

In situ GISAXS Investigations of Multi-responsive Block Copolymer Thin Films during Solvent Vapor Annealing

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Responsive block copolymer thin films are of interest for many applications, e.g. as fast sensors or switchable membranes. They may be based on physical hydrogels formed by telechelic copolymers featuring a stimuli-responsive midblock and hydrophobic end blocks. For temperature-responsive end blocks, a weak gel is formed below their collapse temperature, while a frozen network is formed above [1]. In thin films, a pH-responsive midblock, e.g. a weak polyelectrolyte, may be used to tune the self-assembly process, while a temperature change may be used to immobilize the end blocks and to freeze the so created nanostructure. The latter feature is especially interesting for solvent vapor annealing (SVA), which is a versatile technique to improve long-range order in polymer thin films and alter its morphology, but with the drawback that non-equilibrium morphologies are often difficult to preserve during solvent removal [2,3].

In the present work, thin films from the telechelic pentablock terpolymer P(n-BuMA8-co-TEGMA8)-b-PDMAEMA50-b-PEG46-b-PDMAEMA50-b-P(n-BuMA8-co-TEGMA8) were investigated in-situ during SVA with water using grazing-incidence small-angle X-ray scattering (GISAXS). The endblocks are statistical copolymers of the thermoresponsive TEGMA (triethylene glycol methyl ether methacrylate) and the hydrophobic n-BuMA (n-butyl methacrylate). Increasing the temperature increases its hydrophobicity and thus leads to a reduced mobility. The intermediate DMAEMA (2-(dimethylamino)ethyl methacrylate) block is a weak cationic polyelectrolyte, which becomes ionized at low pH values and assumes a stretched conformation. The permanently hydrophilic poly(ethylene glycol) (PEG) block enhances water solubility. The role of the solvents used for film preparation and for SVA on the structural evolution will be presented.

References

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