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A comparison of the lamellar morphology of melt-crystallized isotactic and syndiotactic polypropylene

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The lamellar morphology of melt-crystallized thin film spherulites of isotactic and syndiotactic polypropylene (iPP and sPP) has been investigated by transmission electron microscopy (TEM) in phase contrast conditions. It is found that the arrangement and orientation of the lamellae depend on the crystallization temperature. The spherulitic crystallization of iPP has changed from dominant radial to cross-hatched lamellae growth with decreasing crystallization temperature. sPP has shown preferred branched growth at high crystallization temperatures, a radial lamellae growth at an intermediate temperature range and non-spherulitic disordered crystal growth at low temperatures. Copyright © 1996 Elsevier Science Ltd.

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Introduction

In recent years the lamellar morphology and spherulitic supermolecular structures of melt-crystallized isotactic polypropylene (iPP), especially of the monoclinic form, has been investigated by light microscopy[1,2] and transmission electron microscopy (TEM)[3,4]. On the largest scale, i.e. on the level of the polarizing light microscope, there exists a variety of spherulite types distinguished by their different birefringence and shape[5–7]. The morphology on the resolution level of the TEM is also complex. The lamellar morphology of iPP changes from radial lamellae to nearly orthogonal 'cross-hatched' lamellae growth, depending on the crystallization temperature[8].

Also, there is a growing interest in the morphology of syndiotactic polypropylene (sPP). Single crystal-like and spherulitic supermolecular structures have been observed by light microscopy[9,10]. On the level of lamellar resolution, structural investigations on sPP single crystals[11,12] and oriented films[13] have been performed, but studies of the lamellar arrangement of spherulites are still rare and have only recently been published[14].

The present study is a transmission electron microscopic investigation of the spherulitic morphology on melt-crystallized thin film samples of iPP and sPP. Depending on the crystallization temperature, the growth of lamellar crystals of both stereoregular polypropylenes has been observed and compared. The crystallization behaviour at very low undercooling of both the polymers differs significantly and will be treated in a separate paper.

Experimental

The iPP used in the experiment was Novolene 1100H (BASF AG Ludwigshafen, Germany). The sPP was kindly supplied by the Fina Oil and Chemical Company. Thin films of both polymers were solution-cast from a 0.1 wt% solution in xylene on the surface of glycerin at different temperatures. The isothermal crystallization temperature is established as the measured temperature of the glycerin, but in our thin film preparation the crystallization temperature may differ from the actual one by approximately 10°C. The films were mounted on copper grids and used directly for TEM observations. A Philips CM200 electron microscope, operated at 200 kV and equipped with a Gatan slow-scan CCD camera, was used for the investigations of the morphology of these samples. The images were printed directly without digital processing of the raw data.

Results and discussion

Figure 1 shows, for comparison, electron brightfield micrographs of the spherulitic supermolecular structures of melt-crystallized thin film samples of iPP. At each crystallization temperature single spherulites are visible and the diameter of the spherulites decreases with decreasing crystallization temperature. Crystallized at high temperatures, the iPP sample contains many holes (*Figure 1a*), because casting the polymer solution on the surface of the glycerin yields high mobility and non-stability of the polymer film. *Figure 2* represents high magnification electron micrographs of the lamellar arrangement of iPP crystallized at the different temperatures. Using phase contrast in underfocus conditions, the darker contrast correlates to the higher density or crystalline areas and the brighter contrast to the lower density or amorphous areas. Isothermal crystallization of iPP at 130°C (undercooling of 40°C) results in preferred radial, straight, long lamellar crystals (*Figure 2a*). Only a few short, tangentially grown, secondary lamellae are visible. When the crystallization temperature decreases to 90°C (undercooling of 80°C), the morphology changes dominantly to the so-called 'cross-hatched' lamellae growth (*Figure 2b*). A homoepitaxial deposition of tangentially grown lamellae on radial crystallized lamellae is characteristic for this

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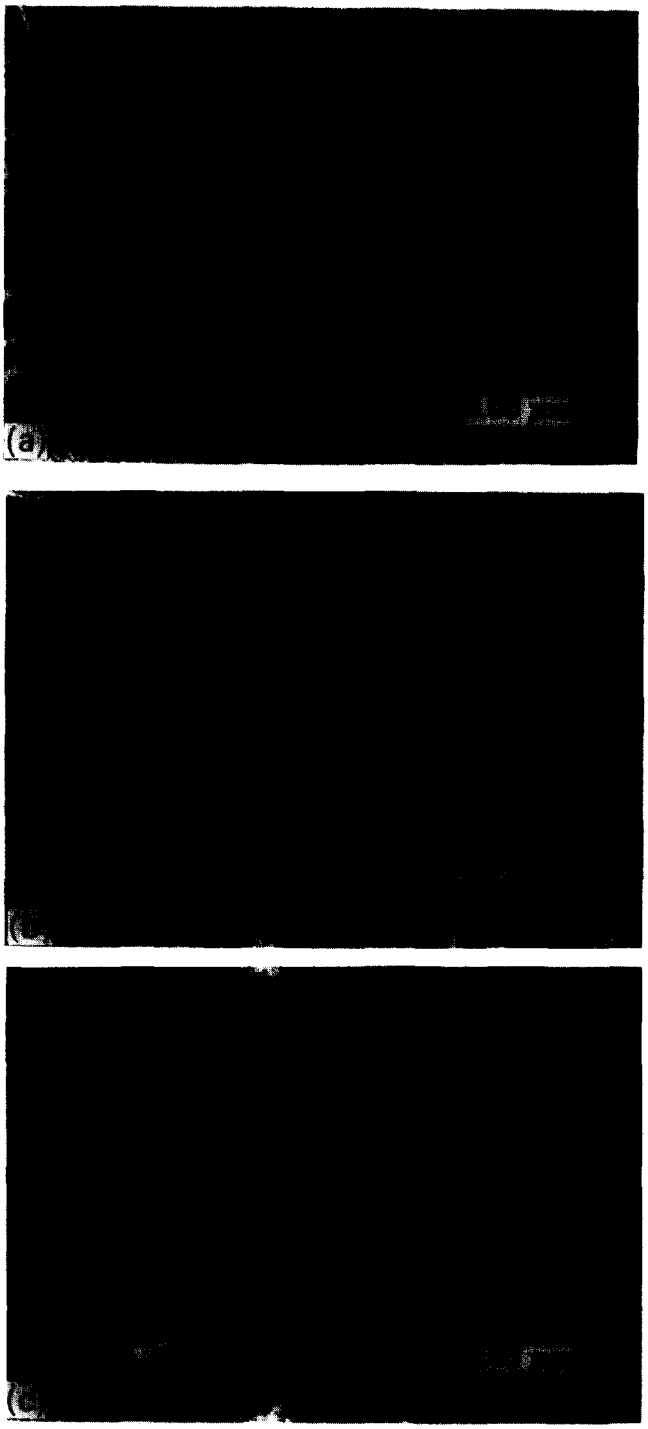

Figure 1 Spherulitic supermolecular morphology of iPP at low magnification. Isothermal crystallization temperatures: (a) $T_C = 130°C$; (b) $T_C = 90°C$; (c) $T_C = 50°C$

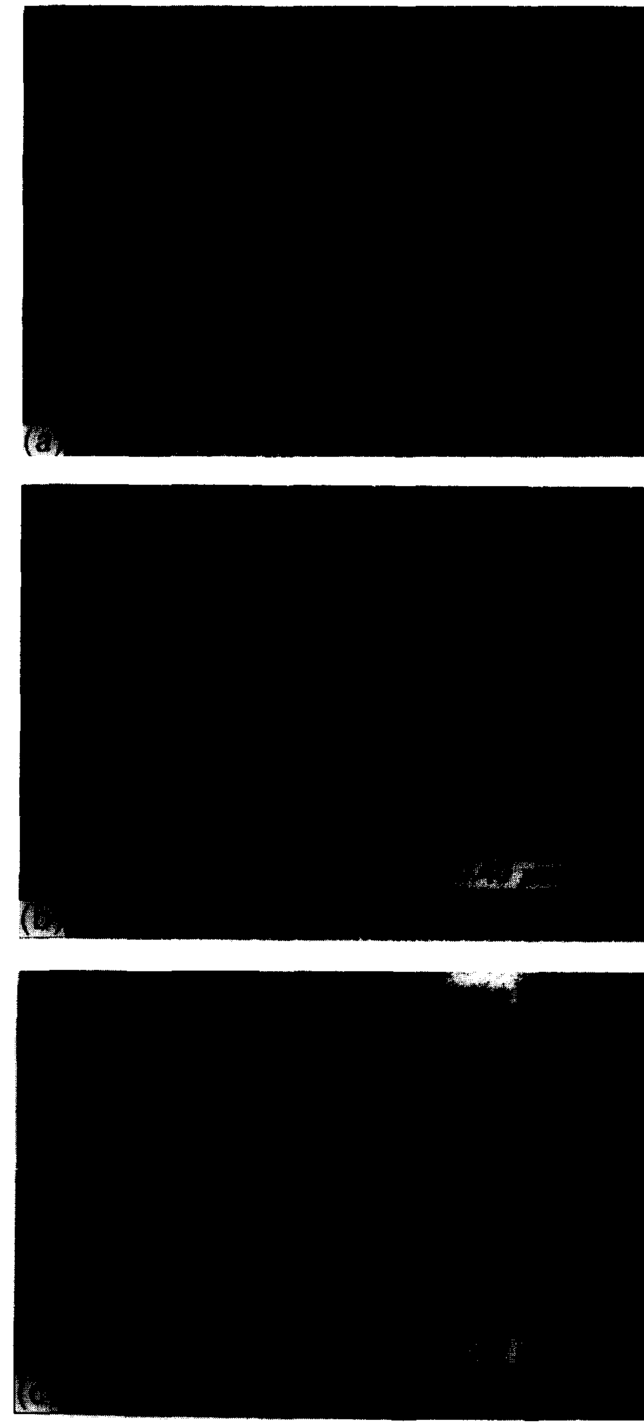

Figure 2 Different lamellar arrangements of iPP at high magnification. (a) $T_C = 130°C$; (b) $T_C = 90°C$; (c) $T_C = 50°C$

morphology[15]. The crystal branch angle of approximately 80° corresponds to parallelism of the *a* and *c* axes in the monoclinic modification of one lattice with the *c* and *a* axes, respectively, of the other. With isothermal crystallization at 50°C (undercooling of 120°C), thin lamellar crystals are visible (*Figure 2c*) and, almost quenched from the melt, nucleation and crystal growth of iPP result in small separated spherulitic supermolecular structures. All the iPP morphologies have exhibited α-modification, indicated from the electron diffraction pattern with its four intense Debye–Scherrer rings.

Figure 3 shows a sequence of electron micrographs of the spherulitic morphology of melt-crystallized sPP. At high crystallization temperatures (*Figure 3a*), as well as at intermediate crystallization temperatures (*Figure 3b*), single sPP spherulites are observable. The morphology at low crystallization temperatures shows, in contrast to iPP, no spherulitic growth (*Figure 3c*), only uniform accumulation of areas of different contrast without recognizable growing centres.

The spherulitic morphology of sPP crystallized at 100°C (undercooling of 40°C) shows predominant branched lamellae growth (*Figure 4a*). Comparable to iPP, an angle of branching is proposed for homoepitactic crystallization of sPP[16], but the

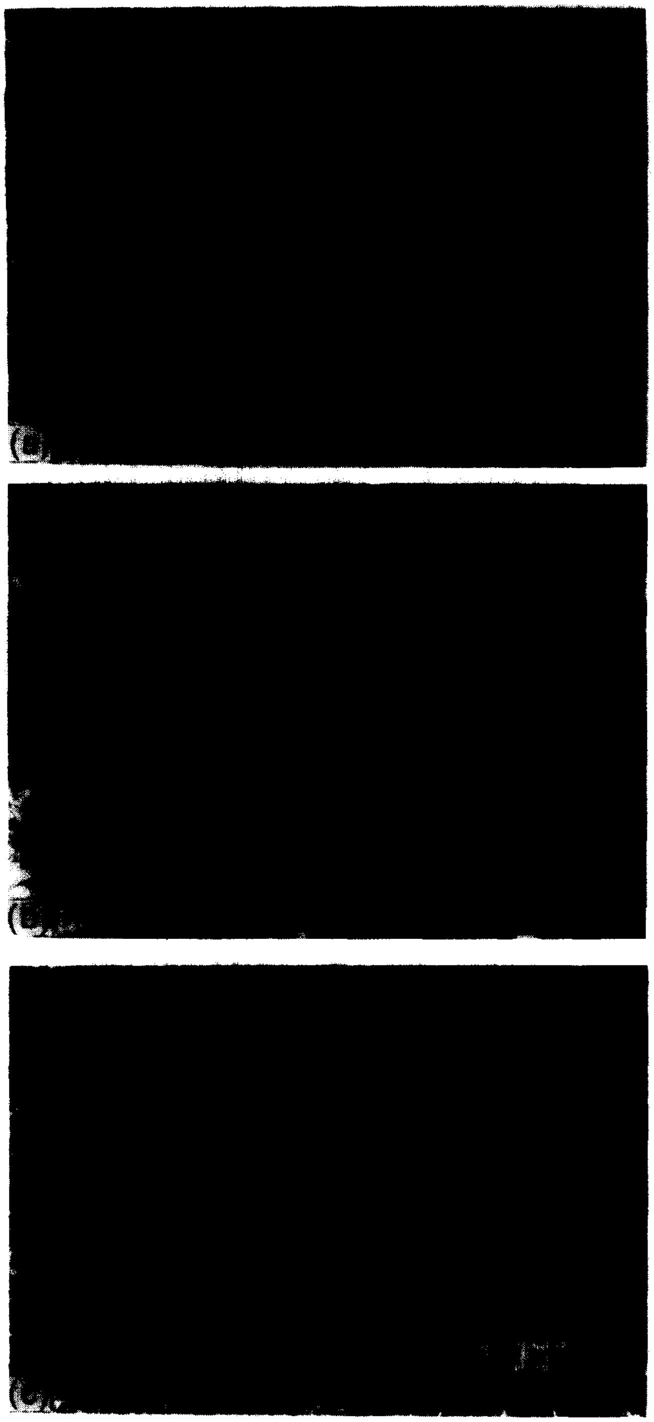

Figure 3 Spherulitic supermolecular morphology of sPP at low magnification: (a) $T_C = 100^\circ C$; (b) $T_C = 90^\circ C$; (c) $T_C = 50^\circ C$

Figure 4 Different lamellar arrangements of sPP at high magnification: (a) $T_C = 100^\circ C$; (b) $T_C = 90^\circ C$; (c) $T_C = 50^\circ C$

lamellae branching in the samples investigated shows several different contact angles. With crystallization at 90°C (undercooling of 50°C), the lamellar morphology of sPP changes (*Figure 4b*). Straight long lamellae of two different spherulites are visible and the investigation of the brightfield micrograph reveals the absence of any branching. When the isothermal crystallization temperature decreases to 50°C (undercooling of 90°C), the lamellae growth behaviour changes again (*Figure 4c*). Accumulations of short and branched lamellar crystals grow closely and, in comparison to *Figure 3c*, no spherulitic supermolecular structure is observable. A very high amount of nuclei and a high crystal growth rate characterize this crystallization behaviour.

The results, described and discussed above, have to be considered under the restriction that the morphology formations appear from solution-cast films and may differ from bulk crystallization. But a strong relevance to bulk crystallization is very likely, as in our observations the morphologies of the iPP correspond closely to those of other published data on bulk crystallization.

Conclusion

The comparison of melt-crystallized thin film iPP and sPP shows different crystallization behaviour, depending on the isothermal crystallization temperature. iPP shows a transition from straight grown lamellae to 'cross-hatched' morphologies with decreasing crystallization temperature. The crystal growth behaviour of sPP changes from branched to straight and again to branched lamellae growth and, at high undercooling, a spherulitic supermolecular structure of sPP is not visible.

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