Supporting Information

Temperature-Induced Reversible Morphological Changes of Polystyrene-*block*-Poly(ethylene Oxide) Micelles in Solution

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Experimental Section

Sample synthesis and preparation. The diblock copolymer PS_{962}-*b*-PEO_{227} was synthesized using living anionic polymerization based on a standard route which is published elsewhere.[1] In brief, the PS precursor was characterized by size exclusion chromatography (SEC) using polystyrene standards and had a M_n^{PS} of 100k g/mol (the degree of polymerization of ~ 962) and a polydispersity of 1.03. The M_n^{PEO} was determined by proton nuclear magnetic resonance to be 10k g/mol (the degree of polymerization of ~ 227). A polydispersity of 1.04 in the overall diblock copolymer was determined by SEC using the universal calibration. The volume fraction of PS blocks was then calculated to be 0.914.

The PS-*b*-PEO block copolymers were first dissolved in anhydrous DMF by stirring at room temperature for a few days to obtain stock solutions of different

copolymer concentrations, and they were then sealed with Teflon tape and stored at room temperature. Anhydrous DMF was filtered using 0.02 μm pore size filters before making the stock solutions.

We first prepared the micellar solution at room temperature using a procedure in which water is added to the block copolymer solution in DMF at an appropriate rate to a final, predetermined water concentration. The details of the procedure have been given elsewhere.[2] For studying the effect of temperature, the micellar solutions in vials were sealed with Teflon tape and kept at the desired temperature in a temperature-controlled oil bath with a digital temperature controller having an accuracy of ± 0.1 °C. During heating and cooling, the micelle samples were equilibrated at the desired temperature for 2 to 4 hrs dependent upon the equilibrating time needed. In order to study the morphological evolution in an isothermal condition where the morphological changes occur, the micelle samples were taken out of the isothermal temperature oil bath at different periods of time for TEM sample preparation (see below).

Transmission electron microscopy. Micelle morphological observations were performed on a Philips TECNAI TEM with an accelerating voltage of 120 kV. Because we need to visualize the morphology in the solution at the particular temperature a small amount of the solution was quenched in excess water at room temperature, after thermal equilibration, to quickly vitrify the PS blocks into its glassy state. A drop from the quenched solution was then placed on the carbon-coated grid. After a few minutes, the excess solution was blotted with filter paper. The grids were dried at room temperature and atmospheric pressure for several hrs before examination in the TEM. Since the PS

blocks were in their glassy state, the "quenched" morphologies were fixed during TEM observation.[3] No staining was used as the self-assembled structures were easily visible in TEM.

Static and dynamic laser light scattering. Laser light scattering (LLS) experiments were carried on a Brookhaven laser light scattering instrument equipped with BI-200SM Goniometer and a PCI BI-9000AT correlator. A Melles Griot 35 mW He-Ne laser was used as the light source (632.8 nm). A cylindrical glass scattering cell with diameter of 12 mm was placed in the center of the thermostated bath with decahydronaphthalene used for refractive index matching. The BI temperature controller can adjust the temperature from 10 to 80 °C (with an accuracy of temperature control of ± 0.01 °C). The system was equilibrated at the desired temperature for two hrs before taking the reading. The glass scattering cells were extensively cleaned by ultrasonication in THF and ethanol to eliminate any dust and impurities. The stock solutions were filtered into the scattering cells through filters with a 0.45 μm pore size. Water was added, dropwise, through a filter with a 0.02 μm pore size.

Turbidity measurements. Turbidity was measured by a Hewlett Packard HP 8453 UV-Visible Spectrophotometer with UV-Visible Chem Station software. The measurements were carried out at a wavelength of 700 nm where the absorption of the aggregates was minimized. The sample vials were sealed with Teflon tape and placed in a temperature cell in which the temperature was controlled by a temperature controller. DMF was used as the reference for all the measurements. The preparation of the solution was identical with those for light scattering.

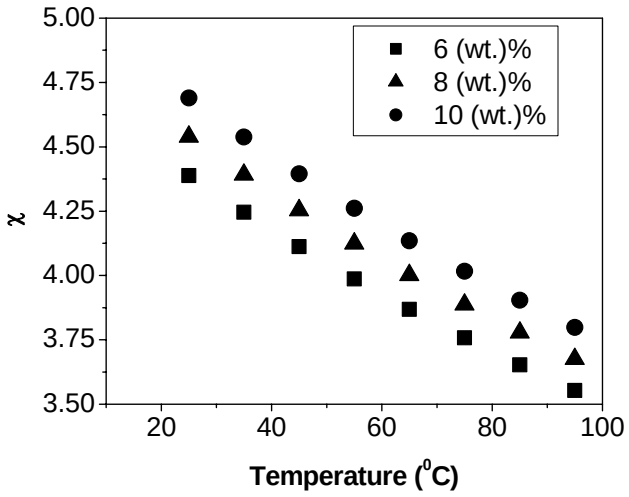

Figure S1 Change in PS-solvent interaction parameter, $\chi_{PS\text{-}solvent}$, with temperature for different water concentrations in DMF/water systems.

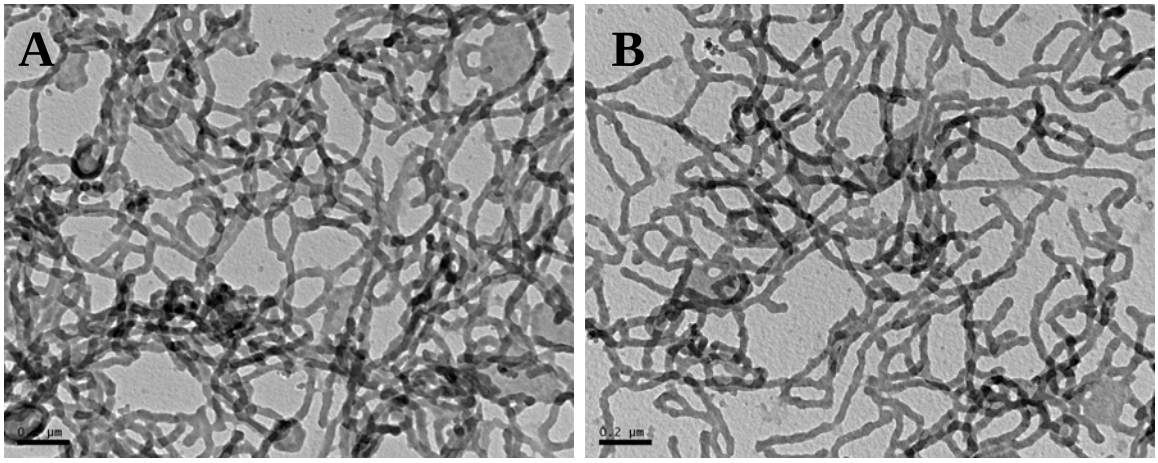

Figure S2 Rod-like cylindrical morphology formed from a system with 0.4 (wt.) % copolymer concentration and 4.35 (wt.) % water concentration in DMF/water in which the original morphology was vesicles: (a) after rapidly heating to 50 ºC and equilibrating for 2 hrs; (b) after rapidly heating to 80 ºC, equilibrating for 2 hrs, and then, quenching to 50 ºC and equilibrating for another 2 hrs.

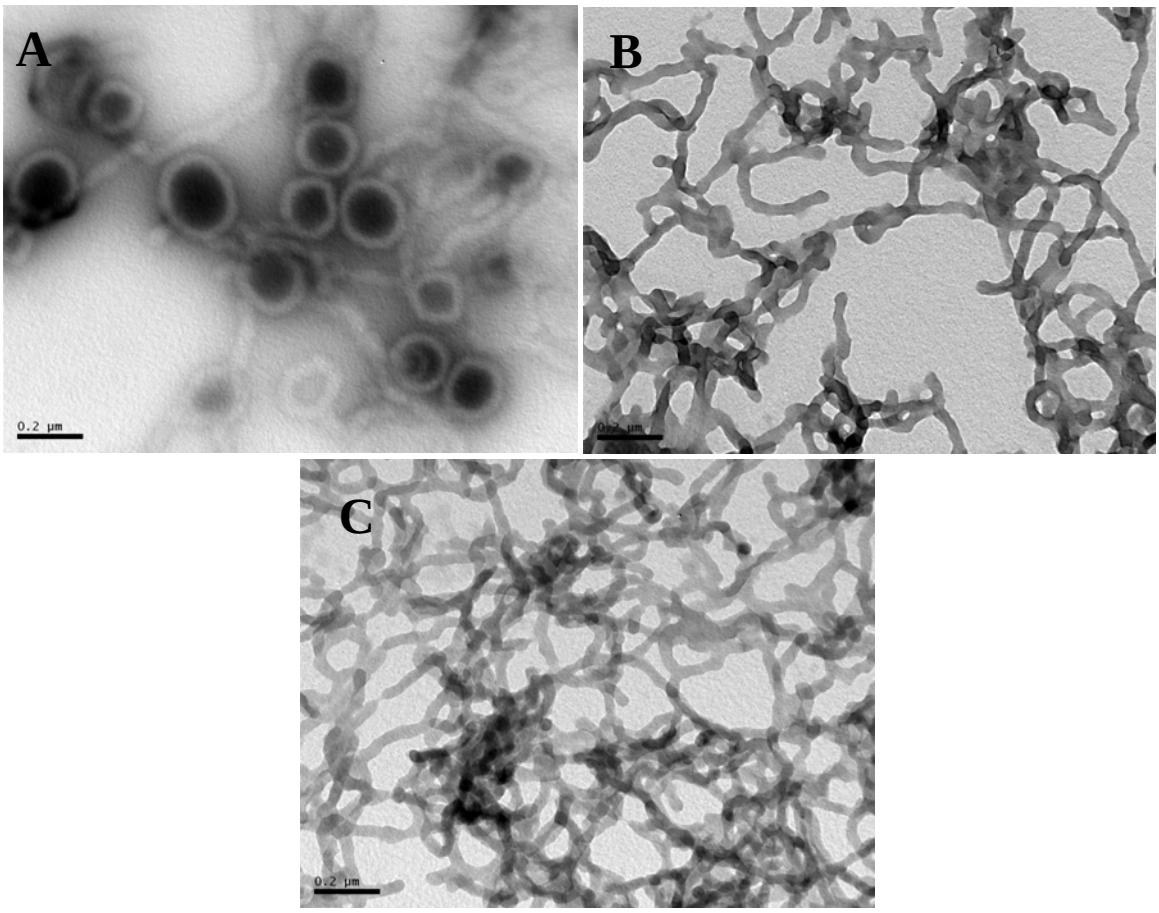

Figure S3 After rapidly heating a system with 0.4 (wt.) % copolymer concentration and 4.35 (wt.) % water concentration in DMF/water in which the original morphology was vesicles at room temperature to 65 ºC, equilibrating for 2h, then quenching to 50 ºC, the morphological changes with time: (a) large compound micelles after 30 min, (b) rod-like micelles after 1h, (c) rod-like micelles after 2h.

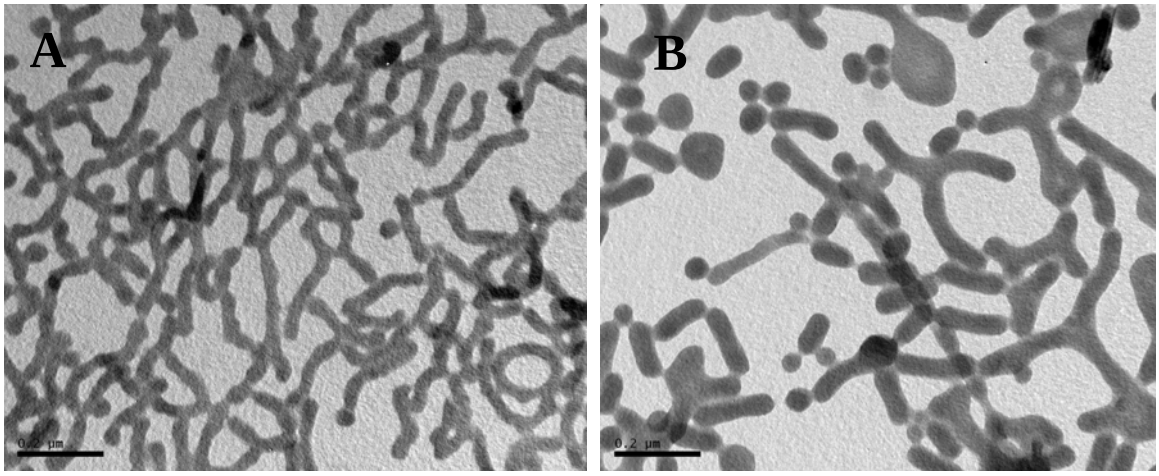

Figure S4 After rapidly heating a system with 0.4 (wt.) % copolymer concentration and 4.35 (wt.) % water concentration in DMF/water in which the original morphology was vesicles at room temperature to 70 ºC, the morphological changes with time: (a) long rods and spheres after 15 min, (b) short rods and spheres after 30 min.

References

1) Quirk, R. P.; Kim, J.; Kausch, C.; Chun, M. S. *Polym. Int.* **1996**, *39*, 3-10.

2) Bhargava, P; Zheng, J. X.; Li, P.; Quirk, R. P.; Harris, F. W.; Cheng, S. Z. D. *Macromolecules* **2006***, 39,* 4880-4888.

3) Zhang, L.; Eisenberg, A. *Polym. Adv. Technol.* **1998**, *9*, 677-699.