Investigation of chain orientation in thin polymer layers by means of grazing incidence X-ray diffraction (GIXD)

A. Meyer, H.G. Zachmann
Instiut für Technische und Makromolekulare Chemie, Universität Hamburg

There exist different chain orientations in thin PEO-films at different distances to the surface as it is revealed by the GIXD measurements at the microfocus beamline BL1/ID13. These measurements were performed at various incident angles Θ_i = 0.05° -0.18° which are well below the critical angle Θ_c = 0.20°. The penetration depth of the evanescent wave which runs parallel to the surface was in a range of 2 -6 nm. The evanescent wave was used to obtain information on the crystallization behaviour dependent on different depth regions of the film. In Fig. 1 one can clearly recognize the crystal reflections. It shows the results obtained under different incidence angles from the same film. The thickness of the film is 66.1 nm. The orientation of the chains changes drastically the the penetration depth of the synchrotrons beam. While the chains are more or less unoriented at the surface, the deeper zones are highly oriented and the chains are lying parallel to the surface and the b axis of the monoclinic lattice perpendicular to the surface. By means of polarizing and interference microscopy it was shown that two dimensional spherulites were formed.

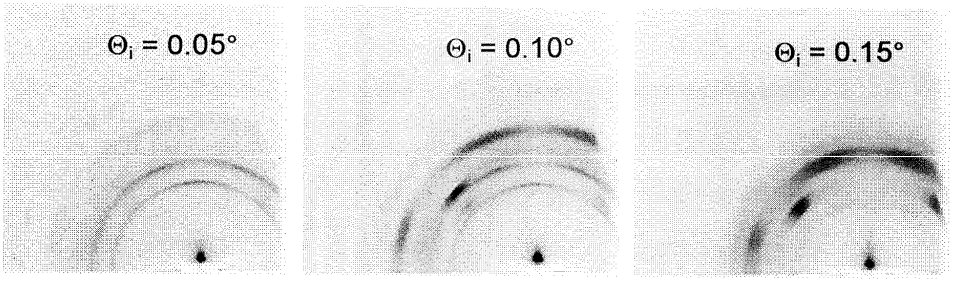

Fig. 1: Different orientations depending on the penetration depth for the same PEO-film

In order to study the influence of the film thickness another experiment was performed using three different concentrations and the same spinning rate (3000 rpm). The scattering was detected by means of a two-dimensional detector. Fig.2 shows the results. As one can see, the change in concentration results in different orientations. In the sample with a thickness of 70 nm (1.5 wt%) again a spherulitic structure is obtained, while in the sample with a thickness of 15 nm the chains are oriented radially symmetric in the plane and the b axis parallel to the

sample surface. The film with a thickness of 40 nm shows an intermediate structure .

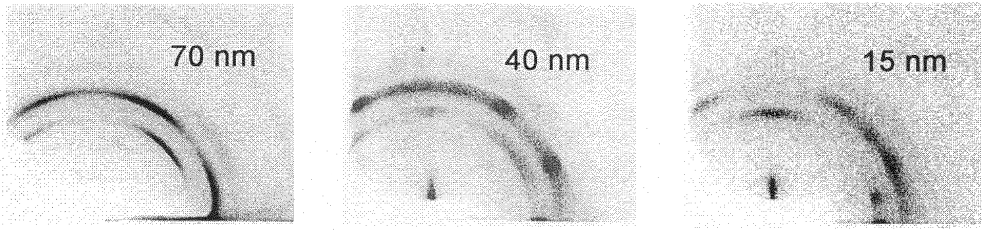

Fig.2: Influence of the film thickness on the orientation in PEO

From this results it is clearly evident that the crystallization behaviour of thin polymer films is different compared to the bulk material. More systematic investigations are necessary to understand the crystallisation process. Furthermore, some pre-investigations of films of PET, PEN and PVDF were performed and show comparable results.