Supporting Information for:

Doubly thermo-responsive ABC triblock copolymer nanoparticles prepared through dispersion RAFT polymerization

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1. Experimental

1.1 Synthesis of the PDMAEMA-TTC macro-RAFT agent.

The polymer of PDMAEMA-TTC was synthesized by RAFT polymerization in 1,4-dioxane using AIBN as initiator and CDTPA as the RAFT agent. Into a 25 mL Schlenk flask with a magnetic bar, DMAEMA (5.00 g, 31.8 mmol), CDTPA (3.50 g, 0.51 mmol), AIBN (25.7 mg, 0.17 mmol) and 1, 4-dioxane (7.2 g) were added. The solution was degassed with nitrogen at 0 ^{o}C for 30 min, and then the flask content was immersed into a preheated oil bath at 70 ^{o}C for 4 h. The polymerization was quenched by rapid cooling upon immersion of the flask in iced water. To detect the monomer conversion, a drop of the polymerization solution was dropped into $CDCl_3$ and subjected to ^{1}H NMR analysis. The monomer conversion was calculated by comparing the integral areas of the protons of the double-bond peaks at δ = 5.56 ppm in reference to the protons peaks of the methylene at δ = 4.07 ppm. To collect the polymer, the flask content was purified by three precipitation/filtration cycles in *n*-hexane at 0 ^{o}C. The product was dried under vacuum at room temperature overnight to afford 4.52 g

(82% yield) of dark yellow polymer.

1.2 Synthesis of the PDMAEMA-*b*-PNIPAM-TTC macro-RAFT agent.

The diblock macro-RAFT agent of PDMAEMA-*b*-PNIPAM-TTC was synthesized by RAFT polymerization in 1,4-dioxane using AIBN as initiator and $PDMAEMA_{30}$-TTC as the macro-RAFT agent. Herein, the synthesis of $PDMAEMA_{30}$-*b*-$PNIPAM_{106}$-TTC was introduced as a typical example. Into a 50 mL Schlenk flask with a magnetic bar, NIPAM (4.69 g, 41.4 mmol), $PDMAEMA_{30}$-TTC (1.50 g, 0.48 mmol), AIBN (19.2 mg, 0.12 mmol), 1,3,5-trioxane (0.37 g, 4.14 mmol) and 1,4-dioxane (18.0 g) were added. The solution was degassed with nitrogen at 0 ^{o}C for 30 min, and then the flask content was immersed into a preheated oil bath at 65 ^{o}C for 3 h. The polymerization was quenched by rapid cooling upon immersion of the flask in iced water. To detect the monomer conversion, a drop of the polymerization solution was dropped into $CDCl_3$ and subjected to ^{1}H NMR analysis. The monomer conversion was calculated by comparing the integral areas of the protons of the double-bond peaks at δ = 5.58 ~ 5.62 ppm in reference to the protons peaks of the internal standard 1,3,5-trioxane at δ = 5.16 ppm. To collect the polymer, the flask content was purified by three precipitation/filtration cycles in *n*-hexane at 0 ^{o}C. The product was dried under vacuum at room temperature overnight to afford 5.20 g (85% yield) of pale yellow and powder-like polymer.

2. Equations

$$M_{n,PNIPAM-TTC,NMR} = \frac{3I_{4.00}}{I_{0.88}} \times M_{n,NIPAM} + M_{n,RAFT} \quad \text{(S1)}$$

$$M_{n,PNIPAM-b-PDMAEMA-TTC,NMR} = \frac{I_{2.56\text{-}2.80} \times DP_{PNIPAM,NMR}}{2(I_{3.88\text{-}4.22} - I_{2.56\text{-}2.80})} \times M_{n,DMAEMA} + M_{n,PNIPAM-TTC,NMR} \quad \text{(S2)}$$

$$Chain\ density = \frac{N_{agg}}{4\pi R^2} = \frac{\pi D^3 d_p N_A}{6M_{n,NMR}} \Big/ 4\pi R^2 = \frac{D d_p N_A}{6M_{n,NMR}} \quad \text{(S3)}$$

3. Characterizations

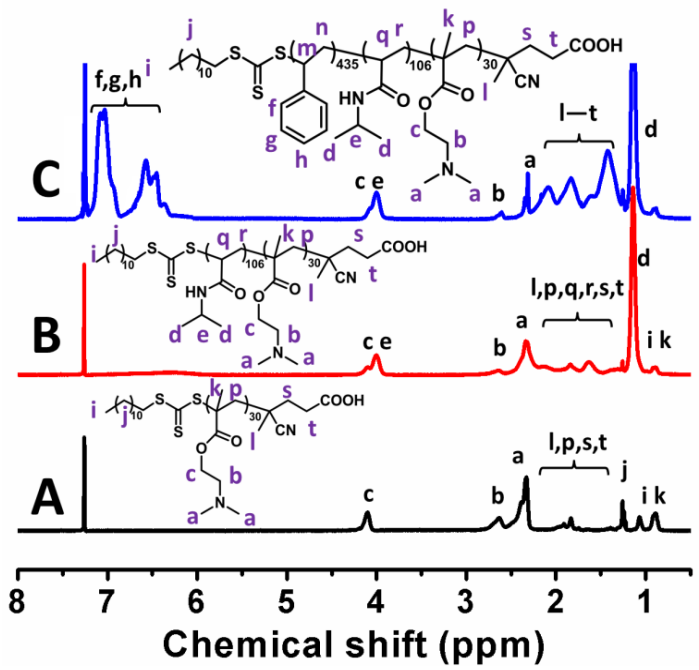

Figure S1. The 1H NMR spectra of PDMAEMA$_{30}$-TTC (A), PDMAEMA$_{30}$-*b*-PNIPAM$_{106}$-TTC (B), and PDMAEMA$_{30}$-*b*-PNIAPM$_{106}$-*b*-PS$_{435}$ (C).

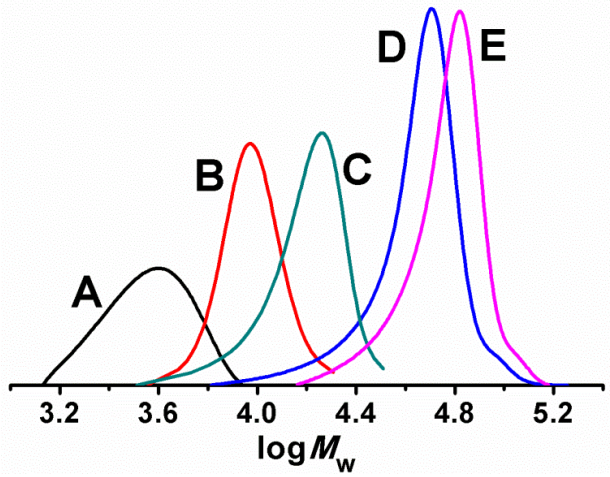

Figure S2. The GPC traces of PDMAEMA$_{30}$-TTC (A), PDMAEMA$_{30}$-*b*-PNIPAM$_{68}$-TTC (B), PDMAEMA$_{30}$-*b*-PNIPAM$_{106}$-TTC (C), PDMAEMA$_{30}$-*b*-PNIPAM$_{68}$-*b*-PS$_{482}$ (D) and PDMAEMA$_{30}$-*b*-PNIPAM$_{106}$-*b*-PS$_{435}$ (E).

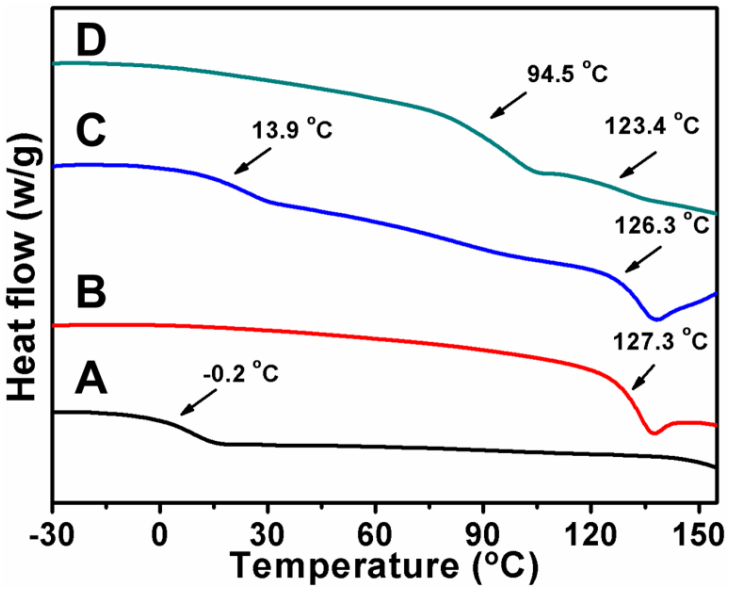

Figure S3. The DSC thermograms of PDMAEMA-TTC (A), PNIPAM-TTC (B), $PNIPAM_{54}$-*b*-$PDMAEMA_{46}$-TTC (C), $PNIPAM_{54}$-*b*-$PDMAEMA_{46}$-*b*-PS_{460} (D).

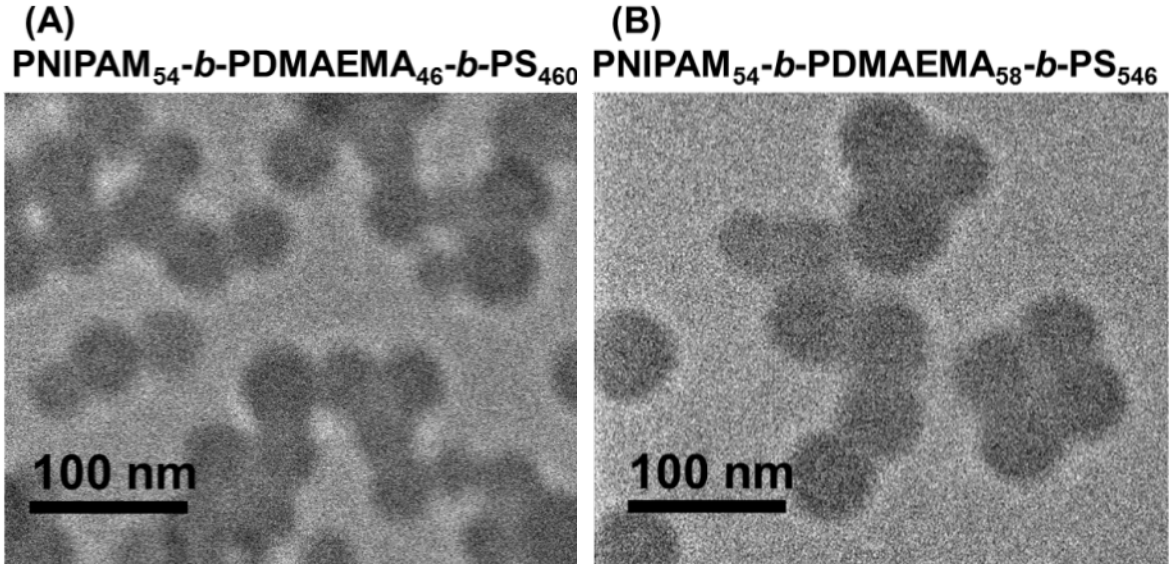

Figure S4. The TEM images of the triblock copolymer nanoparticles of $PNIPAM_{54}$-*b*-$PDMAEMA_{46}$-*b*-PS_{460} (A) and $PNIPAM_{54}$-*b*-$PDMAEMA_{58}$-*b*-PS_{546} (B).

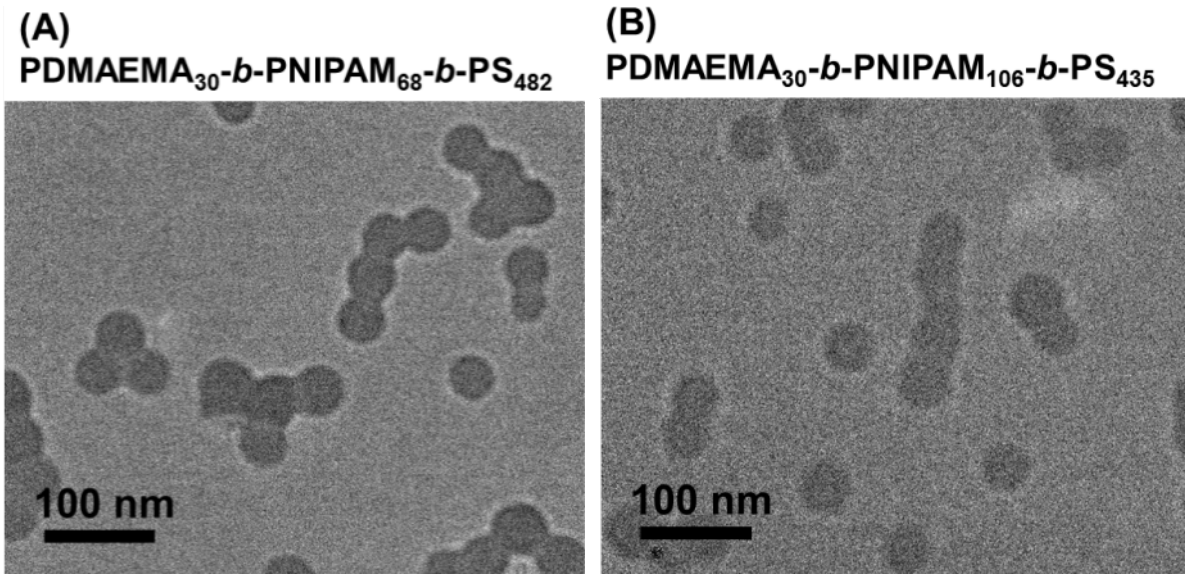

Figure S5. The TEM images of the triblock copolymer nanoparticles of $PDMAEMA_{30}$-*b*-$PNIPAM_{68}$-*b*-PS_{482} (A) and $PDMAEMA_{30}$-*b*-$PNIPAM_{106}$-*b*-PS_{435} (B).

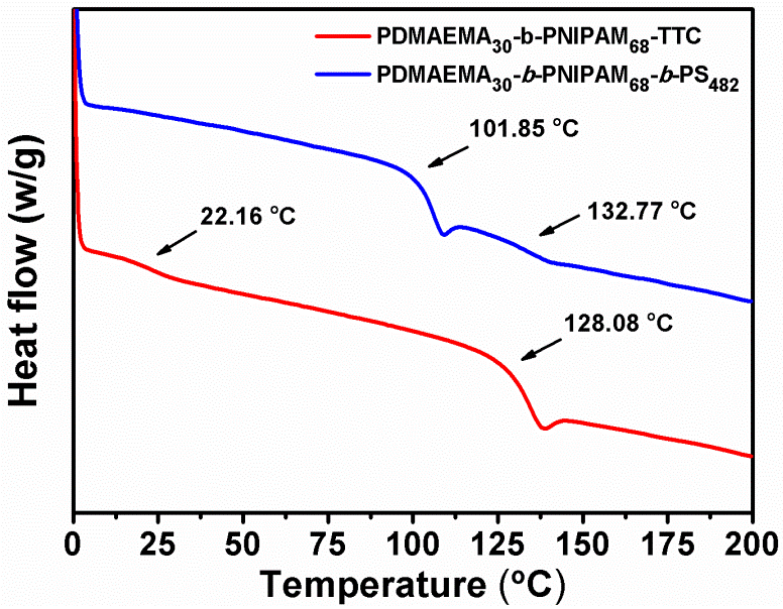

Figure S6. The DSC thermograms of $PDMAEMA_{30}$-*b*-$PNIPAM_{68}$-TTC and $PDMAEMA_{30}$-*b*-$PNIPAM_{68}$-b-PS_{482}.

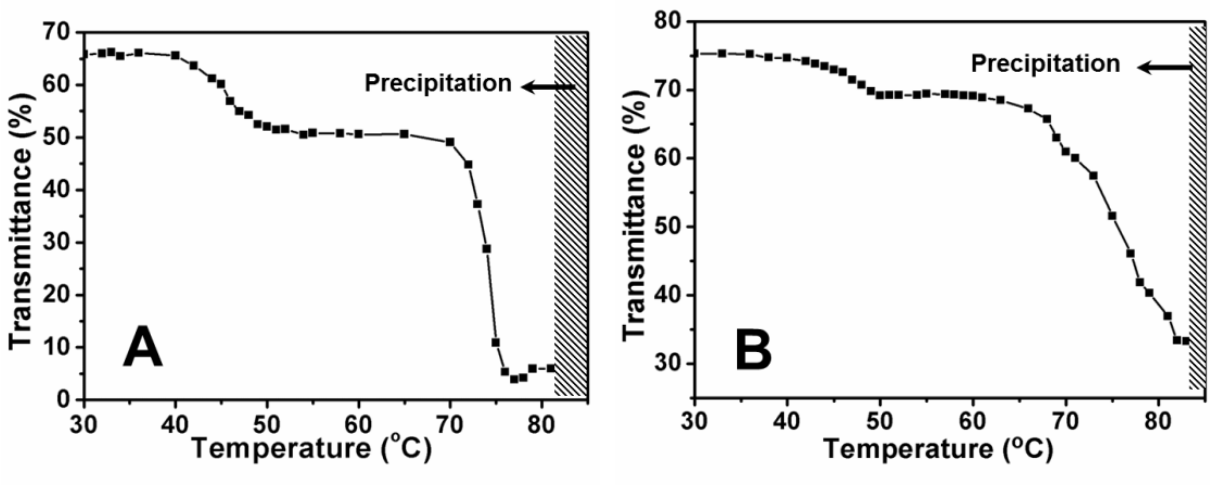

Figure S7. Transmittance *versus* temperature plots for the 0.2 wt% aqueous dispersion of triblock copolymer nanoparticles of $PNIPAM_{54}$-b-$PDMAEMA_{27}$-b-PS_{519} (A) and $PNIPAM_{54}$-b-$_{PDMAEMA58}$-b-PS_{546} (B).

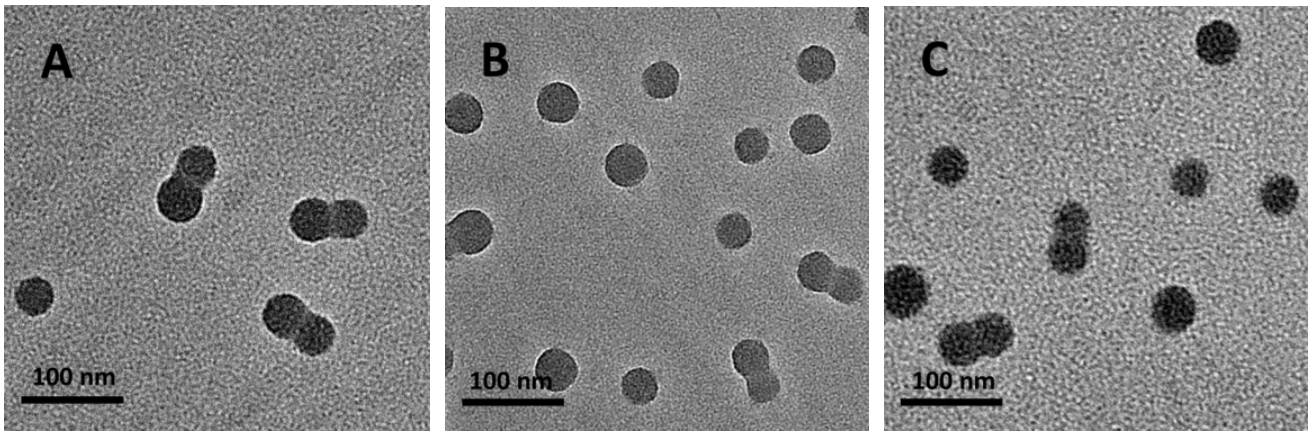

Figure S8. The TEM images of the $PNIPAM_{54}$-*b*-$PDMAEMA_{46}$-*b*-PS_{460} nanoparticles dispersed in water at 30 °C (A), 45 °C (B), and 70 °C (C).

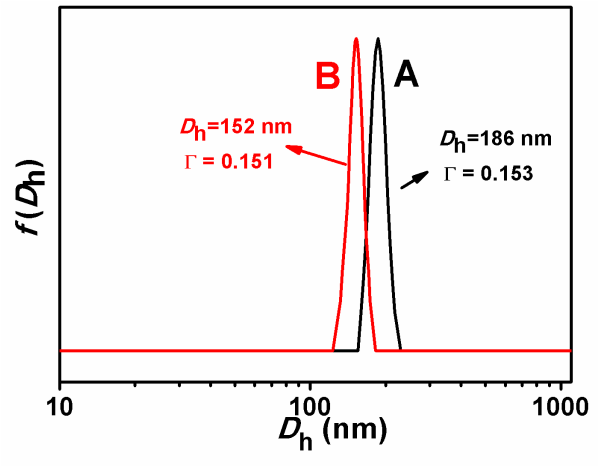

Figure S9. Hydrodynamic diameter distribution $f(D_h)$ of the triblock copolymer nanoparticles of $PNIPAM_{54}$-*b*-$PDMAEMA_{46}$-*b*-PS_{460} (A) and $PDMAEMA_{30}$-*b*-$PNIPAM_{68}$-*b*-PS_{482} (B) dispersed in water at 30 ^{o}C.