

Isotactic Polypropylene Crystallized from the Melt. I. Morphological Study

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ABSTRACT: The spherulitic structure of isotactic polypropylene (iPP) from the melt was studied by polarized light and scanning electron microscopy. From the crystallization morphology, it can be observed that crystallization of iPP from the melt below 132°C forms two types of spherulites, termed α - and β -spherulites. The structure of iPP isothermally crystallized above 132°C shows α -type only. The α -spherulites have a complex crosshatched array of radial and tangential lamellar structures, while β -spherulites have, to some extent, simpler lamellar morphology with lower crosshatching content compared with α -type. However, in α -spherulites the radial lamellar thickness is greater than that of tangential lamellae, but in β -spherulites the radial and tangential lamellae have approximately the same thickness. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1259–1265, 1998

Key words: isotactic polypropylene; crystallization; thermal behavior; morphology; optical microscopy; scanning electron microscopy

INTRODUCTION

Isotactic polypropylene (iPP) structure is one of the most complex commercially developed polymeric materials, because it has a number of crystal modifications^{1–4} such as monoclinic (α), hexagonal (β), and triclinic (γ). The appearance of these three structures is critically dependent upon the crystallization conditions.^{5–8} Actually, commercial iPP grades have crystallized mostly in α modification under the usual thermal conditions with only sporadic occurrence of β -modification formed at low crystallization temperature.⁹ However, Varga^{5,6} prepared pure β -modification in the presence of selective β -nucleation agents under appropriate thermal conditions of crystallization. The γ -modification may form in low molecular weight iPP or in samples crystallized under high pressure.^{7,8} Experimentally observed, melting be-

havior of iPP usually shows multiple melting peaks. The appearance of this melting behavior has been attributed to different factors such as two different spherulitic structures,¹⁰ two different crystal sizes,¹¹ and recrystallization and perfection of the poor crystals during heating.¹² However, it was found with no β -phase, the source of double-peak shapes may be attributed to the recrystallization of the less-ordered α_1 -form, with a random distribution of up and down chain packing with methyl groups, to a more ordered α_2 -form with a well-defined deposition of up and down helices in the unit cell.¹³

The purpose of this study, which is presented in two parts, is to correlate the overall crystallization with melting behavior through the knowledge of spherulitic morphology for iPP crystallized from the melt at different temperatures.

EXPERIMENTAL

Materials

The PP samples used in this work are iPP in pellet form supplied by PSCC at RAPRA, UK. Its molec-

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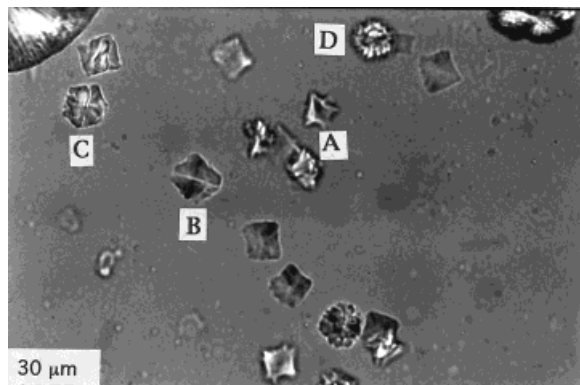


Figure 1 Optical micrograph of iPP sample showing different views of monolayer crystals in early stages of growth at 145°C.

ular mass has been determined, by PSCC, to be $M_n = 4.7 \times 10^4$, and $M_m = 4.2 \times 10^5$.

Optical Microscopy

Samples were prepared by squashing individual pellets between slide and coverslip on a hotplate to the thickness of $\sim 100 \mu\text{m}$. The samples melted under nitrogen flow in a Mettler FP82 hot stage, at 200°C for 1 min, to obtain a crystal-free melt, and then cooled to the crystallization temperature, T_c , and kept there for predetermined crystallization time, t_c . The optical microscopy study was performed on the film specimen while it was on the hot stage at crystallization temperatures without further modification. The resulting objects were observed in the optical microscope under the following conditions: (1) crossed polars, (2) crossed polars with quarter-wave plate, and (3) crossed polars plus compensator.

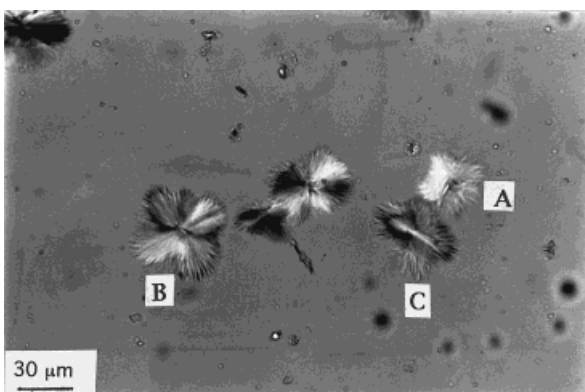


Figure 2 Optical micrograph showing an intermediate stage of growth of iPP at 145°C.

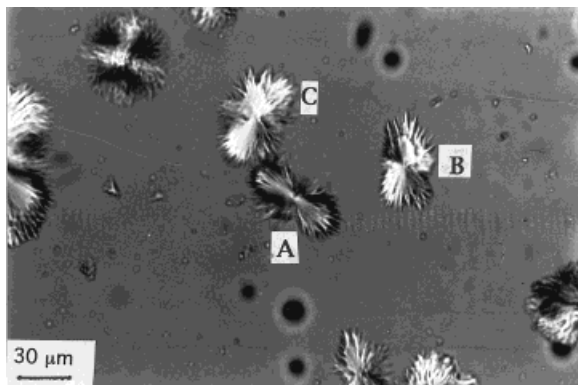


Figure 3 Optical micrograph showing different views of an intermediate stage of growth of iPP at 145°C.

All the resulting objects were photographed by a Nikon 35 mm camera type FX-35 DX and the optical microscope used in this study was a Nikon type (Optiphot Pol).

Scanning Electron Microscopy

The lamellar textures of melt crystallized spherulites of iPP were studied using a Leica Cambridge scanning electron microscope (Stereoscan 360). Samples were prepared for scanning electron microscopy (SEM) in two ways: (1) crystallizing the iPP pellet in the differential scanning calorimetry (DSC) furnace while it is in an uncovered aluminum crucible, and (2) the iPP pellet is squeezed between glass slide and a coverslip on a hotplate, the coverslip then removed and the slide with the iPP film on it is inserted to the DSC hot-stage. In both cases the samples were crystallized at the needed temperature for a predetermined time and then quenched in liquid nitrogen to keep the final structure, followed by sputter coating with gold

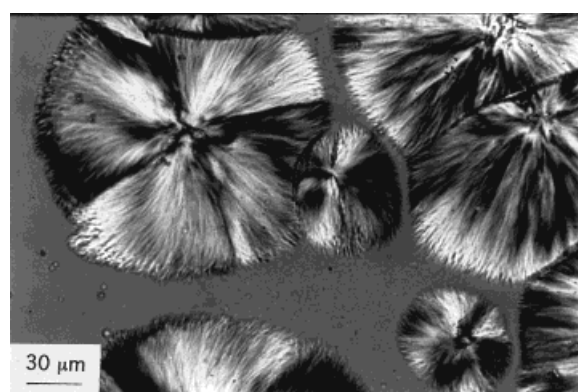


Figure 4 Optical micrograph of iPP sample showing an advanced stage of growth at 145°C.

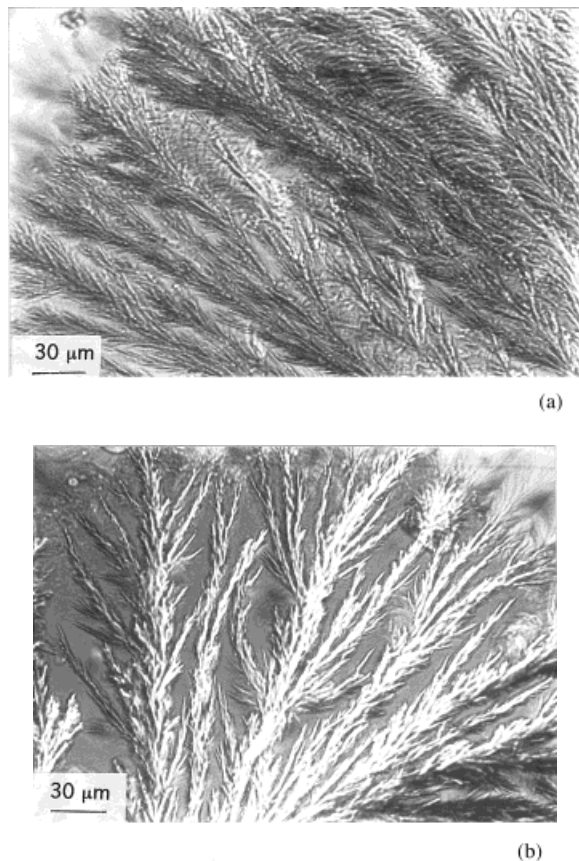


Figure 5 Optical micrograph of iPP sample grown at 132°C. (a) Thin part of the specimen, (b) at the edge of the specimen.

film and then examined by the scanning electron microscope at different accelerating voltages.

RESULTS AND DISCUSSION

Early stages of crystal growth of iPP are seen in an optical microscope for samples crystallized at 145°C for 24 h. Figure 1 shows what is observed in such pictures which are still not a complete objects. In Figure 1 one can see directional views related to an initial square lamella. Below the center there are two square monolayer crystals and their planes parallel to the plane of the picture. Above (A) a similar monolayer appears to change direction by $\sim 25^\circ$. Above (B) an object consists of two parallel monolayers, which may be related to a screw dislocation. With clear inspection of the same object one can see a thinner lamella with normal view to the page. Above (C) there is an object parallel to the plane of the page that appears to have two crossed lamellae perpen-

dicular to the plane of the page, with angle of $\sim 80^\circ$ between them. Such results reveal that the crosshatched morphological pattern, popular at low crystallization temperatures,¹⁴ can be found in the early stages of the growth at a relatively high crystallization temperature (e.g., 145°C). Right of (D) there is an object with multilayers showing development from square habit.

Figure 2 shows an intermediate stage of growth in a different part of the same specimen, the object labeled (A) is observed approximately down the original object plane. As such object develops, four leading groups of lamella grow out from the four sides of the square habit. Object (B), more developed than object (A), begins to spread out of the four sides and starts to have the sheaflike structure. At the bottom sheaf of this object one can see individual dominant lamellae; some of them are approximately parallel and some are splaying apart. For the object seen in (C) the plane is slightly tilted with respect to the plane of the film. Figure 3 shows objects similar to those in Figure 2, object (A) viewed approximately in a perpendicular direction to its plane, which gives a sheaflike section, objects (B) and (C) in the same figure have planes tilted at $\sim 45^\circ$. At the tips of these objects individual lamellae can be identified.

Figure 4 shows more advanced stages of growth for samples crystallized at 145°C for 30 h; the orientation of the original square habit persists in considerable measure to very large dimensions. It shows an object exceeding 150 μm in diameter. In Figure 4, the original square habit of the object lies in the plane of the page. The object is rosette-shaped, with four radiating groups of lamellae. In this case the birefringence rosette must not be confused with the Maltese cross shown by spherulites under linearly polarized light.

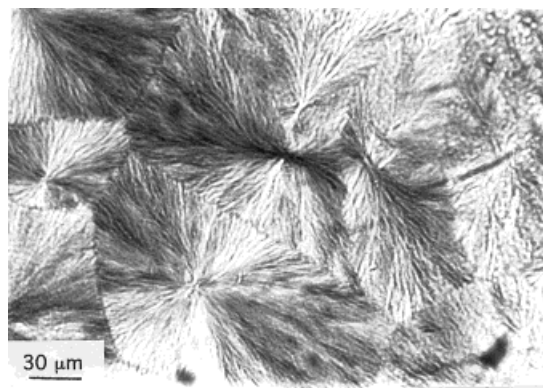


Figure 6 Optical micrograph of iPP sample grown at 105°C.

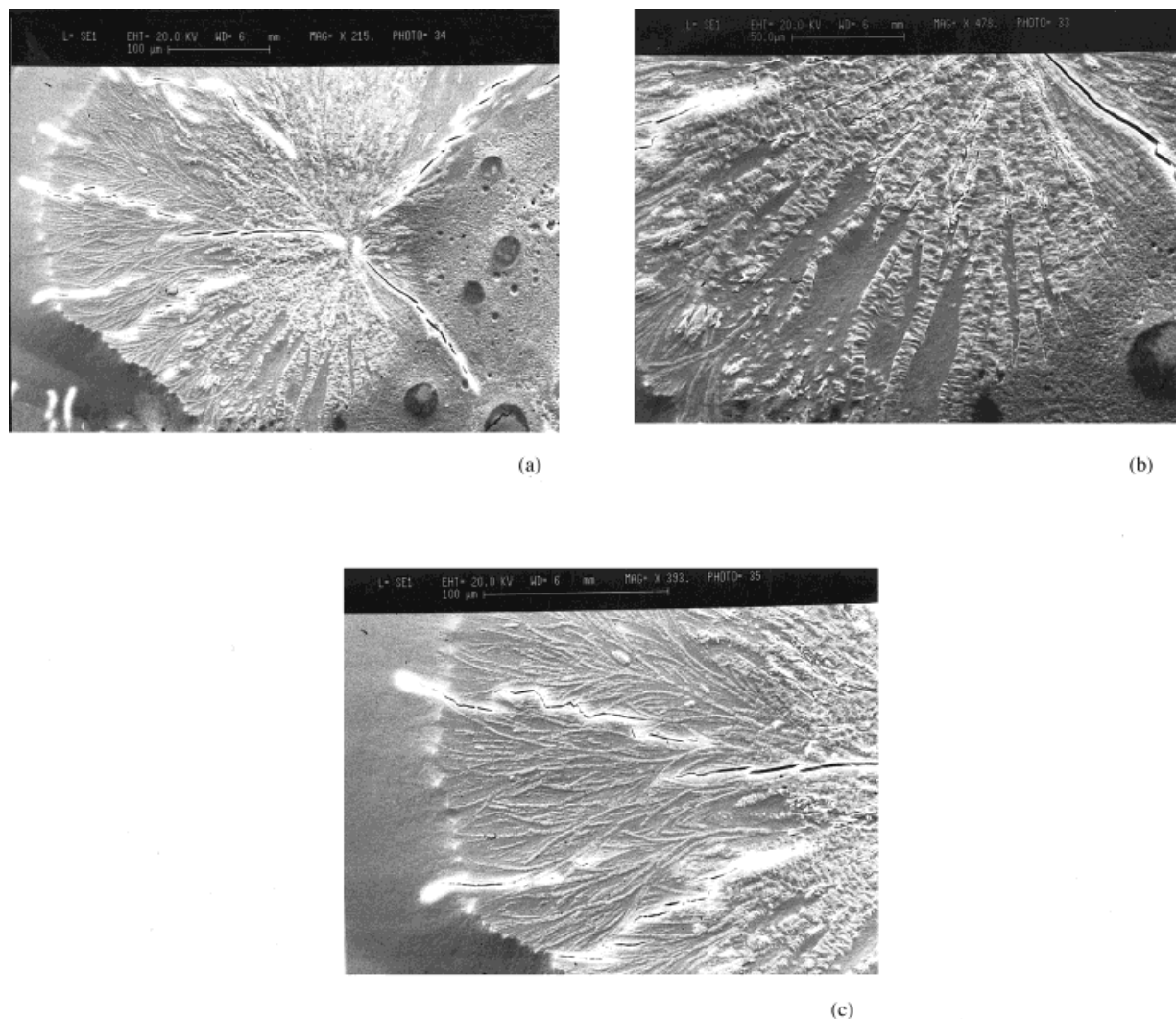


Figure 7 Scanning electron micrograph of α -spherulite at the edge of the specimen grown at 125°C. (a) Low magnification, (b) higher magnification to the lower part of (a), and (c) higher magnification to the left part of (a).

However, the thickness of the sample between the glass slide and the coverslip considerably reduced at the edges due to the material flow during the melting process. In these regions the supply of the crystallizable material is exhausted early, and the objects formed at the boundary of the specimen are immature spherulites with dendritic structures. These objects are crystallized under the same thermal conditions as the spherulites in the melt-rich parts of the sample. Due to the open structure of these objects, more details can be observed than in the spherulites formed in the melt-rich regions concerning the radiating dominant and subsidiary lamellae. The images of such regions for samples crystallized at 132°C are shown in the transmission light micrographs in

Figures 5(a) and (b). The spherulitic structure in Figure 5 is α -type developed by repetitive branching and diverging of lamellae, of branching angles varying from ~ 5 – 40° . The dendritic structure in Figure 5 is similar in appearance to the melt-crystallized poly(epichlorohydrin) dendritic structures grown in thin sections of the film at 80°C,¹⁵ and the monofibrils and small-angle branches of fibrils became visible even by optical microscope.

As the supercooling is increased, nucleation density decreases the spherulitic diameters. Figure 6 shows spherulitic structure of iPP crystallized from the melt at 105°C, formed at the edges of the sample. Due to the lack of crystallizing material at the thin parts of the sample, the formed

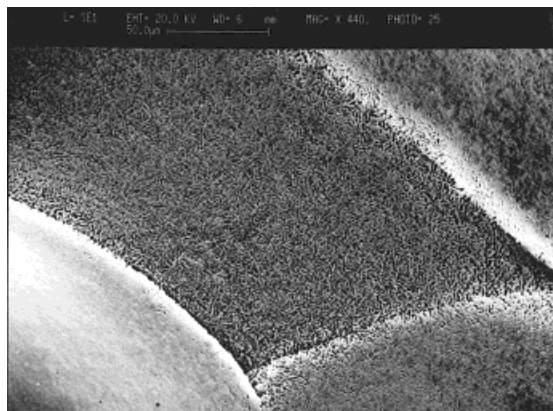


Figure 8 Scanning electron micrograph showing crevice formed from impingement of spherulites grown at 138°C.

spherulites are open and provide clear evidence about branching and deviation from the radiating lamellae. This is demonstrated by the SEM micrographs, Figure 7, which shows a sample crystallized at 125°C for one hour in the hot stage, followed by immediate quenching in liquid nitrogen to preserve the final structure the sample reaches. Figure 7(a) shows α -spherulites formed at the edge of the sample, where the thickness of the sample is small. The picture shows that the crosshatching structure increases as the sample thickness increases, from the left to the right. Figure 7(b) is at higher magnification of the lower part of Figure 7(a), and shows that there are radiating dominant lamellae between short lamellae (cross-hatched) traversing from one dominant lamella to the next. It is consistent with the thin film observations of Padden and Keith¹⁶ which say that the crosshatching lamellae nucleate on the

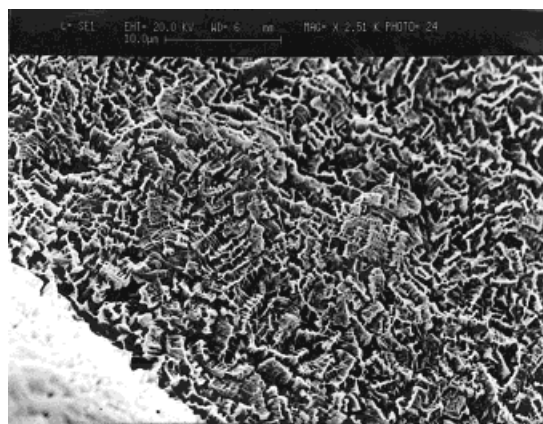


Figure 9 High magnification of the crevice shown in Figure 8.

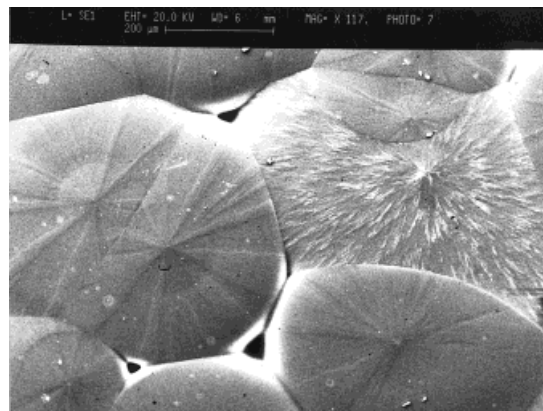


Figure 10 Scanning electron micrograph of iPP sample crystallized at 128°C showing α - and β -spherulites.

side surface of α -lithes and lie in a different plane. This suggestion is also central to the epitaxial relationship of side surfaces giving the angles $80^\circ 40'$ twining angle characteristic of crosshatching. Lotz and Wittmann¹⁷ suggested that the crosshatching lamellae epitaxially grown in iPP occur on the lateral (010) crystallographic plane of the radial lamellae by a satisfactory interdigitation of the methyl groups of facing planes. Figure 7(c) is a view, at high magnification, of the left part of the spherulite shown in Figure 7(a). In this figure three types of lamellae can be identified: dominant, subsidiary, and crosshatched lamellae. There are three basic habits, differing in profiles, of dominant lamellae in this location of the spherulite: (1) planar, (2) slightly curved, and (3) S-shaped lamellae. Such lamellar profiles have been seen previously in melt-crystallized polyethylene.¹⁸ In Figure 7(c), the subsidiary lamellae branch out from the main lamellae at small angles, and continue outward growth until they collide with outer lamellae growing radially. After that, they continue growing radially to maintain the overall orientation.

Figure 8 is a SEM micrograph of melt-crystallized iPP sample at 137°C for 16 h in the DSC. The sample was ~ 1 mm thick, and after the crystallization it was quenched in liquid nitrogen; the surface of the sample was rough due to the crevices between the formed spherulites. During the solidification process the melt has retracted and has gone to feed crystallization of material below the surface. Therefore, the spherulites at the upper surface of the sample do not have spherical symmetry and their top surfaces are flat, while inside the sample the formed spherulites have full symmetry. To see such spherulites, in this case,

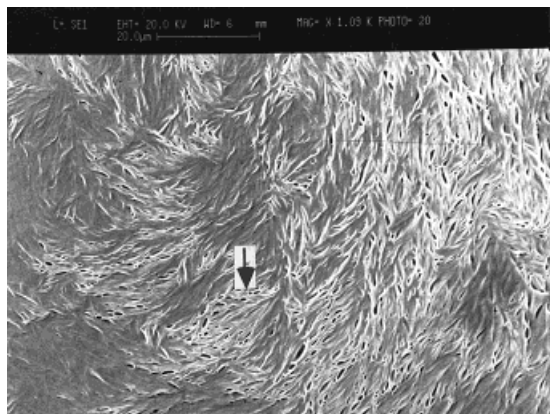


Figure 11 Scanning electron micrograph showing central part of β -spherulite grown at 128°C.

we looked deeply through the crevices, so that the spherulites are seen down the a^* axis (growth direction).¹⁹ Figure 9 shows the spherulite texture inside the crevice, appearing in Figure 8, at higher magnification in this particular region; the vertical look to the sample is down the growing direction (a^* , normal to the page). Through the crevice the contrast of the dominant lamella is increased and the crosshatching between them is highlighted. This allows one to see the crosshatching restricted to lengths between dominant lamellae. It is apparent that the thickness of radial lamellae is greater than that of crosshatching lamellae, as long as the crosshatching phenomenon is observed.

Figure 10 is a SEM micrograph of iPP crystallized from the melt at 128°C. This figure shows two kinds of spherulites. The first is an α -type spherulite with an average diameter $\sim 300 \mu\text{m}$ and exhibits a dark contrast, the second is a β -type spherulite having a larger diameter, $> 400 \mu\text{m}$ diameter in most cases, and appears much brighter in intensity than the α -type. All microscopic observations made in this article suggest that β -type spherulites appear at crystallization temperatures below 132°C, and above that α -type was observed. The proportions of β -type spherulites increases with decreasing the crystallization temperature and it was detected to form sporadically with the α -modification. However, in most cases the β -form does not exceed 15% of the crystallized material. In samples containing both modifications, β -spherulites in most cases have a larger size than α -spherulites, with the concavity oriented toward the α -spherulites. This can be attributed to the higher linear growth of β -spherulite. This difference in growth rate between α - and

β -spherulites was actually verified by Padden and Keith.¹ It appears that the β -spherulite structure is more open and simpler than α -type. Therefore, one can imagine that the faster growth rate of β -type is correlated to their simpler lamellar morphology, compared to the complex crosshatched structure in α -spherulites. The arrangement of the lamellae in β -spherulites is radial with small angles branching, as usually seen in polymeric spherulites. According to Norton and Keller,²⁰ no traces of crosshatched structure was detected. This result disagrees with our finding in β -spherulites, where the crosshatched structure was observed in different parts of β -spherulite, as seen, for example, in the arrowed region of the SEM micrographs (Figs. 11 and 12). However, the crosshatching contents in β -spherulites are much less than those in α -spherulites. On the other hand, SEM observations show that for β -type both radial and crosshatched lamellae have approximately the same thickness, which grow simultaneously.

CONCLUSIONS

Spherulites of iPP crystallized from the melt develop from initial square lamellae by branching probably from screw dislocation and spreading out from four sides to form sheaflike structures. This process continues, producing radiating individual lamellae, within which short lamellae (crosshatched) traverse the distance between two neighboring radiating lamellae, leading eventually to a spherical envelope.

Crystallization of iPP below 132°C produces



Figure 12 Scanning electron micrograph showing edge of β -spherulite grown at 128°C.

both α - and β -spherulites, and above that temperature only α -spherulites form.

Spherulites of the α -form have a more complex structure and higher density of crosshatching lamellae than β -spherulites, which are of open structure and lower density of crosshatching lamellae.

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REFERENCES

1. F. J. Padden and H. D. Keith, *J. Appl. Phys.*, **30**, 1479 (1959).
2. A. Turner-Jones, J. M. Aizelwood, and D. R. Beckett, *Macromol. Chem.*, **75**, 134 (1964).
3. E. J. Addink and J. Beintema, *Polymer*, **2**, 185 (1961).
4. F. J. Padden and H. D. Keith, *J. Appl. Phys.*, **44**, 1217 (1973).
5. J. Varga, *J. Thermal Anal.*, **31**, 165 (1986).
6. J. Varga, *J. Thermal Anal.*, **35**, 189 (1989).
7. H. Awaya, *J. Polym. Sci. Polym. Lett.*, **4**, 127 (1966).
8. A. Turner-Jones, *Polymer*, **12**, 487 (1971).
9. J. Varga, *J. Mater. Sci.*, **27**, 2557 (1992).
10. M. Aboulfaraj, B. Ulrich, A. Danoun, and C. G'Sell, *Polymer*, **34**, 4817 (1993).
11. R. J. Samuels, *J. Appl. Polym. Sci.*, **13**, 1417 (1975).
12. Y. S. Yadav and D. C. Jain, *Polymer*, **27**, 721 (1986).
13. V. Petraccone, G. Guerra, C. De Rosa, and A. Tuzi, *Macromolecules*, **18**, 813 (1985).
14. J. J. Janimak, S. Z. D. Cheng, P. A. Giusti, and E. T. Hsien, *Macromolecules*, **24**, 2253 (1991).
15. K. L. Singfield, J. M. Klass, and G. R. Brown, *Macromolecules*, **28**, 8006 (1995).
16. F. J. Padden and H. D. Keith, *J. Appl. Phys.*, **37**, 4013 (1966).
17. B. Lotz and J. C. Wittmann, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 1541 (1986).
18. D. C. Bassett, *Principles of Polymer Morphology*, Cambridge University Press, Cambridge, 1981, Chap. 4.
19. R. H. Olley and D. C. Bassett, *Polymer*, **30**, 399 (1989).
20. D. R. Norton and A. Keller, *Polymer*, **26**, 204 (1985).