

Isotactic Polypropylene Crystallized from the Melt. II. Thermal Melting Behavior

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ABSTRACT: Isotactic polypropylene (iPP) isothermally crystallized from the melt was studied by differential scanning calorimetry (DSC) and light transmission measurements techniques. When samples crystallized isothermally above 132°C, α -spherulites were formed only; the DSC measurements showed double melting endotherms peak. The first peak represents the melting of crosshatched lamellae in α -spherulites, while the second peak is correlated to melting of the radial and the reorganized tangential lamellae. Below 132°C the iPP showed a broad melting peak endotherm with a melting tail endotherm at the low temperature side. The light transmission measurements showed that the tail endotherm is due to the melting of β -spherulites and the broad melting peak is due to the melting of α -spherulites. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1267–1271, 1998

Key words: isotactic polypropylene; crystallization; thermal behavior; morphology; α -spherulites; β -spherulites

INTRODUCTION

There has been a lot of research on the melting behavior of isotactic polypropylene (iPP),^{1–7} especially on the origin of its multiple melting peaks. In order to explain the phenomenon of this kind, several models have been proposed. Most authors have attributed the higher melting peak to material reorganized during the differential scanning calorimetry (DSC) scan.^{8,9}

In thick samples containing α - and β -spherulites, Aboulfaraj et al.¹⁰ showed that the two different peaks, at 155 and 170°C, represent melting of the β - and α -forms, respectively. When the appearance of the β -phase has been excluded, recrystallization during the heating process^{8,9} and segregation during crystallization¹¹ have been suggested as possible causes of multiple endotherms. Another explanation for the occurrence of

double endotherms was suggested by Martuscelli, Pracella, and Grispino.¹² They suggested that the double melting peak may be related to the existence of processes of primary and secondary crystallization in the sample. The higher melting peak corresponds to the melting of crystals formed during the process of primary crystallization, while the lower peak corresponds to the melting of crystals grown mainly in interfibrillar regions during the secondary crystallization process.

The purpose of this article is to consider whether or not the multiple behavior of iPP cooled from the melt can arise from the melting and recrystallization of a sample distribution of crystals, or from two phases of α - and β -spherulites.

EXPERIMENTAL

Materials

The material of this study is a homopolymer of iPP originally supplied by Polymer supply and

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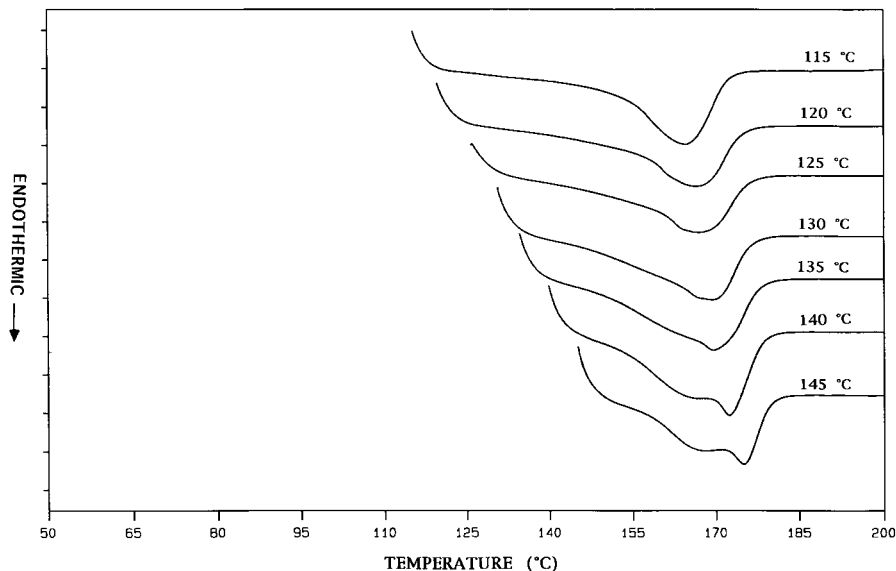


Figure 1 Normalized melting endotherms of iPP samples crystallized isothermally from the melt at different temperatures for 22 h heated from T_c directly.

characterisation centre (PSCC) at RAPRA, Shawbury, UK. Its molecular mass has been measured by PSCC to be $M_n = 4.7 \times 10^4$ and $M_w = 4.2 \times 10^5$.

Differential Scanning Calorimeter

The melting behavior of iPP crystallized from the melt is measured using computerized DSC manufactured by Rheometric scientific (England),

model DSC plus-094. The instrument has nitrogen gas and liquid nitrogen flow lines, the first to achieve an oxygen-free ambient around the sample, and the second for cooling purposes.

For isothermal crystallization from the melt, the samples were first heated to 200°C and held ~ 2 min to obtain crystal-free melt, and then cooled quickly to the crystallization temperature, T_c , and kept there for the predetermined crystallization time, t_c . The lowest T_c used still permitted

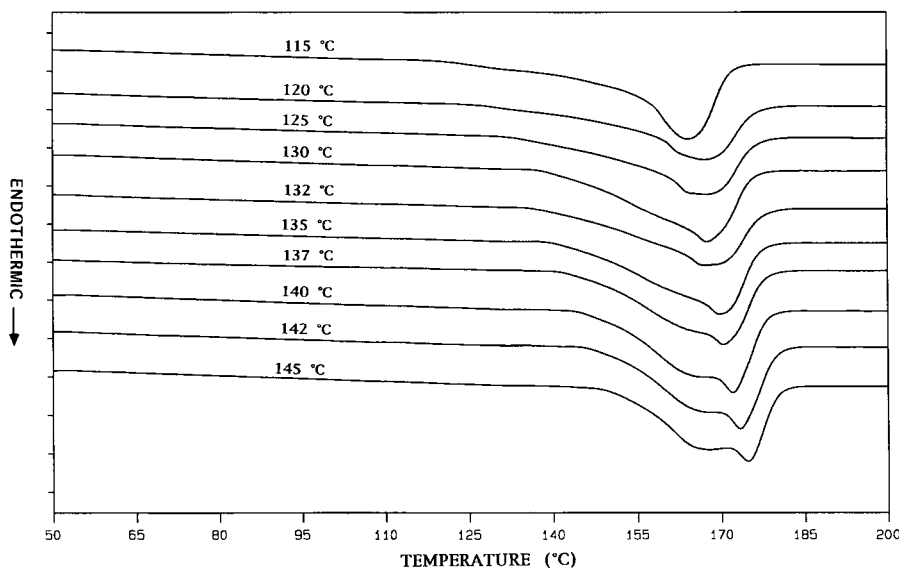
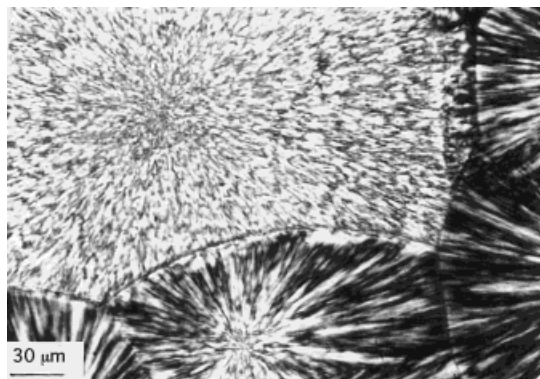
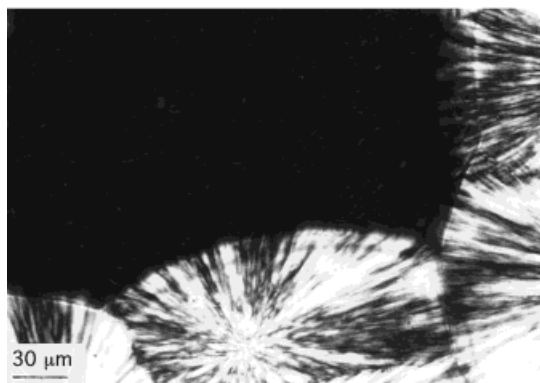


Figure 2 Normalized melting endotherms of iPP samples crystallized isothermally from the melt at different temperatures after cooling to room temperature.



(a)



(b)

Figure 3 Optical micrographs of iPP samples crystallized at 128°C. (a) Showing α - and β -spherulites, (b) showing separate melting of β -spherulite.

thermal equilibration before a noticeable exotherm developed. The isothermal crystallization was followed by cooling quickly to room temperature, then heating to 200°C, or by direct heating without prior cooling to lower temperature.

Optical Microscopy Measurements

The samples for measurements of the relative light intensity between crossed polarizers were made by melting the iPP pellet between glass slide and coverslip. The layer thickness was $\sim 100 \mu\text{m}$. The samples were held for 1 min at 200°C and then quenched quickly to the crystallization temperature. The light microscopic investigations were carried out with a Nikon microscope (Optiphot-Pol) and a mettler (FP82) hot stage that allows observation during isothermal crystal-

lization. The light intensity between crossed polarizers was measured with a photo monitor. A 35-mm camera was used to photograph the spherulitic structure.

RESULTS AND DISCUSSION

Figure 1 shows DSC traces for iPP isothermally crystallized from the melt without cooling at different temperatures for 22 h. At crystallization temperatures of 115, 120, 125, and 130°C the material shows a broad melting peak endotherm with a melting tail endotherm at the low temperature side. As the crystallization temperature T_c increases, the tail and the endothermic peak increase in temperature. Applying a higher crystallization temperature (ranging from 135 to 145°C) produces two melting peaks, and their melting enhances as T_c increases. The heating rate used in these melting runs was 10°C/min, which has been reported as an optimum rate to avoid reorganization or recrystallization influencing the shape and character of the melting endotherm of iPP.¹³

Figure 2 is the same as Figure 1, but in this case the samples were cooled to room temperature before scanning to 200°C. The similarity between the DSC traces in Figures 1 and 2 reveals that the time of the crystallization, 22 h, used was sufficient to crystallize the whole samples for T_c ranging from 115 to 145°C. According to our study

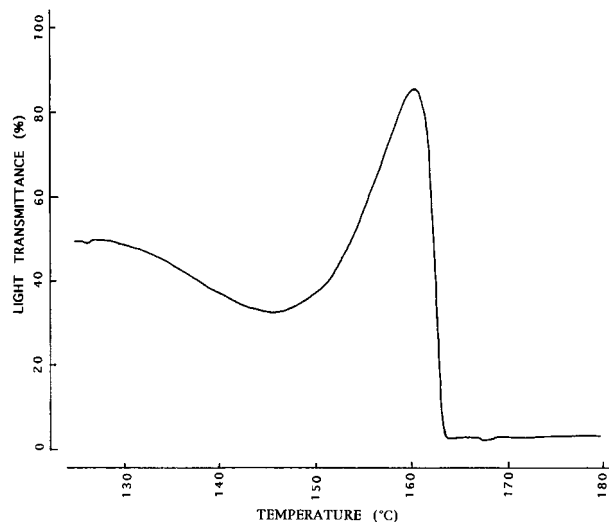


Figure 4 Melting curve of α -spherulite grown at 125°C, scanned at 10°C/min without cooling showing the relative light intensity in an optical microscope using crossed polarizers.

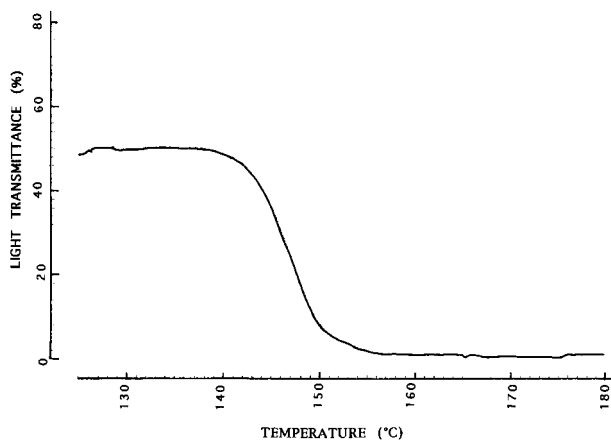


Figure 5 Melting curve of β -spherulite grown at 125°C scanned at 10°C/min with cooling showing the relative light intensity in an optical microscope using crossed polarizers.

in part I, no β -spherulite was found above the crystallization temperature, 132°C. Thus, the source of double-peak shapes should be related to the process involving α -spherulites only. Therefore, the double melting endotherms must be attributed to transitions between different modifications of the α -crystal form. In the literature,^{14,15} the α -form is further classified into two limiting structures by order; a disordered limiting structure (α_1) has a random distribution of up and down chain packing with methyl groups. An or-

dered limiting structure (α_2) has a well defined deposition of up and down helices in the unit cell. The α_1 form is the most widely occurring spherulitic structure, and the α_2 form is derived from the α_1 form by heating.

From the previous study, when the crystallization temperature was below 132°C, α - and β -spherulites were seen in the iPP samples together, and the β -phase represents 10–15% of the crystalline content. In general, the β -spherulites have a larger size than α -spherulites, despite the fact that the β -phase occupies, on the whole, a smaller fraction. Obviously, the melting point of the α -phase is $\sim 12^\circ\text{C}$ higher than that of the β -phase. An optional representation of the melting process is shown in Figure 3. In samples containing α - and β -spherulites, after isothermal crystallization at $T_c = 128^\circ\text{C}$, the two phases are shown in Figure 3(a), while the separate melting of β -spherulites is presented in Figure 3(b). Therefore, one can anticipate that the melting tail endotherm when $T_c < 132^\circ\text{C}$ should be related to the melting of β -spherulites. At this stage we suggest that the main broad melting endotherm peak is composed of two melting peaks due to the recrystallization of the less-ordered α_1 form to a more ordered α_2 form. To confirm the above suggestion, we obtained the melting process of iPP crystallized at 125°C by measuring the relative light intensity of α -spherulites between crossed polarizers applying a heating rate of 10°C/min

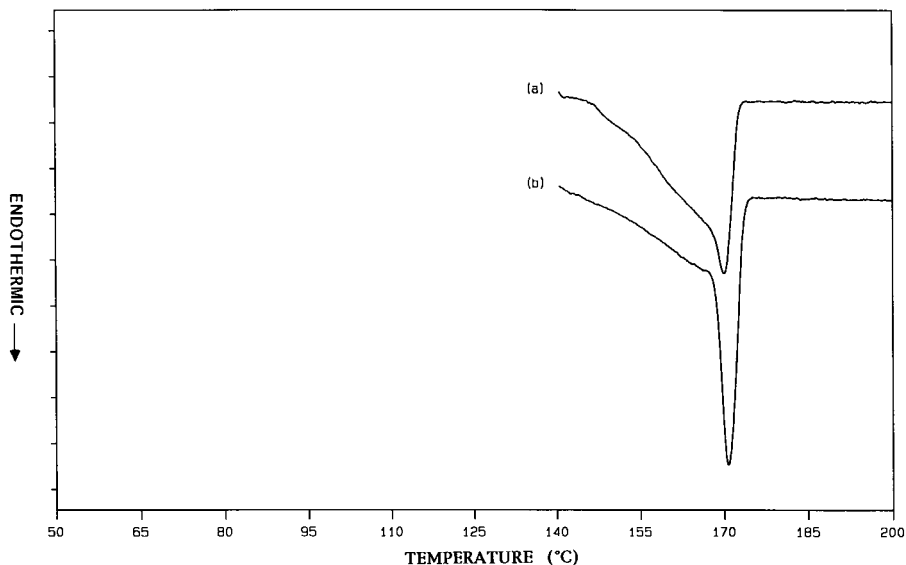


Figure 6 Normalized melting endotherms of melt-crystallized iPP at 140°C for 15 h, scanned at 2.5°C/min. (a) The sample was heated directly from T_c without cooling, (b) heated to 168°C for 1 s, cooled to 140°C, and then heated to 200°C.

(Fig. 4). For the α -phase the melting is reflected in a continuous decrease of the relative light intensity. Shortly before the melting process is finished, an increase in the relative light intensity occurs. In α -spherulites, the crosshatched lamellae grow after the radial lamellae and are thinner (see Fig. 9, part I). Therefore, the relative increase in the light intensity can be explained by a transition from type α_1 to type α_2 spherulites. The transition is related to the melting and recrystallization of the crosshatched lamellae, which are thinner, to form more perfect lamellae.

As revealed from SEM observations in the first part of this study, the crosshatched lamellae in β -spherulites have much lower content in comparison with α -spherulites, and develop at almost at the same time as the radial leading lamellae due to the open structure in the β -spherulites. Therefore, the lamellar thicknesses are similar to each other, so that the crosshatched lamellae in β -spherulites don't reorganize during the heating process, and this can be observed from Figure 5, where the relative light intensity during heating does not show any increment. As seen in part I (Fig. 9), with no β -spherulites the radiating lamellae are thicker than the crosshatched lamellae. Therefore, the lower melting peak temperature corresponds to the fusion of the crosshatched lamellae, while the higher peak corresponds to melting of the radiating lamellae and melting of the reorganized crosshatched lamellae.

Figure 6 shows the melting endotherm of iPP samples crystallized at 140°C for 15 h, scanned at 2.5°C/min. In curve (a) the sample was heated without cooling from 140°C to 200°C, while in curve (b) the sample was heated from 140°C to 168°C for 1 s, at this instant most of the crosshatched lamellae have been melted, and that portion gives the lower melting broad peak in curve (a). The radial lamellae giving the upper melting peak in curve (a) have been recrystallized, and at 168°C, have remained unmolten. The crosshatched lamellae, which melted at a lower melting peak, will now have the opportunity to recrystallize either while holding at 168°C, in which case it will contribute to material melting above 168°C, or upon cooling. This annealing process below the melting point (168°C) leads finally to the increase of the final melting temperature due to thickening of the lamellae.

CONCLUSIONS

The examination of iPP morphology from the melt in part I provides a clear picture of the influence of spherulitic structure on the occurrence of double melting endotherms. The appearance of two melting peaks above 132°C, with no β -spherulites, attributed to two kinds of lamellae, crosshatched and radiating dominant lamellae.

Below $T_c = 132^\circ\text{C}$, the tail endotherm represents the melting of β -spherulite and the broad melting peak was shown to consist of two peaks as established from light intensity measurements, and in this case the broad peak represent melting of crosshatched and radiating lamellae in α -spherulites.

Annealing the sample between the two melting peaks leads to an increase in the final melting temperature due to thickening of the lamellae.

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