

## Supporting information for

### Versatile multicompartment nanoparticles constructed with two thermo-responsive, pH-responsive and hydrolytic diblock copolymers

Shengli Chen<sup>†</sup>, Xueying Chang<sup>†</sup>, Pingchuan Sun<sup>†</sup> and Wangqing Zhang<sup>\*,†,‡</sup>

<sup>†</sup>Key Laboratory of Functional Polymer Materials of the Ministry of Education, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China.

<sup>‡</sup>Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China.

## 1. Experimental Section

### 1.1 Synthesis of macro-RAFT agents

The macro-RAFT agent of PNASME<sub>153</sub>-TTC was prepared by RAFT polymerization under [NASME]<sub>0</sub>:[DDMAT]<sub>0</sub>:[AIBN]<sub>0</sub> = 800:4:1 in 1,4-dioxane at 70 °C for 12 h. Into a Schlenk flask with a magnetic bar, NASME (1.57 g, 10.00 mmol), DDMAT (18.23 mg, 0.050 mmol), 1,3,5-trioxane (internal standard, 90.00 mg, 1.00 mmol), and AIBN (2.05 mg, 0.0125 mmol) dissolved in 1,4-diethylene dioxide (3.18 g, 3.06 mL) were added. The oxygen in flask content was excluded with high-purity argon at 0 °C, and then the polymerization was initiated at 70 °C under magnetically stirring. After 12 h, the polymerization was inhibited by rapid cooling upon immersion of the flask in iced water (-20 °C) and a monomer conversion of 76.5% was obtained. The monomer conversion was determined with <sup>1</sup>H NMR analysis by comparing the integral areas of the monomer protons of C=C-H at  $\delta = 5.60$ -5.80 ppm with that of the 1,3,5-trioxane internal standard at  $\delta = 5.10$ -5.20 ppm. The synthesized polymer was purified by three precipitation-filtration cycles in cold diethyl ether, and was dried under vacuum at room temperature overnight to

afford a pale yellow powder of PNASME<sub>153</sub>-TTC ( $M_{n,th} = 24.3$  kg/mol,  $M_{n,GPC} = 23.7$  kg/mol,  $\mathcal{D} = 1.22$ ).

A similar procedure of RAFT polymerization was also employed to prepare the macro-RAFT agent of P4VP<sub>133</sub>-TTC under  $[4VP]_0:[DDMAT]_0:[AIBN]_0 = 800:4:1$  in ethanol at 70 °C. After 12h, a monomer conversion of 66.5% was determined by <sup>1</sup>H NMR analysis. The synthesized polymer was purified by three precipitation-filtration cycles in cold diethyl ether, and then dried under vacuum at 25 °C overnight to afford a light pink powder of P4VP<sub>133</sub>-TTC ( $M_{n,th} = 14.3$  kg/mol,  $M_{n,GPC} = 13.2$  kg/mol,  $\mathcal{D} = 1.17$ ).

## 1.2 Synthesis of nanoassemblies formed by individual block copolymers

The PNASME<sub>153</sub>-*b*-PS or P4VP<sub>133</sub>-*b*-PS nano-assemblies were prepared by dispersion RAFT polymerization employing PNASME<sub>153</sub>-TTC or P4VP<sub>133</sub>-TTC as macro-RAFT agent under  $[St]_0:[macro-RAFT]_0:[AIBN]_0 = 900:3:1$  similarly with the dispersion RAFT polymerization employing two macro-RAFT agents introduced in Section 2.3. The obtained diblock copolymers are PNASME<sub>153</sub>-*b*-PS<sub>279</sub> (T<sub>153</sub>S<sub>279</sub>,  $M_{n,th} = 53.4$  kg/mol,  $M_{n,GPC} = 50.2$  kg/mol,  $\mathcal{D} = 1.29$ ) and P4VP<sub>133</sub>-*b*-PS<sub>292</sub> (H<sub>133</sub>S<sub>292</sub>,  $M_{n,th} = 44.6$  kg/mol,  $M_{n,GPC} = 42.3$  kg/mol,  $\mathcal{D} = 1.21$ ).

## 2. Equations and Tables

$$M_{n,th} = \frac{[\text{monomer}]_0 \times M_{\text{monomer}}}{[\text{RAFT}]_0} \times \text{Conversion} + M_{n, \text{RAFT}/\text{macro-RAFT}} \quad (\text{S1})$$

where  $[\text{monomer}]_0$  and  $[\text{RAFT}]_0$  represent the concentration of the fed monomer and the RAFT agent,  $M_{\text{monomer}}$  is the molar mass of the monomer,  $M_{n, \text{RAFT}/\text{macro-RAFT}}$  is the molar mass of RAFT/macro-RAFT agent, and the monomer Conversion is determined by <sup>1</sup>H

NMR analysis by comparing the integral areas of the monomer protons of C=C-H at  $\delta = 5.60$ - $5.80$  ppm with those of the 1,3,5-trioxane internal standard at  $\delta = 5.10$ - $5.20$  ppm.

The  $M_{n,NMR}$  of separated diblock copolymers, *i.e.*, PNASME-*b*-PS (eq. S2) and P4VP-*b*-PS (eq. S2) was calculated with the ratio of two blocks by  $^1\text{H}$  NMR analysis (2.6-3.2 ppm corresponding to methyl of the PNASME block and 6.2-7.3 ppm corresponding to phenyl group of the PS block, and 8.0-8.4 ppm corresponding to pyridyl of the P4VP block).

$$M_{n,NMR} = DP_{PS} \times M_{St} + M_{PNASME-TTC} = \frac{I_{2.6-3.2} \times \frac{1}{3}}{I_{8.0-8.4} \times \frac{1}{6}} \times DP_{PNASME-TTC} \times M_{St} + M_{PNASME-TTC} \quad (\text{S2})$$

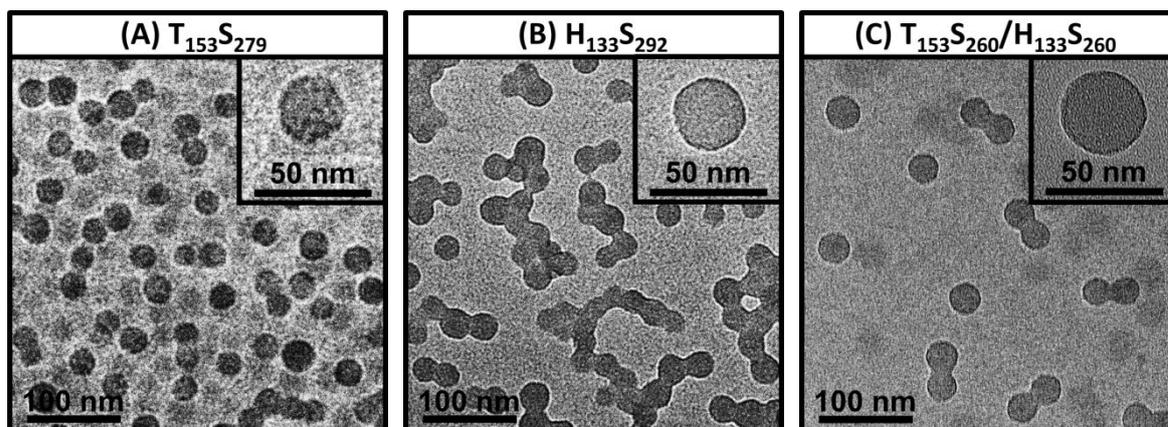
$$M_{n,NMR} = DP_{PS} \times M_{St} + M_{P4VP-TTC} = \frac{I_{6.2-7.3} \times \frac{1}{2}}{I_{8.0-8.4} \times \frac{1}{6}} \times DP_{P4VP-TTC} \times M_{St} + M_{P4VP-TTC} \quad (\text{S3})$$

**Table S1.** Summary of the synthesized MCBNs.

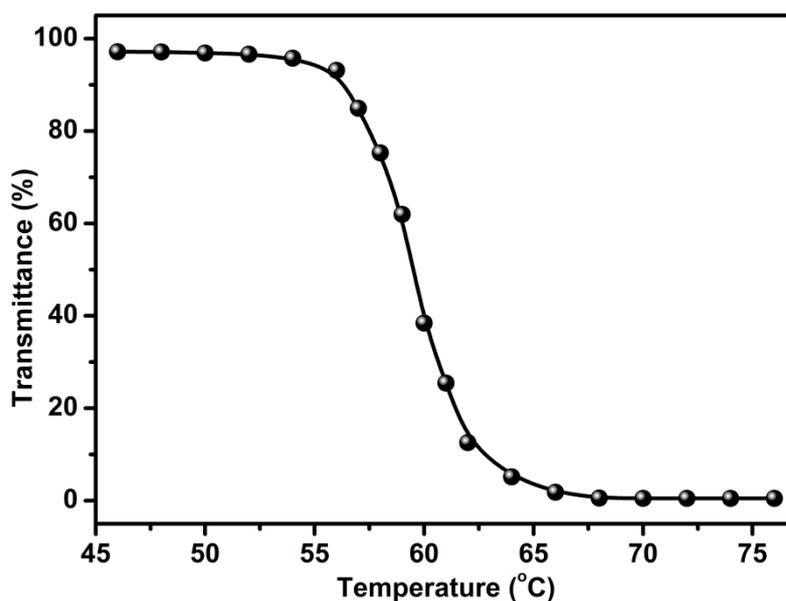
Figures	MCBNs <sup>a</sup>	[St] <sub>0</sub> : [T] <sub>0</sub> :	Conv. <sup>b</sup> (%)	$M_{n,NMR}$ (kg/mol) <sup>c</sup>		$M_{n,GPC}$ (kg/mol)/ $\bar{D}$ <sup>d</sup>		
		[H] <sub>0</sub> : [I] <sub>0</sub>		TS <sup>e</sup>	HS <sup>f</sup>	TS/HS	TS <sup>e</sup>	HS <sup>f</sup>
4B/5B	T <sub>153</sub> S <sub>260</sub> /H <sub>133</sub> S <sub>260</sub>	1800:3:3:1	86.7	50.6	43.9	43.1/1.37	45.2/1.25	40.7/1.21
4A	T <sub>153</sub> S <sub>261</sub> /H <sub>133</sub> S <sub>261</sub>	1800:4:2:1	87.2	51.4	43.4	43.7/1.40	45.5/1.22	39.8/1.19
4C	T <sub>153</sub> S <sub>264</sub> /H <sub>133</sub> S <sub>264</sub>	1800:2:4:1	88.3	50.3	44.5	44.2/1.42	46.6/1.24	41.7/1.28
5A	T <sub>153</sub> S <sub>90</sub> /H <sub>133</sub> S <sub>90</sub>	600:3:3:1	90.1	33.6	23.8	27.4/1.36	30.9/1.18	21.2/1.15
5C	T <sub>153</sub> S <sub>390</sub> /H <sub>133</sub> S <sub>390</sub>	3000:3:3:1	78.2	64.6	57.1	52.3/1.44	58.1/1.31	49.8/1.27
9A-B	T' <sub>153</sub> S <sub>260</sub> /H <sub>133</sub> S <sub>260</sub>	1800:3:3:1	86.7	48.5	43.9	42.7/1.41	44.1/1.20	39.8/1.17

<sup>a</sup> T, H, S and T' denotes PNASME, P4VP, PS and PNAS block, respectively, <sup>b</sup> the monomer conversion was determined by  $^1\text{H}$  NMR analysis, <sup>c</sup> the molecular weight by NMR analysis according to eqs. S2 and S3, <sup>d</sup> the polymer molecular weight and  $\bar{D}$  ( $M_w/M_n$ ) by GPC analysis, <sup>e</sup> TS denotes the separated PNASME-*b*-PS diblock copolymer or the hydrolytic PNAS-*b*-PS diblock copolymer, <sup>f</sup> HS denotes the separated P4VP-*b*-PS diblock copolymer. Note: the MCBNs of T'<sub>153</sub>S<sub>260</sub>/H<sub>133</sub>S<sub>260</sub> was prepared with hydrolyzing from T<sub>153</sub>S<sub>260</sub>/H<sub>133</sub>S<sub>260</sub>.

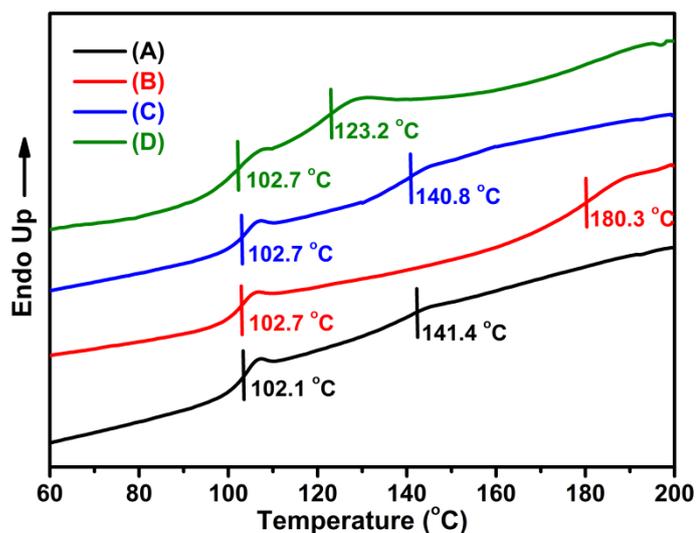
### 3. Supplementary Figures



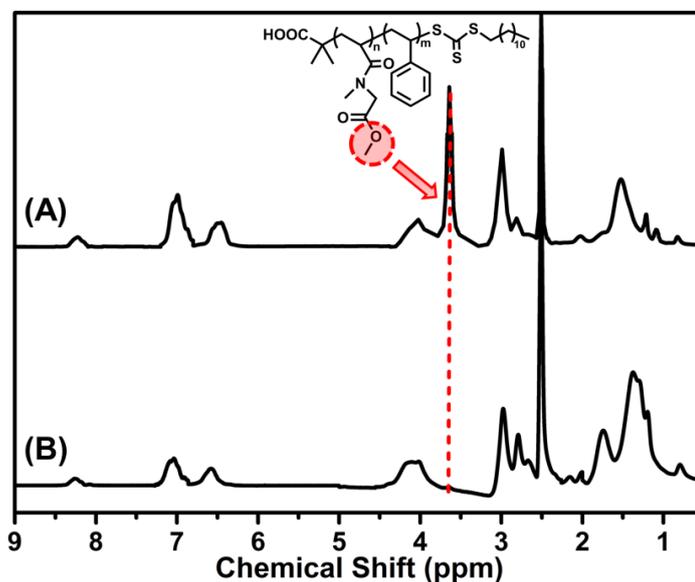
**Figure S1.** TEM images of the non-stained nanoparticles of PNASME<sub>153</sub>-*b*-PS<sub>279</sub> ( $T_{153}S_{279}$ , A), P4VP<sub>133</sub>-*b*-PS<sub>292</sub> ( $H_{133}S_{292}$ , B) dispersed in ethanol/water (80/20 w/w) prepared via dispersion RAFT polymerization employing individual macro-RAFT agents and the PNASME<sub>153</sub>-*b*-PS<sub>260</sub>/P4VP<sub>133</sub>-*b*-PS<sub>260</sub> nanoparticles ( $T_{153}S_{260}/H_{133}S_{260}$ , C) prepared employing two macro-RAFT agents.



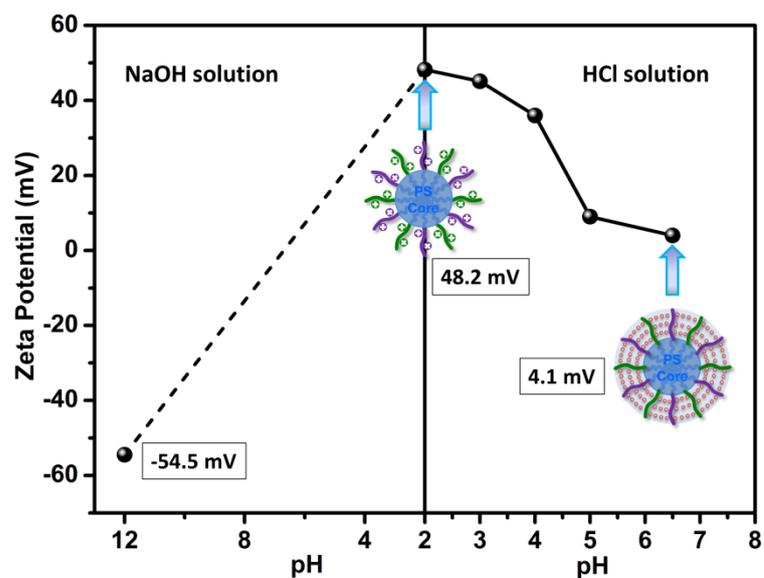
**Figure S2.** Temperature-dependent transmittance of 0.01 wt% PNASME<sub>153</sub>-TTC aqueous solution.



**Figure S3.** DSC thermograms of the PNASME<sub>153</sub>/P4VP<sub>133</sub> (1/1 w/w) blends (A), and PNAS<sub>153</sub>-*b*-PS<sub>260</sub>/P4VP<sub>133</sub>-*b*-PS<sub>260</sub> (B) obtained from hydrolysis of PNASME<sub>153</sub>-*b*-PS<sub>260</sub>/P4VP<sub>133</sub>-*b*-PS<sub>260</sub>, the separated diblock copolymer of P4VP<sub>133</sub>-*b*-PS<sub>260</sub> (C) and PNAS<sub>153</sub>-*b*-PS<sub>260</sub> (D). Note: The glass transition temperature ( $T_g$ ) of PNASME<sub>153</sub> is about 102.1 °C and the  $T_g$  of P4VP<sub>133</sub> is about 141.4 °C.



**Figure S4.** <sup>1</sup>H NMR spectra of the PNASME<sub>153</sub>-*b*-PS<sub>260</sub>/P4VP<sub>133</sub>-*b*-PS<sub>260</sub> nanoparticles before hydrolysis (A) and the PNAS<sub>153</sub>-*b*-PS<sub>260</sub>/P4VP<sub>133</sub>-*b*-PS<sub>260</sub> nanoparticles after hydrolysis (B). Note: the signal of H<sub>2</sub>O (3.33 ppm) in DMSO-*d*<sub>6</sub> was inhibited by water suppression experiment.



**Figure S5.** pH dependence of Zeta-potentials of the  $\text{PNAS}_{153}\text{-}b\text{-PS}_{260}/\text{P4VP}_{133}\text{-}b\text{-PS}_{260}$  nanoparticles in aqueous solution at pH = 12.0, pH = 2.0 and pH = 6.5, respectively. Insets: the schematic structures of nanoparticles in aqueous solution are at pH = 2.0 and pH = 6.5, respectively.