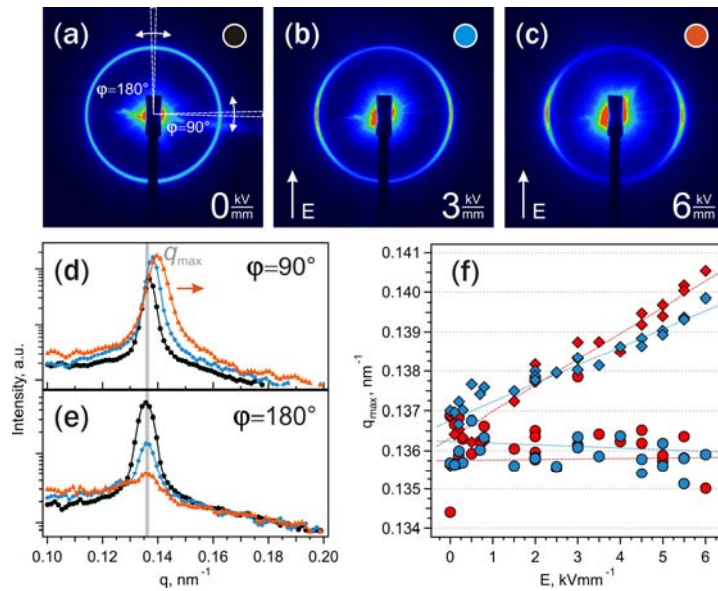




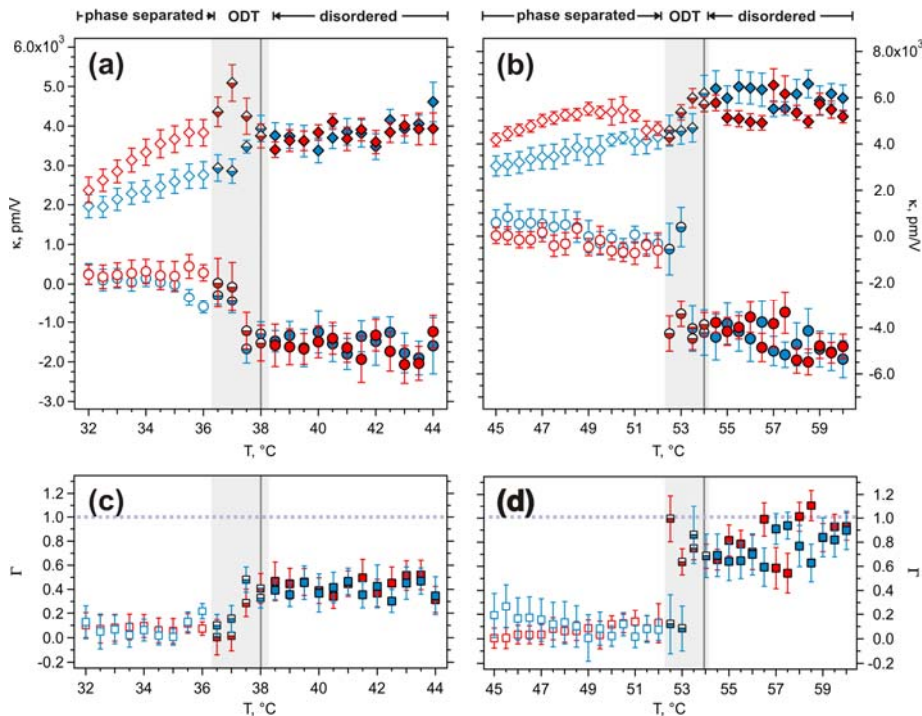
	<b>Experiment title:</b> <b>Electric-Field-Induced Alteration of Domain Spacings of Block Copolymer Systems</b>	<b>Experiment number:</b> SC-2874
<b>Beamline:</b> ID 2	<b>Date of experiment:</b> from: 07.05.2010 to: 11.05.2010	<b>Date of report:</b> 25. Jul. 2011
<b>Shifts:</b> 9	<b>Local contact(s):</b> Dr. P. Boesecke	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Alexander Böker, Christian Pester*, Markus Ruppel*, Heiko Schoberth*, Kerstin Schindler*, Clemens Liedel*, Stephanie Hiltl* (Lehrstuhl für Makromolekulare Materialien und Oberflächen, RWTH Aachen University, D-52056 Aachen, Germany)		

## Report:

This report deals with the beam time of the project SC-2874. As we proposed for this beamtime we investigated the temperature dependence of the electric field induced distortion of poly(styrene-*b*-isoprene) (PS-*b*-PI) block copolymer chain conformations. The polymer was dissolved in toluene at two different concentrations. Our home-built, temperature-controlled capacitor allowed high voltages of up to 8 kV/mm for these measurements and enabled us to measure our sample over a large period of time without solvent evaporation, and unwanted alterations regarding sample concentration. According to our measurements, lamellar block copolymer microstructures are anisotropically distorted by high electric fields. Whilst lamellae parallel to the field vector decrease in size, those with perpendicular alignment increase in size (cf. Fig. 1a-e). This direction, the magnitude and linear character of the effect at hand pointed towards initially unexpected piezoelectric properties of this non-polar, non-crystalline polymer, which, above all, is up to two magnitudes of order stronger than other commercial piezoelectric materials (cf. Fig. 1f). Our temperature dependent measurements furthermore showed that also after melting the polymer microstructures, correlation holes in the disordered sample are anisotropically distorted and show an even higher response to the external stimulus (Fig. 2a,b). From the anisotropic response and its behavior we were able to draw conclusions on the nature of fundamental electric field – polymer chain interaction (Fig. 2c,d). Whilst in the phase separated regime polymer chain morphologies are strongly stretched at the interfaces of their respective morphology, preventing further distortion of perpendicular lamellae, they relax to a more Gaussian state in the disordered phase, which allows pronounced interaction with the electric field. A manuscript summarizing these results has been submitted in may 2011.



**Figure 1** 2-D-SAXS patterns for a 32.5 wt.% solution of PS-*b*-PI in toluene for increasing electric field intensities of 0 (a), 3 (b) & 6 kV/mm (c) at 48 °C ( $T < T_{ODT}$ ). Arrows indicate the direction of the electric field. 5° Angular sections in (a) represent sectors at azimuthal angles  $\varphi=90^\circ$  and  $\varphi=180^\circ$ . 1-D-scattering data represent the evolution of the first-order Bragg maxima for sectors normal,  $\varphi=180^\circ$ , (d) and parallel,  $\varphi=90^\circ$ , (e) to field direction at 0 (black), 3 (blue) & 6 kV/mm (orange). Evolution of  $q_{\max}$  with increasing electrical field intensity (f) for lamellae oriented normal (circles) and parallel (rhombi) to the applied field. Data obtained from heating and cooling cycles (see methods section) are color coded in red and blue, respectively.



**Figure 2** Evolution of the piezoelectric susceptibility with temperature for block copolymer lamellae oriented perpendicular ( $\kappa_{\perp}(T)$ , circles) and parallel to an applied field ( $\kappa_{\parallel}(T)$ , rhombi) for a 30.5 wt% (a) and 32.5 wt% (b) solution of PS-*b*-PI in toluene. The piezoelectric asymmetry  $\Gamma(T)$  for both concentrations (30.5 wt.% (c), 32.5 wt.% (d)) is depicted in the bottom part of the figure. Heating and cooling cycles are color coded in red and blue, respectively. The dark gray line indicates  $T_{ODT}$

for respective block copolymer solution at 0 kV/mm and the dashed line indicates the ideal case of a symmetric electroactive response irrespective of electric field orientation.