Electronic Supplementary Material (ESI) for RSC Advances

Supporting Informations

Synthesis of Block Copolymer

Reagents

4-Cyanopentanoic acid dithiobenzoate was synthesized according to the method reported by McCormick and co-workers.[1] [3-(Methacryloylamino)propyl]trimethylammonium chloride (MAPTAC, 50 wt % in water) and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 98 %) from Aldrich were passed through basic alumina columns to remove the inhibitor. Water was purified using a Millipore Milli-Q system. The other reagents were used as received.

Preparation of PMAPTAC macro-chain transfer agent (macro-CTA)

The preparation of the PMAPTAC macro-chain transfer agent (macro-CTA) is as follows. The MAPTAC aqueous solution (50 wt %, 100 g, 227 mmol) was diluted with 17 mL of water, and then 4-cyanopentanoic acid dithiobenzoate (421 mg, 1.51 mmol) and 4,4'-azobis(4-cyanopentanoic acid) (84.6 mg, 0.302 mmol) were added to this solution. The mixture was degassed by purging with Ar gas for 30 min. the polymerization was carried out at 70 °C for 4 h. The polymerization mixture was poured into a large excess of acetone to precipitate the resulting polymer. The polymer was purified by reprecipitating from methanol into a large excess of acetone. The obtained MAPTAC homopolymer could be used as a macro-CTA to prepare the block copolymers (16.5 g, 33.0 %). The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) for PMAPTAC were estimated by gel-permeation chromatography (GPC) to be 1.28×10^4 and 1.03, respectively. The number average degree of polymerization (DP) for PMAPTAC was 56 as estimated from the M_n.

Preparation of PMAPTAC-b-PDMAEMA

DMAEMA (3.48 g, 22.1 mmol) was dissolved in 26.8 mL of water. The solution pH was adjusted to 6.5 by adding HCl (6.0 M) to the solution. MAPTAC macro-CTA (2.50 g,

0.22 mmol, $M_n = 1.28 \times 10^4$; $M_w/M_n = 1.03$) and 4,4'-azobis(4-cyanopentanoic acid) (12.4 mg, 0.044 mmol) were added to the aqueous solution. The solution was deoxygenated by purging with Ar gas for 30 min. Block copolymerization was carried out at 70 °C for 4 h. The diblock copolymer was purified by dialysis against pure water for one week by changing the pure water twice a day. The diblock copolymer was recovered by a freeze-drying technique (4.97 g, 70.6 %). The M_n and M_w/M_n for PMAPTAC-*b*-PDMAEMA were estimated by GPC to be 1.95×10^4 and 1.06, respectively. The DP estimated from the ^{1}H NMR for PMAPTAC-*b*-PDMAEMA was 74.

Measurements

GPC analysis was performed using a refractive index (RI) detector equipped with a Shodex Ohpak SB–804 HQ column working at 40 °C and the flow rate of 1 mL/min. A 0.3-M Na_2SO_4 aqueous solution containing a 0.5-M acetic acid was used as the eluent. The molecular weights of the sample polymers were calibrated with standard poly(2-vinypyridine) samples of 6 different molecular weights ranging from 5.70×10^3 to 3.16×10^5. ^{1}H NMR spectra were obtained using a Bruker DRX-500 spectrometer operating at 500 MHz.

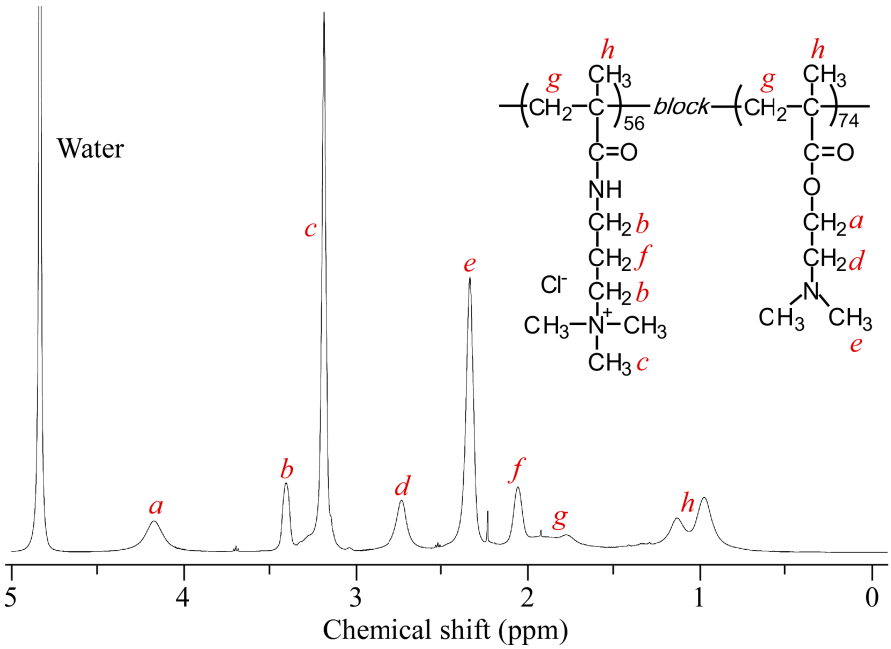

Fig. S1 ^{1}H NMR spectrum for PMAPTAC-*b*-PDMAEMA in D_2O at pH 11.

Fig. S1 shows the ^{1}H NMR spectra for the PMAPTAC-*b*-PDMAEMA in D_2O at pH 11. The resonance bands in the 0.8-1.2 ppm region and at 1.8 ppm are attributed to the methyl protons and the main chain methylene protons, respectively. The composition of the diblock copolymer was determined from the intensity ratio of the resonance bands due to the pendant methylene protons in the DMAEMA block at 4.4 ppm and the trimethyl amino protons of the MAPTAC block at 3.2 ppm. The DP values for the PMAPTAC and PDMAEMA blocks are 56 and 74, respectively.

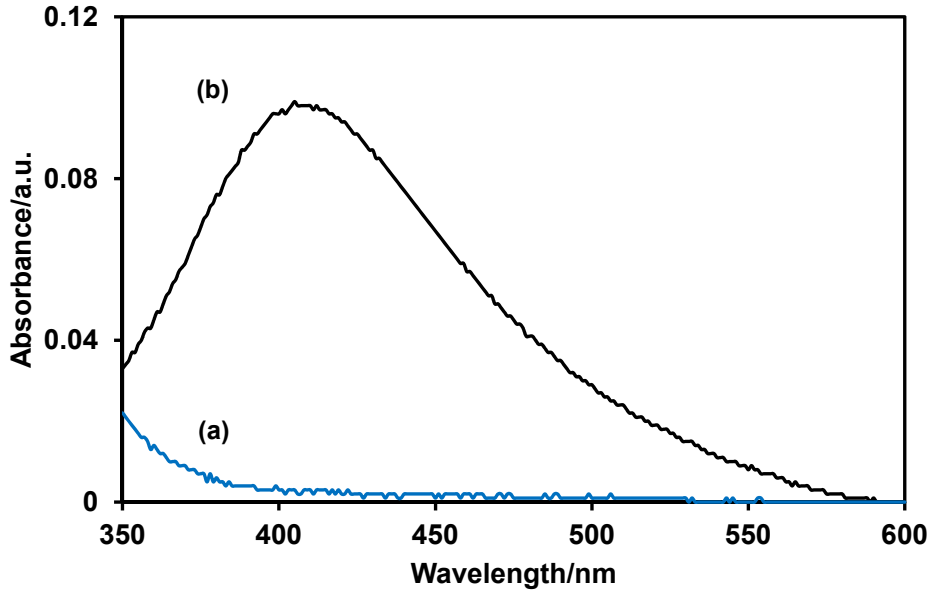

Fig. S2 UV-Visible absorption spectra of (a) the block polymer and (b) Ag nanoparticles formed in the polymer solutions.

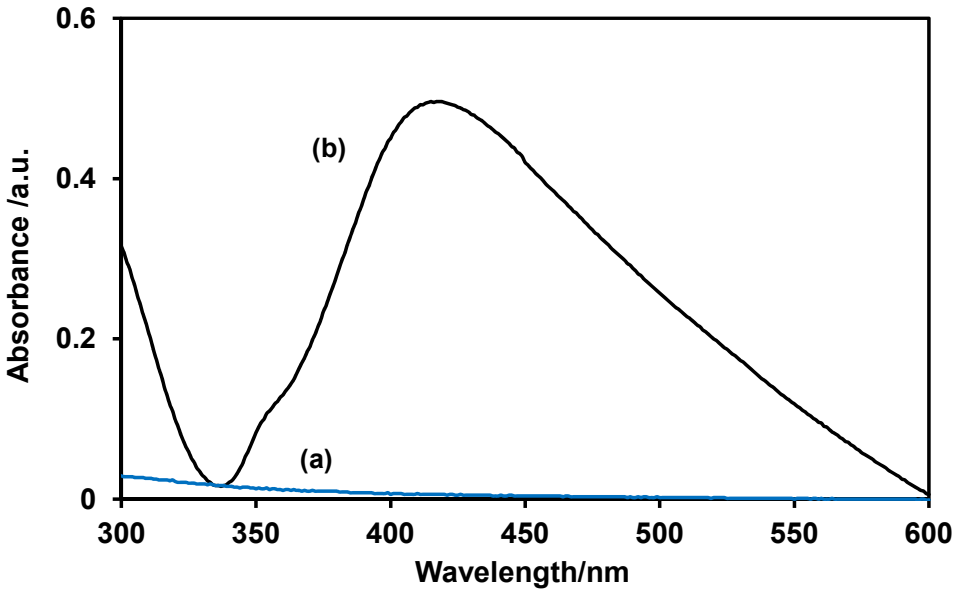

Fig. S3 UV-Visible absorption spectra of PDMAEMA homo polymer (a) before and (b) after adding Ag^{+} ions.

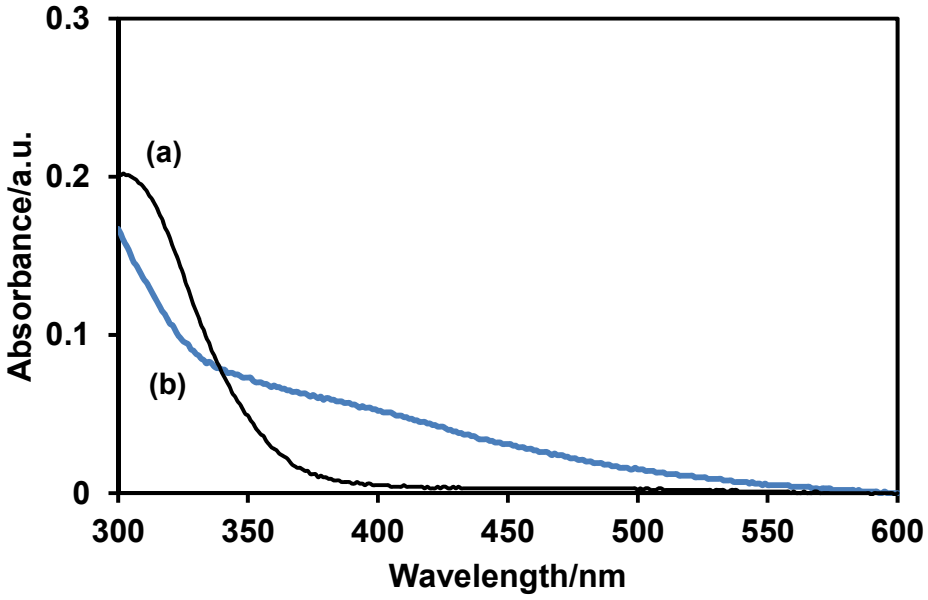

Fig. S4 UV-Visible absorption spectra of PMAPTAC homo polymer (a) before and (b) after adding Ag^{+} ions.

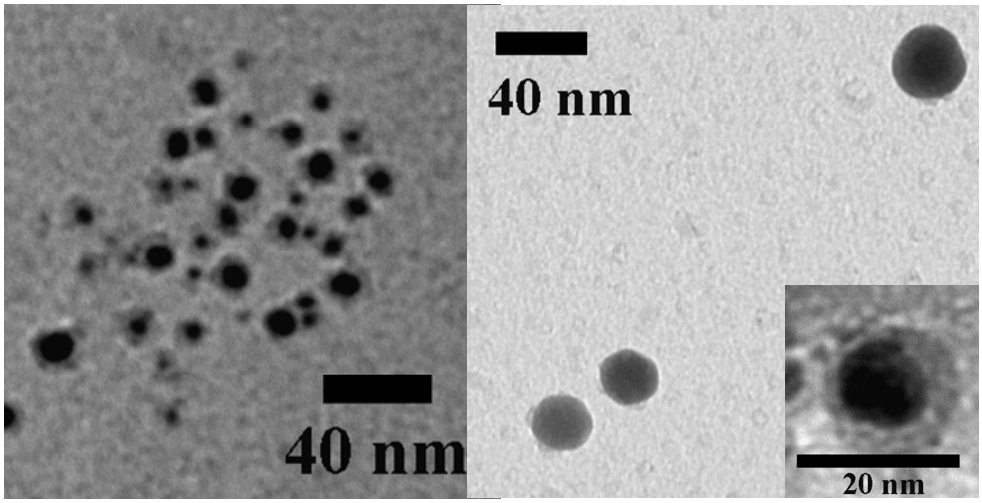

Fig. S5 TEM image of $Ag@SiO_2$ core- shell nanoparticles.

References

1) Y. Mitsukami, M. S. Donovan, A. B. Lowe and C. L. McCormick, *Macromolecules* 2001, **34**, 2248.