Supplementary Material (ESI) for Soft Matter

Supporting Information

Temperature-Induced Reversible Transformation between Toroidal and Cylindrical Assemblies under Shear Flow

Zhida[a,b] Wang and Wei Jiang*[a]

[a] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China*

[b] *Graduate University of the Chinese Academy of Sciences, Beijing 100039, P. R. China*

*to whom the correspondence should be addressed: wjiang@ciac.jl.cn

Experimental Section

Preparation of Micelles

The linear amphiphilic triblock copolymer used in this study is poly(4-vinyl pyridine)-*b*-polystyrene-*b*-poly(4-vinyl pyridine) ($P4VP_{43}$-*b*-PS_{260}-*b*-$P4VP_{43}$, the subscripts indicates the number of repeat units of the blocks; PDI=1.09), which was purchased from Polymer Source Inc., Canada. At first we directly dissolved 0.01 g copolymer in the dioxane/water solvent with 1 ml dioxane and 0.25 ml water respectively in a 5 ml conical flask. The scale of the cylindrical stirring bar used in this study was $\phi 5*15$, i.e., the diameter was 5 mm and the length was 15 mm. The solution was kept stirring for about 96 hours to induce the self-assembly of ring-shaped micelles. Then the solution were heated at different temperature (at the same stirring rate or without stirring for experimental requirement) for about 2 hours (or for varying times for the kinetic studies) to induce the morphological changes. Afterwards a large amount of water (ca. 400%) was added to the resulting solution to quench the micelle morphologies. At this water content range, the structures of the micelles became kinetically locked over the experimental time scale[1]. Finally, the resulting solution was placed in dialysis tubes and dialyzed against distilled water for a few days to remove all of the organic solvent from the solution. Although the PVP block is not soluble in pure water, it is soluble in water below a pH of 5.[2,3] Therefore, during the dialysis process the pH of the distilled water was thus adjusted to 4 by hydrochloric acid (HCl) to keep the colloid solutions from precipitating. The morphology of the micelles was stable during the dialysis process and after the dialysis.

Heating and Cooling Experiments

Rapid heating: We directly putted the small vial containing the toroidal micelle solution into a big oil bath at 60 ^{o}C. We considered that the temperature could be shortly increased to 60 ^{o}C under stirring condition**.**

Slow heating: The system was heated by two steps, i.e., the system was directly heated from 20 ^{o}C to 50 ^{o}C, and kept at this temperature for 2 h, then to 60 ^{o}C.

Rapid cooling: The cylinders formed at 60 ^{o}C are quenched to 20 ^{o}C. We monitored the structure evolution of this solution over time as the solution was kept at 20 ^{o}C.

Slow cooling: We cooled the cylindrical micelle solution from 60 ^{o}C to 20 ^{o}C via two steps. The solution firstly was cooled to 40 ^{o}C and kept at 40 ^{o}C for 12 h, then the same solution was further cooled to 20 ^{o}C and kept at 20 ^{o}C for 48 h. The cooling curve is given in Figure S4. The micelles were extracted from the same solution at different stages. Figure 3e and Figure 3g were obtained by TEM after the micelles cooled from 60 ^{o}C to 40 ^{o}C and kept at 40 ^{o}C for 4 h and 12 h, respectively. Figure 3h was the TEM image of the micelles which were further cooled from 40 ^{o}C to 20 ^{o}C and kept at 20 ^{o}C for 48 h, i.e., the final state in the slow cooling.

Atomic Force Microscopy (AFM)

SPA-300 atomic force microscopy was operated at the tapping mode with a SPI3800 controller (Seiko instruments Industry Co. Ltd.). The tip type was sharpened tetrahedral (R<10 nm, tip height 14 μm) and the contilever used was fabricated from silicon with a spring constant of 2 N/m and a resonance frequency of 70 Hz. To prepare the samples for AFM, a drop of the very dilute solution after dialysis was dropped onto the freshly cleaved mica substrates. All of the samples were dried in air and at room temperature for 1 day before observation. The experiments were all performed in atmosphere and at room temperature.

Transmission Electron Microscopy (TEM)

Regular TEM was performed on a JEOL JEM-1011 transmission electron microscopy operated at an acceleration voltage of 100 kV to directly observe the morphologies of aggregates. A drop of the solution was strawed and placed onto TEM copper grid covered by a polymer support film precoated with carbon thin film. After a while, excess solution was blotted away using a strip of filter paper. The samples were allowed to dry in atmosphere and at room temperature for 1 day before observation.

Dynamic Light Scattering (DLS)

To understand the hydrodynamic radius (R_h) changes of the micelles, dynamic light scattering (DLS) experiments were conducted on a Multi-angle Light Scattering

(MALS) instrument equipped with a digital correlator (QELS [690 nm]) at 90°. Water was firstly filtered with a 0.22 μm Millipore filter into a clean scintillation vial. The stock micelle solutions were filtered through a 450 nm Millipore filter into a clean scintillation vial. All the DLS measurements were carried out at 90° scattering angle at room temperature.

Field Emission Scanning Electron Microscopy (SEM)

SEM measurements were performed on a XL 30 E-SEM (FEG, Micrion FEI PHILIPS) operated at an acceleration voltage of 20 kV. For preparing the samples for SEM, a drop of dilute micellar solution after dialysis was dropped onto the cleaned silicon (Si) wafers. Prior to coating, the silicon substrates were cleaned in a bath of 100 mL of 80% H_2SO_4, 35 mL of H_2O_2, and 15 ml of deionized water for 15 min at 80 °C and rinsed several times in deionized water. The silicon surface was then dried with compressed nitrogen gas. The coated substrates were then dried in air and at room temperature for 1 day to let the micelles set on the Si wafer. Then, the samples were coated with a thin layer of gold (Au). The Au layer coating time and density for all of the samples were under same condition to reduce the standard error of the measurement.

Supporting Figures

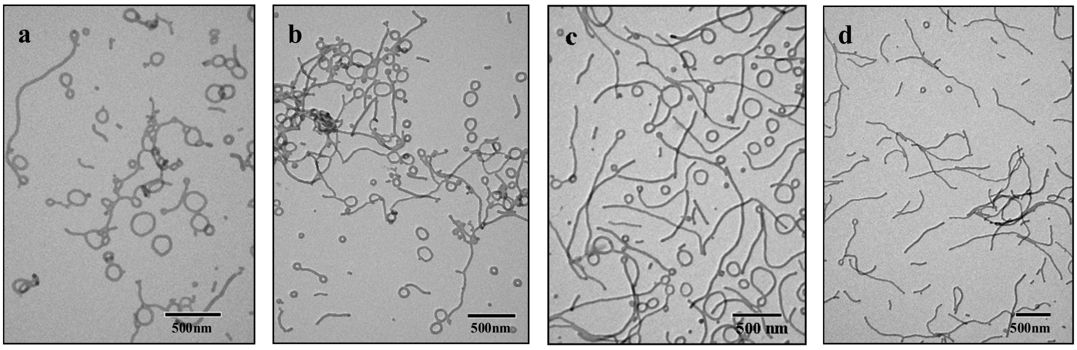

Figure S1. After rapidly heating ring-shaped micelles to 60 ^{o}C under fixed stirring rate of 800 rpm for a system with 0.8 wt % copolymer concentration and 19.3 wt % water content in dioxane/water solvent, the morphological changes with time: (a) 2 min; (b) 10 min; (c) 20 min. (d) 40 min.

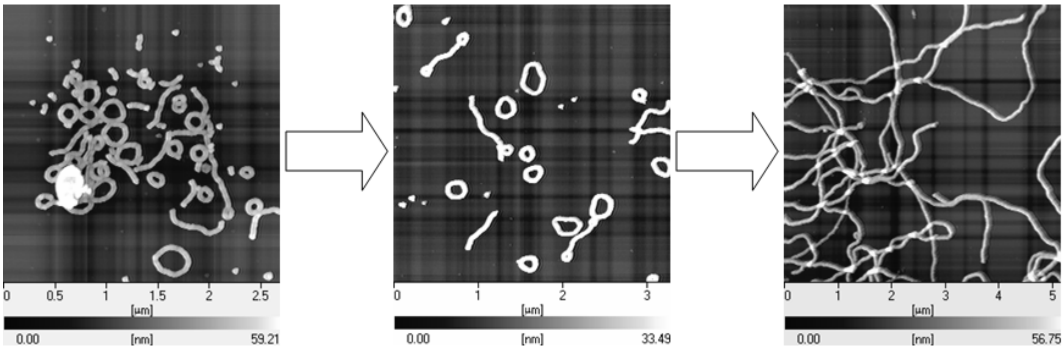

Figure S2. AFM height images of variation of micellar morphology with increasing time at 60 ^{o}C under a fixed stirring rate of 800 rpm for a system with 0.8 wt % copolymer concentration and 19.3 wt % water content in dioxane/water solvent. (a) Toroidal micelles formed at 20 ^{o}C, (b) 10 min, (c) 40 min.

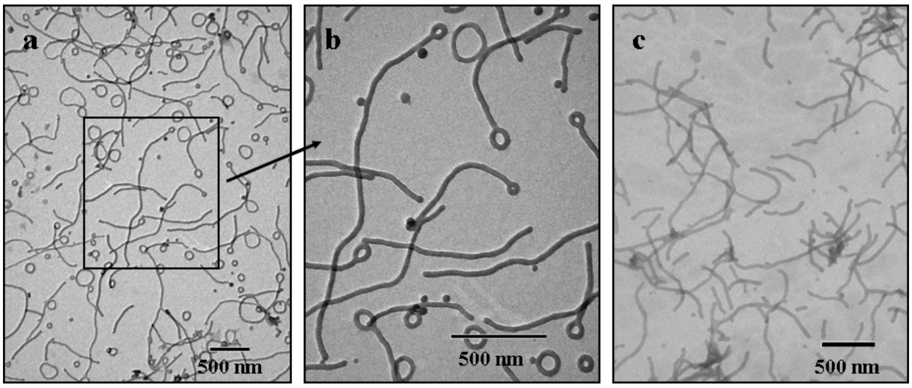

Figure S3. Morphological changes in slow heating under a fixed stirring rate of 800 rpm for a system with 0.8 wt % copolymer concentration and 19.3 wt % water content in dioxane/water solvent. (a) TEM images of ring with long tail as rings were rapidly heated to 50 ^{o}C and equilibrated at 50 ^{o}C for 2 h; (b) is the enlarged part boxed in (a); (c) rod-like micelles after rings were rapidly heated to 50 ^{o}C, equilibrated for 2 h, then heated to 60 ^{o}C and kept at 60 ^{o}C for 2 h.

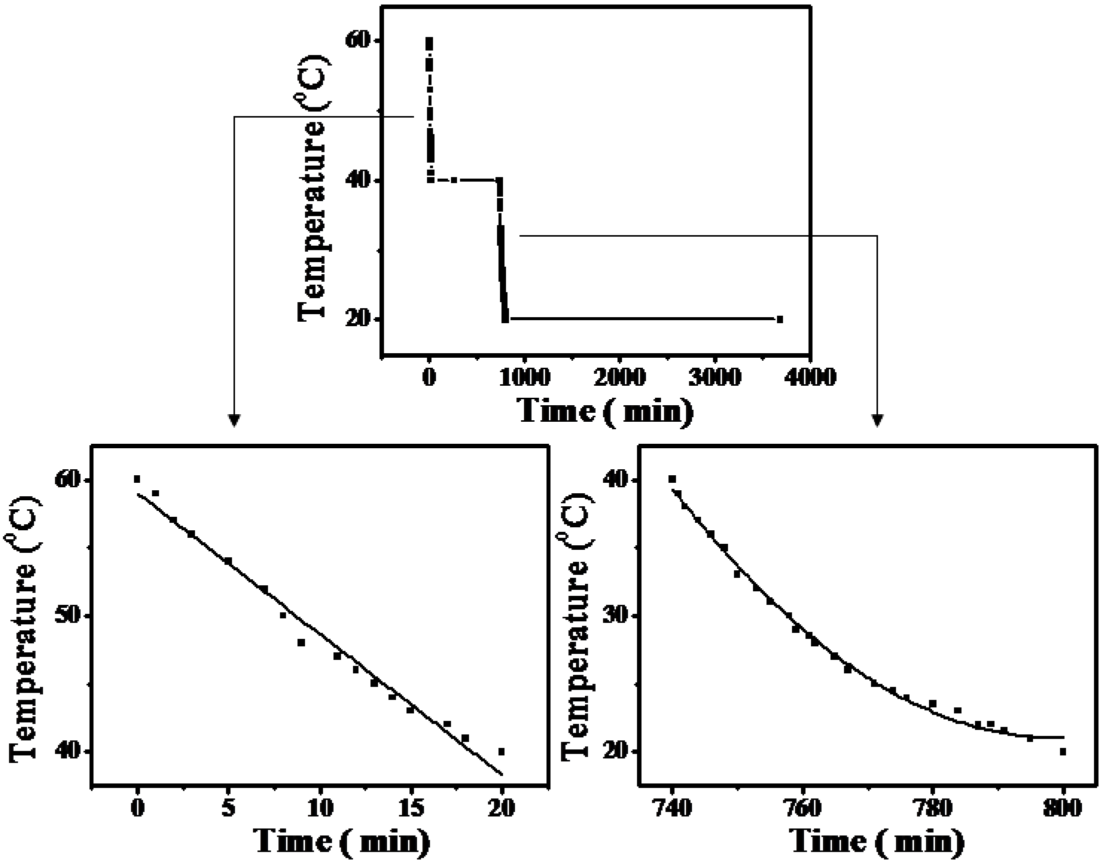

Figure S4. Slowly (two step) cooling curve and local enlarged curves for a system with 0.8 wt % copolymer concentration and 19.3 wt % water content in dioxane/water solvent under a fixed stirring rate of 800 rpm. Temperature decreasing from 60 to 40 °C in 20 min and kept at 40 °C for 12 h, then to 20 °C in 60 min, and kept at 20 °C for 48 h.

Supporting reference

(1) L. Zhang, A. Eisenberg, *Macromolecules*, 1999, **32**, 2239.
(2) J. T. Zhu, W. Jiang, *Macromolecules*, 2005, **38**, 9315.
(3) H. Shen, L. Zhang, A. Eisenberg, *J. Am. Chem. Soc.*, 1999, **121**, 2728.