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Triangular Polymer Single Crystals: Stereocomplexes, Twins, and Frustrated Structures

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ABSTRACT: The crystallographic origins leading to the formation of polymer single crystals with highly unusual triangular shapes are analyzed. Triangular crystals are obtained: (a) for stereocomplexes of poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) crystallizing in a trigonal unit cell with *R*3*c* (or *R*-3*c*) symmetry. In this case, the triangular morphology results from the different molecular characteristics (mainly molecular weight) of the stereoisomer polymers used to form the complex, which in turn introduce different rates of deposition on opposite sides of the (110) crystallographic growth plane and therefore to the triangular morphology. *A contrario*, when molecularly (near) identical stereoisomers are used in equal concentrations, or when an (achiral) *homo*polymer crystallizing in the same crystal structure is used, the growth rates are equal and hexagonal crystals are formed (b) for some multiple twins, in particular triple growth twins of PLLA in its α form (c) for *frustrated* trigonal polymer crystal structures, in which different nucleation sites exist on opposite sides of a given growth plane. This difference in growth rates results from a genuine lack of symmetry of the crystal structure: *triangular crystals are a morphological marker of the frustrated character of the packing in the unit cell*. Further consequences of this frustration, such as differences in lamellar thicknesses for nominally equivalent growth sectors, shed new light on the details of nucleation and growth theories of polymer single crystals.

Introduction

The overall morphology of polymer single crystals is a good, albeit not an infallible, indicator of the symmetry of the underlying crystal structure: tetragonal unit cells give rise to square crystals, hexagonal unit cells give rise to hexagonal cystals, the orthorhombic unit cell of PE leads to lozenge-shaped crystals bounded by {110} growth faces, etc. On this basis, the occurence of triangular single crystals would not be expected, since no known unit cell geometry can be associated with such a morphology.

Having obtained recently triangular single crystals with a number of polymers, we examine in this paper the various reasons for which such triangular single crystals may nevertheless be produced. We consider in particular several observations of one of us[1,2] and of Brizzolara *et al.*,[3] who report triangular crystals for racemic stereocomplexes of poly(L-lactide) (PLLA) associated with its enantiomer poly(D-lactide) (PDLA). These stereocomplexes have attracted considerable interest in recent years because their melting temperatures are about 50 °C higher than those of the corresponding enantiomeric crystals. We have designed a set of experiments which demonstrates that the triangular crystals formed by the racemic mixture rest on an imbalance of rates of attachment of the two polymers on opposite sides of a given growth plane. When these growth rates are equal (e.g. for molecularly identical enantiomers in equal concentrations), hexagonal crystals are formed. Triangular crystals are also observed, less frequently, for the enantiomers. On the basis of new electron diffraction evidence, we show that these triangular crystals are conventional multiple twins and that the triangles simply reflect the near hexagonal packing of the 10_3 helices in a nominally orthorhombic unit cell.

Finally, we demonstrate that triangular or truncated triangular crystal morphologies are expected, and indeed are observed almost systematically, for polymers with *frustrated structures*.[4,5] These frustrated structures are based on trigonal unit cells which contain three threefold *isochiral* helices and in which the (nearly) similar azimuthal setting of two helices differs significantly from that of the third helix. The triangular growth morphology is a logical consequence of these different azimuthal settings, which create different nucleation sites on opposite sides of any given growth plane. Further consequences of the asymmetry characteristic of frustration are illustrated by e.g. different lamellar thicknesses in nominally equivalent growth sectors. The crystal morphology and growth kinetics of frustrated structures thus provide a set of new and highly original data for further analyses of molecular processes involved in nucleation and growth of polymer crystals.

Experimental Section

1. Materials. The samples used in this study have various origins:

Poly(L-lactide) and poly(D-lactide) (PLLA and PDLA) were kindly supplied by Pr. Michel Vert (Montpellier, France), Dr. Nicolas Spassky (Université Pierre et Marie Curie, Paris), and Pr. H. Tsuji, S.-Y. Hyon, and Y. Ikada (Kyoto University). Samples of the latter authors have been used more extensively, as have, in particular, two sets of enantiomers with identical molecular weights (7000 and 19000).[1,2]

Isotactic poly(2-vinylpyridine) (iP2VP) is a sample synthesized and used in the initial investigation of the crystallization behavior of this polymer by Challa and his collaborators.[6] It was kindly supplied by Dr. G. O. R. Alberda van Ekenstein (University of Groningen, Holland). Its molecular characteristics are as follows: >98% isotactic triads; molecular weight (viscosity at 25 °C in methanol), 400 000.

Poly(L-hydroxyproline) was purchased from ICN Pharmaceuticals France, 91893 Orsay Cedex. Its molecular weight (weight average) is 16 000.

2. Methods. Crystallization Techniques. The crystallization techniques are similar to or adapted from those of the

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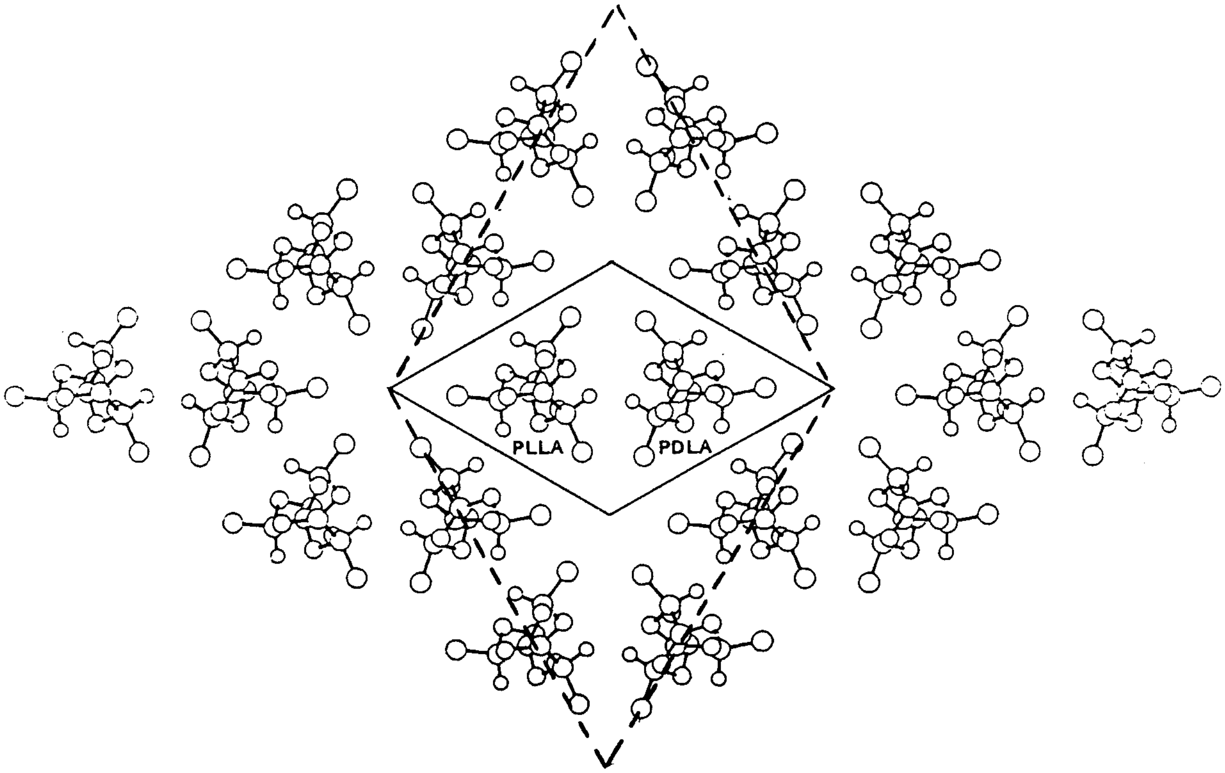


Figure 1. Molecular arrangement of the PLLA/PDLA stereocomplex projected on the plane normal to the chain axis. The triclinic unit cell ($a = b = 9.16$ nm, $c = 0.870$ nm, $\alpha = \beta = 109.2°$, $\gamma = 109.8°$, 2 chains per cell) proposed by Okihara *et al.*[1] (full lines) is a subcell of the larger, newly proposed trigonal unit cell ($a = b = 1.498$ nm, $c = 0.870$ nm, $\alpha = \beta = 90°$, $\gamma = 120°$, 6 chains per cell), with *R*-3*c* symmetry (broken lines).

various previous studies performed on similar materials. PLLA and PDLA and the stereocomplex are crystallized from dilute solutions in *p*-xylene (usually at concentrations of 0.05%) or from thin films cast from the same solvent. Details of the crystallization procedure (temperature and thermal histories) are given in the appropriate legends. As a rule, crystallization of iP2VP is performed from thin films.

Techniques. Electron Microscopy and Diffraction are performed with a Philips CM12 instrument equipped with a 60° rotation-tilt stage. To preserve the sample from rapid damage under the electron beam, most preliminary observations are made at very low magnification, usually by defocusing the diffraction pattern. Bright field and diffraction patterns are recorded on Agfa Scientia EM and Kodak DEF 5 films, respectively.

Results and Discussion

The triangular morphology of single crystals of PLLA and the PLLA/PDLA stereocomplex has been analyzed by Brizzolara *et al.*[3] in terms of the underlying helix conformation and/or crystal structure. We consider first these morphologies in light of our own experimental results and show that they can be explained in terms of very classical, if sometimes unexpected, crystal and growth features.

1. Triangular Crystals of the PLLA/PDLA Stereocomplex. Okihara *et al.*[2] and later on Brizzolara *et al.*[3] have reported that the PLLA/PDLA stereocomplex forms triangular single crystals. These crystals often display screw dislocations which are oppositely oriented relative to the basal lamella, thus generating star-shaped multilamellar aggregates with overall hexagonal symmetry. This morphology has been analyzed by Brizzolara *et al.*[3] in terms of the crystal structure of the stereocomplex, as determined by Okihara *et al.*[1] We recall first the main features of this crystal structure and analysis.

As shown by Okihara *et al.*,[1] the stereocomplex of PLLA and PDLA crystallizes in a triclinic unit cell (Figure 1) with parameters $a = 0.916$ nm, $b = 0.916$ nm, $c = 0.870$ nm, $\alpha = 109.2°$, $\beta = 109.2°$, and $\gamma = 109.8°$. It contains two enantiomorphous helices with threefold symmetry (left-handed 3_2 for PLLA, right-handed 3_1 for PDLA). For the purpose of our analysis, it is however useful to point out that this structure can also be described, perhaps more appropriately, as a *trigonal unit cell* similar to that of isotactic poly(1-butene) (iPBu1) in its Form I or I′ or of isotactic polystyrene (iPS). The triclinic cell used by Okihara *et al.*[1] is a subcell of this larger trigonal cell, which has parameters $a = b = 1.498$ nm, $c = 0.870$ nm, $\alpha = 90°$, $\beta = 90°$, and $\gamma = 120°$ and contains six helices, three right-handed and three left-handed ones (broken lines in Figure 1). Its space group is either *R*3*c* if helices are all oriented in one direction only (isocline helices) or, better, *R*-3*c* if, as is probable, statistical existence of up- and down-pointing (i.e. anticline) helices is considered at each helix site.

It is important to recognize that, whereas the crystal structures of the PLLA/PDLA stereocomplex, of iPBu1 (forms I or I′), and of iPS are strictly equivalent, iPBu1 and iPS are achiral, which means that the crystals are grown from *one and the same molecular species*. On the contrary, the formation of the stereocomplex requires the cocrystallization and, more exactly, the sequential crystallization in successive, alternate growth layers of PLLA and of PDLA, that is of *two different molecular species*. Furthermore, since the melting point of the stereocomplex is significantly higher than that of the stereoisomers, its crystallization range can be (and in many experiments was chosen to be) outside that of the enantiomers: growth of crystals of the stereocomplex is not "polluted" by independent growth of crystals of PLLA or of PDLA.

For future reference, we further recall that the homopolymers, i.e. PLLA or PDLA, crystallize in a stable form with an orthorhombic unit cell of parameters $a = 1.037$ nm, $b = 0.598$ nm, and $c = 2.88$ nm and two helices per cell with the helix conformations left-handed 10_7 for PLLA and its right-handed 10_3 mirror image for PDLA. In addition, an unstable modification of these same polymers is obtained in stretched samples. Its diffraction pattern has been interpreted on the basis of a six-chain orthorhombic cell by Hoogsteen *et al.*[8] Cartier *et al.*[5] showed recently that it is more appropriately described as a trigonal, frustrated cell with three chains. The chain conformation is a threefold helix similar to that existing in the stereocomplexes: 3_2 for PLLA and 3_1 for PDLA. Since this structure is produced by mechanical means only, it will not be featured in the present analysis.

Reverting back to the crystals of the PLLA/PDLA stereocomplex, we illustrate in Figure 2a the triangular morphologies that we obtained, in the present case in thin film growth. Similar morphologies, often more complex, have been reported by Okihara *et al.*[2] and by Brizzolara *et al.*[3] Electron diffraction patterns (Figure 2b) indicate that the growth planes are parallel to (110) (using the new cell), thus providing an experimental support to the calculation of growth rates and crystal morphology made by Brizzolara *et al.*[3] (Incorrect (100) growth planes were indicated in ref 2.) The crystal morphology was calculated by these authors using a module of the Cerius^2 software package by Biosym-Molecular Simulations. It is based on the Bravais−Friedel−Donnay−Harkar method. As indicated by Brizzolara *et al.*,[3] this method actually yields a *hexagonal* shape for the single crystals. Taking into account the correct prediction of the nature of the growth plane, but not of the triangular morphology, these authors were then led to suggest a slightly different molecular growth mechanism for the stereocomplex. As shown in Figure 3, it rests on the triangular geometry of the initial helical stem, on the further triangular geometry of the nucleus formed when three antichiral helices are attached to this initial single-helix nucleus, etc. This growth scheme results in a single-crystal structure composed of two intertwining spirals, one made of a PLLA and one of a PDLA chain. A further advantage of this model is that the (presumably unfavorable) crossing of folds or loops of PLLA and PDLA at the crystal surface is avoided.

However, it is clear that this model, if correct, can only apply to the initial steps of the growth mechanism: for crystals with growth faces several micrometers wide, it is unlikely that the "turn-around" at the triangle corner influences the growth of the whole facet: in other words, the deposition of the various molecules must be considered in the broader framework of nucleation and growth of polymer crystals.

In this context, we note first that since iPBu1 and iPS have the same trigonal structure as the PLLA/PDLA stereocomplex and since their crystals are indeed hexagonal, the prediction of a six-sided single crystal geometry is actually correct *when a single molecular species is involved (here a homopolymer)*. The triangular geometry therefore must be related to the fact that the stereocomplex implies the *cocrystallization of two different molecular species*. The design of experiments to be described now rests on the analysis of the growth processes of two different molecular species in a trigonal unit cell with symmetry $R3c$.

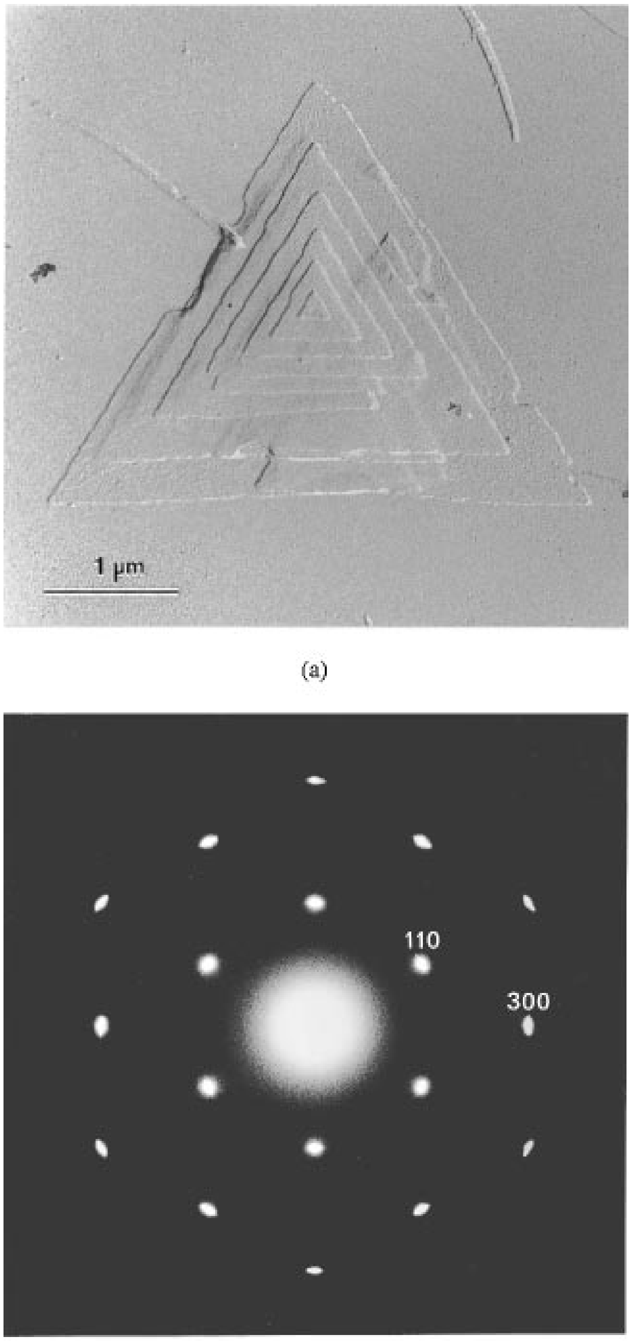


Figure 2. (a) Transmission electron micrograph of a single crystal (actually a double Frank−Reeds dislocation) of the PLLA/PDLA stereocomplex formed by thin film growth at 200 °C. The film is obtained by evaporation of a 1% *p*-xylene solution containing a blend of PLLA and PDLA both of molecular weight 7000 in a $^1/_3$ ratio. (b) Electron diffraction pattern of the crystal as in part a in the proper relative orientation, indexed on the basis of the large trigonal unit cell ($a = b = 1.498$ nm).

Figure 4 illustrates the arrangement of helices in the trigonal unit cell. Helices are schematized as triangular rods, which helps identify their azimuthal setting relative to the growth faces. Opposite hands are distinguished by the presence or absence of shading of the end surfaces. As already illustrated by Brizzolara *et al.*,[3] it is immediately apparent that successive {110}

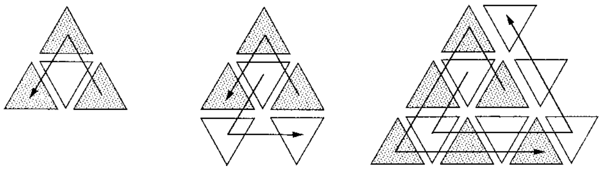


Figure 3. Scheme of the growth mechanism of the PLLA/PDLA stereocomplex single crystal proposed by Brizzolara *et al.*[3] Helices of opposite chirality are shown as shaded and unshaded, respectively. Note the spiral chain path, which involves folds and crystal stems.

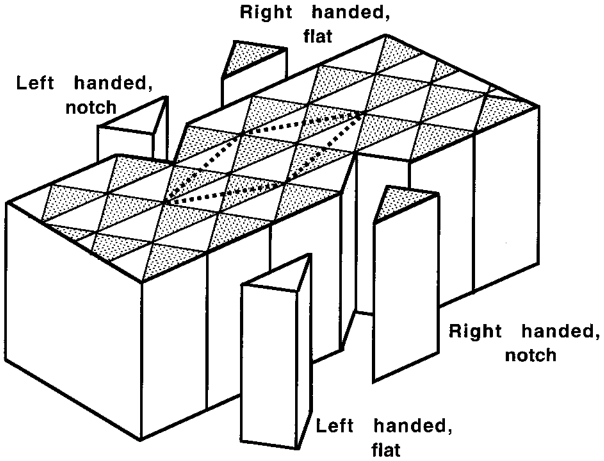


Figure 4. Representation of the arrangement of helices (schematized as triangular rods) in a trigonal unit cell with $R3c$ or $R\text{-}3c$ symmetry (*ab* plane of the cell shown by dashed lines). Note the four deposition possibilities for right- or left-handed helices (two for each helix chirality) and the resulting *polar* nature of the crystal with respect to the chirality of deposition sites.

growth faces are not equivalent with respect to the azimuthal setting of the incoming helical stem: in one growth plane, the incoming helix deposits with one of its corners oriented *away from* the crystal center, whereas in the next layer, it deposits with one of its corners *toward* the crystal center (Figure 4).[11] As a consequence, the rates of deposition (or of growth) of alternate layers must be significantly different. In addition, the {110} growth planes are *polar*. Left-handed and right-handed helices have their corners oriented in opposite senses relative to the growth plane. It follows that *four* deposition rates must be defined to describe the growth of such crystals, which take into account two variables: the helical hand and the deposition either in a notch or on a flat part of the growth surface. Since the slowest deposition rate determines the overall growth rate of the crystal face, it follows that the overall morphology will be determined by the ratio of the slowest growth rates on opposite sides of the (110) growth plane.

For achiral homopolymers (iPS, iPBu1) crystallizing in this packing scheme, the overall rates in opposite growth directions are identical, since any molecule can adopt either right- or left-handed helical conformations: hexagonal crystal geometries are anticipated and indeed observed (Figure 5). However, the situation is quite different for the stereocomplex, since the chirality of any chain dictates the helical hand and therefore sets limitations on the actual deposition site. It follows that differences in molecular constitution (molecular weight, molecular weight distribution, stereoregularity, ...), which are known to affect the growth rates of homopolymers, will also affect the deposition rates of the two stereoisomers. Since however these growth rates materialize on different sides of the (110) growth plane, *any difference in the molecular characteristics of the enantiomers will result in departures from hexagonal crystal geometry toward triangular ones.*

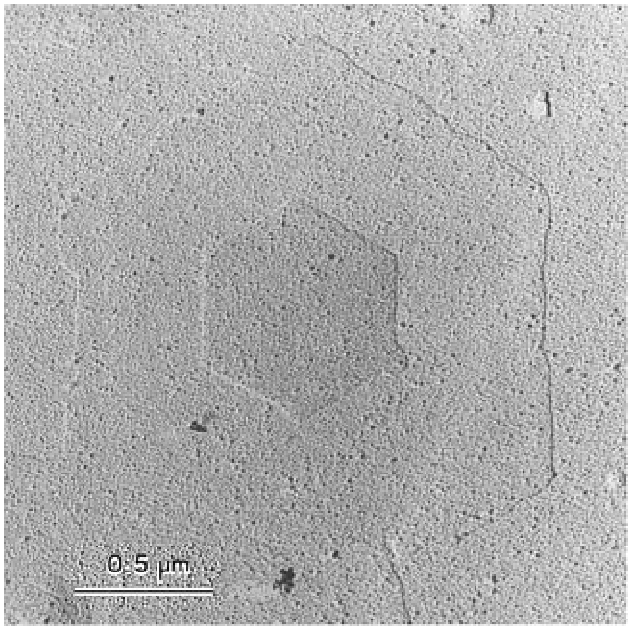


Figure 5. Electron micrograph of a single crystal of isotactic poly(1-butene) in its form I′. Low molecular weight material obtained in a thin film by vaporization and crystallized by slow cooling.

We note in this respect that the triangular stereocomplex crystals shown in refs 2 and 3 are indeed produced with racemic mixtures of PLLA and PDLA of different molecular weights (similar M_ns, but M_ws of 16.000 and 7.000 in ref 3; no indication of molecular weight is given in ref 2). We have repeated these experiments and observed also rounded triangular crystals (grown from solution) with samples of molecular weights 19000 and 7000, respectively.

From the above analysis, hexagonal crystals can be expected for the racemate if the molecular characteristics of the two enantiomers are sufficiently close. We have used an *equimolecular blend* of PLLA and PDLA both *of the same molecular weight* (at least nominally, i.e. within the uncertainties of molecular weight determination) of 7000. The resulting crystal morphology is very *nearly hexagonal*, as illustrated in Figure 6 for solution growth (in *p*-xylene).

Even when the molecular characteristics of the stereoisomers are identical, a further imbalance can be introduced by changing the relative amounts of the two polymers: in bulk or thin film growth, different growth rates are then introduced by different diffusion rates to the growth front. We have systematically observed triangular morphologies in such experiments. A most illustrative example is displayed in Figure 7. In this experiment, a glass slide was first covered with a thin film of PLLA cast from solution. Hexagonal single crystals as shown in Figure 6 were then deposited with their mother liquor on the thin PLLA film. After evaporation of the solvent, the slide was heated at 250 °C, above the melting temperature of the stereocomplex (and therefore also of the PLLA (180 °C)) and recrystallized isothermally at 200 °C. Blending of the stereocomplex with the PLLA results in an excess of PLLA and development of the triangular crystal shown in Figure 7.

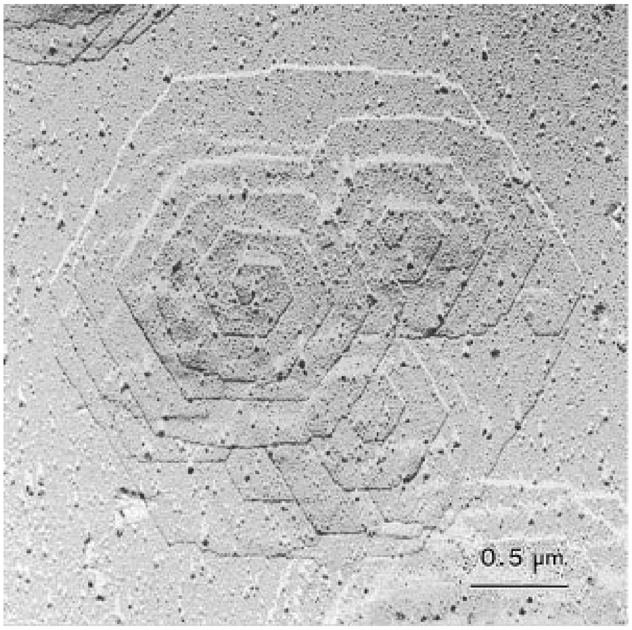


Figure 6. Electron micrograph of a single crystal of the PLLA/PDLA stereocomplex grown from a 0.05% solution in *p*-xylene at 56 °C during 3 days. The solution contains an *equimolecular* blend of the two enantiomers with the *same* molecular weight of 7000.

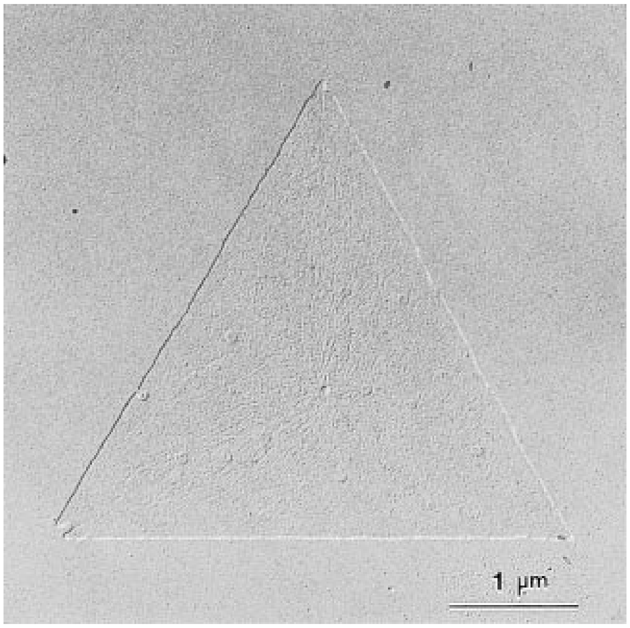


Figure 7. Transmission electron micrograph (replica) of a single crystal of the PLLA/PDLA stereocomplex grown after deposition of a single crystal as shown in figure 6 on a thin film of PLLA (M_n = 7000) and then melted at 250 °C and crystallized for 3 h at 200 °C.

The above set of experiments amply demonstrates that the triangular morphology of PLLA/PDLA stereocomplexes is not associated with a *crystallographic* feature or a particular geometry of the initial nucleus. It rests solely on the polar (with respect to helix chirality) character of the unit cell and on the fact that the growth rates of the two stereoisomers affect opposite sides of the (110) growth plane. The triangular morphology therefore reflects simply an imbalance of growth rates, which may be associated with differences in molecular characteristics (molecular weight, ...) or in rates of diffusion to the growth front when the mixture is off-racemic.

Finally, it is worth pointing the following:

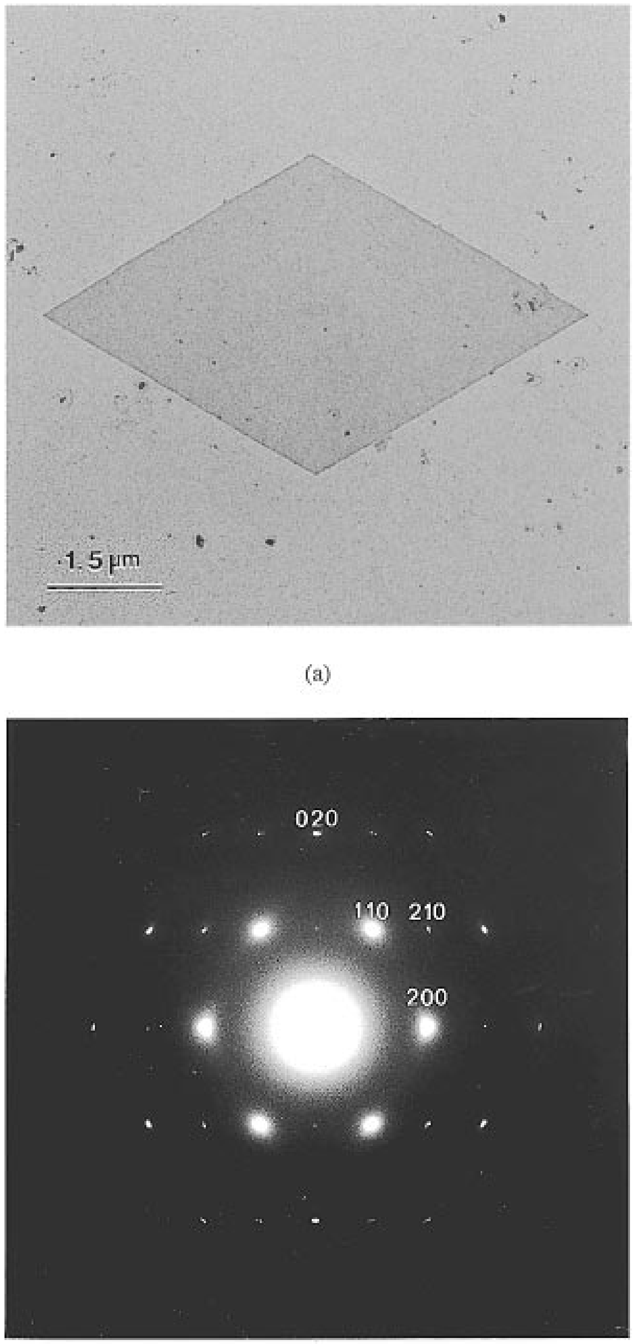
(a) The above analysis is most probably valid for other stereocomplexes which may be formed by racemates of polymers crystallizing in the same unit cell.

(b) The triangular geometry and the transition to hexagonal geometry provide an excellent morphological marker to evaluate the impact of the composition of the near-racemate on growth rates, i.e. on diffusion constants of crystallizing species near a growth front. However, the domain is limited to a range of *relative* growth rates which should not exceed a ratio of 1 to 2. (This ratio stems from the position of the barycenter of an equilateral crystal relative to its base and tip, respectively.) Beyond this ratio, the crystals are uniformly triangular.

(c) Two variables (at least) have been identified which influence the morphology: molecular weight and imbalance of composition. It is therefore possible, in principle, to investigate these two effects by compensating molecular weight imbalance with adequate adjustments of relative concentrations. In other words also, the iso-MW, iso-concentration situation illustrated in Figure 6 is only the central point on a curve which displays the morphology (and in particular the hexagonal one) versus the molecular weight and relative concentration of the stereoisomers.

2. Twins of PLLA or PDLA in the Stable α Modification. For the sake of completeness, we consider now the occurence of triangular crystals of PLLA or PDLA in their stable form (left-handed 10_7 or right-handed 10_3 helix, respectively). PLLA crystallizes in the form of lozenge-shaped crystals very similar to those of polyethylene (PE). As for the latter, the lozenge shape indicates {110} growth faces for the orthorhombic structure of this form. However, numerous crystals have a triangular shape, and the crystals often display overgrowths which are oriented at 180° to the basal lamella: the resulting crystals may therefore be confused with the triangular or star-shaped entities characteristic of the stereocomplexes. The true nature of these crystals is revealed by electron microscopy and electron diffraction. Figure 8a represents a lozenge-shaped crystal, and Figure 9a, a triangular crystal obtained by solution crystallization of a sample of PLLA. The diffraction pattern of Figure 8b indicates that the crystal structure of the lozenge-shaped crystal is orthorhombic, as attested by the characteristic presence of 210 reflections (arrowed). The triangular crystal of Figure 9a has a diffraction pattern (Figure 9b) which, although apparently of hexagonal symmetry, is actually a superposition of three patterns, as in Figure 8b, rotated by 120°. This analysis suggests that the triangular crystal is actually a multiple twin. This is confirmed by the bright field images which distinctly reveal *growth* twin boundaries and associated notches on the three edges of the crystal (arrowed in Figure 9a).

This analysis indicates that the triangular crystals of PLLA or of PDLA are multiple twins. This twinning is particularly easy for PLLA or PDLA due to the geometry of the unit cell: even though the structure must be described as an orthorhombic cell, the ratio of the *a* and *b* cell parameters is equal to $\sqrt{3}$: the packing of the helices is almost hexagonal. Under these conditions, growth twins (which from a crystallographic standpoint can be described as *rotation twins*) are easily produced, and triangular crystals with three *a* axis tips are not uncommon. Note that the situation described here for PLLA or PDLA differs somewhat from that

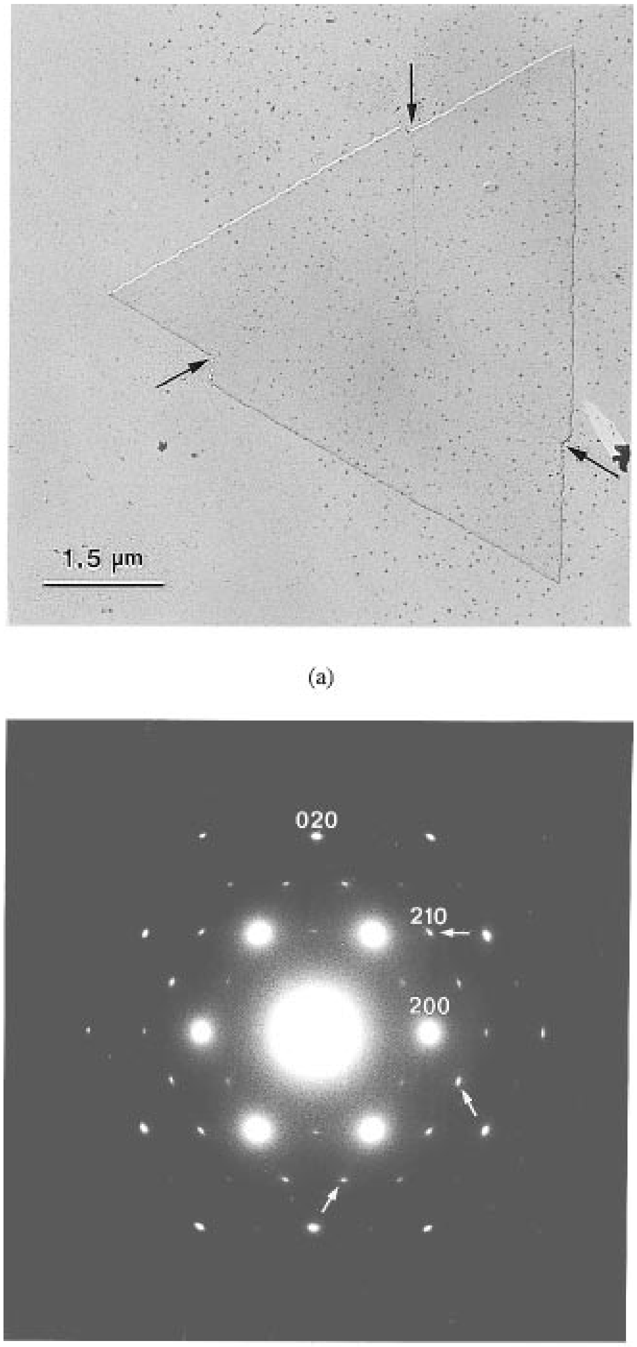


(a)

(b)

Figure 8. (a) Electron micrograph of a single crystal of PLLA (M_n = 7000) grown by slow cooling from 90 °C of a 0.05% solution in *p*-xylene. (b) Electron diffraction pattern of the crystal in part a in the proper relative orientation, with indexing on the basis of the orthorhombic unit cell of PLLA.[1]

analyzed for polyethylene, for which occasional triangular crystals have already been reported:[12] one such example, taken from ref 12, is reproduced in Figure 10. The 2_1 helical shape of PE is less "cylindrical" than the 10_3 helix of PDLA, and the packing is "less pseudohexagonal". Conceivably, a crystal similar to that shown in Figure 9 for PLLA would be created by a triple (310) *reflection* twin in PE. However, the sum of the internal angles would amount to 381.3° (as opposed to 360° for PDLA): such triple twins are not observed for PE. Rather, the crystal shown in figure 10 is a double (310) twin, with an additional infilling sector.[12]

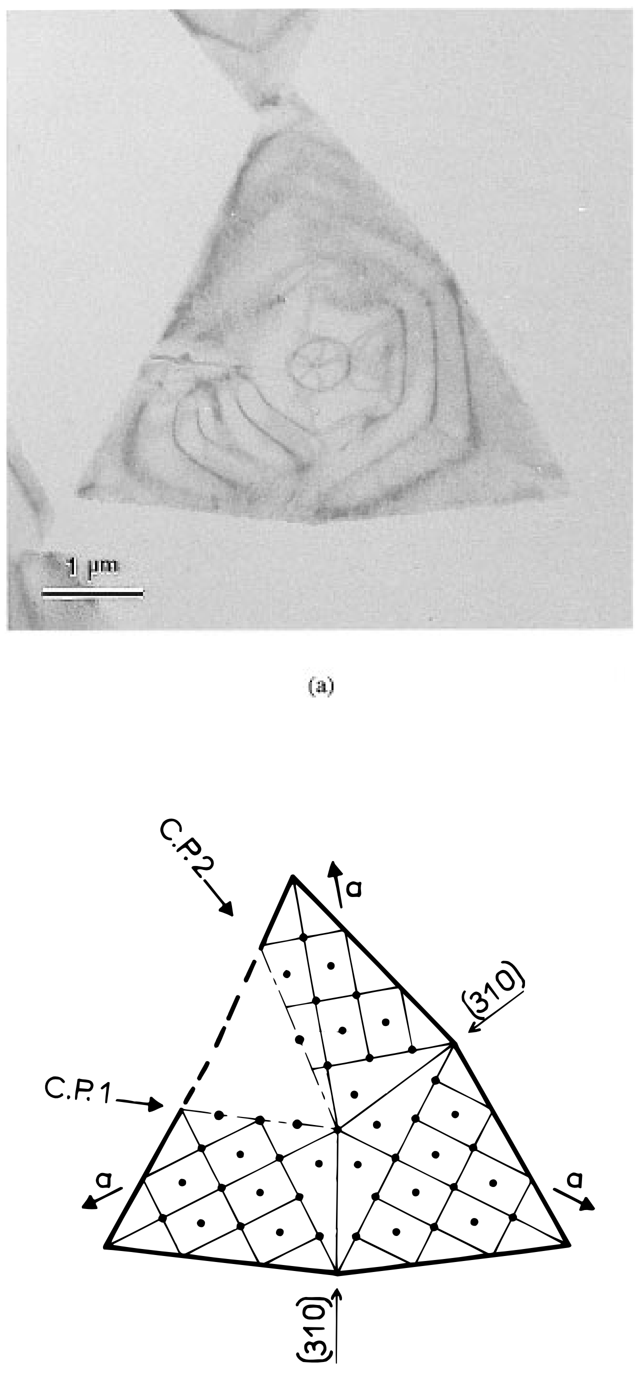


(a)

(b)

Figure 9. (a) Electron micrograph (replica) of a multiple twinned crystal of PLLA obtained under the conditions described in Figure 8a. The three twin planes are marked with arrows. (b) Electron diffraction pattern of the crystal in part a in the proper relative orientation. Indexing of reflections corresponds to the left hand side tip of the crystal in part a, and should be rotated by + and −120° for the two other components of the twin. 210 reflections of the three components are marked with arrows with the orientation of the arrow parallel to the *a* axis of the respective component.

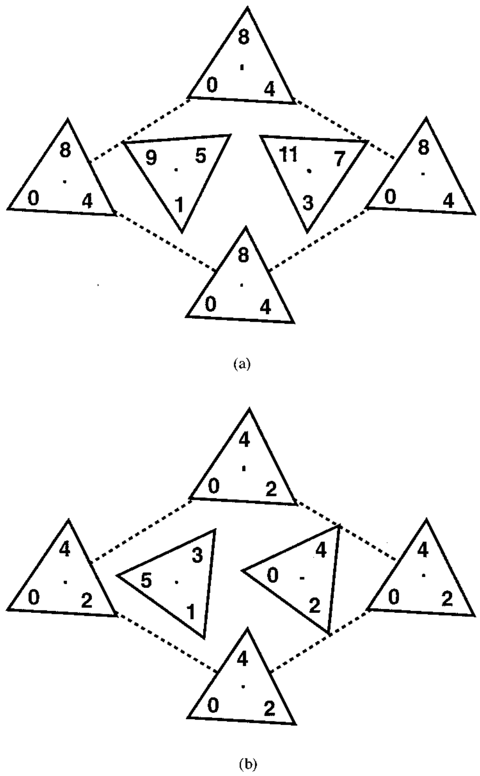
To sum up therefore, the formation of triangular crystals of PLLA rests on a conventional multiple twinning which is very frequent for PLLA in view of its almost perfect pseudohexagonal, but actually orthorhombic packing of 10_3 helices. The origin of this triangular geometry appears more circumstantial than for the stereocomplexes considered above. It is nevertheless of interest to point out its origin, in view of



(a)

(b)

Figure 10. (a) Transmission electron micrograph of a multiple twinned crystal (two (310) twins boundaries) of polyethylene, courtesy of Dr. J. C. Wittmann, Institut Charles Sadron, Strasbourg. The crystals are obtained from a 0.05% w/v solution in tetrachloroethylene by a self-seeding technique. The polymer first dissolved at 120 °C is quickly cooled to 50 °C and then slowly heated at 0.5 °C/min to 92 °C before crystallization at 63.5 °C. (b) Structural analysis of the twin in part a.[12] C.P.: coalescence planes.



(a)

(b)

Figure 11. Schematic trigonal, three_chains unit cell in which the different azimuthal settings of the threefold helices create a frustrated packing. Two models are illustrated which can be described after the orientation of one of their side chains as (a) North−South−South, which applies for iP2VP, and (b) North−West−West, a model developed for, among others, poly-(L-hydroxyproline)[7] and poly(*tert*-butylethylene sulfide).

possible confusion arising from the formation of nearly identical crystals for the polylactide racemate and the optically active polymers.

3. Triangular Single Crystals of Polymers with a Frustrated Structure. As indicated in the introduction, we have identified only one major and genuine crystal structure symmetry (or more rightly asymmetry) which, even for homopolymers, results naturally in triangular crystal morphologies.

The frustrated packing scheme of polymers has been identified for threefold helical polymers packing in a trigonal, three chains unit cell. A further distinctive feature of the structure is that the helices are *isochiral*. Frustration results from the different azimuthal settings of the three helices. Although the details of the various structures may vary from polymer to polymer, the characteristic feature of the structure is that two helices maximize their interactions at the expense of the third helix. As a consequence, the third helix is frustrated, since it is not in its ideal environment. For threefold helices, the frustration manifests itself by the (near) identical setting of two helices, which departs significantly from that of the third one. Two variants of the frustrated packing have been identified, which may be defined after the orientation of one of the side chains of the three helices (in the *c* axis projection, of one of the tips of the triangle which symbolizes the threefold helix) as north−south−south (NSS) or north−west-west (NWW) (or the equivalent north−east−east (NEE)) (Figure 11). It should be pointed out that frustration is a concept that was introduced in 1977 by Toulouse[13] to describe the relative orientation of magnetic spins in antiferromagnetic frustrated systems.

Several chiral and even achiral polymers were found to pack in frustrated structures. Although the structure was not described in terms of frustration, the first and most noticeable structure of a frustrated polymer packing was analyzed back in 1979: it is the structure of isotactic poly(2-vinylpyridine) (iP2VP).[14] The structure was correctly described in terms of a trigonal unit cell with $P3_1$ or $P3_2$ symmetry (depending on the helical hand). The structural repeat unit is composed of three monomer units (one for each helix), and the three helices of the unit cell are generated by the operation of the three threefold axes of the space group. The three monomer units can adopt any position relative to their respective axes and are not linked by any other element of symmetry: the space group adequately describes the frustrated packing. Helices with opposite direction (anticline) can be generated by proper definition of a second monomer unit for each helix site, although some elements of symmetry may link the anticline helices. A packing scheme very similar in its principle to that of iP2VP was proposed recently for the structure of the β phase of isotactic polypropylene (βiPP) independently by Meille *et al.*[15]and by Lotz *et al.*[4] The latter authors further pointed out the frustrated character of the resulting packing scheme. Curiously enough, the two first crystal structures for which the frustrated packing scheme was established deal with *achiral* polymers, whereas the packing scheme is by nature *chiral*. A recent reevaluation or elucidation of several trigonal unit cells including three threefold helices of chiral polymers and biopolymers led to the conclusion that these structures are indeed frustrated ones.[5]

In the present context, the most original feature of frustrated structures is the fact that opposite faces of the densely packed planes (i.e. {110} and {100}) comprise three different deposition (helix) sites corresponding to different azimuthal settings. Furthermore, *the deposition sites are different for opposite faces of a given growth plane*. For example, if we consider the deposition of a first stem on a flat (110) face in the NSS arrangement, deposition on the north face involves most probably a helix which deposits with one of its faces lying “flat-on” (using the nomenclature of Figure 4) on the surface (the deposition of a helix with its tip oriented toward the surface is highly unlikely). This first step is followed by “notches” once the flat-on helix is deposited. On the contrary, on the south face of that same plane, initiation of a new layer most probably involves deposition in a notch (which provides a more favorable nucleation site), followed by two “flat-on” depositions of helical stems. Similar asymmetries in the growth patterns exist for the NWW packing scheme or for (100) growth planes.

The above analysis therefore indicates that the frustrated packing scheme has *a built-in asymmetry* which should be reflected in the development *of crystals with threefold symmetry*, in view of the differences in nucleation mechanisms and energies on opposite sides of densely packed crystallographic growth planes. Indeed, triangular crystals have been observed for (almost) all frustrated crystal structures. Figures 12 and 13 illustrate crystals of isotactic poly(*tert*-butylethylene sulfide) (PTBES) and of poly(L-hydroxyproline) (PHypro), respectively. In both cases, nonfrustrated crystal structures had been proposed. However, they were shown recently to be actually frustrated ones, and the single crystals have been grown to support the frustration with their triangular morphology. Note however that no triangular single crystals of the unstable modification of PLLA can be grown, since this form is not obtained under quiescent conditions: the frustration cannot be supported by morphology, although the fiber pattern provides a clear indication in its favor (i.e. the weakness of the 003 reflection versus the 103 one[5]).

Isotactic poly(2-vinylpyridine) provides yet a further elaboration on this morphology theme. Indeed, depending on crystallization conditions, a number of different morphologies are obtained, all with threefold symmetry: deformed hexagons and truncated triangles. A truncated triangular single crystal is illustrated in Figure 14a. Electron diffraction patterns of such crystals (Figure 14b) indicate that the slow growth faces which bound the triangular crystals are (100), as for PTBES and PHypro; note that these are *not* the most densely packed planes in the trigonal, frustrated unit cell.

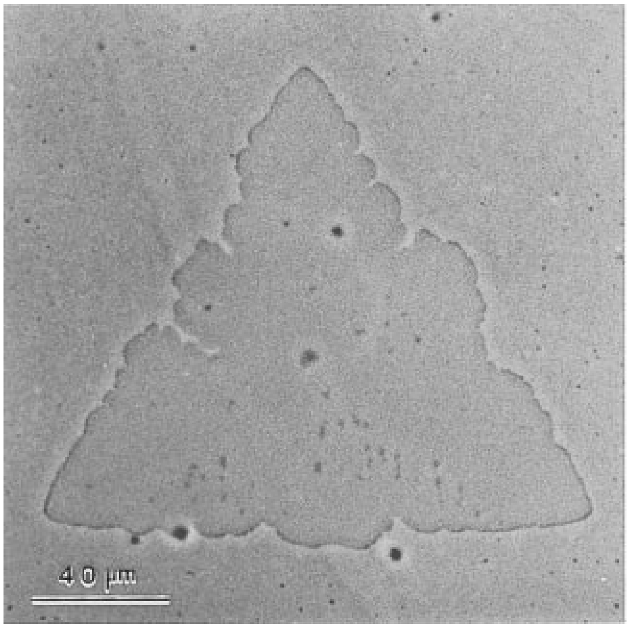


Figure 12. Phase contrast optical micrograph of a single crystal of isotactic poly(*tert*-buthylethylene sulfide) formed by thin film growth at 130 °C. The film is obtained by evaporation of a 1% toluene solution. The growth faces are {100} (they were erroneously indicated to be {110} in ref 5).

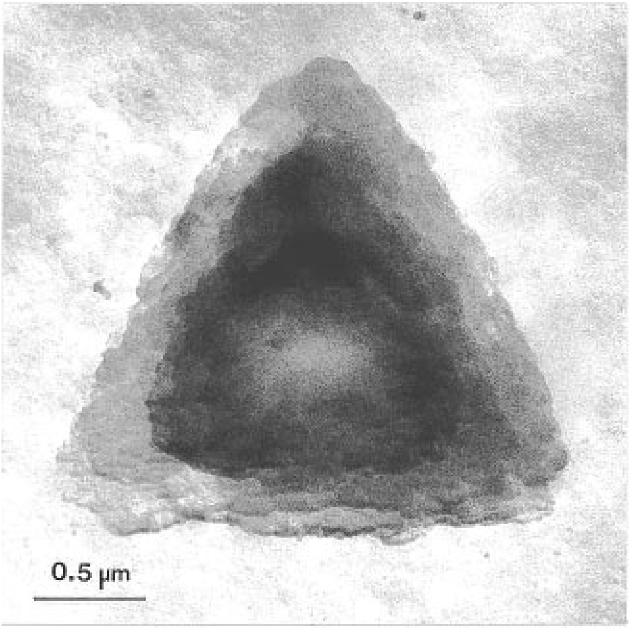
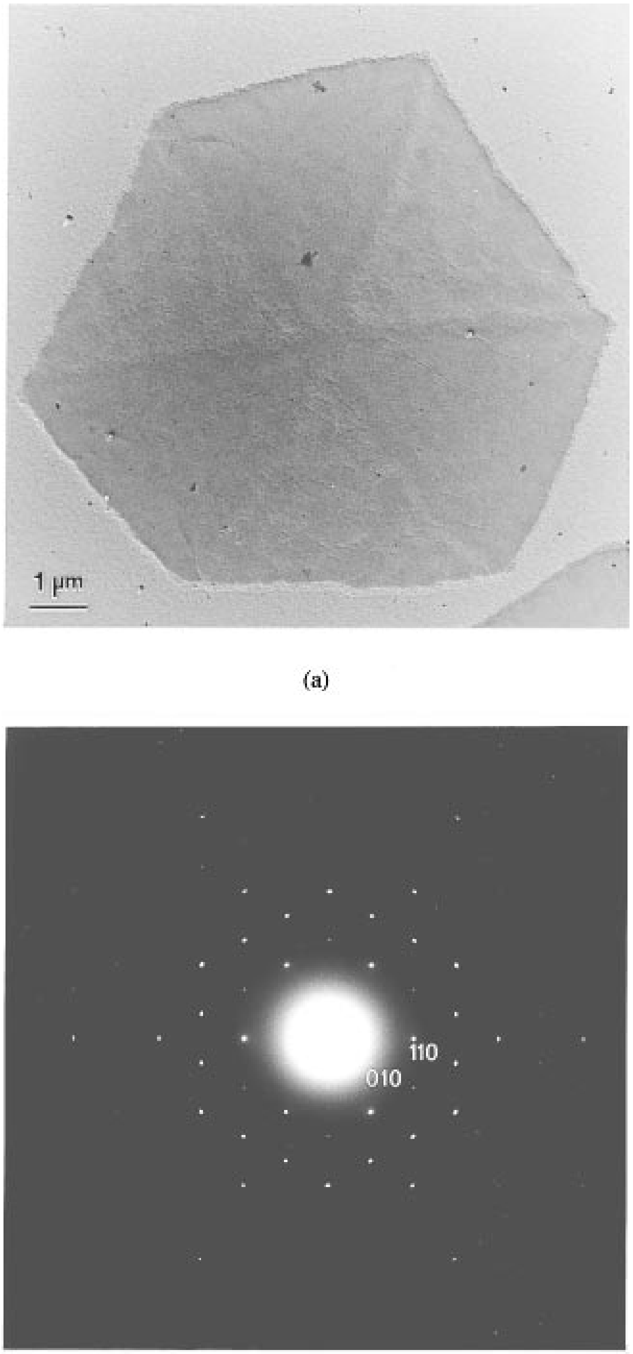


Figure 13. Transmission electron micrograph of a single crystal of poly(L-hydroxyproline) grown from a 0.1% solution in a 1/9 (v/v) mixture of formic acid and ethanol at room temperature.

The crystals of iP2VP further illustrate an original and most intriguing possible feature of single crystals of frustrated structures. As can be seen in the truncated single crystals of Figure 14, *the lamellar thickness is*



(a)

(b)

Figure 14. (a) Electron micrograph of a single crystal of isotactic poly(2-vinylpyridine) formed by thin film growth for 15 h at 200 °C. (b) Electron diffraction pattern of the crystal in part a in the proper relative orientation. Indexing according to the unit cell of Puterman *et al.*[14]

growth sector dependent. Different lamellar thicknesses have been observed for several polymers (PE,[16] syndiotactic polypropylene[17]), but as a rule, these involve different crystal faces (i.e. (110) and (200) in PE, (010) and (100) in sPP) and therefore different lateral energies as well as surface energies (due to different interstem distances and therefore fold lengths). In the present case, the situation is significantly different, since the crystal structure is identical for the opposite sides of the same crystal plane, and deposition must be characterized by the same end surface energies. It results that the differences in lamellar thickness reflect differences in the energy balance when attaching individual stems.

We note in particular that theories of polymer crystal growth have considered so far depositing stems with a parallelepipedic cross section[18] only but not the nearly triangular one of threefold helices. As illustrated in Figure 4 or 11, a threefold helix can be approximated by an elongated rod (of length l) with a triangular section (of edge length a). Flat-on deposition of the rod on the crystal substrate is energetically quite costly, since it *creates* an additional lateral surface characterized by an energy term equal to $al\sigma$. On the contrary, deposition of a helix in a notch is energetically quite favorable, since the system *regains* one lateral surface energy term $al\sigma$: Whereas two lateral surfaces existed prior to deposition of the chain, only one is left after deposition. However, the *global* energy balance (after deposition of the three helical stems which build up the frustrated structure unit cell) must be comparable on opposite sides of any growth plane: evaluation of the global energies involved suggests that the lamellar thicknesses should be equal on opposite growth faces, whereas Figure 14a demonstrates that this is not so. In other words, the different lamellar thicknesses reflect *different partitions* of the total energy between the three stems, i.e. illustrate the impact of energies of attachment at a more local scale, and even at the scale of one stem.

Beyond these more detailed aspects of the growth mechanism, we wish to point out that, on the basis of the above evidences, *the triangular morphology, when observed for a homopolymer—and in particular for a chiral homopolymer—is a very strong, possibly an absolute, indicator of a frustrated packing scheme.* On this basis, we suggest that polymers for which triangular or truncated triangular crystals have been documented (e.g. poly(L-alanine) grown from a trifluoroacetic acid–trifluoroethanol mixture[19]) should be reexamined, and crystal structures based on threefold isochiral helices with a frustrated packing should be considered.

Conclusion

The evidence presented in this paper indicates that, besides relatively straightforward cases of twinned crystals, triangular or truncated triangular polymer single crystals are obtained for trigonal unit cells in which *opposite sides of a given growth plane are not equivalent*.

This nonequivalency may be a *genuine crystallographic feature of the unit cell*. We have identified such asymmetries in the so-called *frustrated packing scheme* observed for several polymers for which three threefold, isochiral helices are assembled in a unit cell with $P3_1$ or $P3_2$ symmetry. The asymmetry stems from the different azimuthal settings of the three helices which build up the unit cell, resulting in different nucleation sites on opposite sides of any given growth plane. Present evidence suggests however that most (or all) of the frustrated polymer crystals are bound by {100} growth faces, which grow at a slower rate than the more densely packed {110} faces.

Triangular crystal morphology is not however an unequivocal indicator of frustration. Indeed, achiral polymers may crystallize in frustrated crystal structures but may form enantiomorphic domains separated by antiphase boundaries. This composite structure results in averaging of the polarity of the growth fronts and therefore in hexagonal or rounded morphology, as observed for the β phase of isotactic polypropylene and the α phase of syndiotactic polystyrene.

A second cause of triangular morphology rests again on a trigonal crystal structure, this time with $R3c$ or $R\text{-}3c$ symmetry. This unit cell is characterized by the fact that right- and left-handed threefold helices are imbricated to create an overall enantiomorphous structure, in which however the settings of right- and left-handed helices are symmetrical relative to the (110) growth plane. Upon crystallization of an *achiral* polymer, which can form right- and left-handed helices, the *same molecules* deposit on opposite sides of the growth plane, and the crystal is hexagonal (growth rates are identical for opposite growth fronts). The crystal structure is however also valid for racemic mixtures of enantiomorphous polymers. In such a case, *two different molecular species* form the right- and the left-handed helices, and they crystallize with their own characteristic rates on opposite sides of the (110) growth plane. An imbalance in growth rates (and therefore triangular morphologies) is created in the case of *disparities in molecular constitution (or concentration)* of the two (co)-crystallizing species. The triangular morphology requires in this case *two* (enantiomorphous) crystallizing species, whereas the genuine crystallographic asymmetry of frustrated structures generates triangular crystals for a *single* polymer.

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(11) Note that this situation is not specific to the trigonal unit cell geometry but rather is a feature of crystal structures in which layers of antichiral threefold helices are involved, e.g. for the monoclinic unit cell of isotactic polypropylene (iPP) in its α phase and more specifically for its lateral (010) growth faces (in which the actual orientation of the helices could be determined by AFM on epitaxially crystallized samples).

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