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# The frustrated structure of poly(L-lactide)

J. Puiggali[a,1], Y. Ikada[b], H. Tsuji[c], L. Cartier[a,2], T. Okihara[a,3], B. Lotz[a,*]

[a]Institut Charles Sadron (CNRS-ULP), 6, Rue Boussingault, F-67083 Strasbourg, France
[b]Research Center for Medical Polymers and Biomaterials, Kyoto University, 53 Kawahara-cho, Shogoin, Sakyo-ku, Kyoto 606, Japan
[c]Department of Ecological Engineering, Faculty of Engineering, Toyohashi University of Technology, 1-1 Tempaku-cho, Toyohashi, Aichi 441, Japan

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## Abstract

The crystal structure formed upon stretching or stroking of poly(L-lactide) is determined by electron diffraction and conformational energy analysis. It rests on a frustrated packing of three three-fold helices in a trigonal unit-cell of parameters $a = b = 1.052$ nm, $c = 0.88$ nm, space group $P3_2$. The frustrated packing is of the type described as North–South–South (NSS). This structure appears to be formed to accommodate the random up–down orientation of neighbor chains associated with rapid crystallization conditions. This randomness introduces structural disorder ($c$-axis shifts and azimuthal setting of neighbor helices). The resultant streaking of the diffraction pattern is modeled. Frustrated packings observed in polymeric systems that depart from three-fold symmetry, and in pseudo-racemates of low molecular weight compounds are discussed.

*Keywords*: Polylactide; Crystal structure; Frustration

## 1. Introduction

Epitaxial crystallization of the enantiomeric forms of polylactide, poly(L-lactide), PLLA or poly(D-lactide), PDLA, of formula $(O–CO–C^*H(CH_3))_n$ described in the preceding paper [1] has led to the recognition of a hitherto-unsuspected crystal modification of this polymer (denoted the γ-phase), with an orthorhombic cell geometry and characterized by the *antiparallelism* of its two chains. However, Eling et al. [2] showed that polylactide forms, upon mechanical stretching of its stable α-form, yet a different crystal phase. Hoogsten et al. [3] suggested for this phase an orthorhombic unit cell ($a = 1.031$ nm, $b = 1.821$ nm) which includes *six* helices with three-fold helical conformation. Given the large size of the cell and number of helices, the detailed arrangement of the latter in the unit-cell could not be worked out. Noting that the cell geometry corresponds very nearly to a hexagonal packing of helices (the $b/a$ ratio is 1.76, i.e. $\approx \sqrt{3}$), Cartier et al. [4] suggested that the six chains, orthorhombic cell can be described as a smaller, trigonal cell that houses three helices. In view of the three-fold helical conformation, of the fact that polylactide is chiral and of the characteristic trigonal unit-cell with three helices, Cartier et al. further suggested that the helix packing probably conforms to the scheme of *frustrated* crystal structures recently uncovered for isochiral three-fold helices [4–8].

In the present contribution, we analyze this crystal structure (which, anticipating results to come, will be referred to hereafter as frustrated, or β-structure). On the basis of extensive crystal packing analyses, we establish the filiation between the new orthorhombic crystal structure described in the preceding paper [1] (the γ-form) and the frustrated structure. More specifically, we conclude that the frustrated structure is formed when the regular pattern of antiparallel chain orientations characteristic of the γ-form cannot be established. In addition, variability in the relative up–down helix orientations introduces a structural disorder (both in the $c$-axis shifts and azimuthal settings of helices), which is reflected by a significant streaking in the diffraction pattern of this frustrated phase.

## 2. Experimental

The samples and investigation procedures are as described in the companion paper [1]. Oriented (fiber) patterns of the frustrated crystal phase were obtained from

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[*] Corresponding author. Tel.: +33-3-88-41-40-46; fax: +33-3-88-41-40-99.

[1] Permanent address. ETSEIB, Department d'Enginyera Quimica, Diagonal, 647 E-08028 Barcelona, Spain.

[2] Present address. ENSCL, Laboratoire GEPIFREM, Cité Scientifique, Bat C7 Av. Mendeleiev, BP108, 59652 Villeneuve d'Ascq, France.

[3] Permanent address. Department of Applied Chemistry, Faculty of Engineering, Okayama University, Okayama 700, Japan.

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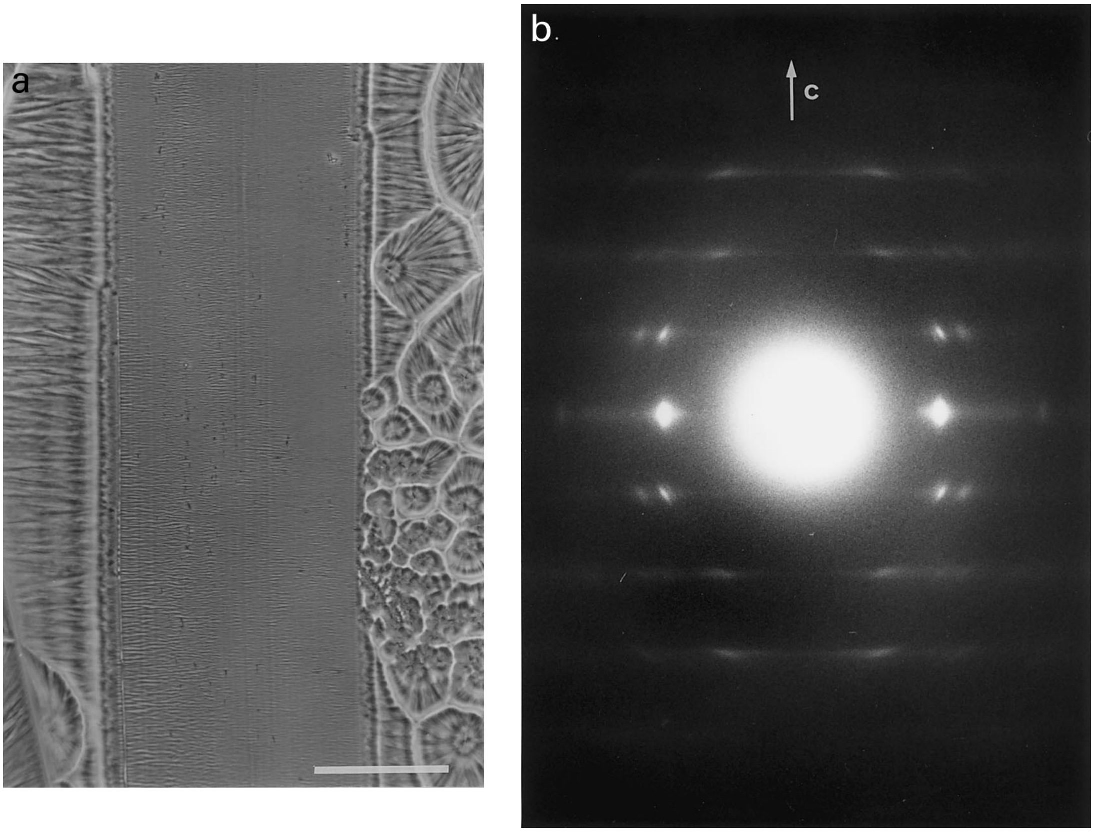


Fig. 1. (a) Thin film of PLLA stroked and annealed at 140°C for 2 h. Note the orientation of lamellae (actually stacks of lamellae) normal to the stroking and chain axis direction (vertical). On the sides of the stroked region, development of so-called transcrystalline regions (growth nucleated by the stroked area), as well as spherulitic growth. Optical micrograph, phase contrast. Scale bar: 100 μm. (b) Electron diffraction pattern of a stroked PLLA film as in (a). Fiber axis vertical.

thin layers of PLLA cast on a glass slide from a dilute solution and positioned on a hot bar with a temperature gradient (a Kofler bench). The films are stroked with a razor blade from the hot towards the colder end of the bar: the molten sample crystallizes while being sheared. Whereas the procedure is not well controlled, it produces, for almost all polymers, the desired fiber orientation in films thin enough (a few tens of nm at most) to be used in transmission electron microscopy. The alternate method (stretching of a PLLA fiber in the stable form) used by the Dutch group [2,3] is more reproducible but the fibers are only suitable for X-ray diffraction analyses. The sample is coated with a film of carbon, floated on water with the help of a polyacrylic acid backing, and examined in a Philips CM12 electron microscope operated at 120 kV. The molecular modeling packages are those developed by Biosym-Molecular Simulations (Cambridge, UK and Waltham, MA).

## 3. Results

### 3.1. Morphology and diffraction pattern of stroked PLLA

The film of PLLA stroked with a razor blade and let to anneal displays very prominent stacks of lamellae oriented at right angles to the stroking direction. Also, the crystallization of the stroked part takes place early-on, since it induces a transcrystalline layer on its edges, which extends into the molten part of the film (Fig. 1a). An electron diffraction pattern obtained from the stroked area is displayed in Fig. 1b. This fiber pattern is similar in every respect to the pattern published by Okihara et al. [9,10] or to the X-ray diffraction pattern reported by Hoogsten et al. [3]. It is distinctly different from that of the “orthorhombic” γ-form obtained by epitaxial crystallization, and analyzed in the preceding paper (Fig. 2a in Ref. [1]) (in the comparison, it should be kept in mind that the pattern of the β-phase, obtained by epitaxial crystallization is not, strictly speaking, a *fiber* pattern). Although the two forms are definitely based on the same three-fold helical conformation of the chain, the *lateral packing of the helices is different*: the 110 and 200 reflections characteristic of the β-phase are merged in a single reflection; additional reflections exist on the first layer line, near the meridian; also, a significant streaking, already noted by previous investigators, is visible on all layer lines.

Since the helix conformation needs not be questioned, derivation of the structure concentrates on the sole lateral

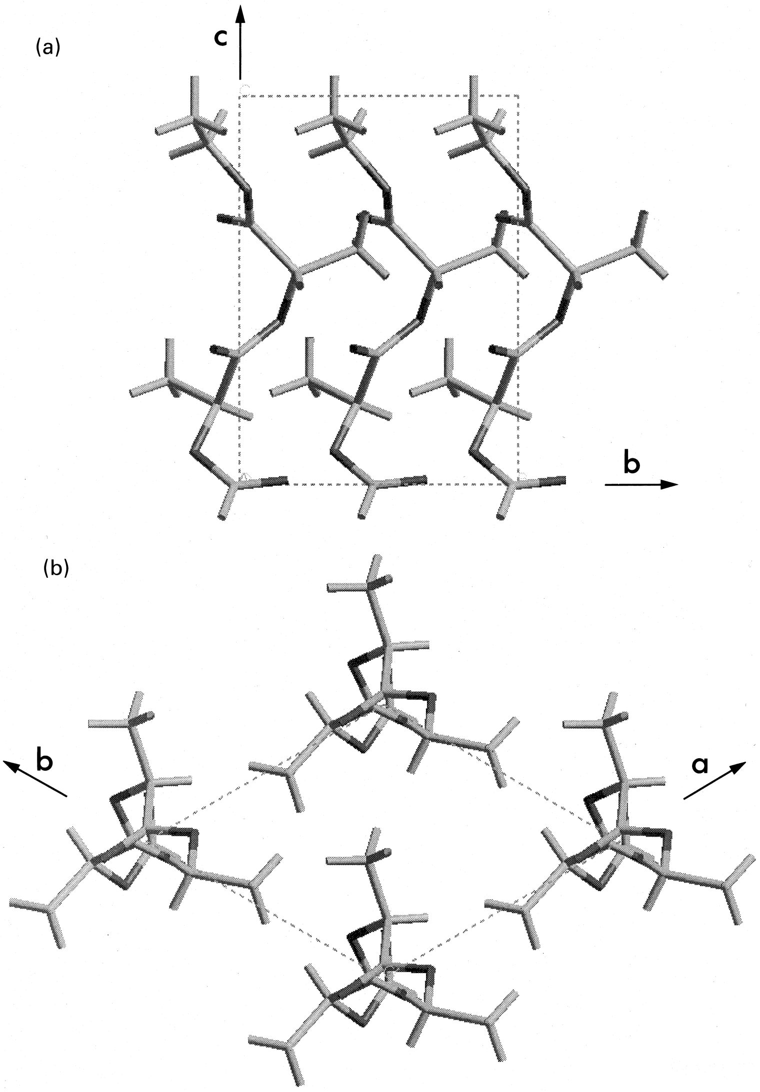


Fig. 2. (a) Model of the minimized orthorhombic unit-cell made of parallel chains, seen along the *a*-axis but assuming parallel chain orientation rather than antiparallel (the latter is shown in Fig. 4b of Ref. [1]). (b) Molecular model of the packing of PLLA chains after minimization of the packing energy of a γ-phase orthorhombic cell (structure in part (a)) represented as a simpler trigonal, one-chain unit-cell. Minimized cell parameters: $a = b = 6.21$ Å, $c = 8.8$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$.

organization of helices in the unit-cell. Determination of this lateral packing would of course be best assessed with the help of single crystals. This is not possible however, neither for the β-phase (only produced so far by epitaxial crystallization) nor for the frustrated structure (produced by stroking or stretching). Structure derivation must therefore rest on the fiber diffraction pattern only.

As indicated in the introduction, Hoogsten et al. [3] in their analysis of the fiber pattern, were led to propose a large orthorhombic cell which must include *six* helices to yield a reasonable crystal density. It is readily apparent that the available diffraction evidence can be interpreted on the basis of a trigonal unit-cell of parameters $a = b = 10.52$ Å, $c = 8.8$ Å, which corresponds to half the large orthorhombic unit-cell, and therefore houses *three* helices.

Derivation of a trigonal unit-cell with the unconventional cell content of *three* helices indicates that the structure of the stroked PLLA belongs to a recently uncovered class of *frustrated* structures [4–8]. In this family of structures, based on trigonal unit-cells with three three-fold chiral helices, two helices maximize their mutual interactions. Such favorable interactions can be repeated between helices organized in a honeycomb lattice, but leave aside the third helix. The latter interacts differently with its six neighbors, which are all part of the honeycomb. The different interactions result in, and show up by different azimuthal settings for the three helices, and in particular for the latter one. The frustrated packing schemes are characterized by several structural or diffraction “markers” that help diagnose their existence. One of them cannot be used in the present case: it is the triangular shape (frequent, but not systematic) of the single crystals grown from solution or from thin films [11].

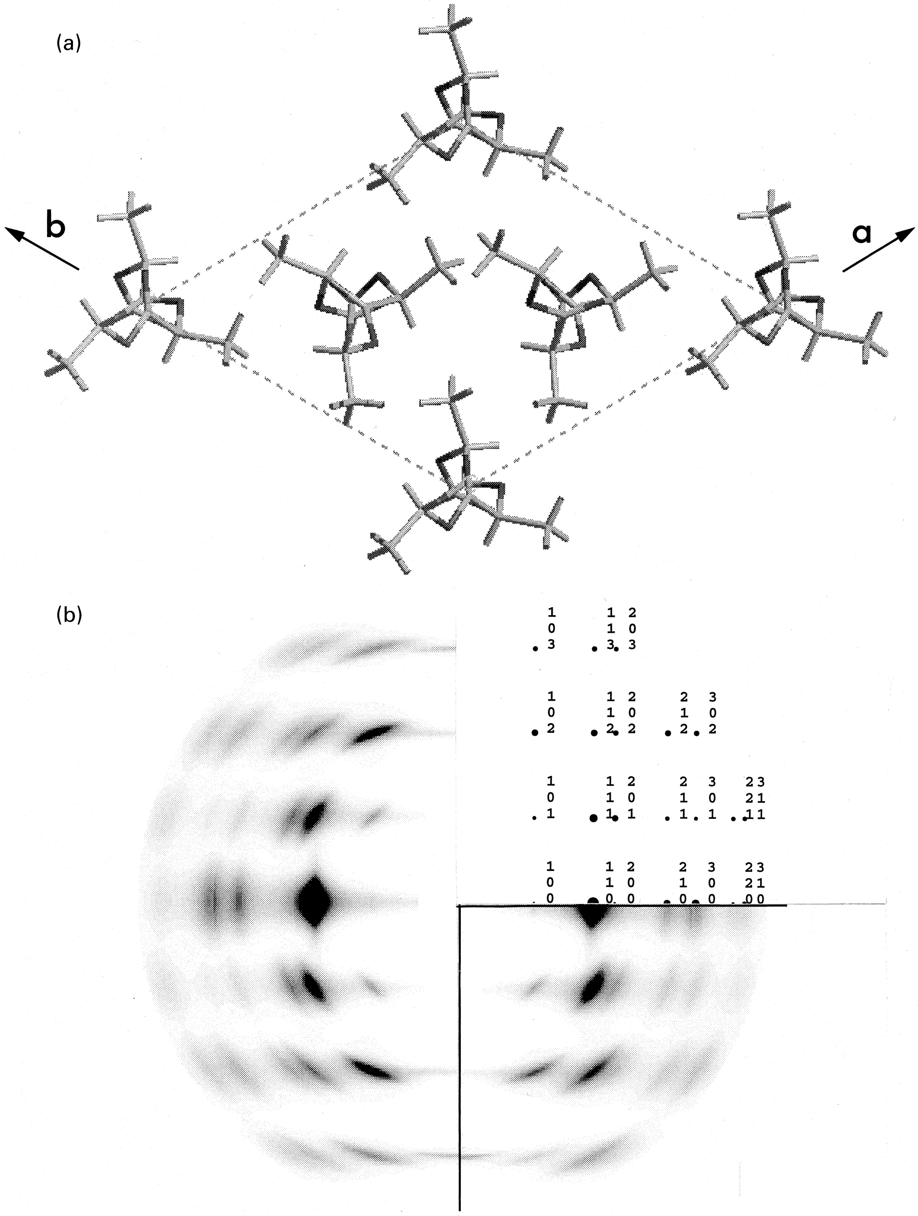


Fig. 3. (a) Crystal structure of the β-phase of PLLA, shown here with three parallel helices. The trigonal, three chains unit-cell displays a frustration of the type NSS. (b) Computed diffraction pattern of the β-phase of PLLA (left-hand side of the figure), and corresponding indexing (top right). The bottom right of the diagram represents one quadrant of the diffraction pattern computed for a crystal structure based on a different setting of the helices, described as NWW. Note the reversal of relative intensities for the 102 and 112 reflections, which is not in agreement with the experimental pattern (Fig. 1b).

A second criterion is the weakness of the 003 reflection in the fiber pattern compared to its neighbor 103 and $\bar{1}03$ reflections. This peculiarity of the diffraction pattern, not observed with standard unit cells based on $P3_1$ or $P3_2$ symmetries (which house only one chain), results from the fact that two helices of the cell are shifted by $c/2$, which implies that their contributions to the 003 reflection cancel out. The fiber pattern of β-poly(L-lactide), while being significantly streaked, displays indeed this feature.

Whereas this first analysis of the diffraction pattern shown in Fig. 1a strongly suggests a frustrated structure, it is of interest to derive the details of the latter starting from the orthorhombic form described in the preceding paper [1]. Indeed, *the crystal polymorphism of PLLA, with two crystal forms based on the same three-fold helix geometry, provides an unusual opportunity to analyze the structural and molecular origin of the frustration.*

### 3.2. Towards the frustrated structure

The crystal structure of the orthorhombic γ-phase analyzed in the preceding paper is based on the fact that two *antiparallel* chains are housed in the cell. The packing of the chains is nearly, *but not exactly,* hexagonal. Using the

Table 1
Fractional coordinates of the β frustrated structure of poly(L-lactide). Unit-cell parameters: $a = b = 10.52$ Å, $c = 8.8$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$. Space group: $P3_2$. Parallel helices are assumed. The three helices are generated from the coordinates of three independent lactide repeat units marked 1–3 in the table

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| 1. C (H) | 0.1284 | 0.1147 | 0.2554 |
| C ($H_3$) | 0.2320 | 0.2701 | 0.3172 |
| O | 0.0461 | 0.1233 | 0.1319 |
| C (=O) | 0.0238 | 0.0197 | 0.3814 |
| O (=C) | −0.0966 | 0.0084 | 0.3965 |
| 2. C (H) | 0.3746 | 0.8059 | 0.2804 |
| C ($H_3$) | 0.3522 | 0.9304 | 0.3422 |
| O | 0.2773 | 0.7361 | 0.1570 |
| C (=O) | 0.3435 | 0.6939 | 0.4065 |
| O (=C) | 0.2218 | 0.5864 | 0.4215 |
| 3. C (H) | 0.7183 | 0.4735 | 0.1742 |
| C ($H_3$) | 0.7068 | 0.6044 | 0.2360 |
| O | 0.6195 | 0.4088 | 0.0507 |
| C (=O) | 0.6795 | 0.3598 | 0.3002 |
| O (=C) | 0.5544 | 0.2579 | 0.3153 |

same packing-energy analysis methods, it is of interest to analyze the impact of chain sense on this structure.

Keeping the orthorhombic geometry of the γ-phase cell, and using *parallel* helices, minimization of the packing energy yields a surprising result: the helices rotate on their axes, and shift along *c*. The minimized structure is characterized by azimuthal settings and *c*-axis shifts of the two helices that are *identical* within fractions of degrees (for the azimuth) and angstroms (for the shift). Further, the *a*- and *b*-axes of the minimized unit-cell are in a characteristic $\sqrt{3}$ ratio: the minimization *has generated an orthorhombic packing which can be reduced to a one chain, trigonal unit cell*, with $P3_2$ symmetry, as illustrated in Fig. 2a and b. The minimized interchain distance (and *a*-axis parameter of the trigonal one-chain unit-cell) is 6.21 Å.

Packing energy analysis, therefore, suggests that *the unit-cell geometry and symmetry of PLLA depends on the chain sense of neighbor helices*. The new feature uncovered by the present analysis is that the antiparallel orientation of helices established for the γ-phase *must* be a regular one, with antiparallel *layers* alternating along *b*- (and *a*) axis directions. Introduction of a helix with the "wrong" sense in such layers creates a local disturbance, and generates an environment which drives the structure towards a trigonal structure. This result is also consistent with, and reflects the fact that anticline isochiral helices of PLLA *are not isosteric*. Indeed, upon chain reversal, and assuming that the location of the most exposed methyl side-chains is preserved, the carbonyl group is located either "above" or "below" this methyl side chain.

The "simple" packing in a one-chain trigonal unit cell of parallel helices derived by packing energy analysis is not however observed experimentally. It is actually highly unrealistic since antiparallelism of chains is imposed by chain folding in lamellar crystals. Rather, a frustrated crystal structure is generated, the structure of which is examined now.

### 3.3. The frustrated structure of PLLA

The coexistence and statistical distribution of parallel and antiparallel neighbor helices is likely, not only as a result of chain folding, but also under "harsh" crystallization conditions. These conditions prevail upon stretching of a fiber, or when stroking, under which the β- or frustrated structure is formed. We suggest therefore that, in the case of PLLA at least, *frustration is the structural response to accommodate a statistical up–down orientation of helices*. This analysis underlines the difficulties of the derivation of the frustrated structure of PLLA, given the variety of local environments of any one helix (parallelism or antiparallelism with each of its six neighbor helices), and assigns limited objectives to the structure derivation. The latter will mainly deal with two issues: determination of the exact frustrated packing scheme, and analysis of the origin of disorder.

#### 3.3.1. The frustrated packing scheme

Previous investigations [4–8] of frustrated structures have revealed that two frustrated packing schemes, characterized by two different sets of azimuthal orientations of helices may exist. The two sets of orientations have been described as North–South–South (NSS) and North–West–West (NWW): the orientations indicate the (approximate) location on a compass of one of the side chains of each of the three helices when seen in *c*-axis projection.

For PLLA, discrimination between the two packing schemes is mainly performed by model building and minimization of the packing energy and comparison of the calculated and experimental diffraction patterns. Standard packages of molecular simulation and packing energies are used, since they have produced very satisfactory structural models when applied to similar problems (e.g. for the frustrated "superstructure" of syndiotactic polystyrene) [8]. In a first analysis and for simplicity, we consider the frustrated packing of three parallel helices, in spite of its shortcomings. Structures that combine different helix senses will be considered in the next section, in connection with the analysis of the structural disorder.

From a comparison of the two alternative NSS and NWW frustrated packings applied to poly(L-lactide), the answer is unambiguous: the NSS is the lowest energy-packing scheme, and that which yields the best agreement with experimental diffraction evidence. The packing energy is −26 kcal/cell, as opposed to −18 kcal/cell for a NWW structure. The NSS model arrived at is actually a rather "pure" structure, with minimal departures from the North and South orientations: 6, −2 and 7°, as defined with the conventional trigonometric sense. Fig. 3a presents the frustrated crystal structure of poly(L-lactide) as derived in the present investigation. The fractional coordinates of the

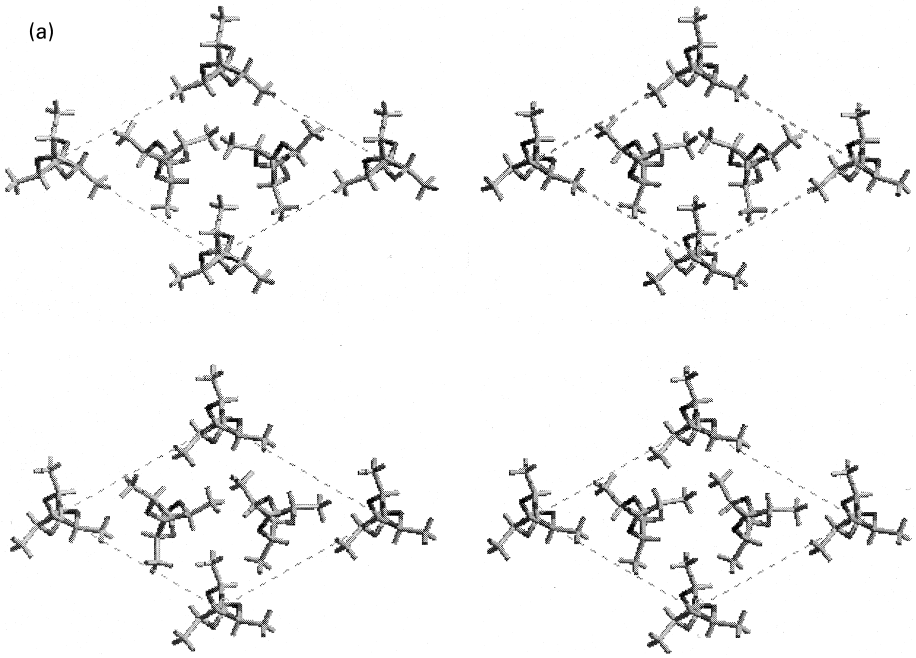


Fig. 4. Impact of chain sense on the setting of chains in the unit-cell and resulting streaking of the diffraction pattern. (a) Four models used in the modelization. They correspond to packing energy minimized structures for various combinations of chain senses (up (U) and down (D)) and at various locations in the unit-cell. The three helices in the (110) plane are, starting from the left helix: UUD, DUD, DDU and DUU. (b) Modelization of the impact of the structural diversity of frustrated structures depending on relative chain sense (illustrated in part (a) for the azimuthal settings only) on the diffraction pattern of the β-phase of PLLA. The various diagrams represent the intensity profiles for the equator and the first three layer lines ($l = 0$–3). The profiles are shown along $h0l$ and scaled in the first column to represent the intensity of the spots. In the second and third columns (the latter for $h1l$), the maximum intensity has been set at 30, to better visualize the streaks.

model are given in Table 1. Fig. 3b represents in its left part the computed pattern of a NSS arrangement, and in the lower right part that of a NWW arrangement. The relative intensities of 102 and 112 reflections on the second layer line provide an unambiguous indication in favor of the NSS packing scheme. Note again that, for simplicity, the structure described by these coordinates corresponds to *parallel* helices. The impact of antiparallelism has a significant bearing on the structural disorder, as analyzed now.

### 3.3.2. Antiparallelism of helices and structural disorder

Antiparallelism of neighbor helices has a significant impact on the chain packing, i.e. on the azimuthal settings and *c*-axis shifts. Similar conclusions were actually reached by Puterman et al. [12] in their analysis of the structure of isotactic poly(2-vinylpyridine) (iP2VP), and more recently in a packing energy analysis of the β-phase of isotactic polypropylene by Meille et al. [13]. This impact can be evaluated by considering a few representative, but simplified situations in which any one helix in the unit-cell is inverted, and is therefore surrounded by six antiparallel helices. Whereas these “academic” situations help grasp the major trends, they cannot however simulate the variety and complexity of helix surroundings which exist in chain-folded lamellae.

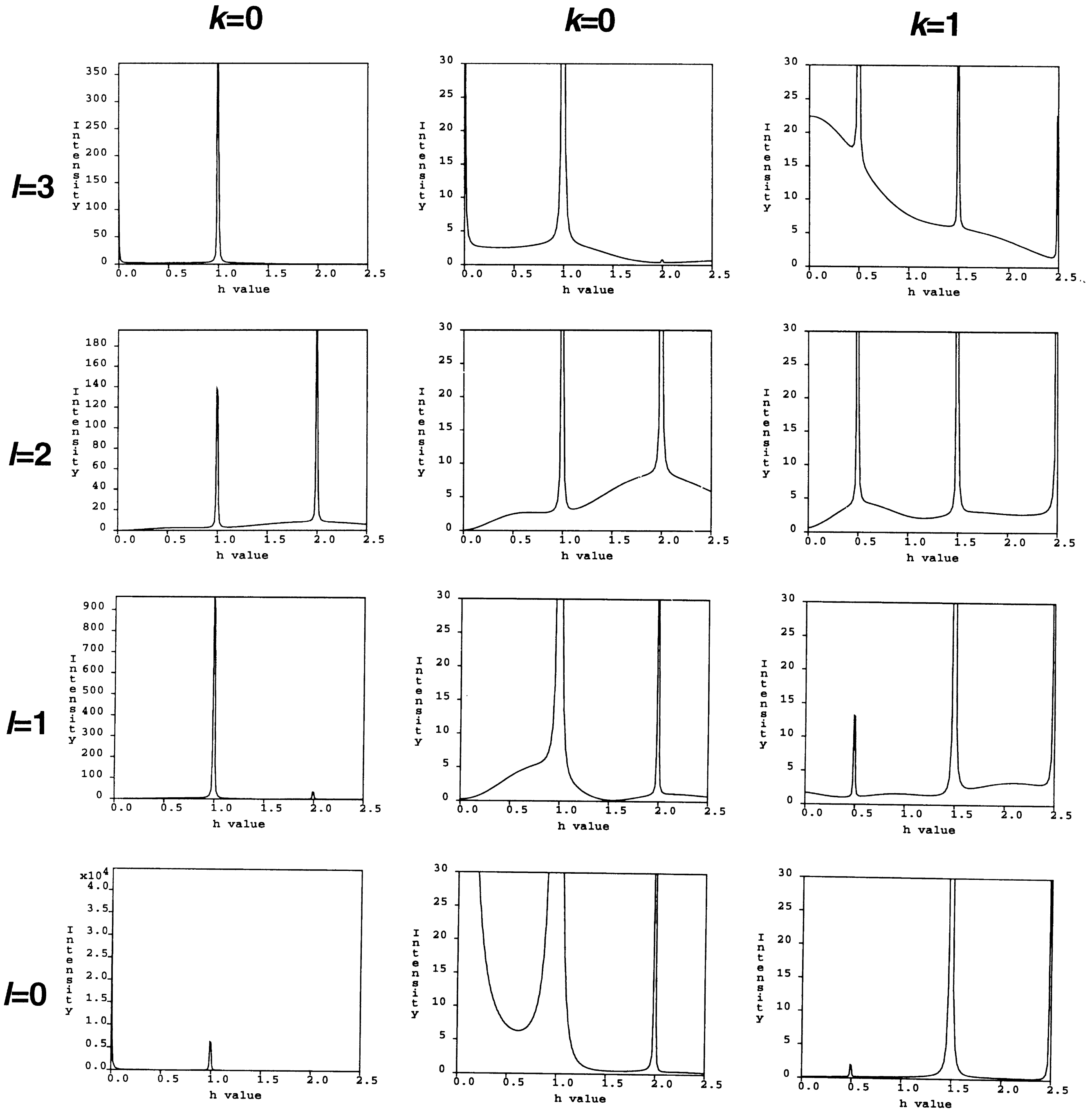
Within the confines of “all antiparallel neighbors” set above, all three helix sites need be considered in frustrated structures: corner and the two center ones. The results are summarized in a condensed form in Fig. 4a.

Inversion of the corner helix (the “North” helix) does not significantly alter the crystal structure: the azimuthal settings of the three helices are virtually maintained at their initial values after packing energy minimization. Helix sense reversal at this site has therefore relatively “mild” structural consequences.

Reversal of the helix sense at one of the center sites (defined here, for convenience, as center left) is similarly of relatively limited consequences. While the azimuthal settings vary somewhat more than in the previous case, the general features of the structure are maintained: in particular, the azimuthal settings of the three helices still conform to the general “North–South–South” scheme.

Helix reversal at the other center site has more impact on the structure. After minimization, the azimuthal settings tend towards NEE. Note that in this process, one center chain site is more affected than the other. In the models displayed in Fig. 4a, it is the center right site. Comparison of the various models shown in Fig. 4a also helps understand the importance and structural impact of helix reversal, notably at one of the center sites. As already indicated, the difference between the two center sites was first established by Putermann et al. [12] in their early structural analysis of iP2VP.

To conclude this section on the structure derivation of the



(b)

Fig. 4. (*continued*)

frustrated β-structure of PLLA, it is clear from the above analysis that a single set of atomic coordinates is insufficient to describe the structure and its complexity: coordinates in Table 1 are given to serve as guidelines for further studies on this system. The limitations just indicated are further illustrated by the analysis of the structural disorder observed in β-PLLA.

### *3.3.3. Disorder in the frustrated structure of poly(L-lactide)*

Fiber patterns of poly(L-lactide) in its β-form suggest a significant structural disorder: they are streaked on all layer lines, in sharp contrast with the α-form, or the newly discovered γ-form. Extensive structural disorder must therefore exist in the fibers or stroked films of the frustrated structure of PLLA.

Structural disorder is frequent, but by no means systematic, in frustrated structures. Poly(*t*-butylethylene sulfide) (PTBES) [6] or iP2VP [12,14] display virtually no disorder. However, the *hk*0 and *hkl* patterns of the β-phase of isotactic polypropylene are significantly streaked [15,16]. For βiPP, a possible origin of the disorder lies in the coexistence of domains made of left- and right-handed helices (separated by antiphase boundaries). Such a disorder has also been considered for the $\alpha''$ form of syndiotactic polystyrene (sPS) by Pradère and Thomas [17]. This "antichiral" origin, conceivable for βiPP or sPS (which are achiral) cannot apply for the chiral PLLA.

The most plausible origin of the disorder appears, therefore, to rest on the structural variability associated with helix sense orientation. This could take various forms, based on the above results on the polymorphism of PLLA: coexistence of small domains with different cell geometries (antiparallel β-phase, "parallel" trigonal one-chain cell) in addition to disorder within the frustrated structure itself. Only the latter is considered here.

Streaks of the diffraction pattern have been modeled using the "Diffraction Faulted" module of the Cerius package. This program generates the packing of up to four different models, and includes various features such as thermal agitation factors, etc. The outputs can be either intensity profiles along certain layer lines, or "reconstructed" diffraction patterns. Adapting the program from a parallel study of the streaking in the *hk*0 pattern of βiPP (Lotz B, et al., to be published), and taking into account certain constraints of the program, the trigonal cell of the frustrated structure is converted in an orthorhombic cell with parameters $a = 18.22$ Å, $b = 5.26$ Å, $c = 8.8$ Å, and the intensity profiles on the various layer lines are calculated for sections of the reciprocal lattice which cross the meridian and the 110 spot, and for sections parallel to this initial section, shifted by $b^*$.

A great number of combinations of structural models have been tested. Only one representative—but by no means unique—combination is presented here, merely to illustrate the features under discussion. The various models tested in the initial runs indicated that the streaking is associated with presence of up- and down chain orientations, i.e. with antiparallelism of helices, as well as with variations in azimuthal settings. In order to generate a packing which combines these features, four models with various up–down combinations and that correspond to the lowest energy models of the previous section have been used, and are displayed in Fig. 4a.

The statistical structure is made of:

- at the corner site, 1 up and 3 down helices;
- at the center left, 3 up and 1 down helices;
- at the center right, 2 up and 2 down helices.

Further, azimuthal orientations are mostly North and South for the corner and center left helix sites, but vary significantly for the center right one, from East to South.

The intensity profiles associated with the above combinations of helices is represented in Fig. 4b, for the equator and three first layer lines (the maximum intensity in the right two columns of the figure has been set to 30, in order to highlight the streaks). The profiles combine sharp spots and continuous streaks, as observed in the diffraction pattern. In particular, the latter are observed on all layer lines, and extend to high reciprocal angles. Whereas the absolute intensity of the streaks remains low compared to the sharp spots, introduction of a thermal agitation factor (e.g. $B = 6$ Å$^2$, typical for this type of structure) would decrease the intensity of the latter, and better account for the actual distribution of intensity (and its partition between streaks and spots) in the diffraction pattern.

Beyond the details of the model used in this analysis and the shortcomings of selecting a restricted (although typical) number of structural models, it needs be restated that models that are based on one set of azimuthal angles only, or on parallel helices only, do not display the same computed streaking, both in position and in intensity: the streaks arise from electron density fluctuations both in the *ab*-plane and along *c* (chain axis direction). The present investigation illustrates the interplay of: (a) packing energy minimization, which leads to a set of frustrated structures with some variability in their details (azimuthal angles, etc.); and (b) simulation of the streaked pattern, which rests on the structures derived in (a). Both analyses point to the impact of randomness of relative chemical and conformational sense (parallelism and antiparallelism) of neighbor helices.

## 4. Discussion

### 4.1. Poly(L-lactide) in the context of frustrated structures of polymers

Frustrated structures have been observed and/or are suspected for many polymers that display a three-fold element of symmetry, and most often for three-fold helices. The structural/conformational reasons that determine the formation of this structure, rather than a more "classical" one, are not yet fully understood. It was already observed that frustration may occur for helices with side-chains protruding only little from the main chain. Several polymers of the general formula $[CH(CH)_3–X]_n$ or $[CH(CH)_3–X–Y]_n$, i.e. with methyl side chains adopt a frustrated structure, either as a stable or a metastable phase: isotactic polypropylene (metastable β-phase), poly(L-alanine) in an unstable modification (possibly solvated), poly(L-lactide) in its β-phase and the alternating polymer of propylene and carbon monoxide (poly(Pro–CO)) (Sen A, Lotz B, et al., unpublished results).

Poly(L-lactide) provides further understanding on the origin of frustration, thanks to the existence of different polymorphs based on the same helix conformation. From the blend of packing energy and diffraction data gained on these systems, it appears that, for PLLA, frustration is very much dependent on relative chain orientation in the unit-cell. An "all-antiparallel" pattern leads to the orthorhombic β-phase, an "all parallel" one to a trigonal one-chain cell (which is not observed). *Frustration appears to be a structural means to accommodate random chain sense in poly(L-lactide)*. This is not too surprising, in view of the fact that antiparallel helices of PLLA are not isostructural: if the methyl group location is maintained in the chain inversion, the CO group is located either above or below that methyl group.

Isotactic polypropylene displays a somewhat similar polymorphism, i.e. exists in two crystal structures (excluding the γ-phase with its non-parallel chain axes) which are both based on a three-fold helices. The situation is more complex, since antichiral helices exist in the α-phase, and the latter as well as the frustrated β-phase can accommodate helix reversals at each site: chain reversal does not introduce the same packing energy penalty, on account of a more "symmetric" chain geometry. Evidence for a trend towards more regular arrangement of chain sense upon annealing of the α-phase has however been established, leading to the so-called $\alpha''$ structure [18].

Whereas the frustrated structure appears as a compromise for the accommodation of random chain sense, the latter has however an impact on this frustrated structure. As a matter of fact, the packing energy results suggest that in the frustrated structure, *antiparallel* arrangement of neighbor helices is favored in all cases over parallel arrangement. However, systematic antiparallelism of any one chain relative to all its six neighbors is impossible in a hexagonal close packed lattice. Interestingly, *this preferred relative orientation of neighbor helices is a potential source of a second, subsidiary frustration in the structure, additional to, and independent from, the primary "physical" frustration manifested in the different azimuthal settings* (the latter being represented by the North–South combination). This second frustration, linked with the chain sense (but not with the specific helix geometry, e.g. three-fold), would therefore parallel more closely the problematic encountered in anti-ferromagnetic systems based on triangular or hexagonal lattices: in such lattices, any one spin cannot be antiparallel to both of its two (or six) neighbors. In polymers, it must however be made clear that the two frustrations need not necessarily be correlated, i.e. that the physical frustration associated with the helix setting (NSS or NWW frustrated schemes) is observed irrespective of relative chain sense. Relative chain sense may induce disorder (as in the case of PLLA) or it may not (at least to any significant or observable level), as for isotactic PTBES [6] or isotactic polyvinylpyridine [14].

### 4.2. Frustration in other polymer systems

Observation of a frustrated crystal structure for yet another polymer raises the issue of the generality of the concept of frustration in polymer science, and its connection with similar or related features observed in other systems. These are now considered briefly.

Frustration has been reported so far only for polymer systems in which the structural unit (helix, or cluster of three chains in sPS [8]; for simplicity, only helices are mentioned in the following) displays an element of three-fold symmetry. This appears most logical, if one considers that frustration results from the establishment of favorable (privileged) interactions between two structural units in a hexagonal lattice. Such interactions can only take place in a honeycomb lattice (on account of the three-fold symmetry of the constituent elements). The honeycomb lattice leaves aside one element out of three, thus the frustrated trigonal unit-cell with three helices.

It may be of interest to consider whether frustration also exists for packings of structural elements that *do not possess the three-fold symmetry*. Whereas this issue has not yet been analyzed in any detail, a literature search indicates at least two polymers with crystal structures, which were, at least implicitly, described as frustrated: these are a substituted polyglutamate and a hexagonal columnar phase of DNA.

The first example deals with poly(γ-*n*-propyl-L-glutamate) (PPLG) which has an α-helix structure (3.6 residues per turn). In the temperature range 150–170°C, this polymer adopts a trigonal unit-cell ($a = b = 24.3\,\AA$) with three helices per cell [19]. Sasaki interprets these data by assuming coexistence of three helices, and determines shifts and azimuthal reorientations of the two central helices relative to the corner one of ±2 Å and ±12°, respectively. These departures generate, what is in effect, a frustrated structure, since the environments of the helices in the cell are different.

The second example deals with a columnar hexagonal phase of DNA in concentrated solutions. For concentrations ranging from 380 to 447 mg/ml of DNA (or for interhelix distance ranging from 29 to 31.5 Å) the DNA adopts a columnar hexagonal phase which is untwisted (at lower concentrations, twisted cholesteric or blue phases are formed). The unit-cell is trigonal and houses three double stranded helices of DNA [20,21]. This structure has been interpreted [20,21] by assuming a shift of the two central helices by $z/6$, but no variation in the azimuthal setting was considered (however, this would be needed in order to account for *hk*0 reflections corresponding to a larger unit-cell). Note however that a recent analysis of similar data led Strey et al. [22] to suggest "chiral angular frustrations in a hexagonal lattice". Their (schematic) azimuthal settings for the three helices would however create an orthorhombic cell rather than the trigonal one, and may need to be revised.

The above-two examples indicate that variants of the frustrated packing scheme considered so far for helices or entities with three-fold symmetry are possible—indeed have already been described. These systems will be analyzed further in the future in order to evaluate the impact of departures from "pure" three-fold symmetrical polymers.

It may well be that for these systems, the overall three-fold symmetry is lost (as manifested, for example, by the triangular shape of single crystals), and that lower symmetries are involved.

Finally, it is worth drawing an analogy of frustrated polymer structures with features encountered in some non-polymeric systems, and namely in so-called pseudo-racemates or anomalous racemates. Although this analogy may appear at first sight curious, since the frustrated structures of polymers described so far are chiral, some racemic compounds display trigonal unit-cells with three structural entities very reminiscent of frustrated polymer structures.

The phase diagram of binary mixtures of enantiomers sometimes displays the existence of pseudo-racemates with compositions D and L in a 2/1 (and 1/2) ratio [23]. Of interest in the present context is the family of organometallic complexes of the type $MX(PPh_3)_3$ (in which Ph stands for phenyl), such as $CuCl(PPh_3)_3$, $CuBr(PPh_3)_3$, $Ir(NO)(PPh_3)_3$, etc. The enantiomers crystallize in the space group *P*3. The racemate is a conglomerate of $D_2L$ and $L_2D$ crystals, described by the authors as an "unbalanced packing of chiral molecules" [24,25]. The crystal structure of the racemate is of special interest since it displays three molecules with three-fold symmetry packed in a trigonal cell. Moreover, the central molecule has a different azimuthal setting than that of its two antichiral neighbors: *the set of azimuthal orientations of this pseudo-racemate corresponds to the characteristic NSS pattern of frustrated polymer structures*. In the present case, antichirality of the central molecule allows better interdigitation of the "side chains" of the structural unit, namely the triphenyl groups with their complicated overall shape. By contrast, the methyl groups (or "flat" aromatic rings, for iP2VP) [12] are relatively featureless and can pack more easily in chiral frustrated structures. In any case, the analogy drawn here between very different systems underlines the structural feasibility, or even interest of frustrated structures in which the coexistence of different environments for *individual* structural elements contributes to, or is at least compatible with the *overall* stability of the structure.

## 5. Conclusion

Poly(L-lactide) provides an exceptional opportunity to analyze the origin of frustration since two different crystal modifications, which share the same helix conformation, have been characterized.

The present study has confirmed an earlier suggestion [6] that the structure of PLLA formed on stroking or by stretching of the "standard" α crystal structure (based on $10_3$ or $10_7$ helices) rests on a *frustrated packing scheme* which we find to be of the type NSS.

Experimental results and packing energy analyses suggest that the specific mode of packing (i.e. cell symmetry) depends critically on the *chain sense* of the PLLA helices: *antiparallel* helices pack *regularly* in an orthorhombic cell observed in the epitaxially crystallized films [1]. Packing energy analysis results suggest that *parallel* helices would tend to pack in a one-chain trigonal unit-cell. However, due to the existence of chain folds, this unit-cell remains hypothetical and would be envisageable only for oligo(L-lactides).

The frustrated structure (trigonal unit-cell, three helices per cell) examined in this paper appears to be a *compromise* structure which is able to accommodate a random orientation of chains imposed by rapid crystallization conditions (stroking or stretching of the α-phase)—even if it introduces some structural packing disorder, as manifested by streaking of the fiber pattern.

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