Supporting Information

to

Reversible Polymer Nanostructures by Regulating SDS/PNIPAM Binding

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EXPERIMENTAL

Materials

Unless otherwise stated, all chemicals were used as received. The solvents used were of either HPLC or AR grade; these included dichloromethane (DCM; Aldrich AR grade), dimethylformamide (DMF; Aldrich, AR grade) and tetrahydrofuran (THF; Labscan, HPLC grade). Activated basic alumina (Aldrich: Brockmann I, standard grade, ~ 150 mesh, 58 Å), MilliQ water (Biolab, 18.2 MΩm), sodium dodecyl sulphate (SDS: Aldrich, 99 %), triethylamine (TEA; Fluka, 99%) and methyl-2-bromopropionate (MBP; Aldrich, 98%) were used as received. Styrene (STY: Aldrich, >99 %) was passed through a basic alumina column to remove inhibitor. *N*-isopropylacrylamide (NIPAM: Aldrich, 97 %) was recrystallized from hexane, and azobisisobutyronitrile (AIBN: Riedel-de Haen) was recrystallized from methanol twice prior to use. RAFT agent methyl 2-(butylthiocarbonothioylthio)propanoate (MCEBTTC) was synthesized according previous procedure.[1]

Techniques

Size Exclusion Chromatography (SEC) Size Exclusion Chromatography measurements were performed using a Waters Alliance 2690 Separations Module equipped with an auto-sampler, Differential Refractive Index (RI) detector and a Photo Diode Array (PDA) detector connected in series. HPLC grade tetrahydrofuran was used as eluent at flow rate 1 mL/min. The columns consisted of two 7.8 x 300 mm Waters linear Ultrastyragel SEC columns connected in series. Polystyrene standards were used for calibration.

Transmission Electron Microscopy (TEM) The nanostructure appearance of the polymer latex was analyzed using a JEOL-1010 transmission electron microscope utilizing an accelerating voltage of 100 kV with spot size 6 at ambient temperature. A typical TEM grid preparation was as follows: A polymerization mixture was diluted with Milli-Q water to approximately 0.05 wt%. A formvar precoated copper TEM grid was then dipped in the diluted latex solution and dried on the filter paper at 25 °C.

^{1}H Nuclear Magnetic Resonance (NMR) Spectroscopy All NMR spectra were recorded on a Bruker DRX 500 MHz spectrometer.

Matrix-Assisted Laser Desorption Ionization-Time-of-Flight (MALDI-ToF) Mass Spectrometry

MALDI-ToF MS spectra were obtained using a Bruker MALDI-ToF autoflex III smart beam equipped with a nitrogen laser (337 nm, 200 Hz maximum firing rate) with a mass range of 600-400 000 Da. Spectra were recorded in both reflectron mode (2000-5000 Da) and linear mode (5000-20000 Da). Trans- 2-[3-(4-tert-butylphenyl)-2-methyl-propenylidene] malononitrile (DCTB; 20 mg/mL in THF) was used as the matrix and Na(CF3COO) (1 mg/mL in THF) as the cation source. Samples were prepared by co-spotting the matrix (20 μL), Na(CF3COO) (1 μL), and polymer (20 μL, 1 mg/mL in THF) solutions on the target plate.

Dynamic Light Scattering (DLS) Dynamic Light Scattering measurements were performed using a Malvern Zetasizer Nano Series 3000HS running DTS software and operating a 4 mW He-Ne laser at 633 nm. Analysis was performed at an angle of 173^o. The sample refractive index (RI) was set at 1.59 for polystyrene. The dispersant viscosity and RI were set to 0.89 and 1.33 Ns/m^2, respectively.

Synthesis and Procedure

(a) Synthesis of PNIPAM$_{43}$-SC(=S)SC$_4$H$_9$ by RAFT Polymerization. NIPAM (15 g, 0.133 mol), RAFT agent MCEBTTC (0.75 g 3.0 x 10^{-3} mol) and AIBN (50 mg, 3.0 x 10^{-4} mol) were dissolved in 30 mL of DMSO. The solution was purged with Ar for 30 min. The reaction solution was then immersed in preheated oil-bath at 60 ^{o}C for 16 h. The reaction was stopped by cooling in ice-bath and exposing the solution to the air. The polymerization mixture was then diluted by 500 mL of DCM and washed five times with Milli-Q water. The organic phase was dried over $MgSO_4$, filtered, concentrated and precipitated in diethyl ether. After filtration, the yellow powder was dried under vacuum at R.T. for 48 h. ($M_{n,SEC} = 4200$), the repeating units was calculated based on ^1H NMR.

^1H NMR ($CDCl_3$, 298K, 500 MHz); 6.47 (b, -N*H*-C=O- of poly(NIPAM) repeating units), 4.62 (b, 1H, -C*H*-SC(=S)S-C_4H_9), 3.97 (b, -NH-C*H*(CH_3)$_2$ of poly(NIPAM) repeating units), 3.66 (b, 3H, C*H*$_3$O-RAFT residual group) 3.34 (b, 2H, -SC(=S)S-C*H*$_2$$C_3H_7$), 1.06-2.45 (b, methylene and methine protons of poly(NIPAM) backbone), 1.12 (b, methyl protons of poly(NIPAM) repeating units), 0.90 (b, 6H, methyl protons of RAFT residual group).

(b) Synthesis of PNIPAM$_{43}$-b-PSTY$_{40}$ Latex by RAFT-mediated Aqueous Dispersion Polymerization. Typically, to a 50 mL Shlenck flask, PNIPAM$_{43}$-SC(=S)SC_4H_9 0.70 g (1.46×10^{-4} mol) and SDS 29.0 mg (1.0×10^{-4} mol) were added in 12.5 ml Milli-Q water and stirred in an ice-bath until the solid dissolved. The solution was purged with Ar for 20 min then STY (0.70 g, 6.72×10^{-3} mol) and AIBN (2.4 mg, 1.46×10^{-5} mol) was added to the solution via a syringe. After further purging with Ar for another 5 min, the reaction vessel was then immersed in a 70 °C oil bath. The reaction solution turned from clear to a two phase yellow solution and then to a white emulsion in a few minutes. After 3.5 h of polymerization, the reaction vessel was removed from oil bath and opened to the air to stop the polymerization ($M_{n,SEC} = 8200$, PDI=1.09).

(c) Temperature Directed Morphology Transformations (TDMT) by Adding Different Amount of Toluene.

Various 3D structures were formed by cooling the above latex below the LCST. Three methods were used to produce these 3D structures. All three methods gave near identical 3D structures when the latex was cooled below the LCST.

(i) *Removal of unpolymerized styrene*. The latex solution was further heated at 70 ^{o}C for 4 h to remove most of the unpolymerized STY monomer. Then 0.5 mL of the copolymer latex solution was then added into a vial containing different amounts of toluene ranging from 0, 10, 20, 50, 80, 100 µL at 25 ^{o}C. This mixture was shaken for 10 s, and allowed to cool to room temperature. The TEM images are given in Figure 1 in the main text.

(ii) *Without removing unpolymerized STY monomer*. 0.5 mL of the copolymer latex solution was added into a vial containing different amounts of toluene, ranging from 0, 10, 20, 50, 80, 100 µL at 25 ^{o}C. The mixture was shaken for 10 s and allowed to cool to room temperature (see Figure S5).

(iii) *Without removing unpolymerized STY monomer and diluting in water*. 0.5 mL of the copolymer latex without removing STY monomer was added into a vial containing 1.67 mL of Milli-Q water and different amounts of toluene ranging from 0, 10, 20, 50, 80, 100 µL at 25 ^{o}C. The mixture was shaken for 10 s and cooled to room temperature (see Figure 2A-D in main text).

(d) SDS Directed Morphology Transformations. The 3D structures prepared above (section (iii) in procedure (c) above) by the TDMT method at room temperature were then treaded with SDS. The amount of SDS added was 3.94 mg, the mixture shaken for 10 s and the resultant structures analyzed by TEM (see Figure 2E-H in main text) and DLS.

(e) SDS Directed Morphology Transformations of worm structures. The copolymer latex solution (0.5 mL) prepared from section (iii) in procedure (c) above was added to a mixture of water (1.67 mL), toluene (10 μL) and increasing amounts of SDS (0 to 1 eq of the cmc) at 25 °C, and the mixture shaken for 10 s. The structures from the resulting mixtures were analyzed by TEM (see Figure S6).

(f) Reorganization of various nanostructures from nanospheres. The nanospheres obtained via the procedure **(e)** (nanoworm cut by adding SDS at 0.8 eq cmc) were freeze-dried to remove toluene and STY monomer. The powdery nanospheres were suspended in Milli-Q water and dialyzed against 1 L of Milli-Q water at 40 °C (dialysis tubing, MWCO = 3500) to remove the SDS. The water was changed 6 times during 24 h. The nanospheres were then recovered by freeze-drying. The powdery nanospheres were re-suspended in Milli-Q water to give an 8 wt % water latex solution and then heated up to 70 °C. 100 μL of this hot latex solution was added to different vials with 0, 2, 4, 10 and 16 μL toluene correspondingly and cooled down to 25 °C. The yielded latex solutions were then characterized by TEM. (see Figure 3 in the paper).

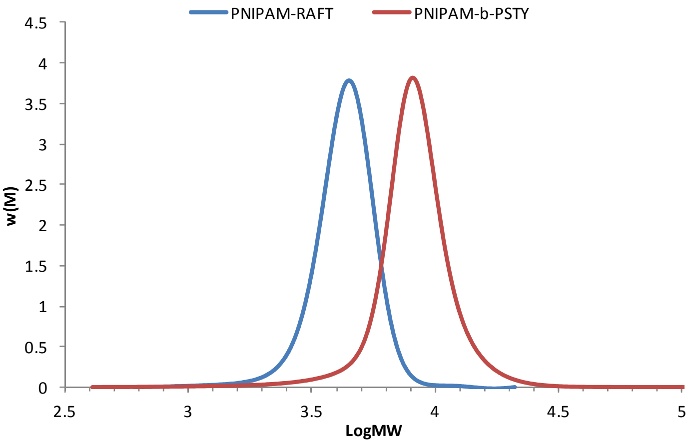

Figure S1. SEC traces of of $PNIPAM_{43}$-RAFT (—) by RAFT solution polymerization in DMSO at 60 °C and $PNIPAM_{43}$-b-$PSTY_{40}$ (—) by RAFT-mediated aqueous dispersion polymerization at 70 °C.

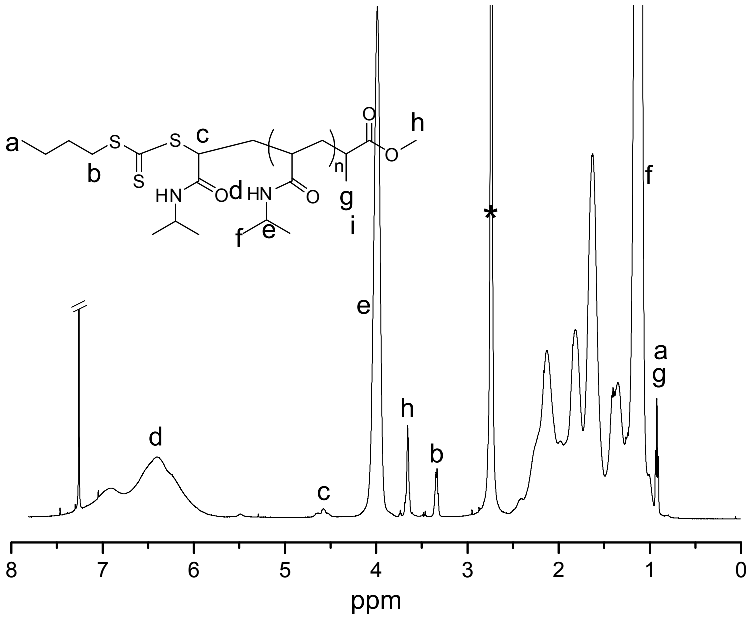

Figure S2. ^{1}H NMR of PNIPAM$_{43}$-RAFT in $CDCl_3$ at 500 MHz, * is water.

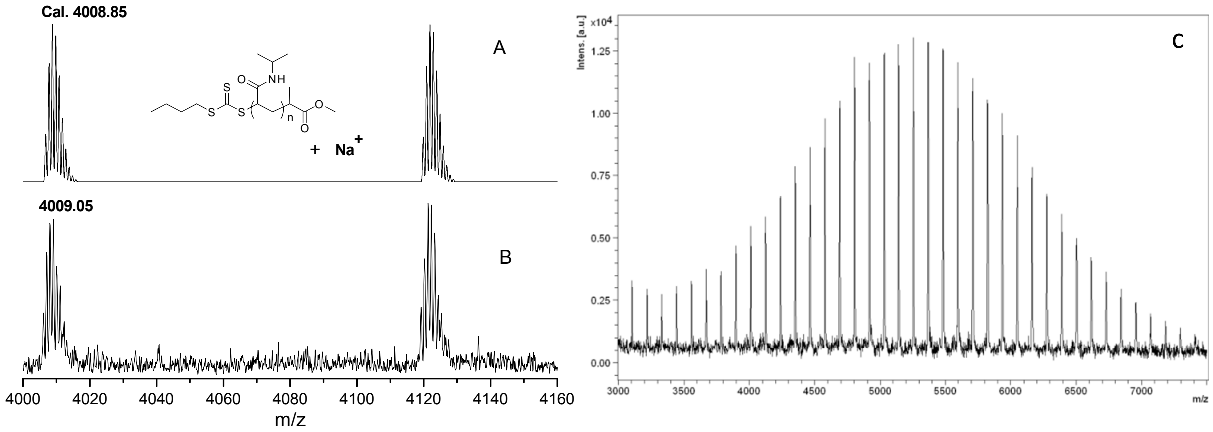

Figure S3. MALDI-TOF-MS of PNIPAM$_{43}$-RAFT synthesized by RAFT polymerization in DMSO at 60 ^{o}C, (A) is calculated isotopic resolution and (B) is recorded resolution and (C) full spectrum.

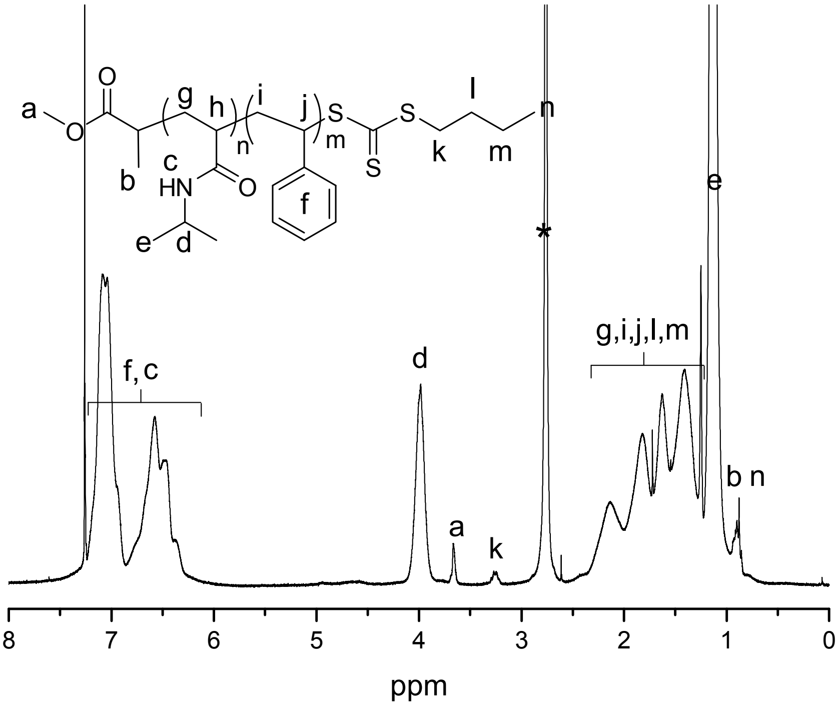

Figure S4. ^{1}H NMR of PNIPAM$_{43}$-b-PSTY$_{40}$ in CDCl$_3$ at 500 MHz which was synthesized by RAFT-mediated aqueous dispersion polymerization * is water.

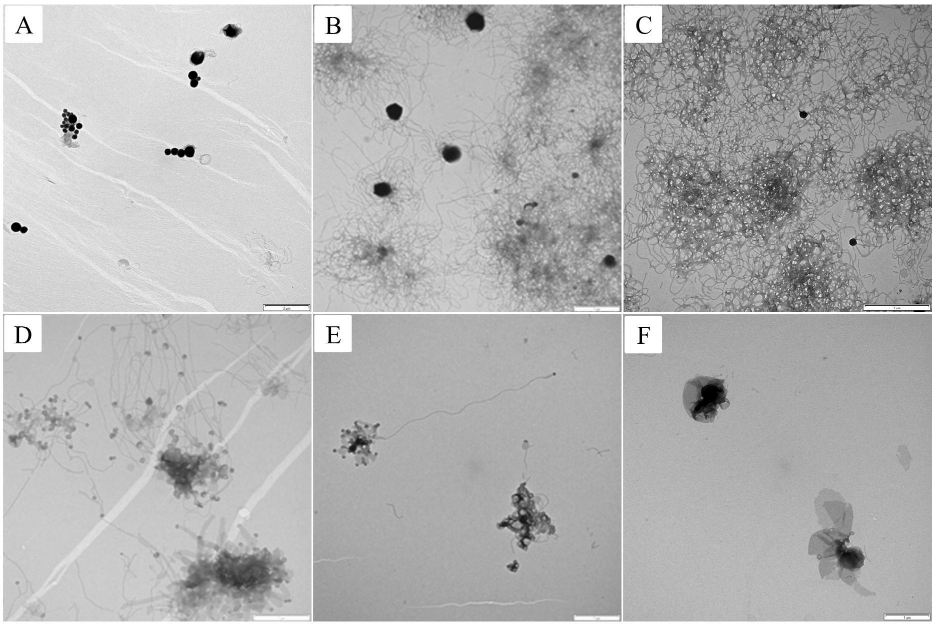

Figure S5. TEM images of temperature directed morphology transformations by adding various amount of toluene to the PNIPAM$_{43}$-b-PSTY$_{40}$ latex solution (~8 wt %) obtained via aqueous dispersion polymerization. A 0.5 mL volume of the polymer latex solution (without removing STY) was added to a mixture of water (1.67 mL) and different amounts of toluene (A) 0 µL, (B) 10 µL, (C) 20 µL (D) 50 µL; (E) 80 µL and (F) 100 µL as plasticizer, and the mixture was allowed to cool further to room temperature. Scale bar 1 µm.

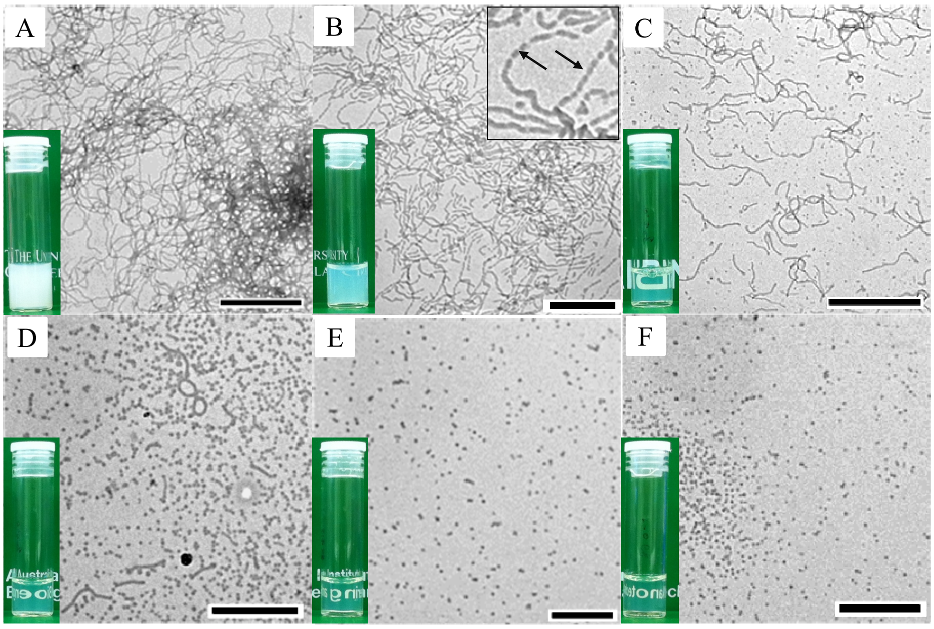

Figure S6. TEM images of TDMT from PNIPAM$_{43}$-b-PSTY$_{40}$ copolymer latex solution by adding 0.5 mL latex to 10 μL oftoluene, water (1.67 mL) and different concentrations of SDS (0 to 1.0 equivalent cmc). (A) 0 eq; (B) 0.2 eq; (C) 0.4 eq; (D) 0.6 eq; (E) 0.8 eq and (F) 1.0 eq; scale bars for (A), and (C) were 1 μm and (B), (D), (E) and (F) were 500 nm. Insets are the photos of the nanostructure solution after being treated with corresponding amount of SDS.

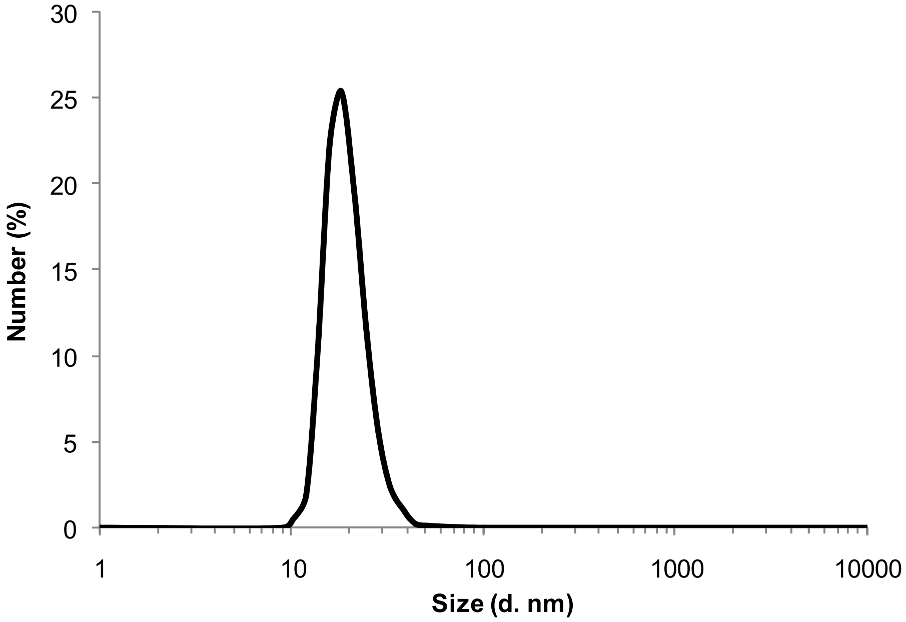

Figure S7. DLS of the nanospheres formed after adding SDS (0.8 eq of the cmc) to the worms and shaken for 10 s before the measurement, D_h=19.2 nm (PDI = 0.22).

(1) Truong, N. P.; Jia, Z. F.; Burges, M.; McMillan, N. A. J.; Monteiro, M. J. *Biomacromolecules* **2011,** *12*, 1876-1882.