

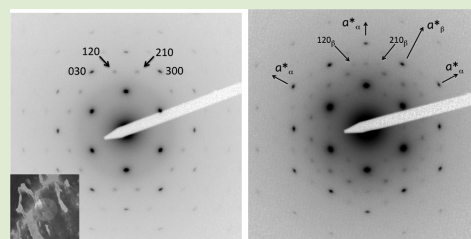
Single Crystals of the Frustrated β -Phase and Genesis of the Disordered α' -Phase of Poly(L-lactic acid)

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Supporting Information

ABSTRACT: The metastable, frustrated β -phase of poly(L-lactic acid) (PLLA) had been obtained so far only by drawing fibers from amorphous PLLA or the stable α -phase. This phase has now been obtained by crystallization in thin films in the form of snow-flake-like crystals produced at high T_c (140 °C). They display the characteristic single crystal diffraction pattern of frustrated polymers with a three-chains, trigonal unit-cell. Also, $hk0$ electron diffraction patterns indicate that crystallization of PLLA at 90 °C takes place in a transient, frustrated β PLLA phase that converts rapidly to α' PLLA. The disorder in α' PLLA stems from the incompatible cell symmetries of the trigonal, three-chains β PLLA and orthorhombic, two-chains α PLLA unit-cells. The disorder in α' PLLA involves shifts of domains along the chain axis and three azimuthal orientations 120° apart that both reflect the initial trigonal/hexagonal symmetry of the parent β PLLA. Recognition of this solid-state transformation provides a logical framework that explains many unusual characteristics of the α' PLLA phase (structural disorder, lamellar thickness and possibly growth rate vs T_c).



Poly(L-lactic acid) (PLLA) presents a complex crystal polymorphism based on different helical conformations (left-handed 10_3 and 3_1 helices). The 10_3 helix is found in the stable α -phase and in a disordered α' variant formed at low T_c ($< \approx 120$ °C).¹ The 3_1 helix is observed only in fibers drawn from the α -phase. It is a frustrated crystal structure with a trigonal cell that houses three helices.² Another orthorhombic γ form also in 3_1 helix conformation has been obtained so far only by epitaxial crystallization.³

The present contribution describes the β frustrated phase as obtained in thin film growth rather than by mechanical means. The novel $hk0$ diffraction pattern fully supports the structure derivation that was made from the sole fiber diffraction information.

This information is also used in a preliminary experiment as a means to investigate the genesis of the disordered α' -phase. This phase has been investigated in considerable detail, but several puzzling features are still not understood. The α' PLLA unit-cell a and b dimensions are slightly larger than those of the more ordered α -phase, indicating a significantly less regular chain packing. Various models of disorder have been considered that involve in particular shifts of small domains parallel to the chain axis.⁴ In addition, the growth rate versus T_c shows a definite hump in the T_c range where α' PLLA phase is produced.⁵ Finally the lamellar long periods are unusually large and show, in the 90–120 °C a curious decrease with increasing T_c .⁶

Our results indicate that α' PLLA results from a crystal–crystal transformation of an initial frustrated β -phase. The samples are either low M_w materials used in previous studies,^{2,3} or a commercial material provided by Pr. Avérous (ECPM Strasbourg). Thin films of polymer are deposited on mica or glass cover-slides from semiconcentrated solutions in p -

xylene or chlorinated solvents. Exploratory crystallization experiments are performed on a Kofler temperature gradient hot bench. More controlled experiments are made under a nitrogen atmosphere in Mettler FP 80 and Linkham HMS600 hot stages. The samples are examined with a Leica optical microscope in phase contrast and polarized light and with a Philips CM12 electron microscope equipped with a MVIII CCD camera (Soft Imaging System; cf, also, SI#1)

Growth of the frustrated β -phase from thin films: Growth of PLLA from thin films yields as a rule the α' -phase when T_c is $< \approx 120$ °C or the α -phase when $T_c > \approx 120$ °C, respectively. Observation of the crystals shown in the inset of Figure 1 came thus as a real surprise. The crystals have snow-flake like characteristics that immediately suggest some form of hexagonal packing or symmetry. The diffraction pattern in Figure 1 indicates that the unit-cell is trigonal and houses three chains. Two landmark reflections (arrowed) are indexed 120 and 210 and are located between the 300 and 030 reflections (cf. SI#2). They are found in diffraction patterns of polymers with frustrated unit-cells, among them, most prominently, the β -phase of isotactic polypropylene.⁷ They are a distinctive and specific mark of the frustration, since they would not exist in any other packing mode known for trigonal unit cells.⁸

What conditions trigger the development of this phase that, again, had not been obtained so far for PLLA except by mechanical means? It seems that the key factor is the use of a chlorinated solvent, in the present case, the high boiling

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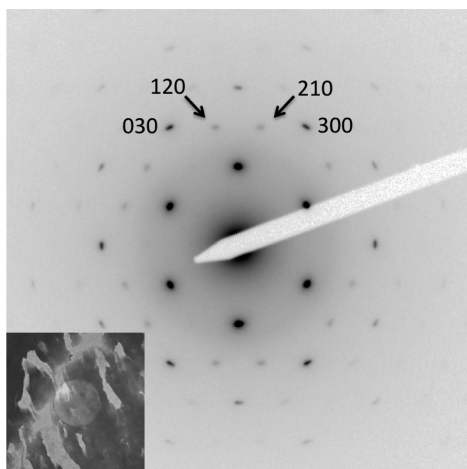


Figure 1. *hko* electron diffraction pattern of a single crystal of PLLA in the frustrated β -crystal modification.

dichlorobenzene. It is likely that traces of the solvent left in the thin film helped induce the formation of the β -phase.

The impact of traces of solvent in producing specific polymer crystal phases is not new. Esters induce the formation of the orthorhombic, chiral phase III of isotactic poly(1-butene) (iPBu1; with 4_1 helices), whereas the “spontaneous”, kinetically favored phase is the tetragonal Form II (with 11_3 helices).⁹ Propylene carbonate is known to induce or at least favor the γ -phase of poly(vinylidene fluoride) (PVDF). As is the case for iPBu1, γ PVDF has a chain conformation different from the stable α PVDF. In a similar way, different solvents, as well as crystallization conditions, can generate a variety of crystal phases of poly(4-methyl-pentene-1).¹⁰

The discovery of experimental conditions (and, apparently, mostly solvent impact) that yield the frustrated β PLLA as a result of a growth process provide a means to investigate this crystal modification on its own right and will help determine, for example, the crystallization kinetics, lamellar thickness, or melting characteristics. These investigations, as well as the impact of other factors (M_w ? Presence/proportion of D residues?) are underway. In the present note, we limit ourselves, using the diffraction information provided by Figure 1, to report on a new finding that sheds light on the genesis of the so-called α' PLLA phase, the “disordered” variant of the stable α PLLA phase obtained by crystallization at low T_c .

Formation of the PLLA α' -phase; A β – α crystal–crystal transformation: The genesis of the α' PLLA phase remains a mystery even though its structure and formation have been investigated repeatedly. The most thorough crystal structure analysis describes small domains that are shifted along the c axis, and considers α' PLLA as a “true phase” (named δ PLLA) as opposed to a phase produced by some transformation mechanism.⁴ Also, a hump in the growth rate versus T_c curve is interpreted as a manifestation of a change in growth regimes, from regime II to regime III, although M. L. di Lorenzo indicates that “the results of Hoffman–Lauritzen treatment ... (and) their treatment (are) not straightforward”.⁵

Figure 2 illustrates a diffraction pattern taken from the outer part of a spherulite of PLLA grown well in the T_c domain in which α' PLLA is produced, here at 90 °C. Although the pattern appears to have clear hexagonal symmetry, it is actually a composite pattern made of three *hko* diffraction patterns of the stable α PLLA phase rotated by 60° or 120°. More interestingly,

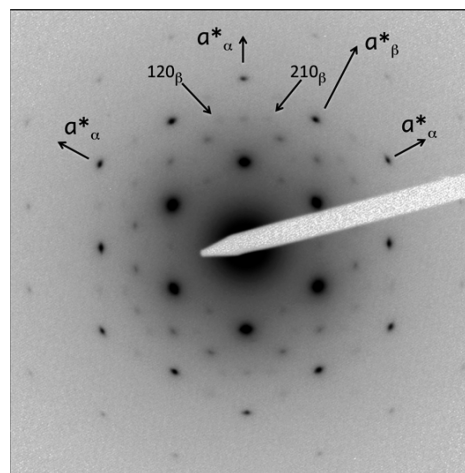


Figure 2. *hko* electron diffraction pattern of the edge of a PLLA spherulite grown in thin film at 90 °C.

this pattern displays, in addition, a set of weak reflections that are the 120 and 210 reflections of the frustrated β -phase (cf. SI#2).

The apparent simplicity of the pattern stems from the fact that in both β PLLA and α PLLA the chains pack on a hexagonal lattice in spite of their different unit-cell geometries (trigonal and orthorhombic) and helix symmetries (3_1 and 10_3). Moreover, the interstem distance is the same: 6.20 Å, which results in dense planes spaced 5.33 Å apart. In view of the different α PLLA and β PLLA unit-cell geometries, the six strongest reflections of the pattern are labeled 200/110 for α PLLA and 110 for β PLLA, respectively. Reflections specific to each phase do exist. For α PLLA, the most prominent ones are the 210 reflections (second ring in Figure 2, cf., SI#2). For β PLLA, only the 120 and 210 reflections are strong enough. Since their position differs from any of the α PLLA reflections, they help reveal the existence of this phase.

The composite diffraction pattern displayed in Figure 2 suggests at once that the α PLLA phase results from a crystal–crystal transformation of an initial β PLLA phase. Similar diffraction patterns have been recorded in all known crystal–crystal transformations. This inference stems from the azimuthal correlation of β PLLA and α PLLA lattices and the existence of three different orientations of α PLLA that reflect the symmetry of the initial β PLLA. The transformation is a very easy one: the (pseudo) hexagonal packing is maintained, and a perfect dimensional match does not require any shift of the stems. Only the helical conformation does change from 3_1 to 10_3 , with the rise per residue decreasing slightly, from 2.93 to 2.88 Å. Such a “mild” transformation appears to take place at 90 °C, shortly behind the growth front, since the β PLLA phase is not detected during crystal growth. It is definitely not a “retarded” transformation as in the case of iPBu1 that involves considerable lattice rearrangements (in chain axis projection, the lattice contracts by nearly 20%, in a highly nonsymmetrical way).¹¹

Recognition of α' PLLA as resulting from a solid-state phase transformation of an initial, transient β PLLA phase provides new insights into the molecular and crystallographic features of this phase. It also supports or helps precise earlier analyses of this phase. Several of these issues are briefly indicated here:

- Infrared investigations by S.-L. Hsu and co-workers had detected the presence of 3_1 helices in nominally

- α' PLLA.¹² The present crystallographic data confirm this earlier observation. At the same time, they indicate that these 3₁ helices are clustered in β PLLA “domains”.
- (b) The *c* axis shifts and structural up–down disorder in α' PLLA are a partial memory of the parent β PLLA phase crystallography. The *c* axis shifts between the three helices are mostly *c*/2 and *c*/3 in β PLLA, whereas the two helices in α' PLLA are related by the 2₁ symmetry. Moreover, the β PLLA unit-cell houses three chains, which does not allow for regular, crystallographic organization of the up–down orientation of stems required by chain folding. Conversion of β PLLA into α' PLLA thus yields by design a “disordered” α' PLLA phase with regard to the up–down helix orientation. The crystallographic cell symmetry of the resulting α' PLLA simply cannot be that of α PLLA. Regular, “crystallographic-symmetry compatible” up–down stem orientation can only be achieved for direct growth in the α' PLLA phase, at high *T_c*. This α' PLLA higher order translates in the well-known slightly smaller unit-cell parameters compared to α' PLLA (≈ 0.1 Å or $\approx -1.5\%$ in chain axis cross section).
- (c) The observation of three orientations 120° apart of the α' PLLA unit-cell in the α' PLLA “phase” points to the impact of an azimuthal disorder in this phase, in addition to the *c* axis shifts of domains mostly considered so far. The azimuthal disorder in turn suggests that the domains are related and limited by twin boundaries. These are most likely (110) twins, since (110) growth twins are frequently observed in solution grown single crystals. Triply (110) twinned α' PLLA crystals are triangular crystals, made of three domains only.¹³ Their *hko* diffraction pattern reproduces very precisely the α' PLLA pattern of Figure 2. For α' PLLA that results from a crystal–crystal transformation, the size of these domains may depend on the crystallization temperature and subsequent processing of the material. It could be down to the tens of nanometers range. In their analysis of an unoriented α' PLLA sample stretched and annealed at 100 °C (thus, that may not result solely from a crystal–crystal transformation), 100 Å size domains were used when modeling the α' PLLA fiber pattern.⁴
- (d) The observed anomalous increase of the lamellar thickness (or long period) for lower crystallization temperatures in the 120–90 °C range simply reflects the fact that they are governed by the metastable β PLLA crystallization process. These longer periods are due to the smaller undercooling of β PLLA at any *T_c* compared to α PLLA. They are maintained during the crystal–crystal transformation and are therefore a permanent β PLLA characteristic of the transformed α' PLLA structure.
- (e) The β PLLA– α' PLLA crystal–crystal transformation may well explain also the anomalous hump in the growth rates versus *T_c* in the 90–120 °C range. It must be stressed that the maximum growth rate deviation is only about twice the expected value for a smooth bell-shaped curve (≈ 8 μm/min rather than ≈ 4 μm/min). Several origins may be considered for this growth rate increase in connection with the present β PLLA– α' PLLA transformation process. If as is likely the transformation reaches the growth front, the substrate growth face has an “unnatural”, larger lamellar thickness than for normal

α PLLA growth in the critical temperature range. Also, the radial growth direction is different in the β PLLA and α PLLA spherulites: in both cases it is a* but corresponding to different lattice orientations. This would provide a means to differentiate the two growth mechanisms by the radial orientation of the diffraction pattern. Finally, twin planes or multiple twin planes linked with the transformation that impinge on the growth front may alter the growth rates. Significant increases in growth rate are documented in such cases. For solution grown polyethylene single crystals, growth rates along the (110) twin plane may be over three times larger than along a.¹⁴ [Note, however, that similar growth rate increases have not yet been reported for the structurally similar α PLLA (orthorhombic cell but near hexagonal chain packing).] The enhanced secondary nucleation at such twin boundaries emerging on the growth face could be analyzed as, or confused with, a regime II to III growth transition, but would have a very different structural origin that is linked with the transformation process.

In conclusion, traces of a chlorinated solvent make it possible to obtain the frustrated crystal structure of PLLA, β PLLA, whereas this phase was obtained so far only by mechanically stretching films of PLLA. Characteristic reflections of this β PLLA phase have been observed in the diffraction pattern of PLLA spherulites crystallized in the temperature range where they are known to be in the so-called α' PLLA (or δ PLLA), a disordered variant of the stable α PLLA. The diffraction evidence (*hko* diffraction patterns with one β PLLA and three α' PLLA unit-cell orientations) indicates that α' PLLA results from a crystal–crystal transformation from a parent, but very transient β PLLA phase. Such a solid-state transformation explains many of the “anomalous” characteristics of α' PLLA: its disordered structure, its uncommon lamellar thickness variation, and possibly also its original growth rate variations with *T_c*.

■ ASSOCIATED CONTENT

📄 Supporting Information

(1) Additional experimental details; (2) Build-up of the diffraction patterns shown in Figures 1 and 2. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00205.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

- (1) Wasanasuk, K.; Tashiro, K. *Macromolecules* **2011**, *44*, 9650–9660.
- (2) Puiggali, J.; Ikada, Y.; Tsuji, H.; Cartier, L.; Okihara, T.; Lotz, B. *Polymer* **2000**, *41*, 8921–8930.
- (3) Cartier, L.; Okihara, T.; Ikada, Y.; Tsuji, H.; Puiggali, J.; Lotz, B. *Polymer* **2000**, *41*, 8909–8919.
- (4) Wasanasuk, K.; Tashiro, K. *Polymer* **2011**, *52*, 6097–6109.
- (5) Di Lorenzo, M. L. *Eur. Polym. J.* **2005**, *41*, 569–575.
- (6) Zhang, J.; Tashiro, K.; Domb, A. J.; Tsuji, H. *Macromol. Symp.* **2006**, *242*, 274–278. Cho, T.-Y.; Strobl, G. *Polymer* **2006**, *47*, 1036–1043. Kawai, T.; Rahman, N.; Go, M.; Nishida, K.; Kanaya, T.;

Nakano, M.; Okamoto, H.; Kawada, J.; Usuki, A.; Honma, N.; Nakajima, K.; Matsuda, M. *Macromolecules* **2007**, *40*, 9463–9469.

(7) Dorset, D. L.; McCourt, M. P.; Kopp, S.; Wittmann, J. C.; Lotz, B. *Acta Crystallogr.* **1994**, *B50*, 201–208.

(8) Lotz, B. *Macromolecules* **2012**, *45*, 2175–2189.

(9) Lotz, B.; Thierry, A. *Macromolecules* **2003**, *36*, 286–290.

(10) Charlet, G.; Delams, G.; Revol, F.-F.; St John Manley, R. *Polymer* **1984**, *25*, 1613. Charlet, G.; Delmas, G. *Polymer* **1984**, *25*, 1619.

(11) Kopp, S.; Wittmann, J. C.; Lotz, B. *J. Mater. Sci.* **1994**, *29*, 6159–6166. Tosaka, M.; Kamijo, T.; Tsuji, M.; Kohjiya, S.; Ogawa, T.; Isoda, S.; Kobayashi, T. *Macromolecules* **2000**, *33*, 9666–9672.

(12) Aou, K.; Kang, S.; Hsu, S. L. *Macromolecules* **2005**, *38*, 7730.

(13) Cartier, L.; Okihara, T.; Lotz, B. *Macromolecules* **1997**, *30*, 6313–6322.

(14) Wittmann, J. C.; Kovacs, A. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 901. Lotz, B.; Wittmann, J. C. In *Materials Science and Technology, Structure and Properties of Polymers*; Cahn, R. W., Haasen, P., Kramer, E. J., Eds.; VCH: Weinheim, Germany, 1993; Vol. 12, Ch. 3, pp 79–151.