Processing of Block Copolymer Thin Films

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Block copolymers (BCPs) have a multitude of applications. One of the intriguing properties of BCPs is that they form regular self-assembled nanostructures in the range of 10 nm to 300 nm. By further treatment such nanostructures can be converted into nanoscaffolds with applications in ultrafiltration [Du] and solar cells [Crossland]. BCP thin films are typically produced be spin coating yielding a high-quality homogeneous coating of the substrate. However, due to the fast drying kinetics during spin coating, the self-assembled structures formed have a lot of defects, and also often deviate from the equilibrium BCP morphology. The classic thermal treatment to resolve these issues cannot be applied to all BCPs, in particular when they have a temperature-sensitive block.

Solvent vapor annealing (SVA) has evolved as an alternative gentler technique. In SVA the polymer is exposed to solvent vapor of a controlled concentration. BCPs can swell in the vapor of a good solvent to more than twice the original film thickness. This way the glass temperature can be lowered close to room temperature and the polymer chains become more mobile. However, the challenge remains in finding a good match between BCP and solvent and finding the best swelling ratio where chains are mobile enough, but still in the strong segregation regime so that there is a driving force towards ordering [Posselt].

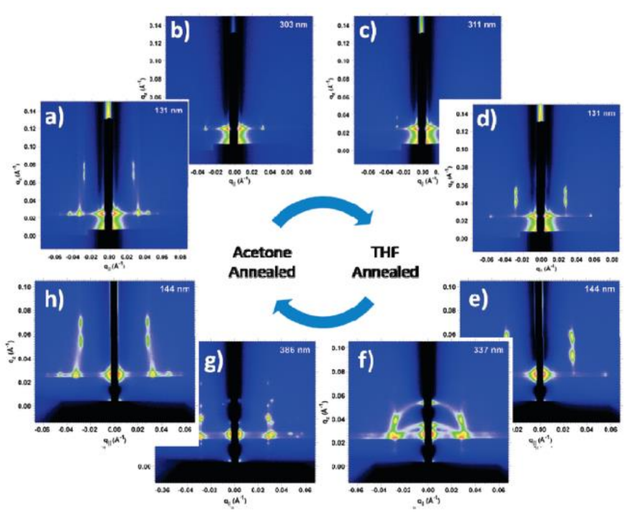

Figure 1: Morphology switching in a BCP via selective (acetone) and nonselective (THF) solvent vapor. The cycle could be repeated at least 3 times. For details see [Paik].

If a good solvent for both blocks is replaced with a selective solvent even more dramatic things can happen: the selective solvent swells on of the blocks more than the other, thus changing the volume ratio of the blocks and driving the swollen film to a different place in the phase diagram. By rapid drying this new morphology can be stabilized albeit the blocks get somewhat squished during removal of the solvent. Using a non-selective solvent in another SVA cycle brings the BCP back to its original phase

[Paik]. Solvent vapor processing can be further modified by using mixtures of selective solvents. This way it is possible to reach even several morphologies from the same polymer by variation of the mixing ratio [Chavis].

In this project we would like to explore the morphologies in PS-*b*-PDMS by using a variety of solvents or mixtures. A solvent vapor annealing setup with an optical film thickness sensor, a spin coater, and a UV/ozone cleaner are available in the Sample Environment Lab at CHESS for initial studies. Through the Ober group also AFM and SEM are available. Materials will be synthesized in collaboration with the Ober group, and then processed at CHESS. When CHESS starts up again in November, we plan to complement these preliminary studies with in-situ x-ray scattering at D-line.

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