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Lamellar Thickening and the Equilibrium Melting Point of Polypropylene

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ABSTRACT: The correct value of the equilibrium melting point of isotactic polypropylene has been determined using small-angle X-ray diffraction. The conflict in the literature between the two very different values obtained through extrapolation of melting point versus crystallization temperature data has been resolved. It is demonstrated through studies of the melting point of polypropylene as a function of crystallization time that the dependence of melting point elevation on supercooling is the opposite of that of polyethylene. The thickening process is shown to be most effective at low supercoolings, leading to abnormally high melting points for specimens crystallized at low supercoolings. The equilibrium melting point of isotactic polypropylene is close to 186 °C. It is believed that the observed behavior is a direct result of polypropylene crystallizing in regimes II and III, unlike bulk linear polyethylene, which crystallizes in regimes I and II. It is suggested that the behavior may be directly related to the length of continuous adjacent reentry folding generated under the different regimes.

Introduction

Polypropylene is a much studied polymer with several unusual features in its crystallization behavior, which have tended to make it more difficult to understand than polyethylene. There have always been two different values of the equilibrium melting point quoted in the literature. Many earlier studies have been complicated by possible effects caused by a lack of close to complete isotacticity; modern polypropylenes are now better than 99% isotactic. Inconsistencies in extrapolated equilibrium melting points must be caused by differences in experimental approaches and errors in extrapolations when care has been taken to choose a microstructurally pure polymer.

The extrapolated values of the equilibrium melting point, $T_m°$, reported in the literature fall into two groups, one around 186 °C and the other around 210 °C.[1-10] Krigbaum[1] and Miller[2] have determined $T_m°$ to be 186 ± 2 °C, whereas Fatou[3] and Monnasse[4] have extrapolated $T_m°$ to 208 °C. Samuels[5] has found two different equilibrium melting points: one equal to 185 °C and the other to 220 °C. His work was based on different molecular orientations within semicrystalline fibers.

Kamide and Yamaguchi[11,12] have observed changes in melting temperature with crystallization time for different molecular weights and fractions of iPP. Their analyses were based on the shift of the peaks of the DSC plots. They noticed that at the same crystallization temperature the degree of shift is proportional to the crystallization time. Furthermore, as the crystallization temperature is increased, the degree of shift is progressively larger. At the end of their analysis they concluded that the changes in melting temperature with time were independent of molecular weight and its distribution. But they did not study the effect of annealing on the equilibrium melting temperature.

In estimations of the equilibrium melting point made using the experimentally determined relation between melting point and crystallization temperature, errors can occur due to lamellar thickening. It has generally been recognized that lamellar thickening can occur at the crystallization temperature and during the heating necessary to obtain the melting curve.[12,13] There is a tendency for the "most accurately determined points", i.e., those produced at low supercoolings, to be high partly because of the long dwell time needed at the crystallization temperature to crystallize a specimen. In turn, this effect results in abnormally high values of the extrapolated equilibrium melting point. Conversely, it is also recognized that points obtained at high supercooling may in fact have been generated during cooling and be characteristic of a dynamic rather than an isothermal crystallization. They, in turn, tend to depress the value of the extrapolated equilibrium melting point.

It has generally been assumed that the thickening ratio (final to initial lamellar thickness) can be determined from the slope of the T_m versus T_c curve, following the schema of Hoffman and Weeks.[14] The crystals produced at high supercoolings are thinner and further away from equilibrium than those produced at low supercoolings. Therefore, their melting points are elevated by the thickening process much more than those crystallized at low supercoolings. In that approach thickening results in a lower slope to the plot, with the equilibrium melting point unchanged. In this paper it will be demonstrated that thickening in polypropylene favors the thicker lamellae and that it causes abnormally high extrapolated values of the equilibrium melting point. The 210 °C estimate of the equilibrium melting point of polypropylene is erroneous and caused by a relatively slow lamellar thickening process that occurs at the crystallization temperature.

Experimental Section

Isotactic polypropylenes, iPP, were supplied by Exxon Corp. and had an isotacticity of >99% as determined by Exxon using NMR methods. The values of M_n, M_w, and M_z were respectively 72K, 257K, and 528K for the first sample and 50K, 151K, and 287K for the second.

Small-angle X-ray scattering, SAXS, studies were carried out at the Center for Small Angle Scattering Research at Oak Ridge National Laboratories using a sample to detector distance of 5 m. Wide-angle X-ray diffraction, WAXD, studies were carried out using a Rigaku Denki diffractometer. Samples were prepared for SAXS and WAXD analysis in a silicone oil bath at different crystallization temperatures. First, the sample was held in one bath at 200 °C, and then it was rapidly transferred to another bath which was set at the desired crystallization temperature.

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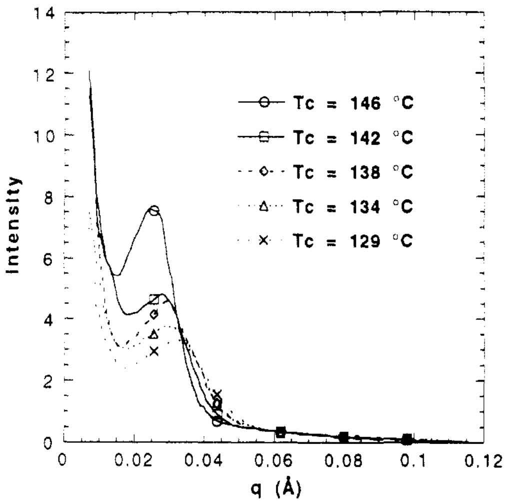

Figure 1. SAXS radially averaged intensity I versus scattering vector q for isotactic polypropylene M_w = 151K isothermally crystallized at atmospheric pressure and several crystallization temperatures.

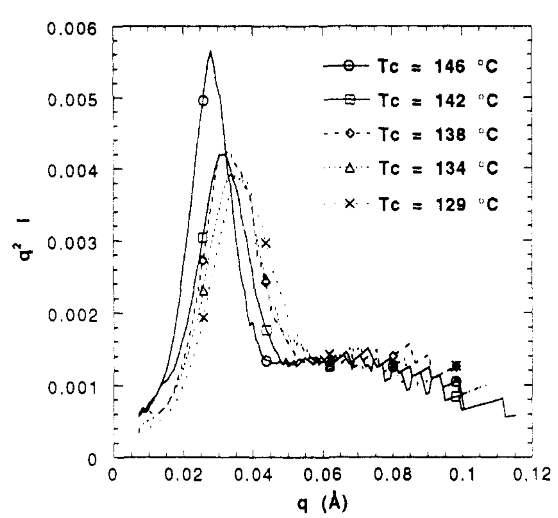

Figure 2. SAXS Lorentz-corrected plots for the data of Figure 1.

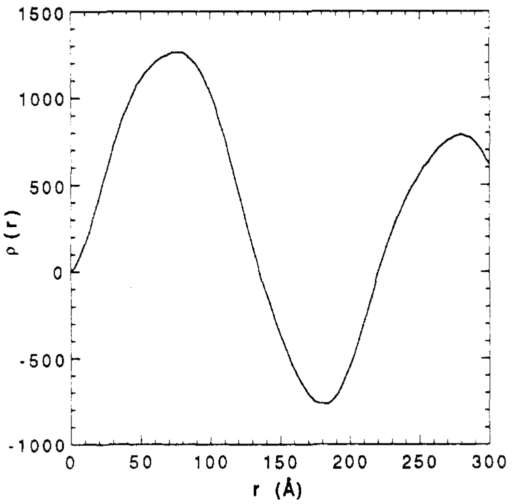

Figure 3. Distance distribution function, $\rho(r)$, for isotactic PP isothermally crystallized at ΔT = 47 °C. SAXS intensity profile recorded at 25 °C.

The sample was removed from the second bath after a time adequate to ensure its complete crystallization. A small part of the sample was taken for melting point determination using microscopy.

Transmitted light intensity determinations of melting point were carried out using a Mettler hot stage mounted on an Olympus microscope under cross-polar conditions. A trinocular was used, one beam passing to a photomultiplier tube attached to a chart recorder and the second to a binocular eyepiece for direct observation. The hot stage was calibrated using an Omega, Type J, calibrated thermocouple. The polymer sample was placed between two glass cover slips. Using another hot stage, the sample was heated to 200 °C, held for 10 min, and then rapidly transferred to the hot stage which was set to the desired crystallization temperature. This procedure ensured the isothermal crystallization of the polymer. For each run the sample was crystallized and then heated at a rate of 10 °C/min, and the melting point of the polymer was recorded.

A Perkin-Elmer Series 7 differential scanning calorimeter, DSC, was also used to determine the equilibrium melting point of iPP. The DSC was calibrated using pure indium as a standard ($T_m°$ = 156.60 °C). The sample was heated to 200 °C and held for 10 min in order to lose its thermal history, and then it was rapidly cooled at a rate of 80 °C/min to the desired crystallization temperature, T_c. The sample was held at the crystallization temperature for 10–70 min depending on T_c, so that enough time was given to grow small crystals, and then melted at a rate of 10 °C/min. Two melting points, the peak and the modified return-to-the-baseline (MRB), were taken each run.

Results

Lamellar Thickness Studies. SAXS data were collected as two-dimensionally averaged scattering intensities. All specimens exhibited circularly shaped two-dimensional plots, indicative of isotropic materials. Figure 1 shows a plot of radially averaged intensity versus scattering vector for the polymer of 151K M_w as a function of isothermal crystallization temperature. As expected, the peak shifts to lower q values as crystallization temperature increases, reflecting the increase in long period. In general, the curves show relatively well defined Bragg maxima. The curves were corrected using the Lorentz geometric factor, the corrected data being shown in Figure 2. Corrected curves typically show a relatively sharp primary peak with occasionally a secondary peak of much lower intensity at higher scattering vector values.

More detailed analysis of SAXS data can be made by performing distance distribution function ($\rho(r)$) and electron density correlation function ($\gamma(r)$) plots. The distance distribution plot gives information on the nature of the scattering. Such analyses (Figure 3) indicate a concentrated system in that a minimum occurs with negative values of the distance distribution. Data for other crystallization temperatures were similar.

A representative electron density correlation function plot is shown in Figure 4 and is typical of a two-plane system with long period variation, lamellar thickness variation, and a diffuse phase boundary. The data are consistent with literature results for other semicrystalline polymers.[15] The long period determined from such a plot was found to be larger than those determined from the observed SAXS intensity profiles. Table 1 gives as a function of crystallization temperature the details of long periods determined from the obtained SAXS intensities, the Lorentz-corrected intensities, and the electron density correlation function.

Lamellar thicknesses were estimated using the traditional method of multiplying the Lorentz-corrected long period by the crystallinity determined from WAXD. A plot of melting point versus reciprocal lamellar thickness is shown in Figure 5. The melting points used here were determined from direct optical microscopy in a hot stage at 10 °C/min.

Dynamic Light Intensity. The melting behavior of α-spherulites of polypropylene is complicated by the presence of thin lamellar branches inclined at 80° to the

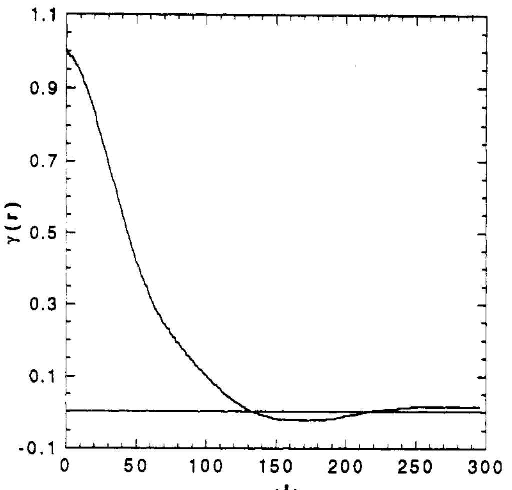

Figure 4. Electron density correlation function, $\gamma(r)$, for isotactic PP isothermally crystallized at $\Delta T = 47$ °C. The SAXS intensity profile was recorded at 25 °C.

Table 1. Comparison of Long Periods Determined from SAXS, Observed Intensity, and Electron Density Correlation Functions[a]

	L, Å (Bragg)		
T_c	LC	obs	$L(\gamma)$
127	184	218	221
129	192	226	226
134	198	248	236
136	210	238	252
137	210	238	266
138	208	248	262
139	210	256	266
140	226	248	267
141	224	256	271
142	230	256	281
143	230	276	256
144	238	276	261
146	248	298	303

[a] T_c is the crystallization temperature (°C). LC is the Lorentz-corrected lamellar thickness from q–q^2I data. Obs is the observed lamellar thickness from q–I data. $L(\gamma)$ is the lamellar thickness from the correlation function γ.

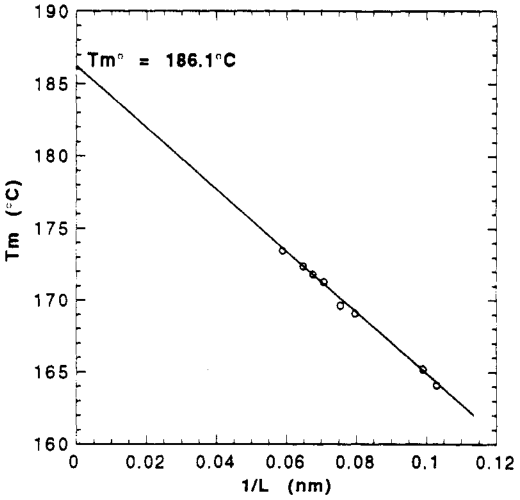

Figure 5. Melting temperature, T_m, from DLM of iPP (Mw = 151K) versus reciprocal lamellar thickness from SAXS using Lorentz-corrected data.[10]

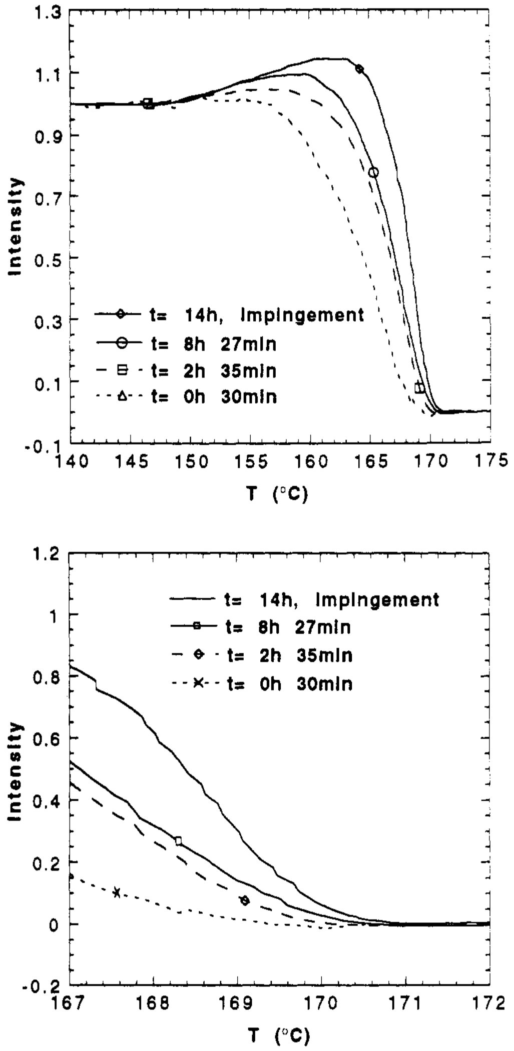

Figure 6. (a) Light intensity, I, versus temperature, T, for different crystallization times, t, at 140 °C. Heating rate: 10 °C/min. (b) Magnification of the end of the melting region of (a). The melting point after 14 h is 1.5 °C higher than after 30 min.

dominant radial lamellae.[16-21] Their angle of inclination leads to a partial compensation of the birefringence arising from the radial lamellae. This effect is responsible for the well-known low birefringence of α-spherulites. During a heating cycle the branches melt at a lower temperature than the dominant lamellae, causing an increase in the birefringence of the spherulites and, hence, of the specimen (Figure 6a). When the radial lamellae melt, the expected decrease in birefringence occurs, permitting an estimate of the melting point to be made as the temperature at which zero birefringence is attained. As a function of the time of crystallization, the temperature at which zero birefringence is attained can be seen to increase (Figure 6a). The latter effect is caused by the lamellar thickening of the radial lamellae, and for the example shown in Figure 6a of 140 °C crystallization there is a difference of 1.5 °C in this value between 0.5 and 14 h of crystallization time (Figure 6b). This effect can be observed over much of the crystallization range. The amount of thickening being greater at low supercoolings, due to the long crystallization times necessary for production of a specimen, has an unduly large effect on extrapolations of the equilibrium melting point.

Clearly, this effect will confuse traditional extrapolations as illustrated in Figure 7, where two extrapolations are performed. First, specimens have been crystallized for long times and at least to impingement. The points fall reasonably well on the drawn line, which is the best fit line for the data points. It can be seen that the extrapolation leads to an equilibrium melting point close to 210 °C. Secondly, specimens were crystallized for very short times and then the melting points determined. In this case it

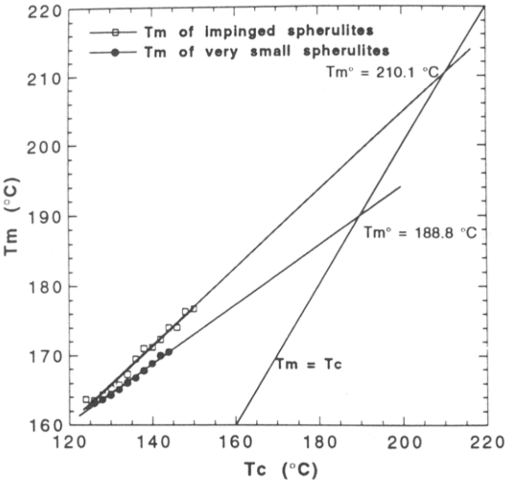

Figure 7. T_m versus T_c for two experiments that yield distinct equilibrium melting temperatures, $T_m°$. The experiments differ only in crystallization time.

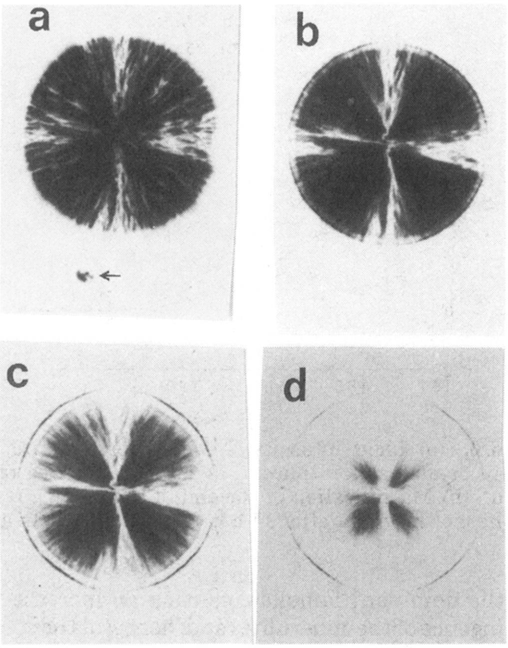

Figure 8. Typical melting of iPP spherulites crystallized below 135 °C and heated at 10 °C/min: (a) crystallized spherulite (T_c = 135 °C for 52 min); (b, c, d) during melting after 3 min 2 s, 3 min 8 s, and 3 min 14 s, respectively. Notice the appearance of the ring and the radial melting. Also notice that from a to b the small spherulite (arrow) has melted.

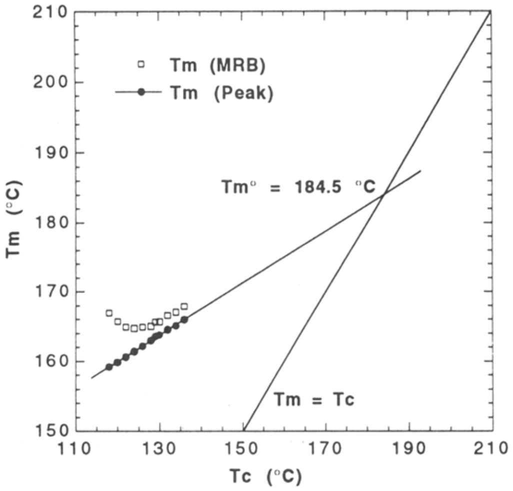

Figure 9. T_m versus T_c, using the peak and the modified return-to-the-baseline (MRB) temperatures from DSC. The data were collected after a short time of crystallization.

was necessary to allow sufficient crystallization for an accurately measurable light intensity trace to be obtained. Obviously, the transmitted intensity is proportional to the crystallinity in the sample and a certain minimum crystallinity was necessary in each case. When plotted, the points give the best fit line shown and an extrapolated equilibrium melting point of 188.8 °C. The equilibrium melting temperature would be more accurate if one could measure the melting temperature characteristic of newly initiated spherulites, but this is very difficult using current instrumentation. The first difficulty encountered is the sensitivity of the light intensity detector. The second problem is the continuous crystallization of the polymer that occurs during heating at a moderate rate such as 10 °C/min from low crystallization temperatures. This effect is manifest in the formation of rings that grow at the edge of spherulites during heating of the specimen (Figure 8). Both of these problems are not easily overcome. Also in Figure 8 one can see the melting of a small spherulite (arrow) preceding the melting of a large one.

When specimens were crystallized for very short times, $T_m°$ was determined to be 184.5 °C (Figure 9) from the peak temperatures using the DSC instrument. The melting points shown in Figure 9 are the peaks of each plot given by the DSC. The peak represents the average melting point compensated by the distribution of spherulite sizes and, hence, lamellar thicknesses. Also, the melting of thin lamellar branches and the rings which were formed during melting were included in the peak measurements. The modified return-to-the-baseline measured the melting point of the rings that developed during heating at 10 °C/min. Such rings were only formed when the isothermal crystallization was below 135 °C. When crystallized at high temperatures (Figure 10) the rings did not form and the return-to-the-baseline temperature could be extrapolated accurately to give an equilibrium melting point close to 186 °C.

Discussion

Although the Hoffman–Weeks plot used is very convenient for equilibrium melting point determinations, it was never claimed that it was a substitute for the primary extrapolation, which must involve an extrapolation of melting point versus lamellar thickness. The latter process is much more lengthy and requires accurate determinations of lamellar thicknesses and crystallinities. This usually entails the use of both small-angle and wide-angle X-ray studies. When such determinations are conducted for polypropylene (Figure 5), they result in an extrapolation which, when best fit, generates an equilibrium melting point of 186.1 °C, which correlates well with the lower value obtained from Hoffman–Weeks plots.

The value of the equilibrium melting point of polypropylene is therefore believed to be close to 186 °C. A more precise evaluation is not easily possible because of the inherent errors in all of the techniques which have to be used. Analyses reported in the literature of the kinetics of crystallization of polypropylene using an equilibrium melting point of 210 °C or above (e.g., refs 4 and 22) need to be reevaluated. The extrapolations producing the equilibrium melting point of 210 °C have all been carried out using established techniques and have been conducted in an acceptable manner. Why then is it so different from the value obtained using small-angle X-ray scattering? The answer lies in the nature of the self-annealing

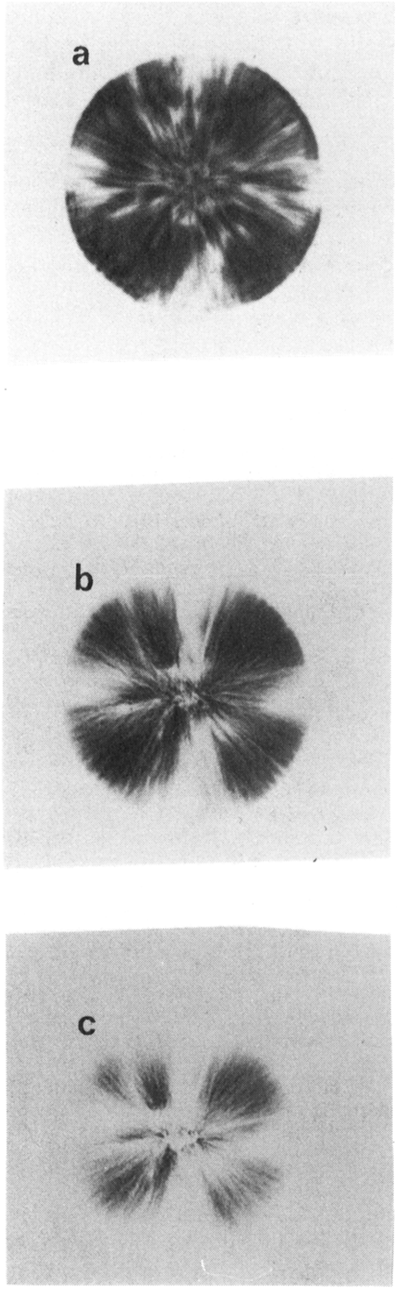

Figure 10. Typical melting of iPP spherulites crystallized above 140 °C and heated at 10 °C/min: (a) crystallized spherulite (T_c = 150 °C); (b, c, d) close to melting. Notice that no ring appears during melting and the spherulite radially melts toward its center.

mechanism occurring at the crystallization temperature. Most studies of self-annealing have considered polyethylene and generally at low supercoolings. The clearly recognized dependence on annealing is that the slope of a curve of melting point versus crystallization temperature is decreased.

In the study reported here the slope clearly increased when long crystallization times were used instead of short ones. However, the crystals produced at the highest supercooling showed only marginal increases in melting point with time. In other words, their thickening process was being inhibited. Crystals produced at low supercooling showed the largest increases in melting point. Furthermore, the line fits for the curves of Figure 7 clearly indicate that the inhibition of the thickening process is dependent on temperature in a somewhat linear fashion. The curve for impinged spherulites is fairly straight above 135 °C but has a much lower slope below that temperature. Indeed, it is relatively close to that for the newly formed spherulites. However, natural scatter of the data prevents any stronger statements from being made, although it is noted that 135 °C is close to the regime II–regime III transition temperature.

The results of the study raise some fairly serious questions regarding the current level of understanding of lamellar thickening processes. First, it has generally been assumed that the thickening coefficient is a constant value, resulting in the melting points of the thinnest crystals being affected the most by an annealing process because they are far from equilibrium dimensions. However, here there is a clear example of the thicker crystals being affected most by the thickening process. It should also be recalled that in earlier studies of poly(ϵ-caprolactone)s[23] the thickest crystals tended to be able to approach equilibrium more easily than thinner crystals. In this case it was assumed that the low molecular weight of the polymer enabled thicknesses approaching complete extension to be reached easily.

The mechanism of thickening must involve a snaking through the crystal of lengths of chain. It is a reasonable assumption that the activation energy of the snaking process should be proportional in some way to the thickness of the crystal because of the length of chain involved dictating the total amount of internal frictional resistance encountered. The results presented here conflict with such a reasonable assumption. Such a model does not allow for the impediment to thickening caused by the presence of some nonadjacent reentry folding, nor does it consider the influence of tie molecules. Analyses of the crystallization kinetics of polypropylene at atmospheric pressure show that the commonly encountered high molecular weight polymer crystallizes in regimes II and III dependent on temperature.[9,24] Regime theory states very explicitly that a change of regime does not interfere with the expected linear dependence of the unthickened lamellar thickness on supercooling. All the experimentation carried out to date on several polymers confirms this conclusion. Regime theory does not deal with any thickening process, but it is possible to infer some reasonable hypotheses regarding the nature of the folded surface and how it varies with regime.

Although some might dispute this statement, it has been generally assumed that regime I conforms most closely to the adjacent reentry surface. In regimes II and III, in which there is multiple nucleation, there is a tendency to incorporate more nonadjacently reentered stems into the surface as well as increasingly larger numbers of nonreentered molecules. This tendency tends to be favored as the supercooling is increased and hence should be greatest in regime III. The type of disordered surface generated is sometimes referred to as an interfacial layer.[25] In any case, disrupting the continuity of adjacent reentry has to present a major obstruction to the lamellar thickening process. It should render the thinner lamellae produced at high supercooling incapable of responding adequately to the thermodynamic driving force for thickening. The data in the literature on thickening of polyethylene crystals consider largely crystals generated under regime I conditions where adjacent reentry dominates the crystallization process. It is therefore suggested that the thickening behavior exemplified by polyethylene crystallized at low supercoolings and characterized by a lower slope to a plot of T_m versus T_c should not be taken as representative of all polymers, but may be typical only of polymers crystallized under regime I conditions where adjacent reentry predominates.

It is remarkable that the break in the T_m versus T_c curve for the impinged spherulites occurs at 135 °C. This value is close to the regime II–regime III transition temperature of 137 °C. Remembering that the data reported have excluded specimens in which crystallization might have occurred prior to reaching the crystallization temperature, it would be reasonable to suggest that the lowest slope demonstrating little or no thickening is characteristic of regime III crystals. The curve giving rise to the slope that generates a $T_m°$ of 210 °C is then characteristic of regime II growth. It therefore appears that lamellar thickening in regime II is characterized by a temperature-dependent thickening coefficient. It is very tempting to suggest that this is giving a measure of the fraction of adjacent reentry folding present in the surfaces, but such a speculation would be virtually impossible to test.

It is possible that a reevaluation of literature data will support the mechanism as being common to many polymers. Most studies show a low or zero slope region at high supercoolings which has been ascribed to nonisothermal crystallization and ignored. Following on the suggestion of the existence of regime transitions, a reevaluation of kinetic analyses proved to be very valuable. Perhaps a similar reevaluation of Hoffman–Weeks plots would be in order.

Conclusions

The effect of lamellar thickening during polymer crystallization on equilibrium melting temperature, $T_m°$, has been investigated. For the same crystallization temperature iPP crystallized to impingement has a higher melting temperature than if crystallized for a lower crystallization time. Since $T_m°$ is extrapolated from these melting temperatures, different values of $T_m°$ are obtained depending on the time of crystallization. The results show that thickening in polypropylene favors the thicker lamellae and that it causes abnormally high extrapolated values of $T_m°$. Therefore, the 210 °C estimate of the equilibrium melting point, even though accurately obtained, is erroneous. In addition, the equilibrium melting temperature that results from the data which are collected at low crystallization times is similar to the one obtained from DSC and SAXS experiments. Unlike polyethylene, the effect of thickening in iPP is greater at low supercooling.

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