

Supporting Information

Synthesis of Poly(dihydroxystyrene-*block*-styrene) (PDHSt-*b*-PSt) by the RAFT Process and Preparation of Organic-Solvent-Dispersive Ag Nanoparticles by Automatic Reduction of Metal Ions in the Presence of PDHSt-*b*-PSt.

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I. Experimental

1. Materials.

3,4-Dimethoxystyrene (DMSt, technical grade, 99%) and 2-cyano-2-propyldodecyltrithiocarbonate (CPDTTC, 97%) were purchased from Sigma-Aldrich. DMSt and CPDTTC were used without any purification. Anhydrous 1,4-dioxane ($\geq 99.0\%$), boron tribromide (BBr_3 , 99.85%), *N,N'*-dimethylformamide (DMF, $\geq 99.5\%$) and dichloromethane (CH_2Cl_2 , $\geq 99.5\%$) were purchased from Wako Pure Chemical Industries, Ltd. 2,2'-Azobis(isobutyronitrile) (AIBN, $\geq 98.0\%$) was recrystallized from methanol and dried *in vacuo* before use. Styrene (St, $\geq 99.0\%$, Wako Pure Chemical Industries, Ltd.) was passed through alumina to remove the inhibitor before use. Poly(styrene-*block*-acrylic acid) was purchased from Polymer Source, Inc.

2. Characterization.

The number-average molecular weight (M_n) and molecular weight distribution of the polymers were measured by using gel permeation chromatography (GPC, HLC-8320GPC, Tosoh Corporation) with polystyrene as standard. THF was used as an eluent at a flow rate of 0.6 mL/min at 40 °C. Conversion of monomer was detected with $^1\text{H-NMR}$ analysis (400 MHz, Bruker). The theoretical molecular weight was calculated from the monomer conversion. Glass transition temperature was measured by using differential scanning calorimetry (DSC, DSC822, Mettler-Toledo International Inc.).

3. Synthetic procedures.

•Synthesis of Poly(dimethoxystyrene)

Typical synthesis scheme of poly(dimethoxystyrene) was shown below.

Poly(dimethoxystyrene) (PDMSt) was prepared by using RAFT polymerization. A schematic

illustration of the block copolymer synthesis is shown in Scheme 1. DMSt (2.03 g, 12.4 mmol), CPDTTC (27.8 mg, 8.04×10^{-2} mmol), 1,4-dioxane (1.03 g) and AIBN (7.1 mg, 4.32×10^{-2} mmol) were added to a glass tube, which was sealed after four freeze-pump-thaw cycles, and then the glass tube was placed in an aluminum block heater at 60 °C for 5 h. After polymerization, the reaction mixture was cooled with liquid nitrogen. The resulting solution was purified by reprecipitation in a large volume of methanol. The yellow precipitate was collected by centrifugation and dried *in vacuo*. The yield was 36.5%. Part of the product was used as a macro-RAFT agent for the synthesis of PDMSt-*b*-PSt. The M_n and M_w/M_n of the PDMSt macro-RAFT agent were 7.10×10^3 and 1.08, respectively. ^1H NMR (CDCl_3): δ 1.11–2.22 ppm (broad, polymer backbone), 3.49–3.92 ppm (broad, methoxy group), 5.76–6.69 ppm (broad, aromatic) (Figure S1 (a)). SEC results were summarized in Figure S2.

•Synthesis of Poly(dimethoxystyrene-*block*-styrene)

St monomer (3.06 g, 29.3 mmol), PDMSt macro-RAFT agent (97.4 mg, 1.28×10^{-2} mmol), 1,4-dioxane (3.00 g), and AIBN (1.15 mg, 7×10^{-3} mmol) were added to a glass tube, which was sealed after four freeze-pump-thaw cycles, and then the glass tube was placed on an aluminum block heater at 60 °C. After polymerization, the reaction mixture was cooled with liquid nitrogen. The resulting solution was purified by reprecipitation in a large volume of methanol. The white precipitate was collected by centrifugation and dried *in vacuo*. Glass transition temperature was observed at 75 and 101 °C (Figure S4). ^1H NMR (CDCl_3): δ 1.05–2.29 ppm (broad, polymer backbone), 3.49–3.92 ppm (broad, methoxy group), 5.76–7.23 ppm (broad, aromatic) (see supporting information, Figure S1 (b)).

•Synthesis of Poly(dihydroxystyrene-*block*-styrene)

PDMSt-b-PSt was treated with BBr_3 to convert the methoxy groups to hydroxyl groups. The diblock copolymer (150 mg, 1.79×10^{-3} mmol) and dichloromethane (5 mL) was added to a glass vial, and then the vial was sealed with a rubber septum. After the solution was cooled to 0 °C, dichloromethane solution containing BBr_3 (0.5 mL, 1.00 M) was slowly added with vigorous stirring. The solution was stirred at room temperature for 12 h. The mixed solution was added dropwise to a large volume of aqueous 1 M HCl. After stirring for 3 h, the white precipitate was collected by centrifugation and dried under vacuum. The sequence was repeated twice. ^1H NMR (DMF): δ 1.07–2.51 ppm (broad, polymer backbone), 5.85–7.48 ppm (broad, aromatic) (see supporting information, Figure S1 (c)).

•Synthesis of Poly(dihydroxystyrene-*random*-styrene)

Random copolymer was synthesized by free radical polymerization. St monomer (2.00 g, 19.2 mmol), DMSt (1.05 g, 6.39 mmol), 1,4-dioxane (3.00 g), and AIBN (42.0 mg, 0.256 mmol) were added to a glass tube, which was sealed after four freeze-pump-thaw cycles, and then the glass tube was placed on an aluminum block heater at 60 °C. After polymerization, the reaction mixture was cooled with liquid nitrogen. The resulting solution was purified by reprecipitation in a large volume of methanol. The white precipitate was collected by centrifugation and dried *in vacuo*. The M_n and M_w/M_n of the PDMSt-b-PSt were 5.33×10^4 and 1.62, respectively. The random copolymer (150 mg, 1.79×10^{-3} mmol) and dichloromethane (5 mL) was added to a glass vial, and then the vial was sealed with a rubber septum. After the solution was cooled to 0 °C, dichloromethane solution containing BBr_3 (0.5 mL, 1.00 M) was slowly added with vigorous stirring. The solution was stirred at room temperature for 12 h. The mixed solution was added dropwise to a large volume of aqueous 1 M HCl. After stirring for 3 h, the white precipitate was collected by centrifugation and dried under vacuum. The sequence was repeated twice. Copolymerization ratio (styrene/

dimethoxystyrene) was determined by ^1H NMR, and it was 2.92.

•Synthesis of Organic-Solvent-Dispersive Metal Nanoparticles

PDHSt-b-PSt diblock copolymer was dissolved in chloroform (1 mL) and DMF (1 mL). AgNO_3 aqueous solution (2 mL, 102.5 mM) was added to the mixture containing the diblock copolymer. The solution was allowed to stand for 12 h at 25 °C, and it turned orange. An excess of Ag ions and polymers were removed by centrifugation. Methanol was added to make the solution to a single phase (The volume ratio of the solution and methanol was 1 : 1), and then centrifugation (12,000 rpm, 10 min, 5 °C) was carried out. After that small amount of DMF (approximately 100 μl) was added to disperse polymer and synthesized nanoparticles, and then deionized water was added (approximately 900 μl). nanoparticles were collected by centrifugation (12,000 rpm, 10 min, 5 °C). The solution was washed by DMF and water twice. Finally, the collected nanoparticles were redispersed in THF. A drop of the Ag nanoparticle dispersion was cast on a Cu grid covered with elastic carbon, and the Ag nanoparticles were observed by using transmission electron microscope (TEM, H-7650, Hitachi High-Technologies Corporation). The diameters of the Ag nanoparticles were estimated from TEM images by using image analysis software (Image J).

II. Results.

1. NMR results.

The chemical structures of the PDMSt macro-RAFT agent, PDMSt-b-PSt and PDHSt-b-PSt were determined by $^1\text{H-NMR}$. The PDMSt macro-RAFT agent and PDMSt-b-PSt were dissolved in CDCl_3 . Chloroform and water peaks were observed at 7.26 and 1.56 ppm, respectively. PDHSt-b-PSt was dissolved in DMF-d_7 . DMF peaks were observed at 2.74, 2.91, and 8.02 ppm, and a water peak was also observed at 3.46 ppm. From $^1\text{H NMR}$ result of block copolymer after treatment with BBr_3 , end groups of block copolymers did not observed due to high molecular weight of the block copolymer. Though, since it is reported that the end functional groups was affected and did not remain intact when BBr_3 reagents were employed¹, end groups lose their functionality after treatment with BBr_3 .

1, A. Isakova, P. D. Topham and A. J. Sutherland, *Macromolecules*, **2014**, 47, 2561-2568

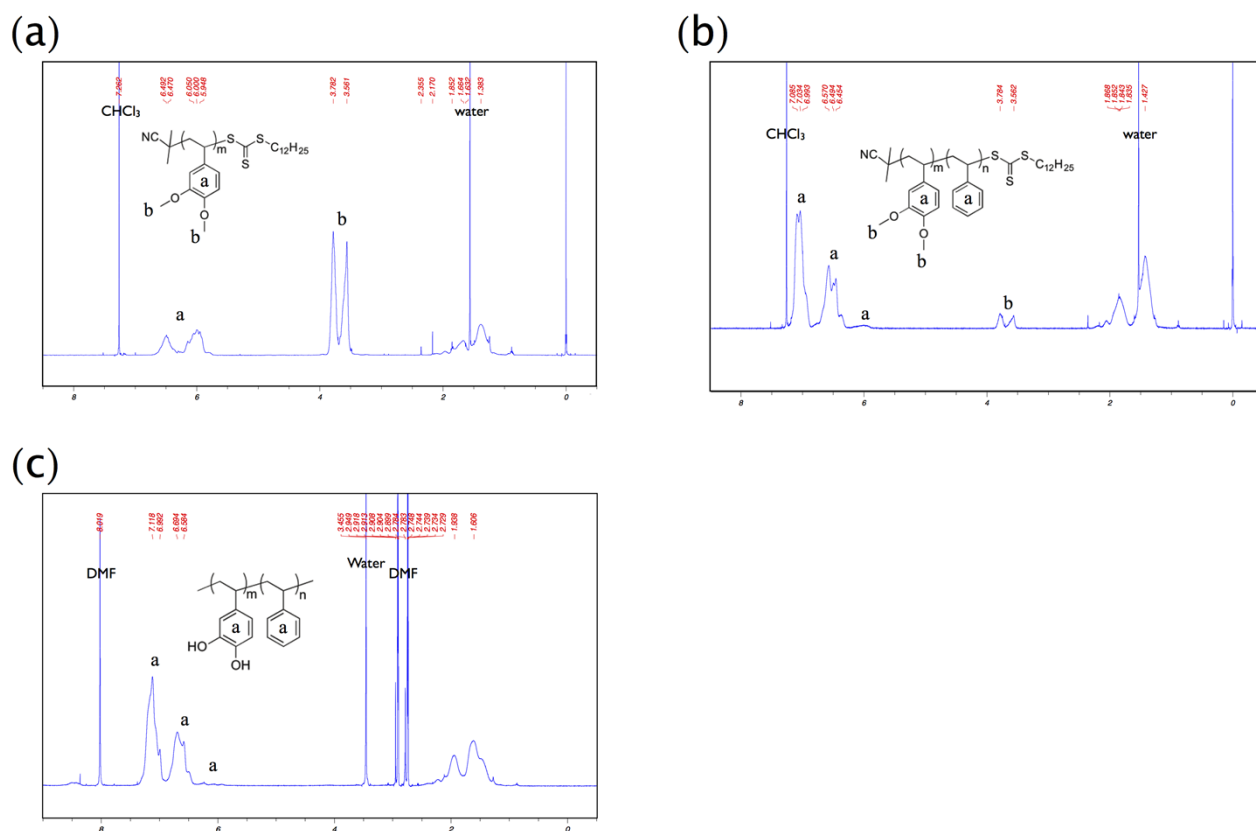


Figure S1. NMR results of (a) PDMSt macro-RAFT agent, (b) PDMSt-b-PSt and (c) PDHSt-b-St.

2, GPC and NMR results of PDMSt.

DMSt monomer reached about 34% within 93 h. The molecular weight distribution, M_w/M_n , of PDMSt-*b*-PSt showed a narrow polydispersity around 1.1. M_n was almost proportional to the conversion. These results indicate that each monomer was polymerized in the living polymerization system.

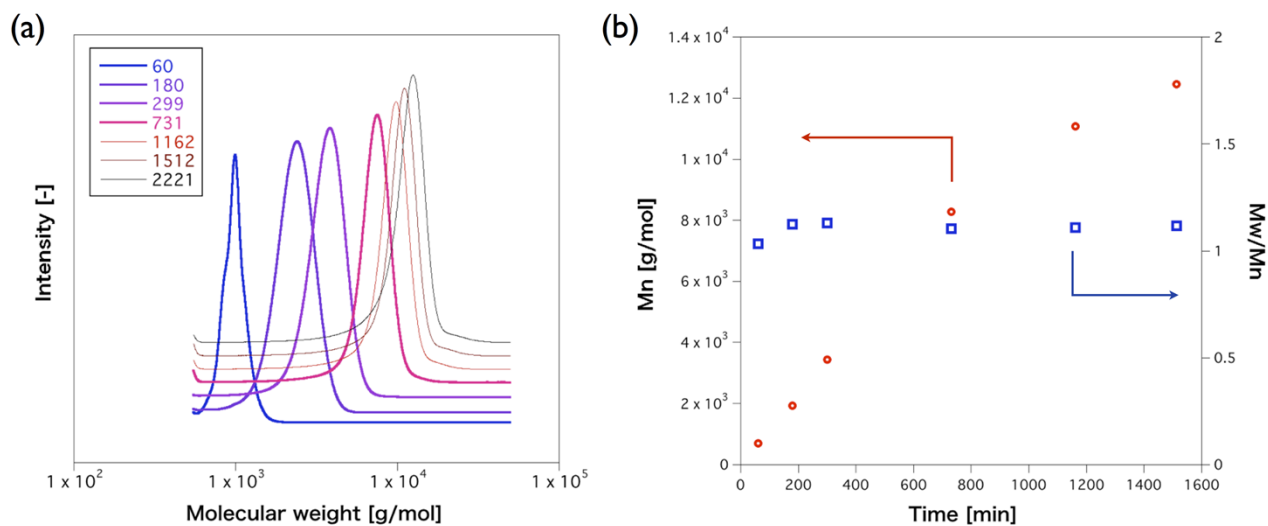


Figure S2, (a) GPC results and (b) M_n (red circles) and M_w/M_n (blue squares) as a function of reaction time.

3. GPC results of the second block polymerization.

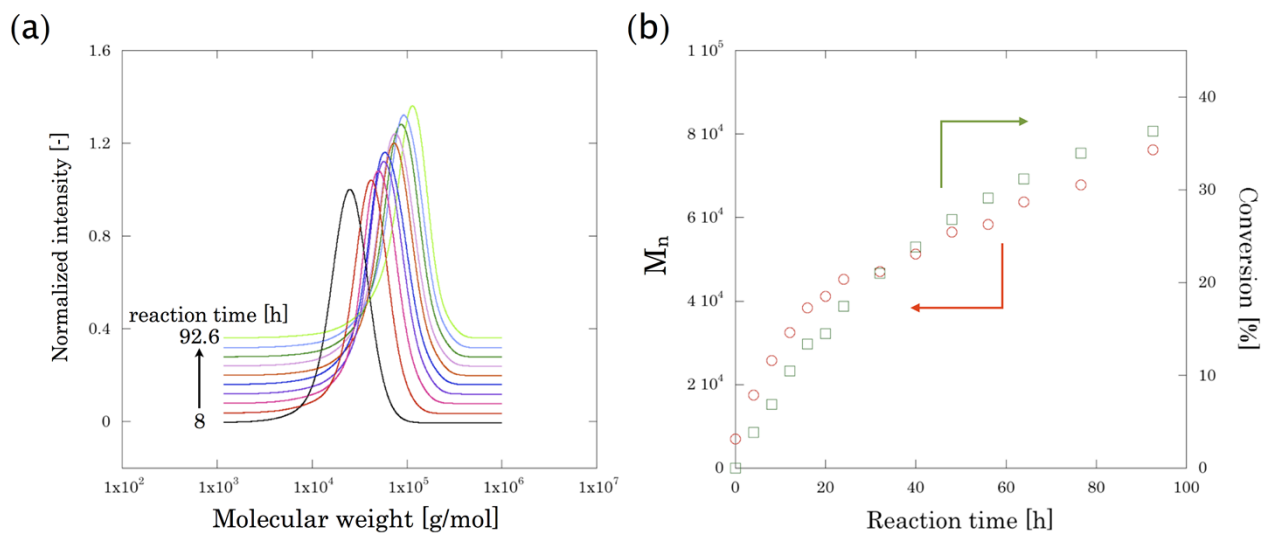


Figure S3. GPC results of the second block polymerization from 8 to 92.6 h.

4, DSC results of PDMSt-b-PSt

Glass transition temperatures were observed at 75°C and 101°C.

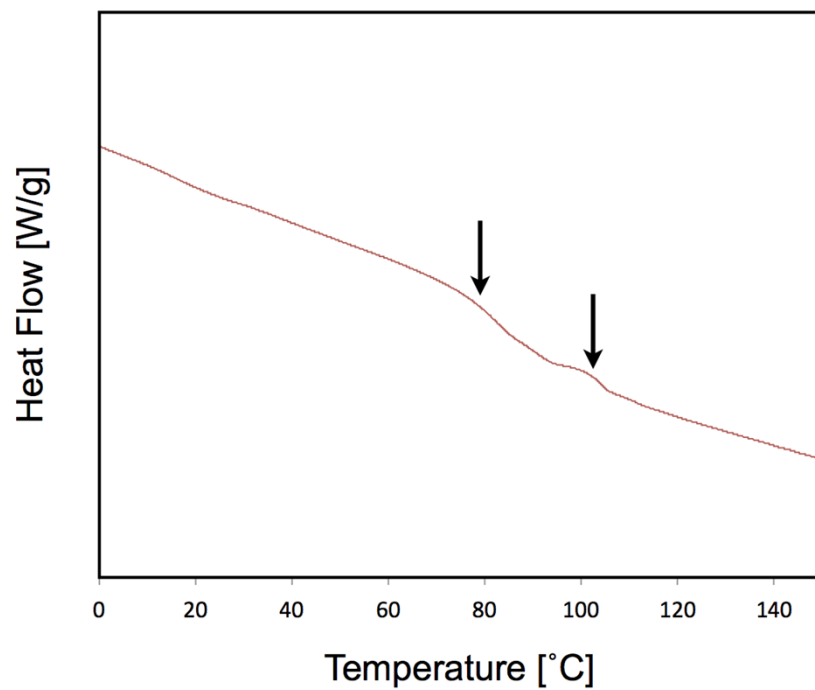


Figure S4, DSC result of PDMSt-b-PSt.

5, TEM images and Photographs of Ag NPs prepared with polymer 1, 2 and 3

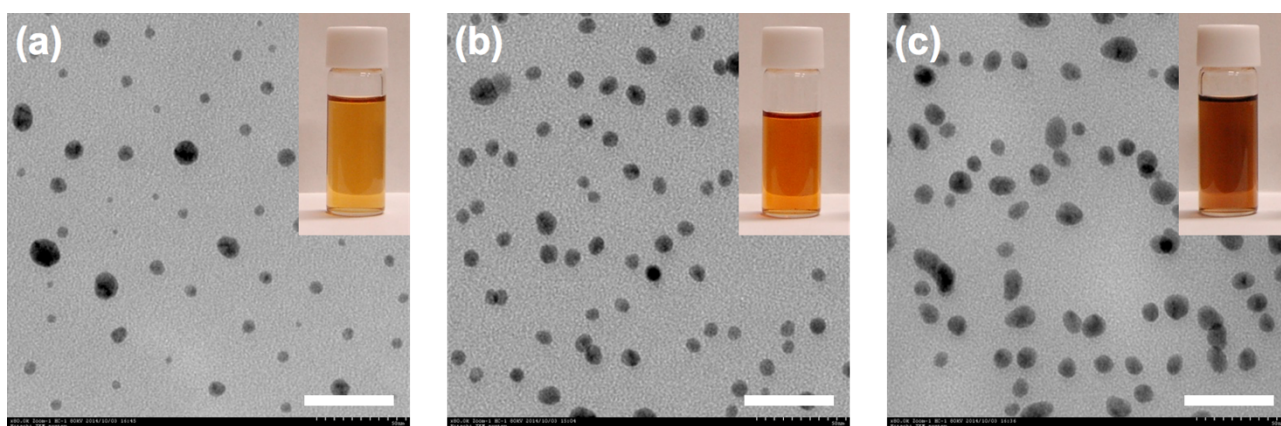


Figure S5, TEM images of Ag NPs and photograph of THE solution containing Ag NPs prepared with (a) polymer 1, (b) polymer 2 and (c) polymer 3. (Scale bars; 50 nm)

6, UV-Vis results of solutions containing poly(styrene-*block*-acrylic acid)

Poly(styrene-*block*-acrylic acid) was used instead of catechol-containing diblock copolymer. M_n of polystyrene and polyacrylic acid segments were 15000 and 4300, respectively. In the case of poly(styrene-*block*-acrylic acid), a peak of plasmonic resonances of silver nanoparticles was not observed. This result suggested that catechol-containing block copolymers can be effective in helping silver nanoparticle formation.

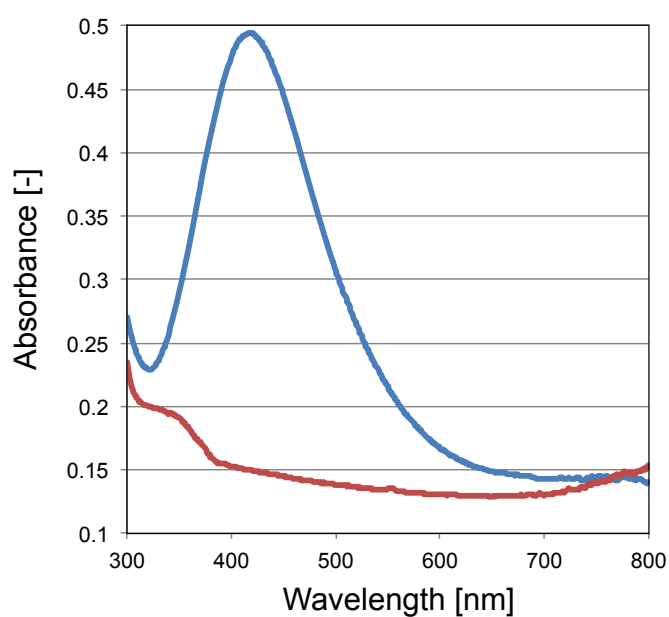


Figure S6, UV-Vis results of polymer 2 (red) and poly(styrene-*b*-acrylic acid).

7, Ag NPs prepared with random copolymer

Ag NPs were also prepared by using random copolymer, which has similar copolymer ratio compared with polymer 3. Size of Ag NPs was measured from TEM images. A histogram and a TEM image are shown in Figure S4. From TEM images, Ag NPs from 1 nm to 25 nm are observed. The histogram shows that NPs prepared with random copolymer has wide dispersity compared with polymer 3.

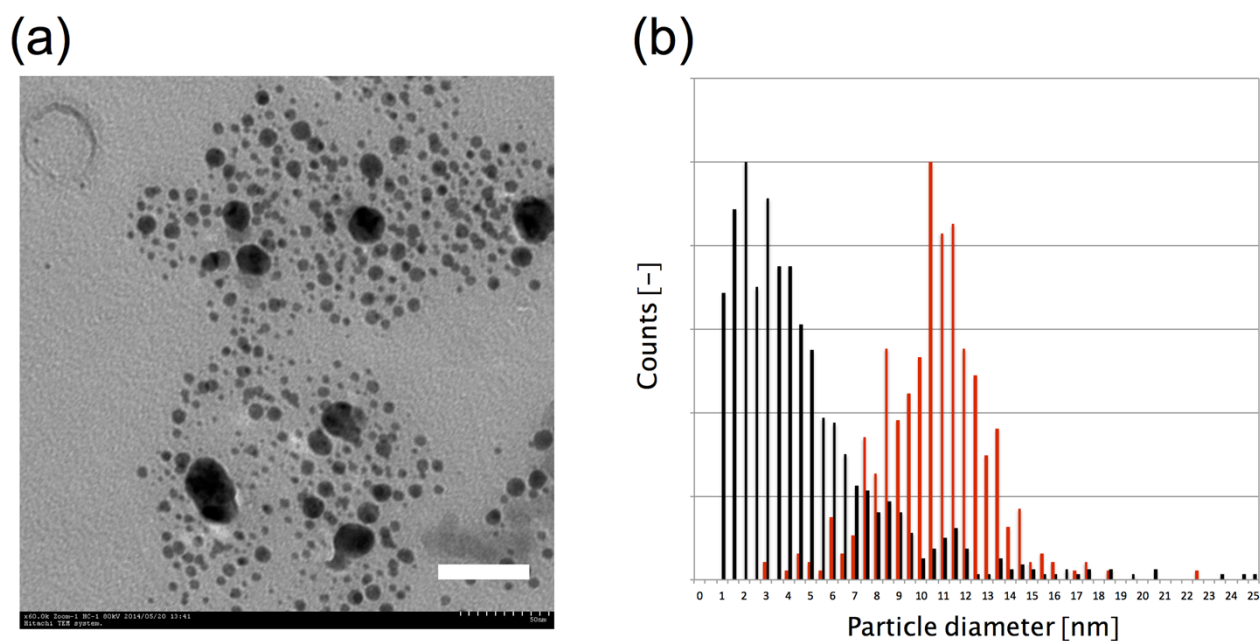


Figure S7, (a) TEM image of Ag NPs prepared with random copolymer, and (b) Histograms of size of Ag NPs prepared with polymer 3 (blue) and random copolymer (black). (Scale bar; 50 nm)

8. TEM image of synthesized Ag nanoparticles.

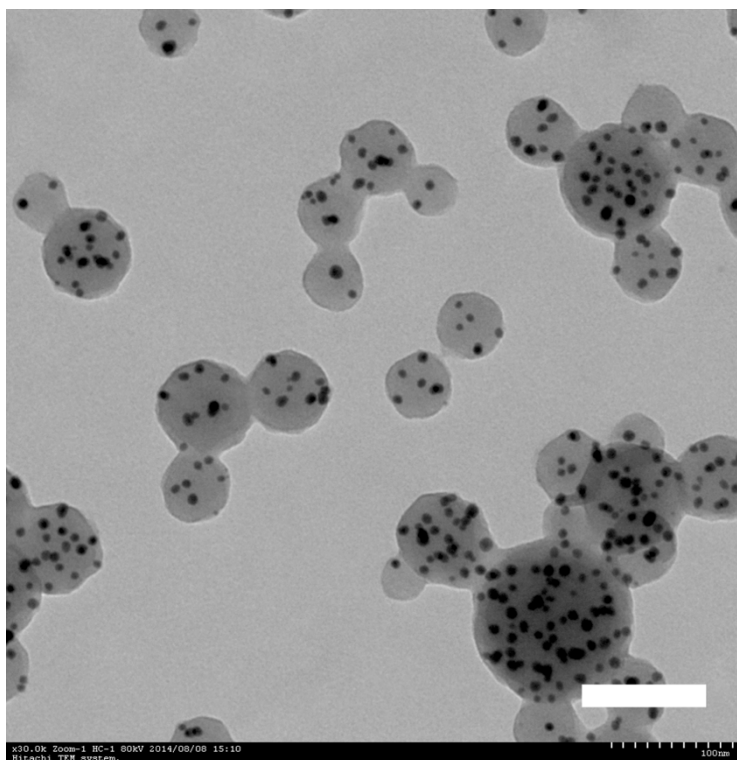


Figure S8. TEM image of synthesized Ag nanoparticles. Scale bar: 100 nm.