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Fusion of Isotactic Poly(propylene)

Tracy W. Huang and Rufina G. Alamo*

Department of Chemical Engineering, Florida Agricultural and Mechanical University and Florida State University College of Engineering, 2525 Pottsdamer St., Tallahassee, Florida 32310-6046

Leo Mandelkern*

Department of Chemistry and Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306-4380

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Introduction. The establishment of the equilibrium melting temperature, T_m^0, of isotactic poly(propylene) has been an elusive and controversial matter for some time. The reported values of T_m^0 have ranged from about 185 to 220 °C.[1−5] These values are based on what has now become conventional extrapolation methods to obtain T_m^0. These methods involve either the determination of the melting temperature as a function of the crystallite thickness (Gibbs−Thomson) or analyzing the relation between the observed melting temperature and the crystallization temperature (Hoffman−Weeks procedure[6]). There are several possible reasons for the wide range in T_m^0 values that have been reported. One, common to all polymers, involves inherent problems in the extrapolations.[7] Other possibilities are specific to isotactic poly(propylene). They involve, among others, the accurate determination of the structural regularity of the chain, interpretation of the multiple endothermic peaks that are invariably exhibited during the fusion of this polymer, use of sufficiently high molecular weight samples, and the heating rates. It is not our intent in the present Communication to sort out the specific reasons for the range in T_m^0 values that have been reported. Rather, we wish to report a unique feature of the fusion of isotactic poly(propylene) that not only has direct bearing in determining the observed melting temperature T_m of a sample crystallized under given conditions, and thus the extrapolation procedures, but is of importance and significance in itself. The phenomenon to be described transcends the problems encountered in the conventional extrapolations to T_m^0.

Experimental Section. Both Ziegler−Natta and metallocene types of isotactic poly(propylene) were studied in this work. The molecular characteristics of the two polymers are given in Table 1. The molecular weight distributions were obtained by standard GPC methods.[8] The concentrations of stereo and regio defects were determined by high-resolution ^{13}C NMR.[9,10] The concentrations of regio defects were calculated from the corresponding NMR peaks.[10−12] The stereo defects were determined from half of the fraction of mmmr pentads.

Table 1. Molecular Characteristics of Isotactic Poly(propylenes) Studied

sample type	M_w	M_w/M_n	total defects[a]	stereo defects[a]	regio defects[a]
Ziegler	271 000	6.1	0.83	0.83	
metallocene	575 000	2.4	0.30	0.08	0.22

[a] Mole percent.

The isothermal crystallizations of all the samples studied here were carried out in thermostated silicone oil baths that were controlled to ±0.1 °C. Compression molded films were placed in vacuum-sealed tubes to prevent degradation during the long-time crystallization. After melting the sample at 200 °C for 10 min the tubes were rapidly transferred to the oil baths that were set at the desired temperature. The isothermal crystallization was halted by quenching into ice water. The isothermal crystallization temperatures varied from 136 to 164 °C. The crystallization times were guided by previous crystallization kinetic studies.[13] The GPC of the samples after crystallization were very similar to those of the original samples, thus indicating that chain scission or degradation upon lengthy crystallization was negligible.

The fusion process was studied by differential scanning calorimetry using a Perkin-Elmer DSC-7 calibrated with indium. Preliminary exploratory experiments were carried out in a Perkin-Elmer DSC-2. The initial thermograms were obtained at a heating rate of 10 K/min. After annealing, the heating rate for fusion was 2.5 K/min. The thermograms did not show any quenching peak, indicating that crystallization was complete at the given isothermal crystallization temperature.

Results and Discussion. The unique lamellar branching of the monoclinic (α) form of isotactic poly(propylene) is well-documented to be the result of a homoepitaxial crystallization.[14] This reference also gives a detailed chronology of earlier observations and interpretations. The structure parallel to the 010 plane of the monoclinic phase is bilayered, each layer made up of helices of the same hand. Successive layers have helices of opposite hand. Tangential branching has been explained by a deposition of the same hand helix on a preexisting 010 face with helices of the same handness. The methyl groups of the 010 face interdigitate with the methyl groups of the contacting helix by a rotation of 100° around the *b*-axis. This rotation allows the *c*-axis of a unit cell in the radial lamellae to be parallel to the *a*-axis of an adjacent one in the transverse lamellae. This epitaxial structure, made of radial and tangential lamellae, presents a unique feature of polymer crystallization that in turn influences the melting process.

One consequence of the epitaxial lamellar crystallization is the observation of two endothermic peaks in thermograms obtained by conventional differential scanning calorimetry.[15] A typical set of thermograms, obtained at 10 K/min, for different crystallization temperatures, are given in Figure 1 for the Ziegler catalyzed polymer. These thermograms are characterized by two endothermic peaks at all of the crystallization temperatures. Detailed studies have identified the origin of the two peaks.[15] The low-temperature endotherm results from a cooperative melting of branched or tangential lamella. The high-temperature one corresponds to the melting of the primary radial lamellae.[15] It was demonstrated that the overall birefringence of the spherulites formed at relatively high crystallization temperatures (T_c > 145 °C) changes during fusion from a mixed-type character to preferentially negative at temperatures corresponding to the peak of the low endotherm. Thus, most of the thinner tangential lamellae melt at this

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* To whom correspondence should be addressed.

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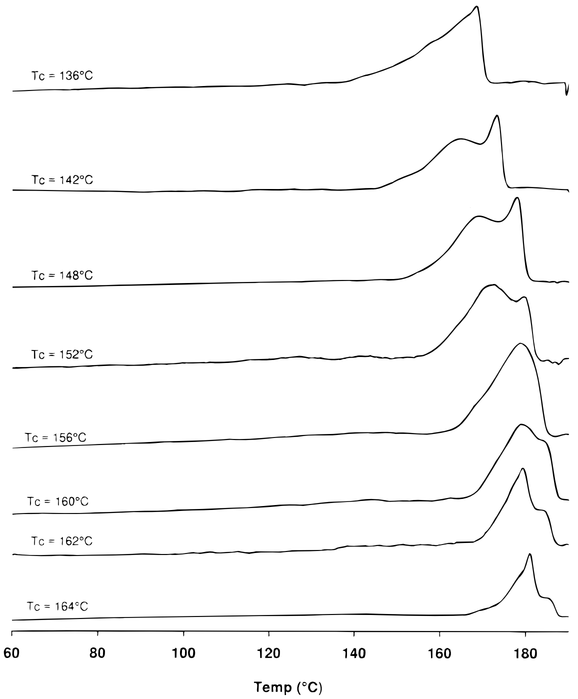

Figure 1. Melting thermograms obtained from differential scanning calorimetry of Ziegler-type isotactic poly(propylene). Isothermal crystallization temperatures are indicated.

temperature. The crystallites formed at temperatures less than about 142 °C show melt−recrystallization during fusion. On melting, the initial mixed-type overall birefringence remains unchanged until complete melting. This indicates that the melting of radial and tangential lamellae, which have approximately the same thickness in this range of crystallization temperatures,[15,16] occurs simultaneously. Epitaxial crystallization and the formation of lamellae branching (cross-hatching) are observed at all crystallization temperatures, including 160 °C and greater.[17]

The interest here is in the details of the fusion process after most of the branched lamellae have melted. Thus, we focus attention on the temperature interval between the two endotherms, as is illustrated in Figure 2. Here, from the thermogram taken from the preceding figure, the region between the two endotherms is expanded for the sample crystallized at 148 °C. The maxima of the two endothermic peaks are located at 168.8 and 178.0 °C following the initial scan at 10 K/min. An annealing temperature of 171 °C, for example, represents a temperature above that of the lower peak but 7 °C below the apparent melting temperature of the dominant lamellae. It is, therefore, a temperature at which tangential lamellae have melted. Samples were held at this temperature for varying lengths of time and then heated (without any cooling) at a rate of 2.5 K/min. The resulting thermograms are also shown in Figure 2. After annealing for 4 min at this temperature, complete melting had not occurred, and a crystallinity level of 16% was retained. As is illustrated in the figure, the crystallinity level decreased with increasing annealing times at this temperature. After annealing at 350 min, less than 1% crystallinity remains, while the sample was completely melted after 450 min of annealing at this temperature. Therefore, in this example, complete melting took place between 350 and 450 min at a temperature 7 °C below the peak melting temperature obtained by a conventional scan at a heating rate of 10 K/min. Reducing the heating rate of the initial scan to 1 K/min only reduces the melting temperature by about 2 °C. Thus, the major reduction in the melting temperature obtained by annealing cannot be attributed to the scanning rate.

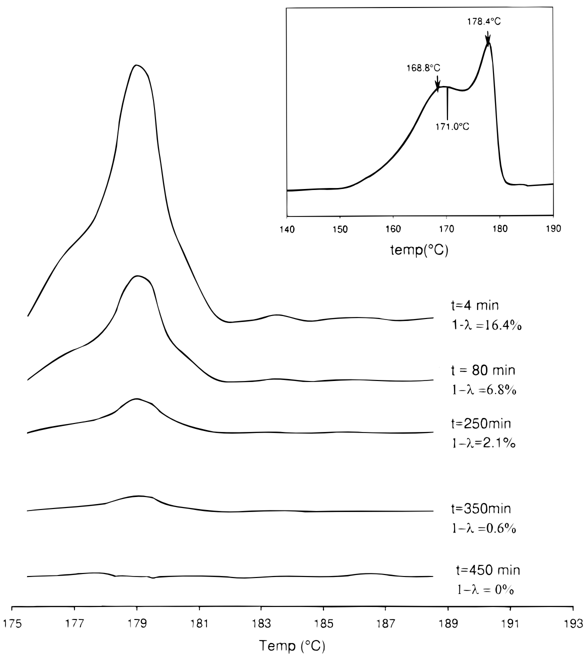

Figure 2. Expanded thermograms from Figure 1 for sample crystallized at 148 °C. Thermograms obtained after annealing same sample at 171 °C for indicated times.

If for the same polymer and crystallization temperature the initial annealing temperature was increased to 173.5 °C, melting was complete after 8 min. These results are typical of both of the isotactic poly(propylenes) studied here, for initial crystallization temperatures higher than about 142 °C. Annealing experiments of samples crystallized at temperatures below ∼142 °C did not show melting kinetics. Depending on the annealing temperature, the polypropylene either melts instantaneously or shows melt−recrystallization. Thus, isotactic poly(propylene) displays significant melting kinetics that is unique in the realm of polymer crystallization. This phenomenon requires the melting of lamellae branching so that the fusion of the epitaxial structure is no longer involved. Thus, what is being observed is a consequence of the instability of the primary radial lamellae, caused by the removal of the epitaxy. The rate of melting depends on the annealing temperature, located between the two initially observed endotherms. The higher this annealing temperature, the more rapid the melting.

We next examine the time, *t*, that is required for complete melting to take place at a given annealing temperature, T_a. Figure 3 illustrates the decrease in crystallinity level with time at a fixed T_a, for samples crystallized at 148 °C. The same type plots are found, irrespective of the annealing temperature, the initial crystallization temperature, or whether a Ziegler or metallocene polymer is involved. From plots of this kind, the time required for melting at a given annealing temperature for a sample crystallized at a specified temperature can be determined.

Of particular interest is the lowest annealing temperature at which the sample would melt after an infinite time. This temperature, defined as T_m^{∞}, repre-

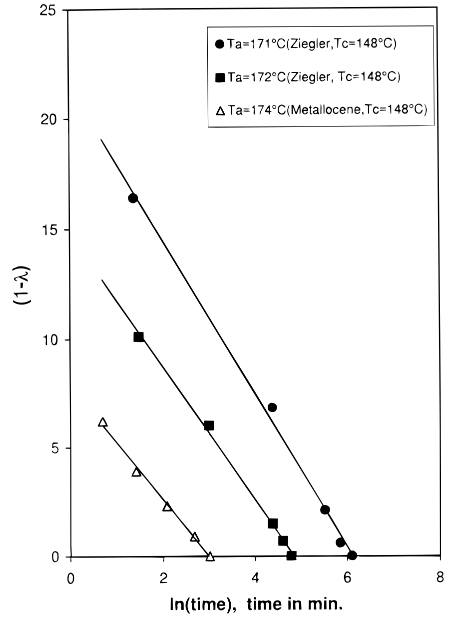

Figure 3. Plot of crystallinity level $(1 - \lambda)_{\Delta H}$ against ln time for Ziegler and metallocene polymers at indicated crystallization and annealing temperatures.

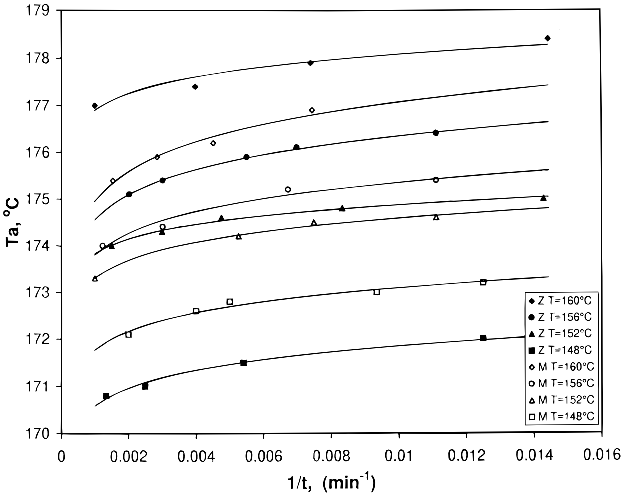

Figure 4. Plot of annealing temperature T_a against reciprocal of time required for melting $(1/t)$ for indicated crystallization temperatures: Ziegler-type polymer, ●; metallocene-type polymer, ○.

sents the true melting temperature of the isotactic poly(propylene) crystallized at T_c. T_m^{∞} should not be taken as the equilibrium melting temperature of monoclinic isotactic poly(propylene). The value of T_m^{∞} can in principle be obtained from annealing temperature−time relations obtained from plots of the type illustrated in Figure 3, i.e., the time needed for melting to be complete at a given value of T_a. The task of determining T_m^{∞} can be in principle accomplished by either a theoretical analysis of the data or an empirical extrapolation. A quantitative understanding of the melting kinetics is not presently available either to allow for a theoretical determination of T_m^{∞} or to guide the extrapolation. Therefore, a purely empirical extrapolation would be required. Rather than attempt such an extrapolation at this time, and a discussion of the T_m^{∞} values thus obtained, we merely indicate the form of the data by a plot of T_a against $1/t$ in Figure 4. The characteristics of the curves are similar to one another. For the same annealing time, the T_a values are greater the higher T_c, and those of the Zigler polymers are greater than the metallocenes at $T_c \geq 152$ °C. A better theoretical understanding of the problem is required before T_m^{∞} can be established with sufficient certainty so that it can be related to T_m^0.

The results that have been presented above indicate that the basic premise of the Hoffman−Weeks extrapolation for T_m^0, which involves analyzing the relation between the observed melting temperature and the crystallization temperature, is not fulfilled by isotactic poly(propylene) of high structural regularity because of the results described above. Hence, it is not surprising that such a large range in values for T_m^0 is obtained when this method is used for isotactic poly(propylene). Literature reports indicate the failure of this extrapolation method with other polymers but for other reasons.[18−20] To invoke the Gibbs−Thomson equation to obtain T_m^0, knowledge of the T_m^{∞} value that corresponds to the crystallite thickness is needed. This information is not as yet available and will be difficult to obtain. On the basis of these new experimental results, discussion of the correct value of T_m^0 for isotactic poly(propylene) is premature. The melting of the radial (thicker) lamellae invokes an unusual dynamic process, that needs to be understood, to determine T_m^0 in terms of T_m^{∞}. This problem is currently being addressed. Also being studied is the influence of structural irregularities on these melting kinetics.

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