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Thermal Behavior and Cononsolvency of the Thermoresponsive Diblock Copolymers PMMA-b-PNIPAM and PMMA-b-PNIPMAM in Aqueous Solution

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Amphiphilic diblock copolymers having a hydrophobic poly(methyl methacrylate) (PMMA) block and a thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) or poly(N-isopropylmethacrylamide) (PNIPMAM) block form core-shell micelles in aqueous solution. The transition temperature of the PNIPMAM block is 43 oC, thus significantly higher than the one of PNIPAM (32 oC), which has been attributed to steric hindrance by the additional methyl group which weakens the intermolecular interactions [1]. Both, the PNIPAM and PNIPMAM blocks are not only sensitive to temperature, but also to the solvent composition. Adding methanol as a cosolvent causes these blocks to collapse, which reduces the transition temperature, i.e. cononsolvency is observed [2]. In contrast, PMMA features the cosolvency effect in water-methanol mixtures, i.e. the solubility of PMMA block is increased by adding the cosolvent methanol [3]. In the present work, we investigate (i) the structure of the self-assembled micelles and the changes upon collapse and aggregation with increasing temperature, and (ii) the effect of methanol using turbidimetry, differential scanning calorimetry (DSC), dynamic light scattering (DLS) and small-angle neutron scattering (SANS). The results reveal the role of the nature of the thermoresponsive block on the thermal behavior and the morphology changes upon temperature and solvent composition.

[1] E. I. Tiktopoulo et al., Macromolecules 28, 7519 (1995).
[2] F.M. Winnik, H. Ringsdorf, J. Venzmer, Macromolecules 23, 2415–2416 (1990).
[3] R. Hoogenboom et al, Aust. J. Chem. 63, 1173-1178 (2010)

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