Further Study on Double-Melting Endotherms of Isotactic Polypropylene

XINYUAN ZHU,[1] DEYUE YAN,[1] SUSHENG TAN,[2] TAO WANG,[2] DONGHANG YAN,[2] ENLE ZHOU[2]

[1] College of Chemistry and Chemical Technology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

[2] Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

ABSTRACT: The origins of the single- and double-melting endotherms of isotactic polypropylene crystallized at different temperatures were studied carefully by differential scanning calorimetry, wide-angle X-ray diffraction, and small-angle X-ray scattering. The experimental data show that spontaneous crystallization occurs when the crystallization temperature is lower than 117°C; thus the lamellae formed are imperfect. At a lower heating rate, the recrystallization or reorganization of these imperfect lamellae leads to double endotherms. On the other hand, when the crystallization temperature is higher than 136°C, two major kinds of lamellae with different thickness are developed during the isothermal process, which also results in the double-melting endotherms. In the intermediate temperature range the lamellae formed are perfect, and there is only a single peak in the distribution of lamellar thickness. This explains the origin of the single-melting endotherm. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 163–170, 2000

Key words: isotactic polypropylene; crystallization; double-melting endotherms

INTRODUCTION

The crystallization and melting behaviors of isotactic polypropylene (iPP) have been extensively studied.[1–18] Interestingly, double-melting endotherms occur at both higher and lower crystallization temperatures, while only a single endotherm exists in the moderate crystallization temperature region. A number of origins for the double-melting characteristics of iPP have been proposed. Kawai[1–2] considered it a type of fractionation during isothermal crystallization. Kim and coworkers[3] attributed the higher melting peak to a crystal fraction with molecular size

higher than a critical value, and the lower T_m was generated when the molecules with high mobility crystallized on quenching after finishing isothermal crystallization at higher temperature. Hoffman et al.[4–5] thought the double-melting endotherms of iPP result from the lamellar thickening on annealing. Recently, the effect of lamellar thickening has been confirmed experimentally by Mezghani and coworkers.[6] The explanation that there are two morphologically different α-forms corresponding to the folded-chain crystal and the extended-chain crystal in the system[7–11] was very attractive. However, Samuels[12] argued that the hypothesis should be rejected because it is hard to form the extended-chain crystal under normal crystallization conditions. He studied the oriented iPP fiber and noticed that it has the same melting behavior as the isothermally crystallized

sample.[12] In 1968 Cox and Duswalt[13] investigated changes in WAXS patterns and concluded that the double endotherms at lower T_c come from the transition of the metastable β-form into a stable α-form. Furthermore, Samuels[12] obtained the ultimate melting point of β-form crystals of iPP, 170°C, by means of the shift of low-temperature endotherms. On the other hand, other authors[3,14] observed double-melting endotherms even for isothermally crystallized iPP with only one phase, that is, the monoclinic α-form. From the experimental results of different heating rates and nitric acid etching, Petraccone et al.[15] attributed the double endotherms of iPP samples isothermally crystallized at 135–150°C to recrystallization, and they excluded the presence of two distinct melting species. However, Corradini et al.[16–18] showed that the crystalline structure of the α-form may show various degrees of disorder in the up and down positioning of the chain; thus the double endotherms were the result of the ordered limiting structure (α_2) having crystallographic symmetry $P2_{1/C}$ and a disordered limiting structure (α_1) having crystallographic symmetry $C2_{/C}$.

Padden and Keith[19] isothermally crystallized iPP in the temperature range 110–148°C and found that positive spherulites are formed below 134°C, negative spherulites are observed above 138°C, and mixed spherulites containing both negative and positive spherulites are present in the range 134–138°C. In terms of the Laurentz–Hoffman regime theory, Manasse and Haudin[14] proposed an interpretation of the morphological change that indicated that the double endotherms might be related to the mechanism of nucleation. Cheng et al.[20] pointed out that there were two almost orthogonal components of the crosshatch, the radial lamellae (mother lamellae) and the tangential lamellae (daughter lamellae). The crosshatched lamellae developed at almost the same time as the radial lamellae at low temperature, so the thickness of the two sorts of lamellae were similar to each other. On the other hand, the crosshatched lamellae grew after the radial lamellae at high temperatures; therefore, the former showed a thinner lamellar thickness.

Even though a lot of effort has been made previously, we are still confused about the double-melting endotherms of iPP because of the contradictory viewpoints and arguments aforementioned. In this work the double-melting behaviors of iPP were studied carefully by using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and small-angle X-ray scattering (SAXS). The experimental results reveal that the origins of the double-melting endotherms for the iPP samples crystallized at lower and higher temperatures are different from each other.

EXPERIMENTAL

Materials and Sample Preparation

The isotactic polypropylene (iPP) used in this study was supplied by Shanghai Jinshan Petrochemical Corp. (Shanghai, China) and had an isotacticity of 96%. The melt flow index was 3.0 g/10 min. A film of melted polymer about 300 μm thick was pressed between two glass slides at 210°C for 5 min in a hot stage to erase the thermal history, and then it was rapidly transferred to another hot stage, which was set at the desired crystallization temperature (T_c). After having crystallized for a time interval that was 1.5 times longer than the isothermal crystallization time measured by DSC, the sample was quenched to 0°C.

Differential Scanning Calorimetry

Thermal measurements and some experiments were carried out on a Perkin–Elmer Pyris-1 series differential scanning calorimeter in a flowing nitrogen atmosphere. The DSC was calibrated using pure indium as a standard. For all experiments the sample weights were approximately 5 mg, and the heating rate was 10°C/min.

Wide-Angle X-ray Diffraction

Wide-angle X-ray diffraction experiments were conducted for all samples with a Philips model PW1700 automatic diffractometer in the deflection mode at 40 kV and 30 mA. The X-ray beam was monochromatized using a graphite crystal. The 2θ-angle region ranged from 6° to 36°, with a scanning rate of 0.05°/min. The diffraction peak positions and widths observed from WAXD were carefully calibrated with silicon crystals. The crystalline form of the crystallized sample could be decided by the WAXD pattern.

Small-Angle X-ray Scattering

The small-angle X-ray scattering intensity of the samples were registered with a Kratky compact camera, the front of which was directly mounted on the top of the cube shield of a stabilized Philips

PW1170 X-ray generator. The Kratky X-ray tube was operated at a power of 1.5 kW. CuKα radiation was used; the monochromatization was performed by the aid of an Ni filter in conjunction with a pulse–height discriminator. Measurements were made by a step-scanning procedure and in the fixed time mode, with a sampling time of 200 s for each step. The number of steps was generally on the order of 250 for each sample. The entrance and detector slits were adjusted respectively to 80 and 200 mm. The explored domain was thus 0.006 nm-1 where $s = 2 \sin \theta/\lambda$, with 2θ representing scattering angle and λ representing X-ray wavelength (1.542 Å). Absorption, sample thickness, parasitic intensity, and electronic noise were taken into account in the standard manner. The scattering geometry used was on the finite-slit-height mode, where the width of the incident beam was comparable to the width of the receiving slit. Corrections were made for the slit-smearing effect with a method proposed by Strob.[21–22] Lorentz correction of SAXS data was implemented by multiplying the intensity by s^2. Using the traditional method of multiplying the Lorentz-corrected long spacing by the crystallinity, the lamellar thickness could be calculated.

RESULTS AND DISCUSSION

The melting behaviors of the crystallized iPP samples had been carefully measured by using DSC in our experiments. The results obtained are similar to those reported by Monasse and Haudin[14]: the double endotherms appear at both $T_c > 136°C$ and $T_c < 117°C$, and there is only a single endotherm peak in the range of $117°C \leq T_c \leq 136°C$. The transition temperature from the single endotherm to double endotherms or vice versa is related to the molecular weight and the isotacticity of the iPP specimen used.[3,5,12,13] The WAXD patterns with different heat history are shown in Figure 1. It is apparent that three strong equatorial α-form peaks of (110), (040), and (130) appear at $2\theta = 13.83°$, $16.90°$ and $18.34°$, respectively; while neither a strong single peak of (hk0) at $2\theta = 16.69°$ nor a strong peak of (120) at $2\theta = 20.10°$, namely β and γ phases, are found.[3,13,23] Moreover, although the crystallization temperature and annealing condition varied, the WAXD patterns are almost unchanging. So, for our experiments, the possibility that the double endotherms result from different crystalline forms can be excluded. On the basis of similarity
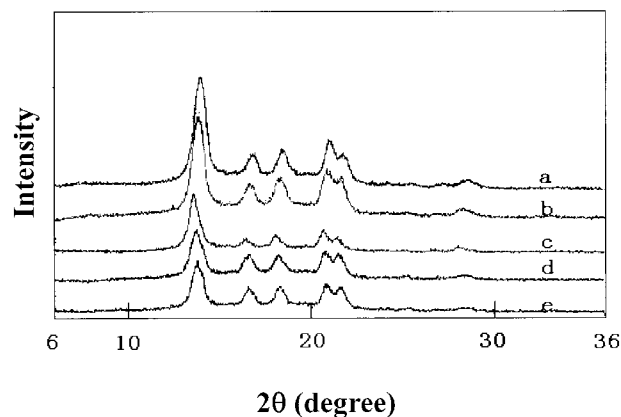

Figure 1 Wide-angle X-ray diffraction patterns of iPP crystallized: (a) at 110°C; (b) at 110°C and then annealed at 162°C for 3 min after quenching to 0°C; (c) at 130°C; (d) at 145°C; (e) at 145°C and then annealed at 170°C after quenching to 0°C.

in melting behaviors, the crystallized samples can be classified into three groups: crystallization at lower temperature ($T_c < 117°C$), at intermediate temperature ($117°C \leq T_c \leq 136°C$), and at higher temperature ($T_c > 136°C$). The three cases are separately discussed below.

Melting Behavior of Samples Crystallized at $T_c < 117°C$

It was extensively reported that the double endotherms appear when the iPP "isothermally" crystallizes at lower temperature.[3,14,24] In order to reveal the origin of the double endotherms at this temperature region, the iPP sample was crystallized at 110°C for 3 min, and the thermograph is shown in Figure 2. The figure indicates that three peaks (peaks I, II, and III) appear during the cooling process. Peak I is in the higher temperature region where the crystallization is impossible to occur at the cooling rate of 80°C/min. Obviously, peak I is the result of apparatus adjustment at the rapid cooling rate and should be unrelated to the double endotherms. This is further confirmed by peak I gradually vanishing with the decrease of cooling rate, just as is shown in Figure 4(a). Peak II is the cooling crystallization peak. It shows that the melt iPP begins to crystallize spontaneously at 117°C before the predetermined crystallization temperature; therefore, the concept of "isothermal crystallization" at a temperature lower than 117°C, which was widely used in literature, is somewhat unrealis-
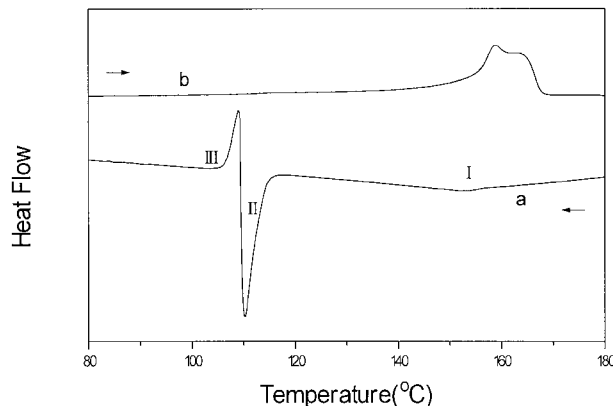
Figure 2   Thermographs of iPP sample crystallized at 110°C for 3 min: (a) cooling thermograph at the rate of 80°C/min; (b) corresponding melting thermograph.

tic. To verify this conclusion, the crystallization and melting behaviors of the iPP sample quenched from the melt were investigated. The DSC thermograph (Fig. 3) shows that only one crystallization peak appears during the cooling process and that the double endotherms still exist. The results of a comparison of Figure 2 with Figure 3 are summarized in Table I. Both the crystallization and melting temperatures in Figure 2 are identical to those in Figure 3, and the enthalpies of single crystallization exotherm and double-melting endotherms are almost unchanged. So spontaneous crystallization does occur during the cooling process when the predetermined crystallization temperature is lower than 117°C, and the subsequent isothermal process has little effect on the crystallization and melting behaviors. In addition, the comparison of Figure 2 with Figure 3 shows that the origin of peak III in Figure 2 is the same as peak I. Thus the double-melting endotherms are only related to peak II in the cooling DSC curve.

Figure 5(a) is the desmeared and Lorentz-corrected small-angle X-ray scattering curve of the iPP sample quenched directly from the melt. Only one population exists in the lamellar thickness distribution, suggesting that the double-melting endotherms may be attributed to recrystallization or reorganization. Further evidence for this come from these observations [see Fig. 4(b)]: (1) By decreasing the cooling rate, the area of endotherm on the lower temperature side increases at the expense of the area of endotherm on the higher temperature side. Finally only one endotherm appears at a very slow cooling rate. But, the sum of the two areas is found to be more or less indepen-

dent of the cooling rate. (2) The lower melting peak shifts toward the high-temperature region with a decreasing cooling rate, while the higher melting peak is almost unchanged. At a higher cooling rate, the spontaneous crystallization results in less perfect lamellae. Thus recrystallization or reorganization happens at a lower heating rate. The peak on the lower temperature represents the melting of the lamellae formed during the quenched process, and the peak on the higher temperature is due to the melting of more stable lamellae derived from recrystallization or reorganization of imperfect lamellae. With a decreasing cooling rate, larger and larger fractions of the sample crystallize perfectly, and the fractions undergoing reorganization decreases. This leads to a decrease in the area of endotherm with a higher temperature, and finally the endotherm disappears completely. In the meantime, the position of the lower melting peak shifts to the higher temperature. If the sample directly quenched from the melt were heated to 162°C at the rate of 10°C/min and then quickly requenched into liquid nitrogen, only one endotherm would appear [Fig. 6(a)], which differs from the thermograph of iPP isothermally crystallized at higher temperature [Fig. 7(b)]. It confirms the occurrence of recrystallization or reorganization—otherwise double endotherms should be observed. This also demonstrates that the recrystallization or reorganization is very fast. If the sample were annealed at 162°C for 3 min, then the melting peak temperature would be higher and the area of endotherm would increase [Fig. 6(b)] due to the lamellar thickening. Busfield and Blake[25] have studied the
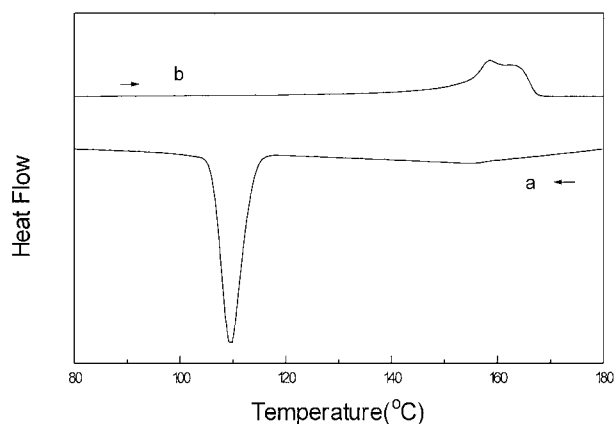

Figure 3   Thermographs of iPP sample quickly quenched to 0°C: (a) cooling thermograph at 80°C/min; (b) corresponding melting thermograph.

Table I Thermal Properties of iPP Samples

	Cooling Process			Heating Process		
Sample	$T_{onset}{}^{a}$ (°C)	T_{peak} (°C)	ΔH_f (J/g)	$T_{peak\,(lower)}$ (°C)	$T_{peak\,(upper)}$ (°C)	ΔH_f (J/g)
Crystallized at 110°C for 3 min	116.93	110.38	85.23	158.89	163.24	74.74
Quickly quenched to 0°C	116.91	110.15	85.29	158.79	163.14	74.93

^{a} T_{onset} is the temperature at which the spontaneous crystallization occurred.

effect of γ-irradiation on iPP samples and found that the main melting-peak temperatures decrease with an increase in the γ-irradiated dose. Corradini and Petracone et al.[16–18] have observed
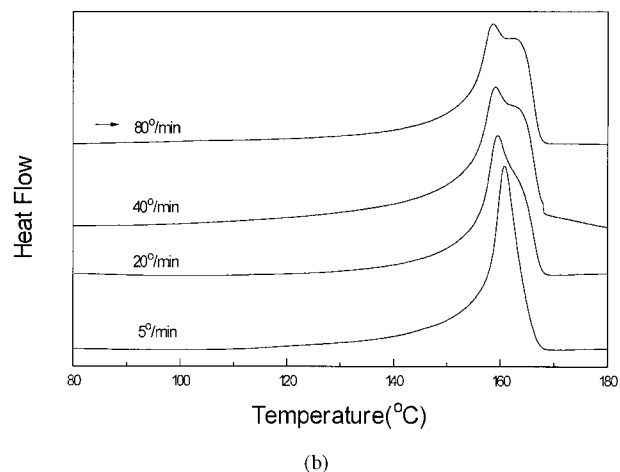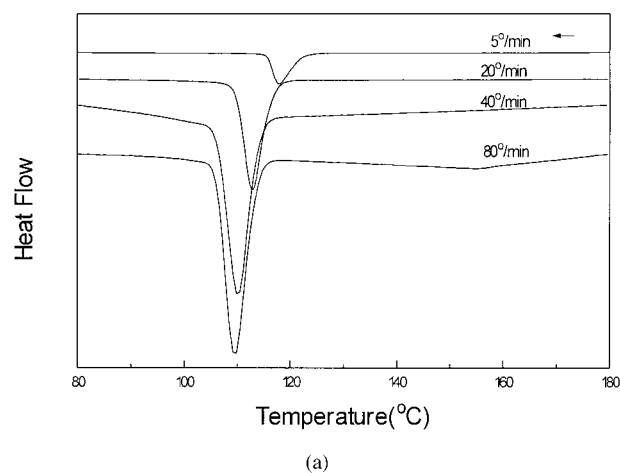

(a)

(b)

Figure 4 Thermographs of iPP sample quickly quenched to 0°C: (a) at different cooling rates; (b) corresponding melting thermographs.

that the crystalline structure of the α-form may show various degrees of disorder in the up and down chain packing with a methyl group: the ordered limiting structure (α_2) having crystallographic symmetry $P2_{1/C}$ and a disordered limiting structure (α_1) having crystallographic symmetry $C2_{/C}$. The α_1-form is the most widely occurring crystal structure for the quenched sample, and the α_2-form can be derived by heating from the recrystallization of α_1-form. By measuring the relative intensity of α-spheralites between crossed polarizers, Qudah[26] has verified the transition from α_1-form to α_2-form. His observations are in accord with our conclusion that double endotherms at lower temperatures come from recrystallization or reorganization.

Melting Behavior of Samples Crystallized at 117°C ≤ T_c ≤ 136°C

In this temperature region the macromolecules have enough time to arrange regularly during the isothermal process, so that the lamellae formed

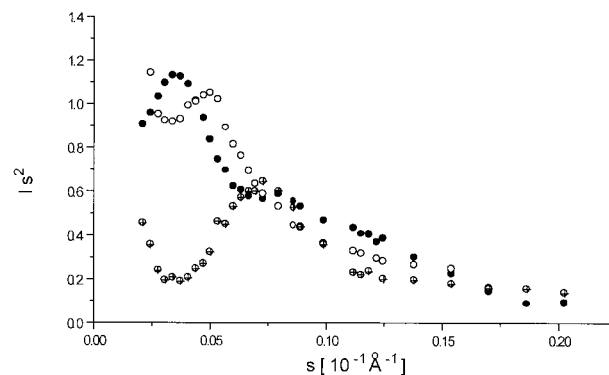**Figure 5** Desmeared and Lorentz–corrected small-angle X-ray scattering curves: (a) quickly quenched to 0°C (⊕); (b) $T_c = 130°C$ (○); (c) at $T_c = 145°C$ (●).
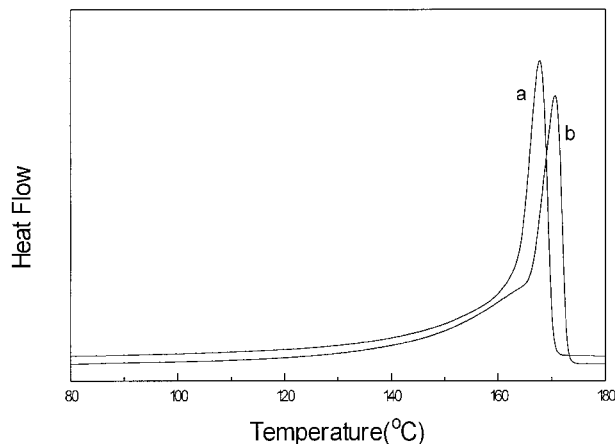
Figure 6 Melting thermographs of iPP sample that was quickly quenched to 0°C, heated to 162°C: (a) and then requenched into liquid nitrogen; (b) annealed at 162°C for 3 min and then requenched into liquid nitrogen.

are more perfect than those crystallized at T_c < 117°C. It seems too hurried for recrystallization (or reorganization) to occur, even at a relatively low heating rate, such as 10°C/min. Figure 5(b) is the SAXS curve of the iPP sample isothermally crystallized at 130°C, which reveals only one peak in the distribution of lamellar thickness. It explains the origin of the corresponding single-melting endotherm. Our transmission electron microscopy observation of this sample also confirmed the similarity of all of the lamellar thick-
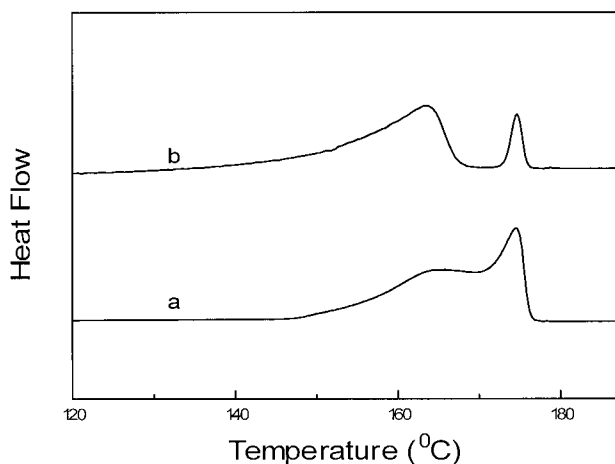

Figure 7 Melting thermographs of iPP sample: (a) isothermally crystallized at 145°C and then quenched to 0°C; (b) isothermally crystallized at 145°C, quenched to 0°C, and then annealed at 170°C for 3 min.
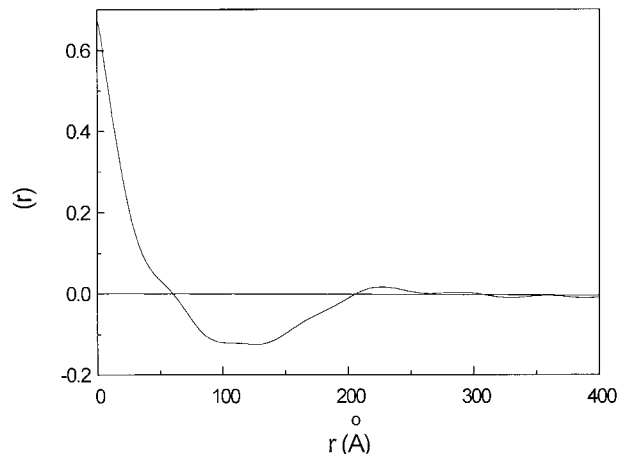

Figure 8 Curve of one-dimensional electron-density correlation function for iPP isothermally crystallized at 145°C.

nesses. This is in agreement with the observation of Cheng,[20] who found that the crosshatched lamellae developed at almost the same time as the radial lamellae in this temperature region, so the lamellar thicknesses were similar.

Melting Behavior of Samples Crystallized at T_c > 136°C

Double-melting endotherms also appear when the crystallization temperature is higher than 136°C. Figure 7(a) is a typical DSC curve, at $T_c = 145$°C. The corresponding SAXS pattern [Fig. 5(c)] exhibits a bimodal distribution with maximum long spacings at 265 Å and 115 Å, and the ratio of the first maximum to the second is not 2. This indicates that two major kinds of lamellae with different thicknesses are present. The one-dimensional electron-density correlation function is shown in Figure 8. Because of the wide distribution of lamellar thicknesses, the self-correlation triangle deviates from a straight line and the most probable spacing is 225 Å.[28,29] Using the permanganic etching technique, Norton and Keller[27] studied the crosshatched feature of iPP and found radial lamellae thicker than tangential lamellae. Later, Cheng[20] proposed that the crosshatched lamellae grew later than the radial lamellae at higher temperatures, thus showing a thinner lamellar thickness. More recently, Mezghani et al.[6] have found that the birefringence of the α-spherulites increases as melting proceeds until reaching a high temperature, which is the direct result of the melting of tan-

gential lamellae; this also demonstrates that radial lamellae are thicker than tangential lamellae. All the aforementioned experimental results show that double endotherms at higher temperatures result from two major, distinct lamellae with different thicknesses.

The annealing experiments provide further evidence of this. If the sample isothermally crystallized at 145°C is annealed for 3 min at 170°C (the temperature between the two melting peaks) and then quickly quenched to 0°C, two melting peaks are also observed, with a highly symmetric peak in the high temperature range as shown in Figure 7(b). Clearly, the thinner lamellae melt and the thicker ones remain during the annealing process. The large peak at the low temperature is produced by the melting of recrystallized lamellae formed in quenching, while the highly symmetric endotherm with a high melting point corresponds to the melting of thicker lamellae.

It is very common that when polymer is crystallized at a relatively high temperature and cooled down to room temperature, a double-melting peak appears because of crystallization during the cooling process (lower melting peak). Kim and coworkers[3] attributed this higher melting peak to the crystal fraction with a molecular size higher than the critical value, and the lower T_m was generated when the molecules with high mobility crystallized on quenching after finishing isothermal crystallization. However, we had noticed that Qudah[26] had done these experiments: (1) the iPP samples were crystallized isothermally at a higher T_c for 22 h and then directly heated to 200°C; and (2) the iPP samples were crystallized at a higher T_c for 22 h, cooled to room temperature, and then heated to 200°C. They found the two thermographs to be almost the same, that is, the double endotherms appeared in both cases. Thus the two kinds of lamellae with different thicknesses are formed during the isothermal process, and the lower melting peak is not the result of the cooling process if the crystallization time is enough long.

Note that the origins of double endotherms of iPP samples are multiple and very complex. Except for recrystallization (or reorganization) and two kinds of lamellae with different thicknesses, several additional factors may also cause the double-melting peak. There is no single reason for the double-melting behavior in iPP; it depends on different crystallization conditions.

CONCLUSIONS

Double-melting endotherms of iPP crystallized at different temperature result from different origins. When the predetermined crystallization temperature is lower than 117°C, spontaneous crystallization occurs just at 117°C during the cooling process; thus, the lamellae formed are imperfect, and the following isothermal process has little effect on crystallization and melting behaviors. At a lower heating rate, recrystallization or reorganization of these imperfect lamellae occurs, which leads to double endotherms. When the crystallization temperature is higher than 136°C, two kinds of lamellae with different thicknesses are developed during the isothermal process. This also results in double endotherms. If the iPP sample isothermally crystallized at 145°C is annealed at a temperature between the two melting peaks, the high-temperature symmetric peak can be separated from its lower counterpart, which further confirms that double endotherms result from two kinds of lamellae with different thicknesses. In the intermediate temperature range the lamellae formed are perfect, and there is only a single peak in the distribution of lamellar thickness; thus only a single-melting endotherm appears in the corresponding thermograph.

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