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Phase transition kinetics in a doubly thermo-responsive block copolymer thin film followed with in-situ neutron reflectometry

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Thermo-responsive polymers can show a strong change in volume towards even slight changes of their surrounding temperature. This behavior makes them promising candidates for the implementation in a manifold application fields such as nano-sensors, artificial pumps and muscles, or optical switches. While the underlying mechanisms of such polymers in solution are well understood, less is known about thermo-responsive polymers in thin film morphology. In our recent work, we follow the phase transition kinetics upon increasing temperature in a doubly thermo-responsive block copolymer thin film via in-situ time of flight neutron reflectometry (TOF-NR). The block copolymer consists of a poly(N-isopropylmethacrylamide) (PNIPAM) block, which shows a lower critical solution temperature (LCST) and a zwitterionic poly(sulfobetaine) (PSB) block, which exhibits an upper critical solution temperature (UCST) that is lower than the corresponding LCST of the PNIPMAM block. A combination of spin-coating and solvent vapor annealing is used to prepare polymer thin films in the range of 30 nm to 150 nm with high homogeneity. At a temperature below the UCST, the polymer film is swollen in D2O atmosphere in order to increase the mobility of the polymer chains. Subsequent, temperature is increased to an intermediate regime (between UCST and LCST) and high regime (above LCST). The kinetic processes (swelling and temperature steps) are followed with high time resolution via TOF-NR. Static measurements and TOF grazing incidence small angle neutron scattering (GISANS) measurements are performed at the beginning and in between the kinetic dynamics in order to gain a complete picture of the swelling and temperature-dependent behavior of the polymer thin film.

Authors: KREUZER, Lucas (TU München, Physik Department, E13); WIDMANN, Tobias (TU München, Physik Department, LS Funktionelle Materialien); BIESSMANN, Lorenz (TU München, Physik-Department E13); MÄRKL, Raphael (TUM Physics E13); MOULIN, Jean-Francois; Dr HILDEBRAND, Viet; Prof. LASCHEWSKY, Andre (Uni Potsdam, IAP Potsdam); PAPADAKIS, Christine (Technische Universität München, Physik-Department, Fachgebiet Physik weicher Materie); Prof. MÜLLER-BUSCHBAUM, Peter (Lehrstuhl für Funktionelle Materialien E 13)

Presenter: KREUZER, Lucas (TU München, Physik Department, E13)

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