

Electronic Supplementary Information for Copolymers of Styrene and Aurum Nanoparticles

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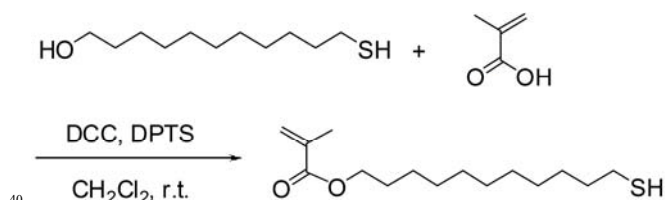
Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

Materials: N,N'-dicyclohexylcarbodiimide (DCC 99%), 4-dimethylaminopyridine (DMAP, 99%), HAuCl₄·3H₂O, sodium borohydride, tri-sodium citrate and 11-mercapto-1-undecanol were purchased from Aldrich and used as received. 4, 4'-Azobis (4-cyanopentanoic acid) (ABCPA, Aldrich, 97%) was recrystallized from methanol and dried under vacuum at room temperature. Styrene and methacrylic acid were purchased from KRS FINE CHEMICAL CO. LT. and purified by distillation at reduced pressure prior to use. Quaternary ammonium free radical initiator was synthesized by a reaction of trimethylamine and 11-bromo-undecan-4, 4'-azobis-(4-cyanopentanoate).^{1, 2} 4-(dimethylamino) pyridinium p-toluenesulfonate (DPTS) was synthesized according to the method reported by Moore and Stupp.³ All the solvents were distilled before use.

Measurements: ¹H NMR measurements were performed on a Varian UNITY-plus 400M nuclear magnetic resonance spectrometer using CDCl₃ (Cambridge Isotope, D 99.8% +TMS 0.03%, CIL) as the solvent at room temperature. The apparent molecular weights and molecular weight distributions of the polymers were determined at 35 °C on a gel permeation chromatograph (GPC) equipped with a Waters 717 autosampler, Waters 1525 HPLC pump, three Waters Ultra Styragel columns with 5K-600K, 500-30K, and 100-10K molecular ranges, and a Waters 2414 refractive index detector. THF was used as eluent at a flow rate of 1.0 mL/min. The number average molecular weights (Mn) and the molecular weight distributions of the polymers were calibrated on polystyrene standards. Transmission electron microscopy (TEM) images were obtained on a Tecnai G2 20 S-TWIN electron microscope equipped with a Model 794 CCD camera (512×512) at an operating voltage of 200 kV.



Scheme S1. A scheme for the synthesis of 11-mercaptoundecyl methacrylate.

Synthesis of 11-mercaptoundecyl methacrylate (MUMA):

MUMA was synthesized by the following procedure as shown in Scheme S1. 1-mercapto-1-undecanol (0.50 g, 2.4 mmol) and methacrylic acid (0.25 g, 2.8 mmol) and 4-dimethylaminopyridinium-p- toluene sulfonate (DPTS, 0.14 g,

0.47 mmol) were mixed in dry CH₂Cl₂ in a round bottom flask equipped with a magnetic stirrer. After the flask was flushed with argon, DCC (0.75 g, 3.7 mmol) was added. The solution was stirred at room temperature for 24 h under argon atmosphere. After the reaction, the DCC-urea was filtered off and washed with CH₂Cl₂. The crude product was purified by liquid chromatography on silica gel, eluting with hexane and ethyl acetate mixtures of increasing polarity to give the final product (299 mg, yield: 45%). ¹H NMR spectrum of MUMA (400 MHz, CDCl₃, δ): 6.02 (s, 1H, H₂C=C(CH₃)), 5.47 (s, 1H, H₂C=C(CH₃)), 4.07 (t, J = 2 Hz, 2H; -OCH₂CH₂); 2.61 (m, J = 8 Hz, 2H; -CH₂SH); 1.89 (s, 3H; H₂C=C(CH₃)); 1.65-1.10 (m, 18H; -(CH₂)₉CH₂SH).

Synthesis of gold nanoparticles (AuNPs) monomer: An aqueous solution (40 mL) of HAuCl₄ (2.5 × 10⁻⁴ M) and tri-sodium citrate (2.5 × 10⁻⁴ M) was prepared in a conical flask, and 1.2 mL of ice cold NaBH₄ solution (0.1 M) was added to the solution at stirring. The solution turned pink immediately after addition of NaBH₄ indicating the formation of AuNPs. The average size measured on the TEM image was around 5 nm (Fig. S1). So the molar number of AuNPs in the solution can be calculated by Equation (1)

$$N = 3m/4\rho\pi R^3 \quad (1)$$

where N is the molar number of AuNPs in the solution; m is the total weight of Au in the solution; ρ is the density of AuNPs; R is the radius of AuNPs. The molar number of AuNPs in this solution is 5.1×10⁻⁸ mol. To prepare AuNPs monomer, 17 μL of THF solution of MUMA (2.9 × 10⁻³ M) was added into the aqueous solution of AuNPs (the molar ratio of MUMA to AuNPs was about 1). In a mixture of toluene and water, AuNPs with long carbon chains (C₁₁) are able to locate at the interface of oil and water. Upon addition of 1% toluene to the aqueous solution of nanoparticle monomers, an emulsion was formed (Vial b in Fig. S2). However for bare AuNPs a clear solution was observed after addition of toluene (Vial a in Fig. S2b). In vial a the phase separation between toluene (upper part of the solution) and water was observed, which means in vial b emulsified toluene droplets were dispersed in aqueous phase. Fig. S3 is a TEM image of dried droplets of AuNPs monomer located initially at the interface of toluene and water and then dried on a carbon-coated copper grid. It was found that the gold nanoparticles were inside the droplet structures but distributed randomly on a copper grid, which confirmed the location of AuNPs monomer at the interface of two liquids.

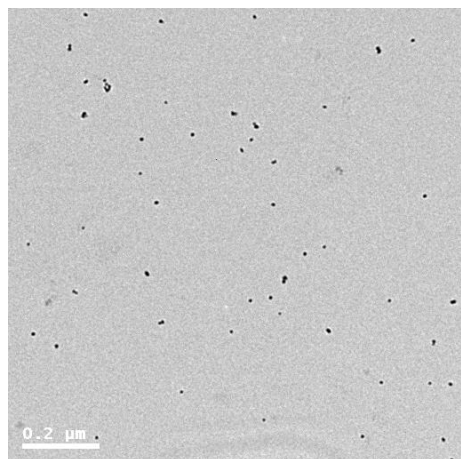


Fig. S1. A TEM image of gold nanoparticles prepared in aqueous solution.



Fig. S2. Images of gold nanoparticle monomers (left) and gold nanoparticles (right) in a mixture of toluene and water. After addition of toluene, an emulsion was obtained for AuNPs monomer solution, and a clear solution was observed for bare gold nanoparticles solution.

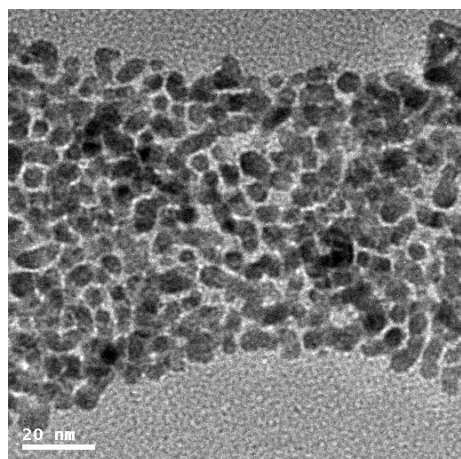


Fig. S3. A TEM image of dried droplets of AuNPs monomer located initially at the interface of toluene and water and then dried on a carbon-coated copper grid.

Free radical copolymerization of styrene and AuNPs

monomer: A typical polymerization was described as follows. An ammonium free radical initiator was dissolved in water (0.017 M) and 1 mL of the solution was added into the aqueous solution of the AuNPs monomer (40 mL). Toluene (20 mL) and styrene (1 mL) were added into the aqueous solution and degassed by bubbling argon gas for half an hour.

The copolymerization of styrene and AuNPs monomer was conducted at 60 °C for 24 h. After cooling down to room temperature the toluene phase was collected and the aqueous phase was extracted by CH₂Cl₂ for two times. The organic layers were combined and concentrated at a reduced pressure. The copolymer was precipitated in methanol, and dried under vacuum. The repeating unit number of styrene in the copolymer was 548 calculated by Equation (2) based on ¹H NMR results

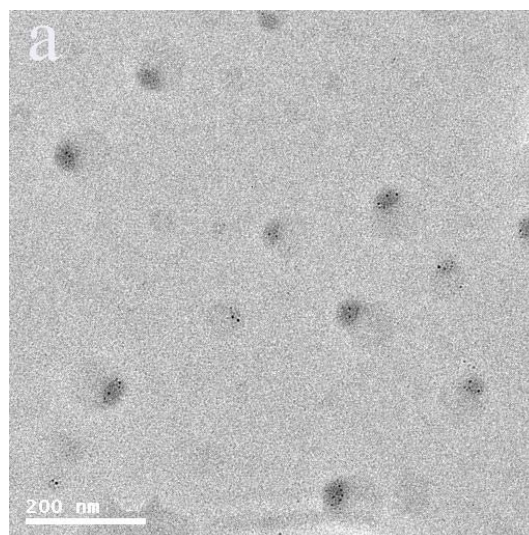
$$n = 2I_a / 5I_b \quad (2)$$

where n is the repeating unit number of PS, I_a is the integral area of the peak corresponding to protons on benzyl rings of PS (6.3 to 7.0 ppm), I_b is the integral area of the peak at 4.24 ppm corresponding to methylene protons adjacent to the quaternary ammonium group at the end of the polymer chains (Fig. 1b). In this research three copolymers with different molecular weights and different number of pendant AuNPs were prepared by using the ammonium free radical initiator (Table S1).

Table 1. Summary of molecular weights and molecular weight distributions of AuNP-co-PS copolymers^a

| Sample | Number of AuNPs ^b | M_n ($\times 10^{-3}$ g·mol ⁻¹) | PDI |
|----------------|------------------------------|--|------|
| AuNP-co-PS-I | 5 | 72 ^c | 1.35 |
| AuNP-co-PS-II | 3 | 31 ^c | 1.47 |
| AuNP-co-PS-III | 1 | 26 ^c | 1.48 |

^a The initiator used in all the free radical polymerizations is quaternary ammonium free radical initiator and the polymerization temperature is 60 °C. ^b Determined by ¹H NMR results ^cdetermined by gel permeation chromatograph based on polystyrene standards.



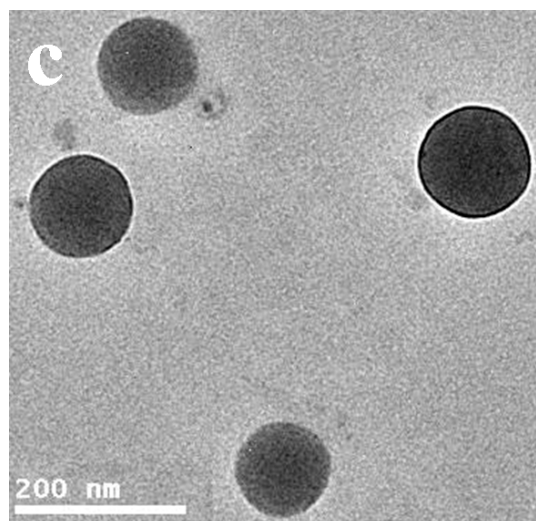
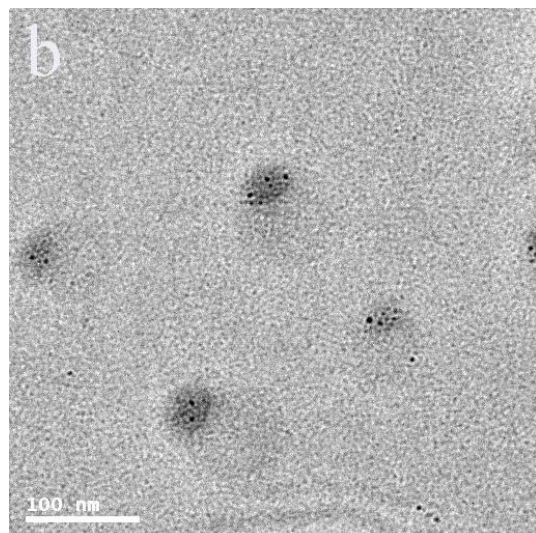


Fig. S4. TEM images of AuNP-co-PS-I copolymer observed at low magnification (image a), high magnification (image b), and the aggregation morphology for aurum nanoparticles copolymers in H₂O. (image c). The specimens were prepared by dipping the copper grids into the copolymer solution and drying in air.

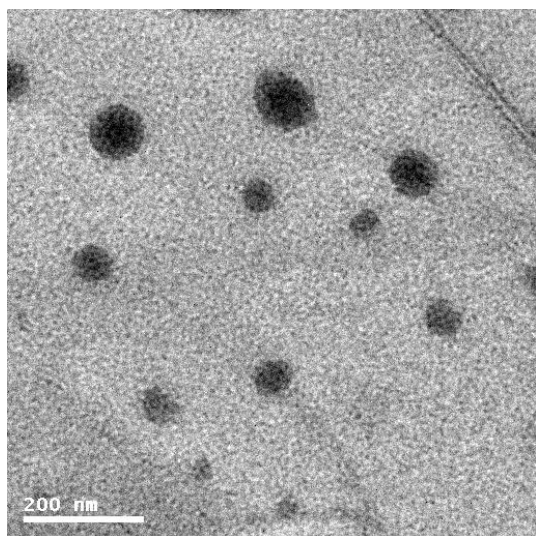


Fig. S5. TEM images of AuNPs-PS copolymer in H₂O.

10 In a controlled experiment a copolymerization reaction was initiated by ABCPA. The details was described as follows: 1 mL of a 0.030 mol·L⁻¹ aqueous solution of ABCPA was added to 40 mL nanoparticles solution. Then 20 mL of dry toluene followed by 0.5 mL styrene was added. The copolymerization
15 of styrene and AuNPs monomer was conducted at 60 °C for 24 h. Fig. S5 shows a TEM image of the self-assembly of the copolymer in water.

References

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