ESRF

Experiment title: Reconstruction of 3D lamellar shape using a combination of micro-focus X-ray diffraction and a tilting stage.	Experiment number: MA-1041

Beamline: BM26B	Date of experiment: from: 01/07/2010 to: 05/07/2010	Date of report: 15/07/2011
Shifts: 12	Local contact(s): Giuseppe Portale	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

M. Rosenthal*, D. V. Anokhin*, Yaroslav Odarchenko*, D.A. Ivanov,

Institut de Science de Matériaux de Mulhouse, CNRS UPR9069, 15, rue Jean Starcky, 68057 Mulhouse CEDEX, France.

Report:

It is generally believed that the polymer crystalline lamella in banded spherulites adopts the shape of the classical helicoid. However, there exist no trivial reasons why they have to do it. It is noteworthy that in the classical helicoid the cross-section profiles in the planes perpendicular to the main axis are straight. Rather, it can be well assumed that other types of cross-section profiles exist, such as S- or C-shapes reported for the case of PE [2] or for poly(trimethylene terephthalate), PTT [3], being of particular importance for the present study. A surface with an S-shaped profile can be constructed for instance by a screw-axis operation on two adjacent arcs. It is clear that the convexity of the S-shape profile directly affects the fiber-angle width of the reflections. Thus, with more and more convex S-profiles, the equatorial reflections will be more often in the reflection conditions. For the limiting case of an S-shape consisting of two adjacent semi-circles, all reflections will be observed permanently. As outlined by *Keith* and *Padden* [4] for the case of PE, there are two possibilities of how the crystalline stems can be arranged in the S- or C-shaped lamellar crystals (cf. Figure 1 (2) and (3)). For the case depicted in Figure 1 (2), the molecular orientation is uniform all the way across the lamellar cross-section, which exhibits curvature toward the lateral outer edges. Thus, the direction of the **c**-axis is invariable everywhere. Since all constitutive unit cells are organized in a strictly parallel way, the equatorial crystallographic reflections won't broaden in the fiber-angle direction. Obviously, the cross-sectional shape with parallel crystalline stems is indistinguishable from a plain flat lamellar ribbon by means of micro-focus diffraction alone, as the diffraction patterns can basically reveal only pointlike reflections having natural width, as it is the case of single crystal diffraction (cf. Figure 1, right). In contrast, for another type of the curved lamellar shape where the crystalline stems keep the same local tilt angle to the lamella normal (cf. Figure 1 (3)), the equatorial diffraction peaks broaden along φ.

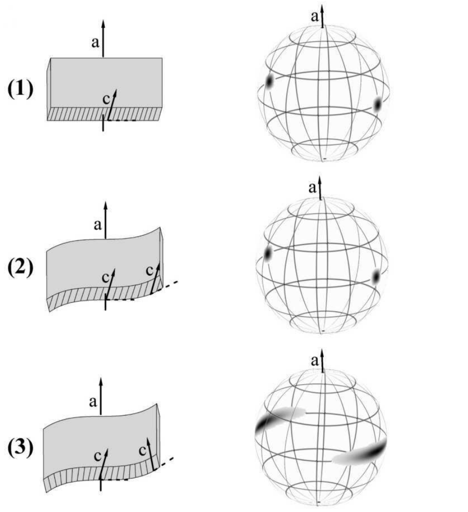

Figure 1. Schematic drawing of twisted lamellar crystals with the corresponding pole figures drawn for an arbitrary equatorial, i.e. 0kl, reflection. The **c**-vector coincides with the crystalline stem orientation. (1) Undeformed lamellar crystal is given for the sake of comparison. (2) Lamella with a curved cross-section in which the crystalline stem directions are all parallel, as described by *Bassett* and *Hodge* [1]. (3) Elastically-bent lamella in which the local tilt angle of the crystalline stems is invariable due to the molecular shearing. This results in varying orientation of the **c**-vector along the lamella cross-section [4].

The experimental data on the fiber-angle broadening of the 010 peak for the meltcrystallized PTT spherulites are shown in Figure 2 (left). After normalization of the maximum integral intensity to unity, it can be seen that the half width of the peaks exceeds 45 deg. Therefore it can be conjectured that the real lamella shape is closer to an S-shaped helicoid than to the classical helicoid with a straight section for the width of the peak is by far larger than its natural width (cf. Figure 2, left, and Figure 1).

Interestingly, there are no significant differences in the peak width with crystallization temperature, whereas the band spacing varies quite significantly. This leads to the assumption that the shape of the helicoid's cross-section is invariant with crystallization temperature. Furthermore, the width of the lamella relative to the band spacing should be also constant in this case. The temperature evolution of the lamellar shape can thus be viewed as a homothetic transformation proportional to the band spacing. The particular shape of the "S" can be conjectured since the shape of the fiber angle broadening corresponds to the histogram of the orientation variation of the stems. The modeling of a real experiment will require another modification to be added. One should take into account possible azimuthal broadening of the reflections which is not directly related to the helicoidal shape. Such broadening can originate, for instance, from non-perfect alignment of the twisting axes or a de-phasing of the twisted ribbons.

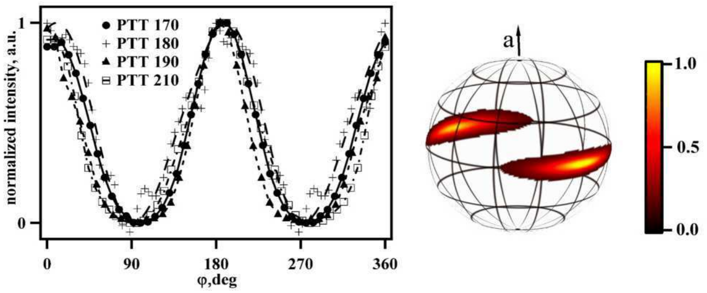

Figure 2. Normalized integral intensity of the 010 refection as a function of the fiber angle φ for different crystallization temperatures of PTT indicated on the graph (left). The curves reveal virtually no variation of the fiber-angle broadening with crystallization temperature. Pole figure corresponding to the 010 reflection (right).

The cross-sectional shape was modeled starting with infinite radius applied to the half width of the ribbon. The results of the simulation are given for three differnt ratios of the lamellar with vs. pitch for a circular S-shape in Figure 3 (bottom). The fiber-angle distribution broadens with increasing the strength of the S-shape, which is in-line with the qualitative consideration given above.The peak broadening observed in the experiment was modeled by simulation using a circular segment S-shaped lamellar helicoid. The parameter describing the circular lamellar deformation is the quotient of the circular radius normalized by the lateral half width of the lamellar ribbon. However, at sufficient approximation the exact profile of the distribution derived from the experiment, as shown in Figure 3 (top), has not been reached with the circular S-shape. The reasons for this could be for example that the exact profile of the S-shape is much more complicated than a circle. A mechanical model taking into account the bending moments of the ribbon due to its finite thickness leads to the bending line dscribed by higher order polynomials. Another reason could be underestimation of the growth axis miss-orientation and other factors leading to convolution effects not accounted for by the model.

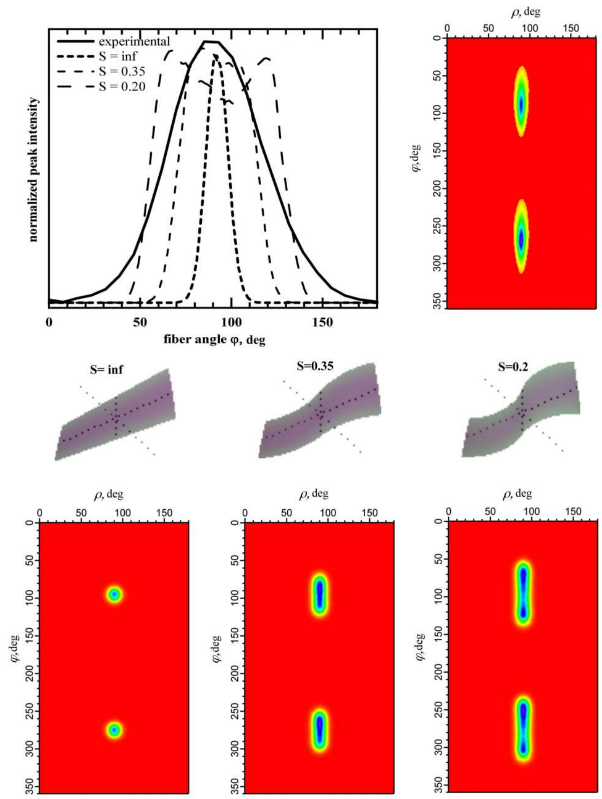

Figure 3. Comparison of the simulated and experimental peak broadening. (Top left) The fiber-angle profile of the equatorial 010 reflection for the experiment (solid) and simulation (dashed). (Top right) Experimental 2D-profile of the 010 reflection. (Middle row) Cartoons of the lamellae with different S-shape parameter indicated above the diagrams and the corresponding 2D plots (bottom row) of the simulated 010 reflection intensity.

Conclusions

It was shown that the cross-sectional profile of the PTT twisted lamellae is not a simple straight section but likely to have a more complicated S-shaped profile. Furthermore, the fiber-angle profile of the equatorial reflections was shown to be invariant of the crystallization temperature indicating that the width of the lamellar ribbon increases homothetically with the band spacing.

References

1 Bassed D.C., Hodge A. M., 1978 Polymer, 19, 469.
2 Bassett D.C., Olley R.H., 1984 Polymer 25, 935.
3 Ikehara T., et al., 2007 J. Pol. Sci. B Pol. Phys., 45, 1122.
4 Keith H.D., Padden Jr. F.J., 1984 Polymer 25, 28.