

Supporting Information

In situ synthesis of the Ag/poly(4-vinylpyridine)-*block*-polystyrene composited nanoparticles by dispersion RAFT polymerization

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Synthesis of P4VP₂₇-TTC. Into a 50 mL Schlenk flask with a magnetic bar, 4VP (8.00 g, 0.0761 mol), DDMAT (0.925 g, 2.54 mmol), AIBN (0.104 g, 0.634 mmol), and ethanol (16.0 g) were added. The solution was initially degassed with nitrogen at 0 °C to remove oxygen, and then the flask content was immersed into a preheated oil bath at 70 °C for 5.5 h. After a given time, the polymerization was quenched by rapid cooling upon immersion of the flask in iced water. The monomer conversion at 90% was determined by ¹H NMR analysis. To check the monomer conversion, once the polymerization was quenched and distributed homogeneously in the polymerization mixture by vigorous stirring, and then a drop of the polymerization solution (about 0.05 mL) was diluted with CDCl₃ (0.5 mL) and subjected to ¹H NMR analysis. The 4VP monomer conversion was calculated by comparing the vinyl signals of 4VP at $\delta = 5.45\text{-}5.55$ ppm with the pyridine signal of P4VP at $\delta = 8.35$ ppm. The synthesized polymer was precipitated into cold diethyl ether, collected by three precipitation/filtration cycles, and then dried at room temperature under vacuum to afford the yellow powder of P4VP-TTC.

Dispersion RAFT polymerization and synthesis of the P4VP-*b*-PS nano-assemblies. The P4VP-TTC macro-RAFT agent mediated dispersion polymerization of styrene in the

methanol/water mixture was carried out at 70 °C with a constant molar ratio of $[St]_0:[P4VP-TTC]_0:[AIBN]_0 = 300:1:0.333$ and with a constant weight ratio of the feeding styrene monomer plus the P4VP-TTC macro-RAFT agent to the methanol/water mixture solvent at 20 wt%. Herein, a typical example of the dispersion RAFT polymerization in the 90/10 methanol/water mixture is introduced. Into a 25 mL Schlenk flask with a magnetic bar, P4VP₂₇-TTC (0.0513 g, 0.0160 mmol), styrene (0.500 g, 4.80 mmol) and AIBN (0.876 mg, 0.0053 mmol) dissolved in the solvent of methanol (1.99 g) and water (0.221 g) were added. The flask content was initially degassed with nitrogen at 0 °C to remove oxygen, and then the polymerization was started by immersing the flask in a preheated oil bath at 70 °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 as discussed in ref. 59, in which a given volume of the colloidal dispersion (1.0 mL) was filtrated twice with a 0.22 μm nylon filter, and then the filtrate was diluted with ethanol and analyzed at 245 nm. To check the resultant P4VP-*b*-PS diblock copolymer nano-objects, a small drop of the colloidal dispersion was deposited onto a piece of copper grid, dried at room temperature under vacuum, and then observed by TEM. To collect the P4VP-*b*-PS diblock copolymer for GPC analysis and ¹H NMR analysis, the P4VP-*b*-PS nano-assemblies were separated by centrifugation of the colloidal dispersion (12500 rpm, 5 min), washed three times with cold diethyl ether, and finally dried at room temperature at vacuum to afford the P4VP-*b*-PS diblock copolymer.

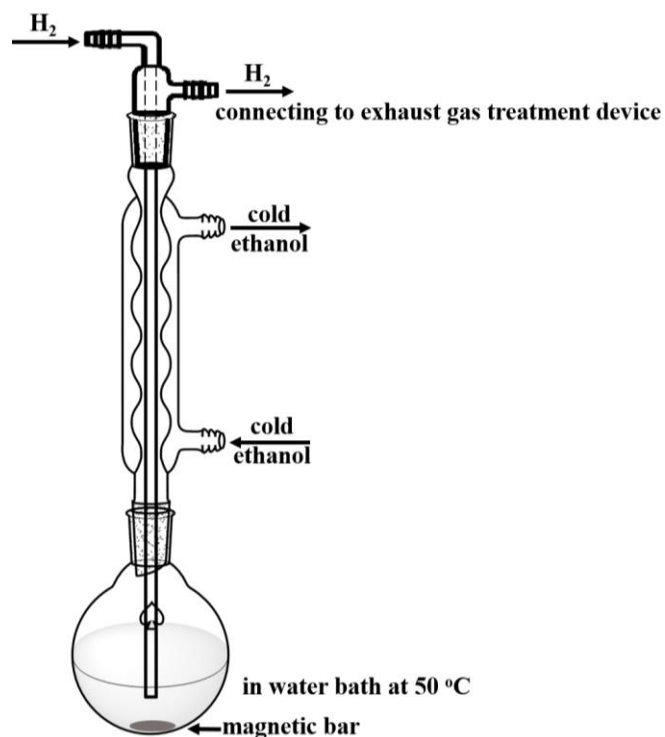


Figure S1. The apparatuses for the synthesis of the Ag NPs.

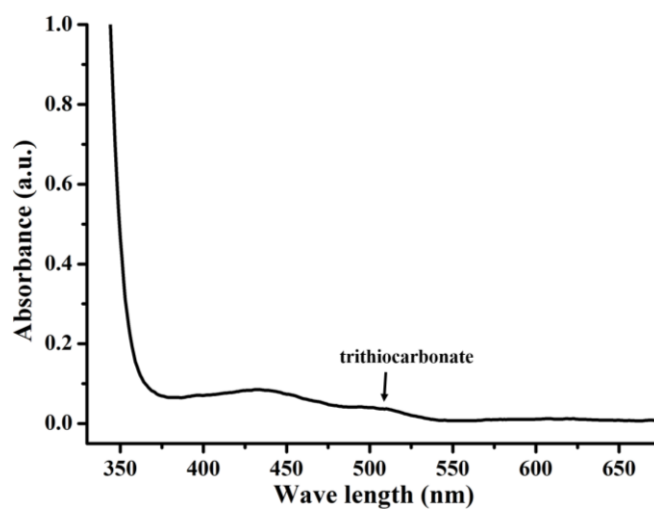


Figure S2. UV-Vis spectrum of P4VP₂₇-TTC.

Figure S3 summarizes the ¹H NMR spectra of P4VP-*b*-PS prepared through the dispersion RAFT polymerization with [Ag]₀: [P4VP₂₇-TTC]₀ = 4:1 at different polymerization time.

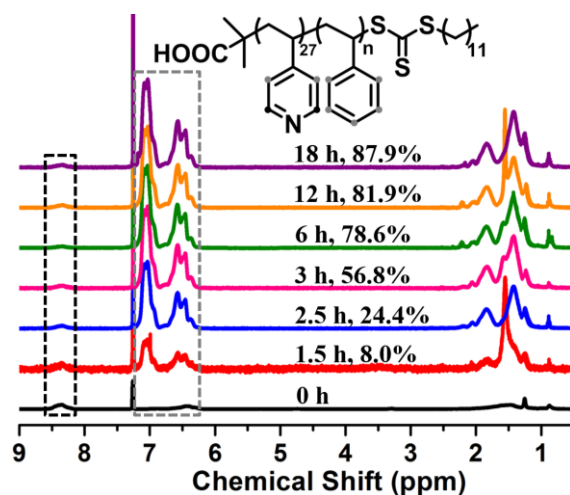


Figure S3. The ^1H NMR spectra of P4VP-*b*-PS synthesized at $[\text{Ag}]_0:[\text{P4VP}_{27}\text{-TTC}]_0 = 4:1$ at different polymerization time.

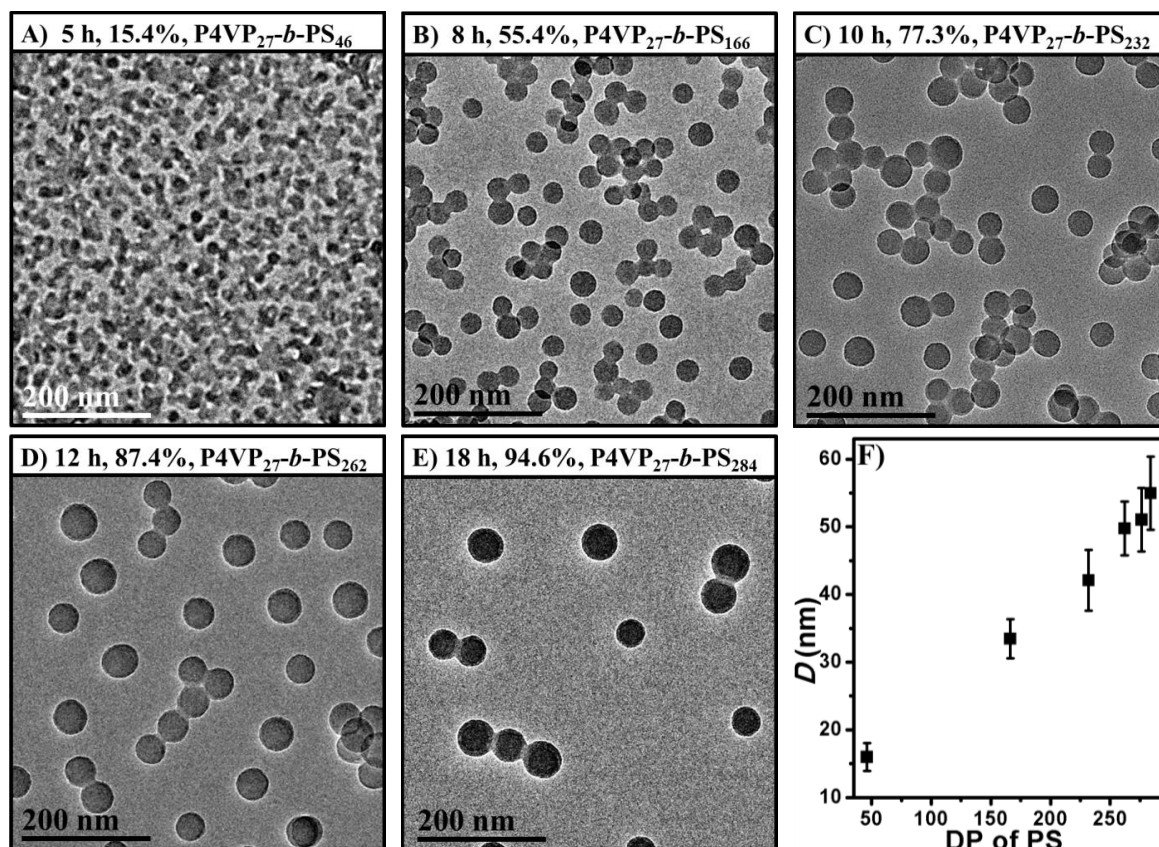


Figure S4. The TEM images of P4VP-*b*-PS synthesized through the dispersion RAFT polymerization at different polymerization time of 5 h (A), 8 h (B), 10 h (C), 12 h (D), and 18 h (E) and the average diameter distribution of P4VP-*b*-PS synthesized at different polymerization time (F).

Table S1. Summary of the P4VP-*b*-PS BCPs prepared through dispersion RAFT polymerization with different molar ratio of the [Ag]₀:[P4VP₂₇-TTC]₀.

Entry	Polymer	[Ag] ₀ :[P4VP-TTC] ₀	Time (h)	Monomer conv. (%)	<i>M_n</i> (kg/mol)			<i>D</i>
					<i>M_{n,th}</i>	<i>M_{n,GPC}</i>	<i>M_{n,NMR}</i>	
1	P4VP ₂₇ - <i>b</i> -PS ₂₇₆	0:1	15	92.1	31.98	34.21	32.73	1.06
2	P4VP ₂₇ - <i>b</i> -PS ₂₇₃	1:1	24	91.1	31.67	68.43	31.80	1.09
3	P4VP ₂₇ - <i>b</i> -PS ₂₇₇	2:1	24	92.4	32.06	77.00	34.75	1.16
4	P4VP ₂₇ - <i>b</i> -PS ₂₈₁	4:1	24	93.8	32.50	242.45	37.66	1.07
5	P4VP ₂₇ - <i>b</i> -PS ₂₉₀	8:1	24	96.8	33.46	242.60	38.84	1.05

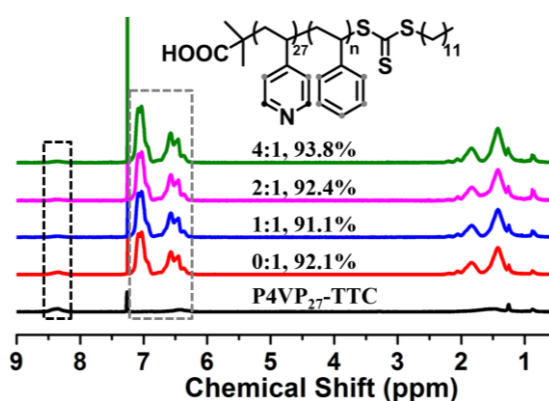


Figure S5. The ¹H NMR spectra of P4VP₂₇-TTC and P4VP-*b*-PS synthesized at [Ag]₀:[P4VP₂₇-TTC]₀ ranging from 0:1 to 4:1 through the dispersion RAFT polymerization.

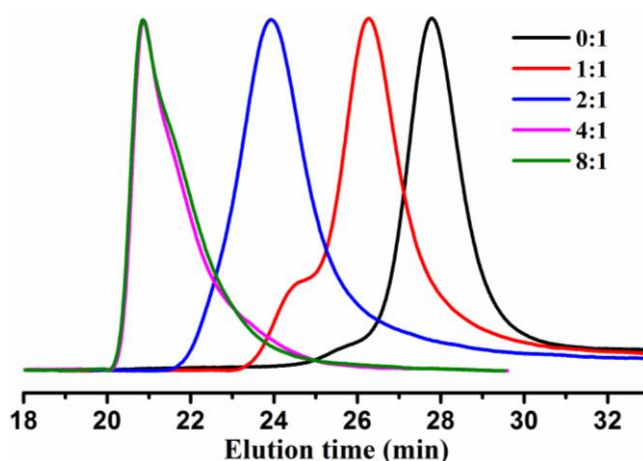


Figure S6. The GPC traces of P4VP-*b*-PS synthesized at [Ag]₀:[P4VP₂₇-TTC]₀ ranging from 0:1 to 8:1 through the dispersion RAFT polymerization.

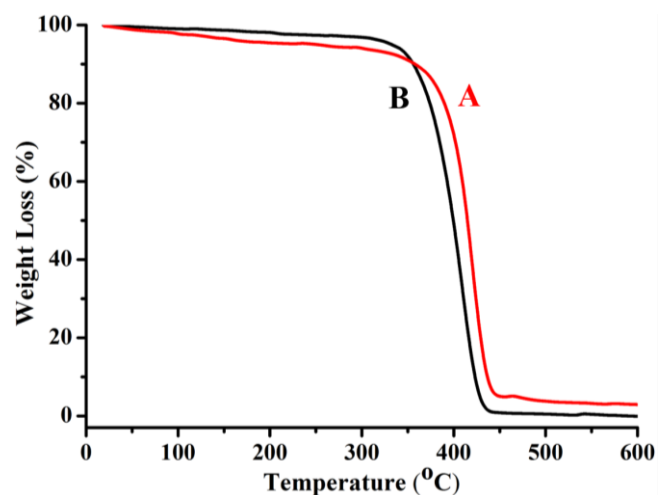


Figure S7. Thermogravimetric analysis (TGA) of the Ag/P4VP₂₇-*b*-PS₂₉₀ nanoparticles synthesized at [Ag]₀:[P4VP₂₇-TTC]₀ = 8:1 (A) and the reference nanoparticles of P4VP₂₇-*b*-PS₂₇₆ synthesized through dispersion RAFT polymerization (B). Note: the TGA analysis was performed on a thermogravimetric analyzer (TG 209, NETZSCH) under nitrogen, with a heating rate of 10 °C /min.