The crystallization of polymers in physically confined environments is a topic of increasing interest because of the required basic understanding of polymer crystallization in nanotechnological applications [1]. Preceding small and wide angle X-ray scattering (SAXS and WAXS) studies have reported the influence of confinement below the μm scale on the crystallization of PET in PET/PC multilayers [2, 3] and on the structure of polypropylene crystallized in confined PP/PS and PP/PA nanolayers [4, 5]. Both systems were prepared by continuous layer-multiplying coextrusion.

This work focuses on the confinement effects and their thermal stability in nanolayered films produced by the above method. To this goal an experimental program involving WAXS and SAXS experiments was designed aiming at the orientation, arrangement and structure of the lamellar crystals as a function of the composition, the film thickness and the layer thickness. Selected samples with PP/PA volume ratios of 70/30, 50/50 and 10/90 and with layer-thicknesses of the PP layers ranging from 40 nm to 1670 nm and the PA layers ranging from 120 nm to 1190 nm, were investigated.

Wide- (WAXS) and small-angle (SAXS) experiments were performed separately in the Soft Condensed Matter Beam Line A2 at HASYLAB (DESY, Hamburg) using a two-dimensional MAR CCD detector. Polymer films were placed with their surfaces parallel and also perpendicular to the X-ray beam. Samples of the control materials (isotactic PP, PA6) were also investigated for comparison.

For the samples placed with their surfaces perpendicular to the X-ray beam, isotropic rings are found in the WAXS pattern. However, if observed parallel to the X-ray beam, a very strong orientation of the lamellar crystals is found. The small thickness of the investigated films requires...
to stack several films in order to increase the scattering volume. It would be of particular interest that the respective orientations of the two constituent crystallisable polymers could well be identified.

In Fig. 1 WAXS diffraction patterns of samples with PP/PA concentrations of 70/30 recorded in parallel to the beam and the coextrusion direction are shown. It can be seen that with reduction of the layer thickness the crystalline reflections become sharper pointing at important effects of the confinement on the lamellar orientation.

For very thin layers of PP as found in samples with concentration ratio 10/90 for instance (Fig. 2a), where the PP layer thickness is in the order of 40 nm, no complete suppression of crystallization is observed. Annealing experiments from RT up to 194°C and back to RT were performed in selected multilayered PP/PA samples. Surprisingly the effect of confinement on the orientation, shown on a 1-D pattern, is preserved after recrystallisation indicating that the layer structure is relatively stable upon melting and recrystallization of the polypropylene layers (Fig. 2b).

Figure 2: (a) WAXS patterns of PP/PA 10/90 nanolayered films with 25.4 µm film-thickness and 40 nm PP layer-thickness. (b) integrated intensity before, during (194°C) and after heat treatment and recrystallization.

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