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Spherulite Morphology of Form III Isotactic Poly(1-butene)

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Introduction. Isotactic poly(1-butene) (iPBu-1) is renowned for its crystal polymorphism, which rests on three different helix conformations: 3_1, 11_3, and 4_1 for forms I (and I′), form II, and form III, respectively.[1,2] Form I, based on the 3-fold helical conformation, exists actually in two variants, named I and I′, depending on the way it is produced. Form I refers usually to a crystal modification that is generated via a solid-state transformation of form II, whereas form I′ refers to the same crystal structure obtained by direct crystallization.[1] The difference may not be trivial, since their melting temperatures have been reported to be significantly different. Form I is the more stable one (T_m about 130 °C) compared to form I′ (reported $T_m \approx 95$ °C).[1] Forms II and III melt at lower temperatures than form I: 124 and 106 °C, respectively.[2−4]

The conditions under which these various forms can be obtained have been investigated in great detail.[1] *Melt crystallization* of iPBu-1 produces usually only form II, which is kinetically favored. This form converts to form I on storage at room temperature. Form I′, the "direct" form with 3-fold helix conformation, has been obtained recently by crystallization in thin films at elevated temperatures (110 °C, 5 days),[5] which casts doubt on the low melting temperatures initially reported for this form.[1] Form III, which is the topic of the present report, has not been produced so far by crystallization from the melt. However, very thin films of all three forms have also been produced by *epitaxial crystallization*, by using appropriate substrates.[6−8]

All three forms can be obtained by *crystallization from solution*, although the proportions of the various forms depend in a complex manner, not yet fully elucidated, on the previous crystallization conditions (solvent, T_c) and annealing/melting of the suspension of crystals.[1,9,10] It seems that some kind of "memory effect", much like that observed more recently for syndiotactic polystyrene,[11,12] is at play in the solutions of iPBu-1. The single crystals have been useful to investigate for example the molecular mechanisms at play in the form II to I transformation.[13,14] The single crystals of form III are lozenge-shaped and very reminiscent of those of polyethylene (orthorhombic unit cell, crystals bounded by (110) growth faces), but they are frequently scrolled ("The lamellae are curled up into tube-like structures while in suspension", to quote Holland and Miller).[1] These single crystals, together with the epitaxially crystallized thin films, have helped refine the crystal structure of form III by electron crystallography.[15] In agreement with an earlier X-ray powder structure determination,[16] form III of iPBu-1 is made of isochiral 4_1 helices packed in an orthorhombic cell (space group $P2_12_12_1$) of dimensions $a = 1.238$ nm, $b = 0.888$ nm, and $c = 0.756$ nm.[15,16]

Since form III has never been obtained by crystallization in the bulk, investigations on this form, for example by NMR, have been performed on sedimented mats of solution grown single crystals.[17−19] Similarly, we have not yet been able to generate a form III-rich bulk phase, even when seeding the melt with the substrate that induces epitaxial crystallization of form III,[6] whereas such a possibility exists, e.g., for the β form of isotactic polypropylene. In other words, the spherulitic morphology of form III iPBu-1 has yet to be established.

In the present report, we describe a means to produce significant proportions of form III of iPBu-1 from the melt and describe some original features of its spherulitic morphology. The procedure is not "clean", however, since some solvent is still used, yet it generates well-defined spherulites of form III. These spherulites display unexpected and original structure and optical properties that are significantly different from those of form II and I. Actually, our experimental procedure derives from initial observations made a long time ago (in the 1960s) by André Kovacs.[20] The results were not published, exploited, or interpreted at the time and were rediscovered only recently.

Experimental Procedure. In the experimental procedure, a film of iPBu-1 is cast on a glass coverslide from a solution and covered with another glass coverslide. A drop of solvent (typically amyl acetate, a mixture of 2-methylbutyl acetate, and *n*-pentyl acetate, Aldrich) is introduced between the two coverslides to wet the edges and surface of the iPBu-1 film. The film is melted on a Kofler bench (a temperature gradient bench) around 140 °C (above T_m of form I, around 130 °C). Crystallization is achieved by sliding the sample along the Kofler bench to lower temperatures. Note that these solvents and/or crystallization conditions have not yet been optimized to improve the form III yield. In the present report, we concentrate on the original features of the morphology and structure of the resulting films (Figures 1−3).

Results. Figure 1a is an optical micrograph of a thin film prepared under the above crystallization conditions and observed under crossed polars. It displays several spherulitic morphologies, which correspond to the various crystal polymorphs of iPBu-1, as also assessed by electron diffraction (cf. later). The spherulites with clearly defined radial symmetry correspond to crystallization in form II (tetragonal cell, 11_3 helix). These spherulites convert on standing to form I. In addition to these "standard" form II spherulites, a tear-drop shaped, weakly birefringent spherulite is also observed. When seen at higher magnification (Figure 1b), these spherulites display concentric extinction rings (here with a periodicity of 5 μm), indicative of lamellar twisting. These are form III spherulites, as shown below. Finally, the sample also contains very small, round, and birefringent objects which are spherulites of form I′ (cf. Figure 1a, better seen in Figure 2a, see below). The relative growth rates of form III and form II may vary considerably depending on the experimental conditions. Growth rate ratios G_{II}/G_{III} *and* G_{III}/G_{II} of up to 170%

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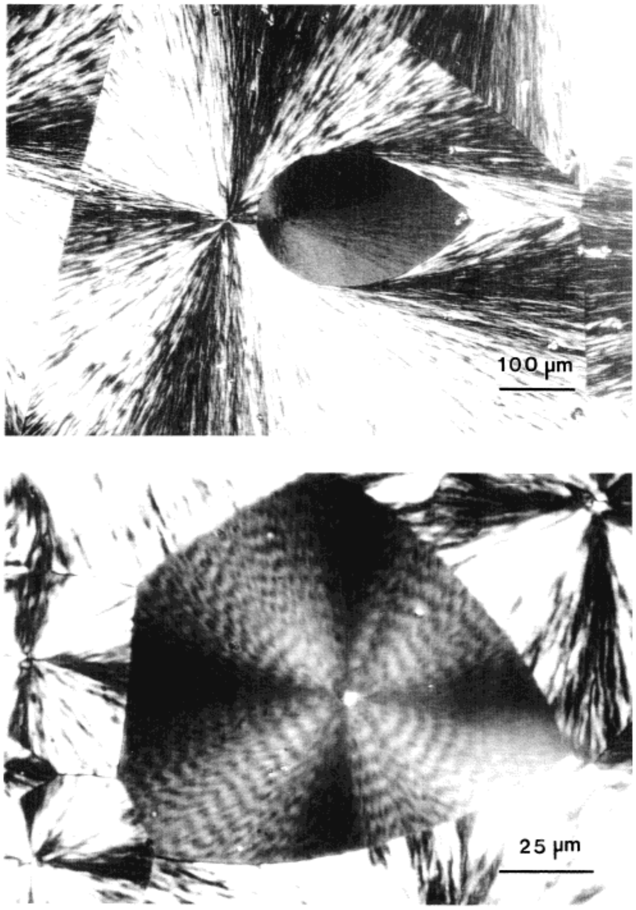

Figure 1. (a, b) Thin film of iPBu-1 crystallized in the presence of amyl acetate, examined in polarized optical microscopy, at two different magnifications. Birefringent spherulites are of form II, possibly already converted to form I. The weakly birefringent spherulites are of form III. Note the ringed structure indicating periodic twist of the lamellae. In (a), the small bright "dots" visible in particular on the right side tip of the form III spherulite are form I′ spherulites, with a much smaller growth rate than either form II or form III spherulites. Under the present growth conditions, the band periodicity (half twist periodicity) is 5 μm, and the form III spherulite growth rate is smaller than that of form II (cf. (a)).

have been observed. As a result, either form II or form III spherulites can be engulfed in the growth of the other form, leading to the classical tear-drop shape of the slower growing spherulites (Figure 1a). In all cases, however, the growth rates of forms II and III are significantly higher than that of form I′.

Figure 2a shows the same three crystal phases and spherulites of iPBu-1 obtained in thinner films under slightly different crystallization conditions, as observed by transmission electron microscopy. The differences in lamellar morphology (twisted and nontwisted lamellae for forms III and II, respectively) is clearly evidenced. Figure 2b shows a Pt/carbon shadowed surface of a spherulite of form III followed by dissolution of the underlying polymer (one stage replica). Again, the cooperative twisting character of the lamellae is clearly evidenced by the sets of concentric rings of lamellae as they stand edge-on at one stage of their twist period.

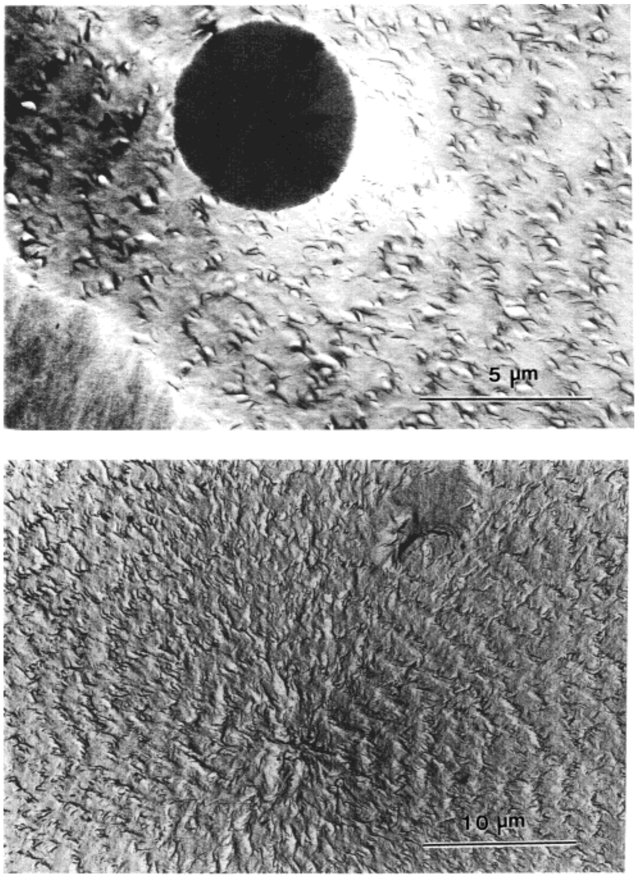

Figure 2. (a) Transmission electron micrograph of a thin film of iPBu-1 crystallized in the presence of amyl acetate and that displays the three crystal phases of iPBu-1. The round, dark object is a spherulite or hedrite of form I′. The uniform, gray area in the lower left corner is part of a spherulite in form II (possibly having experienced transformation to form I). The main field of view shows part of a spherulite in form III. It displays a very prominent banding, indicative of lamellar twisting (half-period of twist: 1.7 μm). The growth rate of form III is here significantly higher than that of form II. Pt/C shadowing. (b) Transmission electron micrograph of a similar thin film of iPBu-1 after shadowing with Pt/C and redissolution of the polymer (one stage replica). The periodic banding visible in Figure 1 arises from the twisting of lamellae.

The crystal modification is best assessed by electron diffraction (Figure 3). The circular objects display the expected diffraction pattern (not shown) with hexagonal symmetry corresponding to the *hk*0 reflections of the trigonal unit cell of form I′.[21] In thin film growth, these objects may be described as hedrites, in Phil Geil's terminology,[22] as assessed by the absence of *hkl* reflections in the diffraction pattern. Nearly flat-on lamellae in thin areas of form II spherulites display a tetragonal diffraction pattern when examined shortly after crystallization. The patterns convert to the hexagonal symmetry of form I when the samples are left to stand and experience the II to I transformation.[13,14,23] In any one small radial growth sector, either "twinned" and "untwinned" form I patterns can be obtained.[1,16,17] Relative orientations of form II and form I patterns result from the constraint of maintaining helical hand during the transformation process.[13,14,23,24] As a result, the radial [110] direction of form II becomes [110] of form I in the transformed spherulites.

The weakly birefringent spherulites yield a diffraction pattern of form III (Figure 3a). For convenience, this pattern is again taken in a very thin part of the film and therefore displays mainly (only) *hk*0 reflections of the orthorhombic unit cell (the 200 and 110 reflections).[15,16] In addition, the *a* axis of the unit cell corresponds to the radial growth direction of the spherulite.

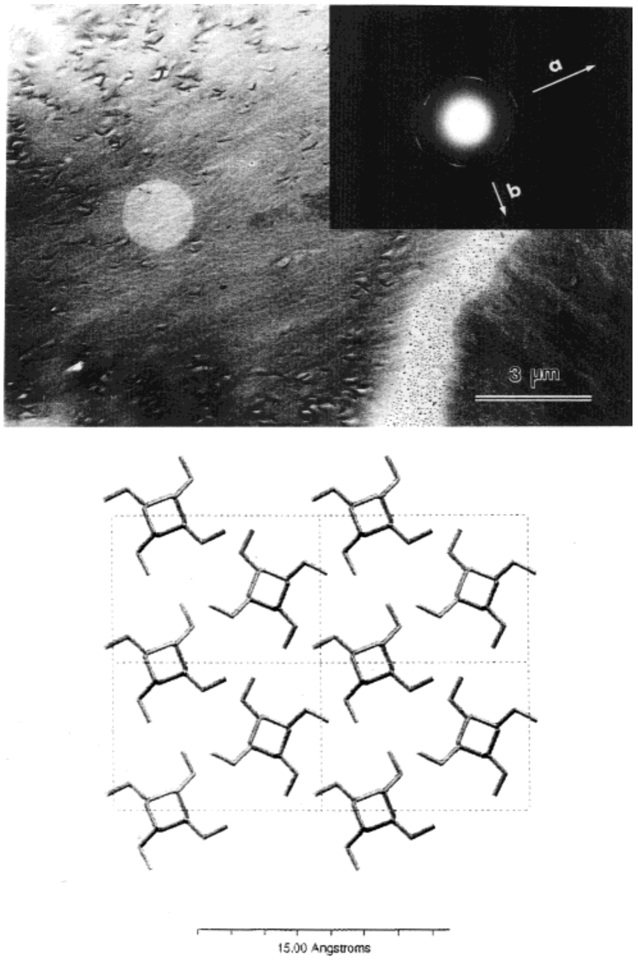

Figure 3. (a) Selected area electron diffraction pattern of iPBu-1 form III spherulite (inset) and the corresponding field of view, taken in the defocused diffraction pattern mode in order to maintain the proper relative orientation. The reflections are *hk*0, indicating that, in the thinner area selected (lighter area), the lamellae are mainly flat-on and the chains are parallel to the electron beam. (b) Crystal structure of isotactic poly(1-butene) form III: orthorhombic unit cell, two chains per cell in 4_1 helix conformation.[15,16] Four unit cells are shown. The *a* axis is radial in the spherulites.

A most conspicuous and original feature of these spherulites is that they are built of *highly twisted lamellae*, as best seen in slightly thicker parts of the film. In Figure 2a, the twist periodicity is about 4 μm (half-periodicity is 2 μm; it is 5 μm in Figure 1b). More interestingly, the origin of this lamellar twisting appears to be quite unconventional in polymer morphology, as examined now.

Lamellar twisting is a frequent feature in polymer spherulites.[25−27] Although the origin of lamellar twisting is still debated,[28−32] the roots rest in structural and/or conformational features of the stems or folds that build up the lamellae.[31,32] Twisting as sometimes observed in achiral polymers (e.g., polyethylene) has a *structural origin*: it is linked with the tilt of the polethylene chains to the lamellar normal and is explained by surface stresses generated by differences in fold conformation on opposite fold surfaces of the lamellae.[31−33] Twisted lamellae are also frequently observed for *chiral polymers*, i.e., polymers that have an asymmetric carbon in their main chain. Well-known examples are the silk fibroin of *Bombyx mori L.*,[34] poly(hydroxy butyrate),[35] and poly(epichlorohydrin).[36] In most (but not all[37,38]) cases, the sense of twist is linked with the *configuration of the asymmetric carbon* in the chain; indeed, enantiomers display lamellar twists in opposite directions. For example, the lamellar twist in silk fibroïn results from the fact that the lowest energy conformation of the L-peptide residues does not yield a “pure” 2_1 helix, but rather a skewed one. Hydrogen bonding between successive skewed chains generates a twisted β sheet, observed very prominently in globular proteins.[32,34] The sheet and resulting crystal twisting can be correlated with the configuration (L- or D-) of the amino acids that build up the *crystalline core* of silk fibroin. More generally, the kind of *configurational chirality* just described imposes that helices adopt a specific handedness, which often translates in specific lamellar twist.

The situation with form III iPBu-1 is quite different. Indeed, *iPBu-1 is a chiral but racemic polymer that can adopt both right- and left-handed helical conformations*. For example, forms I and II can be viewed as “conformational stereocomplexes” in which right-handed helices (3_1 and 11_3, respectively) are surrounded by left-handed helices, and reciprocally. Form III, on the contrary, is an *isochiral* crystal phase: its unit cell houses right-handed (or left-handed) helices *only*. In other words, the lamellar twist observed for form III iPBu-1 conforms to the rule of lamellar twist associated with chirality of the building helices, but *the origin of the helix chirality is conformational rather than configurational*. If this correlation holds true, *the sense of lamellar twist may be used as a “morphological probe” to determine the underlying helix chirality*, much like the lamellar twist in polyethylene can be used to determine the sense of chain tilt.[33]

The formation of spherulites of the chiral polymorph III of iPBu-1 just described is very reminiscent of the β form of isotactic polypropylene (βiPP). Here also, we are dealing with a crystal phase that is isochiral (trigonal, frustrated crystal structure),[39,40] contrary to the conformationally “racemic” α and γ phases. The spherulites of βiPP are also formed of twisting lamellae, but only in a relatively small T_c range, at high temperatures.[41] Furthermore, the degree of twisting is significantly smaller than for form III of iPBu-1 (periodicities in the tens of micrometers are the norm). It is difficult to analyze the origin of this different behavior, which may rest on several causes:

(i) The crystal structure of βiPP is known to display significant structural disorder.[40,42,43] Some disorders may exist within any one isochiral domain (different azimuthal settings of the chains on their axis depending on the local environment of up- and down-chains, etc.). However, coexistence of domains made of left-handed helices and domains made of right-handed helices separated by antiphase boundaries cannot be ruled out. If so, the correlation between lamellar twist and helix hand would no longer apply, since the lamella (as a whole) would behave as a racemate or more exactly as a blend of domains made up of the two enantiomeric helix conformations. If valid, this explanation would imply, a contrario, that growth of form III iPBu-1 selects more drastically the helix hand of the depositing chain, i.e., is more resilient to the formation of enantiomorphous domains separated by antiphase boundaries.

(ii) The trigonal unit-cell symmetry of βiPP results in lamellae that are significantly wider (laterally) than for form III iPBu-1. As the twist period decreases with lamellar width,[26] the “slimmer” lamellae of the orthorhombic form III are likely to twist more easily than those of βiPP.

Whereas the exact causes of lamellar twist in spherulites of chiral, helical polymers are not known, it is of interest to remind, as pointed out in the Introduction, that solution grown single crystals of form III are scrolled.[1] From inspection of the published figures, it appears that the scroll axis is very frequently normal to one set of the lateral (110) growth faces (cf. Figure 6 in ref 4). Scrolling of single crystals and twisting of spherulite lamellae are likely to have, if not identical, at least similar causes. The latter are most probably surface stresses, as has been analyzed in the case of scrolled lamellae of poly(vinylidene fluoride), γ phase,[44,45] or of long chain parafins that bear either a methyl or a butyl substituent in their middle and crystallize in a hairpin fashion.[46] A somewhat similar observation of lamellar twisting in spherulites and scrolled (or at least rolled) single crystals produced from solution has been reported for chiral (*R*)- or (*S*)-poly(epichlorohydrin) by Saracovan et al.[36] The detailed origin of the surface stresses in PBu-1 form III (and more generally in chiral polymers) and their different impact on single-crystal morphology (scrolling) and spherulite lamellae (twisting) needs to be investigated in further detail.[32,36] These stresses may well however result from the constraints set on the fold conformations by the chiral character and/or helical conformations of the chains as they “reach” the fold surface.[32]

Finally, the observed very weak birefringence of the form III spherulites is another feature of interest, very rare in polymer science. Absence of birefringence due to small size and randomness in crystal orientation, as generated for example by homogeneous nucleation upon quenching poly(ethylene oxide)[47,48] or other crystallizable polymers can be ruled out. In the present case, we are most probably dealing with a situation already encountered for the stable, tetragonal crystal phase of isotactic poly(4-methylpentene-1). In the 7_2 helices of this form, the refractive indices along the chain and normal to it are, by coincidence, nearly equal, thus conferring an overall isotropy to the system. In iPBu-1, the three crystal phases have helix geometries that are “stretched” to different extents along the chain axis. The trigonal form I or I′ and tetragonal form II have positive, uniaxial optical indicatrices ($n_c > n_a = n_b$). Form III has a biaxial optical indicatrix (orthorhombic unit cell), but with probably n_a nearly equal to n_b, on account of the very symmetrical 4_1 helix conformation. Compared to forms I and II, the chain conformation is “fatter” and “shorter” in form III. Therefore, the optical indicatrix of form III is “less positive” than those of forms I and II, since polarizabilities along and normal to the helix axis in form III are reduced and increased, respectively. Actually, the three indices in form III appear to be accidentally nearly equal thus providing, besides the well-known example of isotactic poly(4-methylpentene-1), another example of an optically near-isotropic polyolefin crystal modification.

Conclusion. Spherulites of form III iPBu-1 have been obtained from a melt in the presence of amyl acetate, together with the more common form II and I′ ones. The preparation conditions are not “clean” since some solvent is needed that also promotes the formation of form III single crystals in dilute solution. This situation is not however without precedent. Indeed, Keith[49] has pointed out that the most common form of poly(ethylene sebacate) is produced “in the presence of moisture absorbed in the polymer or (in) the presence of sebacic acid often remaining as a contaminant after synthesis”. Under “cleaner” conditions, i.e., *in the absence* of moisture, a new crystal polymorph is formed, together with the more common crystal form.[49]

Under the experimental conditions used, the growth rate of form III spherulites is either larger or smaller than that of form II. Since the crystallization conditions are not well controlled, such variability is to be expected but needs to be explored in further detail. Both forms, however, have growth rates significantly larger than that of form I′. The spherulites are built of highly twisted lamellae (with fastest, radial growth direction along *a*), whereas single crystals of form III grown from solution are scrolled. The nonplanarity of form III lamellae, although different for melt and solution crystallization, is probably linked with the existence of surface stresses and the fact that iPBu-1 form III is a chiral crystal structure.

Spherulites of form III have very little birefringence. Form III iPBu-1 has an orthorhombic cell symmetry. Its optical indicatrix is biaxial, but n_a, n_b, and n_c are coincidentally nearly equal, as is also the case for the stable modification I of isotactic poly(4-methylpentene-1).

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