Single crystals of the frustrated β phase and genesis of the disordered α' phase of poly(L-lactic acid)

Bernard A. Lotz (bernard.lotz@ics-cnrs.unistra.fr)

Institut Charles Sadron (CNRS and Université de Strasbourg) 23, Rue du Loess, BP 84047, 67034 Strasbourg Cedex 2 (France)

Supplementary information.

Supplementary information 1: Experimental

Samples. Crystallographic features at the unit-cell level are investigated. A such, the molecular characteristics (Mw, polymolecularity, possible presence of a small fraction of D residues) should not be of major importance. These factors will be checked in future work. Relatively old PLLA samples provided by Pr. Y. Ikada and Pr. H. Tsuji, with a range of (initial) molecular weights ranging from 7K to 3.4×10^5 have been mostly used. These samples were used in earlier investigations in this laboratory, and their Mw may have decreased on aging (but has not been rechecked). A commercial PLLA (Biomer L 9000, Krailling, Germany) was provided by my colleague Pr. Luc Avérous, ECPM Strasbourg, with the following molecular characteristics: Mn=109 KDa, Polymolecularity 2.75, D-lactide content: ≈8%

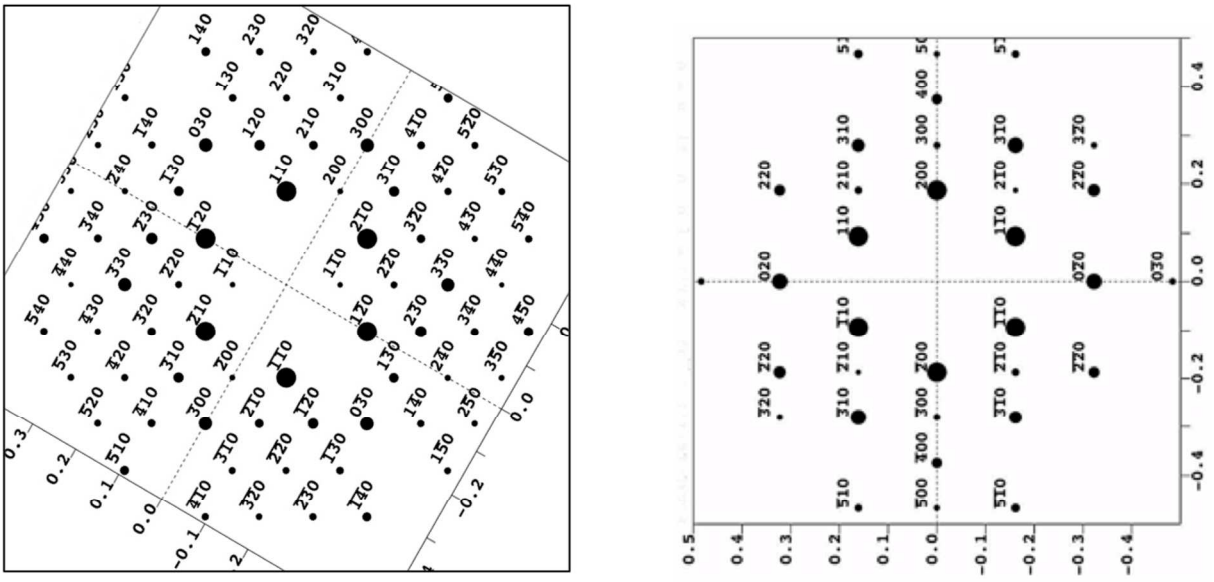
Crystal growth. The single crystals and spherulites are produced in polymer films of various thicknesses cast on a mica or glass cover slide from dilute solutions in *p*-xylene or dichlorobenzene. The films are melted at 180 °C under nitrogen atmosphere, and cooled to the desired crystallization temperatures at 50°C/min. In the early stages of the investigation, exploratory experiments are performed under less well controlled experimental protocols. Films with non-uniform thickness (as opposed to spin-coating) may help reveal unexpected features in samples thinner or thicker than the nominal thickness. Also, using a Kofler bench makes it possible to create very rapid temperature jumps and to cover a range of crystallization conditions in a single experiment, by taking advantage of the temperature gradient.

Investigation techniques. The films are backed with a carbon film, floated off on water with the help of a polyacrylic acid backing, deposited on a copper grid and examined in a Philips CM12 electron microscope. Given the beam-sensitivity of the material, the instrument is operated in the "TEM Low Dose" mode and exploration (scanning) of the morphology is made with the defocused diffraction pattern.

Modeling and analysis of the crystal structures.

Molecular modeling and calculation of the diffraction patterns is performed on a Silicon Graphics Octane workstation, using the Cerius[2] software (Accelrys Inc.)

Supplementary information 2: Analysis of the diffraction patterns.



(a) (b)

Figure S1. Calculated *hk*0 diffraction patterns of (a) the trigonal, frustrated β phase and (b) the orthorhombic α crystal phase of PLLA.

The two diffraction patterns are shown at the same scale. Their uncommon orientation illustrated here corresponds to that adopted in Figures 1 and 2 that is easier to "read".
In Figure S1(a), the reflections that best define frustration (or more precisely the three-chains unit-cell) are the 120 and 210 reflections located between the 030 and 300 reflections. These reflections are arrowed in Figure 1. They can also be seen in Figure 2. In addition, Figure 2 displays the diffraction pattern of the alpha phase (Figure S1(b), but repeated three times, with 60° rotations. The strongest reflections specific to this phase are indexed 210. Due to the quasi-exact hexagonal packing of helices in the alpha phase and the identity of inter-helix spacings in alpha and beta phases, many reflections are superposed and do not help discriminate the different structures/orientations. However, the existence of the composite diffraction pattern and the clear orientational relationship between the mother β phase and the (here three) different daughter α crystal phases is a characteristic systematically found in crystal-crystal transformations.