Melting and Crystallization of Differently Oriented Sets of Crystallites in Polypropylene

N. Stribeck[1], *U. Nöchel*[1], *S. S. Funari*[2]

[1]*Inst. TMC, Dept. of Chemistry, University of Hamburg, 20146 Hamburg, Germany*
[2]*HASYLAB at DESY, 22603 Hamburg, Germany*

Experimental Setup. Wide-angle X-ray scattering is performed in the synchrotron beamline A2 at HASYLAB, Hamburg, Germany. The wavelength of the X-ray beam is 0.15 nm, and the sample-detector distance is 79 mm. Scattering patterns are collected by a two-dimensional position sensitive marccd 165 detector (mar research, Norderstedt, Germany) in binned 1024 × 1024 pixel mode (158.3 µm quadratic pixel size). During the experiments series of scattering patterns are recorded. The cycle-time is 8 s (4 s exposure).

Summary of Scientific Results. Uniaxially oriented polypropylene (PP) is molten and crystallized isothermally from the oriented, quiescent melt. Nucleation and growth of differently oriented sets of crystallites (*c*-set and a^*-set) appear decoupled. After shallow quench crystallization is preceded by (spinodal) decomposition. Evolution is monitored by wide-angle X-ray scattering (WAXS) and compared to results of a SAXS study. Peak integrals (crystallinity) and minimum crystallite size are tracked. In the commercial starting material a^*-set crystallites melt at 158°C. The *c*-set melts at 170°C furnace temperature. After recrystallization both sets melt at 170°C. Isothermal crystallization is divided in two distinct phases. During nucleation the crystallinity stays low. The second phase is dominated by crystallinity growth. At 150°C the *c*-set is seeded first. At 145°C and 140°C a^*-oriented crystallites are the first. The first-seeded set starts to grow first. *c*-set crystallinity is always growing faster than a^*-set crystallinity. The evolution of the SAXS cross-diagram in the growth phase can both be explained by lamellae growing at right angles, and by block merging [1].

New Method: Direct Mapping of Fiber Patterns into Reciprocal Space. The abovementioned scientific results have required the development of an automated data evaluation method for fiber patterns that is suitable for studies in the materials science of soft condensed matter [2]. The development has started from the unexpected finding that the relation [3] used in crystallography to estimate the fiber tilt angle is wrong. The correct equation is readily established [4] after resorting to the geometrical design of fiber diffraction devised by Polanyi [5] (cf. Fig.). Crystallography survives because it refines the mapping parameters manually. With the correct equation we can now construct an automated fiber mapping procedure that is sufficiently accurate for the materials scientist [2]. The automated method tracks the fiber tilt angle during thermal treatment of the fiber (Fig. 2) and maps the recorded pattern into reciprocal space. Now the interesting reflections are always found at the same position where they are readily isolated and automatically evaluated in 3D reciprocal space.

Conclusion. This method permits to automatically evaluate extended series of fiber patterns that are recorded, e.g., in melting and crystallization studies of soft matter. We expect that it will become very useful for the management of extensive data series that will be recorded with high time resolution at PETRA III beamlines.

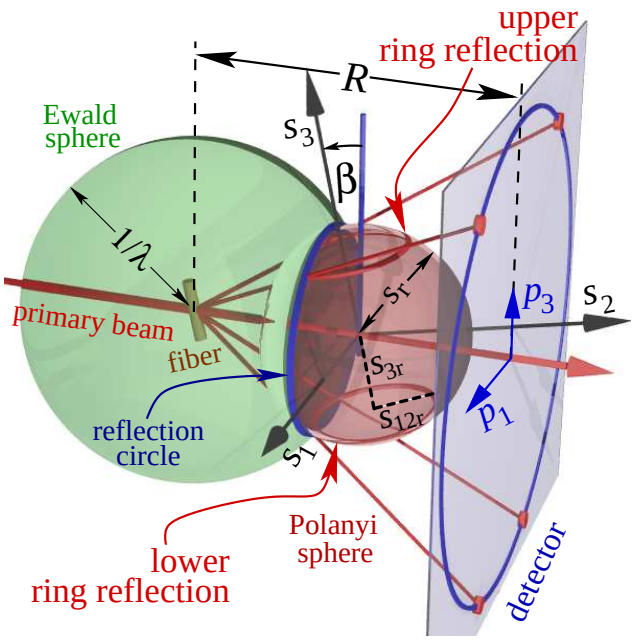

Figure 1: Sketch of fiber diffraction geometry with Ewald sphere and a Polanyi sphere. The intersection is a circle ("reflection circle") that does not even change as the fiber is tilted (tilt angle β). The radius of the Polanyi sphere is chosen to match the magnitude s_r of a model ideal reflection manifested in two rings $(s_{12r}, \pm s_{3r})$. The trihedron (s_1, s_2, s_3) is indicating reciprocal space. R is the distance between fiber and detector. (p_1, p_3) indicates the detector coordinate system

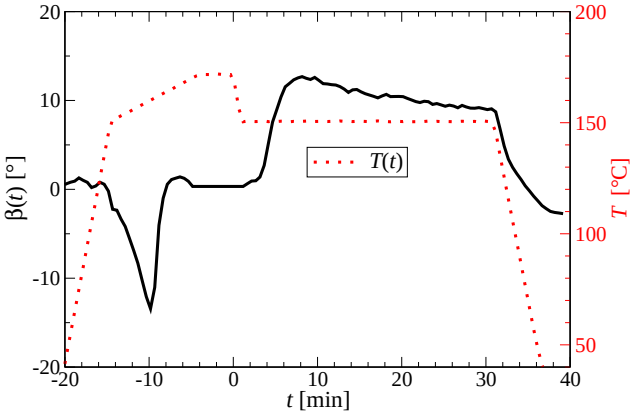

Figure 2: Tilt-angle tracking curve $\beta(t, T)$ from the automatic fiber-mapping procedure in an experiment with long exposure of the patterns (20 s), in which β is changing considerably (HEPP; melt-annealing at 171°C and recrystallization at 150°C)

References

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