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In-operando study of swelling and switching of thermo-responsive polymer films

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Thermo-responsive polymers can exhibit a demixing transition which is of the lower critical solution temperature (LCST) type. The collapse transition of polymers with such LCST behavior is of great interest for applications where a strong change of volume is desired even for small changes of an external stimulus such as temperature. Examples of applications are valves in micro-fluidics, the release of drugs in the body or sensors. A polymer which is a promising candidate in this context is poly(N-isopropylacrylamide), PNIPAM. It exhibits a LCST of about 32 °C that is attributed to alterations in the hydrogen-bonding interactions of the amide group. A polymer with a higher transition temperature as compared to PNIPAM is the thermosensitive acrylate poly(methoxydiethylene glycol acrylate) or PMDEGA. In thin film geometry, such thermoresponsive polymers are of particular interest for use as thermosensitive surfaces, artificial pumps and muscles, light modulation systems and optical switches. The strong volume change translates into a change of the film thickness due to the thin film geometry. We investigate the kinetics of chain collapse of thin thermosensitive films as a function of quench depth. Homopolymer films and amphiphilic block copolymer films are compared. With time resolved neutron reflectivity (NR) we follow the kinetics of the transition from a swollen to a collapsed thermoresponsive film. Within 15 seconds a full NR curve is probed, which allows to determine the evolution of film thickness and of the water content in real time. Thus, we investigate in-operando the switching behavior caused by a thermal trigger. The observed complex three-step switching of the films is discussed.

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