In situ synthesis of thermo-responsive ACB triblock terpolymer nanoparticles through seeded RAFT polymerization

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1 Equations:

$$Conversion(\%) = \frac{5I_{5.16} - 3I_{5.56}}{5I_{5.16}} \quad \text{(S1)}$$

$$M_{n,NMR,\,PDMAEMA-b-PS-b-PNIPAM} = \frac{2(I_{4.22-3.88} - I_{2.57})}{I_{2.57}} \times DP_{PDMAEMA} \times M_{n,NIPAM} + M_{n,NMR,\,PDMAEMA-b-PS} \quad \text{(S2)}$$

2Experimental

2.1 Synthesis of $PNIPAM_{92}$-TTC

The PNIPAM-TTC macro-RAFT agent was synthesized by solution RAFT polymerization. Into a 100 mL Schlenk flask with a magnetic bar, NIPAM (10.0 g, 88.4 mmol), CDTPA (356.7 mg, 0.88 mmol), and AIBN (36.3 mg, 0.22 mmol) dissolved in 1,4-dioxane (35.0 g) were added. The solution was degassed with nitrogen at 0 °C, and then the flask content was immersed into preheated oil bath at 65 °C for 150 min. The polymerization was quenched by rapid cooling upon immersion of the flask in iced water. The monomer conversion of 92% was determined by ^{1}H NMR analysis. The synthesized polymer was purified by three precipitation/filtration cycles in iced diethyl ether, and then

dried under vacuum at room temperature overnight to afford yellow powder of $PNIPAM_{92}$-TTC (8.4 g, 87% yield).

2.2Synthesis of the $PNIPAM_{92}$-*b*-PS_{247}nanoparticles

The macro-RAFT agent of $PNIPAM_{92}$-TTC (0.200 g, 0.0183 mmol), St (0.571 g, 5.49 mmol), and AIBN (1.00 mg, 0.0061 mmol) dissolved in the 85/15methanol/water mixture (3.81 g) were added into a Schlenk flask with a magnetic bar. The solution was degassed with nitrogen at 0 ^{o}C for 30 min, and then the polymerization was performed at 70 ^{o}C under vigorous stirring. After 13 h, the polymerization was quenched by rapid cooling upon immersion of the flask in iced water. The monomer conversion was detected by UV-vis analysis at 245 nm.To check the thermo-response of the triblock terpolymer nanoparticles, these diblock copolymer nanoparticles prepared through the dispersion RAFT polymerization in the methanol/water mixture are transferred into water by dialysis against water at room temperature for three days, diluted with water to form 0.1 wt% aqueous dispersion of the diblock copolymer nanoparticles, and then the transmittance of the aqueous dispersion at a given temperature is checked.

3 Characterizations

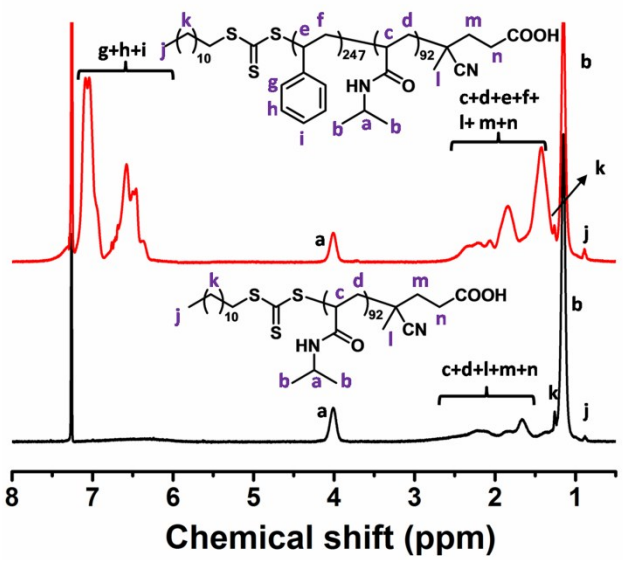

Figure S1 The ^{1}H NMR spectra of the PNIPAM$_{92}$-TTC and PNIPAM$_{92}$-*b*-PS$_{247}$.

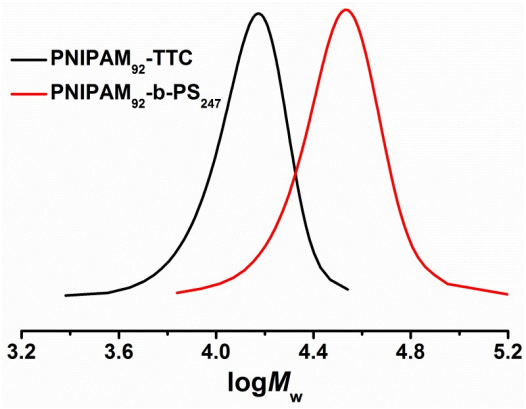

Figure S2 The GPC traces of the PNIPAM$_{92}$-TTC and PNIPAM$_{92}$-*b*-PS$_{247}$.

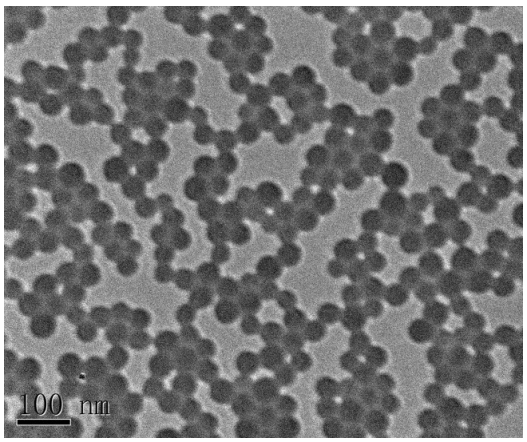

Figure S3. TEM images of the PNIPAM$_{92}$-*b*-PS$_{247}$ diblock copolymer nanoparticles.

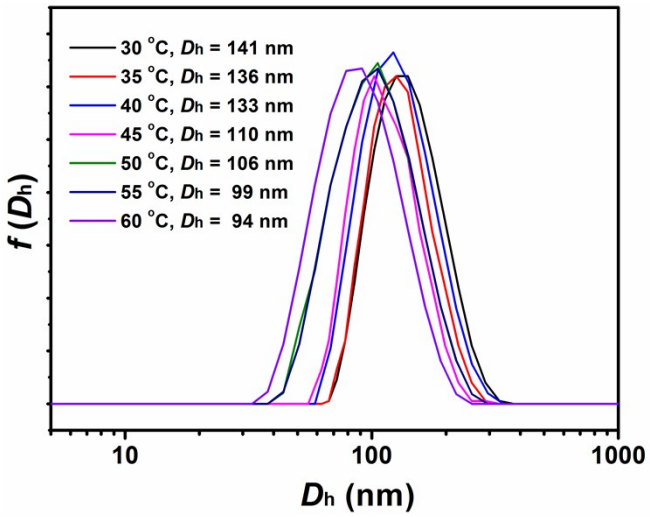

Figure S4. The hydrodynamic diameter distribution $f(D_h)$ of the $PDMAEMA_{96}$-*b*-PS_{266}-*b*-$PNIPAM_{249}$ nanoparticles dispersed in water at different temperatures.