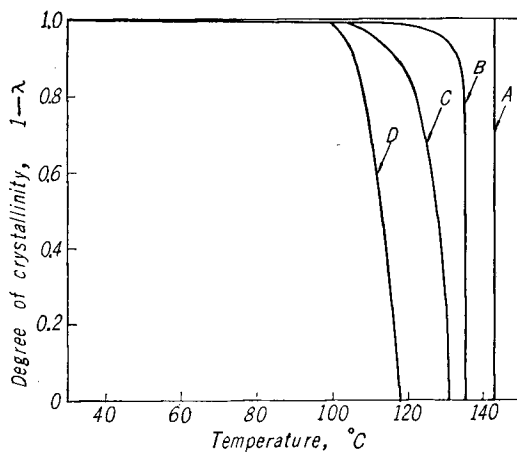
Fig. 4. Degree of crystallinity as a function of temperature for polymer, and polymer-diluent systems, calculated from Eqs. (18) and (23) with $\sigma_e=100$ ergs/ cm² and $T_m^\circ=416.2°K$. Pure polymer system

A : $l=\infty$, $x=\infty$; B : $l=400$Å, $x=1000$
polymer-diluent system ($V_u/V_1=0.2$, $\chi_1=0$)
    C : $l=400$Å, $x=1000$, $v_2=0.9$;
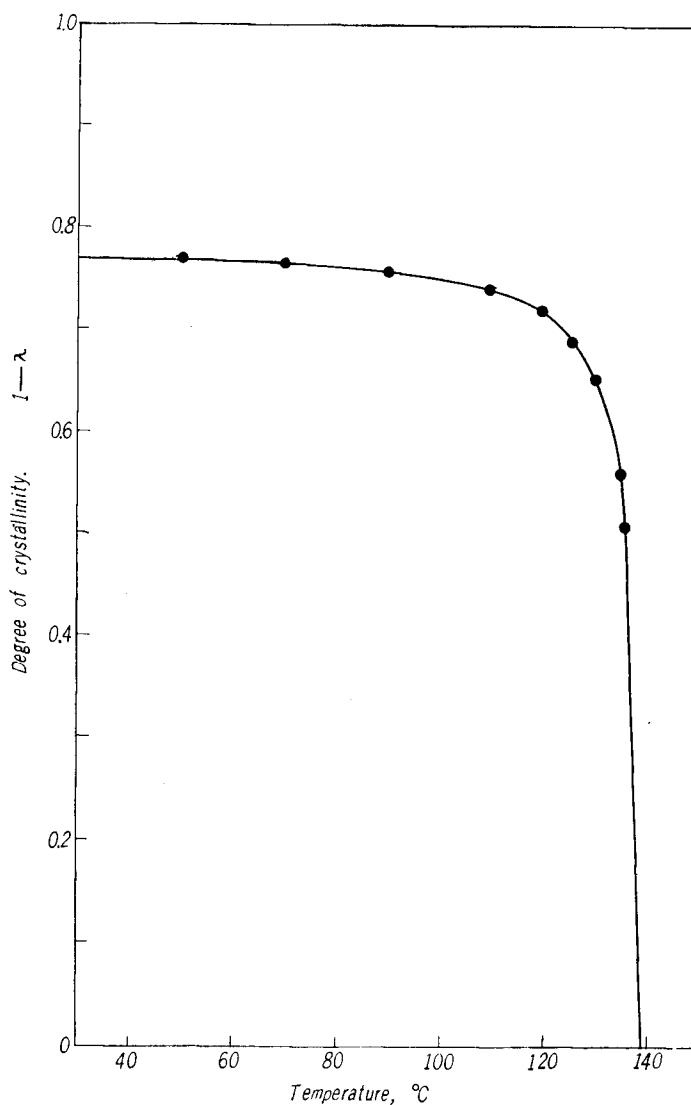   D : $l=400$Å, $x=1000$, $v_2=0.5$,

Fig. 5. Degree of crystallinity as a function of temperature for linear
polyethylene (Marlex 50) crystallized for 40 days at 131.3°C
(Chiang and Flory[18]).

observed actually may be lower than the equilibrium degree of crystallinity.
Mandelkern et al.[17] have reported that the degree of crystallinity of poly-
ethylene crystallized at 130°C is 0.895 in the case of annealing for 40 days
and 0.911 for 400 days. On one side, the curves in Figs. 2, 3 and 4 were com-
puted assuming that the end surface free energy is independent of tempera-

ture. But the surface free energy becomes larger with decreasing temperature, thus at lower temperature far below the melting point the degree of crystallinity should become smaller than he value shown in the figures. Thus the difference in observed and calculated degree of crystallinity may be partly elucidated by the factors mentioned above.

In conclusion, the following points are emphasized from the discussions presented above.

As the melting point of polymer in the absence and presence of diluent may change according to the condition of preparing sample, we propose to use the melting point $T_m^0(l)$ of the polymer of the fold length l which crystallized sufficiently at the highest temperature for crystallization near the melting point, and also the dissolution temperature, $T_m(l)$, at which the polymer of the fold length l is dissolved in diluent by heating, instead of using the results on samples prepared by conventional method[20, 21] in which polymer is dissolved in solvent by heating and then crystallized by slow cooling. These circumstances are clearly showu in Fig. 6[23], in which the crystal-solution phase
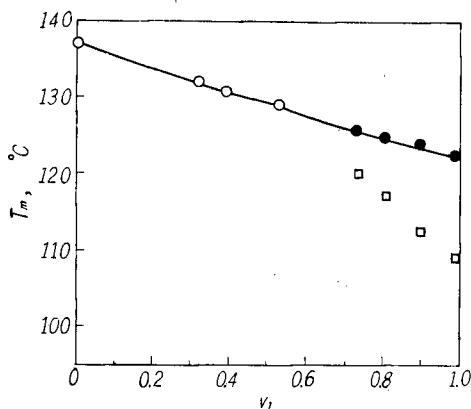

Fig. 6. Crystal-solution phase equilibrium for polyethylene in n-octadecane (Nakajima and Hamada[23]).

○ Melting point of the polymer-diluent mixture crystallized sufficiently near the melting point (determined by dilatometry).

● Dissolution temperature of the melt-crystallized sample (determined by visual method)

□ Dissolution temperature of the sample crystallized from solution (determined by visual method).

equilibrium for polyethylene in n-octadecane is given. Obviously, the dissolution (or melting) temperature of melt-crystallized polymer is significantly higher than that of solution-crystallized polymer, and the difference between the two samples increases with dilution. Recently, similar results were also reported by Flory et al.[19].

The melting point of polymer of infinite fold length and chain length in Eq. (26), T_m^0, to which the effect of end surface free energy is neglected, may be defined as the theoretical melting point. The relation between the fold length l and the melting point of polymer crystal, whose chain length is large, was given by Eq. (26). As obvious from Figs. 2 and 3, the melting

point of polymer crystal strongly depends on the fold length but not much on the chain length, provided the chain length is large[22].

The equations derived here were based on the assumption of regular folded chain crystallite model, but the assumption was used only through the end surface free energy σ_e. Therefore, it is expected that the same equations may be also applicable for polymers consisting of fringed micelle crystallites, if the sample is sufficiently crystallized near the melting point, although the values of σ_e are different for both models.

References

1) F. Hamada and A. Nakajima ; Chem. High Polymers, Japan, in press.
2) F. Hamada and A. Nakajima ; Chem. High Polymers, Japan, in press.
3) P. J. Flory ; J. Chem. Phys., **17**, 223 (1949).
4) A. Keller ; Phil. Mag., **2**, 1171 (1957).
5) L. H. Tung and S. Buckser ; J. Phys. Chem., **62**, 1530 (1958).
6) R. J. Reo, K. J. Smith and W. R. Krigbaum ; J. Chem. Phys., **35**, 1306 (1961).
7) J. I. Lauritzen and J. D. Hoffman ; J. Res. Natl. Bur. Std., **64A**, 73 (1960),
   J. D. Hoffman and J. I. Lauritzen ; J. Res. Natl. Bur. Std., **65A**, 297 (1961).
8) J. D. Hoffman and J. J. Weeks, ibid., **66A**, 13 (1962).
9) R. G. Browm and R. K. Eby ; J. Appl. Phys., **35**, 1156 (1964).
10) S. Iida, H. Sakami, T. Adachi and M. Hori ; 12th Polymer Symposium of the Society of Polymer Science, Japan, Nagoya, November 1963.
11) R. B. Richards ; Trans Faraday Soc., **42**, 10 (1946).
12) "Unsolved Problems in Polymer Sci.", National Academy of Science (1962) pp. 118.
13) P. J. Flory ; J. Chem. Phys., **10**, 53 (1942).
14) V. F. Holland ; J. Appl. Phys., **35**, 59 (1964).
15) N. Hirai et al. ; Chem. High Polymers, Japan, **21**, 173 (1964).
16) T. Kawai and A. Keller ; Phil. Mag., **8**, 1203 (1963).
17) L. Mandelkern, A. S. Posner, A. F. Diorio, and D. E. Raberts ; J. Appl. Phys., **32**, 1509 (1961).
18) R. Chiang and P. J. Flory ; J. Am. Chem. Soc., **83**, 2857 (1961).
19) J. B. Jackson, P. J. Flory and R. Chiang ; Trans. Faraday Soc., **59**, 1906 (1963).
20) P. J. Flory, L. Mandelkern, and H. K. Hall ; J. Am. Chem. Soc., **73**, 2532 (1951).
21) G. B. Gechele, and L. Crescentini ; J. Appl. Polymer Sci., **7**, 1349 (1963).
22) F. R. Anderson ; J. Appl. Phys., **35**, 64 (1964).
23) A. Nakajima and F. Hamada ; Koll-Z., to be published.