Supplementary Information for Walther et al. " Formation of Hydrophobic Bridges between Multicompartment Micelles of Miktoarm Star Terpolymers in Water"

Methods

The polymer used in this study is a miktoarm star terpolymer, bearing three arms of polystyrene (S), poly(2-vinyl pyridine) (V) and polybutadiene (B) , $S_{54}B_{18}V_{28}^{182}$. The subscripts and superscript denote the weight fractions and the overall molecular weight in kg/mol of the terpolymer.

Dynamic Light Scattering (DLS)

Dynamic light scattering was performed on an ALV DLS/SLS-SP 5022F compact goniometer system with an ALV 5000/E cross-correlator and a He–Ne laser (λ_0 = 632.8 nm). Prior to the light scattering measurements the sample solutions were filtered using Millipore or Roth filters (housing: polypropylene, membrane: nylon) with a pore size of 5 μm. All samples were analyzed at high dilution. The data evaluation of the dynamic light scattering measurements was performed with the CONTIN algorithm.

Transmission Electron Microscopy (TEM)

Bright-field TEM was performed on Zeiss LEO 922 OMEGA electron microscope operated at 200 kV. Contrast enhancement of PB over PS was achieved by OsO_4 staining. The sample was deposited by placing a droplet onto a plasma-treated carbon coated TEM grid. Residual liquid was blotted after 15 sec.

For **cryogenic transmission electron microscopy (cryo-TEM)** studies, a drop of the sample dissolved in THF was put on a lacey TEM grid, where most of the liquid was removed with blotting paper, leaving a thin film stretched over the lace. The specimens were instantly vitrifed by rapid immersion into liquid ethane and cooled to approximately 90 K by liquid nitrogen in a temperature controlled freezing unit (Zeiss Cryobox, Zeiss NTS GmbH, Oberkochen, Germany). The temperature was monitored and kept constant in the chamber during all of the sample preparation steps. Afterwards, the specimen was inserted into a cryo-transfer holder (CT3500, Gatan, München, Germany) and transferred to a Zeiss EM922 EF-TEM instrument. Examinations were carried out at temperatures around 90 K. The transmission electron microscope was operated at an acceleration voltage of 200 kV. Zero-loss filtered images (ΔE = 0 eV) were taken under reduced dose conditions (100-1000 e/nm^2). All images were registered digitally by a bottom mounted CCD camera system

(Ultrascan 1000, Gatan) combined and processed with a digital imaging processing system (Gatan Digital Micrograph 3.9 for GMS 1.4).

Additional cryo-TEM images of $B_{11}V_{89}^{100}$ (measured at pH = 2)

The images show core-corona micelles that are not connected by hydrophobic bridges despite their close proximity. The imaging conditions are exactly the same as for the multicompartment micelles.

The micelles can be obtained by direct dissolution in acidic water and are thus of high dynamic nature. Dialysis of the polymer from a common solvent (dioxane) into water leads to similar results.