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

Quanlong Li\textsuperscript{a,b,§}, Lei Li\textsuperscript{a,b,§}, Wenbin Wang\textsuperscript{a,b}, Xiaolei Zhang\textsuperscript{a,b}, Shentong Li\textsuperscript{a,b}, Qian Tian\textsuperscript{a,b}, and Jiaping Liu\textsuperscript{c*}

\textsuperscript{a} State Key Laboratory of High Performance Civil Engineering Materials, Jiangsu Research Institute of Building Science, Nanjing, 210008, China.

\textsuperscript{b} Jiangsu Sobute New Materials Co., Ltd. Nanjing, 211103, China.

\textsuperscript{c} College of Materials Science and Engineering, Southeast University, Nanjing 211189, China.

\textsuperscript{§} These authors contribute equally to this work.

1 Equations:

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

\begin{equation}
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 (S2)
\end{equation}

2 Experimental

2.1 Synthesis of PNIPAM\textsubscript{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 \textsuperscript{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\textsubscript{92}-TTC (8.4 g, 87% yield).

2.2 Synthesis of the PNIPAM\textsubscript{92-}\textit{b}-PS\textsubscript{247} nanoparticles

The macro-RAFT agent of PNIPAM\textsubscript{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 85/15 methanol/water mixture (3.81 g) were added into a Schlenk flask with a magnetic bar. The solution was degassed with nitrogen at 0 °C for 30 min, and then the polymerization was performed at 70 °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.