Supporting Information

Temperature-Induced Ordering and Gelation of Star Micelles based on ABA Triblocks Synthesized via Aqueous RAFT Polymerization‡

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Experimental Section

Materials. All chemicals were purchased from Fischer or Aldrich at the highest available purity and used as received unless otherwise noted. N,N-dimethylacrylamide (DMA) was vacuum distilled and N-isopropylacrylamide (NIPAM) was recrystallized from hexane. 2,2’-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) was used as the initiator (gift from Wako chemicals USA, Inc.). The difunctional chain transfer agent (CTA) 2-(1-Carboxy-1-methylene)sulfanyltiocarbonylsulfanyl)-2-methylpropionic acid (CMP) was used without further purification (gift from Noveon, Inc.).

Synthesis of DMA MacroCTA. Polymerization conditions were followed according to prior literature reports. Briefly, the polymerization was conducted for 3 h at 25 °C in aqueous media at pH 4.7 with an initial monomer concentration ([M]₀) of 0.5 M. A [CTA]₀:[I]₀ ratio of 5:1 was utilized in each polymerization while three ratios of [M]₀:[CTA]₀ were utilized in separate polymerizations, 200:1, 400:1, and 600:1. To synthesize the macroCTA, the following components were added to a 250 mL round bottom flask: DMA, CMP, VA-044 and DI water to bring the final volume to 140 mL. The pH was adjusted to a value of 4.7. The flask was sealed with a rubber septum and purged with nitrogen for 30 min at 5 °C. The flask was then immersed in a 25 °C water bath for 3 h before quenching by rapid cooling and exposure to oxygen. The DMA macroCTA was purified by dialysis and lyophilization.

Chain Extension of DMA MacroCTA. Polymerization conditions were followed according to prior literature reports. Briefly, the polymerization was conducted at 25 °C in aqueous media at pH 5.0 with an initial monomer concentration ([M]₀) of 0.5 M. A [CTA]₀:[I]₀ ratio of 1:1 was utilized in each polymerization. To chain extend the macroCTA, the following components were added to a round bottom flask: NIPAM, DMA macroCTA, VA-044, and DI water to bring the
final volume to 200 mL. The pH was adjusted to a value of 5.0. The polymerization solutions were purged with nitrogen for 30 min at 5 °C. The flasks were then immersed in a 25 °C water bath for 1 h before quenching by rapid cooling and exposure to oxygen. The triblock copolymers were purified by dialysis and lyophilization.

**Gel Permeation Chromatography.** Utilizing triple detection gel permeation chromatography (GPC), $M_n$, $M_w$, and polydispersity indices (PDIs) for (co)polymers were determined. A 20 mM LiBr DMF eluent at 60 °C was used at a flow rate of 1.0 mL/min. Viscotek I-Series Mixed Bed low MW and mid MW columns were utilized on a Viscotek-TDA (302 nm RI, viscosity, 7 mW 90° and 7° true low angle light scattering detectors, 670 nm). The $dn/dc$ of each polymer was determined at 632.8 nm in DMF at 60 °C using a Viscotek refractometer and Omnisec software. The $M_n$ of the inner blocks was determined by taking the difference between the $M_n$ of the triblock copolymer and homopolymer.

**Dynamic Light Scattering.** Dynamic light scattering studies of the block copolymer micelles in aqueous solution were conducted using Malvern Instruments Zetasizer Nano Series instrument equipped with a 22 mW He-Ne laser operating at $\lambda=632.8$ nm, an avalanche photodiode detector with high quantum efficiency, and an ALV/LSE-5003 tau digital correlator electronics system. Samples (1 mg/ml) were allowed to dissolve in deionized water overnight. Temperature was increased from 25 °C to 50 °C in increments of 1 °C. Samples were allowed to equilibrate for 10 min between measurements.

**Rheometric Studies.** Rheological tests were performed with a Rheometrics SR-5000 controlled stress rheometer. A 25 mm cone and plate geometry with an angle of 0.1 radians was utilized for all measurements. An insulated ring was placed around the geometry to prevent water evaporation. Before performing measurements, the polymers were allowed to dissolve overnight.
in either deionized water or 140 mM NaCl/20 mM phosphate buffer. In order to determine the polymers were tested within the linear viscoelastic regime, dynamic frequency sweep experiments were conducted in triplicate (temperature maintained at 50 °C with a water bath, 1 Pa). The storage modulus at 50 °C was determined as the value obtained at 1 rad/s. Samples were allowed to equilibrate for 3 min prior to testing. Dynamic temperature ramp tests were conducted utilizing a Peltier plate to heat the sample at a rate of 1.0 °C min⁻¹. Copolymer solutions were presheared for 2 min at a constant applied shear stress of 5 Pa before dynamic temperature ramp measurements were taken at a frequency of 1 rad/s and stress of 1 Pa. Temperature cycling experiments were conducted using a frequency and stress of 1 rad/s and 1 Pa, respectively. A peltier plate was utilized to cycle the temperature between 25 and 50 °C at a ramp rate of 50 °C min⁻¹.

Small Angle X-ray Scattering. SAXS profiles were acquired using a seal-tube source, a compact Kratky camera with a controlled hot-stage, and a one-dimensional position-sensitive detector. Samples were allowed to dissolve in DI water overnight in a scintillation vial. Samples were subsequently loaded into the samples cell and heated to the acquisition temperature for 1 h before a 30 min SAXS profile was acquired. SAXS traces were acquired under a positive pressure of helium. Data reduction was carried per previous reports to desmear absolute intensity.²,³ CuKa x-rays were employed.

Figure S1. Storage modulus data as a function of frequency for 20 wt% P(DMA$_{93}$-$b$-NIPAM$_{213}$-$b$-DMA$_{93}$) (■), P(DMA$_{93}$-$b$-NIPAM$_{372}$-$b$-DMA$_{93}$) (●), P(DMA$_{197}$-$b$-NIPAM$_{392}$-$b$-DMA$_{197}$) (▲), P(DMA$_{250}$-$b$-NIPAM$_{600}$-$b$-DMA$_{250}$) (▼) gels at 50 ºC.