In–situ USAXS study of oriented polyethylene crystallization

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Abstract. A series of USAXS experiments at beamline BW4 demonstrates that oriented crystallization from a pre–oriented polyethylene (PE) melt results in the same nanostructure as does the isotropic crystallization from a melt without memory. When the material is crystallized with perfect orientation, information on the lateral extension of the lamellae in longitudinal and in transverse direction are obtained. The in–situ data show that the final USAXS diagram with fan–shaped reflections is not related to an orientation distribution of lamellar stacks, but to a correlation between lateral extension and long period (layer thickness). In the beginning thick and extended crystallites with high long periods are formed, and during the course of crystallization the perfection and the long periods are decreasing.

Experimental. USAXS was performed at HASYLAB, BW4. 2D SAXS images were collected by a two-dimensional Gabriel detector. The sample–to–detector distance was 13 m. In order to record data with a sufficient S/N-ratio samples of 3 mm thickness were exposed for 117 s. Detector read–out and data storage took 2.7 s. Thus we recorded one scattering pattern every two minutes. Data were corrected for detector efficiency, incident flux, sample absorption and empty scattering using the data from two ionization chambers.

Results and Discussion. Some of the recorded USAXS patterns are shown in Figure 1. The original injection–moulded rod shows a distinct long period reflection on a pronounced ridge that is extending from top to bottom along the meridian. At 140 $^\circ C$ this structure is completely extinguished, but, anticipating the results of the following experiment, we assume that ”shishs” from highly oriented, extended chains are still present.

During non–isothermal crystallization we observe, first, the formation of extended lamellae with a high long period. At 121 $^\circ C$ the long period streak has grown outward on the meridian, demonstrating the formation of lamellae that are more closely packed. Thereafter (117 $^\circ C$ and lower) the reflection is broadening, predominantly in its outer part. This demonstrates the formation of less extended lamellae with low long periods.

It is worth to notice that, by choosing intermediate melting temperatures, we can observe both isotropic crystallization and perfectly oriented lamellae at the same time (cf. 5th row). This demonstrates that (1) the shishs melt before they have a chance to loose orientation, (2) if the shishs are molten in a specific region of the sample, there is no more oriented crystallization, and (3) the isotropic fraction shows the same crystallization kinetics (scattering intensity distribution) as does the highly oriented fraction of the material. Thus the oriented crystallization is representative even for isotropic material.

In addition we have performed isothermal crystallization experiments that are not demonstrated in this report. Quantitative data evaluation of the nanostructure using the 2D–CDF method has been performed. The initiation of crystallization could not be studied because of the limiting old-fashioned detector (slow, low dynamics).

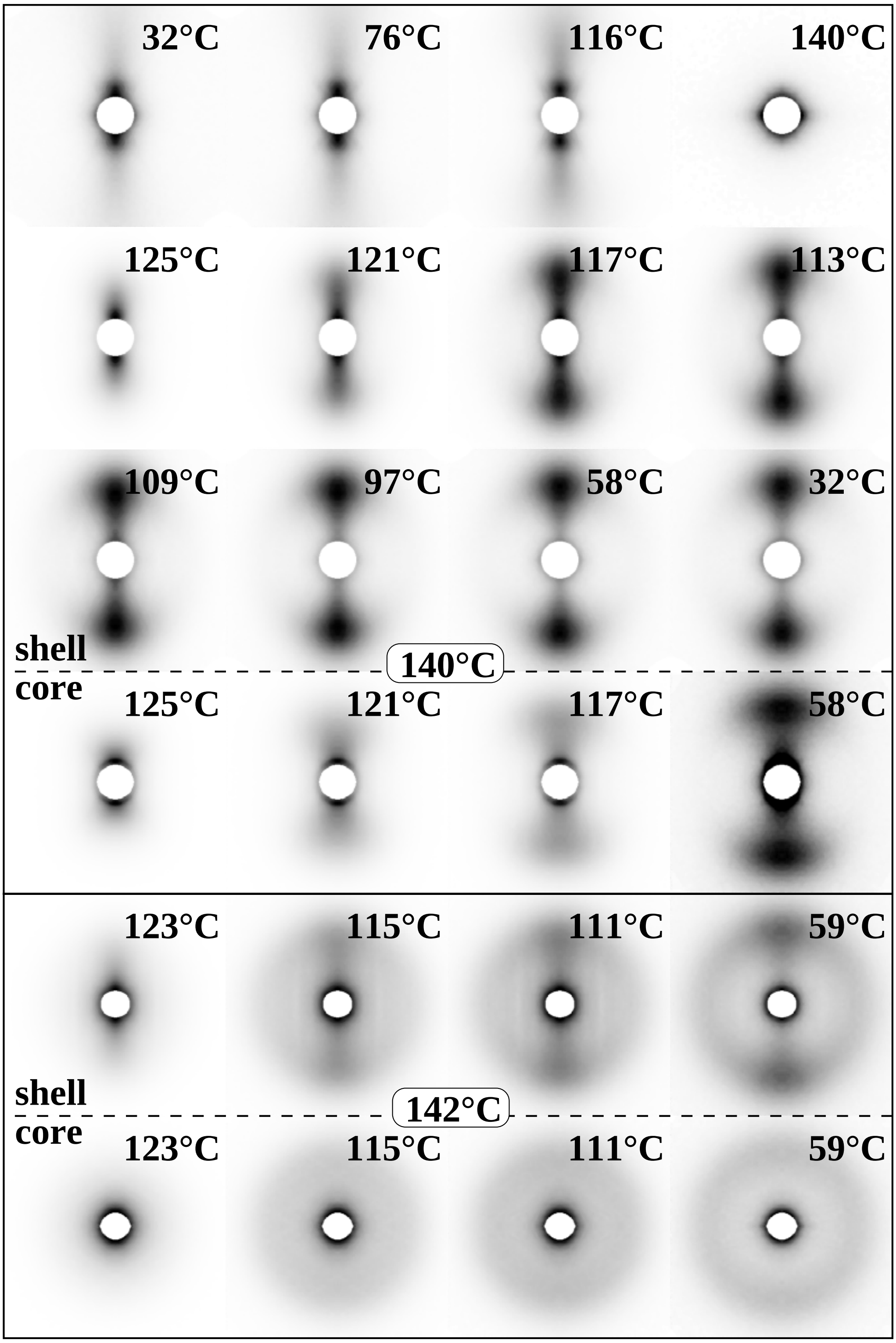

Figure 1: SAXS of the non–isothermal, oriented crystallization experiment (top row: data taken during melting of the oriented PE rods). Both specimens from the shell and the core of the rods are studied. Each pattern shows the interval $|s_{12}|, |s_3| \le 0.04$ nm^{-1}. The four top rows demonstrate data with a melting temperature of 140 $°C$. For the two bottom rows the melting temperature was 142 $°C$. Any kind of sample molten to 150 $°C$ is crystallizing isotropically. Heating and cooling rates: 2 $°C$/min.