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A Re-examination of the Relation between the Melting Temperature and the Crystallization Temperature: Linear Polyethylene

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ABSTRACT: Analysis of the dependence of the melting temperature on the crystallization temperature has been frequently used to estimate the equilibrium melting temperature of a polymer. In the present paper the underlying basis for this extrapolative method is examined in detail. Two distantly different types of nucleation are considered. One is the Gibbs two-dimensional nucleus; the other, certain kinds of three-dimensional nuclei. Thickening, subsequent to nucleation, is also taken into account. Appropriate experiments with linear polyethylenes that have most probable molecular weight distributions, as well as with a molecular weight fraction, were carried out over a wide range in crystallization temperatures. Three distinct regions are observed. The high-temperature region is curved and precludes an extrapolation of the data to the equilibrium melting temperature. Reasons for this behavior are presented. Evidence for its being a general phenomenon is also given. A melting temperature of 141 °C was directly observed for linear polyethylene.

Introduction

The equilibrium melting temperature of a polymer is an important parameter for understanding the crystallization behavior of polymer systems. An accurate value of this quantity is required in the analysis of the crystallization kinetics (establishing the undercooling) and of the melting process. The equilibrium melting temperature, T_m°, of a crystalline polymer is defined as the melting temperature of a perfect crystal formed by infinite molecular weight chains.[1,2] Based on this definition, a direct experimental determination of T_m° is, therefore, not possible for real polymeric systems. To overcome this difficulty, different extrapolative methods have been developed that estimate the value of T_m°. For example, a theoretical analysis of the directly determined equilibrium melting temperatures of oligomeric chains, by Flory and Vrij,[3] allows for an extrapolation of these data to a chain of infinite length and thus to T_m°. An analysis of the melting temperatures of n-alkanes leads to a value of $T_m^\circ = 145.5 \pm 1$ °C for linear polyethylene.[3]

Two extrapolative methods that use the observed experimental melting temperatures of polymers have also been developed and are in common use. One of these involves an extrapolation of the dependence of the observed melting temperature on the crystallization temperature.[4,5] This method is an adaptation of the Gibbs–Thompson equation[6,7] to the melting of crystals with thicknesses significantly smaller than the lateral length.[4] Although it was initially implied that this method was unique to polymer crystals with regularly folded chains,[4] it is in fact generally applicable to both monomers and polymers. It does not depend on the nature of the interfacial structure.[8] In essence, this method consists of relating the thickness of a mature crystallite l, calculated from the Gibbs–Thomson equation, to the thickness, l^*, of the critical nucleus required to initiate crystallization. This concept requires the formulation of l^*, which in turn depends on the assumption of the type of nucleus involved. It also requires knowledge of the thickening process of the crystallite subsequent to the formation of a nucleus of critical size.

The other method, which is in general use, also follows the general theory for the melting of crystals of finite size. Here, the melting temperature is determined as a function of crystallite thickness. The melting temperature that is extrapolated to infinite crystal thickness is taken as the equilibrium melting temperature.

In the present work we shall consider in detail the relation between the observed melting temperature T_m and the crystallization temperature T_c and the extrapolation of these data to T_m°. The experimental focus will be on linear polyethylene. In the initial formulation of the problem the ratio between the thicknesses l to l^* was assumed to be constant with crystallization temperature.[4] The problems that are associated with nonlinear thickening were pointed out by Weeks[9] early on. However, the implications of these observations have not been given serious consideration. The isothermal thickening of linear polyethylene, when crystallized from the melt, is now well documented.[9–14] It was pointed out by Weeks in 1963[9] that the increase in observed melting temperature with increasing isothermal crystallization time is a consequence of the increase in lamellar thickness, which has a logarithmic time dependence. With the large amount of experimental evidence that is now available and the details of the influence of molecular weight and crystallization temperatures,[11–13] it is surprising that a recent report[15] did not recognize the substantial isothermal thickening that occurs in linear polyethylene during crystallization from the pure melt.

In the present work the theoretical basis of the T_m/T_c extrapolation method is re-examined. The isothermal thickening process is also integrated into the analysis. To provide a broader data base, new experimental results were obtained over a larger range of crystallization temperatures than have been reported heretofore. A molecular weight series of linear polyethylenes having a well-defined, narrow distribution were studied, as was a fraction.

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Theoretical Background

The observed melting temperature T_m and the equilibrium melting temperature T_m° are related to one another by the Gibbs–Thomson equation.[6,7]

$$T_m = T_m^\circ[1 - (2\sigma_{ec}/\Delta H_u l)] \qquad (1)$$

In this equation l is the crystallite thickness, σ_{ec} is the interfacial free energy associated with the basal plane of the mature crystallite, and ΔH_u is the enthalpy of fusion per repeating unit.[16] It is assumed here that the lateral dimensions of the lamellar crystallites are much greater than their thicknesses. Equation 1 is quite general. It is applicable to all types of molecules and does not depend on the specifics of the crystallite surface.

The T_m/T_c extrapolation method that is used to obtain the equilibrium melting temperature is based on the fundamental assumption that at low levels of crystallinity the thickness of the crystallite is close to the thickness of the primary, critical nucleus, l^* and can be related to it in a simple, analytic manner. In addition to this assumption, a specific nucleation process needs to be given in order to relate the dependence of l^* on T_c.

It is usually assumed that $l = ml^*$, where m is a constant equal to or greater than unity. There are very many nucleation processes that are consistent with all the reported crystallization kinetic data of polymers. From among them we select two common possibilities for consideration. For a coherent two-dimensional nucleus of the type first described by Gibbs:[6]

$$l^*_{(2d)} = \frac{2\sigma_{en}}{\Delta G_u} \qquad (2)$$

Here σ_{en} is the surface free energy associated with a nucleus of critical size and ΔG_u is the difference in free energy between the liquid and the crystal phase. ΔG_u can be approximated by $(\Delta H_u \Delta T)/T_m^\circ$. Equations 1 and 2 focus solely on the crystallite thickness and the interfacial free energy, i.e., on the role of the crystallite thickness in governing the observed melting temperature. It is assumed that the free energy of fusion per repeating unit, from which ΔH_u is derived, is independent of the level of crystallinity and that the structure of the melt is independent of the level of crystallinity and temperature, except for the usual specific heat effects.

In the case of random copolymers, there is another important factor that needs to be taken into account. Under equilibrium conditions, the melting temperature of a random copolymer represents the disappearance of the longest crystallizable sequences.[1,17] Theory indicates that under real crystallization conditions the observed melting temperature will depend not only on the crystallite thickness but also on the sequence distribution of the crystallizable units in the residual melt. The chemical potential of a chain unit in the melt depends solely on the sequence distribution.[1,17,18] Consequently, it will vary with crystallization temperature, since different length sequences are used to form the crystallites formed at a given temperature. The equations used in the present analysis will then no longer be valid. Therefore, it is not surprising that extrapolation to obtain T_m° for random copolymers by this method cannot be accomplished.[19,20] Since stereoirregular polymers should be considered to be copolymers from this point of view, they also fall into this category. Hence, T_m° values that have been obtained for this class of polymers by this procedure need to be reexamined.

Substituting eq 2 into eq 1 and defining $\beta = \sigma_{ec}/\sigma_{en}$, eq 1 becomes

$$T_m = T_m^\circ\left(1 - \frac{\beta}{m}\right) + \frac{\beta}{m}T_c \qquad (3)$$

which reflects a simple relation between the observed T_m and the crystallization temperature. If both β and m are constant over the complete T_c range of crystallization temperatures, eq 3 leads to a linear relation between T_m and T_c. There are several different ways of interpreting the slope (β/m) of this straight line. If we assume that the thickness of the mature crystallite is the same as the initial critical nucleus ($l = l^*$) and that their interfacial free energies are also equal ($\sigma_{ec} = \sigma_{en}$), then $\beta/m = 1$ and eq 3 becomes

$$T_m = T_c \qquad (4)$$

As was pointed out by Gibbs,[6] such a crystal will not be stable at temperatures infinitesimally above the crystallization temperature. However, stability of this crystal can be assured by allowing l to become greater than l^* ($m > 1$). If β is still assumed to be unity, eq 3 now becomes

$$T_m = \frac{m-1}{m}T_m^\circ + \frac{T_c}{m} \qquad (5)$$

In this case, the slope of the straight line in the T_m/T_c plot could have values greater than zero and less than 1. Theoretically, stability cannot be achieved for $m = 1$ and $\beta > 1$. However, for the case $m = 1$ and $\beta < 1$ it is theoretically possible to attain stability. This latter case is physically unrealistic since it requires that the interfacial free energy associated with a mature crystallite be less than the nucleus from which it is formed.

A second possibility involves three-dimensional homogeneous nucleation[2] or certain types of heterogeneous nucleation.[21] In all of these cases the critical size of a cylindrically shaped nucleus is given by the expression[22]

$$l^*_{(3d)} = \frac{4\sigma_{en}}{\Delta G_u} \qquad (6)$$

When eq 6 is substituted into eq 1, we find that

$$T_m = T_m^\circ\left(1 - \frac{\beta}{2m}\right) + \frac{\beta}{2m}T_c \qquad (7)$$

For this nucleation model, thermodynamic stability is achieved without requiring any further growth in the chain direction or any change in the interfacial free energies.

A similar interplay of possibilities can also be made between β and m for three-dimensional nucleation. For example, if $\beta = m = 1$, eq 7 becomes

$$T_m = \left(\frac{1}{2}\right)(T_m^\circ + T_c) \qquad (8)$$

It is of interest to note that the case represented by eq 8 is identical to having $m = 2$ in eq 5. In that case the thickness of the mature crystallite is twice that of the critical nucleus size. A slope of 0.5 in a T_m/T_c plot does not distinguish between these two cases.

If the interfacial free energies of the crystal and nucleus are assumed to be the same, $\beta = 1$, and $l > l^*$, eq 7 becomes

$$T_m = \left(\frac{2m - 1}{2m}\right)T_m^\circ + \frac{T_c}{2m} \qquad (9)$$

This equation is identical to that originally given by Hoffman and Weeks[4] based on a coherent two-dimensional nucleation process. However, to arrive at this equation, which is also applicable to three-dimensional nucleation (see eq 7), it was necessary to make the arbitrary assumption that the critical nucleus *doubled* its initial thickness before introducing the factor m.[23]

According to eqs 5 and 9, plots of the observed melting temperature against the crystallization temperature, for low degrees of crystallinity, can be interpreted in terms of the type of nucleation involved and the relation between the thickness of the crystallite that actually melts and that of the nucleus from which it develops. If one takes the quantity m as being a measure of the relative thickening and further assumes that it is a constant over the complete interval of T_c, then straight lines should result in a plot of T_m against T_c. For the coherent, two-dimensional Gibbs type nucleus the slope will be $1/m$ with $0 < 1/m < 1$. For the three-dimensional nucleus the slope is $1/(2m)$, with $1/(2m) \leq 0.5$. The nominal value of the slope will reflect the amount of thickening in both types of nucleus.

The inherent instability of the coherent Gibbs-type nucleus, for $m = 1$, $\beta = 1$, was recognized by Hoffman and Lauritzen.[24,25] Since they assumed a nucleus that was comprised of regularly folded chains, the required stability was achieved by taking the average value of fluctuations about l^*. Consequently, eq 2 becomes[24]

$$l^*_{(2d)} = \frac{2\sigma_{en}}{\Delta G_u} + c \qquad (10)$$

were c is approximated by $kT/h\sigma$. Here k is the Boltzmann constant, h is the thickness of one monomolecular layer ($\sim 5 \times 10^{-8}$ cm), and σ is the lateral interfacial free energy. For the crystallization temperature range of 398–405 K for linear polyethylene and with $\sigma = 10$ erg/cm^2, c is essentially constant of the order of 10 Å.[4,26] This procedure will in principle assure thermodynamic stability to a crystallite whose thickness is given by eq 10. By assuming $\sigma_{ec} = \sigma_{en} = \sigma_e$, eq 1 takes the form

$$T_m = T_m^\circ\left[1 - \frac{\Delta T}{T_m^\circ}\left(\frac{1}{1 + c\left(\frac{\Delta H_u}{2\sigma_e}\right)\left(\frac{\Delta T}{T_m^\circ}\right)}\right)\right] \qquad (11)$$

This expression is the same as that given by Morra and Stein[27] following similar reasoning. The significance of eq 11 is that T_m is no longer linear in T_c despite the constant that was added to the initial nucleus.

Taking the quantity $\Delta H_u/2\sigma_e$ as the constant α, eq 11 can be expanded in series to obtain

$$T_m = T_c + \frac{c\alpha(\Delta T)^2}{T_m^\circ} - \frac{c\alpha(\Delta T)^3}{T_m^{\circ 2}} + \ldots \qquad (12)$$

According to eq 12 the magnitude of the deviation from linearity will depend on the values of c and α, the equilibrium melting temperature, and the undercooling (ΔT) at which the crystallization is conducted.

Table 1. Characterization of Linear Polyethylenes

designation	M_W	M_W/M_N
LPE 350	351 000	2.25
NBS 1484	120 000	1.10
LPE 71	71 400	2.22
LPE 40	40 000	1.88

Dalal *et al.*[28,29] took l^* from eq 10 and allowed it to increase by a factor of n to achieve the thickness of the mature crystallite, i.e., $l = nl^*$. Substituting this relation into eq 1 and expanding in series, they obtained[28]

$$T_m = T_m^\circ - \frac{\Delta T}{n}[1 - K\Delta T + (K\Delta T)^2 \ldots] \qquad (13)$$

Here $K = \Delta H_u c/2\sigma_{ec}T_m^\circ$. Equation 13 has the same characteristics as eq 12 and reduces to it for $n = 1$. Allowing the basic Gibbs type of nucleus to thicken for two different reasons as embodied in the quantities c and n is not necessary. The thickening process itself endows the necessary stability to the nucleus and can be made consistent with the observed melting temperature.

Experimental Section

A series of linear polyethylenes having most probable molecular weight distributions and weight-average molecular weights between 40 000 and 351 000 were studied. The polymers were prepared by the method described by Kaminsky *et al.*[30] A linear polyethylene fraction, NBS 1484 with a M_W = 120 000 and M_W/M_N = 1.10, was also studied. The molecular characteristics of these samples are listed in Table 1.

The molecular weights were determined by standard GPC methods. The heating and cooling processes were performed in a Perkin-Elmer differential scanning calorimeter, DSC-2B. Approximately 2 mg of a flat film (~50 μm thick) was encapsulated in a DSC aluminum pan, melted at 150 °C for 5 min, and rapidly quenched, at the highest cooling rate of the instrument, to the predetermined crystallization temperature. After a given time, melting was initiated from T_c, without any previous cooling. The heating rate for all the samples was 10 °C/min, and the melting temperature was taken at the peak of the endotherm. The time allowed at each crystallization temperature was adjusted to obtain a fixed predetermined level of crystallinity.

Results

The linear polyethylene sample having a most probable molecular weight distribution with M_W = 351 000 was crystallized over the temperature range of 121–131 °C to a level of crystallinity of less than 10%. The observed melting temperatures, T_m, are plotted against the crystallization temperatures, T_c, in Figure 1. The experimental points can be represented by the solid curve that is indicated in the figure. At the low T_c values 121–123 °C, there is very little change in T_m with T_c. When T_c is increased from 123 °C to approximately 126.5 °C, the increase in T_m is essentially linear with a slope of 0.49. When these data points are extrapolated linearly to the $T_m = T_c$ line, according to eq 5 or 9, a T_m° value of 144 ± 1 °C is obtained. This T_m° value is in good accord with that previously obtained by similar methods[22,31] and is also expected from the theoretical analysis of Flory and Vrij.[3] However, the T_m values obtained at the highest crystallization temperatures, T_c between 127 and 131 °C, deviate markedly from the

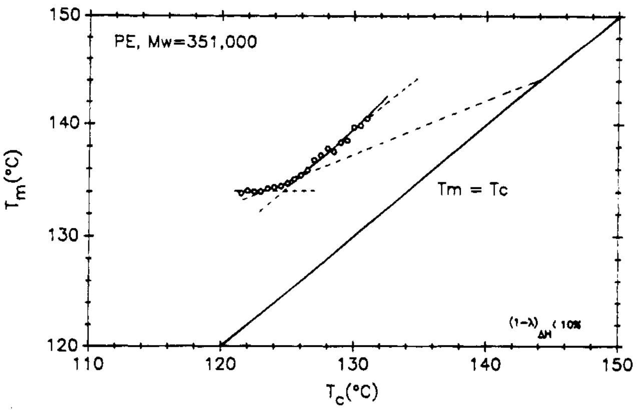

Figure 1. T_m–T_c plot for linear polyethylene (M_W = 351 000; M_W/M_N = 2.25) at levels at crystallinity ≤10%. Solid curve averages experimental points. Dashed lines indicate three regions of the curve as explained in the text.

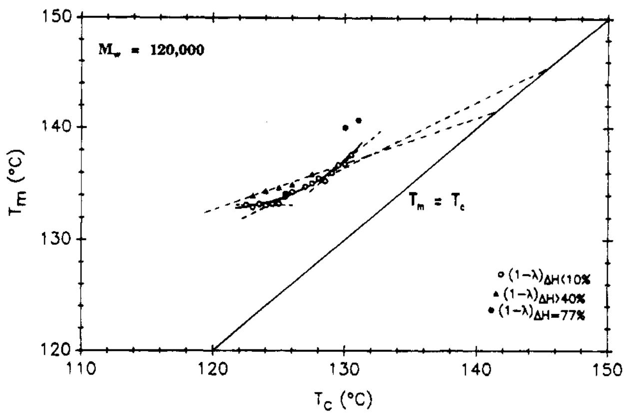

Figure 2. T_m–T_c plot for linear polyethylene (M_W = 120 000; M_W/M_N = 1.10). Three different degrees of crystallinity are plotted. Solid and dashed lines as in Figure 1.

straight-line drawn to represent the data in the 123–126.5 °C range. These data points now parallel the $T_m = T_c$ line. Thus, it is operationally impossible to extrapolate to a T_m^0 value by using the complete range of crystallization temperatures that are available. The experimental results delineate three regions. There is a low-T_c region, where T_m shows very little change; an intermediate-T_c region with a slope close to 0.5; and a high-T_c region, where T_m shows larger increases with T_c and the data parallel the T_m/T_c line. T_m/T_c extrapolations for low levels of crystallinity have been carried out for linear polyethylene fractions[22] and an unfractionated sample.[31] In both works, the observed T_m increased linearly with T_c and extrapolated to about 145.5 °C at the $T_m = T_c$ line. The nonlinear T_m/T_c plot shown in Figure 1 is a feature that has not been observed heretofore in linear polyethylene. This upward curvature was observed in similar plots for poly(tetramethylene oxide)[32] and poly(pivalolactone)[33] and its blends with poly(vinylidene fluoride).[33] It has also been observed in polyethylene blends.[34] In these studies, the deviations from linearity were neglected when extrapolating the data to T_m^0. The upward curvature obviously presents a serious dilemma in utilizing this extrapolative method to obtain T_m^0. For linear polyethylene, where the value of T_m^0 resides as a sound theoretical basis, it is readily apparent which set of data points to use for the extrapolation. However, linear polyethylene is a unique case since a theoretical base does not exist for any other homopolymer. Linear extrapolations are usually made ignoring any deviations of higher T_m values. Consequently, many of the reported T_m^0 values need to be re-examined and analyzed in more detail.

A very important feature that is found in Figure 1 is the high melting temperatures, ≥140 °C, that are obtained at the highest T_c. The crystallization time in this region is of the order of 4000 min. To the best of our knowledge this is the first time that a T_m = 141 °C has been directly observed for linear polyethylene. Even under slow stepwise heating conditions, the highest temperature observed in a fraction was ~138 °C.[35] A T_m of 137 °C was also reported by Weeks[9] after crystallizing an unfractionated sample at 130 °C for almost 20 000 min.

T_m/T_c measurements were also carried out with the narrow polyethylene fraction, sample B. Melting temperatures were obtained over a range of T_c's for two levels of crystallinity, 10 and 40%. In addition, two samples were crystallized to higher levels of crystallinity in sealed glass tubes for a long time (6000 and 21 600 min, respectively, for the low and highest T_c studied) in thermostated oil baths. The results are given in Figure 2. The results for low levels of crystallinity, open circles in the figure, are very similar to those given in Figure 1. The T_m/T_c data can again be divided into three regions. There is a low crystallization temperature region where T_m is essentially constant with T_c. In the intermediate crystallization temperature region there is a linear increase of T_m with T_c. The melting temperatures in this region extrapolate linearly to a T_m^0 value of 145.5 °C with a slope of 0.58. This T_m^0 value is, thus, similar to the other reported values.[22,31] The highest crystallization temperatures give melting temperatures that clearly deviate toward higher values, to the straight line representing the intermediate-T_c range. In this range of crystallization the data can also be represented by a straight line that essentially parallels the T_m–T_c line. Lemstra *et al.*[20] have also discussed their T_m/T_c plots of isotactic polystyrene in terms of three regions. Although the discussion is complicated by the copolymeric nature of the polymer, it is of interest to note that the data for the highest crystallization temperatures parallel the T_m–T_c line. The inability to extrapolate these data raised doubts about using this procedure to obtain T_m^0 for this polymer.

When the level of crystallinity of the polyethylene fraction is increased to slightly more than 40%, the observed melting temperatures also increase. At a given T_c, the increase in T_m varies between 0.6 and 1.7 deg relative to the melting temperatures for the lower degrees of crystallinity. The data can now be represented by a single straight line over the restricted crystallization temperature range that can be reasonably studied. The slope of the straight line is now reduced to 0.41. The straight line extrapolates to a T_m^0 value of 141.5 °C. This value is significantly lower than the one obtained at lower levels of crystallinity. The differences in the extrapolated values for T_m^0, with varying degrees of crystallinity, are the same as those found in earlier reports for linear polyethylene.[22,31] However, the data in Figure 2 encompass a much wider T_c interval. Poly(ethylene oxide)[5] and *trans*-1,4-polyisoprene[36] behave in a similar manner.

The melting temperatures of the fraction crystallized at high temperatures for very long periods were significantly greater than those obtained at low or intermediate levels of crystallinity. As indicated by the closed circles in Figure 2, observed melting temperatures as

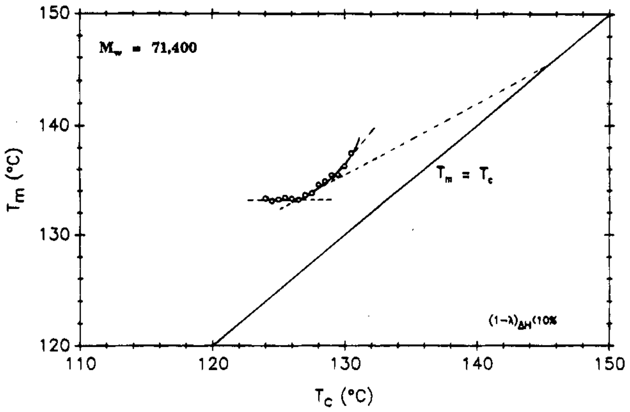

Figure 3. T_m-T_c plot for linear polyethylene (M_W = 71 400; M_W/M_N = 2.22) crystallized at ≤10% crystallinity. Solid and dashed lines as in Figure 1.

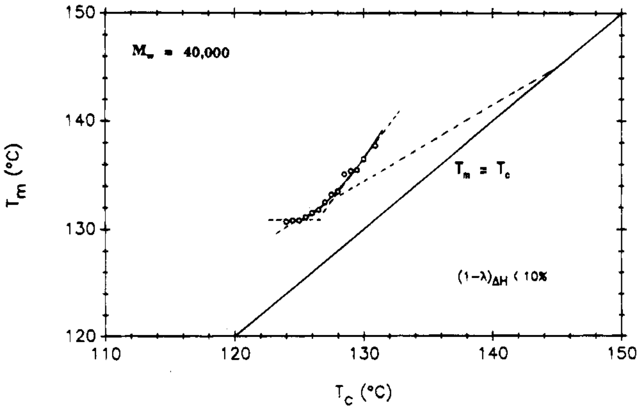

Figure 4. T_m-T_c plot for linear polyethylene (M_W = 40 000; M_W/M_N = 1.88) crystallized at ≤10% crystallinity. Solid and dashed lines as in Figure 1.

high as 141 °C were obtained under these conditions for this sample.

The results of the T_m/T_c plots for the lower molecular weight samples having most probable molecular weight distribution and crystallized to low levels of crystallinity (<10%) are given in Figures 3 and 4. Figure 3 is for a sample M_W = 71 400, while Figure 4 is for M_W = 40 000. Reducing the molecular weight has little influence on the nature of the T_m/T_c plots. Basically, the functional dependence of T_m with T_c is the same as was found for the higher molecular weights. There are also three regions in these curves, and only the intermediate region extrapolates to a reasonable T_m^0 value. The T_m's at the high crystallization temperatures also deviate toward very high values.

Discussion

An examination of the T_m/T_c data that have been reported in the literature for almost all homopolymers shows that the results can be represented either by a single straight line whose slope is the order 0.5 or by such a straight line that is preceded by a region where T_m is essentially constant with T_c. In either case, the extrapolation could apparently be carried out to T_m^0 without any difficulty. The apparent equilibrium melting temperatures for a large number of homopolymers have been determined in this manner.[5,37-43] However, the measurements were not usually carried out to sufficiently high values of T_c so that the upward curvature and deviations from linearity were not observed. Therefore, the validity of the extrapolations is of concern.

The results shown in Figures 1−4 make quite evident that the lack of linearity in the T_m/T_c plots precludes an extrapolation to T_m^0 without adopting arbitrary procedures or ignoring some of the experimental data points. In an effort to understand these results, it is convenient to divide the curves in Figures 1−4 into the three regions that have been described. The samples that are crystallized at the lowest temperatures must traverse a temperature interval, on cooling, where the crystallization rate is extremely rapid. Consequently, crystallites of about the same small thickness will be formed at each T_c in this temperature range. Therefore, T_m will be essentially constant with T_c. This would explain the small changes that are observed in the T_m's in Figure 1 and at comparable low-T_c regions in Figures 2−4. Many other polymers display a similar behavior.[32,37,40,42,44] In the other extreme, at the highest crystallization temperatures, very long times are required to obtain even small amounts of crystallinity (~4000 min at the highest temperatures studied). During this time period the initial nucleus will undergo extensive thickening before even reaching 5−10% crystallinity. The amount of thickening will depend on both the time and crystallization temperature. The resulting crystals will melt at relatively high temperatures. In the intermediate-T_c range, the complications related to either long-time isothermal thickening or rapid crystallization are alleviated. Therefore, in this region the experimental data can be interpreted according to the theoretical developments described by either eq 5 or 9.

In interpreting the linear portion of the T_m/T_c curve, a choice has to be made as to the type of nucleation that is involved. For example, if a Gibbs type nucleus is selected, then the slope of 0.5 in Figure 1 for this region indicates that the thickness of the crystallite that is melting is exactly double that of the initial critical nucleus. However, there is no *a priori* reason for this unique value of m or for its constancy. The linear extrapolation of this portion of the T_m/T_c curve leads to T_m^0 values that are in accord with the theoretical expectations for linear polyethylene. It also follows from eqs 5 and 9 that if m is constant, at any value, over the complete T_c range, then the corresponding plot will be linear and the extrapolation can be accomplished. The theoretical problem to be resolved is why m appears to be a constant over a restricted range in crystallization temperature. The practical problem to be overcome is that the T_m/T_c plot is not linear over a wide T_c range. The increase of m with increasing T_c has been suggested as a possible problem and source of error in determining T_m^0 by this extrapolative method.[9] However, the implications of this possibility were not pursued. It should be noted at this point that the use of eq 12 (where c is a constant) does not explain the curvature in the T_m/T_c plots.

Raman LAM and transmission electron microscopic studies of isothermal thickening during the crystallization of linear polyethylene have demonstrated that the thickening rate increases with the temperature.[12,13] Therefore, m should be greater at the higher T_c values and will lead to relatively higher observed melting temperatures in this range. Given the experimental results and their rationale, it is evident that an unbiased extrapolation of the data cannot be made. If only a linear relation is desired, then one has to *a priori* know at what T_c to cease the measurements. Linear polyethylene represents a unique case since the theoretically expected T_m^0 can serve as a guide to the extrapolation.

The data presented in Figures 1–4 can also be interpreted in terms of eq 9 for different types of three-dimensional nucleation. From the slope of the straight line representing the intermediate region of the curves we obtain $m \approx 1$. Thus, in this temperature region the thickness of the mature crystallite is the same as that of the critical size nucleus from which it develops. However, in this case the crystallite is thermodynamically stable. It should be emphasized that extrapolation of the data to evaluate T_m° is not dependent on the type of nucleation process selected. However, the interpretation of the data is.

The theoretical basis for this extrapolative method requires measurements at the lowest level of crystallinity that is feasible. The effect of increasing the crystallinity level at constant crystallization temperature has been illustrated in Figure 2. When the crystallinity level is increased, the accessible range in T_c is limited because of the excessive time that is involved at the higher temperatures. Although the apparent melting temperatures increase at each T_c, the slope of the resulting straight line is reduced. Hence the extrapolated T_m° value (141.5 °C) is significantly less than the one obtained at the lower crystallinity levels. The results obtained at the lower crystallinity levels, as well as the theoretical analysis, make clear that this T_m° is incorrect. Unfortunately, T_m/T_c data sets that have been reported for many homopolymers have not been restricted to low levels of crystallinity.[37–39,42,45] Linear extrapolations can always be accomplished with this kind of data. However, the validity of the T_m° value so obtained is uncertain.

Several possibilities can be given to explain the increase of the melting temperature with increasing degree of crystallinity at a given T_c.[4,22] The melting of thin crystals followed by recrystallization during heating would be more prominent at the lowest crystallization temperatures where the thinnest crystals are formed.[46,47] With increasing temperature the reorganization on heating is reduced and the melting temperature approaches the one obtained at low degrees of crystallinity. Another possibility is related to crystal thickening during isothermal storage at T_c. An increase in thickness on prolonged storage at T_c can occur by thermal fluctuations which lead to partial melting followed by recrystallization.[48] These processes would be minimized at the lowest possible level of crystallinity that is susceptible to quantitative study because of the time and temperature involved. The result is a lower slope in the T_m/T_c plot. The high degrees of crystallinity and melting temperatures that are observed after long-time crystallization (Figure 2) are consistent with extensive thickening during isothermal crystallization.

Estimates can be made of the relation between the thickness of the crystallite that corresponds to the observed T_m and that of the critical nucleus from which it is formed. The thickness of the crystallite at the low levels of crystallinity was calculated from the Gibbs–Thomson equation (eq 1) by taking $T_m^\circ = 418.5$ K and $\sigma_{ec} = 110$ erg/cm^2. The critical nucleus size was estimated from theory. Initially, a Gibbs type nucleus was assumed and l^* calculated from eq 2. The same value was taken for the interfacial free energy of the nucleus and of the crystal, $\sigma_{ec} = \sigma_{en} = 110$ erg/cm^2. The calculated values of l and l^* are plotted in Figure 5 as a function of temperature. Figure 5a is a plot for $M_W = 352\,000$ and Figure 5b is for the fraction $M_W = 120\,000$. The variations in l and l^* with T_c are very similar in both cases, irrespective of molecular weight or polydispersity. It is quite apparent that the differences between the thickness of the crystal and that of the initial nucleus are not constant with temperature. Rather, these differences are represented by a continuous curve with upward curvature. The differences in dimensions depend on the nucleation type assumed and the values assigned to σ_{en} and σ_{ec}. For example, in the case illustrated, the difference $l - l^*$ for the polyethylene with $M_W = 351\,000$ is 125 Å for the lowest T_c and it increases to 440 Å at the highest T_c studied, 131 °C. If $\sigma_{ec} = \sigma_{en} = 73.5$ erg/cm^2, the difference $l - l^*$ in the same range of T_c reduces to 100 Å at the lowest T_c and 300 Å at the highest one. Taking $\sigma_{ec} = \sigma_{en} = 110$ erg/cm^2, the calculated $l - l^*$ are in the 70–200 Å range for both the fraction and the lower molecular weight samples studied. Clearly, this difference is not a small quantity (~10 Å). It reflects a considerable thickening of the initial nucleus when it is assumed to be of the Gibbs type. Since the quantity c is very small relative to the amount of thickening that occurs, it can be essentially ignored. For all practical purposes, therefore, it is not necessary to consider the fluctuations in the average value of l^*,[24] since the basic Gibbs nucleus is stable at T_c.

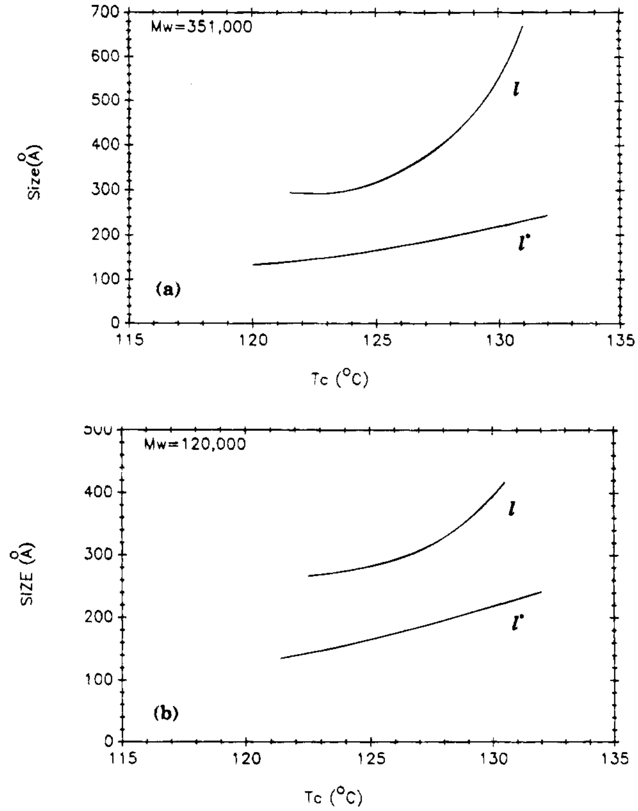

Figure 5. Calculated critical nucleus thickness l^*, according to eq 2, and thickness of the mature crystal l, calculated according to eq 1 with $\sigma_e = 110$ erg/cm^2, $T_m^\circ = 418.5$ K, and $\Delta H_u = 2.8 \times 10^9$ erg/cm^3. The values of l were calculated (a) for experimental T_m's of $M_W = 351\,000$ and (b) for experimental T_m's of $M_W = 120\,000$.

When it is assumed that a three-dimensional type nucleus, adhering to eq 6, is operative, the calculated values of l and l^* are essentially the same in the range of T_c's where the slope of the T_m/T_c plot is approximately 0.5. Figure 6a shows the calculated values of l and l^* for the linear polyethylene with $M_W = 351\,000$. The data are calculated with $\sigma_{ec} = \sigma_{en} = 110$ erg/cm^2. The ratio l/l^* is plotted in Figure 6b. This ratio is effectively

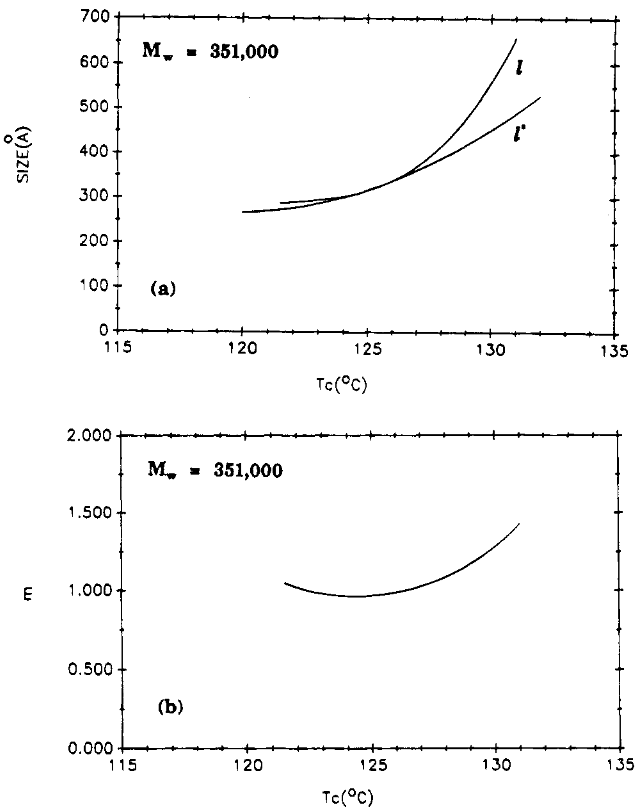

Figure 6. (a) Calculated critical nucleus thickness l^* according to eq 6 and thickness of the mature crystal l for the polyethylene with M_W = 351 000 according to eq 1 with σ_e = 110 erg/cm^2, T_m° = 418.5 K, and $\Delta H_u = 2.8 \times 10^9$ erg/cm^3. (b) Ratio $m = l/l^*$ from the data of (a).

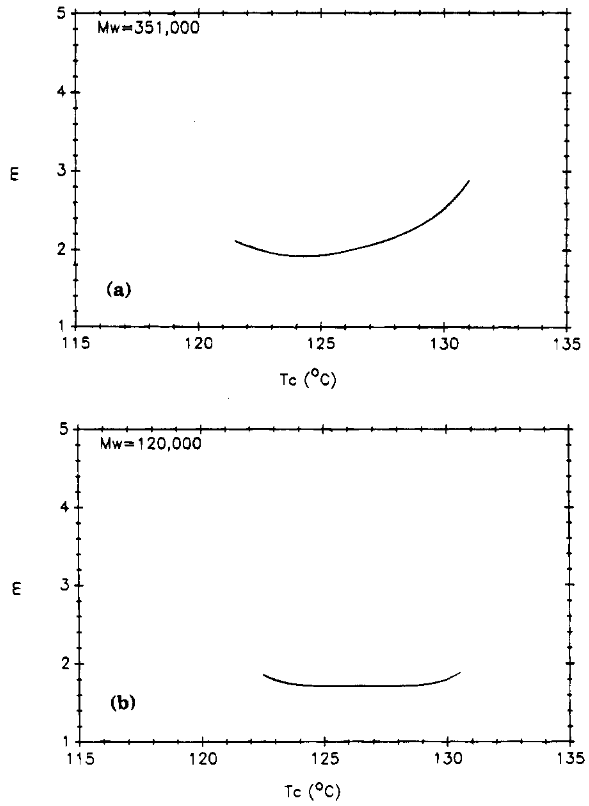

Figure 7. Plot of the ratio $m = l/l^*$: (a) from data of Figure 5a; (b) from data of Figure 5b.

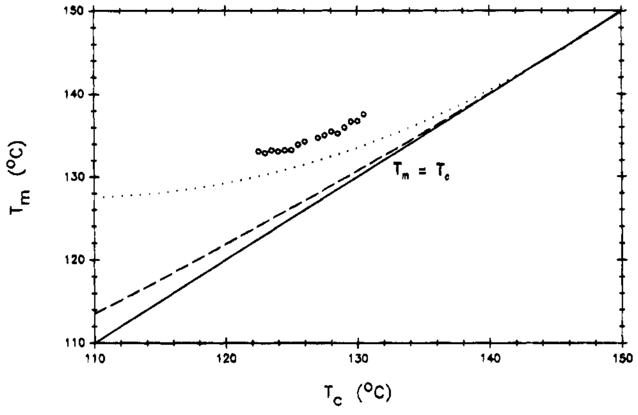

Figure 8. T_m–T_c plot. Open symbols are experimental data for the PE fraction (M_W = 120 000). Solid line, $T_m = T_c$ line. Dashed line, theoretical T_m–T_c curve calculated according to eq 12 for c = 10 Å. Dotted line, same for c = 50 Å. The values σ_e = 110 erg/cm^2, T_m° = 418.5 K, and $\Delta H_u = 2.8 \times 10^9$ erg/cm^3 were used in the calculation.

unity in the T_c region of 120–126 °C. The thickness of the mature crystal that melts is the same as that of the critical nucleus in this region. It increases slightly to 1.5 at the highest T_c studied.

The ratio l/l^* is an important quantity in terms of the theoretical relations given by eqs 5 and 9. This quantity, calculated for a Gibbs type nucleus, is plotted in Figure 7a for the sample having the most probable molecular weight distribution and in Figure 7b for the fraction. Taking different σ_e values does not change this ratio. For the high molecular weight sample in Figure 7a m is essentially constant at about 2 up to T_c of 126 °C. This ratio then increases rapidly to 3 at the higher crystallization temperature. The molecular weight fraction behaves in a qualitatively similar manner. The quantity m is constant, at approximately 1.6, at the lower temperatures and develops upward curvature to m = 1.8 at about 129 °C. The T_c interval in which m is a constant corresponds to where a linear extrapolation can be made to an apparent T_m°. The fact that $m \cong 2$ over a restricted temperature range is a consequence of the type nucleus selected, the parameters characteristic of linear polyethylene, and the low levels of crystallinity that were analyzed. The value of m increases significantly with increasing level of crystallinity. The claim that m is constant with T_c and close to 2 for polyethylene crystallized from the bulk and is independent of the degree of crystallinity cannot be supported.[4,49,50] In fact, the actual value of m depends on the slope of the straight line and the type of nucleation selected.

It is appropriate at this point to analyze in some detail the stability requirement of the two-dimensional Gibbs type nucleus. The calculations illustrated in Figure 5 indicate that the increase in the crystallite thickness that is consistent with the observed melting temperature is very much greater than the quantity $c = kT/\sigma h \simeq 10$ Å that has been adopted to stabilize the nucleus.[24] To further evaluate the assumption made in formulating eq 10, T_m values were calculated according to eq 12 for two different values of c. The results are plotted in Figure 8. Here the dashed line corresponds to c = 10 Å and the dotted line to c = 50 Å. A value of T_m° = 418.5 K was taken for these calculations. Also plotted are the experimental values of T_m for the fraction studied. The experimental data cannot be explained by a small addition to the thickness of the Gibbs nucleus, albeit it has now been rendered stable. Taking σ_e = 110 erg/cm^2, values of c between 65 and 110 Å will be required to interpret the observed T_m for this fraction and between 44 and 70 Å for a $\sigma_e = 73$ erg/cm^2. If this type nucleation is assumed to be operative, substantial growth must take place subsequent to the formation of the critical size nucleus in order to satisfy the observed melting temperatures. The analysis of the data for the most probable molecular weight samples gave very similar results even at very low levels of crystallinity.

Marand and Hoffman[51] analyzed the relation between T_m and the crystallite thickness of the α-phase of poly(pivalolactone) by means of the Gibbs–Thomson equation. From the value of σ_{ec} that was deduced, the thickness of a two-dimensional nucleus was calculated and compared with the measured crystallite thickness. It was found that the thickening ratio also had a value of about 2 and depended on T_c in a similar manner to the plot in Figure 5 (albeit the constant $kT/\sigma h$ is only ~4 Å for this polymer). The only difference was that the undercooling varied from 59 to 79 °C as compared to the much smaller range in linear polyethylene. It was postulated from these results that the equilibrium melting temperature of this polymer cannot be readily determined by the T_m/T_c method. A more recent study with this polymer confirmed this expectation although the point was not emphasized.[33] The results for poly(pivalolactone) and those reported here for linear polyethylene strongly suggest that the nonlinearity in the T_m/T_c plots is a general phenomenon. Consequently, a great deal of caution must be exercised in applying this method. T_m^0 values so determined need to be reexamined. It has already been demonstrated that this method cannot be used to obtain the equilibrium melting temperatures of random copolymers.[19,52]

Conclusions

Experimentally determined T_m/T_c plots of linear polyethylene that encompass a large temperature interval for crystallization have been found for the first time to be nonlinear. These results are contrary to those previously reported and are a consequence of the larger interval in crystallization temperatures that were studied in this work. The higher T_m values found in the high-T_c region are interpreted to result from a large increase in the size of the crystals relative to the initial nucleus size. It has also been calculated, independent of the model assumed, that the ratio between the crystal and the initial nucleus thickness, m, is not constant with crystallization temperature. It in fact increases with decreasing undercooling. This phenomenon, surmised by Weeks,[9] seriously hinders the T_m/T_c extrapolation method to obtain the equilibrium melting temperature of the polymer. The character of the T_m/T_c plots is related to isothermal thickening and is specific for a given polymer. It depends on the undercooling at which crystallization is taking place. Extrapolation to a reasonable T_m^0 can be carried out with the linear polyethylene data obtained at intermediate crystallization temperatures because a theoretical value for T_m^0 has been established. However, this situation does not exist for any other polymers. Therefore, in general, a linear extrapolation is uncertain. A similar nonlinearity in the T_m/T_c plots of poly(pivalolactone),[33] poly(tetramethylene oxide),[32] and some blends[33,34] indicates a similar thickening process at the highest T_c. This phenomenon, therefore, appears to be a general feature of homopolymers.

The quantity m appears to behave in a very similar manner for all homopolymers. It is constant for only a relatively small interval in crystallization temperature. Its value depends on the type of nucleation that is assumed. Values of m close to 2 have been calculated for linear polyethylenes having low degrees of crystallinity when a two-dimensional coherent nucleus is assumed. Values of $m \approx 1$ are calculated if certain types of three-dimensional nuclei are assumed. The conclusion of doubling the thickness of the initial nucleus in order to develop a stable crystallite cannot be made in general.[4]

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