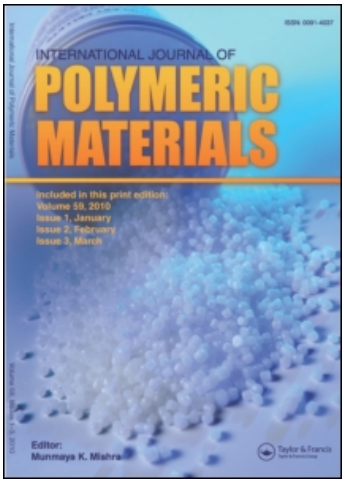

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Spherulitic Morphology of Isotactic Polypropylene and its Melting Behavior

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Spherulitic Morphology of Isotactic Polypropylene and its Melting Behavior

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The crystallization and lamellar morphology of isotactic polypropylene (ipp) have been investigated by thermal analysis and electron microscopy. When ipp samples are crystallized above 132°C, no β-phase was detected and the samples consisted of pure α-spherulites and those showing double melting endotherms, the occurrence of double-peak shapes was attributed to the melting and reorganizing of the radial dominant lamellae, while melting of tangential cross-hatched lamellae belongs to the broad tail endotherm which leads the lower melting endotherm peak.

Keywords: Isotactic polypropylene; Crystallization; Melting behaviour; Spherulites

INTRODUCTION

Isotactic polypropylene (IPP) is known to exhibit several spherulite forms [1–4], namely the monoclinic α-form, the hexagonal β-form and the triclinic γ-form. The α-form is the most stable and prevalent one. The β-spherulite is observed only occasionally during crystallization below 132°C [5, 6] and it appears as a minority constituent of the ipp. When selective β-nucleators are used, higher levels of the β-spherulite can be produced [7, 8]. The γ-modification may form in low molecular weight ipp or in samples crystallized under high pressure.

The melting behaviour of ipp crystallized from the melt has been a complicated issue for quite some time. This is due to the fact that the melting behavior of ipp is affected not only by molecular mass and molecular mass distribution but also by other factors such as

isotacticity and different crystal modifications which includes α, β and γ forms. Experimentally with absence of β-spherulite, the melting behaviour of (ipp) shows double melting peaks. In terms of α-spherulitic structure, the lower melting peak was attributed to the melting of the cross-hatched lamellae and the higher melting peak was attributed to the melting of the radial lamellae [5, 6].

In this paper evidence for lammellar reorganization on heating is observed in α-spherulite when samples are crystallized from the melt. The changes are observed when the samples are partly melted, then recrystallizing, this can occur because melting points are depressed by the lamellar habit according to the Joule–Thomson equation, made explicit for polymer by Hoffman and Weeks [12]. As polymeric solid, generally contain a range of thickness and stability, melting proceeds in stages and it is then possible for a partly molten sample, given time, to crystallize as lamellae thicker than those which had melted. The evidence for lamellar thickening in α-spherulite has come primary from scanning electron microscopy, supported by differential scanning calorimetry.

The aim of this work is to characterize the change of microcrystalline structure of an isotactic polypropylene upon partially melted samples. We attempt to correlate the overall crystallization with melting behaviour through the knowledge of lamellar morphology, so that we hope to achieve a better understanding of crystallization and melting behaviour of (ipp) crystallized from melt.

EXPERIMENTALS

Materials

The materials of this study is a homopolymer of isotactic polypropylene originally supplied by polymer Supply and Characterization Center (PSCC) at RAPRA, SHAWBURY, SHOPSHIRE, UK. Its molecular mass has been measured by PSCC to be $M_n = 4.7 \times 10^4$ and $M_w = 4.2 \times 10^5$. The samples were received in the form of pellets.

Differential Scanning Calorimeter

The melting behaviour of the melt-crystallized (ipp) was examined using a Mettler Differential Scanning Calorimeter (DSC) model FP85.

The samples about 5 mg were melted at 200°C for 2 min in order to eliminate any thermal history of the material, then were cooled quickly to the crystallization temperature T_c and maintained at that temperature for predetermined crystallization time, before heating directly to 200°C at a rate of 10°C/min. However, in another case after the sample was isothermally crystallized from the melt at T_c, it was heated quickly to 155°C for 2 min to melt part of the sample, after that the sample cooled quickly to T_c, then heated without any delay to 200°C at a rate of 10°C/min.

Scanning Electron Microscopy

The lamellar textures of melt-crystallized samples of (ipp) were studied using a Leica Cambridge scanning electron microscope (SEM)(stereoscan 360). Samples were crystallized from the melt in the DSC at 128°C for 30 min, 140°C for 8 hrs and 155°C for 5 days then quenched in cold water. In order to study the effect of the partial melting behaviour on the spherulitic structure, the sample crystallized at 128°C for 30 min, and 140°C for 8 hrs were directly heated to 155°C for 2 min, and for sample crystallized at 155°C for 5 days, it was heated to 159°C for 2 min, then the samples were quenched in cold water. After that, the samples were coated with gold in an automatic sputter coater. Then transferred to the SEM for morphological studies.

RESULT AND DISCUSSION

The scanning electron micrograph given in Figure 1, shows typical view of the microstructure of (ipp) crystallized from the melt at 128°C for 30 min. From this picture α and β phases are easily distinguishable. α ipp spherulites are small and exhibit a dark contrast. On the other hand, β-spherulite in the middle of the figure has larger diameter and appears with a much brighter intensity. β-spherulite is metastable relative to α-spherulite ($T_m = 155$°C *vs.* 170°C), grows upto 70% faster than α-spherulite in a range extending from 141°C to 105°C, and outside this range, the α phase grows faster [13]. Looking down deeply through the crevices between the formed spherulites, one can see spherulites with full symmetry, so that the

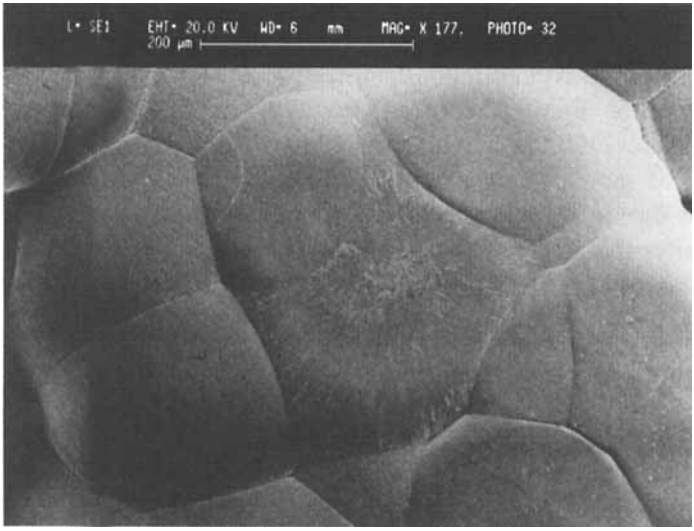

FIGURE 1 Scanning electron micrograph showing general views of spherulitic structure of ipp crystallized from the melt at 128°C.

spherulites are seen down the growth direction. At higher magnification, through the crevices the two types of spherulites are seen to contain different lamellar structures, the lamellae appear as nearly rectilinear and cross-hatched in α-phase, (Fig. 2), while they seem to be sinuous and probably curved in the other type, (Fig. 3).

As shown in Figure 2, α-spherulite exhibits a lamellar branching that is unique among most of the crystallizable polymers. This branching leads to both radial and nearly tangential orientation of lamellae in spherulitic growth. Such lamellar branching manifests itself under nearly all crystallization temperatures. Its impact decreases in melt crystallization below 100°C [13] or above 160°C [14]. The filiation between dominant and cross-hatched lamellae was correctly assigned to eptiaxial interactions in the *ac* faces by Keith and Padden [15] with *a* and *c* axes of one set of lamellae parallel to the *c* and *a* axes of the other set.

Figure 4 shows the DSC endotherms traces of (ipp). Curve a in Figure 4 shows a broad peak of endotherm of melt crystallized ipp at 128°C for 30 min, annealing the same sample at low temperature within the endotherm, such as 155°C for 2 min, followed by

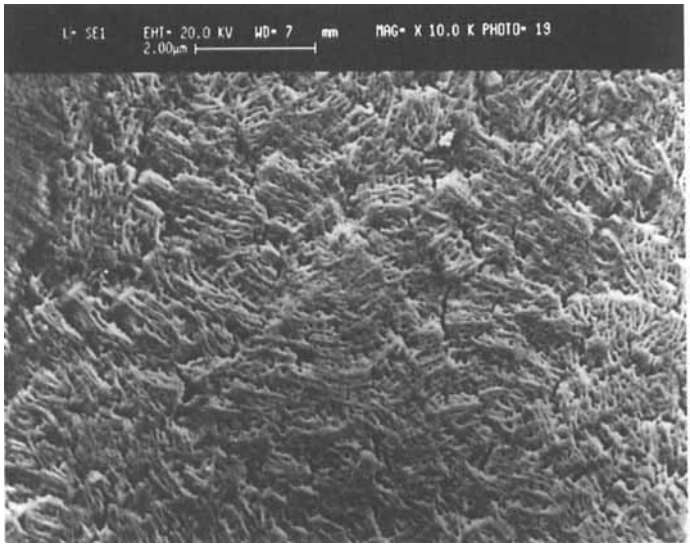

FIGURE 2 Scanning electron micrograph showing cross-hatching structure of α-spherulite for ipp crystallized at 128°C viewed down the a-axis.

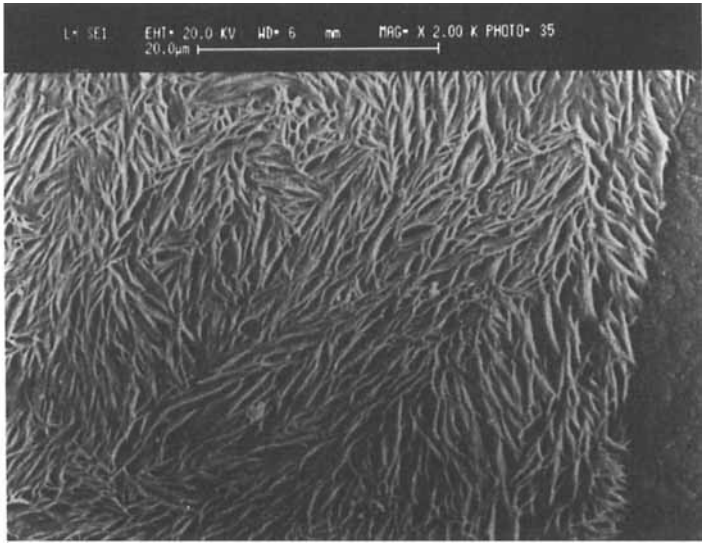

FIGURE 3 The texture of β-spherulite of ipp crystallized at 128°C.

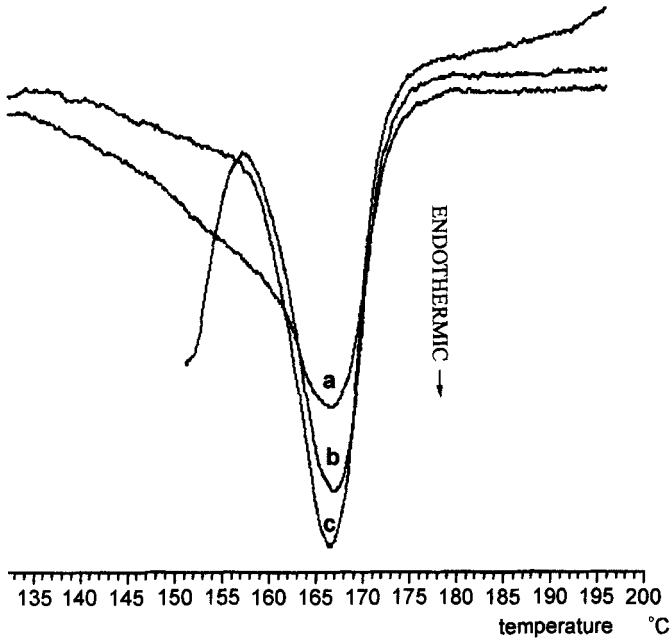

FIGURE 4 Normallized melting endotherms of melt-crystallized ipp at 128°C for 30 min measured at 10°C/min. (a) As crystallized. (b) Annealed at 155°C for 2 min, heated without cooling. (c) Annealed at 155°C for 2 min then cooled to 128°C.

heating to 200°C (Fig. 4 curve *b*), or cooling quickly to 128°C then heating (curve *c*) changes the melting trace so that there is no longer marked melting before 155°C, but at this temperature the new curves rise to accommodate within the old curve. Evidently, the crystalinity of the cross-hatched lamellae which had melted below the annealing temperature has been vanished from the spherulitic structure when the sample crystallized at 128°C and annealed at 155°C for 2 min. The similarity between curve *b* and *c* in Figure 4 reveals that the cooling process to 128°C after annealing at 155°C has no effect on the melting behavior of (ipp).

This trend applies when the (ipp) is crystallized at 140°C for 8 hr (Fig. 5 curve *a*). Once the cross-hatched lamellae are melted after annealing at 155°C then heating directly to 200°C, curve *b*, or cooling the sample to 140°C, curve *c*, upon reheating to 200°C, the double melting behaviour still exists with no broad melting endotherm.

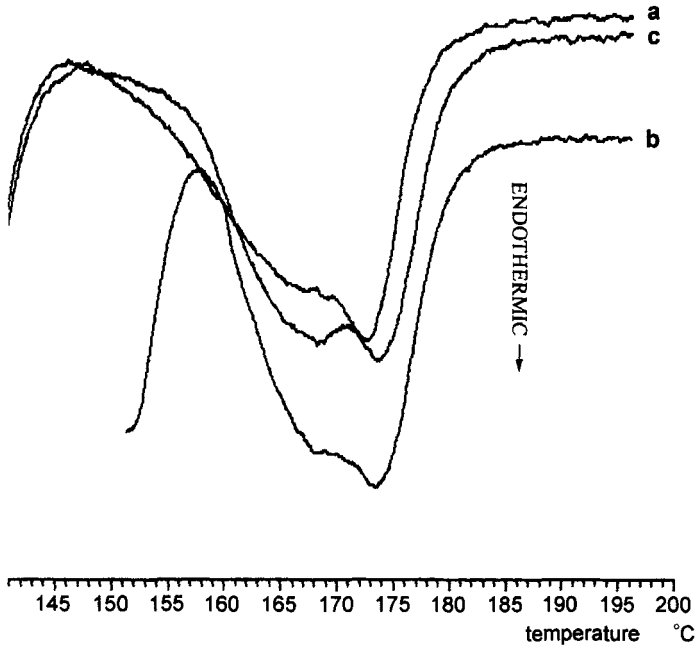

FIGURE 5 Normallized melting endotherms of melt-crystallized ipp at 140°C for 8 hrs measured at 10°C/min. (a) As crystallized. (b) Annealed at 150°C for 2 min, heated without cooling. (c) Annealed at 155°C for 2 min then cooled to 140°C.

It is interesting to note that with no β-phase, the double melting behaviour is not affected by the annealing process at 155°C, therefore the melting of cross-hatched lamellae does not belong to the lower melting peak as one can expect. It can be suggested that the melting of cross-hatched lamellae belongs only to the endotherm of the broad tail which leads the lower melting peak.

This assumption is supported by scanning electron microscopy when the sample is crystallized at 128°C, then heating quickly to 155°C for 2 min, followed by quenching in cold water. The resulting structure (Fig. 6) reveals only the dominant lamellae without any sign to the presence of the cross-hatched structure. At higher magnification (Figs. 7 and 8) for samples annealed at 155°C after crystallization from melt at 128°C and 140°C, respectively, when the cross-hatched lamellae has been excluded from the spherulitic structure, the source of double-peak shape as shown in Figure 5 curve *b*

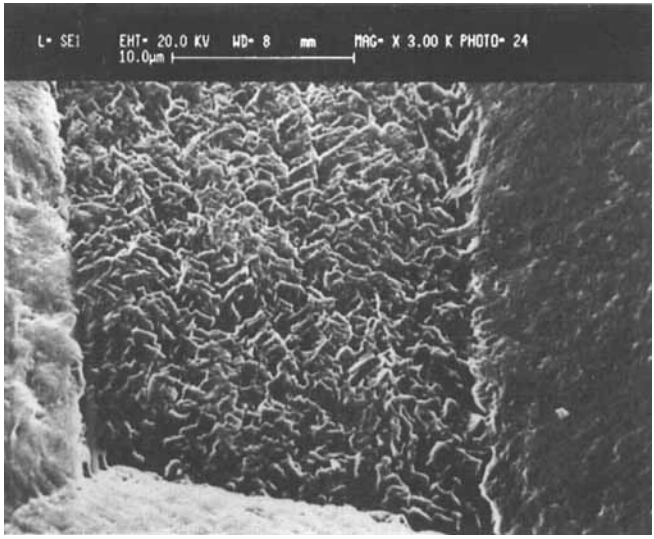

FIGURE 6 Scanning electron micrograph showing α-spherulite inside crevice formed from impingement of spherulites grown at 128°C, annealed at 155°C for 2 min, then quenched in cold water.

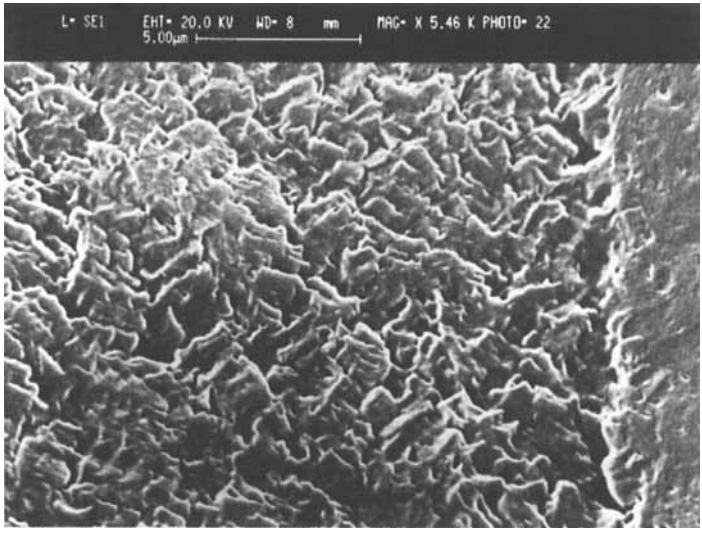

FIGURE 7 High magnification of the crevice shown in Figure 6.

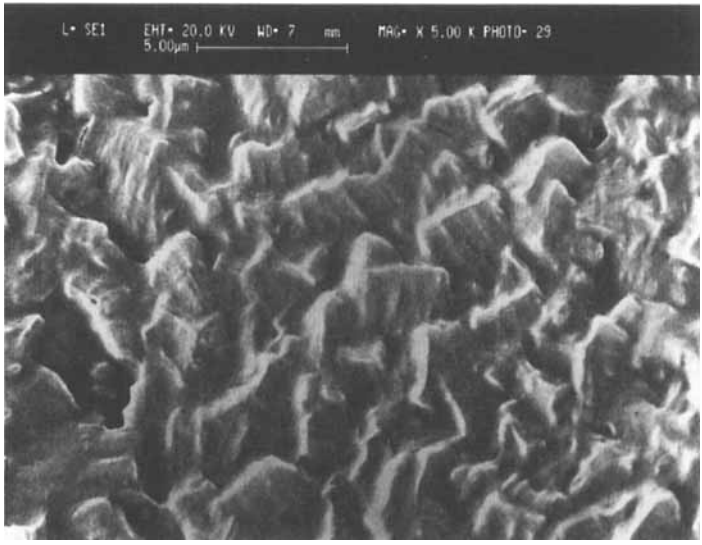

FIGURE 8 α-spherulite showing radial lammellae only, viewed down the *a*-axis. The sample was crystallized from melt at 140°C for 8 hrs, annealed at 155°C for 2 min, then quenched in cold water.

and *c* should be related to processes involving radial lamellae only. In the literature ipp double melting endotherms have been attributed to the transition from type α_1 to type α_2 spherulites [16, 17]. In fact, the two types of α-spherulites proposed by Padden and Keith [1] are distinguishable by the different degrees of cross-hatching. Without the cross-hatched lamellae, the spherulite should be a type α_2. According to that, melt crystallization of ipp samples at 128°C and 140°C, after annealing at 155°C for 2 min as shown in Figures 7 and 8, produces α_2-spherulite since the tangential lamellae are melted and the radial lamellae are only remain apparent.

From both the above observations, melting behaviour and electron microscopy, it is found that the lower melting peak represent the melting of the radial dominant lamellae crystallized isothermally, the upper melting is caused by reorganization of the dominant lamellae during the melting scan, since the heating rate allows the radial lamellae to be annealed and perfected continuously, and consequently attain a certain degree of perfection to become more

thicker, and thus gain a certain degree of stability. As a result, they reinforce the metastability during the heating process and finally melt at higher temperatures.

When we look down the growth direction of α-spherulite (a-axis) for (ipp) sample crystallized isothermally for 5 days at 155°C, the cross-hatching structure is still seen (Fig. 9), and the lamellar thickness of the radial lamellae is greater than that of the tangential lamellae. A spectacular manifestation of the lamellar branching is shown in (Fig. 10) for sample crystallized from the melt at 155°C, where the a-axis lies in the plane of the page. At higher magnification (Fig. 11), in addition to radial lamellae there are two types of the tangential lamellae seen, the first type is sweeping several radial lamellae and approximately has the same thickness as the radial lamellae. The second type is thin cross-hatching lamellae and restricted to lengths between adjacent dominant lamellae. When the sample is heated to 159°C, all of the thin cross-hatching lamellae are melted as shown in Figure 12, but the radial and the tangential sweeping lamellae remain very evident in the spherulitic structure. This is consistent with the

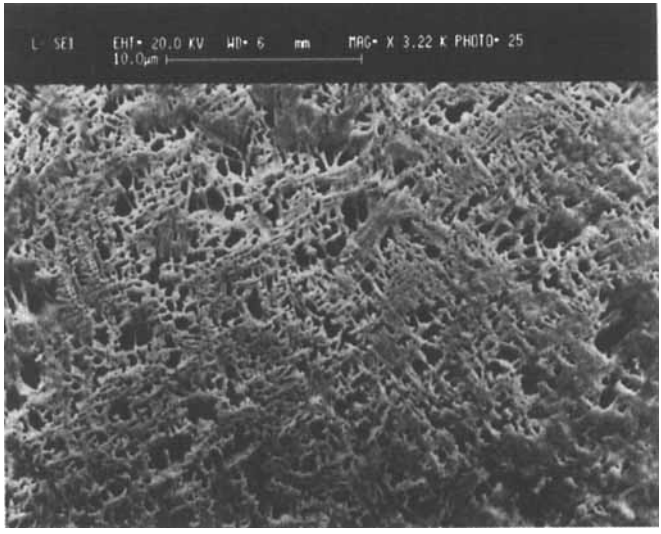

FIGURE 9 Cross-hatching texture of ipp grown from the melt at 155°C for 5 days. Viewed down the a-axis.

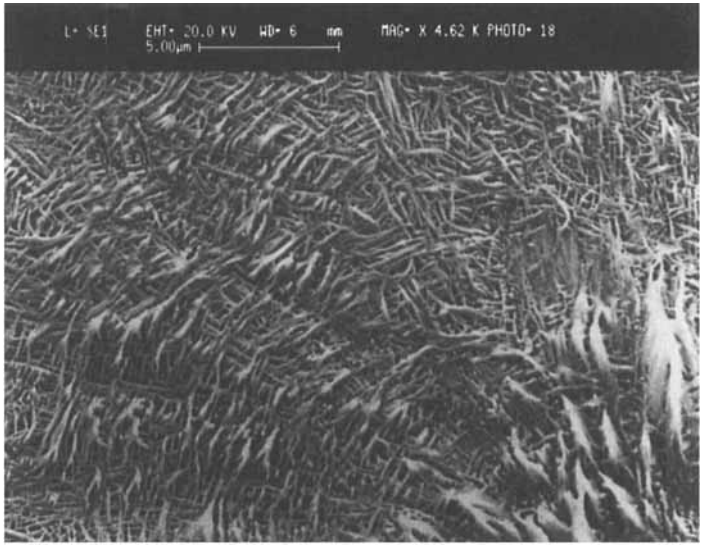

FIGURE 10 Scanning electron micrograph of α-spherulite crystallized at 155°C for 5-days. Note the profuse branching of lamellae at constant 100° or 80°.

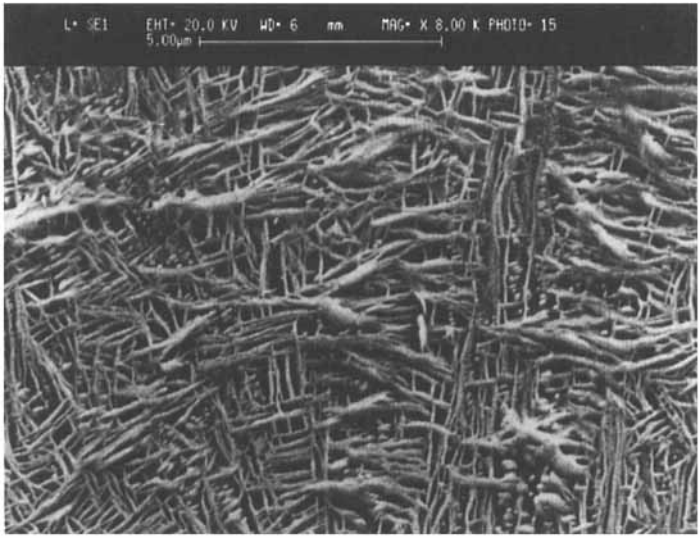

FIGURE 11 High magnification of α-spherulite such as shown in Figure 10. Note that there are three types of lamellae, radial, tangential lamellae sweeping several radial lamellae, and thin cross-hatching lamellae between the adjacent radial lamellae.

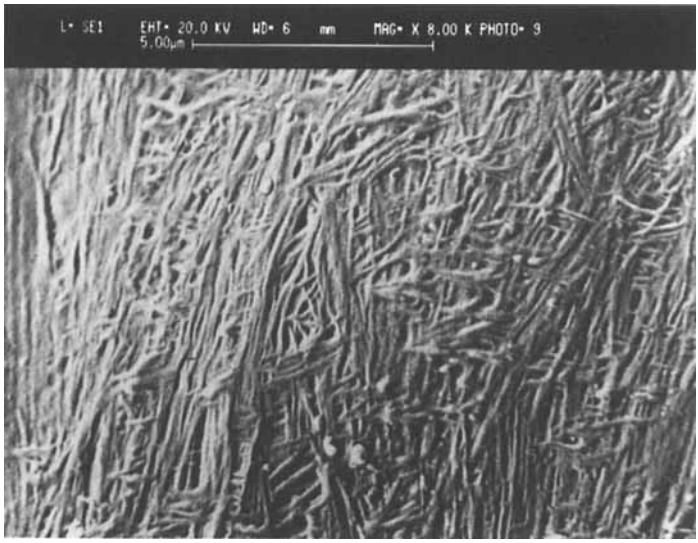

FIGURE 12 Scanning electron micrograph of α-spherulite grown at 155°C for 5-days then annealed at 159°C for 2 min. Note that the thin cross-hatching lamellae are melted from spherulitic structure.

result obtained for samples crystallized at 128°C and 140°C when they are annealed at 155°C.

CONCLUSIONS

On the basis of the results presented above, it is clear that the spherulitic structure of (ipp) depends on the thermal history. Isothermal crystallization from the melt showed that when β-phase is excluded, the spherulitic structure is α_1 type consists of radial and tangential lamellae. Upon annealing the melt-crystallized samples (128°C and 140°C) at 155°C, the tangential lamellae are melted, and the resulting spherulites are α_2 type. The melting behaviour indicates that the melting of the tangential cross-hatched lamellae belong to the low broad melting endotherm tails in the DSC curves. In the case of the double-peaks shape the lower peak was attributed to the melting of the radial lamellae and the upper peak is caused by its reorganization.

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