



Experiment title: Kinetics and mechanisms of electric field induced orientation of block copolymer solutions under strong confinement

Experiment number:
SC-1497

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Report:

In the present study, we have investigated in detail the influence of the degree of initial order on the microscopic route towards domain alignment. In a plate capacitor arrangement, we vary the plate spacing between 3.8 mm and 0.3 mm. The micro domains align parallel to the capacitor plates and the degree of order improves with decreasing capacitor spacing. At the same time the process of reorientation slows down by about an order of magnitude as the capacitor spacing is reduced. Moreover, below 0.9 mm, grain rotation is completely suppressed and domain reorientation can only be achieved via nucleation and growth.

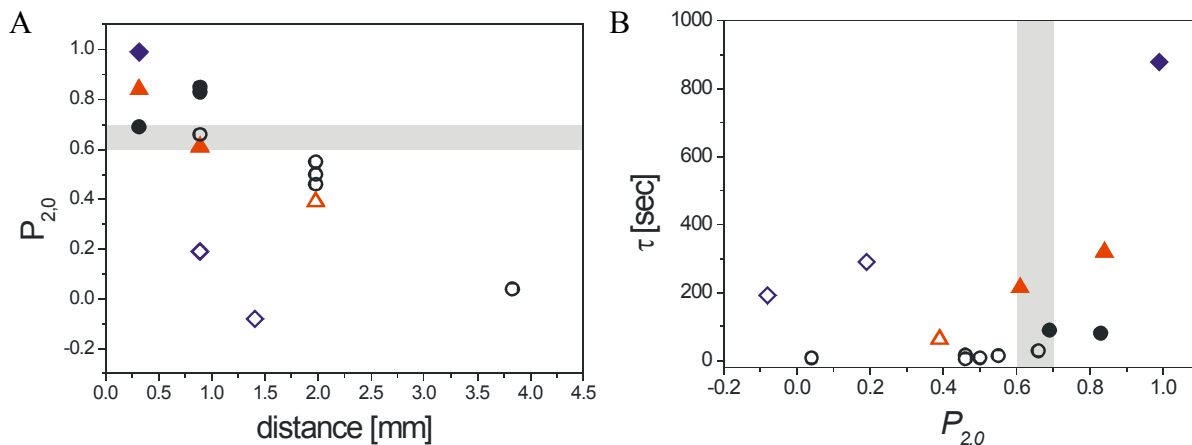


Figure 1: A) Initial order parameter as a function of the electrode spacing for solutions of $S_{50}I_{50}^{100}$ in toluene at 1 kV/mm: \diamond = 55 wt.-%, \triangle = 50 wt.-%, \circ = 35 wt.-%. Full symbols relate to nucleation and growth as the dominant mechanism, while open symbols refer to grain rotation.
 B) Experimental time constants τ as a function of the initial order parameter for solutions of $S_{50}I_{50}^{100}$ in toluene at 1 kV/mm: \diamond = 55 wt.-%, \triangle = 50 wt.-%, \circ = 35 wt.-%. Full symbols relate to nucleation and growth as the dominant mechanism, while open symbols refer to grain rotation.

In summary, it has been found that both the reorientation pathway and the reorientation kinetics for lamellar microdomains in an external electric field strongly depend on the degree of order present prior to the application of the field. Samples of the same concentration but different initial order not only exhibit different mechanisms of orientation but also proceed at different rates. For intermediate degrees of order, where orientation proceeds via both pathways, we find that the dominating mechanism dictates the overall rate of reorientation. We observe consistently that for all systems rotation of lamellae by defect movement is faster than reorientation by nucleation and growth of new domains. Based on our results, we may conclude that above a certain initial orientation parallel to the electrodes the defect density is too low to allow for rotation of domains. In addition, the pressure on the well-aligned lamellae (as pointed out already by Onuki and Fukuda)¹ is larger than for less aligned samples and therefore leads to undulation instabilities which finally serve as nucleation centers for the growth of grains oriented parallel to the external electric field. This leads to a switch in orientation mechanism with increasing initial microdomain orientation from rotation to nucleation and growth. The data from this beamtime will be published soon.²

References

¹ Onuki, A.; Fukuda, J. *Macromolecules* **1995**, *28*, 8788-8795.

² Schmidt, K. et al. "The Influence of Initial Order on the Microscopic Mechanism of Electric Field Induced Alignment of Block Copolymer Microdomains" *Macromolecules*, **2005** submitted.