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ORIGINAL CONTRIBUTION

J. Varga
G.W. Ehrenstein

High-temperature hedritic crystallization of the β-modification of isotactic polypropylene

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Dr. J. Varga (✉) · G.W. Ehrenstein
Friedrich-Alexander-Universität
Erlangen-Nürnberg
Lehrstuhl für Kunststofftechnik
Weichselgarten 9
91058 Erlangen, Germany

Abstract High-temperature crystallization of the β-modification of polypropylene (β-iPP), induced by an active β-nucleating agent, was studied by polarizing light and scanning electron microscopy (SEM). It was established that, in the early stage of crystallization of β-iPP, hedrites were formed as precursors of the spherulitic crystallization. Hedrites seen flat-on are characteristic hexagonal formations (hexagonites) with low birefringence. The central core of hedrites had positive birefringence. Hedrites seen edge-on were rod-like formations with strong negative birefringence which would transform into a radially symmetric spherulitic form through sheaf-like and then oval (ovalite) arrangements. According to the SEM micrographs, hedrites are clusters of multilayer lamellar crystallites. On the surfaces of lamellae hexagonal etch pits appear referring to screw dislocations. They are responsible for branching and proliferation of lamellae. Hedrites may reach considerable sizes (several hundred micrometres) presumably due to a coordinated cooperative growth of lamellae. There is an unequivocal correlation between the character of birefringence and the morphological structure shown by SEM of hexagonites, rods, ovalites and spherulites. It was demonstrated that, at temperatures of isothermal crystallization higher than the critical $T(\beta\alpha)$, mixed polymorphic structures of α- and β-modifications were formed.

Key words Polypropylene – β-nucleation – spherulite – hedrite – hexagonite – ovalite – β to α growth transition – polarizing light microscopy – scanning electron microscopy

Introduction

The investigations on the preparation and on the properties of the β-modification of isotactic polypropylene (β-iPP) have been intensifying in the last decade due to the ascertainment of more efficient new β-nucleating agents [1, 2]. The presence of active β-nucleating agents makes it possible to study the high-temperature crystallization of β-iPP at a low extent of supercooling and to reveal its more detailed supermolecular structural characteristics. β-iPP crystallizes into spherulitic structure. According to an early observation of Padden and Keith [3], depending on the temperature of crystallization, negative radial or negative banded (or ringed) β-spherulites are formed during the melt crystallization. Morphological feature, kinetics of growing, and the formation of β-spherulites structure (apart from its very early stage) were essentially discovered [1, 2 and references in them].

The spherulitic crystallization of β-iPP was investigated at a relatively high extent of supercooling since its formation was detectable only under these conditions. Few data are available in the literature for the high-temperature crystallization of β-iPP [4–7]. Some characteristics of the high-temperature crystallization of β-iPP were revealed by means of stepwise isothermal crystallization [2, 4, 5]. In this regime, the further growth of β-spherulites formed at a lower temperature was studied at a higher temperature step. A crossover temperature was found, $T(\beta\alpha) = 140\,^{\circ}\mathrm{C}$, above which the feature of the spherulitic growth was changed. It was established that if the second temperature step of a stepwise crystallization was higher than $T(\beta\alpha)$, α-nuclei were formed on the growing fronts of β-spherulites and propagated into α-spherulitic segments ($\beta\alpha$-transition of growth). These α-spherulitic segments successively blocked up the room for further growth of the β-spherulite [2, 4, 5], resulting in characteristic $\beta\alpha$-twin spherulites. The frequency of formation of α-nuclei increased considerably with elevating the temperature of crystallization, T_c. This phenomenon is readily reproducible as supported later by Fillon et al. [7]. The temperature $T(\beta\alpha)$ has an essential kinetic aspect. The growth rate of α-modification (G_α) becomes equal to that of β-modification (G_β) just at $T(\beta\alpha)$. Above this temperature, G_α is higher than G_β [1, 2, 4, 5]. This statement was confirmed by Shi et al. [6] by the determination of the growth rate of β-iPP at high temperatures, in the presence of active β-nucleating agents while no $\beta\alpha$-transition was mentioned. It should be noted that the kinetic requirement of the $\beta\alpha$-transition of growth, i.e. $G_\alpha > G_\beta$, was met only above $T(\beta\alpha)$ [4]. This change in the growth rate ratio between the α- and the β-modification as well as the appearance of a $\beta\alpha$-transition above $T(\beta\alpha)$ seemed to support the assumption that the temperature $T(\beta\alpha)$ might be regarded as the principal upper limit temperature of the formation of β-iPP [1, 2, 5].

According to our optical microscopic studies on the high-temperature isothermal crystallization of polypropylene in the presence of an active β-nucleating agent, a hedritic structure was formed which was easily resolved on the optical level. It is worth mentioning that accidental occurrence of β-hedrites was referred in the literature earlier [2, 8, 9]. Hedrites are regular polygonal formations composed of lamellar crystallites. They are transient arrangements between polymeric single crystals and spherulites [9].

The spherulitic crystallization is a general feature of polymers while the formation of hedrites is rare. One of the most comprehensively studied example is isotactic polystyrene [10–12] which forms hedritic structures in a wide range of temperature as revealed by polarized light (PLM), transmission (TEM) and scanning electron microscopy (SEM).

In the present paper, polarized light and scanning electron microscopic investigations on *the high-temperature hedritic crystallization of β-iPP* are presented.

Experimental

The experiments were performed with a commercial homopolymer of propylene, Tipplen H523 (Tisza Chemical Works, TVK, Tiszaújváros, Hungary). Dehydrated calcium pimelate was used as the β-nucleating agent [1, 13] which is capable of producing the pure β-modification of iPP under appropriate conditions. The concentration of the nucleating agent was 0.01–0.5% by weight. Polymer films of 10–40 μm thickness were used as test samples, moulded between two glass plates after heating at 220 °C in order to eliminate the thermal and mechanical history of the sample. Morphological characteristics of crystallization were studied in polarized light by means of a Dialux 20 (Leitz) microscope equipped with a Mettler FB82 type hot stage. The feature of optical birefringence was determined by a first-order red filter (λ-plate). The events of crystallization were recorded to coloured slides. The present paper shows their black-and-white copies.

Scanning electron microscopic investigations were conducted by means of a Cam Scan CS 24 instrument, for the more comprehensive discovery of the sub-structure of hedrites. Test samples had been crystallized isothermally between two glass plates. At certain stages of crystallization, the samples were suddenly quenched by placing them on cold metal plates. This technique fixed the momentary structure of hedrites embedded into a microcrystalline environment. The samples were etched by the method of Olley and Bassett [14, 15] with potassium permanganate at room temperature for 24 h.

Experimental results and discussion

Optical microscopic studies of the hedritic crystallization

In the early stage of the high-temperature isothermal ($T_c = 130$–$143\,^{\circ}\mathrm{C}$) crystallization of β-nucleated iPP, formations of β-modification are produced with different shapes, mainly "*hexagonites*" (hexagonal plates with weak birefringence), "*rods*" (needle crystals with strong negative birefringence) and "*ovalites*" (oval formations developed from the needles) as shown in Figs. 1–3. Depending on T_c, α-spherulites of negative or mixed optical character are also formed at lower or higher proportions as a concomitant phase. It should be noted that the conventional definition of the sign of birefringence is based on the differences in refraction indices between the longitudinal and transversal direction for the rod-like crystal and between radial and tangential directions for the spherulites. Now the signs of birefringence of ovalites and hexagonites are given upon the convention for spherulites. Since the refraction index is generally higher in the direction of polymer chains than in

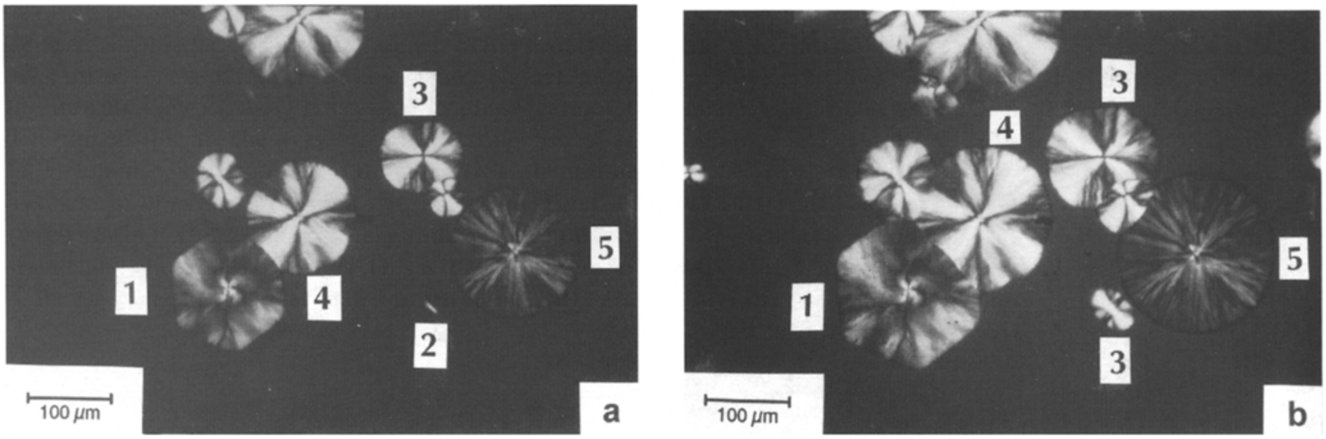


Fig. 1 Formations of various shapes and their growth in β-nucleated iPP samples (a) $T_c = 135\,^\circ C$, $t_c = 50$ min; (b) $T_c = 135\,^\circ C$, $t_c = 62$ min). Marks: (1) β-hexagonite, (2) β-needle crystal, (3) β-ovalite, (4) β-spherulite, (5) α-spherulite

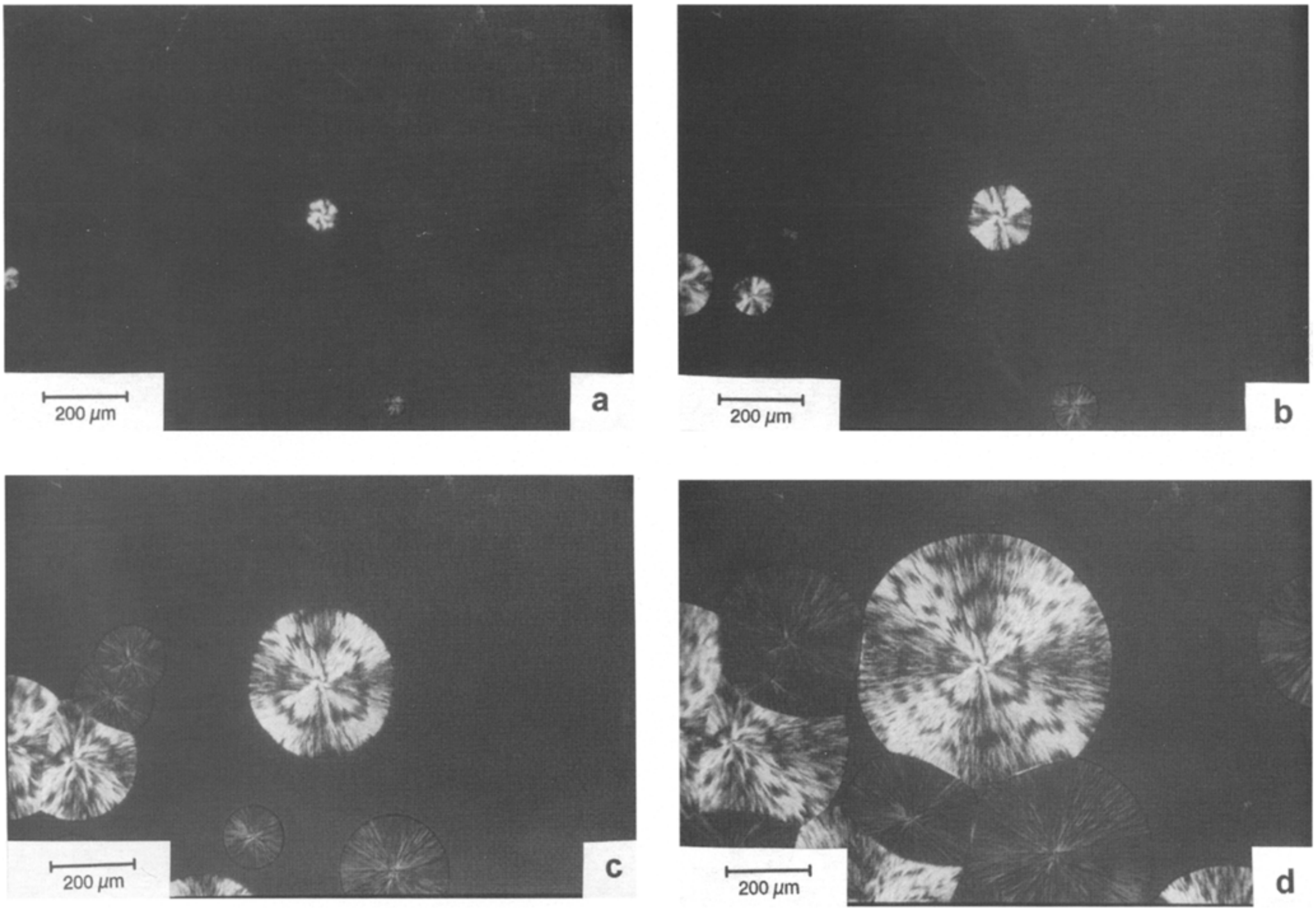


Fig. 2 Banded β-spherulite developed from hexagonite, crystallized in the presence of a trace of β-nucleating agent. $T_c = 130\,^\circ C$, durations of crystallization: (a) $t_c = 8$ min, (b) $t_c = 18$ min, (c) $t_c = 54$ min, (d) $t_c = 80$ min

the perpendicular direction, the sign of birefringence refers to the sterical position of the chains.

A hexagonite corresponds to a hedrite that is seen flat-on. During the high-temperature crystallization, hexagonites may reach a considerable size (several hundred μm) as shown in Fig. 1. At lower T_c values, vertices of hexagonites are getting rounded during the growth transforming into round-shaped spherulites (Fig. 2).

Hexagonites have low birefringence referring to the fact that the polymer chains are almost perpendicular to the plane of the sample. However, a core of positive birefringence can be observed in the center of the hexagonites (as indicated by the central clear region in the hexagonite in the black-and-white picture). The positive optical character is getting weaker with the increasing distance from the center until it turns into a slightly negative birefringence. The crystalline habit of the hexagonal hedrites firmly reflects the symmetry conditions of the (pseudo) hexagonal unit cells of the β-modification [16]. The rod-like formations in the initial stage of crystallization correspond to hedrites viewed edge-on. The growing rod-like crystals form sheaf, then oval (ovalite), and finally circle (spherulite) structures (Fig. 1). All these formations have strong negative birefringence. This refers to the fact that the molecular chains are lying nearly in the plane of the sample with tangential orientation. It is worth mentioning that, besides the two extreme formations (rods and hexagonites), several intermediate arrangements with highly different optical character and birefringence may occur in the crystallizing sample.

As it was mentioned above, *hedrites* might be transformed into spherulites in the later stage of growth, i.e. they could be regarded as the *precursors of β-spherulites*. The lower the temperature of crystallization is, the earlier is the stage of growth which brings switching the hedritic crystallization to the spherulitic one. In Fig. 2 the transition of a hexagonite into a negative banded spherulite is presented. The characteristic feature of a spherulite formed in this way is that it contains a core of positive birefringence at its centre. On the other hand, the central regions of spherulites formed from needle crystals have always negative birefringence.

It should be pointed out that the earliest stage of formation of α- and β-modifications of spherulites has several common features. Binsbergen and de Lange [17] as well as Olley and Bassett [18, 19] observed *square-shaped hedrites*, i.e. *quadrites* as the precursors of α-spherulites. α-Quadrites lying flat-on have low birefringence like β-hexagonites while quadrites seen edge-on are strongly birefringent rods which have, however, positive birefringence, in contrast to β-rods. (These observations make the α- and β-modifications distinguishable in the very early stage of their formation). A quadrite consists of a grid-like array of lamellar lath-like crystallites intercrossing each other almost perpendicularly (at an angle of 80° 40′). The positive birefringence of α-rods can be attributed to the dominance of chains longitudinal to the rods in the orthogonal projection of the molecular chains in the quadrites standing on their edges [17–19].

In the presence of dehydrated calcium pimelate, used as the β-nucleating agent, a lesser or greater amount of β-iPP is formed at high T_c, up to about 145 °C, i.e. above $T(\beta\alpha) = 140$ °C which we consider to be the theoretical upper limit [1, 2]. However, the proportion of the β-modification reduces rapidly with increasing T_c, accompanied by changes in the polymorphic composition and character of the individual supermolecular formations. At T_c levels below $T(\beta\alpha)$, individual morphological structures of pure β-modification are formed (Figs. 1 and 2) while, during the isothermal crystallization above $T(\beta\alpha)$, $\beta\alpha$-transition appears at a higher or lower frequency on the boundary of the growing β-phase along with formations containing α-segments. Such a case is shown in Fig. 3. At a temperature of the isothermal crystallization slightly above $T(\beta\alpha)$, the formation and growth of a few segments of α-spherulites can be observed on the central β-hexagonite. The boundary lines are straight between the hexagonite and the segments of α-spherulites which are more clearly perceptible after melting the β-phase. Similarly, $\beta\alpha$-transition also occurs on the surface of growing β-hexagonites if the temperature of the second step of the stepwise isothermal crystallization is higher than $T(\beta\alpha)$. The sites of α-nuclei are random, i.e. the secondary $\beta\alpha$-nucleation has no favored crystallographic sites. During a stepwise crystallization, α-segments of spherulites are more frequent in the vicinity of the vertices of the hexagonites.

The above experimental results are essentially in accord with the earlier observations [2, 4, 5]. However, the investigations on the high-temperature isothermal crystallization revealed that the formation of β-nuclei and a partial growth of the β-phase were possible in the presence of an active β-nucleating agent even above $T(\beta\alpha)$ (at least not too far from it). Consequently, in spite of the fact that above $T(\beta\alpha)$ a $\beta\alpha$-transition takes place and the growth rate of α-modification is higher than that of β-modification, a certain amount of β-iPP may be formed. It can be attributed to the relatively low frequency of the secondary $\beta\alpha$-nucleation which takes place only in the more advanced stage of growth at temperatures not far from $T(\beta\alpha)$ (Fig. 3). It is notable that similar conclusions were drawn from the experimental studies on the isothermal crystallization of random copolymers of propylene [20]. However, our earlier statement that $T(\beta\alpha)$ is the theoretical upper-limit temperature of formation of β-iPP [1, 2] should be revised on the basis of the present investigations on the high-temperature isothermal crystallization. Accordingly, $T(\beta\alpha)$ is the upper temperature above which pure β-iPP cannot be formed. It can be established from these experimental results that β-iPP can be prepared at much higher temperatures than supposed in the earlier studies with nucleating agent-free iPP [3, 21].

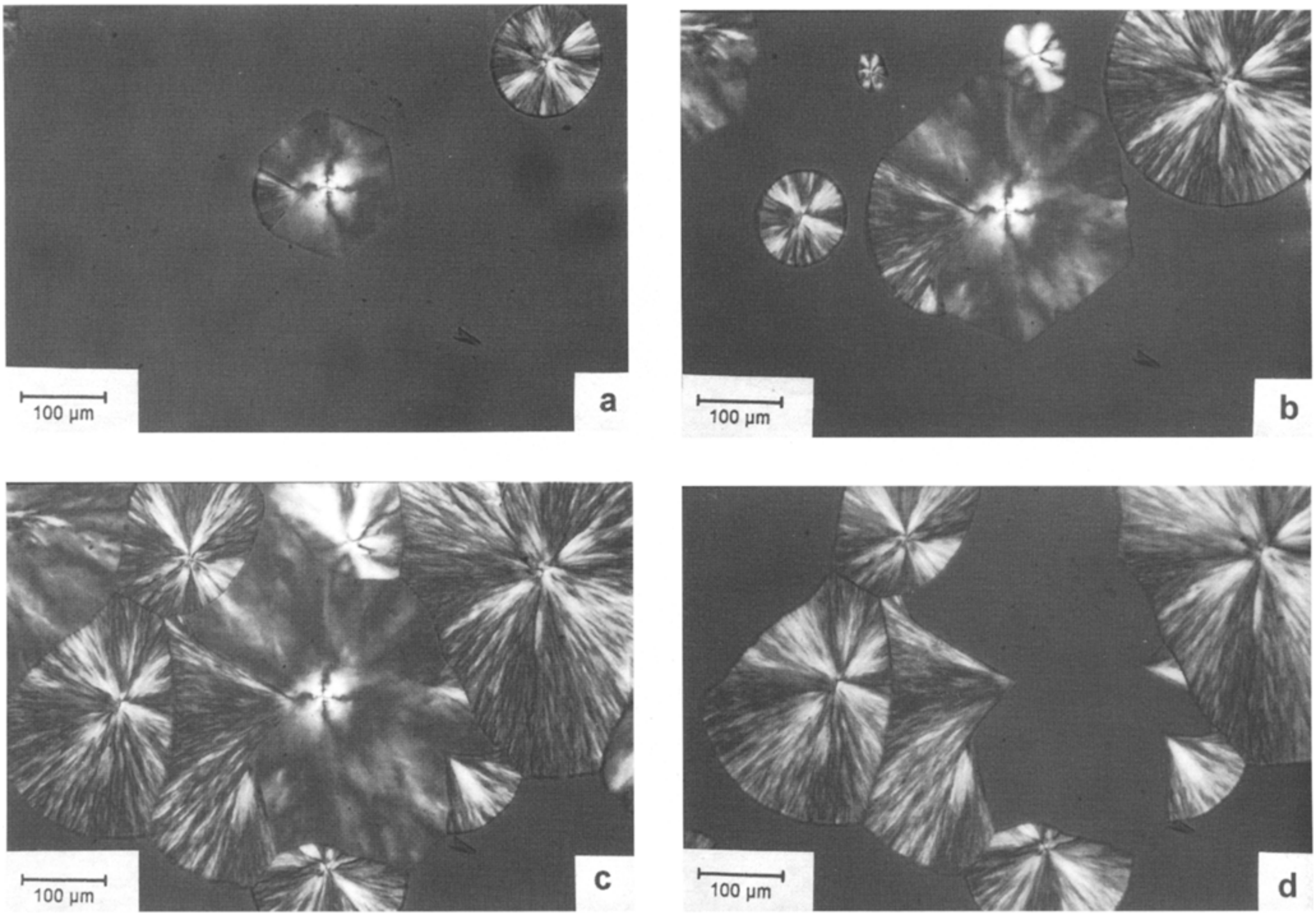


Fig. 3 $\beta\alpha$-Transition on the growing front of the β-hexagonite crystal and growth of the α-spherulite segments during the crystallization above $T(\beta\alpha)$. Temperature of crystallization: $T_c = 141\,^\circ\mathrm{C}$, durations of crystallization: (a) $t_c = 175$ min, (b) 310 min, (c) 500 min; (d) the residual structure after melting the β-phase

Investigations on the morphology of hedrites by SEM

In Fig. 4 a hexagonite and some parts of its structure are shown. It can be established from the SEM micrograph that β-hedrites are multilayer clusters of lamellar crystallites, similar to several observations in the morphology of polymers [8, 10]. The fan-like arrangement of lamellae is nearly parallel to the plane of the hexagonite situated around a central axis perpendicular to the plane of the hedrite (Fig. 4b). On the surface of the lamellae hexagonal formations (etch pits) appear which refer to a screw dislocation (Fig. 4c). TEM studies of β-lamellae lying flat-on revealed such surface formations earlier [15, 21, 22]. These formations are responsible for the branching and proliferation of the lamellae in accord with the assumption of Bassett and Vaugham [10] for the morphological construction of isotactic polystyrene. It was concluded from a great deal of SEM micrographs that the number of screw dislocations on the surface of the lamellae increased with decreasing T_c. It may be supposed that branches of lamellae on these dislocations lead to an early randomization of the hedritic structure of lower T_c levels.

Figure 5 shows the structure of an ovalite developed from a rod-like precursor which appears like a human face. In this case, the plane of the hexagonite is perpendicular to the sample and is coincident with the symmetry plane of the "face". It can also be established that the majority of lamellae in the ovalites is seen edge-on (Figs. 5a and b). However, around the "eye" on the "face", lamellae are lying flat-on (Fig. 5c). The top-view of lamellae standing on the edge is C-shaped, i.e. they are curved (Fig. 5b).

The course of formation of the structure and the successive randomization of hedrites can be followed in the pictures of Fig. 6 which reflect the frozen transient states at the different stages of growth. Figure 6a shows a formation in the very early stage of growth consisting of lamellae standing on the edge. It can be seen that lamellae leave the plane of the hexagonite due to the branches that cause

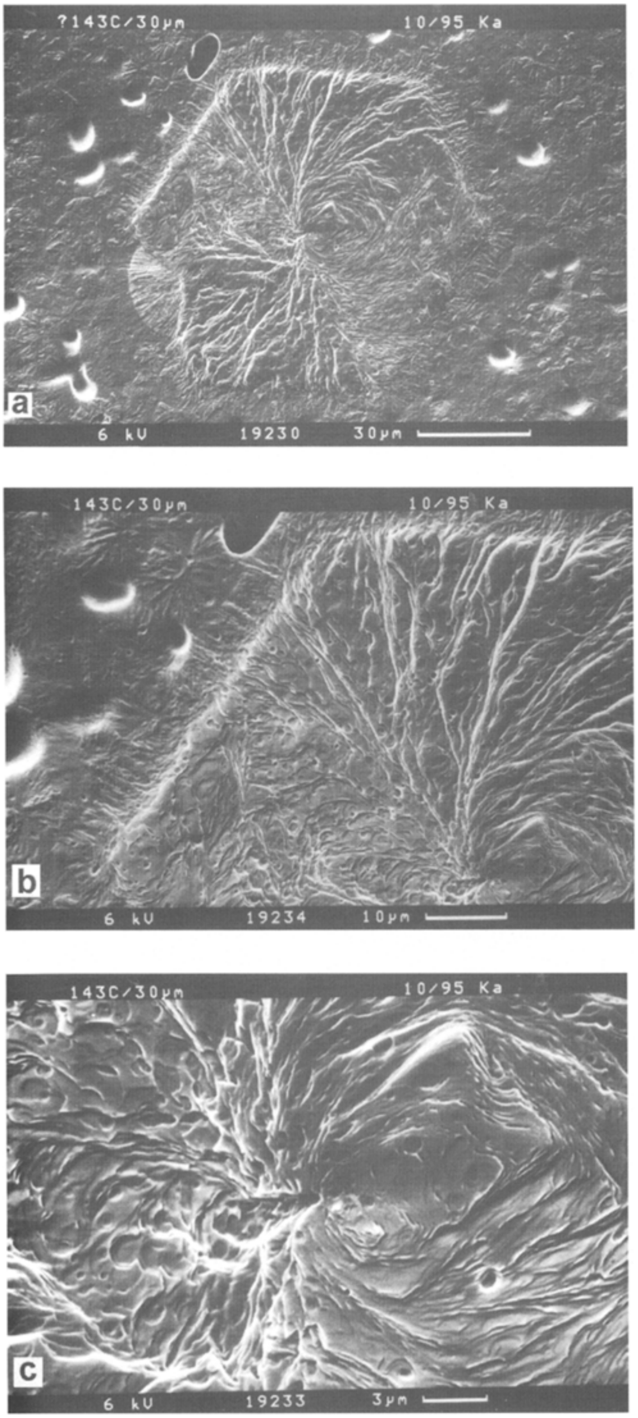


Fig. 4 SEM micrograph of the lamellar structure of β-hexagonite and some details of its morphological structure (b, c). $T_c = 141$ °C

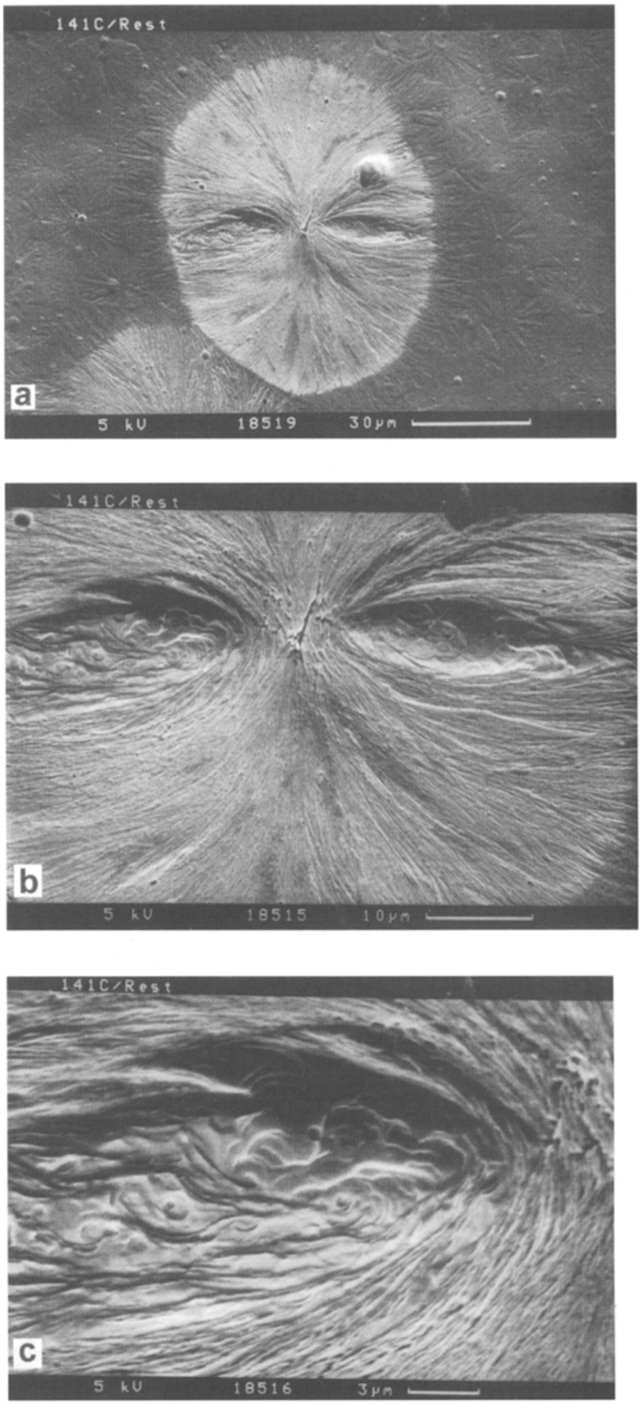


Fig. 5 Ovalite developed from the rod-like precursor (a) and some details of its morphological structure (b, c). $T_c = 141$ °C

splaying of their parallel arrangement. Such formations that are similar to those shown in Fig. 6a are called axialites in the literature [10–12]. A formation in a transient state of the growth between axialite and ovalite is presented in Fig. 6b. Due to the branches of lamellae, two formations develop symmetrical to the plane of the hexagonite, like a flower-cup (Fig. 6c). It is inevitable then, from Fig. 6c, that lamellae are cup-shaped having

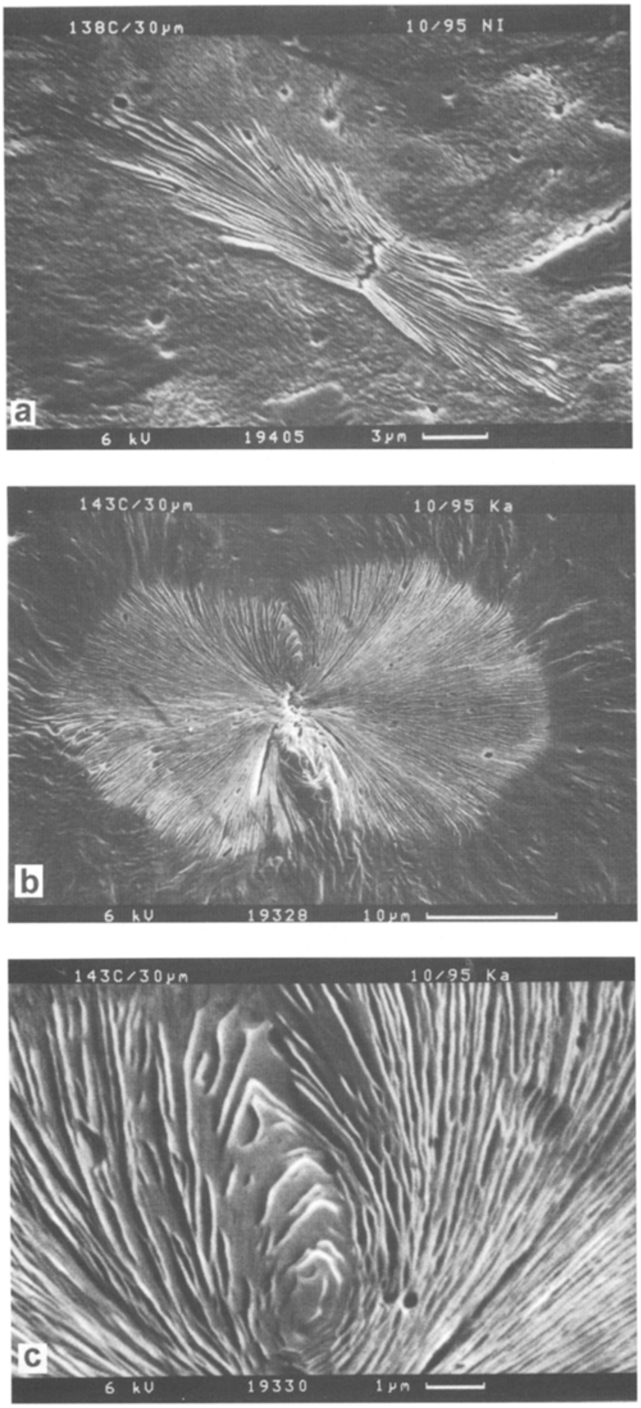


Fig. 6 Randomization of hedrites: (a) an axialite-like formation formed in the early stage of growth. $T_c = 138\,^\circ\mathrm{C}$. (b) and (c) a transient formation between the axialite and ovalite (b) and its lamellar structure (c). $T_c = 143\,^\circ\mathrm{C}$

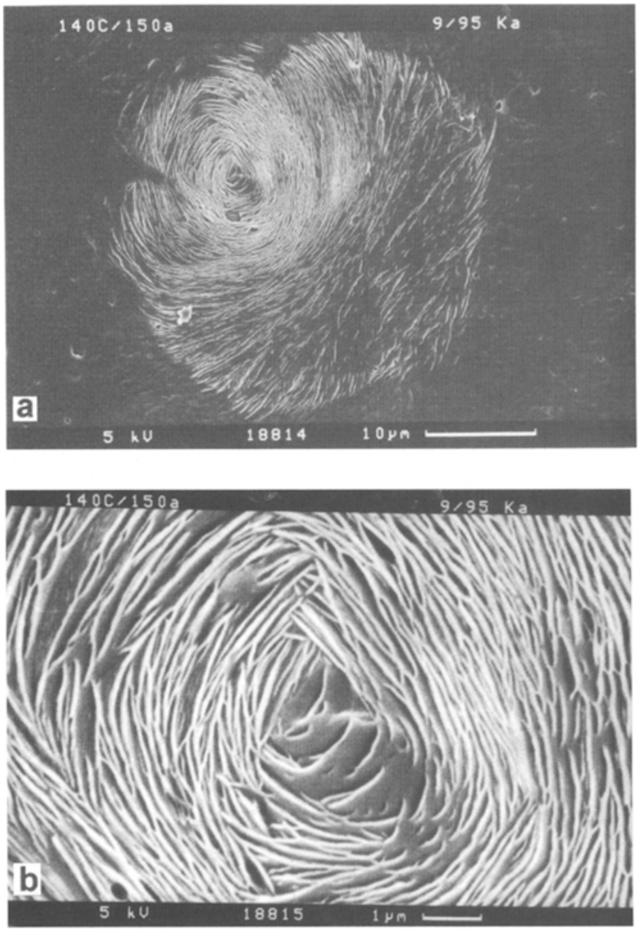
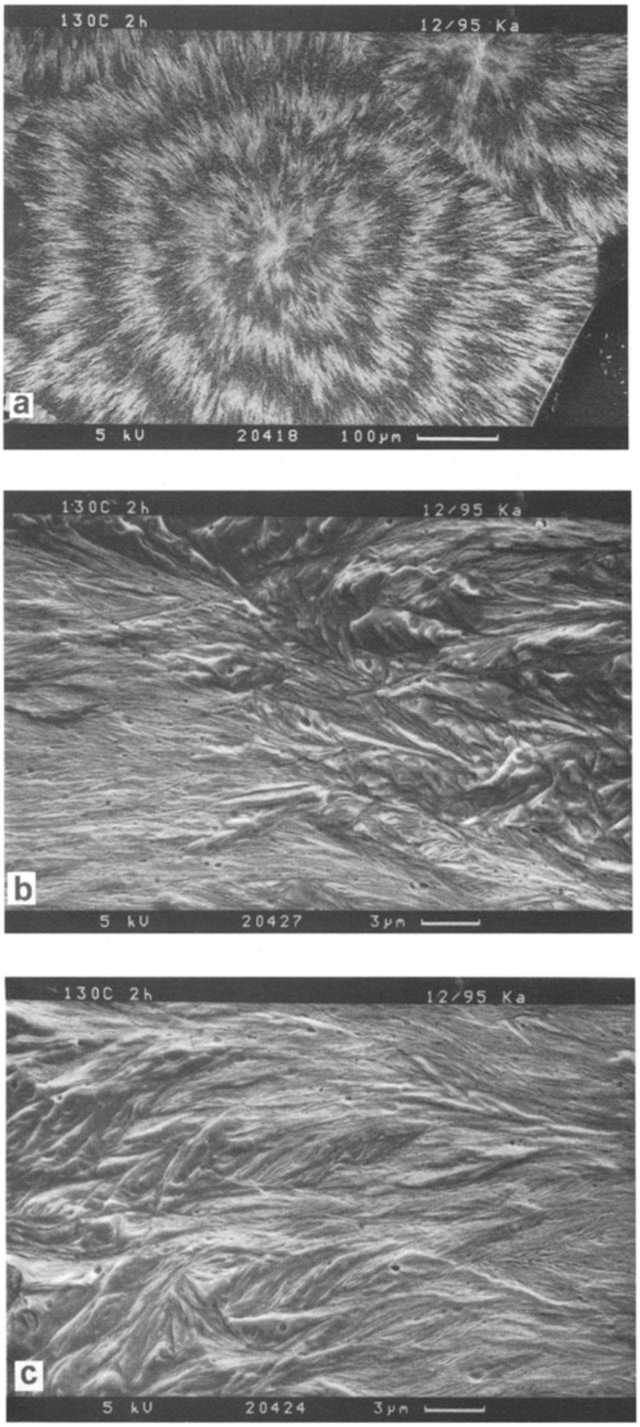


Fig. 7 Hexagonite tilted out from the plane of the sample (a) and the structure of its central zone (b) $T_c = 143\,^\circ\mathrm{C}$

two-dimensional curvatures. According to the SEM micrographs, the hedrites formed by crystallization in the thin (10–40 μm) melt film are not situated exactly at parallel or perpendicular positions to the plane of the sample in most cases. In these instances more or less asymmetric formations are produced which are different from the above ones. They are dominant in the partially crystallized samples. In Fig. 7a a hexagonite is shown slightly tilted from the plane of the sample but having straight border lines as preserved partially. In this spatial position, an interesting detail of the structure can be observed. Figure 7b is a close top-view of the "flower-cup" structure around the central symmetry axis perpendicular to the plane of the hexagonite. This micrograph is a spectacular picture of the branches and curvatures of the lamellae.

Hexagonites preserve their regular geometry even in the later stage of growth in spite of the formation of a multilayer cluster due to branching of the lamellae. It should be assumed, therefore, that the growth of lamellae is a coordinated and cooperative process. This coordinated growth may also occur at lower T_c levels, in the stage of spherulitic growth after randomization of the original hedritic structure, during which the banded structure of β-spherulites is produced due to a coordinated twisting of the bundle of the growing lamellae (Fig. 2). In Fig. 8, a banded spherulite formed at 130 °C and some characteristics of its lamellar structure are shown. In the dark bands, lamellae lying flat-on are dominating while the clear bands represent the dominance of lamellae standing on edges (Figs. 8b and c). The clear bands in the SEM micrograph refer to the effect of edges of crystallites. Twisting of lamellae in the intermediate regions between the dark and clear bands is illustrated in Figs. 8b and c where it is clearly perceptible that the lamellae standing on the edges lean to the plane of the sample while those lying initially on planes tilt out from the plane of the spherulite. It can also be established that the arrangement of lamellae is not completely regular due to a randomization at lower T_c levels. High-resolution micrographs of lamellae viewed flat-on and edge-on are shown in Figs. 8d and e, respectively. The screw dislocations on the surface of lamellae are easily perceptible in the high-resolution micrograph (Fig. 8d) while Fig. 8e is illustrative for the branches of lamellae viewed edge-on.



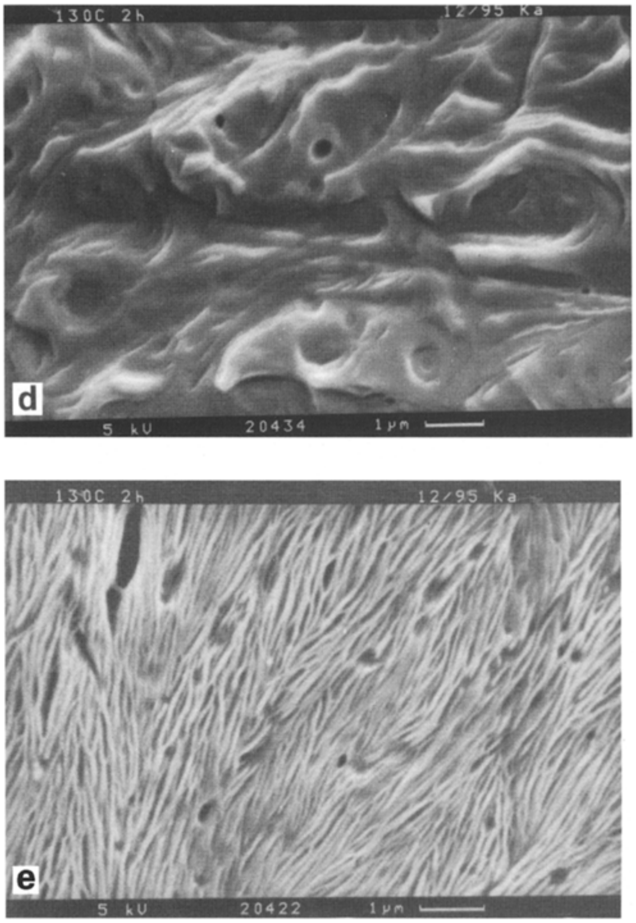


Fig. 8 Characteristics of a banded β-spherulite (a) and its lamellar structure (b–e). $T_c = 130$ °C. (Interpretation in the text.)

The morphological structure of β-iPP has several similarities to that formed during the crystallization of isotactic polystyrene at low extent of supercooling [10–12]. In both the cases, hexagonal multilayer lamellar structures are produced attributed to the screw dislocations on the surface of the lamellae. However, growing lamellae in β-iPP are twisted leading to the formation of banded β-spherulites after the randomization of the hedritic structure.

An unequivocal correlation exists between the lamellar structures of hexagonites, rods, ovalites, and spherulites, as shown in SEM micrographs and the feature of their birefringence observed by polarizing light microscopy. Lamellae lying flat-on and those standing edge-on are dominating in zones of low (e.g. hexagonites) and of high (e.g. ovalites) birefringence, respectively. The positive birefringence of the central zone of hexagonites can be deduced from the radial direction of the orthogonal projection of the polymer chains in lamellae that leave the plane of the hexagonite. Consequently, hedrites, rods, axialites and ovalites correspond to the projections of hexagonal multilayer lamellar crystallites in various stages of growth to different sterical directions. Their growth is restricted when crystallized in thin melt film, thus, they appear as characteristic individual formations. Increase in the thickness of the sample promotes the transition from hedrite to spherulite due to the lesser sterical restraints. In bulk crystallization no such sterical restrictions exist, which favours the formation of a uniform pattern of the spherulitic structure. Hedritic crystallization (i.e. structure) takes place if the growing crystal fronts are impinged prior to their transition to spherulitic structures, fixing the hedritic structure because of the steric restriction of propagation.

The experimental observations inevitably reveal that the central zone of β-spherulites has a hedritic structure. The inhomogeneous structure of the center of β-spherulites, observed by Norton and Keller [21] by TEM studies, is deduced from the fact that their growth is induced by precursors having hedritic structure.

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