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Cononsolvency in PNIPAM-based block copolymer thin films

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The diblock copolymer PMMA-b-PNIPAM forms micelles in aqueous solution that exhibit a reversible shell collapse transition at the lower critical solution temperature (LCST). This thermo-response can be moderated by introducing organic cosolvents such as methanol, ethanol or acetone. In thin film configuration, their multi-responsive behavior makes NIPAM-based polymers promising systems for vapor-sensitive nanosensors and actuators. We prepare thin films with a large PNIPAM block and perform swelling experiments in a custom chamber. The film response is probed for mixed vapors of different solvent and cosolvent content, while the temperature is held constant in order to purely probe the cononsolvency effect. Morphological changes, as well as the swelling kinetics related to the uptake of solvent and cosolvent into the film, concentration gradients and the development of swelling ratio and refractive index are investigated with a focus on spectroscopic reflectance (SR) and in-situ time-of-flight neutron reflectometry (TOF-NR). Running sequential experiments with protonated and deuterated compounds allows us to extract the individual distributions of solvent and cosolvent in the film by contrasting SLD profiles from static TOF-NR curves. SR can be used to monitor the film thickness in real time as well as to use as a feed parameter in batch fits of kinetic TOF-NR data. First results show that cononsolvency-related behavior is transferrable from solution to thin film systems.

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