Melting Process and the Equilibrium Melting Temperature of Polychlorotrifluoroethylene

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A new method of estimating the equilibrium melting temperature, T_m, of a polymer is described, and applied to polychlorotrifluoroethylene (PCTFE). Experimentally determined values of the so-called observed melting point, T'_m(obs), are plotted as a function of the isothermal crystallization temperature, T_x. When freed of secondary effects, such as recrystallization, the data fit a straight line of positive slope on a T'_m(obs) versus T_x plot, T_x being the abscissa. This line is then extrapolated to its intersection with the line T'_m(obs) $=T_x$. The temperature at this intersection is T_m. This intersection is at 224 °C for PCTFE, and T_m is quoted as 224 ± 1 °C. (The highest melting point actually attained for a specimen was 218.2 °C.) The value of T_m estimated using the extrapolation procedure is compared with that estimated using the customary method of slow stepwise warming.

A theoretical justification is given for making the type of plot mentioned above. The most important assumption used in the theory is that one of the dimensions of the growing crystal retains a value rather close to that of the appropriate growth nucleus during an isothermal crystallization, the other two dimensions being large in comparison. Combination of this with the fact that the relevant dimension of the growth nucleus will vary as the reciprocal of the degree of supercooling leads to the prediction of melting points that increase linearly with crystallization temperature. The assumption that one of the dimensions of the crystal retains a value fairly close to that of a growth nucleus can readily be justified on the basis of polymer crystal growth with chain folds. Its justification in the case of the customary bundlelike mode of crystallization is less clear. It is demonstrated experimentally that even the largest detectible crystals in PCTFE are only about 70 percent thicker than a primary nucleus, when secondary effects are minimized.

The application of the theory to systems other than PCTFE is discussed briefly, and some preliminary measurements on polyethylene mentioned. Some points relating to the shape of the melting curves of highly crystalline polymers are also brought out.

1. Introduction

The present investigation was begun largely because of our interest in learning more about the factors that influence the melting behavior of polychlorotrifluoroethylene (PCTFE) specimens that were crystallized in bulk. Such factors as the rate of heating used in the melting run, the initial degree of crystallinity, and the temperature of the original crystallization were studied. One basic fact emerged early in the work: the temperature of the original crystallization had an important influence on the experimentally observed melting point. Under appropriate experimental conditions, the observed melting point, T'_m(obs) increased markedly and nearly linearly as the crystallization temperature, T_x, was increased. It naturally occurred to us that such data might be extrapolated in such a way as to permit the equilibrium melting temperature, T_m, to be determined. The concept that T'_m(obs), T_m, and T_x might be simply related to one another was apparently first mentioned by Lauritzen and Hoffman [1][1]. For a simplified model, they showed that T'_m(obs) $=(T_m+T_x)/2$. A somewhat more general derivation is given in the present paper. The melting point data on PCTFE are extrapolated to obtain an estimate of T_m. A number of secondary effects, such as the recrystallization that may occur on slow warming, are discussed.

It is of interest to know the equilibrium melting temperature of a polymer for a number of reasons. Among these is the fact that this quantity is required in the analysis of crystal growth rate data in order to establish the degree of supercooling $\Delta T = T_m - T_x$. The results of our studies on the isothermal growth of spherulitic crystallization in PCTFE at various temperatures will be reported shortly [2].

The equilibrium melting temperature of a polymer may be defined as the melting point of an assembly of crystals, each of which is so large that size (i.e., surface) effects are negligible, with the provision that each such large crystal is in equilibrium with the normal polymer liquid. (Small crystals will tend to melt well below T_m.) A further provision is that the crystals at the melting point have the equilibrium degree of crystal perfection consistent with the minimum of free energy at T_m. The melting phenomena may take place at too high a temperature if the liquid polymer is oriented to an appreciable extent.

The above definition of T_m for a polymer is in principle similar to that for the true melting point of a pure compound of the nonpolymeric type, whether it be a molecular, ionic, or metallic crystal. However, the formation within a reasonable period of time of polymer crystals that are sufficiently large to meet the requirement that surface effects be negligible presents a most difficult practical problem. Polymers as they are ordinarily crystallized tend to melt out well below T_m because the crystals are

[1] Figures in brackets indicate the literature references at the end of this paper.

small, and perhaps somewhat too imperfect. The result is that an attempt to make a direct measurement of T_m for a polymer is not necessarily rewarded by a result that is sufficiently free of crystal size effects.

Before going on to give the theory and the analysis of the data, it is useful to indicate in a preliminary way the point of view that will be taken concerning the combination of circumstances that (a) causes the observed melting point of a linear polymer of high molecular weight to increase with increasing crystallization temperature and (b) renders it improbable that the equilibrium melting temperature can actually be attained in a real polymer specimen in an experiment of reasonable duration.

From nucleation theory we know that a dimension x of either a primary or secondary (growth) nucleus will vary as $1/(\Delta T)$. If the nucleus grows on all its faces, a large crystal that will melt extremely close to the true melting point will form. This is evidently what occurs with ordinary crystals. On the other hand, if some restriction on growth exists for one dimension, so that the resultant crystallite continues to maintain this dimension at a small value close to x while growing to large size in the other two, the crystal will melt out well below T_m. Thus, if one dimension of a polymer crystal persisted at or near the value appropriate to a nucleus during the growth process, it is seen that the observed melting point would be distinctly higher the greater the temperature of crystallization. As noted earlier, PCTFE exhibits such behavior. (Preliminary work reveals that similar behavior occurs for polyethylene.) The first systematic study showing an increase of melting point with an increase of crystallization temperature was that of Wood and Bekkedahl on natural rubber [3,4].

Even if one dimension of a polymer crystal remained at a value x near the primary or secondary nucleus size while growing to large size in the other two dimensions, it is readily seen that a large and high melting crystal would in theory be formed by carrying out the crystallization very near to T_m where ΔT is small. However, crystallization of a polymer specimen within a few degrees of T_m, so that it would be certain to melt within say 1 or 2 °C of T_m, will generally be prevented by kinetic factors. The growth rate of polymer crystals is nucleation rather than diffusion controlled anywhere near to T_m, with the result that the rate of crystallization becomes exponentially slower as the crystallization temperature is raised. Depending on the polymer, the rate of isothermal crystallization generally becomes excessively slow somewhere between 5 and 20 °C below even the nominal melting point. On this basis, one must expect to be frequently confronted with the problem of the depression of the observed melting point well below the true equilibrium melting temperature because of small crystal size. In a slow warming run, certain secondary mechanisms, to be discussed in some detail later, may operate in such a manner as to permit a further increase of crystal size. However, these effects (melting out followed by recrystallization; chain

mobility in the crystal) will tend to be increasingly ineffective the higher the temperature. Hence, it is to be expected that even the slowest of the warming rates useful in practice may not lead to a specimen which actually melts at T_m, even though the dependence of T_m''(obs) on T_x will be more subdued than with more rapid warming.

A slow stepwise warming technique has been advocated by Mandelkern [5,6] as a method of attaining or closely approaching T_m in a real polymer specimen. From an operational standpoint, this method places emphasis on secondary processes such as the recrystallization that occurs with very slow warming as a method of obtaining large crystals and a high melting point in a specimen, rather than on initially crystallizing at the highest practicable temperature to achieve the same end. The question naturally arises as to how close the results obtained with the slow stepwise warming technique, as it is applied in practice, are to both the T_m value obtained by the extrapolation method, and the actual melting points of specimens obtained with initial crystallization at a high temperature. In order to obtain information on these points, a slow stepwise warming run was carried out on PCTFE. Data on polyethylene are also discussed in connection with this problem. Evidence is cited that suggests that the slow stepwise warming technique, as it has been employed in practice, gives melting points that are at least a few degrees below T_m.

The data on PCTFE analysed in this paper lead to the definite conclusion that one dimension of the crystal is small and close to that of a nucleus. (The preliminary data on polytheylene lead to a similar conclusion.) A discussion is given concerning the origin of this phenomenon. One of the models discussed is that of polymer crystal growth with chain folds, and the other is the familiar bundlelike model of polymer crystal growth. It is indicated that the retention of one dimension of the grown crystal near that of a growth or primary nucleus can be defended on theoretical grounds for a folded crystal, but that difficulties arise in the case of the bundlelike system. On this and other grounds, it is concluded that it is highly probable that the melting behavior of PCTFE is to be explained in terms of the model with chain folds.

2. Theory

2.1. Crystals With Chain Folds

The principal objective of this section is to derive an expression relating the observed melting point T_m''(obs) of a polymer with chain folded crystals to the crystallization temperature T_x and the equilibrium melting temperature T_m. The general type of experiment to which the theory applies is the following. A specimen is crystallized isothermally at T_x after being cooled from the melt. The melting point T_m''(obs) relevant to T_x is determined by warming the specimen at a specified rate by a method which locates the temperature at which the last detectible trace of crystallinity disappears. The experiment is then repeated for different T_x values.

The development given mentions the theoretical justification for assuming that one dimension of a folded crystal retains a value close to that of a primary or growth nucleus. Consideration is also given to the secondary mechanisms, such as recrystallization, that may occur in experimental studies and allow some increase in this restricted dimension. The shape of the melting curves is also discussed.

Consider the free energy of formation of a crystal with chain folds of the type shown in figure 1a. Define the dimension l as the step height of the crystal, and denote the other two dimensions a and b. Let σ and σ_e be the lateral and end surface free energy, respectively. Then the free energy of formation of a crystal may be written as

$$\Delta\phi_c = 2ab\sigma_e + 2al\sigma + 2bl\sigma - abl(\Delta f), \qquad (1)$$

where (Δf) is the free energy difference between the supercooled liquid phase and the bulk crystal phase. The latter quantity may be written

$$\Delta f = \frac{(\Delta h_f)(\Delta T)}{T_m} = \frac{(\Delta h_f)(T_m - T_x)}{T_m} \qquad (2)$$

to a sufficient approximation.[2] The quantity (Δh_f) is the heat of fusion in erg cm^{-3}. The quantities a, b, and l are in cm, and the surface free energies are in erg cm^{-2}. Thus $\Delta\phi_c$ is given in ergs for the whole crystal.

By setting $\Delta\phi_c = 0$, one finds

$$T_m'(l) = T_m \left\{ 1 - \frac{2\sigma_e}{(\Delta h_f)l} \right\} \qquad (3)$$

for the melting point of a folded crystal where l is small compared to a and b [1,7]. The equilibrium melting temperature is seen to correspond to a crystal that has very large a, b, and l dimensions.

Even in the case where a and b are only several times larger than l, eq (3) is a fair approximation because σ_e will in general be substantially larger than σ. The ratio σ/σ_e will usually be within a factor of 2 or so of 0.1 [7]. The quantity σ_e will usually lie between 25 to 40 erg cm^{-2} to perhaps 150 to 175 erg cm^{-2}, depending on the work required to make a fold, and the cross-sectional area of the polymer molecule [7]. Thus, the terms $-4\sigma/(\Delta h_f)a$ and $-4\sigma/(\Delta h_f)b$ which appear in the exact form of eq (3) will be less important than the term $-2\sigma_e/(\Delta h_f)l$ even if a and b are only a few times larger than l. In the case $a \gg l$ and $b \gg l$, eq (3) may be regarded as exact.

For completeness, the terms $4a\epsilon + 4b\epsilon$ where ϵ is the edge free energy in erg cm^{-1} could have been included in eq (1), but this would not have affected the result for $T_m'(l)$. The edge free energy reflects the extra work that may be required to cause a fold

² The expression $\Delta f = [(\Delta h_f)(\Delta T)/T_m][T_x/T_m]$, which takes account of the fact that the entropy difference between the supercooled liquid and crystalline phase falls below $(\Delta h_f)/T_m$ when $T_x < T_m$ is somewhat more accurate than eq (2). (See Ref. [9]). However, we need not complicate the analysis at this point by using the more accurate expression for (Δf) if it is understood that the results may require modification if T_x/T_m falls much below about 0.9.
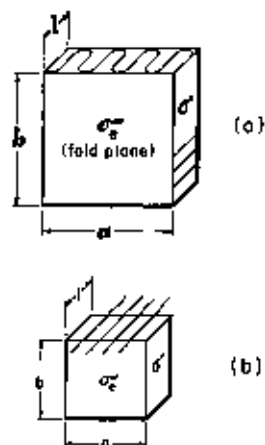

FIGURE 1. *Models of polymer crystals.*

(a) Lamellar crystal with chain folds.
(b) Bundlelike crystal.

to lie on a flat surface in from the fold plane, rather than in the plane of the chain folds or even outside it [1,7].

The assumption $\Delta\phi_c = 0$ is equivalent to the statement that the melting of crystals of finite size occurs when the free energy of the crystal, surface energy included, is the same as that of the supercooled liquid.

We must now pause and ask if it is reasonable to assume that l remains at a small value while the folded crystal grows to large dimensions in the a and b directions.

There is a strong theoretical justification for this restriction of l in the case of polymer crystals grown in the chain folded pattern. This has been discussed in detail in a series of three papers by Lauritzen and Hoffman [1,7], and Lauritzen [8]. Reference [1] deals mainly with the formation of chain folded platelets in dilute solution. Reference [7] deals with the formation of chain folded crystals in bulk, and how aggregates of such crystals can form typical lamellar spherulites. Reference [8] treats the problem of the fluctuation of step height within a given folded crystal as it grows in the a and b direction. The following is a summary of a number of points relevant to the present discussion concerning crystallization with chain folds. The original papers should be consulted for details.

It can be shown that at a given degree of supercooling the step height of the growth nucleus will not fall below $2\sigma_e/(\Delta f)$, because no increase of stability even with extended growth in the a and b directions is achieved thereby. (It is easily seen from eq (1) that $\Delta\phi_c$ always has a positive value when $l = 2\sigma_e/(\Delta f)$ no matter what values are assigned to a and b. Thus a stable crystal with this step height, i.e., one with $\Delta\phi_c$ negative, cannot be formed). If the edge free energy ϵ is included in the calculation, this lower limit becomes $l = (2\sigma_e + \epsilon/b_o)/(\Delta f)$, where b_o is the thickness of the monomolecular growth layer.

The explanation of why the l dimension of the growth nucleus will not increase markedly as the folded crystal grows to large size in the a and b dimensions is based on the fact that the maximum steady-state growth rate in the a and b dimensions refers to a certain value of l. The value of l that leads to the maximum growth rate is [1,7]

$$l_g^* = \frac{(2\sigma_e + \epsilon/b_0)}{(\Delta f)} + \frac{kT}{b_0\sigma}. \tag{4a}$$

The quantity $kT/b_0\sigma$ will generally run from 10 to 30A. If l for a given crystal becomes temporarily larger than l_g^*, the activation barrier becomes high, thus reducing the rate of crystal growth in the a and b directions. For a relatively large value of ϵ, eq (4) will be

$$l_g^* = \frac{4\sigma_e}{(\Delta f)} = l_p^*, \tag{4b}$$

where l_p^* is the step height of a primary (homogeneous) nucleus. Crystals with values of l in excess of those given by eqs (4a) and (4b) will occasionally occur, but these will not grow as rapidly in the a and b directions as those with a step height l_g^*. Once a chain folded crystal is formed, it will not tend to grow rapidly in the l direction because of the folds.[a] Through fluctuations, a step height that is too large will gradually tend toward l_g^* as growth in the a and b directions takes place [8]. The tendency of the step height of a folded crystal to maintain itself close to that of the growth nucleus is also predicted by the theoretical studies of Frank and Tosi [10] and Price [11].

At a supercooling of 20° C, eqs (4) predict values of l_g^* in the neighborhood of roughly 50 to 500 A [7]. There is no restriction to such a small value implicit in the model for growth in the a and b directions. Thus, there is a theoretical justification for the assumptions a>>l and b>>l used in the derivation of eq (3) for a polymer crystal formed on the chain folded pattern.

The considerations outlined above provide a reasonable theoretical justification for the assumption that the mean value of the step height l of a folded crystal will maintain itself at a value close to that of a primary or growth nucleus, while the other two dimensions become much larger. The various factors that can lead to a preponderance of crystals with chain folds over bundle-like crystals during crystallization from the supercooled bulk phase are discussed in some detail in reference [7].

From an experimental standpoint, there is ample reason to consider polymer crystals with chain folds for material crystallized from dilute solution. Keller [12] has clearly demonstrated that the platelets formed under these conditions are chain folded when removed from the solution and dried, and that the step height increases with decreasing supercooling as required by eqs (4a) and (4b). The question of

whether chain folded crystals exist in polymer crystallized from the supercooled bulk phase has proved to be more difficult to answer. Recently however, Geil has demonstrated that chain folds must exist in polypropylene crystallized from the melt [13]. This work provides strong experimental confirmation of the view that the lamellae in spherulites consist of chain folded crystals (cf. ref. [7]). Any chain folded structures formed in bulk will doubtless possess some chains protruding from the plane of the chain folds, and chains of a similar character forming interlamellar links.

We return now to the question of the application of eq (3) to melting point data. The melting point T_m' (obs) is defined operationally as the temperature where the last detectible trace of crystallization disappears. For crystals at the melting point defined in this way, the value of l that is relevant in eq (3) is not the average value of l, but rather a somewhat larger value that represents the thicker and therefore the higher melting crystals in the system. In this situation, it is convenient to assume that

$$l = \beta l_p^* = \beta \left\{ \frac{4\sigma_e T_m}{(\Delta h_f)(T_m - T_x)} \right\}, \tag{5}$$

where l_p^* is given by (4b) and β is a constant. This states simply that the mean step height of the crystals that melt out last, i.e., those corresponding to T_m' (obs), is β times as large as the mean step height of a primary nucleus, or the mean step height of a growing crystal with fairly large ϵ.

Some discussion of the expected values of β and the implications of this approximation is necessary.

The theory of chain folded nucleation and growth suggests a rather narrow number distribution of step heights n(l) of the general type shown in figure 2 by the dashed line. The particular distribution illustrated was calculated on the assumption that the grown lamellae have the same step height distribution as that of the primary (homogeneous) nuclei
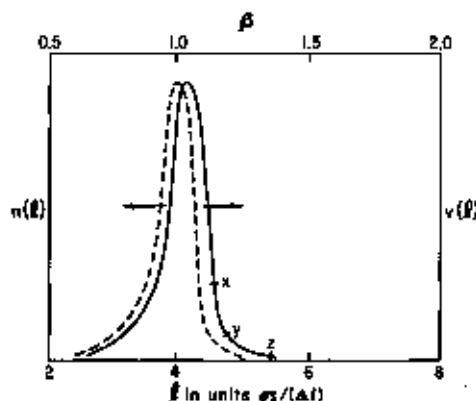

FIGURE 2. *Distribution of lamellar thickness for crystals with chain folds (schematic).*

- - - - denotes number distribution n(l).
———— denotes volume distribution v(l).

x, y, and z indicate increasing β with increasing detector sensitivity.

[a] In some cases, diffusion mechanisms involving chain mobility in the crystal may allow a gradual increase of l in a grown crystal with the passage of time. This effect is discussed later in the paper.

[1, 7]. This corresponds to the case where the growth nucleus has a large ϵ. The assumption that the step height distribution of the grown lamellae is the same as that of the primary nuclei is crude. However, a detailed calculation [8] of the distribution of step heights formed in the growth process within a given lamella, and the deviation of the average height of each lamella compared with the rest, gives a distribution which for the present purpose has similar properties. Hence our general conclusions concerning β will not rest on the assumption of homogeneous initiation.

It is seen in figure 2 that there is a rather sharp maximum in $n(l)$ at $l_x^* = 4\sigma_e/(\Delta f)$. However, some crystals are thinner than l_x^*, and a significant number are thicker. It is the melting of these thicker crystals that will be observed near the melting point as it has been defined. However, for the purpose of analysing melting points obtained from specific volume-temperature $(\overline{V} - T)$ curves, we must really ask what the volume of such crystals is, rather than the number. We may in general expect the thicker crystals to have a larger volume, thus shifting the righthand side of the volume distribution function $v(l)$ slightly to the right in the plot shown in figure 2 (see solid curve). Thus, for the case where the mean step height of the growing crystal is $l_x^* = 4\sigma_e/(\Delta f)$, we must expect β to be somewhat in excess of unity. Further, the sensitivity of the detector will have an influence on the observed value of β. This is shown in figure 2 at points x, y, and z, which correspond to slightly different β values. Thus, in the case of large ϵ, we may expect β to be near or slightly greater than unity. In the case where ϵ is negligible, β may be expected to be somewhat below unity.

Insertion of (5) into (3) gives

$$T_m'(\text{obs}) = T_m(1 - 1/2\beta) + \frac{T_x}{2\beta}. \qquad (6)$$

This equation describes a family of straight lines on a plot of $T_m'(\text{obs})$ *versus* T_x. *The equilibrium melting temperature is the intersection of one of these lines with the line* $T_m'(\text{obs}) = T_x$. A schematic plot of $T_m'(\text{obs})$ against T_x for some β values is shown in figure 3.

The expression $T_m'(\text{obs}) = (T_m + T_x)/2$ given earlier [1] corresponds to the case $\beta = 1$.

The depression of the observed melting point below the equilibrium melting temperature predicted by eq (6) for even the higher range of β is quite large. Equation (6) was derived on the basis that no secondary processes enter and cause l to increase as the polymer is stored, or while it is being warmed during the melting run. Such processes can be imagined, and their effect is discussed below.

Melting out of Thin Crystals followed by Recrystallization

According to eq (3) a given chain folded lamella, or portion of a lamella, will melt out as the polymer is heated. The thinner lamellae, or sections thereof, will melt out first. The (possibly somewhat oriented) supercooled liquid produced by a melting crystal at $T_m'(l)$ during the warming process will tend to recrystallize at $T_x'(l)$, forming a crystal with the larger value of l characteristic of this higher crystallization temperature. This new and thicker lamella will have a higher $T_m'(l)$ value than the one originally melted out. The recrystallization will tend to be slower the higher the temperature because it involves a nucleation mechanism.[a] As a consequence, for a specified warming rate, the $T_m'(\text{obs})$ values obtained for high T_x values are apt to be more nearly correct than those obtained for low T_x values. Thus a β value obtained under conditions where recrystallization occurs during the warming process will tend to be too large. Also, the value of T_m obtained by extrapolation of melting data involving recrystallization is apt to be somewhat low. These two features are illustrated schematically in figure 3 in conjunction with the case $\beta = 1$ (see dotted line).

The effect of recrystallization after melting out can be lessened by increasing the rate of warming during the melting run.

Possibility of Isothermal Increase of l Resulting from Chain Mobility in a Folded Crystal

In the derivation of eq (6), it was assumed that the step height l remained at a certain value, originally determined by the crystallization temperature, until it was melted out. This assumption implies that the polymer chains comprising the folded crystal have insufficient mobility to permit the rather complex rearrangements that would be required to permit the step height of a folded crystal to increase while still in the crystalline state. This assumption is probably correct in at least some

[a] Detailed investigations of the recrystallization process carried out by Kovacs and coworkers verify this statement (private communication from Dr. A. J. Kovacs, Strasbourg).
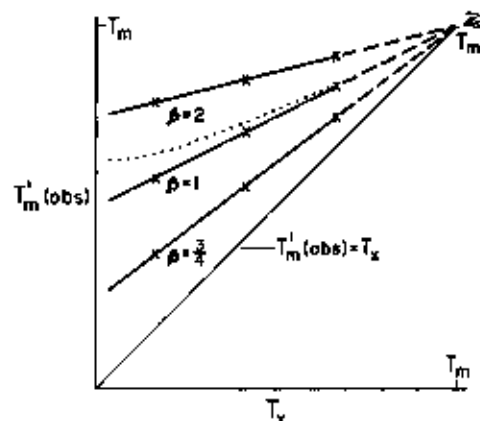

FIGURE 3. *Theoretical $T_m'(\text{obs})$ versus T_x plot.*

x—x—x denotes $T_m'(\text{obs})$ versus T_x for various β values in experimentally accessible range (no secondary effects assumed).

.... illustrates type of effect caused by recrystallization or chain mobility effects for $\beta = 1$ line.

cases, but in others the mobility of the chains might permit an isothermal increase of the step height on prolonged storage. The driving force for the increase of the step height will always exist below $T_m'(l)$ for a lamellar crystal as it is formed in the kinetic crystal growth process. (It should be recalled that a folded crystal possesses a small and temperature-dependent mean step height l_x^* because a crystal of this step height has the maximum rate of growth in the **a** and **b** directions, and *not* because a crystal with this step height is the most stable at the crystallization temperature from a thermodynamic viewpoint [1,7]). In view of the fact that a thin chain folded lamellar crystal could increase its stability (and hence, its melting point) by becoming thicker, through complex chain rearrangements fostered by chain mobility in a crystal, it seems useful to indicate how this would affect the present analysis. Reneker has suggested some interesting mechanisms involving defects such as point dislocations that could lead to a slow increase of l for folded crystals [14].

If gradual thickening due to mobility of segments in a folded crystal occurred, the melting points corresponding to various T_x values would all be raised somewhat, the effect on $T_m'(l)$ being least at the higher crystallization temperatures because of the greater thickness of the lamellae. In this sense, the effect of mobility would resemble the effect of recrystallization (increased β, low extrapolated T_m value). There is, however, one important difference between the two effects: thickening of a lamella due to chain mobility in the crystal (if it occurs at all) could take place anywhere in the interval T_x to $T_m'(l)$, whereas thickening of a lamella due to melting out followed by recrystallization could occur only after a lamella had been heated to $T_m'(l)$. Thus, if the observed melting point (at a given warming rate) depends markedly on the residence time at T_x, isothermal thickening of the lamellae due to chain mobility should be suspected. If the observed melting points are insensitive to the residence time at T_x, but are dependent on the melting rate, then the existence of simple melting out followed by recrystallization is indicated. (This does not preclude some increase of step height due to chain mobility effects at low T_x values at residence times shorter than those that are experimentally practicable.)

From this standpoint, the most reliable melting point data for the determination of T_m and β for a polymer where either or both effects occur to a measurable extent would be obtained on specimens where the initial crystallinity was low (short residence time at T_x), where fairly rapid melting rates were used, and where the greatest reliance is placed on $T_m'(obs)$ data obtained for high T_x values.

The effect of orientation of the polymer liquid will be to increase the $T_m'(obs)$ values. Such an effect may occur in samples where orientation is initially present due to severe stress applied to the melt phase, but this can generally be circumvented. Also, the crystallization process itself may locally orient the supercooled liquid phase of the polymer somewhat. Where a fast melting run is found to be necessary to minimize recrystallization and lamellar thickening resulting from chain mobility, some residual effect of orientation may appear, but this should be minimized by making measurements on specimens of low initial crystallinity.

In its simplest interpretation, the process we have termed "melting out" refers to the conversion of a crystal of a specified step height at a certain temperature given by equation (3) to a thermodynamic state of identical free energy and a molecular state similar to that of the normal supercooled liquid at the same temperature. While the chain molecules in the normal supercooled liquid may well be somewhat alined locally, this interpretation certainly implies a considerable disorientation of the chains during the "melting out" process. (This does not necessarily imply, however, that any ensuing recrystallization process will lead to a crystal with a different crystallographic orientation than the one originally melted out. For example, the presence of undestroyed nuclei in the form of unmelted lamellae, or portions of a lamella, could easily lead to the same orientation for the newly-formed crystal.) A more complex process than this might actually occur when at a certain temperature the free energy of a lamella, or portion thereof, becomes equal to that of the normal supercooled liquid. For example, a very thin (and nearly unstable) crystal might, when heated slightly find the route to a larger step height more rapid through the chain mobility mechanism than through the melting out with disorientation→recrystallization mechanism. In this case, the distinction we have drawn between the melting out→recrystallization, and the increase of step height through chain mobility, mechanisms would become rather artificial. Nevertheless, for a crystallization conducted fairly close to T_m, where the step height is large, one must expect the disappearance of the crystals on warming to correspond to the formation of liquid-like polymer in a state of disorientation at least fairly similar in nature to the normal supercooled liquid.

Despite the possibilities for an increase of step height after the formation of a folded crystal, it is commonly to be expected that a system of chain folded crystals will exhibit a marked dependence of melting point on the original crystallization temperature. In the limiting case where secondary effects resulting from recrystallization and chain mobility are minimized by appropriate experimental techniques, values of β ranging from somewhat below to somewhat above unity should be found, and a reliable value of T_m determined by the extrapolation method. When these secondary effects enter, β will be larger than normal, and the extrapolated T_m value will be somewhat low.

Shape of the Melting Curves

The theory indicates that the sharpness of the melting process near T_m will increase as the crystallization temperature is increased. This is a natural

consequence of the fact that T_m'(obs) approaches T_m less rapidly than does T_x. This is illustrated schematically in figure 4 for the case $\beta=1$ on the assumption that no recrystallization or chain mobility effects occur during the melting run. The actual shape of the melting curve was drawn in such a manner as to conform to the type of distribution function for $v(l)$ shown schematically in figure 2. The small wing on the right-hand side of the $v(l)$ distribution may in some cases manifest itself as a small "tail" on the melting curve near the liquidus line as shown in the inset in figure 4.

It can be shown to a first approximation that the breadth of the melting process, say as measured by the function $dT/d\overline{V}$ somewhat below T_m'(obs), will vary approximately as ΔT. Recrystallization and chain mobility effects will in general tend to sharpen the melting curves.

The foregoing discussion indicates from a theoretical standpoint that one way to achieve a very sharp melting point for a polymer of very high molecular weight, i.e., one that reproduces the typical sharp first-order phase transition characteristic of the melting of pure non-chain molecular crystals,[5] would be to crystallize the polymer at very low supercooling. However, the rapidly decreasing rate of crystallization as T_m is approached (which culminates in a rate that is zero at T_m), together with the tendency of the step height to maintain itself, must be expected to defeat the actual attainment of either the equilibrium melting temperature or the very sharp equilibrium melting curve. The melting of each individual crystal of step height l at $T_m'(l)$ is properly regarded as a sharp first-order phase transition. The melting curve of a real polymer with a distribution of l is represented here as the sum of a vast number of such events, and may be designated as a "diffuse" or "unsharp" first-order transition (cf. remarks of Mandelkern on the melting of linear homopolymers [15]).

2.2. Bundlelike Crystals

The model is illustrated schematically in figure 1b. The length is denoted l, and the other two dimensions a and b. The end surface free energy is called σ_e, and the lateral surface free energy is called σ. (Note that bold face symbols are used for chain folded crystals, and ordinary face type for bundlelike crystals).

The free energy of formation of a bundlelike crystal may be set down in a manner analogous to eq (1). Using steps similar to those noted in section 2.1, one obtains

$$T_m'(l)=T_m\left\{1-\frac{2\sigma_e}{(\Delta h_f)l}\right\} \qquad (7)$$

as the melting point of a bundlelike crystal that has large a and b dimensions and a small l dimension. The same result is obtained if the crystal is assumed to be a cylinder of revolution about the l direction.
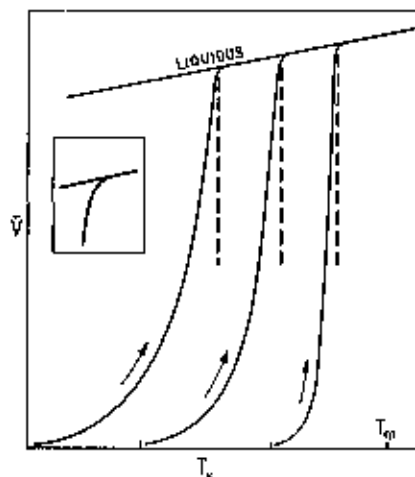
FIGURE 4. *Theoretical melting curves (schematic).*

The curves are based on the type of distribution shown in figure 2. Increasing T_x sharpens melting process. Inset shows "tail" that may appear near liquidus line.

The length of a homogeneous nucleus for such a crystal is

$$l_p^*=\frac{4\sigma_e}{(\Delta f)}. \qquad (8)$$

The length of a coherent lateral growth nucleus is $l_g^*=2\sigma_e/(\Delta f)$. These results are in general similar to those obtained for the corresponding folded crystal. Both l_p^* and l_g^* vary with temperature as $1/\Delta T$.

One could proceed from eqs (7) and (8) to derive an expression for a bundlelike crystal formally equivalent to eq (6) *only* in the case where it is reasonable to define β by the relation $l=\beta l_p^*$. Recalling that we are interested in explaining cases where T_m'(obs) is clearly well below T_m when T_x is in the practicable crystallization range, it follows that l must retain a value reasonably close to that of either the primary or growth nucleus length, i.e., β must be reasonably close to unity. (Values of β between 1 and 2 are found in the present study.) To the best of our knowledge, the assumption that the l dimension of a bundlelike crystal will retain a value fairly close to l_p^* or l_g^* as the crystal grows to large size in the a and b directions has never been justified on theoretical grounds. If the assumption $l=\beta l_p^*$ cannot be justified for the bundlelike mode of growth, then it would follow that the melting behavior of a polymer that conformed to an expression of the form of eq (6), with β in the stipulated range, would most appropriately be interpreted in terms of the chain fold model, where such a β value can readily be justified.

We have considered several conceptions of how the growth of a bundlelike crystal might be much slower in the l direction than in the a and b directions. The result is that it appears to be difficult to defend the assumption $l=\beta l_g^*$ with β anywhere near unity for a bundlelike crystal. The following describes the approaches used:

(1) A calculation of the growth rate in the l direction, and in the a and b directions, was made using classical nucleation theory. The effect of entanglements was ignored, and it was assumed that no cumulative strain existed at the bundle ends. This model implies a more rapid growth rate in the l direction [7], since the end surface free energy of a polymer crystal is generally agreed to be much larger than the lateral surface free energy. This model evidently does not correspond to the crystal habit exhibited by most real polymers, which generally grow most rapidly in the two directions tranverse to the chain axes, rather than in the chain axis direction.

(2) The assumption that the cumulative strain that may occur in the diffuse end surface of a bundlelike crystal might abort growth in the l direction was examined [7]. In the bundlelike system, polymer chain molecules actually pass through the end surfaces, and connect the crystalline and supercooled liquid phases together. Since there is a density difference between the two phases, cumulative strain may exist in the end of the bundle. This model raises a serious question concerning whether a *large* bundlelike crystal can be formed at all, and definitely rules out of existence a strictly bundlelike crystal with a flat end surface where the chains are perpendicular to this surface. The concept of cumulative strain does not imply that the restriction on growth in the l direction would be such as to allow l to be even approximately proportional to l_l^* or l_2^*. Crystals aborted by cumulative strain would in general tend to melt quite close to the crystallization temperature. Rather than giving a clue as to the melting behavior of bundlelike crystals, this model suggests one important reason why crystals with chain folds form instead. Crystals with chain folds effectively evade strain resulting from the density difference of the supercooled liquid and crystal phases, since relatively few chains pass through the end (folded) surfaces.

(3) The concept that chain entanglements cause a bundlelike crystal to cease growth in the l direction once it has reached the nucleus length was examined. This special assumption does not appear to be readily justifiable. The same type of entanglements that one must assume are continually resolved as the critical-sized nucleus is being built up would have to suddenly become exceedingly effective just as the length l_2^* was attained. Recalling that l_2^* is strongly dependent on temperature, such a mechanism for the persistence of the one dimension of a bundlelike crystal near l_2^* seems improbable.

On the basis of the above, it is regarded as unlikely that the interpretation of the melting behavior of a polymer conforming with eq (6) with β values in the general vicinity of unity is to be based on a bundlelike model. To derive the analogue of eq (6) for the bundlelike model, the arbitrary assumption $l = \beta l_2^*$ with $\beta \sim 1$ has to be introduced, and this apparently has no clear justification.

As noted previously, the typical lamellar structures so often seen in polymers crystallized from the unoriented melt are most readily explained in terms of growth of a substantially chain folded character

[7, 13]. Thus, in cases where it is known that the melting process refers to the disappearance of typical lamellar spherulitic structures on warming, the chain fold model discussed in 2.1 is clearly more appropriate than the analogous treatment with the bundlelike model.

3. Experimental

3.1. Materials

The specimens of PCTFE, $-(CF_2CFCl)_n-$, that were used in this work were laboratory samples of Kel-F grade 300 polymer that were kindly supplied to us by the Minnesota Mining and Manufacturing Company. The number average molecular weight was stated to be about 415,000. The polymer was supplied in the form of molded sheets about 2 mm thick. When crystallized as described below the polymer is highly spherulitic.

3.2. Melting Runs With High $\chi_{initial}$ and Moderately Slow Melting

The objective of this part of the study was to determine, with moderately slow warming, the melting point of PCTFE specimens that had been isothermally crystallized to a high degree of crystallinity, χ.

A sample weighing from 1 to 3 g was first heated in an air bath far above any possible value of T_m to a temperature denoted T_l in order to establish a reproducible thermal history. (T_l was usually 305 °C.) Then it was quickly suspended in a silicone oil bath which was operating at the crystallization temperature, T_x, and an isothermal crystallization carried out to the desired degree of crystallinity. The temperature of the sample in the bath was known to better than 0.1 °C.

Melting data were obtained on such specimens by warming them in the silicone oil bath, and plotting the specific volume—temperature ($\overline{V}$–T) curves. The specific volume data were precise to within 0.0002 cm^{3}g^{-1}. This was sufficient to detect a melting point T_m''(obs) corresponding to the disappearance of all but the last four tenths of a percent of crystallinity. Details concerning the apparatus used have been given elsewhere [16]. The T_m''(obs) values cited are accurate to within about 0.2 °C.

In carrying out the melting run, the sample was first warmed rapidly from T_x to about 205 °C in an attempt to minimize recrystallization. The melting point T_m''(obs) was then determined with moderately slow warming above 205 °C. Counting from the time 205 °C was reached, most of the melting runs were carried out within 4 to 6 hours, but a few were carried out over a period of many days in order to check the effect of the rate of heating. In all these runs, most of the time above 205 °C was spent in carefully approaching the melting point. The degree of crystallinity at the beginning of each warming run, $\chi_{initial}$, was calculated from the specific volume using the crystallinity scale established by Hoffman and Weeks [16].

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T_x values from about 170 to 200 °C were practicable with the above procedure. It is difficult to carry out an isothermal crystallization much below 170 °C on a sample of convenient size because of self-heating attending the rapid crystallization. Above about 200 °C, the rate of crystallization becomes intolerably slow.

In a few cases, the melting points were determined by mounting the crystallized specimens on a hot stage on a polarizing microscope, and observing the temperature at which birefringence disappeared.

For most of the runs, the samples were cooled to room temperature after crystallizing at T_x, and then rewarmed and the melting curve obtained. It was demonstrated that this did not alter $T_m''(\text{obs})$, as it relates to T_x, by carrying out similar runs without first cooling to room temperature. The hierarchy of small crystals introduced below T_x on cooling to room temperature simply melt out first when the sample is rewarmed.

The initiation of the crystals in the samples is principally by heterogeneous nucleation. The bulk crystallization isotherms follow the Avrami relation, $\chi = 1 - \exp[-Zt^n]$, where t is time, with $n=2$ to $n=3$, for the first 30 to 50 percent of the crystallization. The crystallization becomes much less rapid as the temperature is increased. Thus the rate constant Z has the strongly negative temperature coefficient characteristic of a nucleation controlled growth mechanism. The $n=3$ exponent results from three-dimensional growth, mainly spherulites in the body of the specimen born at or near $t=0$. In thin samples with a large amount of surface, an $n=1$ component due to surface nucleation causes the overall bulk isotherm to tend toward $n=2$. Above $\chi=0.4$ to 0.5, the crystallization rather abruptly slows down with the consequence that long periods of time are required to attain high χ values.

3.3. Melting Runs With High χ_{initial} and Fast Melting

After conducting the investigation described above and analysing the data, it became apparent that recrystallization and other secondary effects had almost certainly increased some of the melting points somewhat.

In order to reduce recrystallization and other secondary effects during the melting process as much as possible, and thereby obtain $T_m''(\text{obs})$ values that reflected the T_x values more precisely, a rapid melting procedure was adopted.

Specimens were heated to T_1 and then crystallized at T_x as described in section 3.2. Then they were placed (without first cooling to room temperature) in a silicone oil bath operating quite close to the anticipated melting point, i.e., 1 or 2 °C below the $T_m''(\text{obs})$ value obtained with a moderate warming rate. It was then determined, usually by the volume-temperature ($\bar{V}-T$) technique, whether or not the sample had melted out when it came to the temperature of the bath. By successive experiments with baths at closely spaced temperatures, $T_m''(\text{obs})$

could be rather closely bracketted. This procedure is equivalent to a melting run of about 20 minutes duration, most of this interval being spent very close to $T_m''(\text{obs})$.

3.4. Melting Runs With Low χ_{initial} and Fast Melting

These runs were carried out primarily with the aim of determining the effect of storage time on the melting points for a given rate of melting.

The runs were carried out in the same manner as those described in section 3.3, except that the specimens were not allowed to crystallize as long prior to being melted out.

As noted in section 3.2, the runs with high χ_{initial} values ($\chi=0.40$ to 0.65) and moderate melting rates were carried out on specimens about 2 mm thick and weighing about 3 g. In these experiments, and in the high χ_{initial} runs with rapid melting, the $\bar{V}-T$ method detects the disappearance of all but the last 0.4 percent of crystals. However, in this low χ_{initial} runs ($\chi=0.05$ to 0.11) the sensitivity was less, partly because somewhat smaller samples were used, but mostly because of the lower crystallinity. The sensitivity in these runs was such that the observed melting point corresponded to 3 percent crystallinity in the specimen. After some investigation of the slopes of the $\bar{V}-T$ curves in the melting range, it was found that adding 0.6 °C to each observed melting point gave a $T_m''(\text{obs})$ value that corresponded to the disappearance of all but the last 0.4 percent of the crystals. This correction is actually somewhat smaller the higher T_x, but adding the constant value 0.6 °C gives results accurate to about ± 0.2 °C in the experimental range, which is sufficient for the intended purpose.

3.5. Melting Point by the Slow Stepwise Warming Method

A specimen of PCTFE was initially crystallized at 180 °C. (The melting run was carried out with the specimen suspended in silicone oil so that the specific volume could be measured.) It was then warmed to a higher temperature and allowed to stand until the specific volume appeared to settle down to a "rest" value. Then the temperature was raised again, and the process repeated. The total duration of the melting part of the run was 35 days. The average rate of warming was 5 °C per day up to 205 °C, 1 °C per day up to 210 °C, and 0.5 °C per day up to the melting point.

3.6. The Melting Point of Specimens Crystallized at High Temperatures Using Seeds

The objective of this part of the work was to obtain the highest actual melting temperature for a specimen of PCTFE using the general concept that a high isothermal crystallization temperature will lead to a high melting point.

As indicated in section 3.2 the rate of crystallization becomes so slow around $T_x = 200$ °C in the normal runs that it is not convenient to carry out isothermal crystallizations at higher temperatures. Therefore seeds from a previous crystallization were used to accelerate the crystallization process.

The seed crystal run was carried out in the following manner. First, the specimen was heated to 305 °C and then crystallized isothermally at 180 °C to a degree of crystallinity of over 0.5. Then it was warmed to a T_1 value of 215.6 °C. This melted out the vast majority of the crystals present, and gave a specific volume that was indistinguishable from the liquidus. However, numerous seed crystals were present. (The presence of seed crystals was indicated by the fact that the subsequent crystallization at a specified value of T_x was considerably more rapid than the crystallization would have been at the same T_x in a normal run.) The sample was then transferred from the T_1 bath to another bath operating at T_x, and the crystallization carried to a fairly high χ value. Then the melting point was determined from a $\overline{V} - T$ curve with a moderate warming rate as described in section 3.2.

4. Results

Three typical melting curves for PCTFE of the type that were used to obtain the $T_m'(obs)$ versus T_x data are shown in figure 5. The particular ones
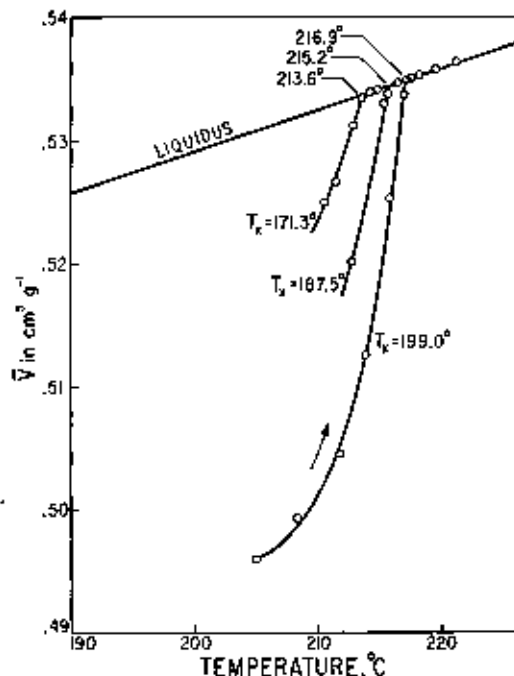

FIGURE 5. *Melting curves of PCTFE obtained for runs with high $\chi_{initial}$ and moderate melting rate.*

Note increase of $T_m'(obs)$ and increase of sharpness of melting process with rising T_x.

shown refer to the high $\chi_{initial}$ runs with moderate melting rate. The melting point relevant to each T_x value is seen to be clearly defined within narrow limits, and the definite character of the increase of $T_m'(obs)$ with increasing T_x is also clearly evident. The other types of runs yield melting curves (not shown) that also lead to clearly discernible melting points.

The $T_m'(obs)$ versus T_x data for each of the three types of runs mentioned in sections 3.2, 3.3, and 3.4 are given in table 1, together with certain other information. The data are plotted in figure 6.

TABLE 1. $T_m'(obs)$ versus T_x data for PCTFE [a]

Initial melt temperature, T_1	Isothermal crystallization temperature, T_x	χ at T_x after crystallization, $\chi_{initial}$	Approximate time required to attain $\chi_{initial}$	Observed melting point, $T_m'(obs)$	Remarks
°C	°C			°C	
305	169.6-170.2	~0.40	~5 min	213.3	T_x measured with thermocouple in sample.
305	171.3	.49	20 min	213.5	T_x certain to about 0.5 °C.
305	172.5-173.0	~.40	5½ min	213.9	T_x measured with thermocouple in sample.
305	179.8	.49	20 min	213.8	----------------
305	190.2	.52	1 hr	214.1	----------------
305	187.5	.49	85 min (est)	215.2	----------------
305	190.1	.53	10 d	215.2	----------------
305	190.2	.49	93 min	215.4	----------------
305	195.8	.55	16 hr	216.4	----------------
305	196.0	.65	2 d	216.0	----------------
325	198.0	.65	34 d	216.9 / 217.2	{Melting point from $\overline{V}-T$ data. / Melting point determined optically.
305	199.6	.53	4 d	216.9	----------------

B. Runs with high $\chi_{initial}$ and fast melting [b]

305	172.6-173.0	~0.40	5½ min	211.2	Melting point obtained visually.
305	180.1	.48	20 min	212.8	----------------
305	185.0	.50	45 min	213.4	----------------
305	190.1	.48	90 min	214.6	----------------
305	196.7	.54	15 hr	216.5	----------------
305	199.5	.50	3 d	217.3	----------------

C. Runs with low $\chi_{initial}$ and fast melting [c]

305	185.9	0.07 (est.)	8 min	212.9	----------------
305	199.8	.05 (est.)	17 min	213.6	----------------
305	192.0	.09	51 min	215.0	----------------
305	193.6	.09	101 min	215.0	----------------
305	196.1	.11	5.2 hr	215.8	----------------
305	199.3	.09	15.6 hr	216.8	----------------
305	201.6	.09	66 h	217.3	----------------

[a] Unless noted otherwise, the $T_m'(obs)$ data were obtained from $\overline{V}-T$ curves.
[b] In these tables the directly observed $T_m'(obs)$ data are given, and refer to the disappearance of all but the last 0.4 percent of crystals.
[c] The $T_m'(obs)$ data given in this table have all been increased by 0.6 °C above the value actually observed in order to correspond to the disappearance of all but the last 0.4 percent of crystals. The values actually observed referred to the disappearance of all but the final 3 percent of crystallinity.

Table 2 gives the results of the runs mentioned in sections 3.5 and 3.6 where, with previous seeding, crystallization at the highest practicable temperature was used to attain high melting points for PCTFE. Also shown in the same table is the result for the slow stepwise warming run on PCTFE,
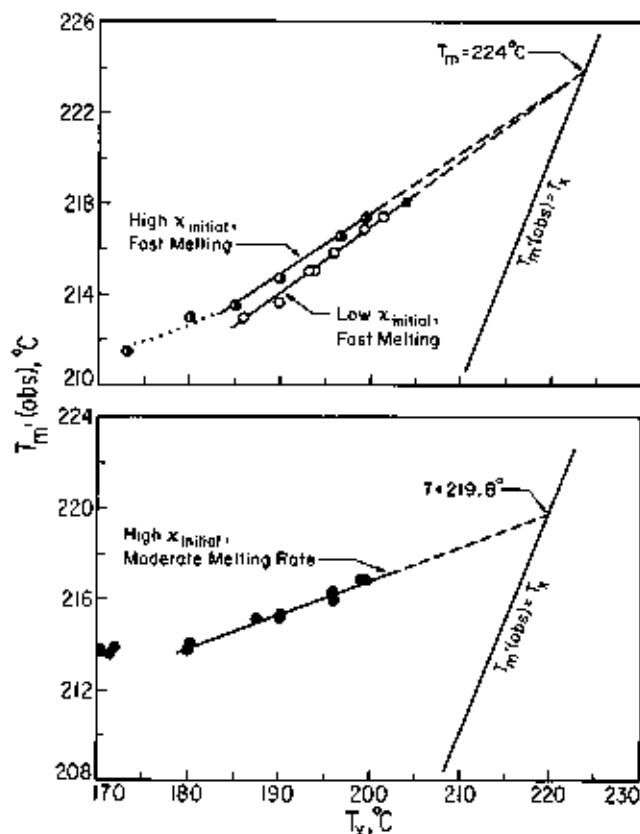
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FIGURE 6. $T'_m(obs)$ versus T_x plots obtained for PCTFE.
——————— shows best straight line that fits data in experimentally accessible region, ——————— shows extrapolation to line $T'_m(obs) = T_x$.

The upper diagram shows data where recrystallization effects are minimized except where noted by dotted line. The lower diagram shows data that are strongly affected by recrystallization, except at the highest T_x values.

Point ■ is seed crystal run from table 2.

TABLE 2. Additional melting point data on PCTFE

A. Melting point obtained using seed crystals to attain fast crystallization at high T_x

Seeding temperature [a]	Isothermal crystallization temperature, T_x	χ at T_x after crystallization, $\chi_{initial}$	Time at T_x required to attain $\chi_{initial}$	Observed melting point, $T'_m(obs)$	Remarks
°C	°C			°C	
				218.0	Melting point from $\bar{V}-T$ data, moderate melting rate.
215.8	203.9	0.36	7 d		
				218.2	Optical melting point, moderate melting rate.

B. Melting point by slow stepwise warming method

Original crystallization temperature	Melting point ($\bar{V}-T$ method)	Time required for run	Remarks
°C	°C		
190	216.4	25 d	Slight discoloration observed toward end of run; specimen sorbed small amount of silicone oil.

[a] Thermal history prior to seeding: Sample heated to 305 °C, crystallized to high χ at 190 °C, and then warmed to seeding temperature. The sample was then lowered to T_x and crystallized for the time indicated.

5. Analysis and Interpretation of Melting Data of PCTFE

5.1. Preliminary Observations on $T'_m(obs)$ Versus T_x Data

The optically determined melting point, and that obtained on a portion of the same specimen from $\bar{V}-T$ curves, are very nearly the same. This is evident from certain entries cited in table 1. This result was also confirmed in a number of other studies not specifically reported. This provides a useful check of the data. However, the optical melting points have not been used in the analysis of β, or in estimating T_m by the extrapolation method.

It is evident from table 1 that heating to the T_i values in the range indicated for a given type of run erased the previous thermal history of the specimen so far as the dependence of $T'_m(obs)$ on T_x is concerned.

Although the main point of this paper is not that of differentiating between the effects on the melting point of melting out followed by recrystallization on warming on the one hand, and any isothermal increase of crystal size on storage at T_x due to chain mobility effects on the other, it will prove useful to comment briefly on this prior to undertaking the main analysis. Orientation effects are also discussed.

It is readily seen from table 1 and figure 6 that in the rapid melting runs there is a small effect of residence time at T_x: the high $\chi_{initial}$ run is from 0.5 to 0.8 °C above the data for low $\chi_{initial}$. This implies that a small increase of the smallest crystal dimension due to chain mobility may have occurred isothermally at T_x in the high $\chi_{initial}$ run, where the residence time was substantially longer. Some of the increase of $T'_m(obs)$ in the rapid melting run with high $\chi_{initial}$ may be a result of residual liquid phase orientation arising from the crystallization process itself, but this is not considered likely (see below).

The $T'_m(obs)$ data for runs with high $\chi_{initial}$ and moderate warming rates are well above any of the rapid melting run data for T_x values in the range 170 to ~185 °C. (Compare upper and lower diagrams in fig. 6.) Some of this excess in the melting point values for the moderate melting rate runs could be due to an increase of crystal size of the same general character that takes place on isothermal storage, but the greater part of it is probably a result of melting out followed by recrystallization during the warming part of the runs. Mandelkern and coworkers have clearly demonstrated in certain polymers (see for example [5]) that an incremental increase in temperature from T_i to T_f leads first to a distinct increase of volume at T_f followed by a slow decrease. This was interpreted as melting out of small crystals followed by recrystallization to form larger crystals. The initial increase of volume at T_f noted by these workers is in our opinion much too large to be ascribed solely to chain mobility effects: an increase of step height due to chain mobility leads, in the first approximation, only to a change of the shape of a crystal, and not its total

volume. Similar volume changes were noted in PCTFE in specimens warmed rapidly from room temperature to a fixed temperature fairly near the melting point, showing that melting out of small crystals followed by recrystallization can in fact occur in this polymer.

Near and above $T_x = 198$ °C, all three types of run give very similar melting points, showing a general lack of sensitivity to heating rate and residence time. Even the seed crystal run in table 2 is consistent in this respect. Our general conclusion from the above is that, for T_x values above 198 °C, the $T_m'(obs)$ data as obtained are essentially free of significant recrystallization and chain mobility effects.

Between a T_x of 185 and 198 °C, each rapid melting run is evidently a simple linear continuation of the $T_m'(obs)$ versus T_x points above 198 °C, where the data are evidently mostly free of secondary effects as noted above. Accordingly, we conclude that the melting points obtained with fast melting from $T_x = 185$ °C up to the highest T_x values employed are most representative of the original crystallization mechanism.

When considered as a whole, the present evidence for PCTFE indicates that melting out followed by recrystallization is a substantially more important cause of an increase of step height (and hence $T_m'(obs)$) after the lamella is originally formed than the chain mobility effect. In accord with the expectations cited in section 2.1, all the secondary effects are minimized at high temperatures for a wide range of storage times and warming rates. The fact that recrystallization is minimized at lower temperatures by rapid melting is also in accord with expectation.

Finally, we must concern ourselves with the possibility that abnormal liquid orientation effects have artificially raised the $T_m'(obs)$ values. First we indicate that the specimens exhibited no marked birefringence after melting out at $T_m'(obs)$. It was concluded from this that there was never any serious degree of orientation in the specimens on a macroscopic scale. Any liquid orientation would have to be on a local scale, presumably induced by the crystallization process. From the standpoint of $T_m'(obs)$ versus T_x data, one would expect orientation of this type to manifest itself in the following way: under equivalent conditions of initial crystallinity and crystallization temperature, a fast melting run should give a higher $T_m'(obs)$ than a slow run because of the greater opportunity for randomization of orientation in the slow run. Just the reverse occurs in PCTFE.

5.2. Determination of β

The $T_m'(obs)$ versus T_x plots used to determine β are shown in figure 6.

A least-squares fit of the data in the straight line region yields the following equations where the temperature is in °C:

$$T_m'(obs) = 187.17° + 0.1486\ T_x \qquad (9)$$

(180.2 to 199.6 °C for high $\chi_{initial}$, moderate melting rate)

$$T_m'(obs) = 163.22° + 0.2709\ T_x \qquad (10)$$

(185.0 to 199.5 °C for high $\chi_{initial}$, fast melting)

$$T_m'(obs) = 157.89° + 0.2952\ T_x \qquad (11)$$

(185.9 to 201.5 °C low $\chi_{initial}$, fast melting).

TABLE 3. *Estimates of T_m by extrapolation method and values of β for PCTFE*

Run	β	Temperature at intersection of extrapolated $T_m'(obs)$ versus T_x line and line $T_m'(obs) = T_x$
		°C
Low $\chi_{initial}$, fast melting	1.69	224.0
High $\chi_{initial}$, fast melting	1.85	223.9
High $\chi_{initial}$, moderate melting rate	(3.36)	(219.2)

The value of β obtained from eqs (9–11) using eq (6) are shown in table 3.

The value $\beta = 1.69$ obtained with the fast melting run with low $\chi_{initial}$ is in reasonable agreement with the theoretical expectations mentioned in section 2.1. This result means that even the largest detectible crystals in the system are only about 70 percent thicker than the mean value of a primary nucleus (or a growth nucleus with large ϵ). The rapid melting run with high $\chi_{initial}$ gives $\beta = 1.85$, which is still not far from theoretical expectation. The slightly greater β value in this case may be a result of chain mobility effects due to the longer residence time at T_x. (The run with high $\chi_{initial}$ and moderate melting rate is known to be strongly affected by recrystallization at low T_x, and is included principally to show how abnormally large β values will be found when such data are analysed.)

We regard the remarkable tendency of the step height of even the largest observable crystals in the system to maintain values close to the nucleus dimension during the crystallization process in PCTFE as being most readily understood in terms of the crystals with chain folds. As discussed in section 2.1, a β value running from somewhat below to somewhat above unity can be given a reasonable direct theoretical justification for a system of chain folded crystals, but no such justification seems to have been given for the bundle-like model.

Further evidence that the chain fold model is appropriate to the case of melting phenomena in PCTFE is as follows. PCTFE crystallized in bulk is known to be spherulitic [2, 17], and definite evidence is available showing that the spherulitic texture in this polymer is distinctly lamellar [18, 19]. Our microscopic observations have shown that melting points obtained from $\overline{V}-T$ curves may be closely identified with the disappearance of the last vestige of the lamellar spherulitic crystallinity. Since the basic features of lamellar spherulites are most reasonably interpreted in terms of structures possessing chain folds [7, 13], it follows that the melting behavior described for PCTFE is most appropriately interpreted in terms of chain folded crystals.

5.3. Estimate of T_m by Extrapolation Method

The general situation with regard to the extrapolation of the $T_m'(obs)$ versus T_x data to the line $T_m'(obs) = T_x$ is shown in figure 6.

Table 1 brings out the enormous increase of crystallization time that is incurred by raising T_x. This places an upper limit on the $T_m'(obs)$ value that can be achieved in a run of reasonable duration. An examination of figure 6 shows that to obtain an observed melting point of 220 °C, the crystallization would have to be carried out close to 210 °C. Our studies of the kinetics of crystallization of PCTFE [2] indicate that without seeding it would take at least one year to achieve a crystallinity of 10 percent at this temperature. (The rate constant Z mentioned in section 3.2 varies approximately as $\exp[-\Delta H^*/RT] \exp[-K_1/T^2(\Delta T)]$, and the latter term, which has a strongly negative temperature coefficient, is dominant anywhere near T_m. Hence there is a very rapid increase in the time required to achieve a given degree of crystallinity as the crystallization temperature is raised.) Seeding might be used to shorten the time, but long crystallization times would still be needed.

The data obtained with a long residence time at T_x (high $\chi_{initial}$) and moderate melting rates lead to an intersection at $T = 219.8$ °C (table 3). This may be safely regarded as a lower limit for T_m, since recrystallization is known to have raised $T_m'(obs)$ at the lower T_x values, and thus artificially lowered the point of intersection.

As noted previously, the most reliable value of T_m should be found with data obtained by rapid melting of specimens with low $\chi_{initial}$, since recrystallization and chain mobility effects are then minimized. Also, in fast melting runs, the effects of residual orientation should be minimized by employing low initial crystallinites. The run with low $\chi_{initial}$ and rapid melting gives $T_m = 224.0$ °C. The rapid melting run with high $\chi_{initial}$ gives the practically identical result $T_m = 223.9$ °C. One gathers from this that any orientation, chain mobility, and recrystallization effects that occurred in the high $\chi_{initial}$ run as compared with the low $\chi_{initial}$ rapid melting run were either compensatory or small.

Accordingly, the "best" value of the equilibrium melting temperature of PCTFE as obtained by the extrapolation method is quoted as

$$T_m = 224 \pm 1 \text{ °C}. \qquad (12)$$

The standard deviation of each of the fast melting runs is only 0.5 °C at T_m. The larger error of ± 1 °C is used to allow for other factors, for example undetected curvature in the $T_m'(obs)$ versus T_x lines used in the extrapolation.

Note that the estimated value of T_m is about 6 °C above the highest melting point actually obtained on any PCTFE specimen (see $T = 218.2$ °C run in table 2). It will be seen subsequently that this state of affairs is not unique to PCTFE.

The present study provides a simple explanation for the low melting points in the range 212 to 215 °C that have been reported in the past for PCTFE. When PCTFE samples of ordinary size, say 2 to 5 mm thick, are heated well above the melting point, and then allowed to cool in air, most of the crystallization tends to take place between 165 and 175 °C. This happens because the crystallization is rapid in this region, and because the heat evolved is sufficient to maintain a specimen of the size mentioned in this range for a time. (The heating and cooling procedure described corresponds to the molding → cooling procedure often used in practice). A glance at table 1 shows that a sample crystallized in this range will melt between about 212 and 215 °C, depending on the melting rate.

5.4. Shape of Melting Curves

Some evidence was obtained suggesting that the breadth of the melting process diminishes as the crystallization temperature increases, i.e., as ΔT decreases, as shown schematically in figure 4. An example of this behavior is seen in figure 5: The quantity $dT/d\overline{V}$ near the liquidus is clearly larger for the $T_x = 171.3°$ curve than it is for the $T_x = 199.0$ °C curve. To a rough approximation, $dT/d\overline{V}$ for these runs appears to vary as ΔT. However, there was considerable scatter in the $dT/d\overline{V}$ data for these high $\chi_{initial}$ runs with moderate melting rates. It seems probable that much of this scatter was due to the secondary effects that occurred during the melting process. No $dT/d\overline{V}$ data of the required accuracy were obtained with fast warming rates.

A number of the melting curves for high $\chi_{initial}$ with moderate melting revealed a small "tail" of the type depicted in the inset in figure 4. This tail corresponds to the melting out of something less than the last one or two percent of the crystals and usually occurred over a range of less than one degree.

6. Discussion

6.1. Comparison of Extrapolated T_m Value With That Estimated by the Slow Stepwise Warming Method

It has been recommended that the equilibrium melting temperature of a polymer be measured by slow stepwise warming [5, 6]. The polymer may be initially crystallized under any of a number of conditions. The stepwise warming is to be carried out so that the specific volume settles down to its "rest" value after each incremental increase of temperature. The method evidently relies in large part on melting out followed by recrystallization and other secondary effects to achieve large and high melting crystals. This method of estimating T_m is discussed below in the light of the present work.

In the case of PCTFE, it appears that the "T_m" value of 216.4 °C obtained by the slow stepwise warming method is somewhat below the true equilibrium melting temperature. This statement holds even if one questions the T_m value of 224 °C obtained by the extrapolation method, since specimens melting at 218.0 to 218.2 °C can be made rather

easily by crystallizing the polymer at high temperatures (table 2). Thus, the melting point obtained by the slow stepwise warming method is at least 1.6 °C low. If the extrapolation method is valid, as the present study suggests, then the melting point obtained by the stepwise warming method is about 7.5 °C below T_m.

The slow stepwise warming run carried out on PCTFE may not be a completely fair test of the method. Some silicone oil was taken up by the specimen, and some discoloration possibly indicative of slight degradation was observed. On this basis, the melting point of 216.4 °C might be thought to be lower than that which would be found in a more ideal stepwise warming run of the same duration. Note, however, that the isothermal run of 34 days duration mentioned in table 1(A) does not lead to a melting point that is out of line with those found in much shorter runs. (The specimens in the shorter runs did not become discolored or take up any significant amount of silicone oil.)

In order to check further on the relative value of the stepwise warming method and the extrapolation method, we initiated a study on linear polyethylene (Marlex 50). Here the T_m value found from a T_m'(obs) versus T_x plot was compared with (a) the value $T_m = 137.5 \pm 0.5$ °C found by Quinn and Mandelkern for Marlex 50 by the stepwise warming method [6], and (b) the convergence temperature of the orthorhombic form of the n-paraffins as determined by the careful analysis of Broadhurst [20], which includes new data on n-$C_{94}H_{190}$. A detailed report of both the T_m'(obs) versus T_x studies (still in progress) and the convergence temperature work will be given elsewhere, but the following brief summary is relevant here.

The observed melting point for polyethylene increases markedly with increasing T_x, corresponding to $\beta \cong 1$ in eq (6). At this writing, the extrapolated value of T_m is 143 ± 2 °C. (A somewhat more precise value may be expected when the work is completed.) This compares favorably with the convergence temperature of 141.1 ± 2.4 °C found by Broadhurst. The latter may be taken as an independent estimate of T_m, since the crystal structure of polyethylene is orthorhombic. As in PCTFE, secondary effects attributable to recrystallization and chain mobility in the crystal were found. A specimen crystallized at $T_x = 130.0$ °C for two weeks (high $\chi_{initial}$, moderate warming rate) gives T_m'(obs) $= 137.7$ °C, which is practically identical to the result obtained by Quinn and Mandelkern using the slow stepwise warming technique.

The T_m'(obs) versus T_x plot containing the point T_m'(obs) $= 137.7$ °C has a definite positive slope similar to that found in PCTFE, and gives a strong impression that crystallization at a higher temperature would give a significantly higher melting point. This would, of course, take a long time to verify because of the rapidly diminishing crystallization rate, but the implication remains clear.

From the above, it seems improbable that T_m is below 140 °C for linear polyethylene, suggesting that the slow stepwise warming method, as applied

in this case, gave a melting point that was at least 2.5 °C below T_m. Our present best estimate is that T_m for polyethylene is about 3.5 to 5.5° C above the melting point given by the slow stepwise warming method, i.e., T_m is between 141 and 143 °C.

It is considered that the value $\beta \cong 1$ found for polyethylene implies that crystallization with chain folds occurs in this polymer.

Some further discussion of the slow stepwise warming method is of interest.

The stepwise warming technique has a tendency to yield the same melting point for polymer crystallized in a variety of ways and at different temperatures prior to the start of the slow stepwise warming run. This result is readily understandable in terms of the concepts outlined in this paper.

Assume for the sake of discussion that two specimens are at hand, and that the one consists mostly of small crystals formed at high supercooling, and the other of medium-sized crystals formed at moderate supercooling. By the time that both specimens have been warmed to a temperature sufficient to melt out the medium-sized crystals, the small ones will also have melted out. Then the recrystallization and other secondary effects occurring in both specimens on sufficiently slow warming will tend to occur under conditions of equivalent supercooling. Thus, the larger crystals formed at these higher temperatures must be expected to eventually develop a quite similar size distribution in each case. Then at some temperature near (but still below) T_m, the negative temperature coefficient of the recrystallization and other secondary mechanisms will in the allotted time effectively prevent the formation of still larger crystals, and the melting point consistent with the patience of the investigator will have been reached. Because of the similarity in crystal size, both specimens will melt close to the same temperature, but this temperature will be somewhat below T_m. Interestingly, the sameness of the observed melting point with slow stepwise warming for a polymer initially crystallized in various ways has been cited as evidence that the melting temperature so found was in fact the equilibrium melting temperature. Such evidence could actually mean merely that the largest crystals in the preparation were of roughly the same size, and is not adequate as a proof of the attainment of T_m.

In view of the foregoing, it is considered improbable that the slow stepwise warming technique, as it has been applied in practice, actually gives the equilibrium melting temperature. The slow stepwise warming technique has the advantage of simplicity, and obviously minimizes orientation effects, but the presently available evidence is that melting points obtained in this way are apt to be several degrees below T_m.

The present work presents an alternative to the slow stepwise warming technique if the objective is to obtain the highest melting point for a real specimen in a given period of time. The bulk of the allotted time is spent in an isothermal crystallization at the highest temperature where a reasonable

amount of crystallization will develop. Then the specimen is warmed and the melting point determined. The latter step would most wisely be carried out on several specimens for a series of moderate and fairly slow warming rates. Seeding may be used to achieve an increased rate of crystallization at high T_x values if feasible. This general procedure forms large crystals in the specimen in the beginning, and does not rely largely on secondary mechanisms to achieve the same end. The present evidence suggests that this method is at least as efficient in producing a high melting point in a specimen in a given period of time as the slow stepwise warming technique. It should be understood that T_m cannot actually be attained by either method in a real specimen because of the extreme slowness of both crystallization and recrystallization near T_m, and the tendency of the step height of a chain folded crystal to maintain itself (see section 6.3).

The extrapolation method of estimating T_m proposed in this paper is not without its pitfalls. In order to avoid recrystallization and other secondary effects, it is desirable to use fairly rapid melting rates. However, the use of such melting rates may fail to allow residual orientation effects in the liquid to disipate, and thus increase the observed melting points somewhat. In the case of PCTFE this effect is evidently small enough so that it is not unambiguously identifiable. It is believed that residual orientation would in any case be subdued by dealing with samples of low crystallinity. The evidence is that the extrapolation method, as applied using low $x_{initial}$ and fairly rapid melting, is accurate in the case of polyethylene, and it is likewise believed correct within the stated limits of error for PCTFE. Nevertheless, investigations with other polymers should not for the time being be confined merely to runs with low $x_{initial}$ and rapid melting, since unusually large secondary or orientation effects may appear in some instances. The proposed extrapolation method has the distinct advantage of being associated with a simple theory whose main points (such as a linear increase of T_m''(obs) with increasing T_x) can be verified in the region where the kinetics of crystallization allow data to be obtained. The method also provides additional information of interest, for instance that concerning β.

6.2. Crystal Size Versus Volume Imperfections as Principal Cause of T_m''(obs) Falling Below T_m

The treatment in this paper deals with the lowering of the melting point of a polymer that is caused by a restriction of one crystal dimension, l, to a small size. This restriction is incurred in the original isothermal crystallization. Thus, crystal size rather than volume imperfections have been taken as the main source of the fact that T_m''(obs) falls well below T_m. We must now raise the question concerning whether this point of view is reasonable in PCTFE.

Geil has found from electron micrographs that the lamellae in an air-cooled specimen of PCTFE are approximately 250 A thick [19]. As noted earlier, a specimen that is air-cooled tends to crystallize at around 175 °C, corresponding to $\Delta T \simeq 50$ °C. This work may be taken as proving the existence of very thin crystals in PCTFE of the general type that must be expected to have a melting point many degrees below T_m.

A simple calculation using eq (3) may be used to lend credence to this statement. For PCTFE, we have $T_m = 497.2$ °K, $\Delta h_f = 9.1 \times 10^8$ erg cm^{-3} [21]; further, $l \simeq 250$ A $= 2.5 \times 10^{-6}$ cm for polymer that is air cooled. The quantity σ_e in eq (3) must be estimated. Recent theoretical studies suggest that the lower range of σ_e for chain folded crystals will be 25–50 erg cm^{-2} [7]. (A value in this range is also consistent with the surface free energy parameters obtained from studies of the radial growth rate of PCTFE spherulites [2].) Using $\sigma_e = 40$ erg cm^{-2} in eq (3), it is found that the melting point of the crystal of average thickness will be about 17.5 °C below T_m. Considering the fact that the observed melting point refers to the largest crystals in the system, we would estimate with $\beta = 1.7$ that the depression should be about 10 °C, corresponding to T_m''(obs)$= 214$ °C. This is close to what is observed for air-cooled specimens (section 5.3).

The foregoing calculation is tendered as a partial justification for analysing the present experiments in terms of crystal size effects, rather than ascribing the observed depressions incurred by low crystallization temperatures mainly to volume imperfections. The latter may exist in excess concentration, and play some role in lowering the observed melting point, but it is very doubtful that this role is the major one. No crystal is "perfect" at its melting point, and a polymer crystal at this temperature must be expected to have an equilibrium concentration of volume defects, e.g., a certain number of small chain ends incorporated in the lattice. However, such equilibrium defects are not to be considered as lowering the melting point. From our point of view, the important "imperfections" that influence the melting behavior of high molecular weight linear polymers with no stereochemical irregularities are the high energy chain folded surfaces and the thinness of the crystals.

6.3. The Concept of the Equilibrium Melting Temperature

The present work does not in any way deny the existence of an equilibrium melting temperature for a highly crystallizable linear polymer. It does however bring out the reasons why this temperature will be impossible (or at least exceedingly difficult) to attain in a real polymer specimen. These reasons are:

(1) One dimension of a polymer crystal, l, is small and varies with the crystallization temperature as $1/(\Delta T)$ because of the nature of the nucleation-controlled growth mechanism in chain folded systems.

(2) The smallness of this one dimension is sufficient to significantly reduce the melting point.

(3) Attempts to produce crystals with a large l dimension by crystallizing at high temperatures,

i.e., small (ΔT), are rendered difficult and eventually impracticable by the rapidly increasing crystallization times involved as ΔT is diminished. This effect is again due to the nucleation controlled character of the growth process.

(4) Efforts to increase the l dimensions of the chain folded crystals by recrystallization and other secondary mechanisms (using either prolonged storage or slow warming) are increasingly inefficient as the melting point is approached. Near the melting point, nucleation effects strongly inhibit recrystallization, and the large lamellar thickness together with the existence of the folds prevent internal diffusion (chain mobility) from further increasing the step height.

In short, our studies strongly suggest that T_m could be closely approached (say within 1 or 2 °C) in a real specimen only in an experiment of extraordinary duration. In this situation, we have turned to estimating T_m using a method that essentially extrapolates to the temperature appropriate to infinite l. Despite its lack of attainability in a real specimen in an experiment of reasonable duration, T_m is clearly to be regarded as a real property of thermodynamic significance.

The present work suggests that the true equilibrium melting curve for a linear polymer of very high molecular weight with no stereochemical irregularities would strongly resemble the very sharp first-order transition commonly associated with ordinary pure molecular crystals. The equilibrium melting curve refers to the melting of an assembly of crystals, each having very large a, b, and l dimensions. The melting of each such crystal would refer to the equilibrium G (infinite crystal)$=G$ (liquid) at T_m, where G is the Gibbs free energy. As noted earlier, it is unlikely that such a state will be readily attained in a real polymer system. However, the increasing sharpness of the melting process in PCTFE and polyethylene that is observed as higher and higher initial crystallization temperatures are employed points to the validity of the above concept. The melting point of a small polymer crystal refers to the metastable equilibrium G (small crystal)$=G$ (slightly supercooled liquid) at $T'_m(l)$, or $T'_m(obs)$ if the larger crystals in an assembly are considered. As long as the time scale is specified, so that no change of crystal size takes place during the melting experiment, and provided that the slightly supercooled liquid is in its normal state, $T'_m(obs)$ is also a quantity of thermodynamic significance. There is no fundamental objection to applying thermodynamics to metastable equilibria.

7. References

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