DISTINCT TIME REGIMES DURING VAPOR TREATMENT OF THIN DIBLOCK COPOLYMER FILMS: A TIME-RESOLVED IN-SITU GRAZING-INCIDENCE SAXS STUDY

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Diblock copolymers in the melt spontanously self-organize into mesoscopically ordered structures. Often, their functionalization involves vapor treatment. In order to characterize possible structural changes of the films, in-situ and real-time grazing-incidence small-angle scattering (GISAXS) is of great value. We have investigated the structural changes of thin films of lamellar poly(styrene-*b*-butadiene) (P(S-*b*-B)) diblock copolymers having initially the lamellae parallel or perpendicular to the substrate surface [1] upon treatment with solvent vapor. The measuring times at CHESS D-line were as short as 10 s, allowing investigations of the early stages of film swelling [2].

We have found that the response to vapor depends crucially on the initial lamellar orientations and the solvent quality and selectivity. For instance, in films with the initial parallel orientation, the lamellae swell upon vapor treatment with toluene, a good and close to non-selective solvent, but after a few minutes spontaneously deswell again (Fig. 1). This change is accompanied by undulations of the lamellar interfaces and restructuring of the lamellar stack. We attribute these observations to the tendency to a more globular chain conformation during swelling [4], leading to deswelling and an increase of the number of lamellae stacked. Complex processes are thus encountered during vapor treatment of block copolymer films.

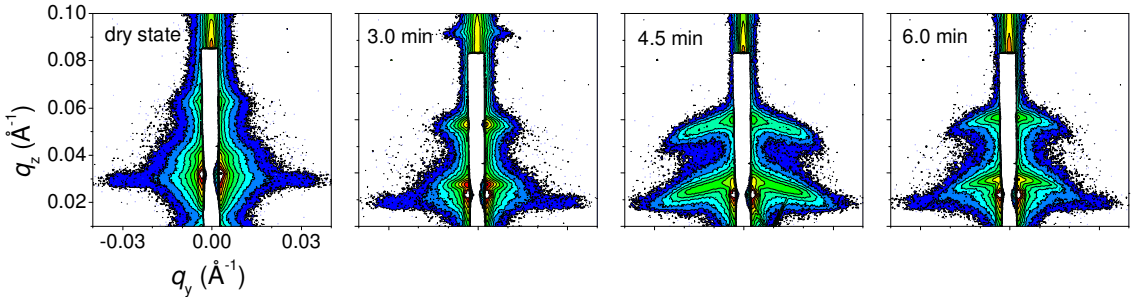

Fig. 1: 2D GISAXS images of a film with initial parallel lamellar orientation in the dry state and during vapor treatment with toluene. Initial lamellar thickness 189 Å, incident angle 0.22°.

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