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α and β phases of isotactic polypropylene: a case of growth kinetics 'phase reentrency' in polymer crystallization

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The α and β phases of isotactic polypropylene form a pair of crystal phases which are characterized by the fact that the less stable β phase has a faster growth rate than the more stable α phase in a large central part of the crystallization range. Both phases share the same three-fold helical conformation, and growth transitions can take place between the two phases: thermal treatments needed to observe the transitions are described. The crystallographic relationship at the transition point is established with single crystals of the β phase subjected to appropriate temperature jumps, and the possible structural origin of the faster growth rates is indicated. The growth transitions taking place at the upper and (mainly) lower ends of the crystallization range have a profound impact on the melting and recrystallization of the β phase. These processes are reviewed, based on the extensive work of Varga (*J. Thermal Analysis* 1989, **35**, 1891) and of Fillon *et al.* (*J. Polym. Sci., Part B: Polym. Phys.*, 1993, **31**, 1407). © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The α and β phases of isotactic polypropylene (αiPP and βiPP) constitute an interesting pair of phases which display what amounts to a growth kinetics-determined case of phase reentrency, better known in phase diagrams of liquid–crystalline materials. This unusual situation stems from a combination of factors. (a) The two phases are based on the same three-fold helical conformation of the chain. As a result, growth transitions between the two phases are structurally feasable, and are indeed observed. (b) Whereas βiPP is the metastable phase (it melts at ≈ 155 as opposed to ≈ 170°C for αiPP), its growth rate is larger (by up to 70%) than that of αiPP over most of the 'usual' crystallization range. (c) However, as shown by Varga[1], and on account of its higher melting temperature, αiPP grows faster than βiPP at high temperatures, above a critical temperature T^* (141°C). (d) Moreover, at low temperatures, i.e. very close to the maximum of the growth rate (G) *versus* crystallization temperature (T_c) curve, the αiPP growth rate exceeds again that of βiPP (*Figure 1a*). This very feature—faster growth rate of αiPP relative to βiPP in a second, low-temperature domain (located between the second critical temperature T^{**} of ≈ 100–105°C and the temperature of homogeneous nucleation of ≈ 80°C)—is, with respect to growth rates, equivalent to the reentrency of phases in liquid–crystalline materials. In the latter case, reentrency is defined as the property of a given phase (usually a nematic phase) to be stable both at higher and at lower temperatures than a second phase (usually smectic)[2] (*Figure 1b*).

The α and β phases of iPP therefore provide an opportunity—so far unique in polymer science—to investigate the structural foundations and consequences of two different growth transitions between phases, especially since these growth transitions can be monitored by appropriate temperature jumps. In the present paper, we analyze the crystal growth and melting behavior of the αiPP–βiPP pair. For this purpose, we draw on extensive work by Varga, who has brought to light many of its unusual aspects[1,3]. We develop the analysis by using some of our own work in this area: an earlier work which established that the low temperatute T^{**} determined by Varga is associated with a $\beta \rightarrow \alpha$ growth transition[4], and more recent work on the frustrated nature of the βiPP crystal structure[5] and the crystallographic relationship between the two phases[6]. Based on the knowledge of both crystal structures, we analyze the β–αiPP growth transitions. Finally, we illustrate (after Varga[1]) the original and complex melting and recrystallization behavior of βiPP, and analyze it in terms of the α phase nucleation potential of high and (mainly) low-temperature growth transitions[7].

EXPERIMENTAL

The experimental results have been obtained over a period of several years, and many details can be found in original publications. The samples have diverse origins. Samples mostly used were provided by ELF-Atochem and Exxon Chemical International. Molecular weights are in the 10^5 range. The d.s.c. investigations were performed with a Perkin-Elmer DSC 4 instrument and were part of a program aimed at establishing an 'efficiency scale' for (heterogeneous) nucleating agent[8,9]. In this scale, 'ideally' nucleated polymer samples are produced by partial melting of the polymer, leaving crystalline fragments which, on further cooling, act as 'ideal' nuclei (same chemical nature, same crystal structure, excellent dispersion as a result of partial melting) for the final crystallization of iPP[9].

Nucleating agents of βiPP are γ-quinacridone[10] (commercialized by Hoechst under the trade name of E3B) and dicyclohexylterephthalamide (DCHT), a nucleating agent recently patented[11]. The epitaxial relationship of iPP on these agents has been investigated by electron microscopy

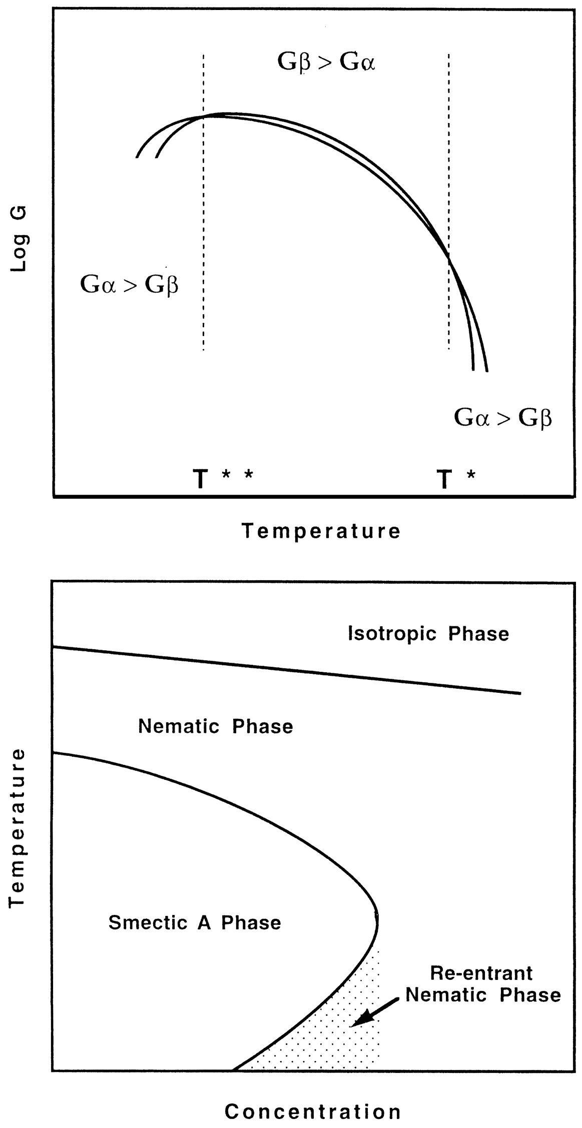


Figure 1 (a) Schematic representation of growth rates of α and β phases of iPP as a function of crystallization temperature. (b) Schematic representation of the phase diagram of a blend of cyanohexyl- and cyanooctyloxybiphenyl which displays phase reentrency (after Ref. [2])

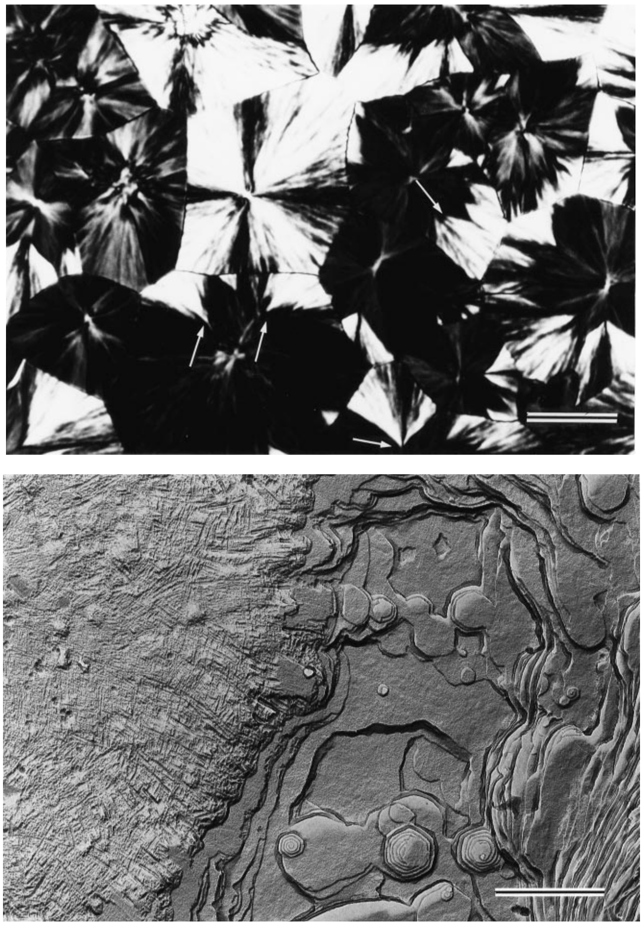


Figure 2 (a) Optical micrograph (crossed polars) of α phase (dark) and β phase (highly birefringent) spherulites of iPP. Note several transitions from α to β phase during spherulite growth (arrowed). Scale bar: 100 μm. (b) Internal lamellar architecture of the α and β phase spherulites of iPP as revealed by permanganic etching. Note the profuse lamellar branching (nearly at right angle) in the α phase spherulites (upper left), and the 'normal' lamellar morphology of the β phase with its characteristic hexagonal screw dislocations when lamellae are seen flat on (center) or edge-wise (lower right). Electron micrograph, replica of a permanganically etched sample, Pt/C shadowing ($\mathrm{tg}\theta = 1/3$). Scale bar: 1 μm

and diffraction and by AFM[12] (using methods already applied to the epitaxy of the α phase)[13] and the data used to solve the crystal structure of βiPP by electron crystallography using direct phasing techniques[14].

Recent investigations of the β–α growth transitions have been performed by growing βiPP single crystals in thin films from the melt[6]. βiPP was nucleated by DCHT crystals, growth took place at 125°C in a Mettler FP80 heating stage under nitrogen atmosphere; additional growth was produced at various temperatures (up to 154°C for a high-tacticity sample!), and the sample was partially melted in order to better highlight the orientational relationship between the two phases. Optical and electron microscopic observations were made with a Zeiss Photomicroscope and Philips CM12 microscopes, respectively.

RESULTS AND DISCUSSION

The high-temperature T* *and low-temperature* T** *β–α growth transitions*

α and β phases of isotactic polypropylene are easily distinguishable in polarized light microscopy, in view of their very different optical properties. βiPP spherulites are highly birefringent, as a result of a 'conventional' spherulite architecture, with radiating lamellae, and tangential orientation of the molecular stems in the lamellae: the spherulites are negatively birefringent as are, for example, polyethylene spherulites ($n_{\mathrm{radial}} < n_{\mathrm{tangential}}$) (*Figure 2a*). αiPP spherulites have usually a much weaker birefringence, as a result of a specific mechanism of lamellar branching. This branching has been analyzed at a crystallographic and molecular level[15–17], and results from a homoepitaxy in the *ac* plane[18]. It generates a pattern of interwoven lamellae which are either radial or tangential in the spherulites (the angle between the two sets of lamellae is nearly 100°, i.e. corresponding to the β angle of the monoclinic unit-cell) (*Figure 2b*). As a result, the birefringence of αiPP spherulites depends on the relative proportions of radial and tangential lamellae[18–21]. It is positive for high density of branching (*Figure 2a*), but may become negative when branching density decreases, both at high temperatures ($T_c > 138$°C) (cf. *Figure 3*) or at low temperatures ($T_c < \approx 90$°C, cf. *Figure 4*)[7]. As a result, α–β and β–α growth transitions are best observed by polarized light microscopy. However, these transitions are only observed

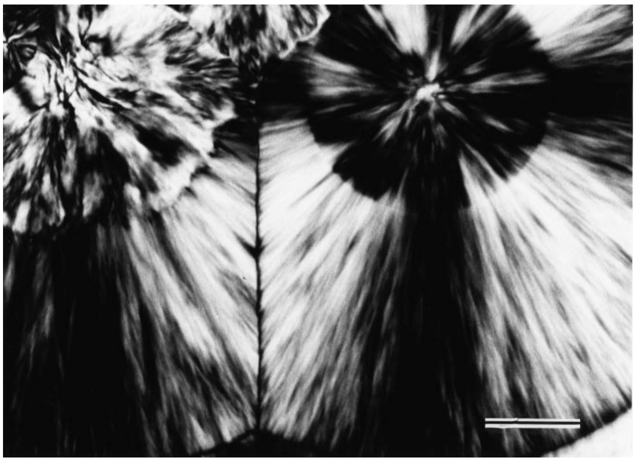


Figure 3 Growth transition to the α phase revealed by optical microscopy (crossed polars) taking place when a β phase spherulite (upper left) crystallized between T^{**} and T^{*} is subjected to a temperature jump above T^{*} (141°C). For the α phase spherulite (upper right), additional growth with higher birefringence is linked to reduced lamellar branching at high temperature. Scale bar: 50 μm

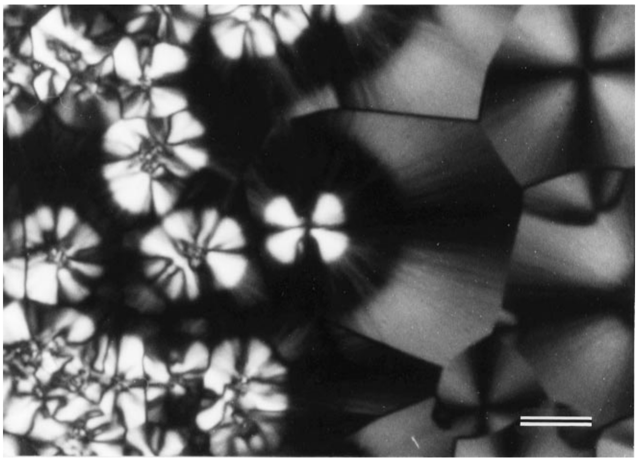


Figure 4 Growth transitions revealed by optical microscopy (crossed polars) taking place when β phase spherulites, while growing between T^{**} and T^{*}, are subjected to progressively lower crystallization temperatures. The vertical row of β phase spherulites on the left are initiated with E3B deposited on the film in a powder form (they are actually part of the author's fingerprint). Growth transitions to a phase with high and low frequency of branching is indicated first by additional growth with low and later 'intermediate' birefringence. Spherulites have started growth at various stages of the cooling process in the non-nucleated, right part of the picture. Scale bar: 10 μm

when the transition induces the fast-growing phase: if the slow growing one were produced, it would be quickly engulfed and 'swallowed' by the fast growing one. As a consequence, α–β and β–α growth transitions are only observed in specific T_c domains.

$\alpha \rightarrow \beta$ growth transitions are observed between ≈ 100 and ≈ 141°C. They are quite infrequent, but have been used, when crystallization takes place in a temperature gradient, to generate βiPP monodomains with 'transcrystalline' orientation[22], which proved useful in solving the βiPP crystal structure[23] (cf. also *Figure 1a*).

$\beta \rightarrow \alpha$ growth transitions can be induced by appropriate temperature jumps in the upper and lower domains of T_c, where α growth is faster. This stepwise crystallization was first used by Varga[3] to demonstrate the existence of, and investigate the high-temperature T^{*} $\beta \rightarrow \alpha$ growth transition (*Figure 3*). The low T^{**} growth transition was first observed by Lotz *et al.*[4] by applying a similar technique, thus establishing the 'phase reentrency' discussed in this paper. The formation of α phase nuclei at low temperatures had been postulated by Varga[1] in his analysis of the complex melting and recrystallization of βiPP. Given the fast growth rates of iPP at low T_c, the growth transition had not been recognized in spherulites growing under 'normal' conditions, since growth is completed in the sample well before it reaches this temperature range. It was, however, observed[4] when quickly cooling a thin film in which βiPP spherulites were growing. Further growth then takes place in concentric rings at progressively lower temperatures, and reveals the existence of growth transitions by sudden changes in spherulite birefringence. A typical experiment (*Figure 4*) therefore reveals that: (a) a $\beta \rightarrow \alpha$ growth transition takes place at a temperature which Lotz *et al.* associated with the low temperature T^{**} transition determined by Varga[1]; (b) whereas the α phase spherulites are positively birefringent when T_c is near T^{**}, they become negatively birefringent at lower T_c, most probably as a result of reduced impact of lamellar branching. This 'optical' transition (within the same crystal phase growth[7]) takes place at ≈ 90°C (*Figure 4*). On further cooling, spherulitic growth is arrested due to the onset of profuse 'homogeneous' nucleation, which for iPP is known to take place near ≈ 80°C[24]: the onset of a dark background, indicative of profuse nucleation (not observed in *Figure 4*) provides a morphological indicator of the actual temperature reached by the sample at this final transition point.

Structural aspects of the growth transitions

The above experiments illustrate convincingly the existence and the specificities of the α–β and β–α growth transitions. They need to be analyzed in terms of the structural relationship between the two crystal phases at the transition point, and with regard to the origin of the faster growth rate of the less-stable β phase.

Orientational relationship of the two lattices at the transition point. In order to establish the structural relationship between the two phases, we have recently attempted to induce the growth transitions at the edges of *single crystals* of the β phase[6] (a somewhat similar approach was pioneered by Rybnikar[25]). The mutual orientation of the two phases can be established by a simple analysis of the morphology, since the growth faces of βiPP single crystals are known to be (110) and the α phase crystals are lamellae elongated in the a^{*} axis direction.

A most instructive optical micrograph of a β crystal in which the β–α growth transition was induced by a T-jump above T^{*} (high T_c growth transition) is shown in *Figure 5*. The features of interest are the small, elongated α phase crystals near the outer edges of the (hexagonal) β phase crystal, and more specifically their orientation parallel, or at a 60° angle to the outside (110) growth faces of the β phase single crystal. This morphological indication (fully supported by electron diffraction patterns) indicates that, in the growth transition, the (110) plane of βiPP remains parallel to the (040) plane of αiPP.

The above structural relationship can be analyzed in terms of interacting helices in the α and β unit-cells, since the α phase structure is known since the 1960s[17] and the structure of βiPP has been solved recently[5,23,14].

αiPP is known to have a monoclinic unit-cell ($a = 6.65$ Å, $b = 20.80$ Å, $c = 6.5$ Å, $\beta = 99.8$°) with layers made of

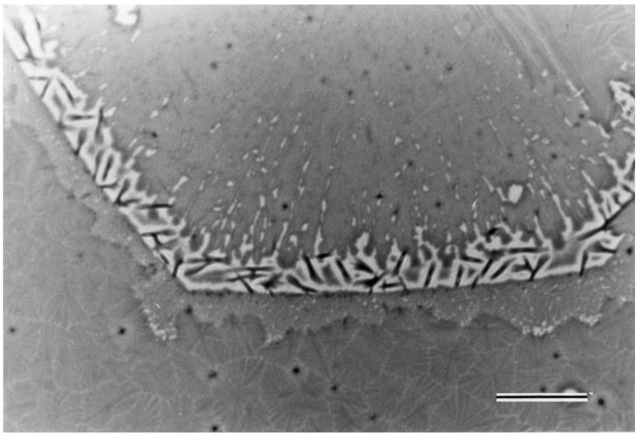


Figure 5 Phase contrast optical micrograph of a hexagonal single crystal of βiPP crystallized at 125°C for 10 min, and at 145°C for 60 min. α phase crystals have developed at the edge, but inside the β phase crystal contour, in the form of elongated laths, extended in the a^* axis of the unit-cell. Note the characteristic orientation of these laths either parallel, or at 60° to the (110) edges of the hexagonal βiPP single crystal. Scale bar: 20 μm

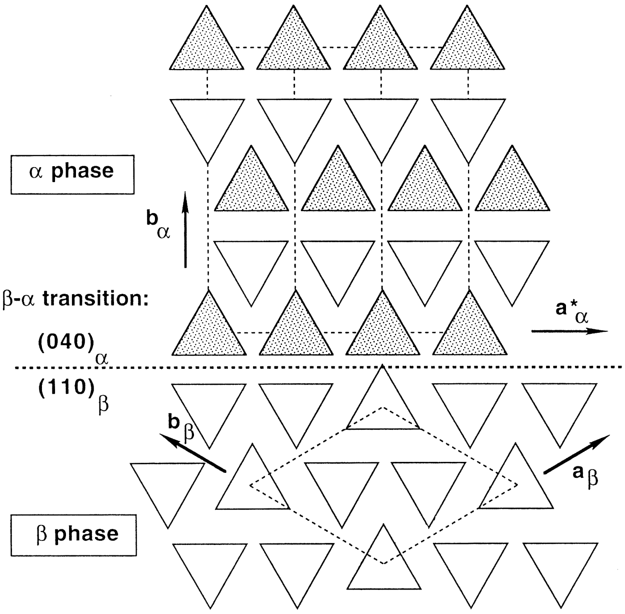


Figure 6 Schematic representation of the structural relationship between β and α phases of iPP which maintains the densely packed $(110)_\beta$ and $(040)_\alpha$ planes parallel, in agreement with the indications of *Figure 5*. Transition from α to β phase would require reorientation of one helix (that shown at the corner of the β phase cell). β–α transition would require deposition of helices of opposite hand (shown shaded)

isochiral helices parallel to the *ac* plane. Alternate layers are antichiral, and further differ by the azimuthal settings of the chains: the tips of the triangle which schematize the helices in *c* axis projection are oriented towards the $+b$ and $-b$ directions of the unit-cell (*Figure 6*).

βiPP has a highly unusual crystal structure, with a trigonal unit cell in which three isochiral helices adopt a frustrated packing[5]. Indeed, the helices have different azimuthal settings, with tips of the helices oriented North, South and South (NSS), or, in another version of the frustrated packing, NWW. Since iPP is chiral but racemic, domains made of right-handed helices only must coexist with domains made of left-handed helices only, the different domains being separated by antiphase boundaries. Coexistence of such domains gives rise to serrated (110) growth faces in single crystals, i.e. every macroscopic (110) growth front actually includes structurally equivalent (1–20) and (–210) growth planes.

With respect to the α–β growth transition, we note (*Figure 6*) that the contact face corresponds to the most densely packed planes of the two phases (interhelix distances: 6.5 and 6.35 Å in α- and βiPP, respectively), that are both made of isochiral helices, and which differ merely by the different azimuthal setting of one helix out of three. Reorientation of this helix accompanied by a small shift along the *c* axis would therefore be sufficient to generate a small patch of the other, faster growing phase, and of further development of that other phase. The β–α transition would be a slight variant of an antiphase boundary between two domains of β phase made of helices of opposite hand. Generation of a 'viable' α phase domain would however have to take place on the (1–20) and (–210) microfacets, since the fast growing αiPP a^* axis would then be oriented at 30° only to the normal of the macroscopic (110) βiPP growth face (cf. *Figure 5*).

The above analysis (made for the high T^* growth transition, but probably valid also for the low T^{**} transition as well) therefore underlines that small perturbations only are needed to switch from α to β phases, thus providing a structural foundation to the observed frequency of this transition. Note however that a similar experimental approach for the reverse transition (which is probably similar in its molecular details) cannot be supported by comparable experimental evidence since it is spontaneously much less frequent, and cannot be induced by appropriate temperature jumps.

Structural origin of the faster growth rate of βiPP. Beyond the general observation that the less-stable phase tends to grow faster than the more-stable one the faster growth rate of βiPP in most of the crystallization range seems to have an identifiable structural origin, which can be traced down to its specific, frustrated crystal structure.

Growth rates are mainly controlled by the rate of 'secondary nucleation', i.e. the rate of creation of a new growth plane by deposition of an initial stem on an existing, completed growth face (or at least on a section of it, depending on the growth regime). On this basis, the structure of the β phase of iPP provides for a constant and favorable secondary nucleation site. Indeed, the different azimuthal settings of the chains imply that, on one side of the (110) growth face at least, a favorable nucleation site exists: it stems from the fact that one helix can be attached on the growth front with its 'tip' (in chain axis projection) entering a 'notch' of the substrate (growth) face (in *Figure 6*, the notch exists between two helices with their tips oriented South). This situation is very favorable indeed, since deposition of such a stem results in the *regaining* of (roughly) one lateral surface energy term, σal, whereas deposition on a flat surface (instead of in a notch) would involve the creation of such a term for a triangular helix (it is equal to 2σal for helices with square cross-section usually considered in crystallization theories). No similar situation exists on the possible growth fronts of the α phase, especially for (110) growth faces. For the α phase lateral (040) growth planes, two different secondary nucleation rates must be considered, since the azimuthal orientation of helices in successive (040) planes differs: one plane does indeed correspond to the deposition of helices in notches, but the next one corresponds to an unfavorable situation with creation of lateral surface energy terms. This latter, presumably slower deposition rate controls, of course, the overall growth rate. By contrast, and as already indicated, favorable secondary nucleation in notches is possible for *every* growth plane in the β phase, which, we suggest, accounts for the larger growth rate of the β phase over the α phase one in most of the crystallization range of iPP.

Impact of the β–α growth transitions on β phase melting and recrystallization

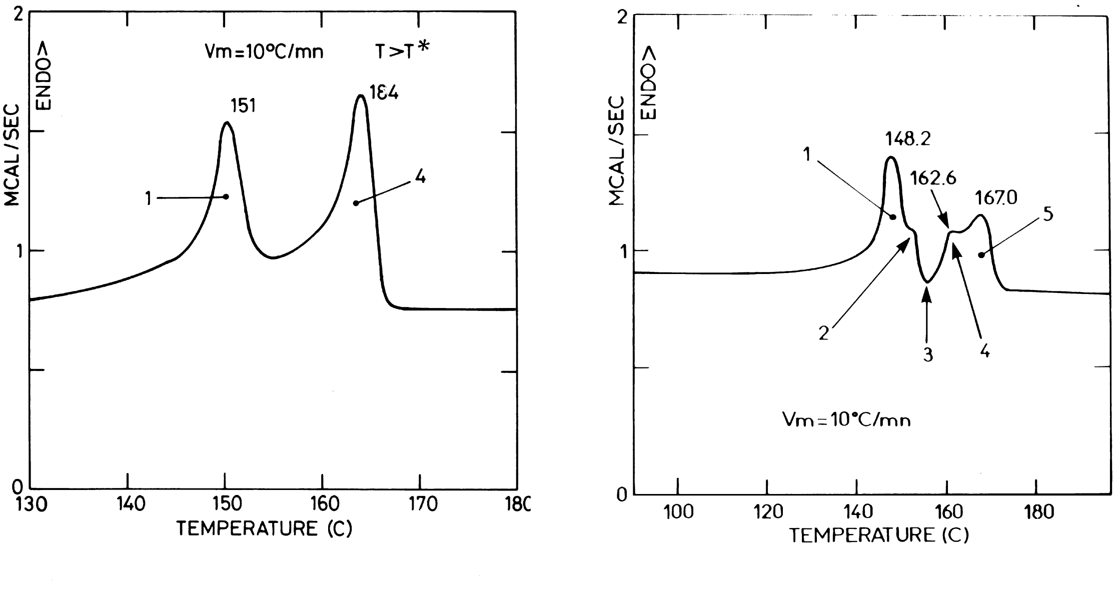
Melting of the β phase in a standard d.s.c. run may be a complicated process[1]. Indeed, melting of βiPP begins in a temperature range in which the αiPP growth rate is still significant. The molten βiPP experiences not only recrystallization in a more-stable β phase (as is observed in all polymers) but also, if and when α phase nuclei are present, recrystallization in the thermally much more stable α phase. Since the two growth transitions just described do generate such α phase nuclei, it is of interest to investigate their impact on the melting process of βiPP.

Investigation of the melting of βiPP involves, by necessity, crossing the high temperature T^* α–β growth transition temperature, which implies that, during every melting experiment, such α phase nuclei are necessarily formed. It turns out, however, that this high-temperature growth transition is much less effective in producing αiPP nuclei than the low-temperature T^{**} transition. It was, indeed, the anomalies of the βiPP melting behavior that led Varga[1] to suspect the existence of a specific low-temperature α phase nucleation mechanism, which was ultimately associated with a growth transition[4].

In order to illustrate the relative potential for αiPP nucleation of the high T^* and low T^{**} growth transitions, two melting curves of an iPP sample crystallized at 125°C are shown in *Figure 7*. The sample contains β and α phase spherulites. The latter, used as a reference in the melting process, do not interfere with the β–α recrystallization process: since the density of α nuclei in β spherulites is high or very high upon recrystallization, the edges of the α phase spherulites, which act as nucleation sites for the molten βiPP, have only a marginal effect in the recrystallization process. For all practical purposes, the two populations of α and β spherulites may be considered as being separate and non-interactive.

High melting T^* growth transition. As already indicated, the T^* temperature is always crossed on heating. If a growth transition takes place, recrystallization of the molten βiPP will take place in the α phase and, on account of the much larger crystallization range of αiPP, over a much larger temperature interval than recrystallization in the β phase. In other words, melting of βiPP is by necessity accompanied by some recrystallization in the αiPP phase on α nuclei generated during the heating after crossing the high T^* transition. All experimental evidence suggests, however, that this growth transition has a very limited impact on the melting process of βiPP, which in turn suggests that the density of growth transition sites in the βiPP spherulites is very limited. This is supported by optical microscopy observations by Varga[26], which show that the number of growth transitions on the outside of β spherulites after a T-jump is very small indeed: one micrograph displays about 10 transition points for a spherulite of diameter apparently in the 50–100 μm range (no scale bar is given). Of course, the density of transition points increases when the temperature reached after the T-jump is higher but, at the same time, the growth rate of αiPP is reduced, thus limiting their impact. Also, lower heating rates allow more numerous growth transitions to take place, and leave more time for a phase growth: the recrystallization process becomes observable in the βiPP melting peak.

For all practical purposes, we may consider that the melting curve obtained at a heating rate of 10°C/min, while still 'contaminated' by some (unavoidable) β–α growth transitions, and therefore a recrystallization, is close to representing a 'pure' β melting curve, as illustrated in



(a) *(b)*

Figure 7 D.s.c. melting curves of β phase spherulites subjected (b) or not (a) to a cooling below the critical temperature T^{**}, at which the β to α growth transition takes place. Note the fairly 'pure' melting of the β phase in (a), and in (b) the considerable recrystallization of the melting β phase into the α phase (step 3), which itself melts at the higher temperature (step 5). Reproduced from Ref. [7], with permission

Figure 7a. Actually, using a concentration of (α phase) nuclei *versus* crystallization temperature on recrystallization, we have established that $\approx 10^9$ αiPP nuclei per cm^3 are produced in βiPP spherulites upon crossing *T** during a heating run at 10°C/min (this figure is, however, obtained on cooling the sample after self-seeding in the α phase melting range, and depends therefore on a more complicated process than mere creation of growth transition sites above *T**). As is shown now, this figure contrasts sharply with concentrations of α phase nuclei produced below *T***.

Low T** *growth transition.* All experimental evidence indicates that the low *T*** growth transition is a much more efficient 'αiPP nucleator' than the high *T** one in βiPP spherulites. During a 'standard' crystallization of iPP, this *T*** temperature ($\approx$ 100°C) is normally crossed, whether as a result of room temperature storage or in conventional d.s.c. crystallization protocols, in which a low final temperature is often used to be 'on the safe side' with respect to crystallization completion. The unexpected outcome of this 'safe' protocol is to generate a very high density of α phase patches at all the lamellar edges within, and at the periphery of, β phase spherulites. These α phase patches are actually produced well within the so-called secondary crystallization of the β phase spherulites. Although most of the crystallization, whether primary or secondary, is completed when the sample reaches 100°C during a typical cooling run at -10°C/min, enough crystallizable material remains to create the α phase nuclei. Further confirmation of this assertion comes from a careful set of experiments reported by Varga[1], who also was first to point out this particular behavior: he showed that the formation of α phase nuclei is significantly reduced when a sample crystallized above *T*** is carefully annealed (and always maintained above *T*** during annealing) prior to cooling below *T***. For such a sample, generation of α phase overgrowth as a result of β–α growth transition is reduced since virtually no crystallizable material is left in the sample.

To summarize therefore, cooling of βiPP spherulites below *T*** ($\approx$ 100°C) generates, during the normal process of secondary crystallization, profuse β–α growth transitions. The α phase represents only a small amount of material, but it is highly dispersed since it 'decorates' all the edges (intra- and inter-spherulitic) of the β phase lamellae which build up the spherulites. This α phase fraction would remain undetected and undetectable by usual structural investigation techniques (powder X-ray diffraction, optical properties, etc.). Its existence is, however, highlighted (and as a result evidenced) by its α phase nucleating effect on melting of the β phase spherulites which 'host' these α phase patches.

The impact of the α phase patches is illustrated in *Figure 7b*, which should be compared to *Figure 7a*. The two figures illustrate the melting of essentially the same samples, crystallized under similar conditions, and heated at the same rate. The sample of *Figure 7b* has been subjected to a cooling below *T*** prior to melting. The much more significant recrystallization into the α phase after β phase melting (cf. the characteristic exotherm, indicated as step 3) illustrates the much higher concentration of α phase nuclei generated by the excursion below the low *T*** growth transition. Evaluation of the number of α phase nucleation sites is difficult. We have examined the transformed spherulites after permanganic etching, and found a spherulite size in the μm range, or smaller. Although this procedure does not specifically evaluate the number of αiPP nuclei generated during cooling below *T*** (since the α phase newly formed during the heating stage is partially melted and recrystallized), it indicates a very high density of 10^{13}–10^{14} nuclei/cm^3. As a result, also, the transformed β spherulites are essentially transparent (non-birefringent), due to the small spherulite size (*Figure 8b*, to be compared to *Figure 8a*).

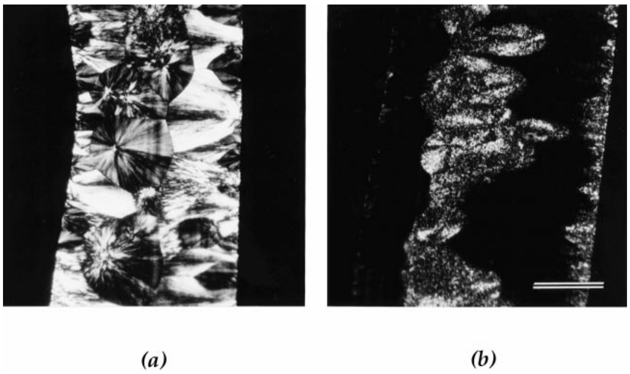


Figure 8 Optical micrographs (crossed polars) of α and β phase iPP spherulites submitted to an 'excursion' in a temperature range below *T***, before (a) and after (b) partial melting in the αiPP melting range and recrystallization. The transcrystalline β phase is nucleated from the surface, and α phase spherulites develop in the center of the thin film, seen in cross-section. The very high concentration of α phase nuclei in the initial β phase spherulites shows up through the absence of birefringence in (b), as a result of the very small size of the spherulites formed ($\Phi < 1$ mm), whereas the initial α phase spherulites have only partly melted and display a morphological 'memory effect'. Scale bar: 100 μm. Reproduced from Ref. [7], with permission

To summarize, the partial melting and recrystallization experiments of β spherulites have provided the first indication[1] of a curious recrystallization behaviour which helped detect the presence of highly dispersed α phase patches within β phase spherulites through their role as a nucleating entities during β phase melting. This unusual recrystallization behavior has triggered experiments which helped establish a second, low-temperature β–α growth transition, which would have been missed otherwise, and which confers the 'phase reentrency' character to the growth kinetics of iPP.

CONCLUSION

The β and α phases of isotactic polypropylene constitute a unique pair of phases which display a complicated pattern of growth transitions, relative thermal stabilities and relative growth rates. With respect to growth rates alone, this behavior is much akin to that of reentrant phases, as the growth rate of αiPP is larger than that of βiPP, not only at high temperatures but at low temperatures as well, the latter feature defining reentrency. This complexity is best illustrated by the α phase recrystallization phenomena taking place during β phase melting, which depends on growth kinetics and thermal history 'memory' effects. The observed behavior has been analyzed and rationalized in terms of two growth transitions taking place at low (*T***) and at high (*T**) crystallization temperatures. The existence of such growth transitions is critically linked with several favorable structural features, in particular with the fact that: (a) α and β phases are based on the same helix geometry; (b) the latter, β phase crystal structure provides for a favorable, self-repeating nucleation site at the growth front which 'boosts' its growth rate beyond that of the α phase over a very large crystallization range; (c) the two phases are not interconvertible in the solid state (on account of their different helix chiralities), which precludes the possibility for the less-stable phase to merely be a transient, unstable phase during crystal growth of the stable phase. Finally, growth transitions between different phases appear unlikely for crystalline polymers the structural polymorphism of which is based on different helix geometries: indeed, the behavior described and analyzed in this paper, although general in its principle, has been observed so far only for the pair of α and β phases of isotactic polypropylene.

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