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Supporting information for

Doubly thermo-responsive nanoparticles constructed with two diblock copolymers prepared through two macro-RAFT agents co-mediated dispersion RAFT polymerization

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1. Separation of the PNIPAM-*b*-PS/PDMAEMA-*b*-PS mixture

The PNIPAM-*b*-PS/PDMAEMA-*b*-PS mixture (0.5 g) was dissolved in dichloromethane (2.5 mL), and the polymer was precipitated in iced diethyl ether (10 mL). The supernatant solution and the precipitate were collected, resepctively. The solvent in the supernatant solution was removed by rotary evaporation under reduced pressure at 30 ^{o}C, and the polymer was analyzed by ^{1}H NMR analysis, in which the signals ascribed to both PNIPAM-*b*-PS and PDMAEMA-*b*-PS were detected (^{1}H NMR spectra are not shown herein). The collected precipitate was dissolved in dichloromethane (2.5 mL) again, and the polymer was precipitated in iced diethyl ether (2.5 mL), collected by centrifugation (12500 r/min, 10 min), dried under vacuum at room temperature for 24 h, and then characterized by GPC analysis and ^{1}H NMR analysis (seeing in Figure S2).

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

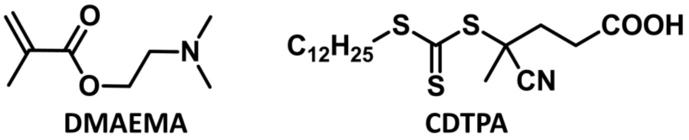
The PNIPAM-TTC macro-RAFT agent mediated dispersion polymerization of styrene was performed in the 85/15 methanol/water mixture at 70 ^{o}C under $[St]_0$:$[Macro\text{-}RAFT]_0$:$[AIBN]_0$ = 1800:6:1 with a constant weight ratio of the fed styrene monomer to the solvent at 15%. Typically, the macro-RAFT agent of $PNIPAM_{92}$-TTC (0.200 g, 0.0183 mmol), St (0.574 g, 5.52 mmol), and AIBN (0.503 mg, 0.0031 mmol) dissolved in the 85/15 methanol/water mixture (3.82 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 a given time, 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.

3 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 85/15 methanol/water mixture at 70 ^{o}C under $[St]_0$:$[Macro\text{-}RAFT]_0$:$[AIBN]_0$ = 1800:6:1 with a constant weight ratio of the fed styrene monomer to the solvent at 15%. Typically, the macro-RAFT agent of $PDMAEMA_{61}$-TTC (0.100 g, 0.010 mmol), St (0.312 g, 3.00 mmol), and AIBN (0.275 mg, 0.0017 mmol) dissolved in the 85/15 methanol/water mixture (2.08 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 a given time, 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.

Figures and Results.



Scheme S1. The chemical structure of DMAEMA and CDTPA.

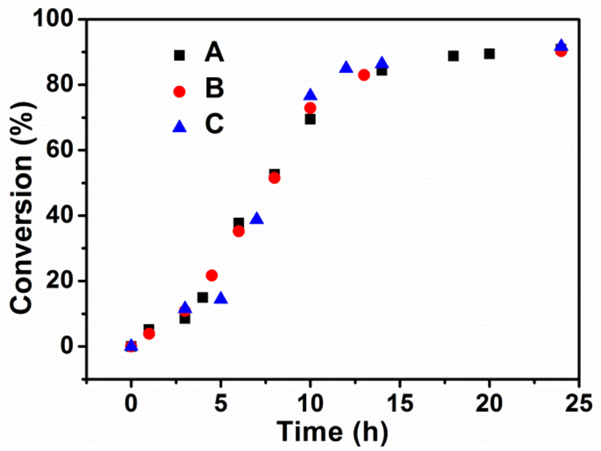


Figure S1. The monomer conversion-time plots for the two macro-RAFT agents co-mediated dispersion polymerization (A), the macro-RAFT agents of PNIPAM$_{92}$-TTC (B) and PDMAEMA$_{61}$-TTC (C) mediated dispersion polymerization.

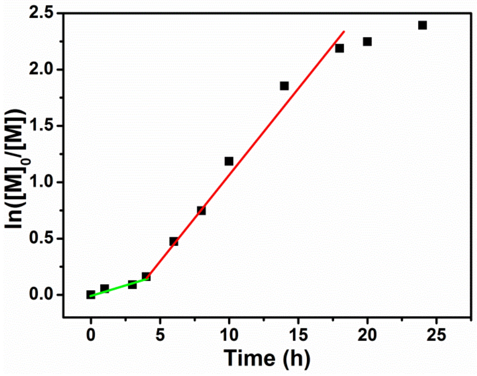


Figure S2. The ln([M]$_0$/[M])-time plots (A) for the dispersion RAFT polymerization of styrene in the presence of the two macro-RAFT agents (molar ratio = 1:1) of PNIPAM$_{92}$-TTC and PDMAEMA$_{61}$-TTC.

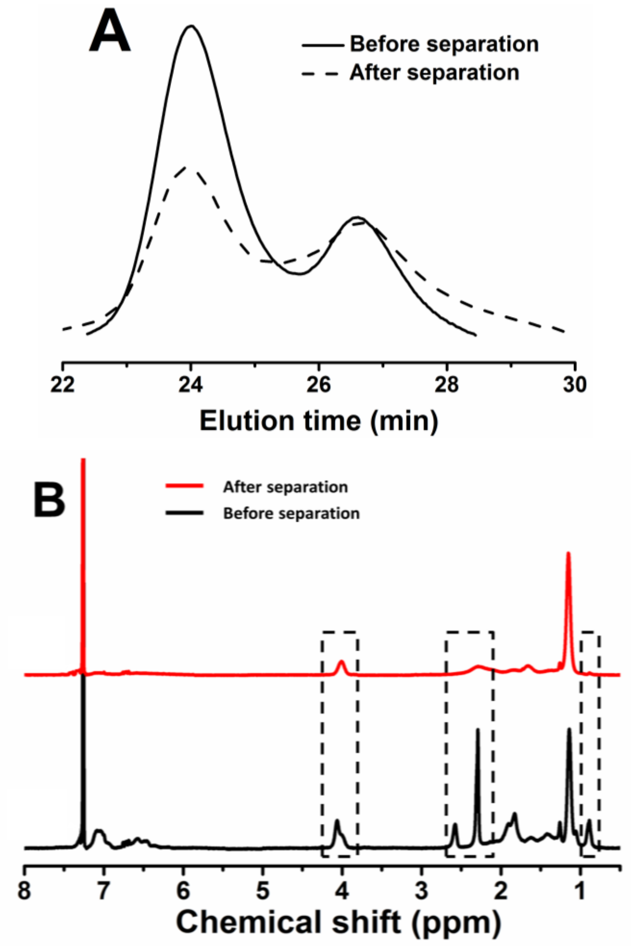


Figure S3. GPC traces (A) and the ^{1}H NMR spectra (B) of the PNIPAM-*b*-PS/PDMAEMA-*b*-PS mixture before and after separation washing with iced diethyl ether. Note: the PNIPAM-*b*-PS/PDMAEMA-*b*-PS mixture was prepared at 4 h polymerization time.

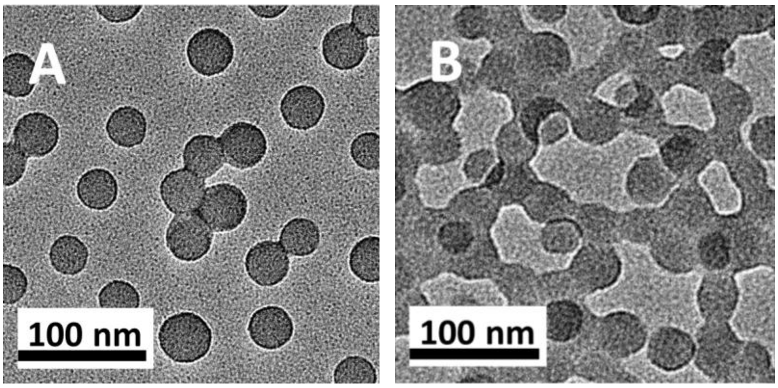


Figure S4. The TEM images of the diblock copolymer nanoparticles of PNIPAM$_{92}$-*b*-PS$_{275}$

(A) and PDMAEMA$_{61}$-*b*-PS$_{265}$ (B).

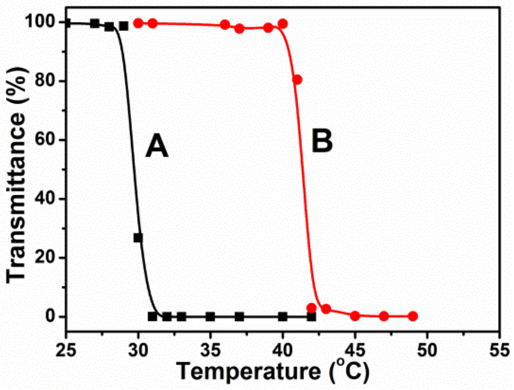


Figure S5. The transmittance versus temperature plots for the 0.01 wt% aqueous solution of PNIPAM$_{92}$-TTC (A) and PDMAEMA$_{61}$-TTC (B).