

Structure and morphology of poly(propylenes): a molecular analysis

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The progress made in the understanding of the crystal polymorphism and morphology of isotactic and syndiotactic poly(propylene) (iPP and sPP) is reviewed. In 1960, the crystal structure of the stable form of iPP, the α phase, was already solved and the general principles of polyolefin chain conformation and crystallography established. The molecular analysis of the lamellar branching of α iPP—a case of homoeptaxy specific to this polymer and this crystal form—was given in 1986. The γ phase of iPP, solved in 1989, is the first and so far unique example of a polymer structure with non-parallel chain stems. The β phase is the first example of a frustrated structure in polymers, and rests on packing of isochiral helices in the unit-cell. The stable, high temperature form of sPP described in 1988 is based on full antichiral packing of helices, whereas the original structure corresponds to another limiting (but not experimentally observed in pure form) case based on packing of isochiral helices. Details of the molecular structure of iPP and sPP, such as the hand of individual helical stems and setting of chains, are accessible by crystallographic considerations which make use of molecular markers provided by the α - α and α - γ epitaxies in iPP or by direct visualization by atomic force microscopy. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The invitation to give a presentation for this anniversary meeting of *Polymer* indicated that it 'may also briefly describe the development state of (the) subject area some 35 years ago'. It offers, therefore, an ideal opportunity to present the progress made in our understanding of the structure and the morphologies of isotactic and syndiotactic poly(propylenes) (iPP and sPP), which happen to have reached near completion only recently. In particular, the two lesser common crystalline modifications of isotactic poly(propylene), the β and the γ phases, which were discovered^{1,2} just before this journal was launched, were solved only in 1994 and 1989, 35 and 30 years after their initial observation—a nearly perfect match with the time span suggested for this presentation.

iPP and sPP are ideal systems to analyse the rules which govern the conformation of polyolefins and their crystallographic packing. Indeed, since they bear a side chain, their main chain conformation is representative of a number of polyolefins with longer and bulkier side chains. At the same time, the position of the methyl group is uniquely determined by the backbone conformation: the rules which govern packing of helices are not blurred by possible conformational flexibility inherent to longer side chains. Given these constraints and their relatively simple helical shapes, the structural versatility of sPP and particularly iPP is truly

astonishing. It is for the most part based on both original combination of helices with different hands and/or on original packing schemes which could not be solved by conventional structure analysis.

The present contribution will develop in some detail the *molecular aspects* of the various crystal modifications of iPP and sPP. It will focus on the ability to determine the *helical hand* within the structure, either by a simple reasoning which blends crystallographic and morphological aspects (for the lamellar branching of α iPP) or by the use of modern near field microscopies, namely atomic force microscopy (AFM). Its scope, therefore, differs somewhat from that of extensive reviews by Brückner *et al.*³ on the polymorphism of isotactic poly(propylene) which was moreover written before the resolution of the β structure of iPP, and the review of Rodriguez-Arnold *et al.*⁴ on the structural and crystallization aspects of syndiotactic poly(propylene). Since this paper concentrates on the molecular aspects, it will not deal with many important aspects of the bulk crystalline structure of iPP as investigated in particular by Bassett *et al.*⁵ or the melting and transformation of the α and β phases of iPP as studied by Varga *et al.*⁶ and ourselves⁷.

THE STRUCTURES AND MORPHOLOGIES OF ISOTACTIC POLY(PROPYLENE)

Polymorphism based on packing of isostructural helices

The crystalline polymorphism of isotactic poly(propylene) involves only one helical conformation,

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a three-fold helix with 6.5 Å chain axis repeat distance. In the light of the recent solutions of its β and γ phases, this polymorphism appears to rest, besides the 'classical' α phase, on the most original packing schemes of helices ever encountered in synthetic polymers. In this section we consider four different topics: (i) the α phase crystal structure, as first established by Natta and Corradini in 1960⁸. This textbook structure is ideally suited to develop the principles of chain conformation and chain packing of polyolefins; (ii) a molecular analysis of the lamellar branching characteristic of this α phase; (iii) the γ phase structure, its original non-parallelism of chains, the similarities with the α phase lamellar branching and the α - γ phases epitaxial relationship; (iv) the β phase and its original frustrated structure.

The α phase structure of iPP

The crystal structure of the most common crystal phase of iPP—the α phase (α iPP)—as established by Natta and Corradini⁶ is reproduced in Figure 1. The overall geometry of the cell is monoclinic, with parameters $a = 6.65$ Å, $b = 20.96$ Å, $c = 6.5$ Å, $\beta = 99^\circ 80'$. It must be noted that, except for a small shift of chains along the c axis and small adjustments of cell parameters, this structure has been confirmed by all subsequent studies^{9,10}.

The structure helps illustrate the classical principles underlying the structure of polyolefins:

- the chain conformation is a ternary helix based on tg^+ and g^-t conformations which avoid methyl-methyl steric conflicts characteristic of extended isotactic chains and lead to left-handed and right-handed helices, respectively.

- the packing of helices is such that any helix interacts mostly with helices of opposite hand. It follows that α iPP is based on an alternation, in the b axis direction, of layers parallel to the ac plane and made only of left-handed, or only of right-handed helices.
- two helices are shown on each site by full and dashed lines, indicating that any site can be occupied by either an 'up' or a 'down' pointing helix; this sense is defined by the orientation of the C(H) – C(H₃) bond relative to the helix axis. Provided that the methyl groups are positioned at the same place, the shapes of the molecular envelopes of 'up' and 'down' helices are nearly identical or, to put it in more appropriate terms, anticline isochiral helices are nearly isostructural.

This isostructuralism is not perfect, however, and well annealed α iPP displays reflections which indicate a bias toward a more regular alternation, along the b axis direction, of *anticline ac bilayers*, each bilayer being made of two layers of antichiral helices. The progressive elucidation of this structural preference and the major contributions towards its analysis by, among others⁸, the group of Corradini in Naples¹¹ have been reviewed in considerable detail by Brückner *et al.*³. Beyond acknowledging this possibility, we will *not* consider in the following the issue of up or down orientation of helices, but concentrate on the *helical hand*.

- a final issue, essential for the analyses developed in the next sections, deals with the azimuthal orientations of helices on their axis, i.e. on the setting angles relative to the a and b crystallographic axes. For every helical turn, each 3_1 helix has one methyl group pointing in either the $+b$ or the $-b$ direction, and two methyl groups in a plane parallel to the ac plane. This creates

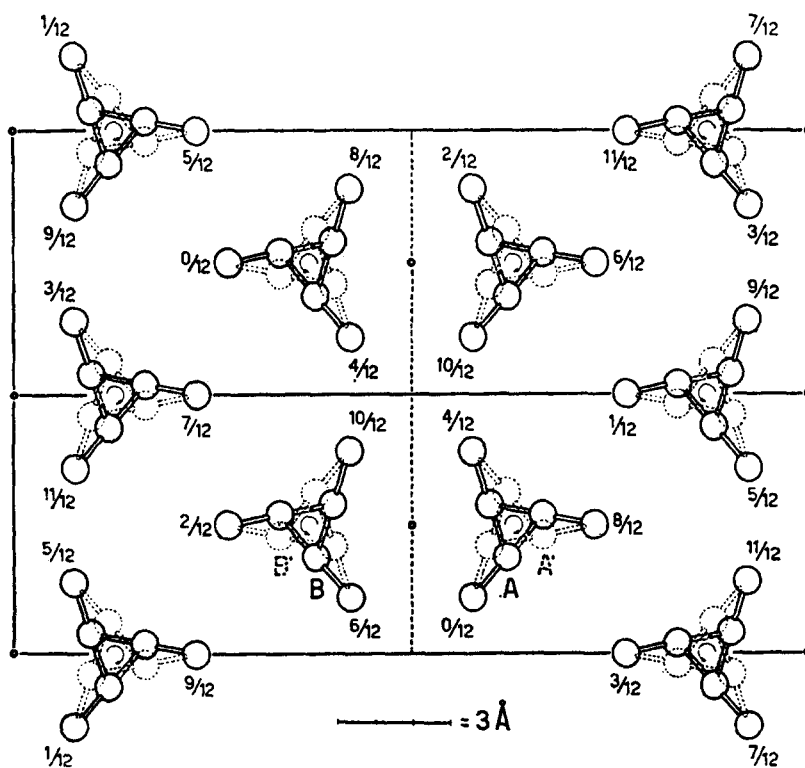


Figure 1 Crystal structure of the α phase of iPP as determined by Natta and Corradini. Two unit cells are shown. a^* axis vertical, b axis horizontal. The crystal structure includes statistical occupation of every chain site by either an up- or a down-pointing chain (anticline isochiral helices). Reproduced from ref. 8

four distinct *ac* faces, two as seen from the $+b$ and two from the $-b$ direction, for which the *hand* and *setting angle* of helices is different. As can be seen in Figure 2, these faces obey a very simple *structural rule*: in the nearly lozenge shaped *ac* face, and irrespective of the actual helix hand, the *exposed helical path is parallel to*:

- the *long* diagonal of the *ac* lozenge when *one* methyl group is exposed, and
- the *short* diagonal of the *ac* lozenge when *two* methyl groups are exposed.

This rule is schematized in a simple mnemonic form in Figure 3 by arrows (the helical path) oriented parallel to the long and short diagonals of the lozenge *ac* plane and supporting one or two circles (the exposed methyl group(s)), respectively. Note that the actual hand of the helix bearing this (or these) methyl group(s) will then depend on the helix axis being oriented parallel to one or the other cell edges. This rule will help analyse the molecular origin of the characteristic lamellar branching of α iPP described next.

Lamellar branching of α iPP

α iPP exhibits a lamellar branching that is unique in polymer crystallography, and also unique to this specific crystal form. This branching manifests itself under all

crystallization conditions: (a) in solution crystallization, it results in the formation of interwoven arrays of lamellae, a structure described as 'quadrites' by Khoury¹²; (b) a spectacular manifestation is shown in thin film growth in Figure 4; (c) this branching leads to both radial and nearly tangential orientation of lamellae in spherulitic growth: the α iPP spherulites may therefore display a highly unusual positive optical character, which is not expected from the optical properties of the crystal lattice; (d) in fibres, a component with its chain axis nearly at right angles to the fibre axis may develop for intermediate or slow take-up speeds. *Lamellar branching is therefore an intrinsic property of α iPP* which manifests itself under nearly every crystallization condition. Its impact decreases in melt crystallization only at very high ($> 160^\circ\text{C}$)¹³ or very low ($< \sim 90^\circ\text{C}$)¹⁴ crystallization temperatures.

This lamellar branching was observed in the early 1960s¹⁵. Solution-grown quadrites were extensively studied and the link with spherulitic growth established by Khoury¹². The filiation between mother and daughter lamellae was correctly assigned to epitaxial interactions in the *ac* faces by Keith and Padden¹⁶ with the *a* and *c* axes of one set of lamellae parallel to the *c* and *a* axes of the other set, and Binsbergen and de Lange¹⁷ correctly concluded that the epitaxial interactions correspond to

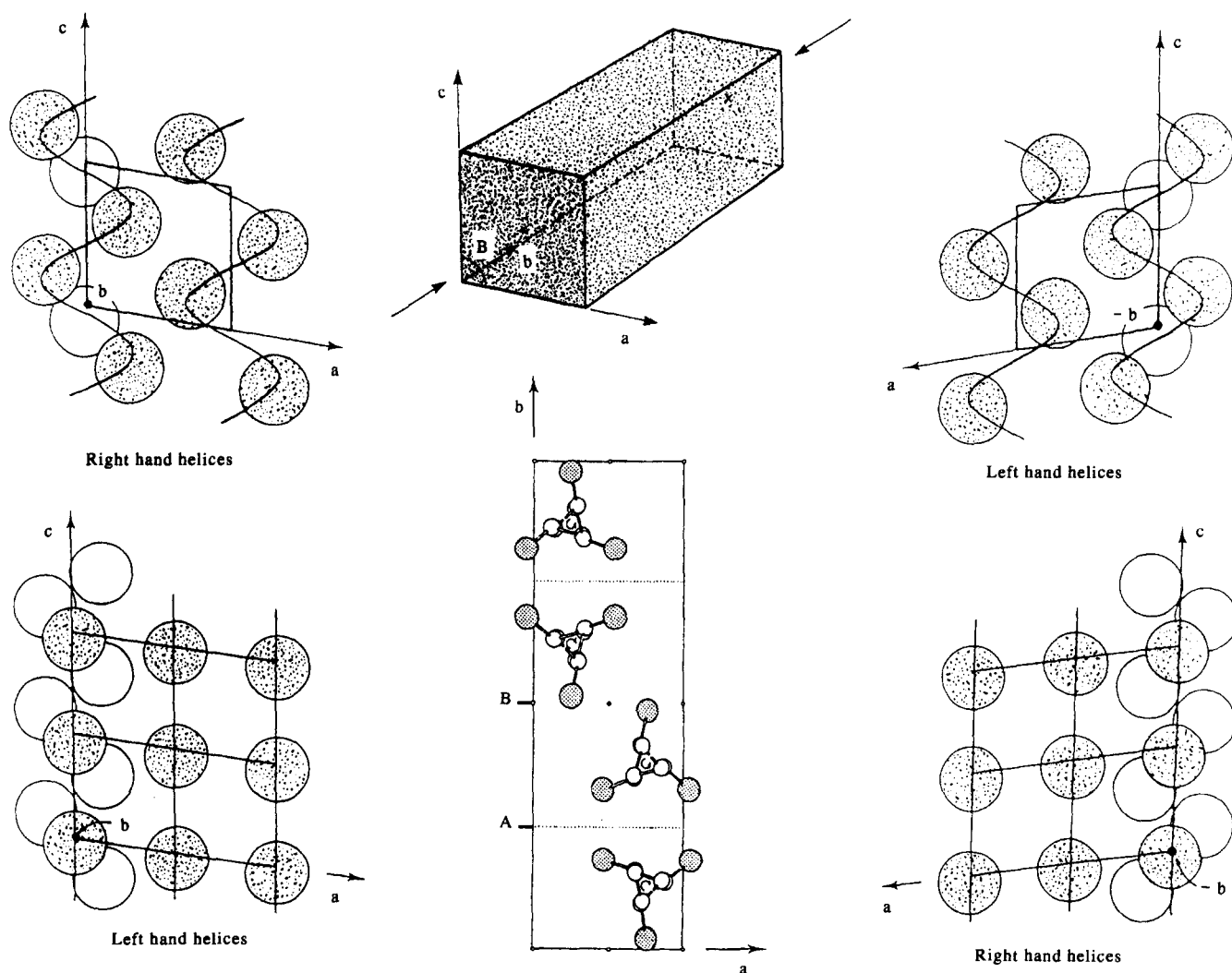


Figure 2 The different exposure faces of the α phase of iPP as seen from the $+b$ and $-b$ directions (left and right hand sides of the figure, respectively). Faces A and B (indicated in the centre lower figure) have low and high densities of exposed methyl groups, respectively. Reproduced from ref. 21

'a fit of molecular subgroups', i.e. to an interdigitation of methyl groups in the contact planes.

The complete molecular picture of the epitaxy was established only nearly 20 years later¹⁸ when the role of the *hand of helices interacting in the contact plane* was clarified: branching takes place *whenever* two successive *ac* layers are made of chains of the *same* hand, whereas the crystallographic unit cell requires that they are of *opposite* hand.

In a shorthand form, the argument is as follows¹⁸: consider the nearly perfect interdigitation of the methyl groups of two different, facing *ac* layers across the contact face marked B in *Figure 5*. Presence of only one methyl group indicates that in both layers the facing helical paths are parallel to the long diagonal of the *ac* face. If (as shown in the right hand side of the figure) the

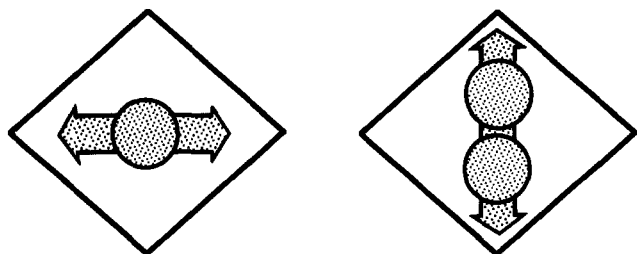


Figure 3 Simplified representation of the exposed helical path in the *ac* plane of the α phase of iPP. The actual helical hand depends on which of the cell edges the helix axis is parallel to

helix axes are parallel to the same cell edge, the helices are of opposite hand (remember that the back of the front helix is seen) and the normal crystal structure is created. If the helix axes are parallel to different cell edges, the helices are of the same hand. Chain axes are mutually rotated by the β monoclinic angle, and a daughter, branch lamella may be created from this initial nucleus: lamellar branching is thus a manifestation of a 'mistake' in the strict alteration of helical hands in successive *ac* layers.

The reasoning just developed for face B is equally valid for face A with two methyl groups. In our initial analysis¹⁸, an ambiguity therefore remained about the exact nature of the contact face, and face A was considered as more probable. This ambiguity has now been removed through the elucidation of the γ phase structure (cf. below) and recent atomic force microscopy of epitaxially crystallized α iPP.

Epitaxy of iPP on a substrate of benzoic or nicotinic acid leads to a quadrite-type interwoven array of α iPP lamellae standing edge-on. Dissolution of the benzoic acid substrate leaves the iPP contact face exposed (*Figure 6a*). When examined by AFM^{20,21}, it revealed a lozenge type pattern of methyl groups 6.5 Å apart (*Figure 6b*). This pattern, similar to the 'four' face of dice is characteristic of faces B. Faces A would display a denser array of methyl groups more akin to the 'five' face of dice. This result suggests that the *ac* face with lowest density of methyl groups is more likely to be involved in epitaxial interactions. Proof of its implication is the



Figure 4 Electron micrograph of a thin film of the α phase of iPP crystallized on a mica sheet at $\approx 130^\circ\text{C}$ and shadowed with Pt/C. Note the profuse branching of lamellae at a constant 100° or 80° angle. This lamellar branching is at the root of the unusual optical properties of spherulites of the α phase. Scale bar: $5\ \mu\text{m}$

homoepitaxy leading to lamellar branching was actually provided by the resolution of the γ phase structure.

Before dealing with the γ phase, it is worth emphasizing that the lamellar branching of α iPP is in essence a molecular marker which helps us gain an intimate knowledge of the molecular structure which has *no equivalent* for any other crystalline polymer. Specifically, *the right or left hand and the setting angle of every helical stem in α iPP can be determined by a simple analysis of the branching habit.* This analysis was first given in a (half page!) legend of Figure 9 of ref. 18 and does not seem to have attracted much attention. In particular, it is never mentioned—much less developed—in recent reviews on iPP morphology.

It may therefore be useful to present again the—actually rather straightforward—reasoning which blends morphological and structural aspects (cf. Figure 7).

In an α iPP quadrite or spherulite, mother and daughter lamellae are 100° (the β monoclinic angle) or 80° apart. In each set of lamellae, the chain axis c is parallel to the lamellar normal. Since this chain axis is parallel to the a axis of the other set of lamellae (as a result of the epitaxial relationship), the a axis orientation in *each set of lamellae* can be determined *morphologically*: it is parallel to the lamellar normal of the other set of lamellae. This relationship helps position unambiguously the lozenge shaped ac unit-cell relative to the quadrite. Combining this information with the helical paths indicated in Figure 3, it is clear that exposed helical paths bearing *two* methyl groups are parallel to the bisector of the *acute* angle of the quadrite and paths bearing *one* methyl group are parallel to the bisector of the *obtuse* angle of the quadrite.

Knowing further that the actual chain axis orientation is parallel to the lamellar normal in each set of lamellae, it is evident that lamellae oriented to the upper right in

Figure 7 are made of layers of right-handed helices in which two methyl groups face the viewer, alternating with layers made of left-handed helices in which only one methyl group faces the viewer. The hand of helices is opposite in the set of lamellae oriented to the upper left. In other words, the α iPP unit cell is seen from the $+b$ direction in the former and from the $-b$ direction in the latter set of lamellae.

Finally, note that a 180° rotation of one set of lamellae along any one of the bisectors generates the other set of lamellae: this operation corresponds to a rotation twin, as already mentioned by Khoury¹² who, however, did not develop the molecular analysis outlined here.

The γ phase of iPP: structure, morphology and relation with the α phase

The γ phase of iPP had remained rather elusive for many years. It is not usually observed as a different phase, but (co)crystallizes with and within the α phase spherulites. It was first mentioned by Addink and Beintema in 1961², who observed an additional reflection in X-ray powder patterns of low M_w iPP. It was later obtained by crystallization of 'conventional' iPP under high pressure^{22,23} (probably on account of its slightly higher density) and of iPP with a few per cent of comonomer at atmospheric pressure²⁴. The chemical and physical requirements of its formation are the subject of ongoing research, which has been revived by the recent availability of well defined iPP copolymers produced by metallocene catalysts²⁵.

The crystal structure of γ iPP has long remained a puzzle. No fibre patterns are available (cf. below) and electron microscopic studies indicate that it crystallizes on the lateral ac faces of α iPP (α - γ lamellar branching). A structural similarity, or at least compatibility, with the α phase was suspected and a triclinic unit-cell,

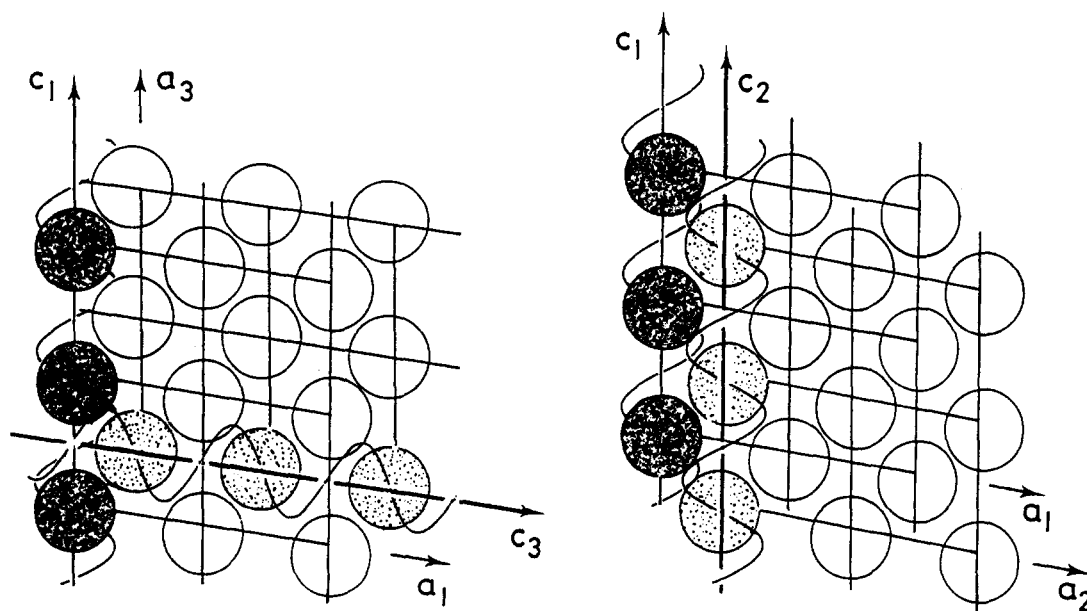


Figure 5 Molecular analysis of the epitaxial deposition of helices leading to the lamellar branching in the α phase of iPP. The methyl groups of one helix of the substrate crystal are shown heavily shaded and are seen from the *front* (the helix axis is behind the methyl groups). The methyl groups of one of the depositing chains are shown lightly shaded, and are seen from their *back* (the helix axis, shown as a heavy line, is in front of the methyl groups: this inverts the helix hand as would be determined from Figure 3). If the substrate and depositing helix axes are parallel to the same edge of the cell, their hands are opposite (crystallographic packing, right hand side of the figure). If they are parallel to different cell edges, the helices are of the same hand (epitaxial packing, left hand side). The interactions of methyl groups of facing planes are essentially similar in the two situations

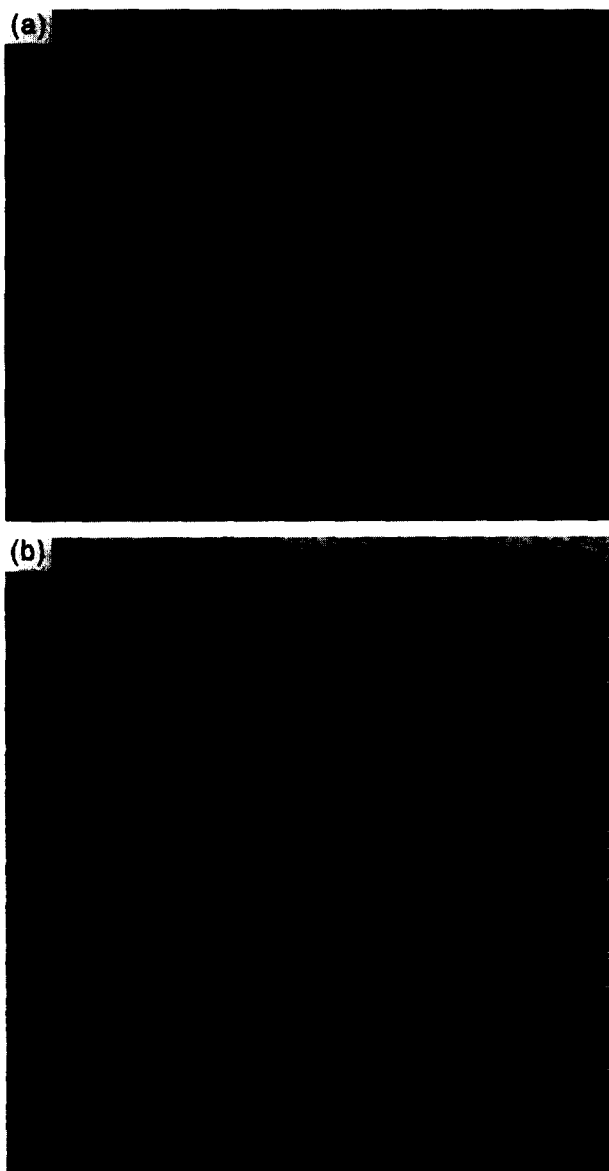


Figure 6 (a) Thin film of the α phase of iPP epitaxially crystallized on benzoic acid. The benzoic acid substrate has been removed by dissolution in methanol, and the iPP film shadowed with Pt/C. α iPP produces edge-on lamellae oriented at 80° or 100° to each other as in quadrites since the ac contact surface is involved in the epitaxy with the substrate. Reproduced from ref. 20. (b) AFM picture of an area as in (a) taken when probing the sample immersed under water (wet cell). The three dark stripes oriented at 1 o'clock indicate the orientation of the fold surfaces of the edge-on lamellae: this AFM picture is almost properly oriented relative to (a) but images only one set of three parallel lamellae of that picture. The pattern of exposed methyl groups appears as an almost square array of dots $\approx 6.5 \text{ \AA}$ apart. Within any lamella, rows of methyl groups normal to the fold surfaces belong to the same helical stem. Size of area: $35 \times 35 \text{ nm}^2$. Reproduced from ref. 21

corresponding to a slightly deformed α phase unit-cell was long assumed for the γ phase^{24,26}.

The real breakthrough in our understanding of the γ phase structure dates from a paper published by Meille and Brückner in 1989²⁷. These authors reevaluated the geometry of the proposed triclinic cell on the basis of improved X-ray powder pattern data and published electron diffraction data²⁸. They noted that the triclinic cell is a sub-cell of a much larger face-centred orthorhombic unit cell with parameters $a = 8.54 \text{ \AA}$, $b = 9.93 \text{ \AA}$, $c = 42.41 \text{ \AA}$. The relationship between the

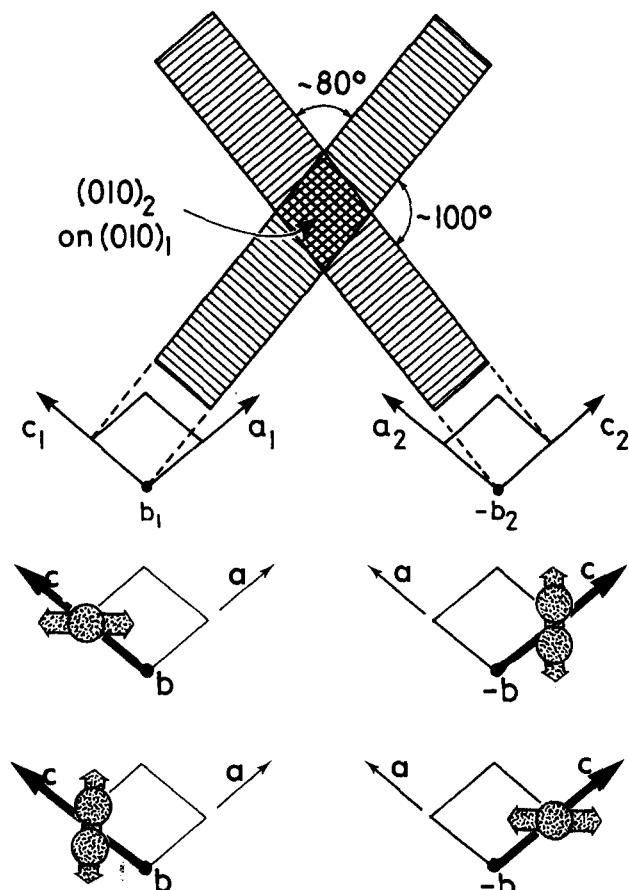


Figure 7 Molecular analysis of the hand and setting of three-fold helices by using the quadrite-type habit of the α phase of iPP. The orientation of the chain axis normal to the lamellar surface helps orient the a and c (or c and a) cell edges of the ac face of α iPP. Combined with the information on the orientation of the helical path contained in Figure 3, the hand and setting angle of all the helical stems in the quadrite can be derived

two cells is such that the c axis of the smaller cell is parallel to the diagonals of the ab plane of the larger cell. Carrying on this analysis, Meille and Brückner were led to propose a structure which departs from common tenets of polymer crystallography, in that *the chain axes in the structure are not parallel* (Figure 8). For a development of the crystallographic arguments and the details of the structure, the reader is referred to the original papers^{27,29} and the review of Brückner *et al.*³

The basic feature of the γ phase, which leads to the non-parallelism of chains, can be summarized in simple terms with reference to the α phase lamellar branching analysed above: across the contact faces B (which involve one methyl group per unit cell) the homoepitaxial deposition (at an angle of 100°) of a layer of isochiral chains is *always preferred* over the 'crystallographic' (parallel chain axes, leading to α iPP) deposition of a layer of antichiral helices. Across contact faces A however, parallelism of chain axes and therefore packing of antichiral layers prevails. As a result, *the structure is made up of a succession of bilayers tilted 80° or 100° to each other*: the 2_1 screw axis leading to rotation twin and lamellar branching in α iPP has become a crystallographic element of symmetry in the γ phase unit-cell and the chain axes are parallel to the diagonals of the ab face.

Revolutionary as it may look, this structure makes

sense in many respects:

- on a local scale no steric conflicts exist, as interdigitation of facing arrays of methyl groups is respected;
- it accounts in simple terms for the α - γ filiation under normal growth conditions: the interacting α and γ faces are indeed isostuctural;
- it explains several important structural elements of γ iPP. In particular, γ iPP crystallizes in an apparently 'normal' lamellar structure. Yet, as indicated by Meille *et al.*²⁹, the lamellar surface must bear a specific relationship with the unit-cell crystallography: it must be *symmetrically oriented with respect to the two chain orientations*, i.e. γ phase lamellar fold surface *must* be parallel to one of the bisectors of the α phase quadrite lamellae. They are indeed parallel to the bisector of the acute angle: the γ phase lamellae therefore branch at a 40° angle to the α phase lamellae and the chains in the γ phase lamellae are tilted at 40° to the lamellar normal²⁸;
- it helps resolve the ambiguity about interacting *ac* faces in α iPP quadrites¹⁸. Indeed, an alternative model in which the epitaxial deposition occurs on crossing contact faces *A* in *Figure 2* shows significantly poorer agreement with X-ray intensity data²⁹;

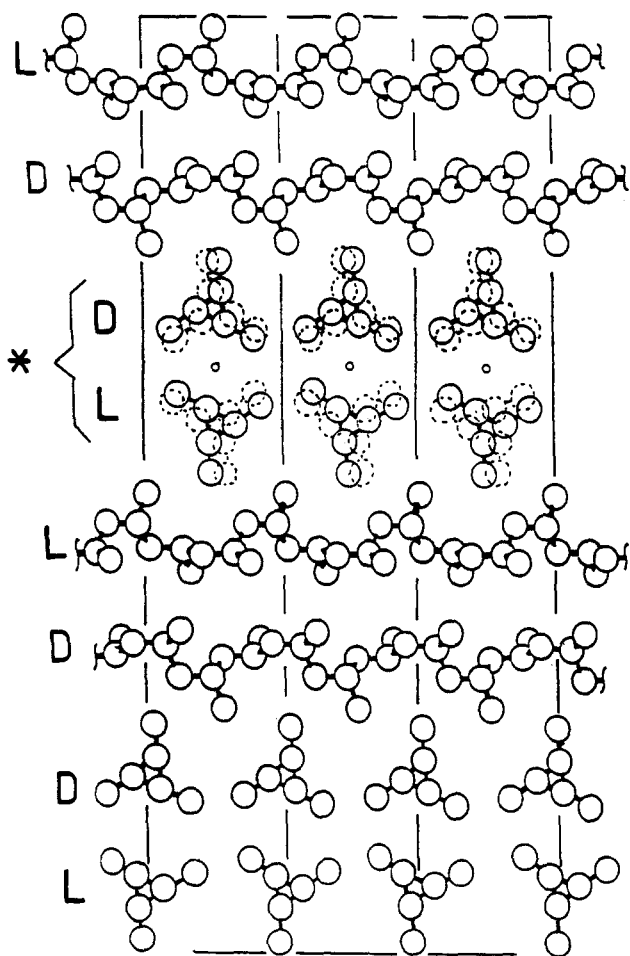


Figure 8 Crystal structure of the γ phase of iPP as determined by Brückner and Meille. The hand of helices is indicated as *L* (evogyre) and *D* (extrogyre). The building bilayer unit of the structure is identified by a bracket and an asterisk and further illustrates the possibility of statistical substitution of anticline helices, as for the α phase. Reproduced from ref. 27

- it accounts for the growth habit of γ phase lamellar single crystals, which are elongated along their *c* axis, which is normal to the two chain orientations. Indeed, 'due to the crossing of chain axes along *a* and *b*, stratification along *c* is a most likely event occurring during crystallization'³.

It should be noted however that all γ phase spherulites reported so far have positive birefringence, as do α phase spherulites²⁵. This optical character suggests that the spherulites are made of a framework of radiating α phase lamellae on which γ phase lamellae branch³. Were the spherulites made of γ phase only, the γ *c* axis would be most likely radial. In that case, all γ phase chains would be tangential to the spherulite surface, and the birefringence would be negative.

The above arguments constitute strong support, but not a direct proof of the revolutionary feature of the γ iPP structure, i.e. the non-parallelism of chains. We therefore attempted to obtain direct experimental evidence through selected area electron diffraction on γ iPP single crystals³⁰. Specifically, flat-on γ phase crystals grown in thin films were tilted at \pm and -40° around their *c* axis. The resulting diffraction patterns, taken along the two different, but crystallographically equivalent chain-axes directions, should be identical: they are indeed³⁰, and more recent dark field pictures support this symmetry³¹ (*Figure 9*). Also, the exploration of the complete reciprocal space of the single crystals confirms the position, assignment, and intensities of all the reflections calculated for this structure with non-parallel chains³⁰.

Finally, and keeping in line with the molecular analysis developed for the α iPP quadrites, it should be noted that growth of a single γ phase lamella on an α phase lamella provides (even in the absence of α phase lamellar branching) a *morphological marker* which helps determine the orientations of the short diagonal of the α phase *ac* plane and, therefore, the *a* axis orientation. It is then possible to deduce the hand, chain axis orientation and setting angle of every helical stem in the composite α - γ crystal by a reasoning similar to that developed for the α phase. For example, for the tilt of the γ phase lamella indicated in *Figure 10*, the contact faces of the α and γ phases on the right-hand side of the α phase lath involve left-handed helices interacting through their 'type-four' faces.

The β phase of iPP: a first illustration of frustration in polymer crystallography

Whereas in bulk crystallized iPP γ and α phases are usually intermixed within any one spherulite and are therefore difficult to distinguish, the β phase produces well individualized negatively birefringent spherulites admixed with, and therefore clearly recognizable from, the weakly birefringent or positive α phase spherulites. β iPP is metastable relative to α iPP ($T_m \approx 155^\circ\text{C}$ vs 170°C), grows up to 70% faster than α iPP in a temperature window extending from 141°C to 105°C (outside this window, the α phase grows faster^{6,7}), but is nucleated less profusely than α iPP, although nucleating agents which induce the formation of β iPP are known and have been patented.

Elucidation of the structure of β iPP has been a considerable challenge. From its discovery in 1959¹, it

was clear that the structure had some form of hexagonal symmetry. However, the diffraction pattern of single crystals displays a number of reflections which require a large unit-cell. Turner-Jones and Cobbold³² were led to suggest a hexagonal unit-cell with parameters $a = b = 19 \text{ \AA}$, $c = 6.5 \text{ \AA}$ even though a one chain cell would allow a sterically acceptable packing of chains^{2,32}. This large cell includes nine chains, and it is not clear how such a large number of chains can be arranged in the unit-cell (proportion of left- and right-handed helices, mutual arrangement, etc.). An excellent account of the problems raised by the structure of β iPP prior to its resolution is given by Brückner *et al.*³

The structure was finally solved in 1994, independently by Meille *et al.*³³ and by Lotz *et al.*³⁴ Both teams reached the same structural solution: a trigonal cell with parameters $a = b = 11.01 \text{ \AA}$, $c = 6.5 \text{ \AA}$ containing three isochiral helices (Figure 11). An essential characteristic of this structure, which makes it so far unique among crystalline polymers, is that it is frustrated³⁴. As such it does not comply with the rules of 'classical' crystal-

lography which postulates structural equivalency. Indeed, examination of Figure 11 indicates that the three helices do not have similar azimuthal orientations since the corner chain is rotated by $\sim 180^\circ$ (or, in view of the three fold symmetry of the helices, by $\sim 60^\circ$) relative to the two middle chains.

This frustrated structure has a well known counterpart in two dimensions: it is the diced lattice or dual Kagomé lattice³⁵. This lattice is one answer (but not a solution) to the problem created when one attempts to pack black and white dots on a close-packed hexagonal lattice, with the additional requirement that every dot of any one colour be surrounded by dots of the opposite colour. This is of course impossible, and a regular array which introduces relatively (acceptably?) small perturbations is the dual Kagomé or diced lattice (Figure 12). In this arrangement, the black dots are frustrated since they have three white and three black neighbours instead of the required six white ones. Frustration is, however, a much more general concept and occurs whenever vicinal conditions are incompatible with packing requirements.

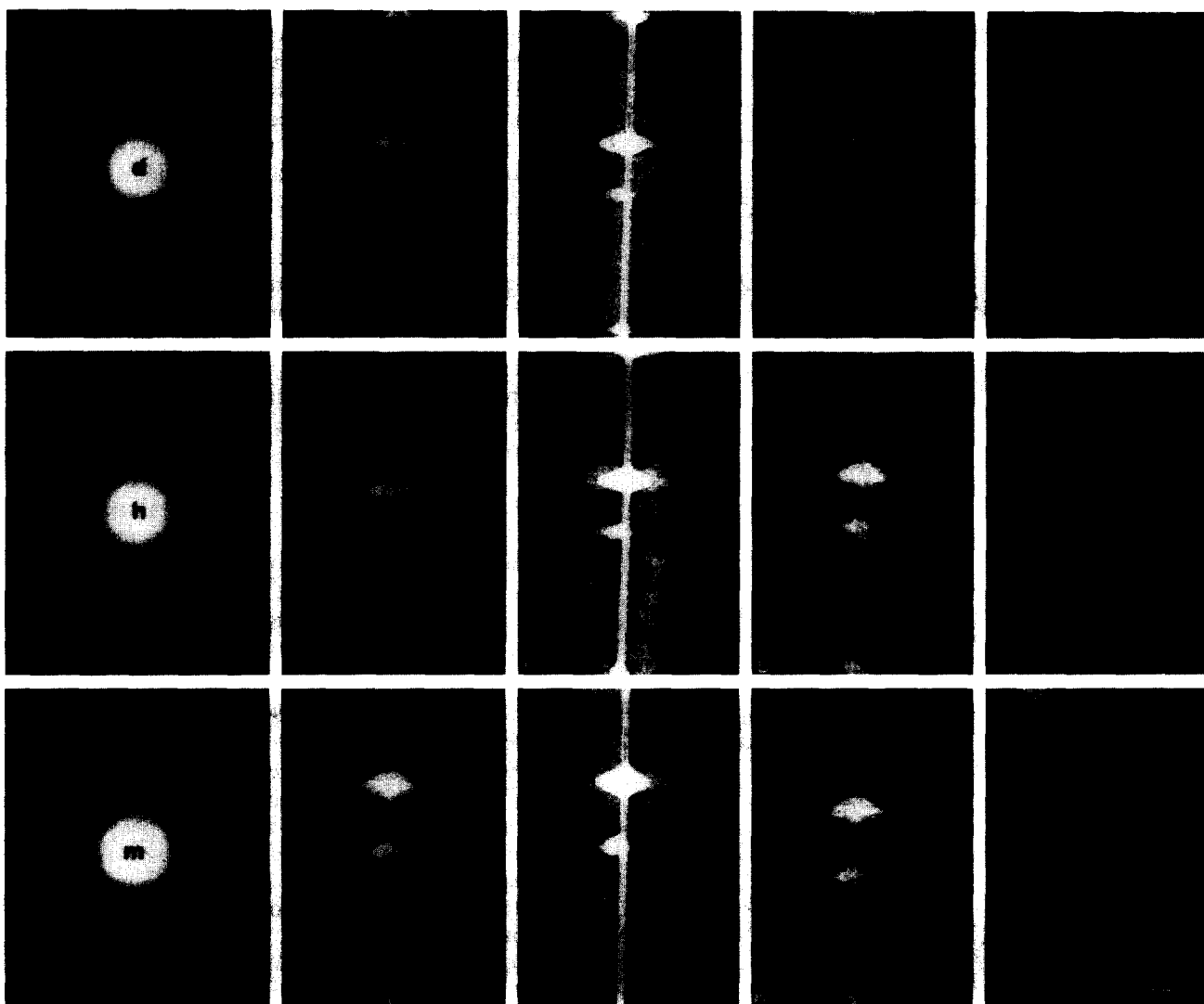


Figure 9 Diffraction patterns (left hand side of the figure), dark field images (a–c, e–g and i–k), and bright field electron micrographs (d, h, m) of composite α - γ single crystals of iPP grown in thin film on a mica sheet (the lettering of the images indicates the reflection in the diffraction pattern (or primary beam) that has been used for the imaging). The triangular, flat-on γ phase crystals of interest have grown on both sides of the central (vertical) spine of composite α - γ phases. They are observed at 0° tilt in the bottom series of pictures; in the two other sets, they are tilted around a horizontal axis by $+40^\circ$ and -40° in order to bring the electron beam parallel to the two different chain axes of the γ phase. Note the similarity in the two diffraction patterns, indicating that the γ phase 'has no fibre pattern'³⁰

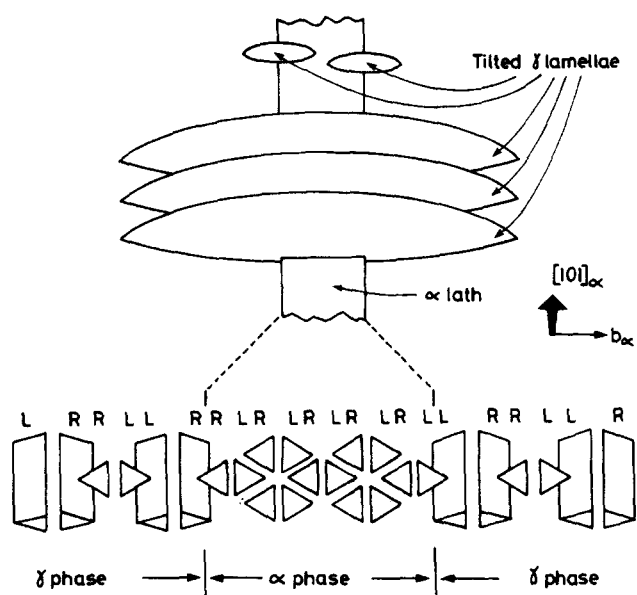


Figure 10 Molecular analysis of the helical hand in composite α - γ phase crystals of iPP. The top drawing corresponds to an enlargement of the central, vertical spine in Figure 9 (which appears as dark and bright in Figure 9d, h, m and b, f, j, respectively). The tilt of the γ phase lamellae determines the α phase a axis orientation, and the helical hand on the lateral faces follows. Since α and γ phase interact through their 'type-four' faces, the phases are in contact through left-handed helices on the right side of the α lath and right-handed helices on the left-hand side of the lath. Reproduced from ref. 30

The concept was introduced in 1977 by Toulouse³⁶ to describe the relative orientation of spins in crystal lattices, and frustrated structures are found in numerous magnetic systems. It is in particular observed in helical magnetic systems of the type ABX_3 which also pack in three-'chains' (or more appropriately three-helix) unit-cells similar to that of β iPP³⁷.

Several issues raised by the frustration of β iPP are still under investigation. These include:

- the perturbations introduced by up-down orientation of chains. Since the molecular envelopes of anticline chains are not strictly isostructural (cf. above), azimuthal reorientations and/or small lateral shifts of chains may be necessary³³. These may in turn be responsible for the characteristic streaking of $hk0$ single crystal diffraction patterns of β iPP.
- the coexistence of, and limits between, domains of different chiralities. Possible 'twin planes' or antiphase boundaries between domains made of left- and right-handed helices can be envisaged^{33,34}, but will require further experimental support.
- an analysis of the molecular features and/or energetic criteria that favour frustrated structures over other, crystallographically simpler packing schemes which are not observed, yet are sterically acceptable. Why are these features favourable enough to induce a crystal structure in which an achiral polymer behaves as if it were chiral, i.e. gives away the *a priori* more favourable possibility of packing antichiral helices? Actually, crystallization of achiral or *racemic* helical polymers in chiral crystal structures (not frustrated) is rather

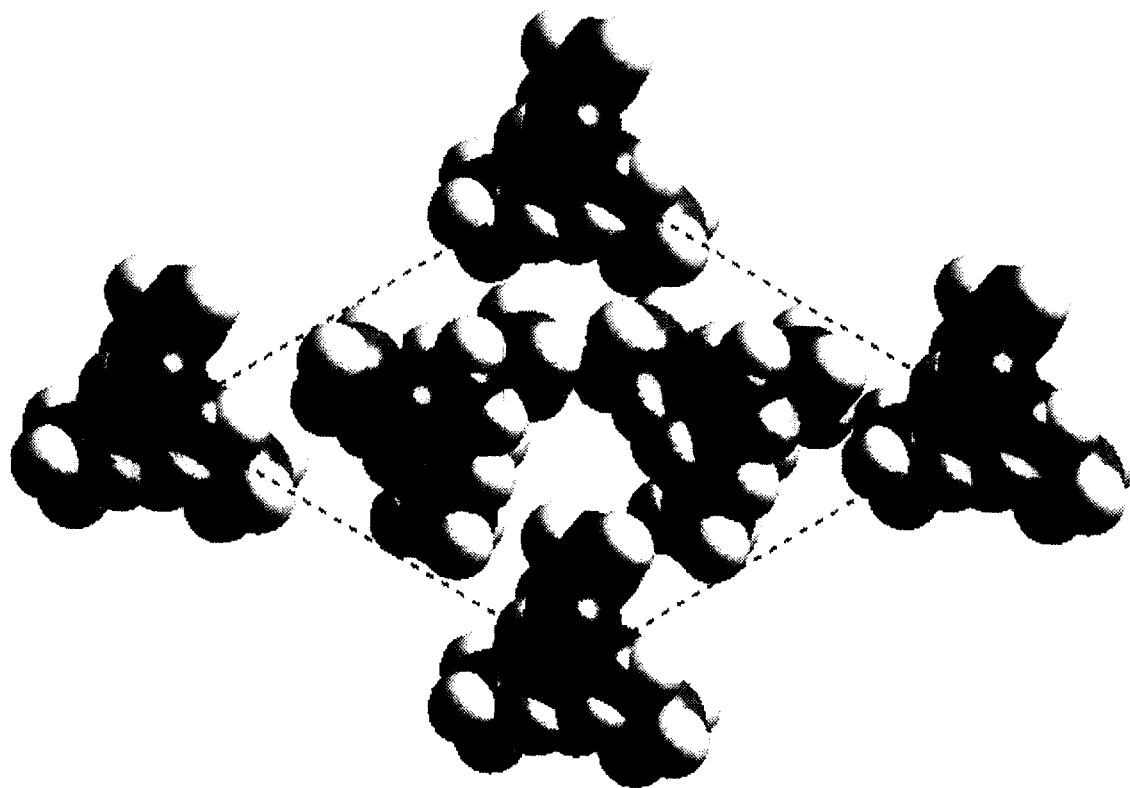


Figure 11 Computer molecular model of the crystal structure of the β phase of iPP according to ref. 34 (generated with the Cerius 2 molecular modelling software package for materials research, Molecular Simulations, Inc., Cambridge, UK). Three iso-chiral, isocline chains are represented. Note the different setting of the corner chain relative to the centre chains. Frustration does not result from chirality (the helices are iso-chiral), but from this different setting, which creates different environments for the three chains. The relative chain orientation (clincity) is an additional, independent source of frustration, and results in small variations of the setting angle of the helices

frequent and an analysis of the energetic and entropic factors which favour such packing modes has been addressed recently³⁸.

In a broader perspective, frustration is a concept which was clearly missing in polymer crystallography. It is therefore of interest to reinvestigate the structure of crystalline phases or polymorphs based on three-fold helical geometries which have remained unsolved or which were solved only approximately. We are presently undertaking such analyses, targeting as a first priority chiral polymers for which isochirality is imposed by the molecular configuration. A first list of polymers from which the crystal structure or at least that of one of the polymorphs appears to benefit from this analysis includes poly(*t*-butyl thiirane), poly(L-lactide), derivatives of cellulose (e.g. polytertiobutylcellulose) and poly(L-hydroxyproline)³⁹.

SYNDIOTACTIC POLY(PROPYLENE)

Polymorphism based on chain conformation and chain packing

Some samples of sPP had been synthesized in the early days of the Ziegler–Natta polymerization. They helped establish the basic features of sPP chain conformation and crystallography^{40,41}. The interest in sPP has been revived by the recent development of so-called fourth generation Ziegler–Natta and metallocene initiators⁴². Since large scale production of sPP requires merely a change of the initiator systems in existing industrial plants, sPP has become in recent years a ‘new’, commercially available polymer.

The very first structural investigations performed in the 1960s helped confirm the predictions of conformational analysis: although sPP can exist in an all-*trans* conformation^{40,41}, the stable structure is based on a sequence of conformations (ggtt)₂, leading to a molecular shape much akin to that of a rectangular staircase with *c* axis repeat distance of 7.4 Å (Figure 13). The distinctive feature of this conformation is that successive CH₂s in the chain have different environments: one CH₂ experiences two γ -*gauche* effects, which show up by the splitting of the CH₂ resonances and the 5 ppm downfield

shift of the CH₂gg⁴³. This use of n.m.r. to determine the molecular conformation of a polymer chain without any prior knowledge has been developed in many textbooks.

The possibility to blend gg and tt sequences within the same chain has been further illustrated by the recent discovery and elucidation of a rather exotic crystalline phase of sPP, obtained from an all *trans* conformation upon absorption of solvent vapour⁴⁴. The structure has a triclinic unit cell with parameters $a = 5.72$ Å, $b = 7.4$ Å, $c = 11.6$ Å, $\alpha = 73.1^\circ$, $\beta = 88.8^\circ$ and $\gamma = 112^\circ$. The molecular conformation is of the type (g₂t₆g₂t₂)_n, in which the two extended stretches are not of the same length⁴⁵. It should be mentioned that a similar conformation has been suggested recently as a possible defect in the stable phase of sPP based on (g₂t₂)_n conformation⁴⁶. However, no crystal phase based on more symmetrical conformations of the type (g₂t_{4n+2})_{2n} has been observed so far.

Our involvement with the structure of sPP is, once again, centred on the *helical hand*. The crystal structure established by Corradini *et al.*⁴¹ is based on the orthorhombic cell with parameters $a = 14.4$ Å, $b = 5.6$ Å, and $c = 7.4$ Å, space group *C*222₁. It is a *C*-centred cell composed of helices of one hand only (either all right- or all left-handed). When we examined single crystals of sPP produced in thin film at high temperature, we observed diffraction patterns which correspond to the same dimensions of the *ab* projection, but are incompatible with a *C*-centred cell: they suggest instead a *B*-centred cell (Figure 14)^{47–49}. The structural origin of this difference lies solely in the packing of helices of different hands. Whereas *C*-centring is consistent with packing of isochiral helices, *B*-centring requires that helices in facing *bc* layers be of opposite hand. The packing may be even more complicated, and the unit cell doubled in the *b* direction to 11.6 Å, if helical hand also alternates along that direction. These two possibilities cannot be distinguished on the basis of *hk0* diffraction patterns alone, but the presence of specific *hkl* reflections indicate unambiguously that the stable phase of sPP is based on full antichiral packing along both *a* and *b* axes. The unit cell has therefore *b* parameter doubled to 11.6 Å and a very symmetric space group *Ibca*.

sPP provides an unmatched opportunity to check perturbations introduced by the packing of helices of different hands within a crystal lattice. This opportunity arises from the facts that:

- the helical shape is rectangular in chain axis projection and the unit-cell orthorhombic. Contrary to hexagonal packing, the perturbations are apparent in one direction only
- the symmetry of the chain conformation is such that no ‘up’ and ‘down’ helix sense can be defined, as was the case with the 3₁ helices of iPP;
- the packing of antichiral and isochiral helices leads to well defined situations, illustrated by the two limiting structures: that established by Corradini *et al.* (with $b = 5.6$ Å, *C*-centred cell) and that with *Ibca* symmetry and $b = 11.2$ Å. The two structures differ essentially, in chain axis projection, by shifts of $b/4 = 2.8$ Å along the *b* axis of successive layers.

Such perturbations are indeed observed when sPP is crystallized at relatively low T_c : the *hk0* diffraction patterns display streaks along the 02*k*0 layer lines, the

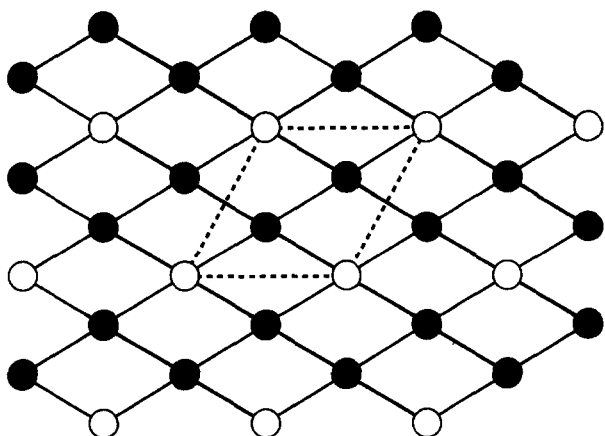


Figure 12 The frustrated dual Kagomé or diced lattice. Note that this lattice can be described by the repetition of a three-dot lattice similar to the β phase of iPP (dashed lines). Adapted from ref. 35

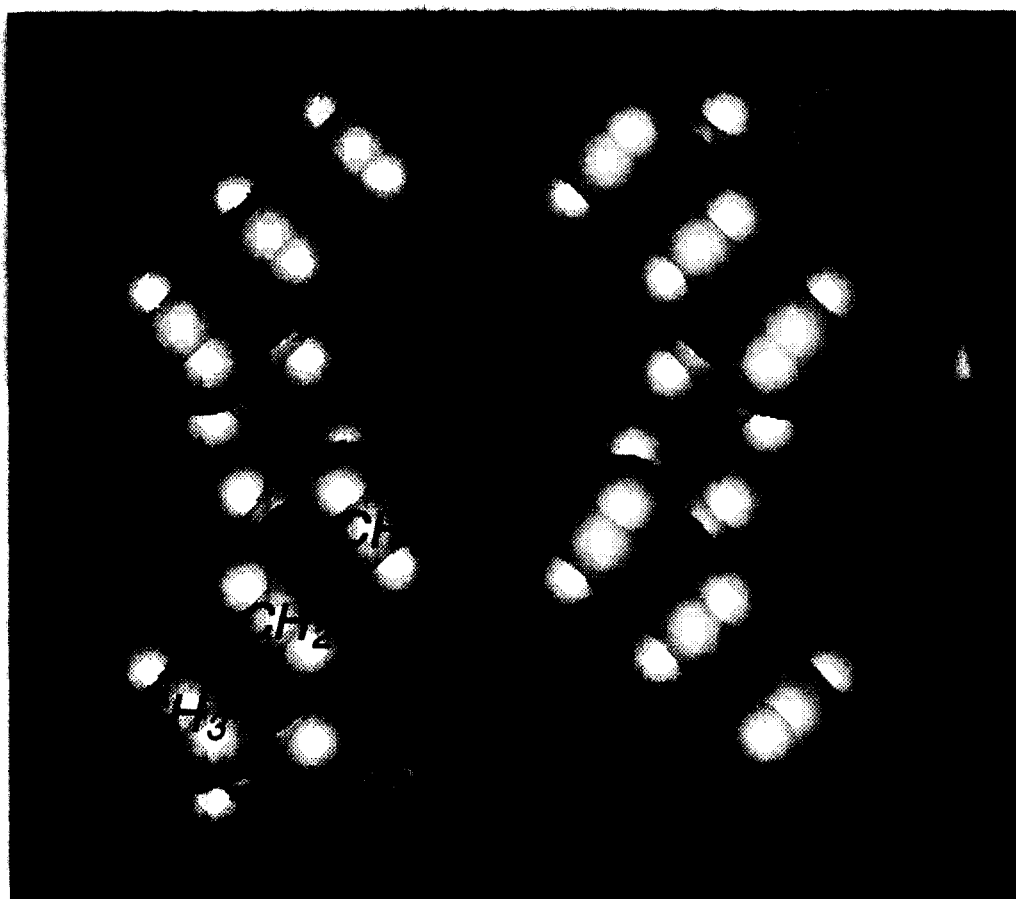


Figure 13 Molecular models of syndiotactic poly(propylene) in $(ttgg)_n$ conformation seen along the a axis, i.e. showing the prominent n -pentane-like units imaged in AFM and used to reveal the helical hand. In the $Ibca$ space-group, the left-handed helix (on the right of the figure) is located in the niches formed by the right-handed helix, thus creating the stagger visible in *Figure 16b*. Reproduced from ref. 53

streaks becoming more intense at low T_c s. They have been accounted for by an increasing impact of the above shifts of layers along the b axis, which are themselves linked to 'mistakes' in the hand of depositing chains (*Figure 15*)⁵⁰⁻⁵².

Finally, sPP has provided an unusual opportunity to observe the *hand of individual helices in real space* by atomic force microscopy. This opportunity arises from the fact that the gg conformational part of the helix, which is visible in the bc plane of the structure, projects two successive CH_3 side groups in opposite directions along the c axis, and actually along the helical path (*Figure 13*). As a result, the two CH_3 s and the middle, main chain CH_2 form an elongated feature resembling an extended n -pentane unit which, given the CH_3 resolution now reached by AFM, should be visible with this technique.

sPP has been crystallized epitaxially on linear polyphenyls (p -ter- or p -quaterphenyl) which have ac parameters matching closely those of the bc face of sPP. After dissolution of the polyphenyl, the exposed bc contact face of sPP is probed by AFM. The best results are obtained when using a so-called 'wet cell', i.e. when probing the sample immersed in water, in order to reduce the tip-sample interactions⁵³. The resulting pictures—even unfiltered ones—clearly show the characteristic, elongated n -pentane units tilted at some 45° to the molecular axis (which is itself tilted at about 1 o'clock in *Figure 16a*). Due to this tilt, left-handed helices, with

their n -pentane units oriented nearly normal to the tip scanning direction (horizontal in *Figure 16a*) are better resolved than right-handed helices. However, the distance between left-handed helices ($\approx 11 \text{ \AA}$) and helical pitch ($\approx 7.4 \text{ \AA}$) corresponds clearly to the stable, high temperature structure of sPP. Furthermore, Fourier filtered pictures reveal the stagger between right- and left-handed helices (*Figure 16b*) characteristic of the $Ibca$ space group⁵³.

The AFM study of sPP therefore reveals for the first time the *hand of arrays of individual helical stems embedded in their crystallographic environment*. sPP is, admittedly, a rather favourable case since, due to the $(ggtt)_2$ conformation and the 'rectangular' c axis projection of the helix, side chain CH_3 s contribute to highlight the underlying helical path, and create a 'flat' elongated feature which is well adapted to AFM examination. However, these first results indicate that epitaxial crystallization, which helps select well defined crystallographic faces with a suitable flat geometry¹⁹ can be validly associated with AFM examination of the contact faces. Epitaxial crystallization removes potential ambiguities in the analysis of AFM pictures since the interpretation is 'guided' by the crystallographic knowledge of the structure and the epitaxial relationship, both determined by electron diffraction¹⁹. Taken together, they provide a valuable combination of preparation and investigation techniques capable of revealing submolecular details which were out of reach only a few years ago.

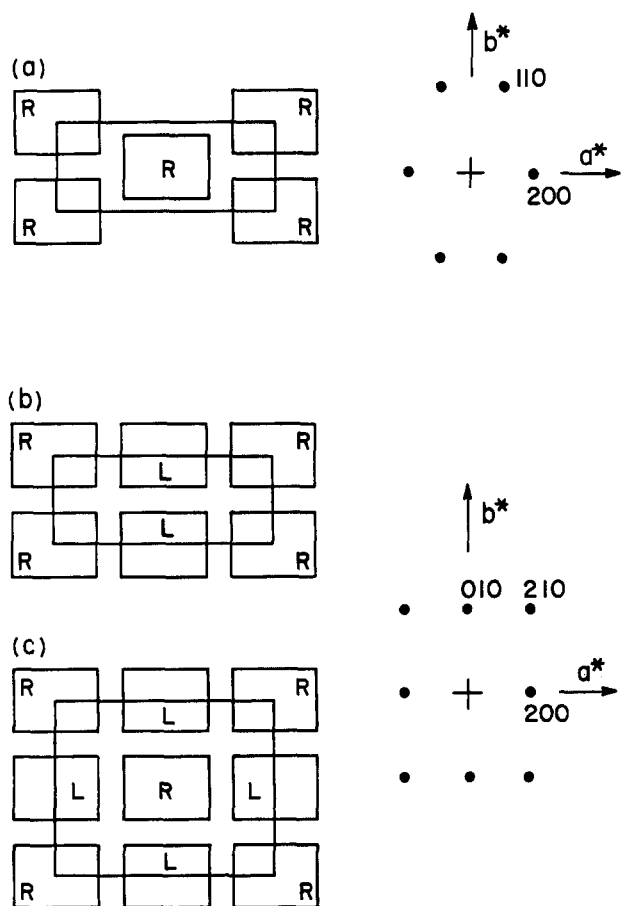


Figure 14 Schematic representation of the two limiting packing modes of syndiotactic poly(propylene): fully isochiral⁴¹ and fully antichiral structure with expected $hk0$ diffraction patterns. The fully antichiral structure is the stable one at high temperatures, while the fully isochiral counterpart is not experimentally obtained. Adapted from ref. 47

CONCLUSION

The last 35 years have witnessed a considerable development of our understanding of the structures and morphologies of stereoregular polyolefins, and of poly(propylenes) in particular. This progress has been significant in the last 10 years for both iPP and sPP. The distinctive feature of this progress is that, although most reasonings and techniques are of a crystallographic nature, our understanding of the features and behaviour of molecular stems is truly physical. It is this aspect that we have tried to convey in this presentation by insisting on the 'molecular analysis'. For example, the lamellar branching of α iPP can be described, quite appropriately, as a rotation twin. However, progressive elucidation of the exact nature of the contact face goes beyond this 'simple' description, and reaches a true (*sub*)molecular level. Further, the implications and constraints linked with the deposition of a stem 100 Å long at right angles to the 'normal' orientation on a growth face are numerous, even if not developed here: the necessity for a crystallographically smooth surface precludes such a deposition in the so-called growth regime III, etc.

The very long time span needed to solve the crystal structures of the β and γ phases of iPP is certainly related to their highly original features and the fact that none of these structures is amenable to 'conventional' polymer fibre science. The *non-parallelism of chains* in γ iPP is a revolutionary feature introduced in polymer science by

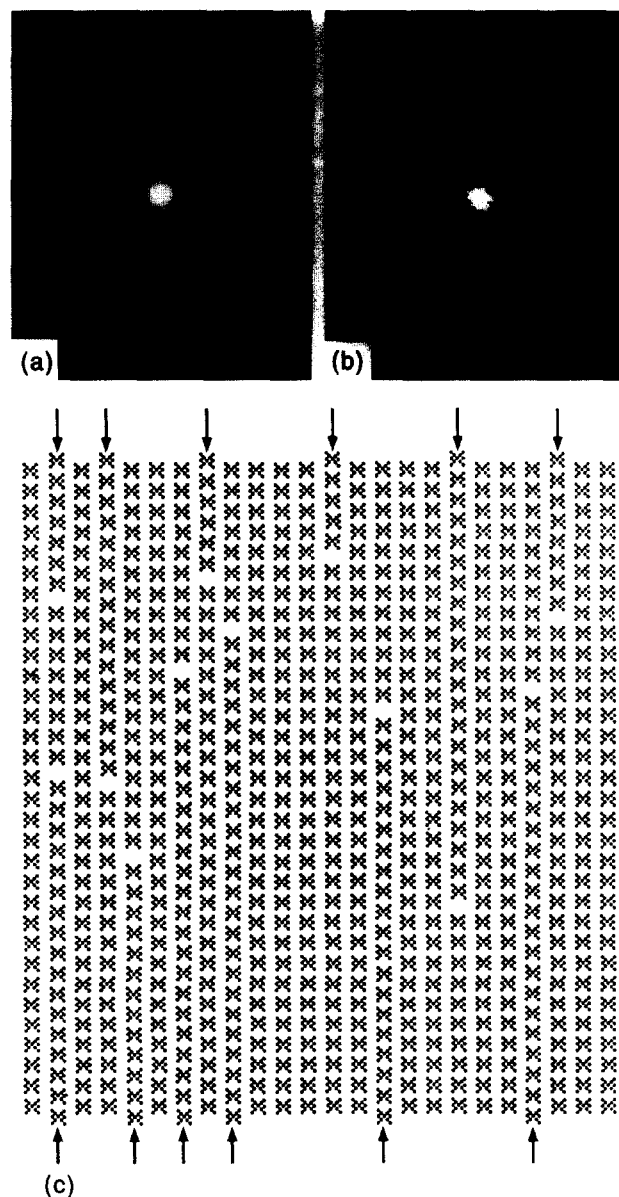


Figure 15 (a) 'Streaked' electron diffraction pattern of an sPP single crystal grown in thin film from the melt at 125°C. (b) Optical diffraction pattern (illustrating the formation of the streaks along the $02k0$ layer lines) of (c) a mask used to simulate packing defects ($b/4$ shifts) generated by deposition of helices with the 'wrong' hand. Adapted from ref. 50

Brückner and Meille²⁷. Although non-parallelism is known in shorter chain aliphatic molecules, its implications for *chain folded* polymers are not yet fully analysed: further work is actively pursued in this area. However, the structure of γ iPP is likely to remain a curiosity in polymer crystallography. Its molecular and structural foundations lie in the exceptionally symmetric and regular array of methyl groups created by the close packing, at ≈ 6.5 Å intervals of isochiral helices with a ≈ 6.5 Å helical pitch. If comparable symmetries of contact faces exist in other polymers, they are more likely to generate occasional epitaxial deposition, i.e. lamellar branching similar to that of α iPP.

The main characteristic of the β phase structure of iPP—its *frustration*—is a concept that was missing in the field of polymer crystallography. Such frustrated structures are based on isochiral helices, and it is surprising that the achiral iPP 'gives away' its ability to

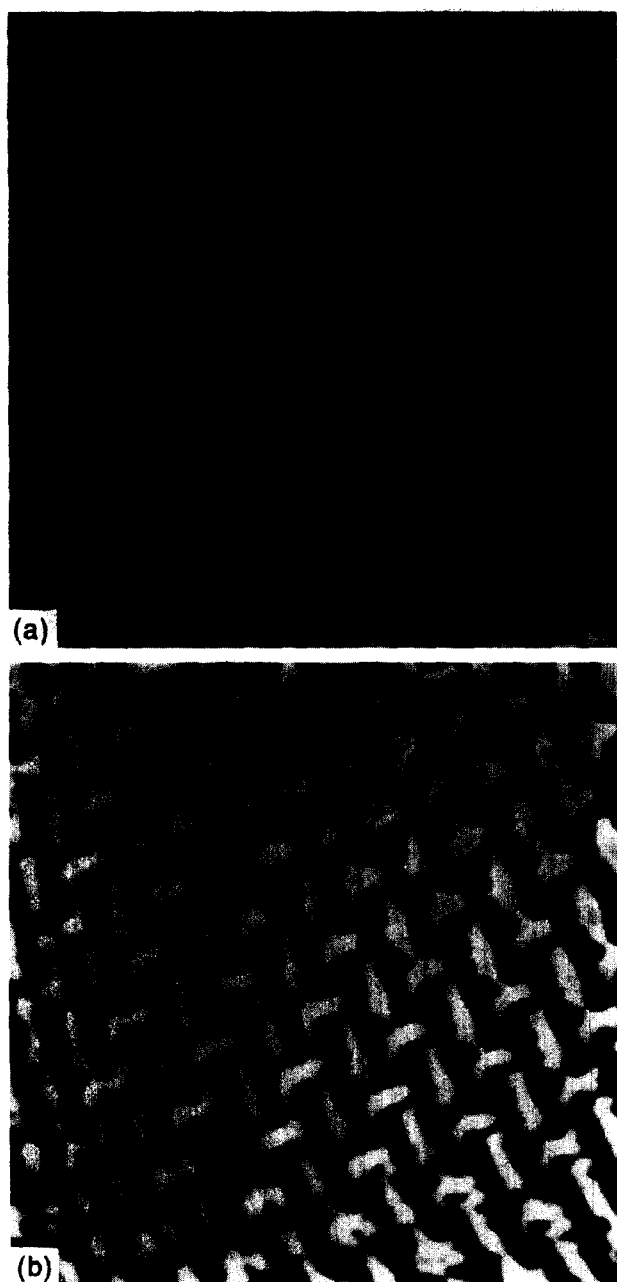


Figure 16 (a) Unfiltered AFM picture of the *ac* contact face of sPP epitaxially crystallized on *p*-terphenyl. Imaging conditions: under water. The helix axes are orientated at 1 o'clock and the *n*-pentane units of left-handed helices orientated at 11 o'clock are better visualized than those of right-handed helices, orientated at 2 o'clock, i.e. more parallel to the scanning direction. Image area: $14.5 \times 14.5 \text{ nm}^2$. (b) Fourier filtered image of the upper left corner of (a). Note that the right-handed helices now appear more clearly than in (a). Size of area: $6.5 \times 6.5 \text{ nm}^2$. Reproduced from ref. 53

exist in left- and right-handed helices, and generates a chiral structure. This chiral structure further grows at significantly higher rates than the α structure over a wide temperature range. With the availability of a correct structural model, a prerequisite is now fulfilled for further work to understand the molecular and conformational features which favour this form, analyse the implications in terms of constraints on chain folding⁵⁴, estimate the origin of its lower thermal stability, etc. The concept of frustration is also of help in the analysis of unsolved or poorly solved structures of polymers, especially chiral ones³⁹.

Finally, syndiotactic poly(propylene) had provided us with an ideal polymer conformation and crystal packing to check, in the absence of any other interference (e.g. chain orientation), the impact of helical hand on the crystal structure. The existence of two well characterized limiting structures—full antichiral packing favoured at high crystallization temperatures, impact of isochiral packing at low T_c —, the easy coexistence of the two packing modes and corresponding generation of well defined defects at intermediate T_c s provide us with a palette of structures and impacts of structural defects.

The molecular analyses of iPP and sPP performed so far combine crystallographic considerations and direct visualization via AFM. Crystallographic considerations take advantage of morphological indicators provided in particular by homoepitaxial interactions in α and γ iPP. Successful as they are, they are not easy to apply to other polymers, since their morphology does not display similar molecular markers.

The prospects for AFM (and STM) examination of polymers are much more open, and several teams are active in this area. When undertaking such research, however, the amount of truly original information accessible with this technique must be carefully evaluated. The two AFM investigations described in this report illustrate the problem just raised: determination of the exact nature of the contact face of α iPP (Figure 6) can be solved only by direct probing of the surface, i.e. by AFM. To the contrary, observation of alternating helical hands in sPP (Figure 16), even if it helps see for the first time the hand of arrays of helices embedded in their crystallographic environment, merely confirms the crystal structure determined unambiguously by electron diffraction. It may, rightly, be considered as a technical prowess rather than a scientific advance. Yet, such studies are necessary steps towards further use of AFM to explore finer details (e.g. conformational and packing defects) and are at the root of a better insight into the submolecular structure of polymers.

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