What high pressure can teach us about block copolymer micelles with a thermoresponsive shell

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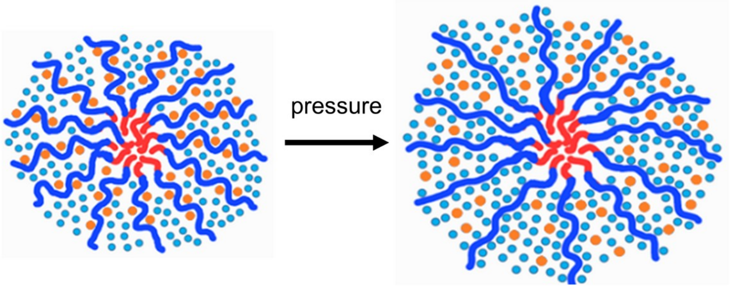
In dilute aqueous solution, thermoresponsive diblock copolymers with a hydrophobic and a thermoresponsive block self-assemble into core-shell micelles. Here, we investigate the self-assembly behavior of the model diblock copolymer PMMA-*b*-PNIPAM consisting of a short permanently hydrophobic poly(methyl methacrylate) and a long thermoresponsive poly(*N*-isopropylacrylamide) block. Synchrotron small-angle X-ray scattering reveals that, below the cloud point T_{CP}, spherical micelles are formed, having a PMMA core and a hydrated PNIPAM shell. Above T_{CP}, the micellar shell dehydrates, and the micelles contract and form aggregates.[1] Adding methanol as a cosolvent leads to strong changes of the micellar structure, which is due to the superposed co-nonsolvency effect of PNIPAM and the enhanced solvation of PMMA.[2] Applying pressure to an aqueous micellar solution of PMMA-*b*-PNIPAM is a tool to alter the hydration behavior of the PNIPAM block. In neat water, we find that not only the value of T_{cp}, but also the transition behavior depends on pressure.[3] In a water/methanol mixture, intricate behavior is found when pressure is varied, both below and above T_{cp}. The observed changes in this system can be traced back to the change of the solvation behavior of PNIPAM homopolymers under pressure, i.e. a replacement of adsorbed water on the PNIPAM segments by methanol molecules, as pressure is increased.[5,6] The pressure-induced alteration of the properties of the micellar shell and the correlation between the micelles allows investigating the relation between these effects.



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