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Cononsolvency-Induced Collapse Transitions in Thin PMMA-b-PNIPAM and PMMA-b-PNIPMAM Films

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Stimuli responsive thin films combine the advantages of polymers in bulk, i.e., their increased stability and of polymer solutions, i.e., their fast response and therefore are attractive for a wide range of applications. Towards future applications, we investigate the not yet well understood phenomenon of cononsolvency. For this we prepared thin films of the thermoresponsive diblock copolymers PMMA-*b*-PNIPAM and PMMA-*b*-PNIPMAM which exhibit cononsolvency induced collapse transitions when organic cosolvents, like acetone or methanol, are introduced into the surrounding atmosphere. The chemical structures of NIPAM (*N*-isopropylacrylamide) and NIPMAM (*N*-isopropylmethacrylamide) differ by an additional methyl group, which is able to influence the film collapse kinetics on a macroscopic scale. The macroscopic changes during the swelling and collapse transitions were investigated by spectral reflectance (SR) and verified through time-of-flight neutron reflectometry (ToF-NR) measurements. On a more molecular level we further elucidate the underlying mechanism by *in situ* Fourier-transform infrared spectroscopy (FTIR) measurements to gain further insight into the origin of the cononsolvency effect.

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