Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Supporting Information for:

In situ synthesis of thermoresponsive 4-arm star block copolymer nano-assemblies by dispersion RAFT polymerization

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1. Dispersion polymerization employing PNIPAM$_{58}$-TTC and synthesis of the PNIPAM$_{118}$-*b*-PS$_{125}$ linear block copolymer nano-assemblies

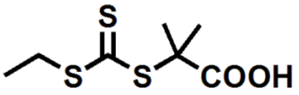
The PNIPAM$_{58}$-TTC mediated dispersion polymerization of styrene was performed under $[St]_0$:$[PNIPAM_{58}\text{-}TTC]_0$:$[AIBN]_0$ = 900:3:1 with monomer concentration at 10 wt % in the 80/20 methanol/water mixture. Into a 25 mL Schlenk flask with a magnetic bar, PNIPAM$_{58}$-TTC (0.1091 g, 0.0160 mmol), St (0.5 g, 4.8 mmol), and AIBN (0.8760 mg, 0.0053 mmol) dissolved in the 80/20 methanol/water mixture (4.5 g) were added. After the flask content being degassed with nitrogen at 0 ^{o}C, the polymerization was initiated by immersing the flask into the preheated oil bath at 70 ^{o}C under stirring. After a given time of interval, the polymerization was quenched by rapid cooling upon immersing the flask into ice water. The monomer conversion in the dispersion RAFT polymerization was detected by UV-vis analysis at 245 nm as discussed elsewhere. The resultant colloidal dispersion of the PNIPAM$_{58}$-*b*-PS nano-assemblies was dialyzed against methanol for 3 days to remove the residual St monomer (molecular weight cutoff: 3500 Da). The removal of St was judged by the UV-vis analysis of the dialysis solution at 245 nm. The PNIPAM$_{58}$-*b*-PS block copolymer was collected by directly removing the solvent in the methanol dispersion of the PNIPAM$_{58}$-*b*-PS nano-assemblies through rotary evaporation under reduced pressure, and then dried under vacuum at room temperature for ^{1}H NMR analysis and gel permeation chromatography (GPC) analysis. The PNIPAM$_{118}$-*b*-PS$_{125}$ nano-assemblies were synthesized at the molar ratio of [St]$_0$:[PNIPAM$_{118}$-TTC]$_0$:[AIBN]$_0$ = 390:3:1 under the same condition for 8h.

2. Equations

$$M_{\mathrm{n,th}} = \frac{[\mathrm{monomer}]_{\mathrm{o}} \times M_{\mathrm{monomer}}}{[\mathrm{RAFT}]_{\mathrm{o}}} \times conversion + M_{\mathrm{RAFT}} \qquad (\mathrm{S1})$$

$$L_{\max} = \left(\frac{2}{3}\right)^{\frac{1}{2}} nl \qquad l = 1.54\ \text{Å} \qquad (\mathrm{S2})$$

3. Scheme



Scheme S1. The structure of EMP.

4. Figures

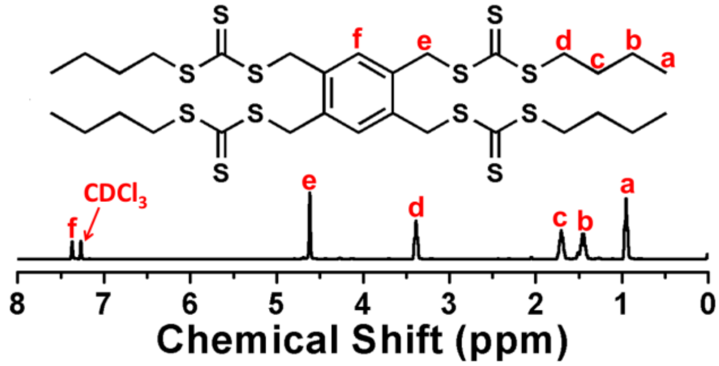


Figure S1. ^{1}H NMR spectrum of 1,2,4,5-tetrakis-(butyltrithiomethyl) benzene.

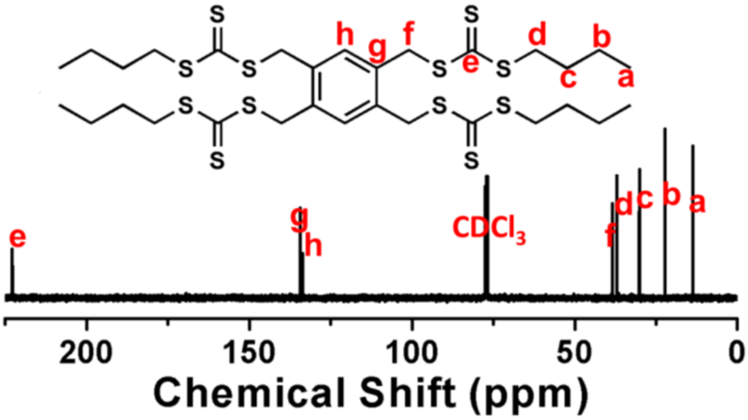


Figure S2. ^{13}C NMR spectrum of 1,2,4,5-tetrakis-(butyltrithiomethyl) benzene.

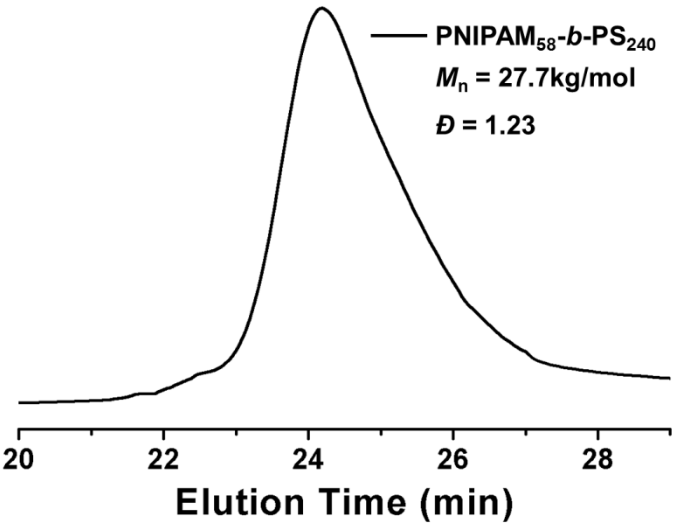


Figure S3. GPC trace of PNIPAM$_{58}$-*b*-PS$_{240}$.

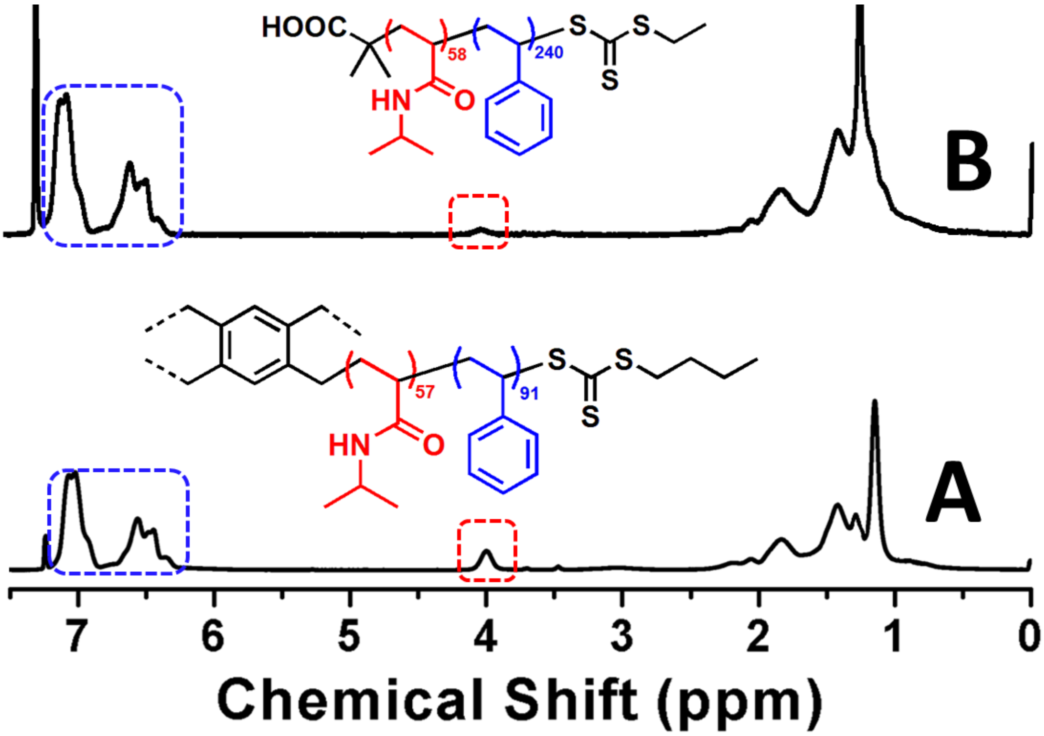


Figure S4. ^{1}H NMR spectra of (PNIPAM$_{57}$-*b*-PS$_{91}$)$_4$ (A) and PNIPAM$_{58}$-*b*-PS$_{240}$ (B).

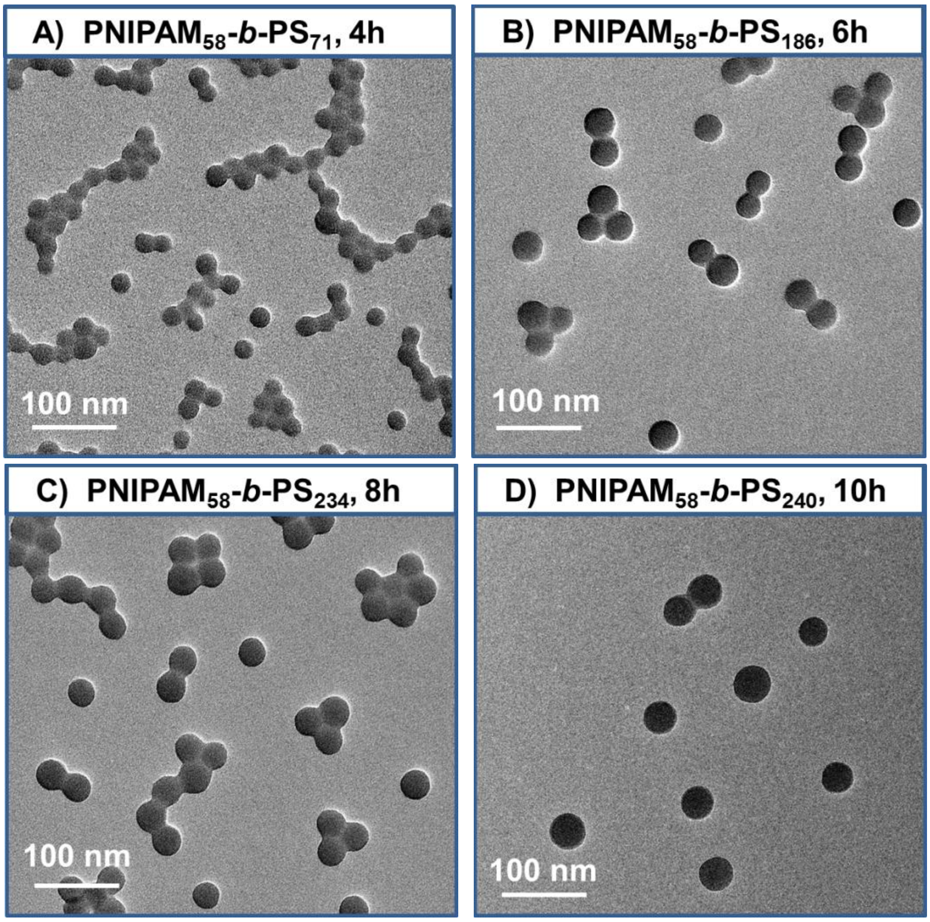


Figure S5. TEM images of the PNIPAM-*b*-PS linear block copolymer nanospheres prepared at the polymerization time of 4 h (A), 6 h (B), 8 h (C) and 10 h (D) through dispersion RAFT polymerization employing the monofunctional PNIPAM$_{58}$-TTC.

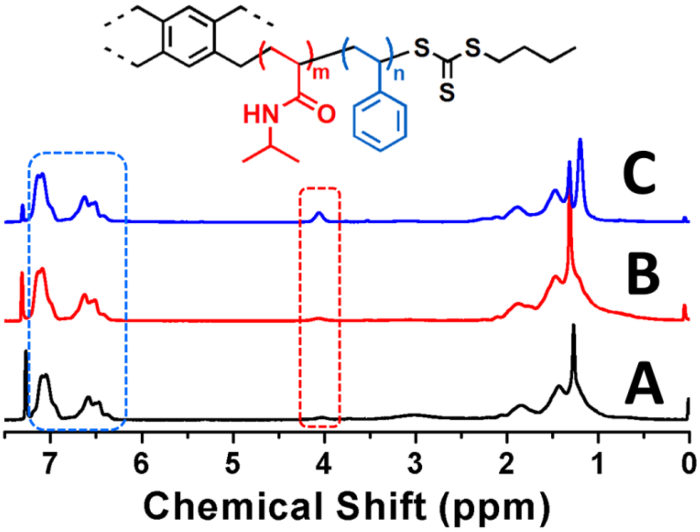


Figure S6. ^{1}H NMR spectra of (PNIPAM$_{29}$-*b*-PS$_{266}$)$_4$ (A) (PNIPAM$_{57}$-*b*-PS$_{255}$)$_4$ (B) and (PNIPAM$_{122}$-*b*-PS$_{263}$)$_4$ (C).

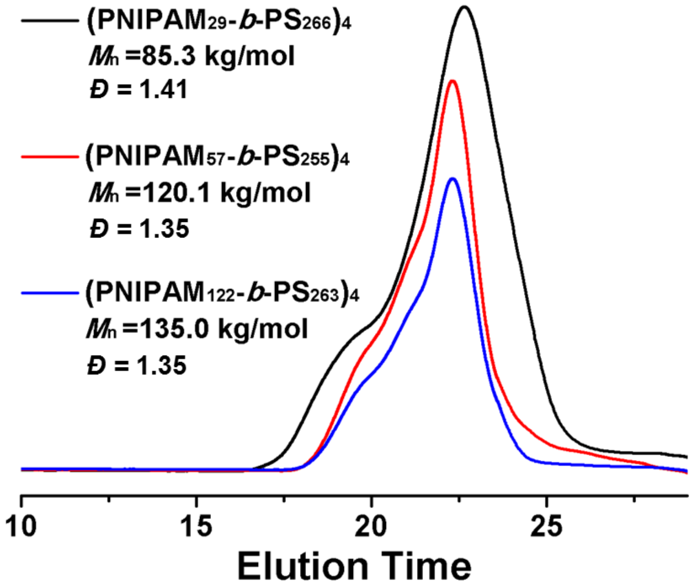


Figure S7. GPC traces of the 4-arm star block copolymers of (PNIPAM$_{29}$-*b*-PS$_{266}$)$_4$, (PNIPAM$_{57}$-*b*-PS$_{255}$)$_4$ and (PNIPAM$_{122}$-*b*-PS$_{263}$)$_4$.

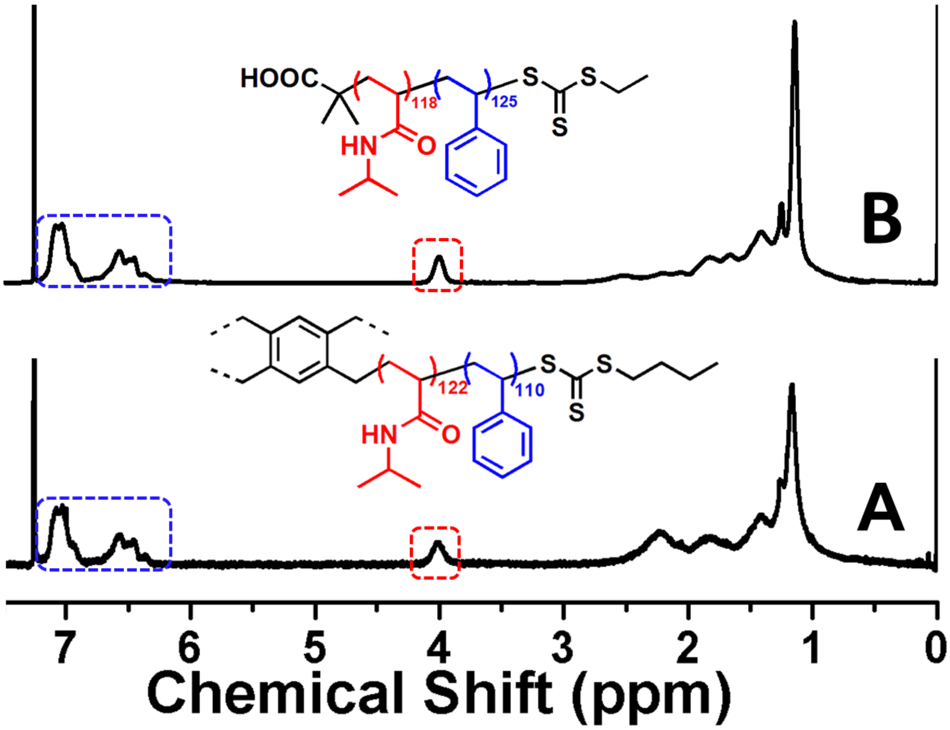


Figure S8. ^{1}H NMR spectra of (PNIPAM$_{122}$-*b*-PS$_{110}$)$_4$ (A) and PNIPAM$_{118}$-*b*-PS$_{125}$ (B).

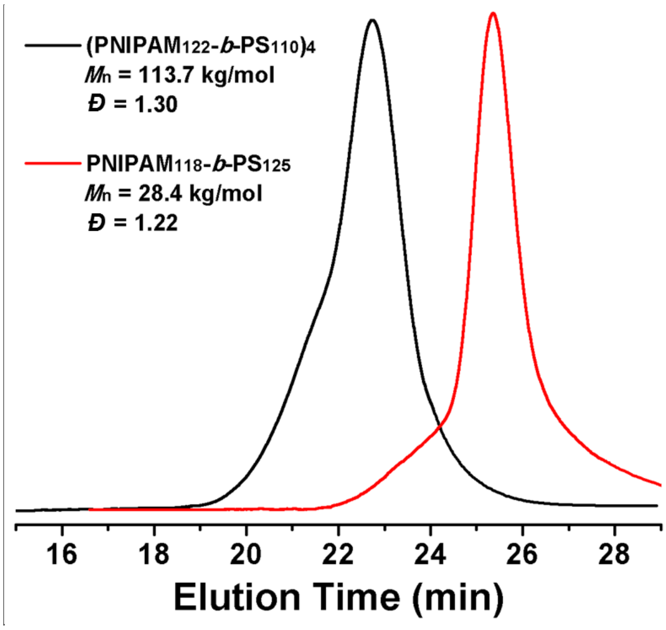


Figure S9. GPC traces of $(\mathrm{PNIPAM}_{122}\text{-}b\text{-}\mathrm{PS}_{110})_4$ and $\mathrm{PNIPAM}_{118}\text{-}b\text{-}\mathrm{PS}_{125}$.