Electric field induced structural fluctuations in ordered, lamellar block copolymers: First results from TOF-Measurements on AMOR/SINQ

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We studied the effects of a weak electric field on a layered, lamellar block copolymer micorphase structure. Using the time-of-flight (TOF) mode on the AMOR reflectometer we were able to measure the specular reflectivity as well as the diffuse scattering intensity over a large range of reciprocal space. The observed increase in the diffuse scattering intensity shows the existence of electric field induced deformations of the layered structure. These undulations are believed to play an important role for the phenomen of electric field induced orientation of block copolymer microdomains.

Lamellar microphase structures formed in a symmetric diblock copolymer can be oriented by an external electric field [1] [2]. While the mechanism of orientation is not yet well understood, it is believed that the electric field induces an instability connected with structural fluctuations or undulations leading eventually to a disruption of the original structure which then allows alignment to set in. In our experiments we investigated these undulations in films of different thicknesses with and without application of an electric field. The undulations cause diffuse scattering which can be mapped using the TOF-mode of the AMOR reflectometer. Our results show that the fluctuations always exist due to thermal excitation but can be strongly enhanced by application of an electric field. The film thickness was shown to be an important parameter.

For our experiments we used a partially deuterated diblock copolymer polystyrene-block-polymethylmethacrylate [P(dS-b-MMA)] with a symmetric volume fraction $f_{PS} = 0.5$, and a molecular weight $M_n = 75000\,\mathrm{g/mol}$. Without field in equilibrium the lamellar structure is aligned parallel to the substrate due to interfacial interactions. Electric fields with a strength of some V/μm were applied for several hours to induce deformations of the original structure. The samples were quenched by cooling below T_g and then measured ex-situ.

While for our first beam time we were using the monochromatic mode of the experiment, later on the time-of-flight mode became available, which turned out to be necessary for a mapping of the diffuse scattering intensity. Part of the beamtime was used to establish the correct instrumental setting for time-of-flight (TOF) measurements on our samples. Two reflectivity curves measured on the same sample but in the two different modes of the instrument are shown in Fig. 1.

Undulations in the lamellar structure correspond to a perturbation of the layers and lead therefore to an enhanced off specular scattering, which was measured by performing longitudinal diffuse scans, as illustrated in the inset of Fig. 1. In TOF-mode a whole scan can be measured simultaneously. We observed a shift in the peak position when the incident angle ω_0 is larger than the scattering angle $\theta = 1.0$, which we attribute to refraction effects. Some example curves are shown in Fig. 2. Here refraction effects were corrected and all curves have a common peak position at about 0.0204 Å^{-1}, corresponding to a lamellar period about 310 Å.

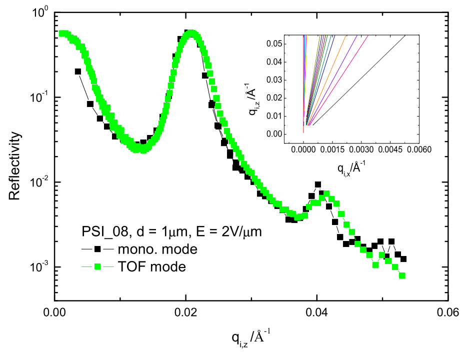
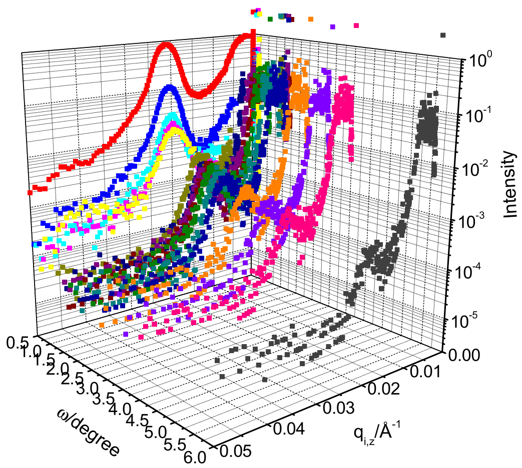
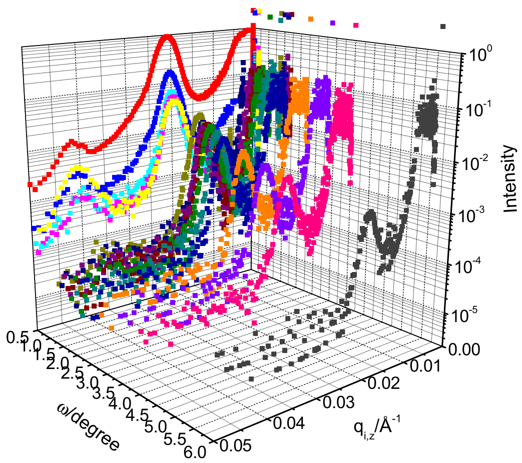


Figure 1: Specular reflectivity as a function of q_z (after correction for refraction effects) of sample PSI_08 obtained in monochromatic mode resp. time-of-flight (TOF) mode. The results are consistent, in TOF-mode the resolution can be largely varied by the setting of slits and pulse width. The inset illustrates schematically how specular and longitudinal diffuse scans probe the intensity in reciprocal space.

While some diffuse scattering is always present due to thermally excited structural fluctuations, the off specular intensity is clearly enhanced after application of an electric field as can be seen in Fig. 2b (see next page). We could also show that the diffuse scattering is also stronger in thick films than in thinner films. A more extended, systematic study which was not possible in the beam time allocated so far, is clearly necessary for a quantitative investigation of the effects shown here.



(a) PSI_05, $d = 1\,\mu$m, $E = 0\,$V / μm



(b) PSI_08, $d = 1\,\mu$m, $E = 2\,$V / μm

Figure 2: Effect of an electric field on the diffuse scattering intensity of a layered block copolymer film (PdS-b-MMA). The lines of different colors correspond to longitudinal diffuse scans taken at different angles of incicidence of the primary beam. The red line represents the specular reflectivity. The others are the longitudinal diffuse scattering as shown in the inset of Fig. 1. The diffuse intensity is caused by lateral perturbations in the layered structure caused by undulations, roughly on a micrometer length scale. The diffuse intensity visible in figure (a) is considerably enhanced after application of an electric field as shown in figure (b). The increase of the diffuse scattering intensity proves the existence of a deformation of the structure caused by the electric field induced fluctuations. (Both films have a thickness of 1m.)

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Work fully performed at SINQ
Proposal-number: I/01L-12
Instruments: AMOR