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Annealing of Diblock Copolymer Thin Films using Solvent Vapor Mixtures

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Block copolymers self-assemble into nanostructures. Solvent vapor annealing (SVA) is an efficient method to improve the long-range order or to alter the morphology in block copolymer thin films.

In the present work, SVA is carried out on thin films from a polystyrene-b-poly(dimethyl siloxane) (PS-b-PDMS) diblock copolymer. For annealing, vapor mixtures of toluene and n-heptane were used, which are weakly selective for PS and highly selective for PDMS, respectively. The morphological changes were investigated by in-situ, real-time grazing-incidence small-angle X-ray scattering (GISAXS). Varying the vapor composition during the annealing cycle results in a lamellar morphology and cylinders with different orientations. Using the scattering contrast, the distribution of the two solvents in the microphase separated thin film can be determined. This information can be transferred to a phase diagram and be related to the observed morphologies during annealing.

The results show that solvent exchange during SVA gives control over the morphology, and that the scattering contrast can be used to track the distribution of two solvents in a phase separated thin film experimentally.

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