

Switching kinetics of thermoresponsive micellar hydrogels

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Thermoresponsive polymers have received increasing attention as they respond with a strong volume change to a small change of temperature across the lower critical solution temperature (LCST). They are of great interest for medical applications as well as for controllable nanoporous membranes [1]. An example for a thermoresponsive polymer is poly(monomethoxy diethylenglycol methacrylate) (PMDEGA) which has an LCST between 30 °C and 50 °C depending on the concentration.

We investigate triblock copolymers which have two short hydrophobic polystyrene (PS) endblocks and a longer hydrophilic PMDEGA middleblock (Figure 1). In aqueous solution, they form flower-like core-shell micelles or, above the critical gel concentration micellar hydrogels. When heated above its LCST, the PMDEGA block becomes hydrophobic and releases water from the micellar shell, which consequently collapses, similar to poly(*N*-isopropyl acrylamide) based triblock copolymer systems [2,3]. The structural changes of the polymeric hydrogels upon fast heating and cooling through the LCST are investigated with small-angle x-ray scattering (SAXS).

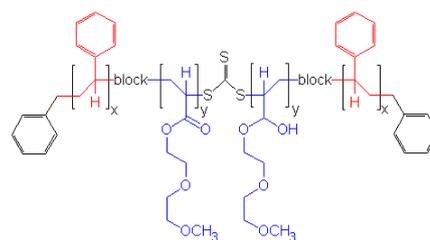


Figure 1: PS-*b*-PMDEGA-*b*-PS triblock copolymer

Time-resolved SAXS experiments were performed at beamline A2, HASYLAB at a wavelength $\lambda = 0.15$ nm and a sample-to-detector distance of 1.04 m. A MarCCD detector was used. A custom-made sample holder allowed heating from the fully swollen into the fully collapsed regime within approx. 25 s. Two copolymers were investigated: PS₁₁-*b*-PMDEGA₈₂-*b*-PS₁₁ and dPS₁₀-*b*-PMDEGA₁₀₀-*b*-dPS₁₀ with fully deuterated PS-blocks. Copolymer concentrations of 50 mg/ml, 200 mg/ml and 300 mg/ml in D₂O were chosen, i.e. in the micellar solution and micellar hydrogel state. Every 30 s, an image was taken.

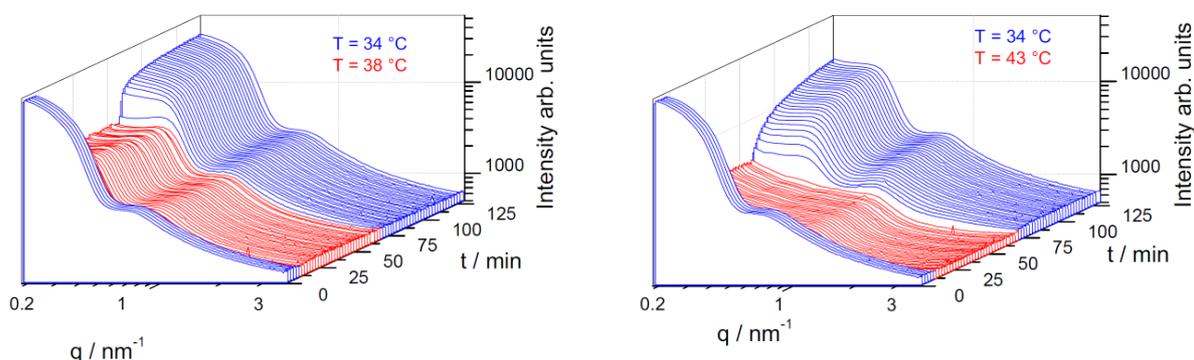


Figure 2: SAXS curves during temperature jumps from a) 34 °C (blue) to 38 °C (red) and back and b) 34 °C (blue) to 43 °C (red) and back for PS₁₁-*b*-PMDEGA₈₂-*b*-PS₁₁ in H₂O at a concentration of 300 mg/ml

Scattering curves for two different jump depths are shown in Figure 2 for PS₁₁-*b*-PMDEGA₈₂-*b*-PS₁₁ at 300 mg/ml. The samples were kept at 34 °C for 5 min, then they were quickly heated to 38 °C (Figure 2a) or to 43 °C (Figure 2b). After 35 min at high temperature, they were quickly cooled back to 34 °C.

For PS-*b*-PMDEGA-*b*-PS triblock copolymers, the matrix scattering is expected to dominate, due to the high scattering contrast between H₂O and PMDEGA. Upon heating, the collapse takes place within 30 s after the temperature jump, which corresponds to the heating time of the sample-holder. The collapse is finished after 90 s. Moreover, during the first 90 s after the jump, the correlation peak moves from 0.6 nm⁻¹ to 0.9 nm⁻¹. From small-angle neutron scattering experiments, it is known that strong forward scattering at small *q*-values arises above the LCST. These findings indicate that the collapsed micelles pack more closely than in the swollen state, and they form clusters above the LCST.

Two major differences are noticed for the two jump depths: For the target temperature of 38 °C, one can still observe the structure factor of core-shell micelles in the collapsed state. At 43 °C (Figure 2b), in contrast, the structure factor vanishes, which points to a dissolution of the PS spheres in the PMDEGA matrix in the clusters. Moreover, upon cooling, the system needs more time to relax to the original state than from 38 °C, i. e. it takes long time for the clusters to dissolve again and for the micelles to re-form.

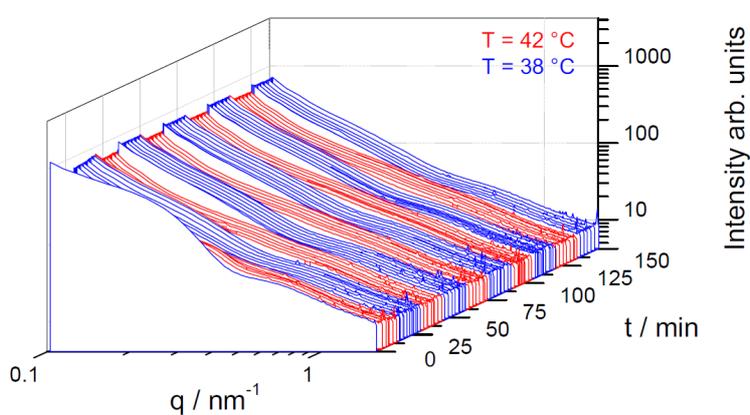


Figure 3: Time-resolved scattering curves during cyclic switching between 38°C (blue) and 42°C (red) for P(S-*d*₈)₁₀-*b*-PMDEGA₁₀₀-*b*-P(S-*d*₈)₁₀ in D₂O at a concentration of 300 mg/ml.

Moreover, we have investigated the reversibility of the structural changes observed. Figure 3 shows a sequence of 6 cycles between 38 °C and 42 °C. In the first cycle, the scattering curve differs from the subsequent ones, i.e. the kinetics are different. During heating, the micelles collapse rapidly and form clusters, whereas upon cooling the clusters need long time to dissolve again, which hinders the swelling of the micellar shell.

We conclude that triblock copolymers form micellar hydrogels in H₂O and D₂O and show thermoresponsive behavior. Time-resolved synchrotron SAXS allowed us to follow the collapse kinetics on a large range of length scales. The kinetics of the structural changes depend on the jump depth and whether the sample is heated up or cooled down.

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References

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