



**Experiment title:** Block copolymer microphases in solution in the presence of an AC electric field – Influence on ODT and frequency dependence of Orientation

**Experiment number:**  
SC-1262

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**Report:**

Based on our previous investigations on the orientation behavior of block copolymer microdomains subjected to an external electric field<sup>12,3,4</sup>, we studied the influence of the field on the order-disorder transition temperature ( $T_{ODT}$ ) in our block copolymer samples. Thus, we conducted heating and cooling experiments in a temperature-controlled sample cell. First results are presented below. For a cylindrical PS-*b*-PI block copolymer (PS cylinders in PI matrix), we find  $T_{ODT}(3 \text{ kV/mm}) < T_{ODT}(\text{no field})$ . In several consecutive heating cycles,  $\Delta T_{ODT}$  was determined to range between 0.6 and 1.1 K.

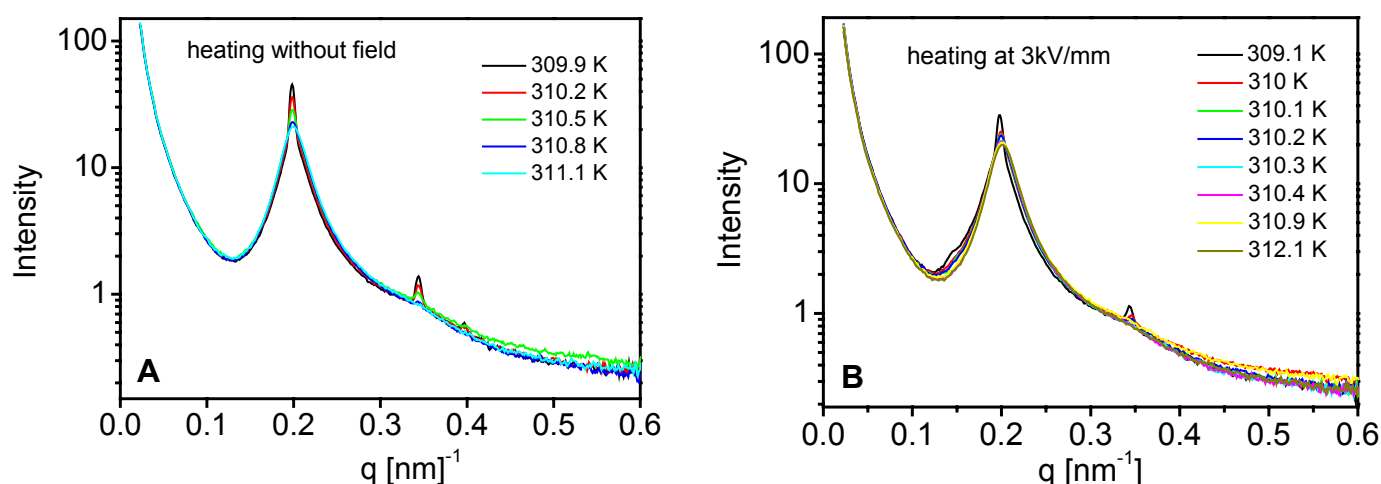


Figure 1: Heating cycle of a cylindrical PS-*b*-PI ( $M_w = 90 \text{ kg/mol}$ ; 55 wt.-% in toluene) without (A) and with (B) an applied electric field of 3 kV/mm.

The corresponding SAXS profiles are shown in Figure 1. Evaluation of every single 2D scattering image revealed the evolution of the orientational order parameter,  $P_2$ , as drawn in Figure 2 versus the temperature of the sample cell. In all cases, order was lost around 310 K, which coincides with the disappearance of the higher orders in the scattering profile and broadening of the first order peak, from which  $T_{ODT}$  was determined.

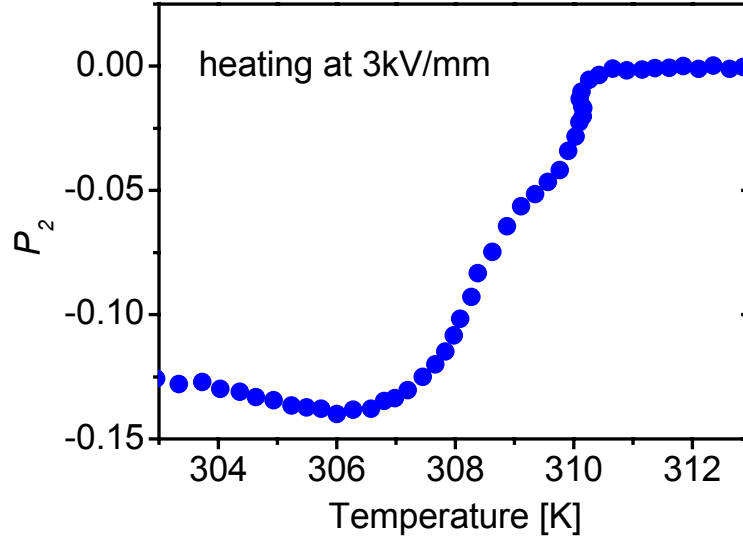


Figure 2: Evolution of orientational order parameter: Heating cycle of a cylindrical PS-b-PI ( $M_w = 90$  kg/mol; 55 wt.-% in toluene) with an applied electric field of 3 kV/mm (see Fig. 1B).

The second set of experiments dealt with the frequency dependence of the microdomain orientation. It has to be noted that there are some technical limitations associated with the present setup, as it is by far not trivial to generate a well-controlled AC field at voltages up to 10kV. At this time a maximum of 5Hz was feasible. The current setup is subject to constant improvement.

We investigated a well-studied lamellar system.<sup>2,3</sup> Depending on the concentration, we found different response frequencies as shown in Figure 3A/B.

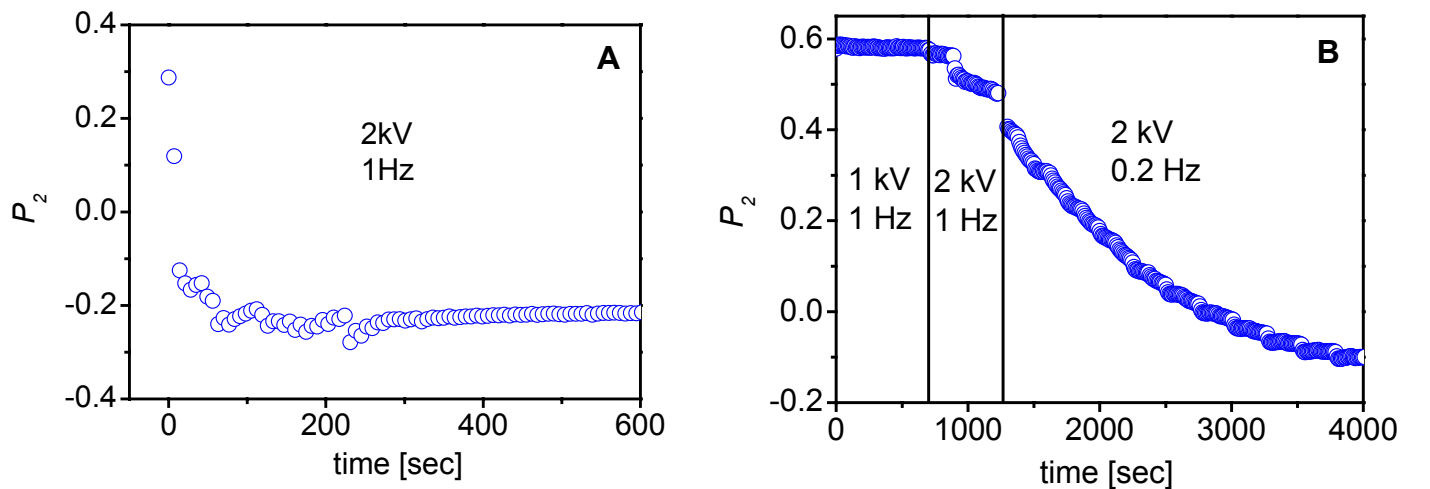


Figure 3: Evolution of orientational order parameter: frequency scan of a lamellar PS-b-PI ( $M_w = 100$ kg/mol; A: 35 wt.-%; B:55 wt.-% in toluene) in a 2 mm capacitor.

The larger the overall time constant,  $\tau$ , for the reorientation of the respective system,<sup>3</sup> the smaller the frequency needed to effectively align the microdomains parallel to the electric field vector. In the case of the 35 wt.-% solution was observed reorientation at 1Hz, whereas a frequency as low as 0.2 Hz was necessary for the higher concentrated sample.

In this experimental series, the feasibility of the proposed measurements has been shown. For future investigations, the temperature control for the ODT measurements and the AC field generator will be substantially improved.

## References

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Reply to Comment on: “Microscopic Mechanisms of Electric-Field-Induced Alignment of Block Copolymer Microdomains”  
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