

Supporting Information for:

Thermo-responsive ABA triblock copolymer of PVEA-*b*-PNIPAM-*b*-PVEA

showing double LCST in the methanol/water mixture

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1. The ^1H NMR spectrum of VEA

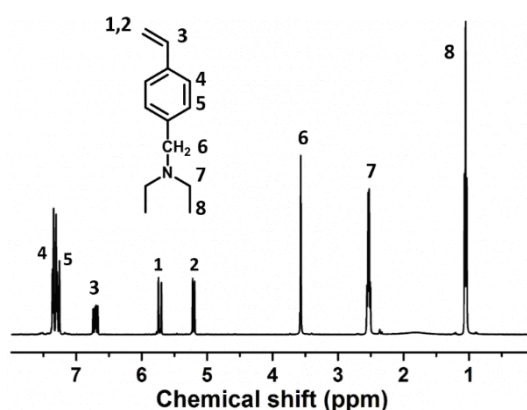


Figure S1. The ^1H NMR spectrum of VEA

2. Synthesis and characterization of PNIPAM₁₈₃ by RAFT polymerization

Into a Schlenk flask, NIPAM (1.3584 g, 12.0 mmol), BDMAT (0.0171 g, 0.060 mmol), AIBN (3.28 mg, 0.02 mmol), and 1,4-dioxane (2.8 mL) were added. The solution was initially degassed with nitrogen at 0 °C for 30 min, and then the flask content was immersed into a preheated oil bath at 70 °C. After 100 min, the reaction was quenched by cooling to 0 °C, an aliquot was withdrawn to determine the

monomer conversion by ^1H NMR analysis. The NIPAM monomer conversion was calculated according to eq 2. The synthesized polymer was precipitated into cold diethyl ether and dried at room temperature under vacuum.

The ^1H NMR spectrum and GPC traces of the synthesized PNIPAM₁₈₃ are shown in Figure S2 and S3, respectively.

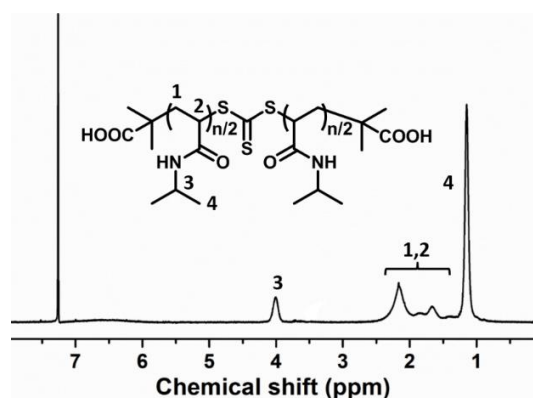


Figure S2. The ^1H NMR spectrum of PNIPAM₁₈₃.

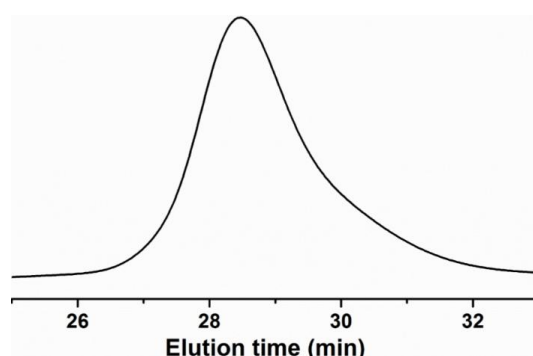


Figure S3. The GPC traces of PNIPAM₁₈₃.

3. Solubility of PVEA₄₀ in the methanol/water mixture

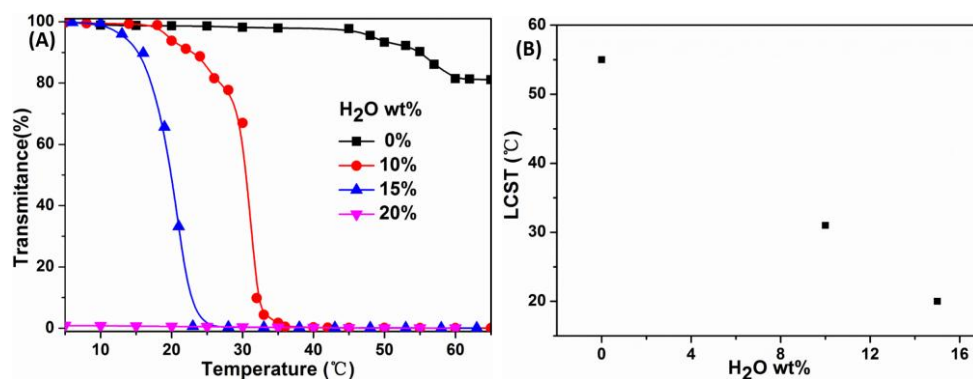


Figure S4. Transmittance versus temperature plots (A) and the water content dependent LCST of PVEA₄₀ (B) in the methanol/water mixture. The polymer concentration is 1.0 wt%.

4. Solubility of PNIPAM₁₈₃ in the methanol/water mixture

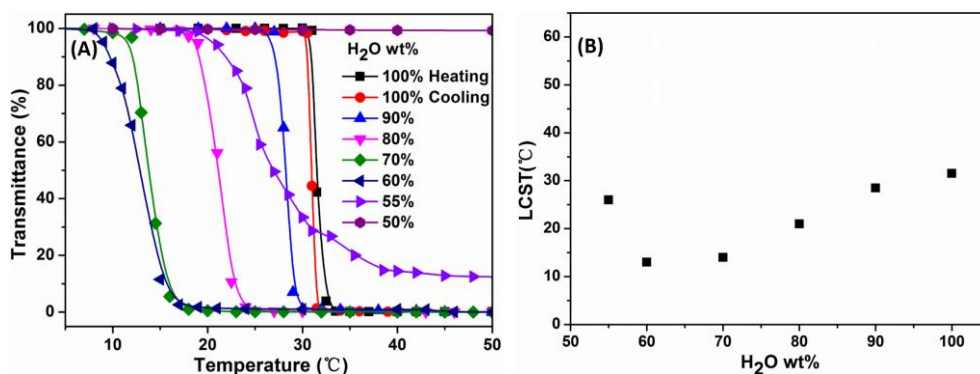


Figure S5. Transmittance versus temperature plots (A) and the water content dependent LCST of PNIPAM₁₈₃ (B) in the methanol/water mixture. The polymer concentration is 0.1 wt%.

5. Dilution of the PVEA₃₂-*b*-PNIPAM₁₉₀-*b*-PVEA₃₂ micellar dispersion

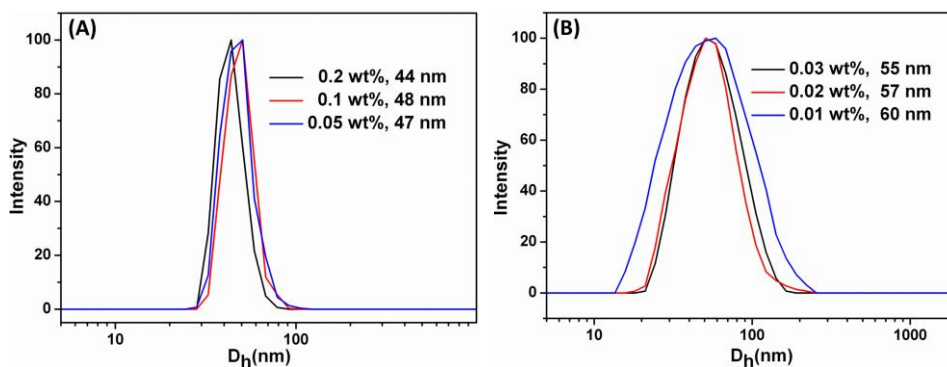


Figure S6. The intensity-weighted hydrodynamic diameter (D_h) distribution of the V₃₂N₁₉₀V₃₂ triblock copolymer (A) in the 80/20 methanol/water mixture at 50 °C and (B) in water at 20 °C.

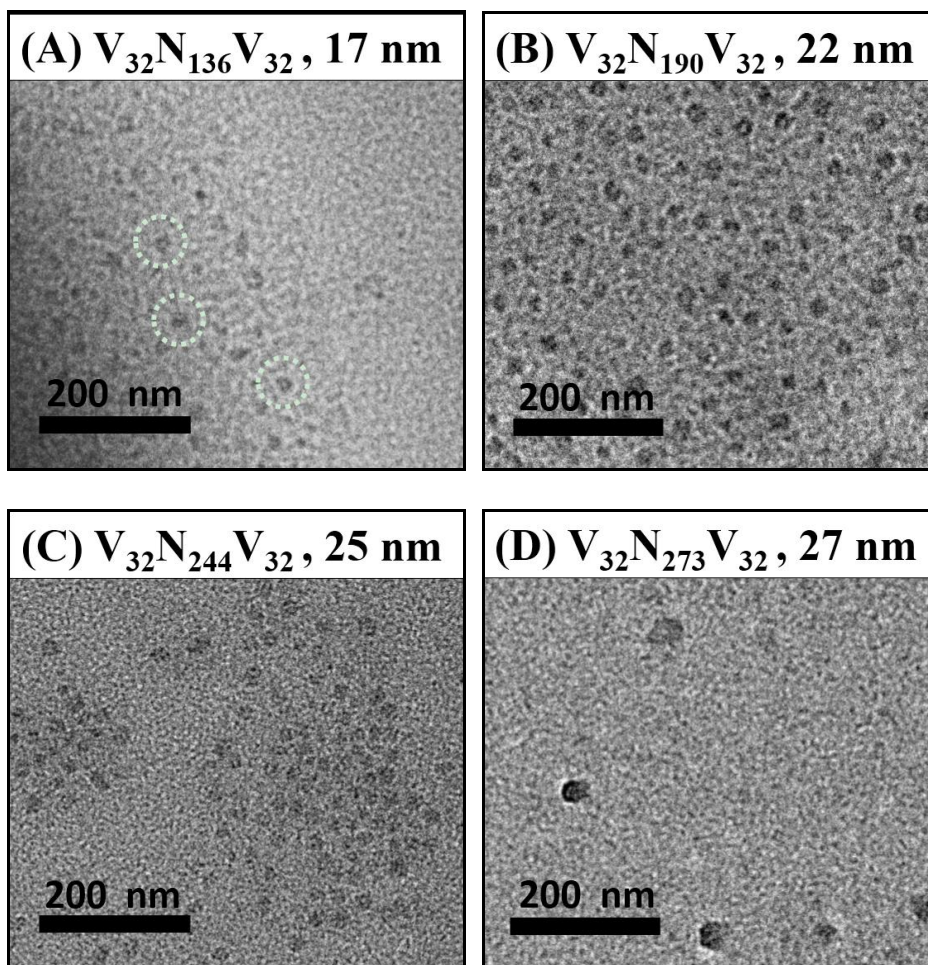


Figure S7. TEM images of the triblock copolymer micelles of $V_{32}N_{136}V_{32}$ (A), $V_{32}N_{190}V_{32}$ (B), $V_{32}N_{244}V_{32}$ (C) and $V_{32}N_{273}V_{32}$ (D) in water at temperature (20 °C) below the LCST of the looped PNIPAM corona.