



	Experiment title: Large Area Domain Alignment of Block Copolymer Films under the Influence of Electric Fields: Domain Orientation and Orientation Kinetics	Experiment number: SC-795
Beamline: ID 2A	Date of experiment: from: 28.04.2001 to: 01.05.2001	Date of report: 31. August 2001
Shifts: 9	Local contact(s): Volker Urban	<i>Received at ESRF:</i>
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Report:

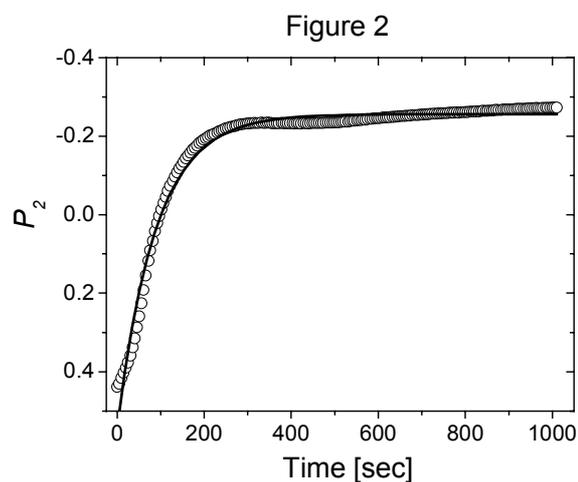
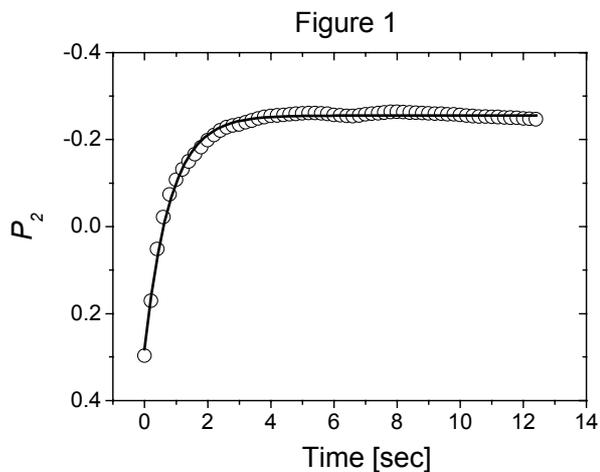
The preparation of highly oriented high molecular weight copolymers or copolymers of more complex architectures (multiblock copolymers, star copolymers, etc.) from melt is rather difficult if not impossible, due to their high melt viscosities. Therefore, we aim to explore alternative approaches, which circumvent this limitation.

Recently [1], we investigated the microdomain alignment of block copolymers during preparation from solution by virtue of an external electric DC field. Bulk samples cast in the presence of an electric field exhibited lamellar microdomains highly oriented parallel to the electric field vector, as shown by small angle X-ray scattering (SAXS) scanning electron (SEM) and transmission electron microscopy (TEM).

In order to elucidate the underlying kinetics of the orientation process, we have performed in-situ Synchrotron-SAXS investigations of the orientation behavior of diblock and triblock copolymer solutions as a function of polymer concentration and electric field strength. (Model systems: polystyrene-*b*-polyisoprene ($S_{50}I_{50}$, $M_n = 80000\text{g/mol}$) in toluene and polystyrene-*b*-poly(2-hydroxyethyl methacrylate)-*b*-poly(methyl methacrylate) ($S_{47}H_{10}M_{43}$, $M_n = 82000\text{g/mol}$) in THF).

We find reorientation (from parallel to the electrodes to parallel to the electric field vector) of lamellar and cylindrical microdomains in the external electric field at concentrations between 30 and 50 wt.-% starting slightly above the order-disorder concentration (ODC). For most data sets, the reorientation kinetics can be fitted by a simple exponential law with time constants varying from a few seconds slightly above ODC to some minutes with increasing concentration.

From the experimental results we can determine an optimum concentration range around the ODC, in which the interplay of chain mobility and gain in free energy in the electric field leading to an improved preparation of highly anisotropic bulk polymer samples.



In the following we summarize the major results of our experiments. In order to evaluate the kinetics of orientation, we calculated the orientational order parameter P_2 from the scattering data and fitted the resulting graph to a simple exponential law. For the SI system we found time constants between 0.8 sec (32.5 wt%) and 14 sec (40 wt%) when subjected to an electric field of 2 kV/2 mm in a specially designed capacitor. At higher concentrations (e.g. 50 wt%) a voltage of 5 kV/2 mm has to be applied in order to induce an electric field driven orientation. Figure 1 shows as an example the reorientation of a 32.5 wt% solution of the lamellar $S_{50}I_{50}^{80}$ block copolymer at 2 kV/2 mm (The black line shows the exponential fit). This represents a remarkably fast reorientation as has not been observed before. The fast shutter at the ID 2A beamline therefore is indispensable to resolve this process very clearly.

The SHM system exhibits a much slower kinetics (time constant of 89 sec for a 35 wt% solution at 1kV/1mm), but in this respect we were able to show that the incorporation of a short PHEMA block strongly enhances the interaction with the electric field as a similar block copolymer of polystyrene-*b*-poly(methylmethacrylate) (SM) so far did not show any response to the external field. This is in contrast to experiments conducted in the melt which can be attributed to an effective reduction of the difference in the dielectric constants of the blocks $\Delta\epsilon$ by the solvent, leading to an aligning force of the electric field which is significantly smaller for block copolymer solutions than for melts. Nevertheless, we were able to show with the in-situ SAXS observations that indeed this low driving force is sufficient to lead to predominant alignment of the microdomains parallel to the electric field vector. Moreover we could identify a threshold voltage for each system at which reorientation takes place. We can conclude that the measurements at the ESRF helped us to develop an experimental protocol to create block copolymer bulk samples with large monodomains with an orientational order parameter P_2 of up to -0.4.