Melting and Recrystallisation of Oriented PVDF Studied by USAXS

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Synopsis. In our screening study on crystallisation mechanisms of oriented polymer materials we have successfully studied an oriented poly(vinylidene fluoride) (PVDF) material during temperature treatment at beamline BW4. Highly oriented scattering patterns are observed (Fig. 1). After heating to a temperature slightly above the melting point the USAXS pattern is completely erased, but the melt is conserving orientation memory. Thus oriented crystallisation is observed when the temperature is reduced, and the mechanisms of lamellae formation, growth and arrangement can be studied in real time. Quantitative image data evaluation by means of the multidimensional chord distribution function analysis[1] is in progress.

Experimental. Highly oriented strips of PVDF (SOLEF 6010/0001, (Solvay Inc., France)) of 2 mm thickness were prepared by channel-die extrusion. The material was wrapped in aluminium foil and studied in the standard furnace of beamline BW4. Sample-to-detector distance was 13195 mm, exposure 60 s and cycle time 70 s. A two-dimensional mar-CCD detector was used for data collection with the resolution set to 2048 × 2048 pixels in multi-read modus. Ionisation chambers were placed directly before and after the sample in order to obtain exact data for the computation of the absorption coefficient and thus for the correction of the machine background. Machine background was measured with two layers of aluminium foil in the sample holder.

In order to preserve the high uniaxial orientation, the samples were slowly melted to the optimum melt annealing temperature (175°C). Then they were crystallised non-isothermally (cooling rate: 1 °C/min) and isothermally at different temperatures for 20 min. Thereafter the isothermally crystallised samples were quenched (20°C/min) to room temperature.

First results. At 175°C the nanostructure has completely melted (Fig. 1). In the beginning of every isothermal crystallisation experiment we observe evolution of a meridional streak related to thick and oriented lamellae with a broad thickness distribution which are uncorrelated. This is similar to the observations with polyethylene[2], and is best described by a random car-parking process[3, 4, 5]. The length of the streak is growing during the isothermal period showing that the late crystals are thinner than the early ones. A “peak maximum” is only observed at the end of the isothermal phase at high scattering angle. This shows that only the late crystals are not placed at random, but are growing in the centre of a gap between already existing lamellae. At low isothermal crystallisation temperature the long period distribution is broader than at high isothermal crystallisation temperature. During quenching and in the course of non-isothermal crystallisation the long period peak is constantly moving outward on the meridian.

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1This was the maximum exposure that was possible without overloading the detector when set at high resolution. At low resolution the maximum exposure for our PVDF is 15 s.
Figure 1: The evolution of the USAXS patterns of a SOLEF PVDF (Polyvinylidene fluoride) during its melting and isothermal crystallisation at different temperatures, as well as during its non-isothermal crystallisation.

References