

Micelles of Polybutadiene-*b*-Poly(ethylene oxide) in Methanol, Cyclohexane, and Methanol + Cyclohexane

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We have studied the self-assembly of a polybutadiene-*b*-poly(ethylene oxide) diblock copolymer in methanol, in cyclohexane, and in the partially miscible binary mixture of methanol + cyclohexane. Molecular probe experiments indicate that PB₈₉-*b*-PEO₁₃₂, where the subscripts indicate the number of monomers of each polymer in the copolymer, forms micelles with PEO cores and PB coronas in pure cyclohexane, and micelles with PB cores and PEO coronas in pure methanol. In both pure solvents, dynamic light scattering indicated that the copolymer forms coexisting spherical and cylindrical micelles. In the binary solvent mixture, only spherical micelles are observed. In the methanol-rich phase, spherical micelles form over a wide range of temperatures. In the cyclohexane-rich phase, spherical micelles are present only near the liquid-liquid critical temperature of the mixture. At the critical solvent composition, spherical micelles form in the single-phase region above the critical temperature. Size exclusion chromatography showed that for the binary solvent mixture, the copolymer distributes mostly into the methanol-rich phase, and this preference becomes more pronounced as the temperature decreases.