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 $^1$H NMR spectrum of VEA

![Figure S1. The $^1$H NMR spectrum of VEA](image)

2. Synthesis and characterization of PNIPAM$_{183}$ 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into a preheated oil bath at 70 °C. After 100 min, the reaction was quenched by cooling to 0 °C, an aliquot was withdrawn to determine the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 $^1$H 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 $^1$H NMR spectrum and GPC traces of the synthesized PNIPAM$_{183}$ are shown in Figure S2 and S3, respectively.

![Figure S2. The $^1$H NMR spectrum of PNIPAM$_{183}$.](image)

![Figure S3. The GPC traces of PNIPAM$_{183}$.](image)

3. Solubility of PVEA$_{40}$ in the methanol/water mixture
**Figure S4.** Transmittance versus temperature plots (A) and the water content dependent LCST of PVEA$_{40}$ (B) in the methanol/water mixture. The polymer concentration is 1.0 wt%.

4. **Solubility of PNIPAM$_{183}$ in the methanol/water mixture**

![Transmittance versus temperature plots](image)

**Figure S5.** Transmittance versus temperature plots (A) and the water content dependent LCST of PNIPAM$_{183}$ (B) in the methanol/water mixture. The polymer concentration is 0.1 wt%.

5. **Dilution of the PVEA$_{32}$-b-PNIPAM$_{190}$-b-PVEA$_{32}$ micellar dispersion**

![Intensity-weighted hydrodynamic diameter distribution](image)

**Figure S6.** The intensity-weighted hydrodynamic diameter ($D_h$) distribution of the V$_{32}$N$_{190}$V$_{32}$ 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.