Supporting Information

A new strategy to prepare thermo-responsive multicompartment nanoparticles constructed with two diblock copolymers

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1. Experimental

1.1 Dispersion RAFT polymerization of styrene in the methanol/water mixture in the presence of the PVEA-TTC macro-RAFT agent

The PVEA-TTC macro-RAFT agent mediated dispersion polymerization of styrene was performed in the 95/5 ethanol/water mixture at 70 ^{o}C under $[St]_0$:[PVEA-TTC]$_0$:$[AIBN]_0$ = 1200:4:1 with a constant weight ratio of the fed styrene monomer to the solvent at 20%. Typically, the macro-RAFT agent of PVEA-TTC (0.168 g, 0.0096 mmol), St (0.300 g, 2.88 mmol), and AIBN (0.395 mg, 0.0024 mmol) dissolved in the 95/5 ethanol/water mixture (1.50 g) were added into a Schlenk flask with a magnetic bar. The solution was degassed with nitrogen at 0 ^{o}C, and then the polymerization was performed at 70 ^{o}C under vigorous stirring. After 32 h, the polymerization was quenched at 60.3% by rapid cooling upon immersion of the flask in iced water. The monomer conversion was detected by UV-vis analysis

at 245 nm. The diblock copolymer was centrifuged (12500 r/min, 30 min), washed with hexane (20 mL × 3), and dried under vacuum for 24 h for further gel permeation chromatography (GPC) analysis and ^{1}H NMR analysis.

1.2 Dispersion RAFT polymerization of styrene in the methanol/water mixture in the presence of the PDMAEMA-TTC macro-RAFT agent

The PDMAEMA-TTC macro-RAFT agent mediated dispersion polymerization of styrene was performed in the 95/5 ethanol/water mixture at 70 ^{o}C under $[St]_0$:[PDMAEMA-TTC]$_0$:$[AIBN]_0$ = 1200:4:1 with a constant weight ratio of the fed styrene monomer to the solvent at 20%. Typically, the macro-RAFT agent of PDMAEMA-TTC (0.206 g, 0.016 mmol), St (0.500 g, 4.81 mmol), and AIBN (0.658 mg, 0.0040 mmol) dissolved in the 95/5 ethanol/water mixture (2.50 g) were added into a Schlenk flask with a magnetic bar. The solution was degassed with nitrogen at 0 ^{o}C, and then the polymerization was performed at 70 ^{o}C under vigorous stirring. After 24 h, the polymerization was quenched at 50.8% by rapid cooling upon immersion of the flask in iced water. The monomer conversion was detected by UV-vis analysis at 245 nm. The resultant dispersion was dialyzed against water for three days (molecular weight cutoff: 7000 Da) to remove the residual St monomer. The polymer aqueous dispersion was extracted with dichloromethane (50 mL × 3), and then the organic phase was collected and dried over anhydrous magnesium sulfate overnight. After filtration of magnesium sulfate and removal of the solvent, the polymer was collected and dried under vacuum at room temperature overnight for further gel permeation chromatography (GPC) analysis and ^{1}H NMR analysis.

2. Equation

$$M_{\mathrm{n,PVEA-TTC,NMR}} = \frac{I_{3.48}\times 20}{\frac{I_{1.26}}{2}\times 2} \times \frac{1}{2} \times M_{\mathrm{n,VEA}} + M_{\mathrm{n,RAFT}} = \frac{5I_{3.48}}{\frac{I_{1.26}}{2}} \times M_{\mathrm{n,VEA}} + M_{\mathrm{n,RAFT}} = \frac{5\times 4.00}{0.43} \times M_{\mathrm{n,VEA}} + M_{\mathrm{n,RAFT}} \quad \text{(S1)}$$

$$\frac{n_{\mathrm{PVEA-PS}}}{n_{\mathrm{PDMAEMA-PS}}} = \frac{I_{3.48}/\mathrm{DP_{PVEA}}}{I_{4.07}/\mathrm{DP_{PDMAEMA}}} \quad \text{(S2)}$$

3. Characterizations

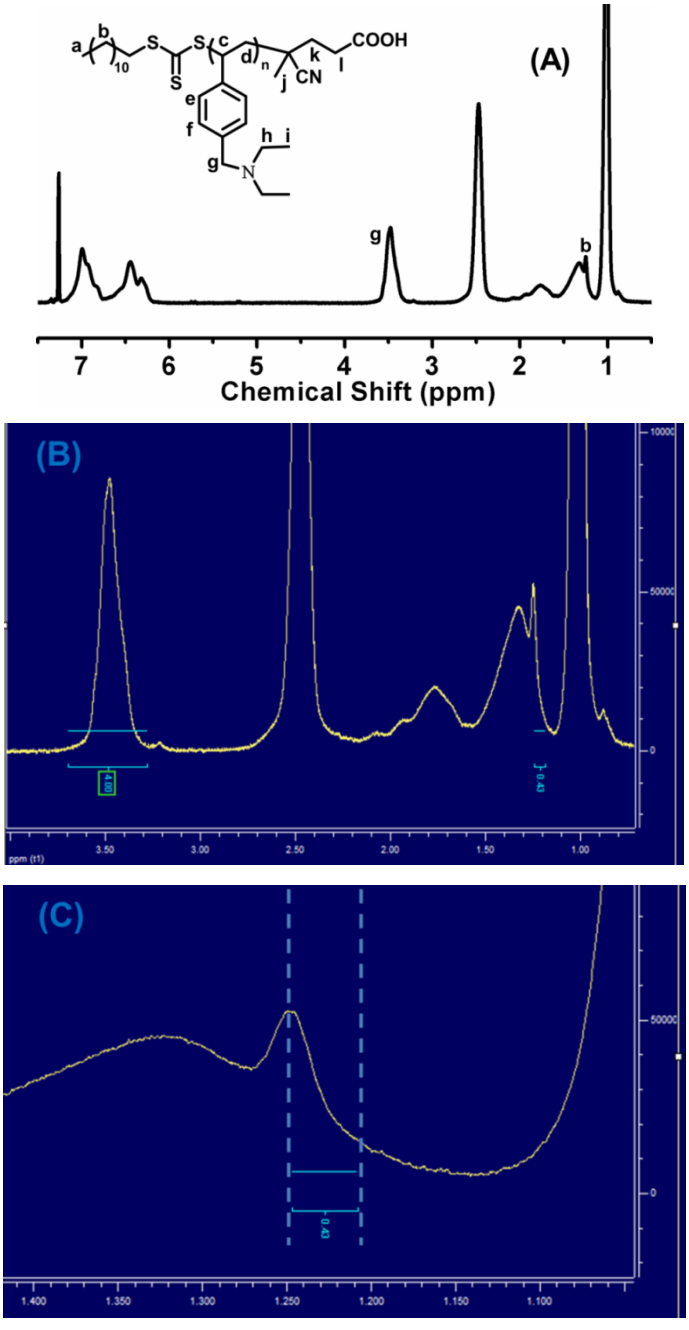

Figure S1. ^{1}H NMR spectra of $PVEA_{50}$-TTC.

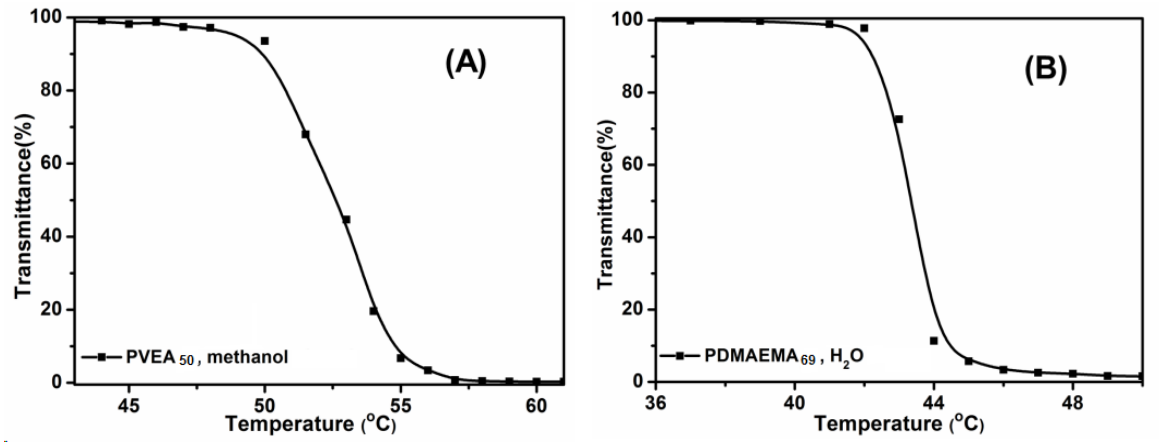

Figure S2. The transmittance *versus* temperature plots for the methanol solution of $PVEA_{50}$-TTC (0.4 wt%) (A) and the aqueous solution of $PDMAEMA_{69}$-TTC (0.1 wt%).

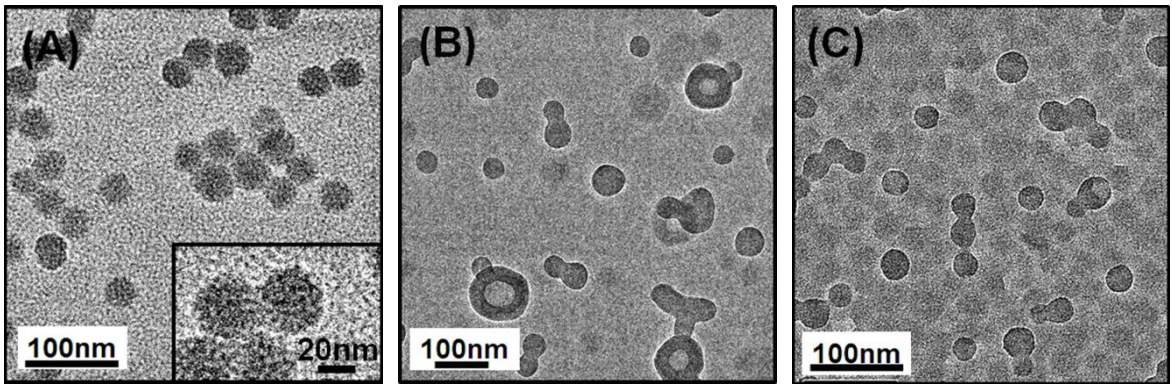

Figure S3. Representative TEM images of the two diblock copolymer of $PVEA_{50}$-*b*-PS_{373}/$PDMAEMA_{69}$-*b*-PS_{186} (A), $PVEA_{50}$-*b*-PS_{390} (B), $PDMAEMA_{69}$-*b*-PS_{162} (C).

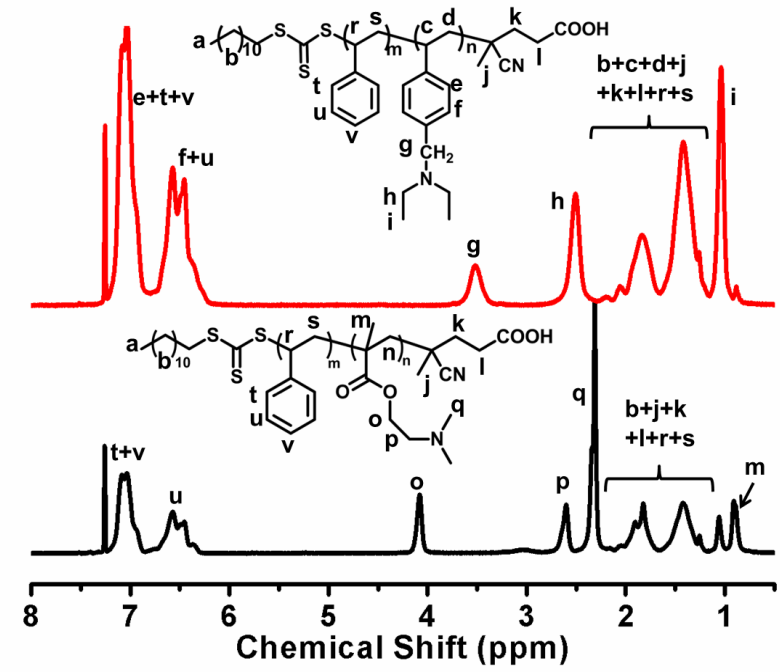

Figure S4. ^{1}H NMR spectra of PVEA$_{50}$-*b*-PS$_{390}$ (A) and PDMAEMA$_{69}$-*b*-PS$_{162}$ (B).

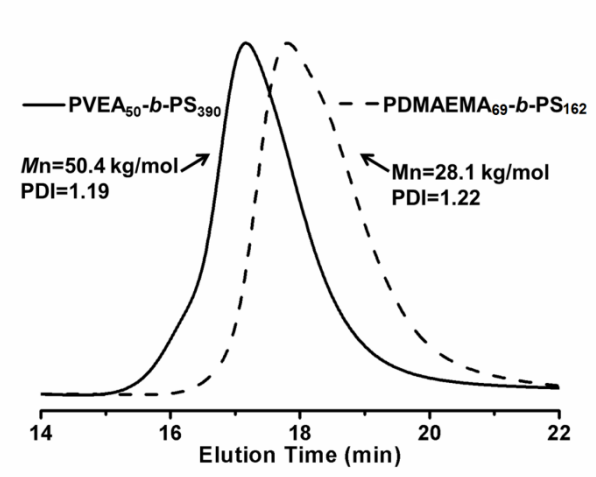

Figure S5. GPC traces of PVEA$_{50}$-*b*-PS$_{390}$ (A) and PDMAEMA$_{69}$-*b*-PS$_{162}$ (B).