Supporting

In situ synthesis of diblock copolymer nano-assemblies via dispersion RAFT polymerization induced self-assembly and Ag/copolymer composite nanoparticles thereof

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1. Figure S1

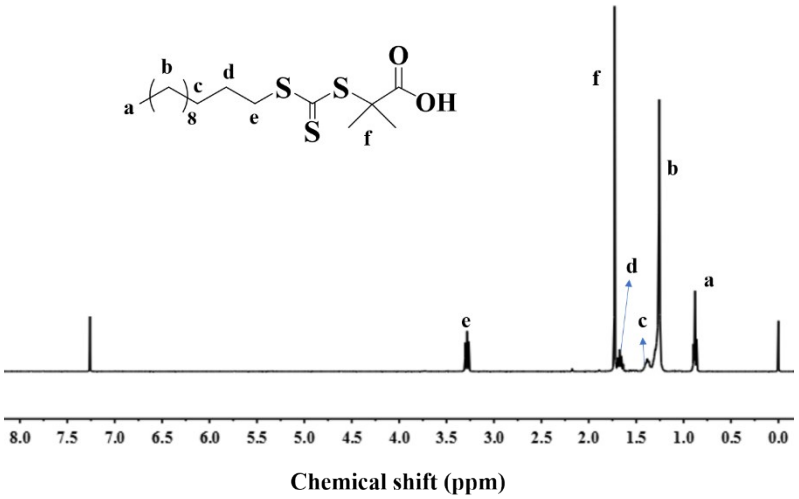

Figure S1 The ^{1}H NMR spectroscopy of DDMAT

2. Figure S2 and Equation S1

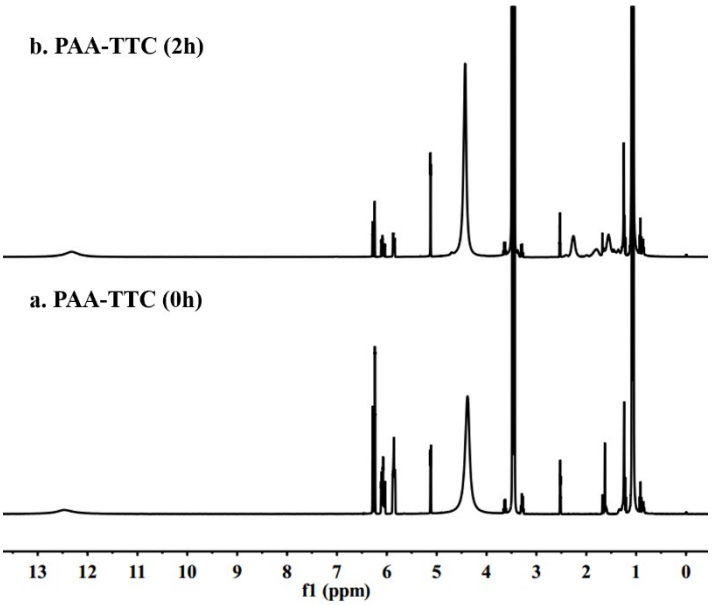

Figure S2. The ^{1}H NMR spectra of the polymerization solution before and after the RAFT polymerization of AA. Polymerization conditions: [AA]/[DDMAT]/[AIBN] = 25:1:0.2; AA (2.565 g, 3.563×10^{-2} mol); ethanol (10 g); 70 °C.

$$\text{Conversion}_{AA(2h)}\,\% = 1\text{-}\textbf{Error!} \qquad \textbf{Equation S1}$$

3. Figure S3

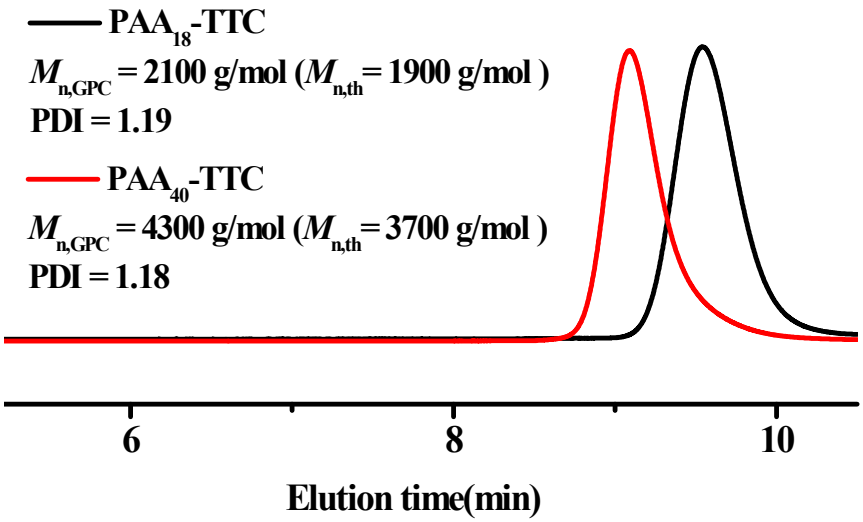

Figure S3 The GPC traces of the methylated PAA_{18}-TTC (A) and PAA_{40}-TTC (B).

Polymerization conditions: (A) [AA]/[DDMAT]/[AIBN] = 18:1:0.2; AA (1.846 g, 2.56×10^{-2} mol); ethanol (10 g); 70 °C; 11h. (B) [AA]/[DDMAT]/[AIBN] = 40:1:0.2; AA (4.104 g, 5.7×10^{-2} mol); ethanol (15 g); 70 °C; 8h. Note: The $M_{n,th}$ is the values of the methylated copolymer.

4. Figure S4

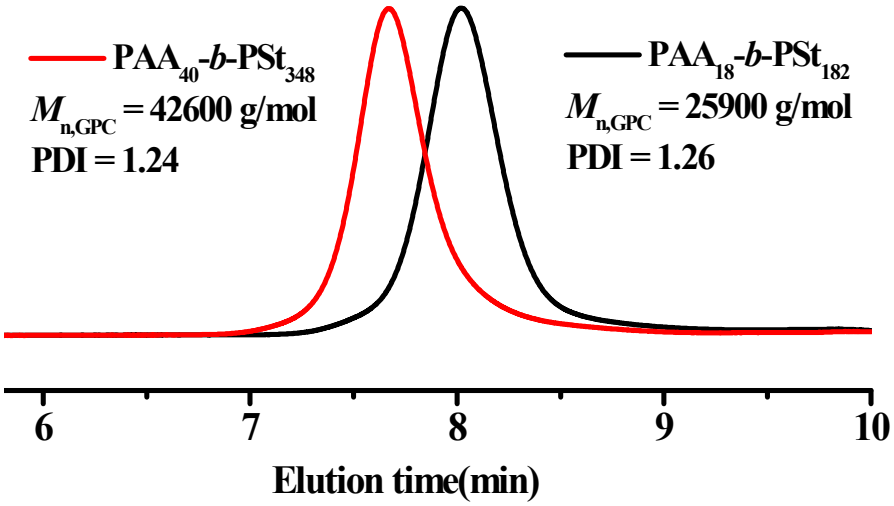

Figure S4 The GPC traces of the methylated PAA_{18}-*b*-PSt_{182} (A) and PAA_{40}-*b*-PSt_{348} (B). The PAA-*b*-PSt nano-objects prepared through the individual PAA-TTC macro-RAFT agents mediated dispersion polymerization at 23 h. Polymerization conditions: (A) [PAA_{18}-TTC]/[St]/[AIBN] = 1:200:0.2; St (7.41 g, 9.5×10^{-2} mol); ethanol/water (53.675 g, 70/30 w/w); 70 °C. (B) [PAA_{40}-TTC]/[St]/[AIBN] = 1:350:0.2; St (17.29 g, 1.663×10^{-1} mol); ethanol/water (53.675 g, 70/30 w/w); 70 °C.

5. Figure S5

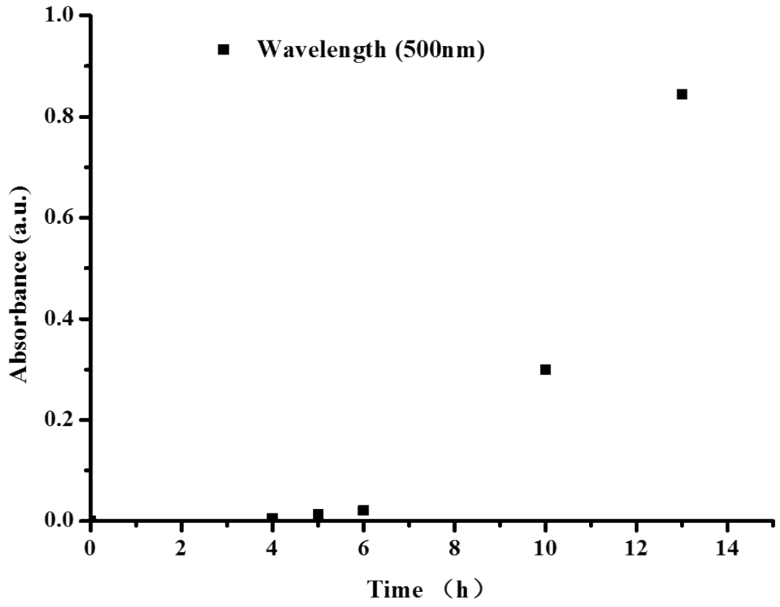

Figure S5 UV–Vis absorption intensity (ca.500 nm) of polymerization solution at different reaction time.

6. Figure S6

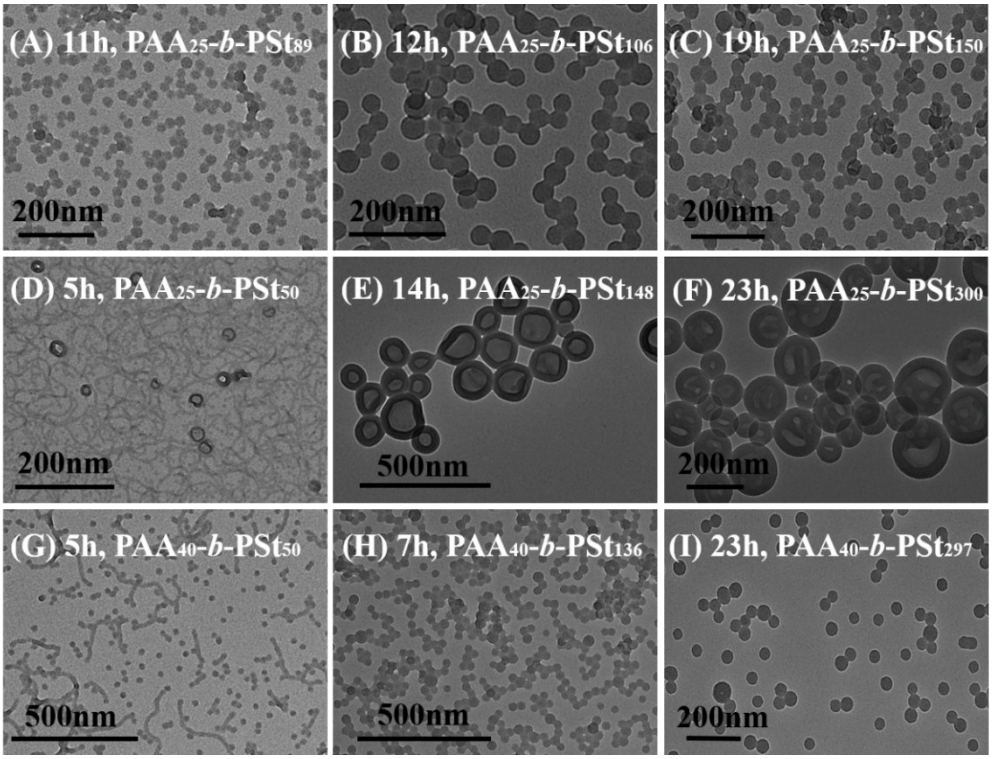

Figure S6 The morphology evolution of the PAA-*b*-PSt nano-objects prepared through

the PAA-TTC macro-RAFT agents mediated dispersion polymerization in different polymerization conditions: (A-C) [PAA_{25}-TTC]/[St]/[AIBN] = 1:150:0.2; St (7.41 g, 7.125×10^{-2} mol); ethanol/water (53.675 g, 70/30 w/w); 70 °C. (D-F) [PAA_{25}-TTC]/[St]/[AIBN] = 1:300:0.2; St (14.82 g, 1.425×10^{-1} mol); ethanol/water (53.675 g, 70/30 w/w); 70 °C. (G-I) [PAA_{40}-TTC]/[St]/[AIBN] = 1:300:0.2; St (14.82 g, 1.425×10^{-1} mol); ethanol/water (53.675 g, 70/30 w/w); 70 °C.

7. Figure S7

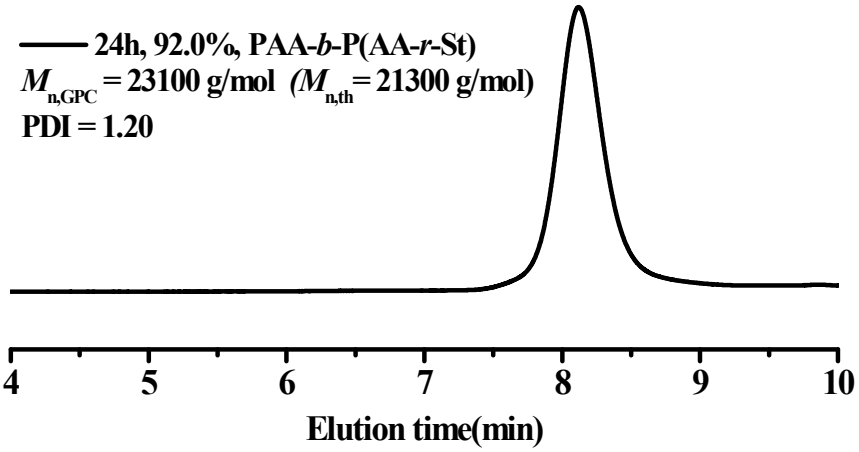

Figure S7 The GPC trace of the methylated PAA-*b*-P(AA-*r*-St). Polymerization condition: [AA]/[St]/[DDMAT]/[AIBN] = 25:200:1:0.2; St (9.88 g, 9.5×10^{-2} mol); ethanol/water mixtures (53.675 g, 80/20 w/w); 16.7% w/w solid content; 70 °C. Note: The AA conversion for PAA-TTC was about 72% determined by ^{1}H NMR after 2h, and used it for the next polymerization of styrene without further purification.

8. Figure S8

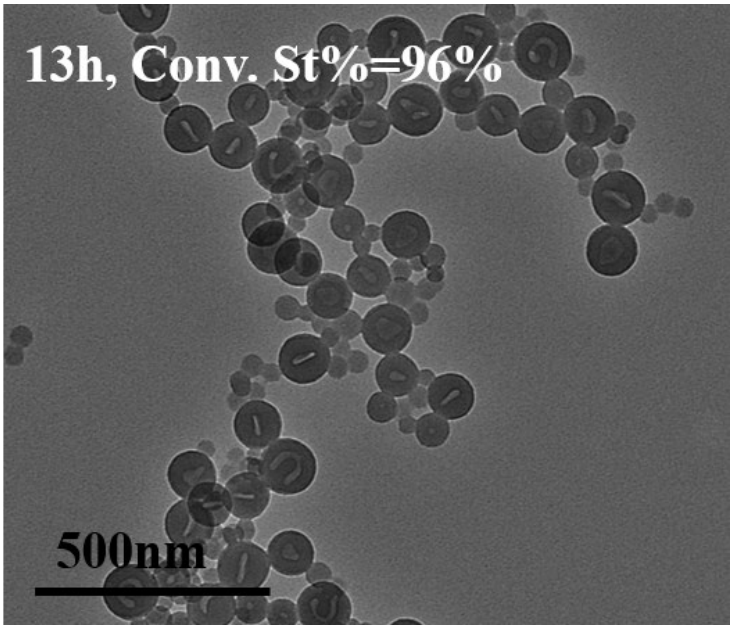

Figure S8 The final morphology of the PAA-*b*-PSt nano-objects prepared through the PAA-TTC macro-RAFT agents mediated dispersion polymerization. Polymerization conditions: [PAA_{25}-TTC]/[St]/[AIBN] = 1:200:0.2; St (9.88 g, 9.5×10^{-2} mol); ethanol/water (53.675 g, 70/30 w/w); 70 °C. Note: the PAA_{25}-TTC was synthesized at the molar ratio of [AA]/[DDMAT]/[AIBN] = 25:1:0.4, and the conversion of AA was above 97% determined by ^{1}H NMR after 5h.

9. Table S1

Table S1 The effect of residual AA on aggregates morphology in various water/ethanol mixtures [a]

Ethanol/water (w/w)	Time (h)	Conv. (%)	Morphology	D[b] (nm)	D_{DLS},nm (PDI)[c]
100/0	48	45.7	vesicles /worms	(1～2)×10^3	1994 (0.199)
90/10	33	94.8	vesicles	228	206 (0.224)
80/20	24	92.0	vesicles	175	168 (0.167)
70/30	13	89.1	lacunal nanospheres /vesicles	138	156 (0.005)

[a] Polymerization conditions: [AA]/[St]/[DDMAT]/[AIBN] = 25:200:1:0.2; St (9.88 g,

9.5×10^{-2} mol); either ethanol or various ethanol/water mixtures (53.675 g); 16.7% w/w solid content; 70 °C. Note: The AA conversion for PAA-TTC was about 72% determined by ^{1}H NMR after 2h. [b] Measured by TEM. [c] Measured by intensity-average DLS.