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PMMA-b-PNIPAM thin films display cononsolvency driven response in mixed water-methanol atmospheres

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The diblock copolymer PMMA-b-PNIPAM forms micelles in solution that feature a permanently hydrophobic core and a thermo-responsive shell. While a typical shell collapse transition can be induced via a temperature stimulus at the LCST, the PNIPAM block is also sensitive to the composition of the surrounding solvent. Although water and organic cosolvents individually act as good solvents to the PNIPAM chain, mixtures of both act as bad solvent. As a consequence, the transition temperature shifts as a function of the molar fraction of the cosolvent. For PNIPAM, well-known examples of cosolvents include simple alcohols such as methanol or ethanol as well as acetone. We demonstrate that the cononsolvency effect is transferrable from solution to thin film systems. PMMA-b-PNIPAM films swollen in saturated water vapor show a swelling and collapse at the exchange of the surrounding atmosphere to a mixed vapor of water and cosolvent. The film kinetics are investigated with a focus on time-of-flight neutron reflectometry (TOF-NR) and spectral reflectance techniques. In order to differentiate between water and cosolvent distributions along the films'vertical, sequential experiments with deuterated and non-deuterated water and cosolvent are performed. Complementary FTIR measurements reveal the hydration and cosolvent exchange process at the PNIPAM amide and alkyl functional groups.

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