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Beamline: ID 2A	**Date of experiment**: from: 5.9.2001 to: 8.9.2001	**Date of report**: 16. August 2002
Shifts: 9	**Local contact(s)**: Volker Urban	*Received at ESRF:*

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Report:

The key to an understanding of the reorientation behavior of block copolymer microdomains in solution is the knowledge of the underlying microscopic mechanisms contributing to the rearrangement of domains. In contrast to the case of shear alignment of block copolymers, which has been studied by a variety of different experimental techniques like in-situ birefringence[1], in-situ small angle neutron scattering[2,3] and ex-situ small angle x-ray scattering (SAXS)[4-6], only little is known about the relevant microscopic processes playing a role during block copolymer alignment in the presence of an electric field.

In the following, we report on real-time SAXS experiments on concentrated block copolymer solutions aiming to study the kinetics of microdomain orientation in the presence of an electric field and to elucidate the underlying microscopic processes. Synchrotron SAXS combines the advantages of the above mentioned in-situ techniques (high time resolution of 0.1 sec) with the detailed information on the microscopic state of order, typical for a high quality scattering experiment. We identify two distinct microscopic mechanisms, each of which dominates the reorientation process in a certain regime of polymer concentration and temperature.

The polymer consists of 52 wt.-% polystyrene and 48 wt.-% polyisoprene with a total number average molecular weight M_n = 80000 g/mol and a polydispersity M_w/M_n = 1.02 (SI-80). The polymer was dissolved

in toluene with concentrations ranging between 30 and 80 wt.-%. The alignment experiments were performed in a home built capacitor with gold electrodes (electrode distance d = 2 mm) at temperatures between room temperature and 80 °C. A d.c. voltage of 2 kV was applied across the electrodes resulting in a homogeneous electric field pointing perpendicular to the direction of the X-ray beam.

If an electric field is applied across the two electrodes, the scattering pattern changes significantly. As can be seen from the snap shots taken at different times after switching on the d.c. voltage, the anisotropic pattern (lamellae parallel to the electrodes) first turns into an isotropic ring of weak intensity (Figure 1B, t = 6 s) before two distinct peaks are formed at around $\varphi = 90°$ and $\varphi = 270°$ (lamellae parallel to the electric field vector) at later times (Figure 1C, t = 34 s). The complete set of data is displayed in Figure 2A, where the intensity of the (100) peak is plotted as a function of φ for increasing time t. Clearly an almost complete destruction of the initial peaks is seen at early times followed by the built-up of new peaks at around $\varphi = 90°$ and $\varphi = 270°$, respectively.

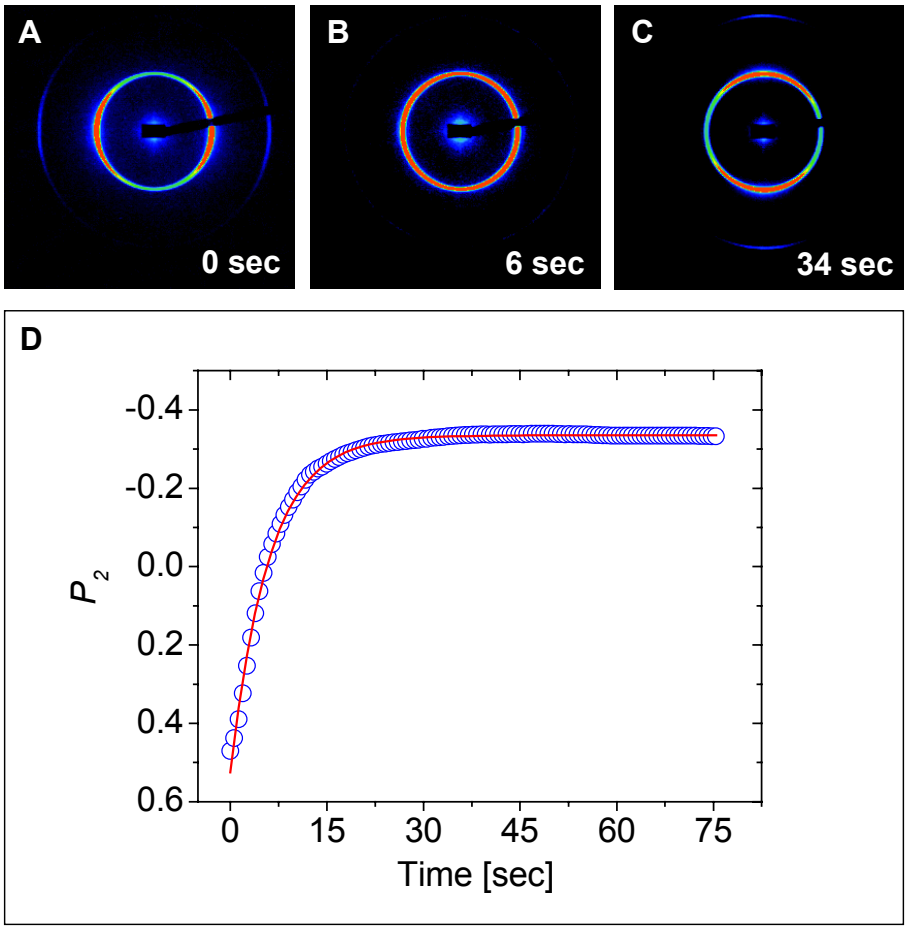

Figure 1: *(A-C) Two-dimensional SAXS patterns of a 35 wt.-% solution of the SI-80 diblock copolymer in toluene taken at room temperature prior (A) and after application of an electric field (E = 2 kV/2 mm) (B, C). (D) Time dependence of the orientational order parameter P_2. The solid line is a least-squares fit to the data according to single exponential decay with $P_{2,0}$ = 0.52, $P_{2,\infty}$ = -0.32, and τ = 5 sec.*

We note that a *qualitatively* different reorientation behavior is observed if the polymer concentration is significantly increased. This is shown in Figure 2B for a polymer solution with ϕ_{pol} = 50 wt.-%. In contrast to the situation described above, the initial scattering peaks are not destroyed as the electric field is applied,

however, they merely rotate from their original positions at $\varphi = 0°$ and $\varphi = 180°$ towards their final positions at $\varphi = 90°$ and $\varphi = 270°$, respectively. The peak intensities decrease slightly during the rotation process and eventually increase again after the final orientation has been reached. For intermediate concentrations (not shown here), a superposition of both behaviors is observed. Interestingly, we can retain the original mechanism, if we increase the temperature. This can be seen in Figure 2C and D, where the reorientation behavior of a sample with $\phi_{pol} = 47.5$ wt.-% is shown at two different temperatures. While a shift of the peaks dominates at lower temperatures ($T = 27$ °C, Figure 2C), at higher temperatures a destruction of the initial signals is followed by a build-up of two new peaks at well-defined positions around $\varphi = 90°$ and $\varphi = 270°$, respectively ($T = 80$ °C, Figure 2D). Again, at intermediate temperatures both behaviors coexist.

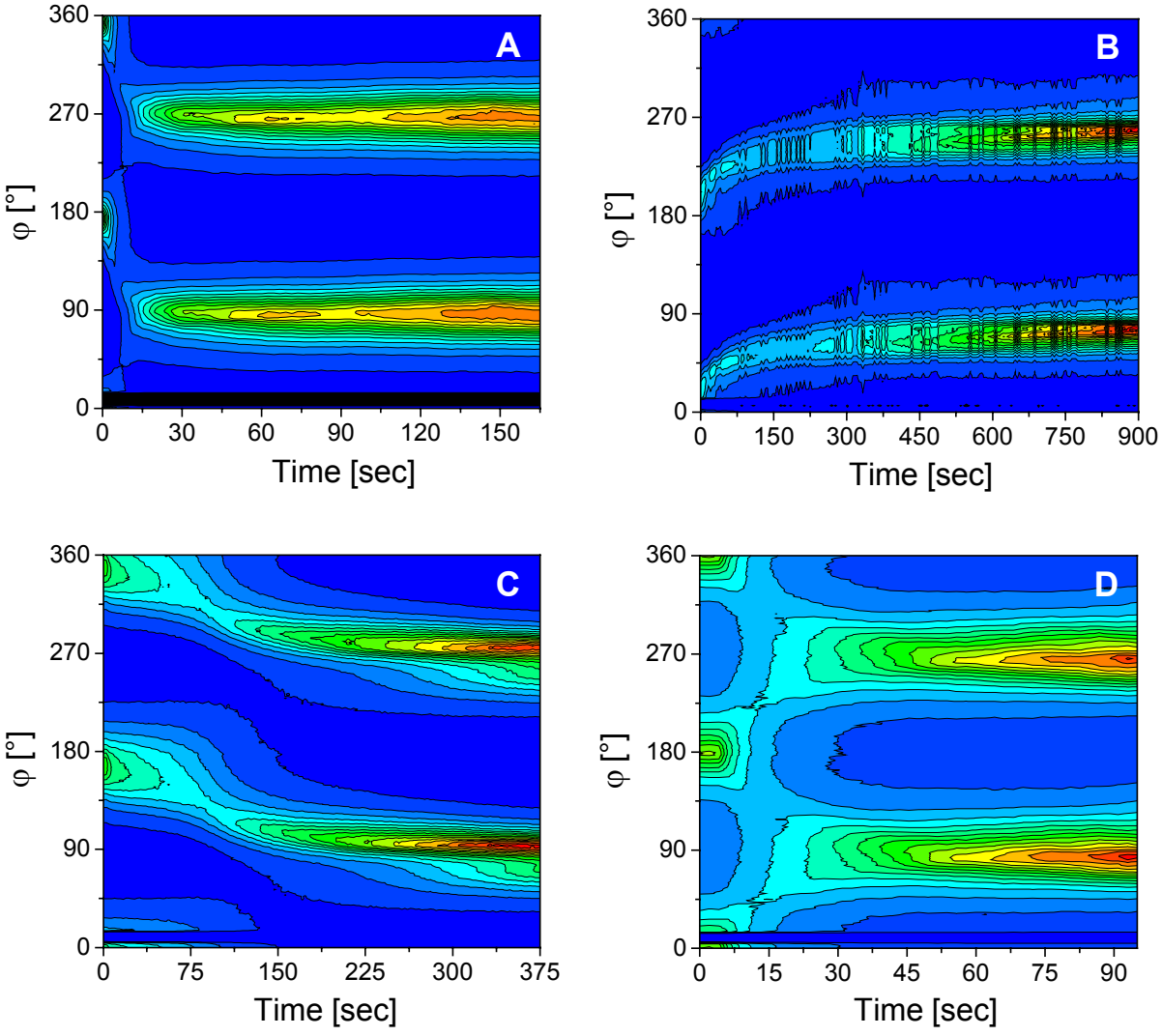

Figure 2: Azimuthal angular dependence of the scattering intensity at 2 kV/2 mm. (A) 35 wt.-%, T = 25°C, (B) 50 wt.-%, T = 25°C, (C) 47.5 wt.-%, T = 27°C, (D) 47.5 wt.-%, T = 80°C.

These findings point to two different underlying mechanisms responsible for microdomain reorientation in the presence of the electric field. Close to the ODT, i.e. at low concentrations and high temperatures, microdomains aligned parallel to the electric field grow at the expense of those aligned parallel to the electrodes. Intermediate orientations, however, are not observed. This behavior matches the notion of the *migration of grain boundaries*, which has previously been described for microdomain alignment under shear[5]

and which was assumed to play a role in electric field experiments as well[7-9]. In this case, one lamella grows at the expense of another with a significantly different orientation by motion of a tilt boundary (wall defect) between them, leading to a direct transfer of scattering intensity between widely separated azimuthal angles φ.

Further away from the ODT, i.e. for high concentrations and low temperatures, the scattering pattern seems to be preserved and merely shifts into the new orientation. This observation points to the *rotation of entire grains*, with a broad size distribution ranging between a few to some hundred microns as determined by birefringence microscopy, as an alternative orientation process. In contrast to the migration of grain boundaries, microdomain orientations intermediate between the original and the final orientations are observed. At the same time no increase in isotropic scattering is observed.

A more detailed description of this work will be published elsewhere[10].

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