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Effect of pressure on the micellar structure of PMMA-*b*-PNIPAM in a water/methanol mixture

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In aqueous solution, amphiphilic block copolymers consisting of a short permanently hydrophobic poly(methyl methacrylate) (PMMA) and a long thermoresponsive poly(*N*-isopropyl acrylamide) (PNIPAM) block self-assemble into spherical core-shell micelles. At atmospheric pressure, the micellar shell of PMMA-*b*-PNIPAM strongly dehydrates and shrinks above the cloud point T_{cp} of PNIPAM. However, when pressure is applied, the dehydration of the PNIPAM shell is less strong. Besides temperature and pressure, the addition of a water-miscible co-solvent affects the self-assembly behavior of PMMA-*b*-PNIPAM. At 0.1 MPa, adding a small amount of methanol (10 % v/v) leads to softening of the PMMA core and a slight shrinkage of the PNIPAM shell [1]. Here, we present the phase behavior and the pressure- and temperature-dependence of the micellar structure of PMMA₂₁-*b*-PNIPAM₂₈₃ in a 90:10 v/v D₂O/CD₃OD mixture in a pressure range between 10 and 250 MPa. Turbidimetry shows that adding methanol to PMMA-*b*-PNIPAM in D₂O shifts the maximum of the coexistence line to a higher pressure and temperature. Synchrotron small-angle X-ray scattering reveals that the size of the micellar core decreases with increasing pressure, which is particularly pronounced for pressures of 200 MPa and above. At all pressures studied, the micellar shell shrinks only slightly when heating across T_{cp} .

[1] C.-H. Ko, C. M. Papadakis et al., *Macromolecules* 54, 5825-5837 (2021).

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