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## Catalytic performance in 4-nitrophenol reduction by Ag nanoparticles stabilized on biodegradable amphiphilic copolymers

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### ABSTRACT

Biodegradable copolymers have received much more attention in the last decades due their potential applications in the fields related to environmental protection, medicine, agriculture, and the chemical processes. Silver nanoparticles (Ag NPs) were prepared via reduction of silver nitrate ( $\text{AgNO}_3$ ) using biodegradable amphiphilic copolymers in aqueous solution. The micelles were constructed from the amphiphilic copolymer composed of poly(2-ethyl-2-oxazoline) and poly( $\epsilon$ -caprolactone). The Ag NPs with a diameter of 10–15 nm were found to show a comparable high catalytic activity toward the reduction of 4-nitrophenol (4-NP) in the presence of an excess amount of  $\text{NaBH}_4$ . The synthesized Ag NPs-loaded copolymer exhibits high catalytic activity for the reduction of 4-NP to 4-aminophenol.

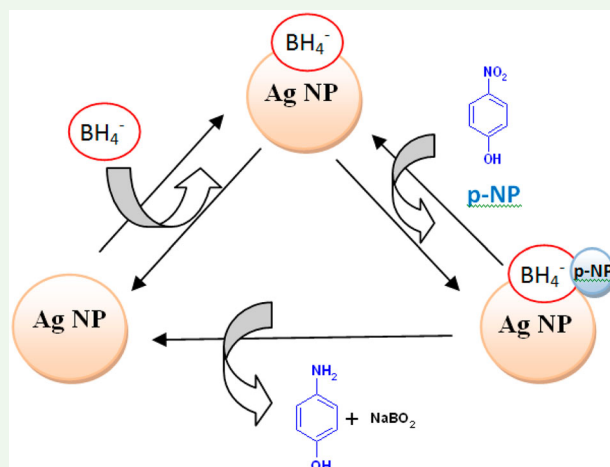
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### KEYWORDS

Silver nanoparticles; amphiphilic copolymer; poly(2-ethyl-2-oxazoline); poly( $\epsilon$ -caprolactone)



### Introduction

Recently, metal nanoparticles have been a subject of much intensive research because of their unique properties and potential applications in many areas, such as catalysts, sensors, medicine electronics, and so forth (1, 2). Among the various metal nanoparticles, silver nanoparticles (Ag NPs) have a wide range of application in various fields of industry biomedicine, antibacterial activity, imaging, and nanophotonics as well as surface-enhanced Raman scattering detection (3–7). Especially, Ag NPs are attractive for catalysis under mild conditions because their high surface area-to-volume ratio allows efficient utilization of expensive metals. Recent reports

have demonstrated that Ag NPs can be used as catalyst for reduction reactions (8, 9). For example, He et al. synthesized Ag-deposited silica-coated magnetic nanoparticles with average particle sizes of 10–20 nm for catalytic reduction of p-nitrophenol by  $\text{NaBH}_4$  (8). The catalytic reduction of p-nitrophenol has been extensively studied involving various noble metal nanoparticles, such as Au, Ag, Pt, and Pd (10–15). Compared with Au, Pt, and Pd, Ag is inexpensive as well as possesses good chemical and physical properties (16).

Stability of the nanoparticles is an important issue and supported metal nanoparticles as catalytic systems have potential to show greater efficiency. Several methods

have been developed for the synthesis of metal nanoparticles (17). More recently, the synthetic method using polymers as template has been reported on immobilization of Ag NPs (18, 19). Several methods have been developed to stabilize Ag NPs in the polymeric matrix. Among those techniques, chemical reduction is the most frequently used strategy by adding a reducing agent (e.g.  $\text{NaBH}_4$ , sodium citrate, ascorbate, or  $\text{LiAlH}_4$ ) to reduce silver precursor such as silver nitrate ( $\text{AgNO}_3$ ) in aqueous solution (20, 21).

Biodegradable polymers are considered to be an invaluable material because of the applications in diverse fields, such as packaging, food, agriculture, consumer products, medical appliances, industry, building materials, polymeric nanocomposites, and aerospace materials. In polymeric nanocomposites, the combination of polymer and nanomaterials results in materials that are highly homogenous resulting in the development of novel nanomaterials with unique and excellent properties (22). On the other hand, amphiphilic copolymers, such as block copolymer, are one kind of excellent support for metal nanoparticles, such as Ag NPs, due to the nature of micelles and small size (23). Polymeric micelles formed in the aqueous phase through self-association of amphiphilic block copolymers have attracted great interest. The micelles based on amphiphilic copolymers are as nanoreactors to fabricate metal nanoparticles (23, 24). An important new class of block copolymer is based on poly(2-alkyl-2-oxazoline) as biodegradable copolymers. Block copolymers were synthesized based on poly(2-ethyl-2-oxazoline) (POX) as the hydrophilic block and poly(L-lactide) or poly( $\epsilon$ -caprolactone) (PCL) as the hydrophobic block (25, 26).

In this work, we reported the preparation of Ag NPs stabilized by the amphiphilic block copolymer in water by adding reducing agent  $\text{NaBH}_4$ . The amphiphilic copolymer, containing POX as the hydrophilic block and PCL as the hydrophobic segment, could self-assemble into micelles which served for the Ag NPs fabrication. The resulting Ag NPs were characterized by UV/Vis spectrum, and the morphology of the as-synthesized nanoparticles was investigated by transmission electron microscopy (TEM). The result showed that the Ag NPs formed by coordination reduction can be effectively applied in catalytic reaction.

## Results and discussion

The synthesis and characterization of POX-PCL amphiphilic copolymers were performed following a literature procedure (27).  $\text{CH}_3\text{I}$  was able to initiate the ring opening polymerization of 2-ethyloxazoline and homopolymers POX were obtained. Polymerization was

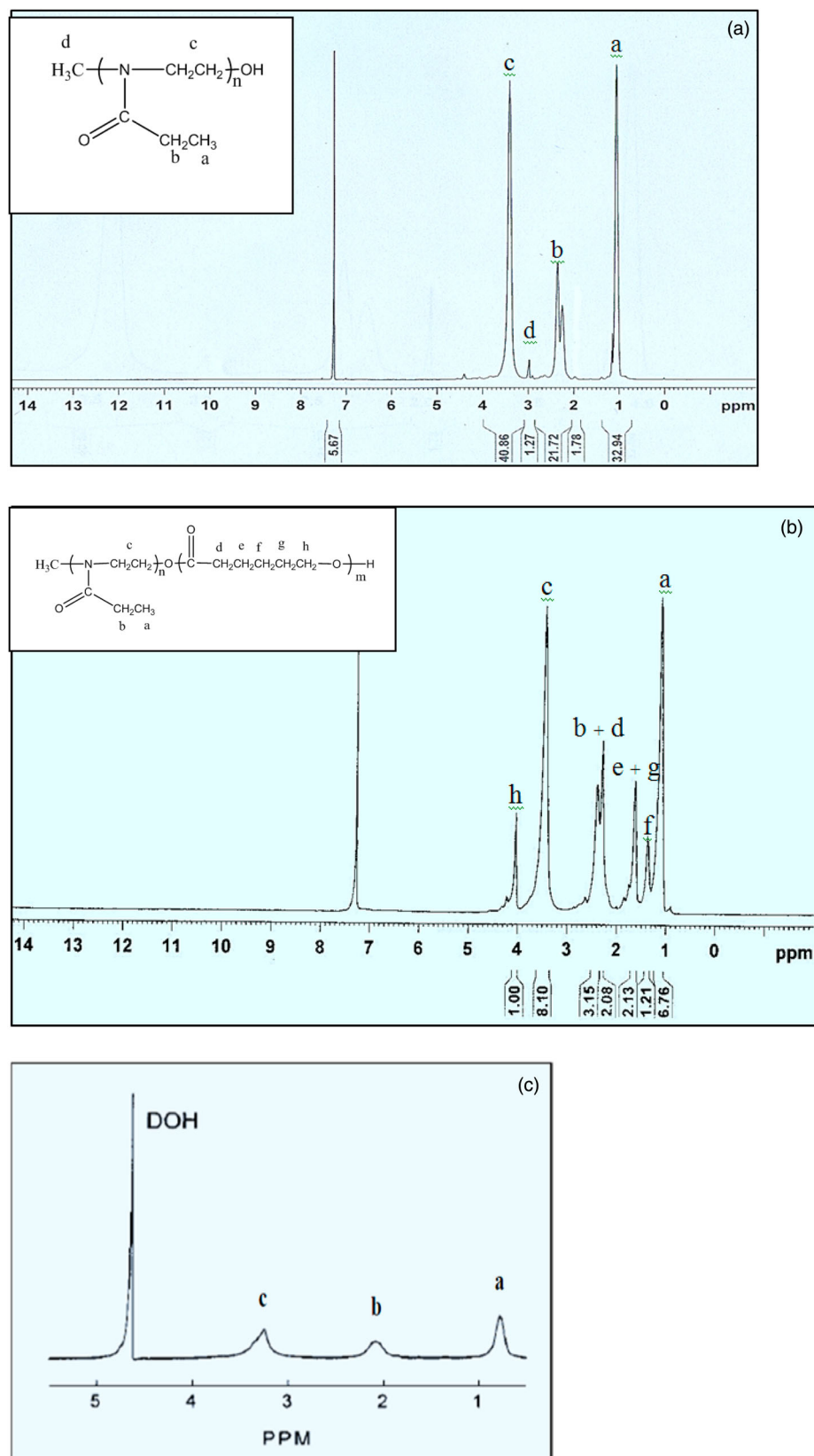
quenched using methanolic KOH, and hydrophilic polymers containing hydroxyl end functional groups (POX-OH) were obtained.  $\epsilon$ -Caprolactone was then polymerized using the hydroxyl end functional groups of POX and diblock copolymers containing hydrophilic POX, and the hydrophobic PCL blocks were synthesized. The molecular weights and block compositions of the amphiphilic diblock copolymers were determined by the analysis of  $^1\text{H}$  NMR spectra, as shown in Figure 1. The molar ratios of repeating units in POX were determined by the peak integration ratios of methyl protons initiator (3 ppm) and  $\text{COCH}_2\text{CH}_3$  (1 ppm). Molecular weights of polymers were 3000 (Figure 1(a)). The molar ratios of repeating units in POX and PCL blocks in the copolymers were determined by the peak integration ratios of methyl protons (1.1 ppm) in POX and  $\text{CH}_2\text{OCO}$  (4.05 ppm) in the PCL block. Molecular weights of copolymers were 4000 (Figure 2(a)). The micelle formation of diblock copolymers in an aqueous phase was confirmed by Nuclear Magnetic Resonance spectroscopy. Figure 1 shows the  $^1\text{H}$  NMR spectra of POX-PCL micelles in  $\text{CDCl}_3$  (a) and  $\text{D}_2\text{O}$  (c). While the resonance peaks from both PCL segment and POX block were clearly observed in  $\text{CDCl}_3$ , the peaks of PCL block disappeared in  $\text{D}_2\text{O}$ , which indicated the limited molecular motion of PCL block surrounded by the hydrophilic POX segment. This result confirms the micelle formation of POX-PCL amphiphilic copolymers in an aqueous phase (27).

The preparation of the Ag NPs stabilized by the POX-PCL diblock copolymers is shown in Scheme 1. The amphiphilic copolymer first self-assembled into micelles in the aqueous solution. Polymeric micelles derived from amphiphilic block copolymers of POX and PCL were prepared in an aqueous phase. Then a certain amount of  $\text{AgNO}_3$  was directly added into the micelle solution. After reaction, the solution turned from colorless to golden yellow color. The reduction of silver ions ( $\text{Ag}^+$ ) to Ag NPs was achieved via coordination reduction by  $\text{NaBH}_4$ .

Figure 2 shows the UV/Vis spectra of the Ag NPs stabilized by the copolymers. The absorption band of Ag NPs appeared at  $\sim 400$  nm (22). Before adding  $\text{AgNO}_3$ , no absorption peak was present in the UV/Vis spectra.

TEM image of Ag NPs stabilized by copolymers is shown in Figure 3. These nanoparticles with a diameter of 10–20 nm, exhibited the spherical or sphere-like shape. However, the micelles formed by POX-PCL copolymers could not be observed by TEM, which was considered to be more sensitive to the electron-rich metal particles than copolymers. Similar phenomena were also observed in previous studies (22, 28).

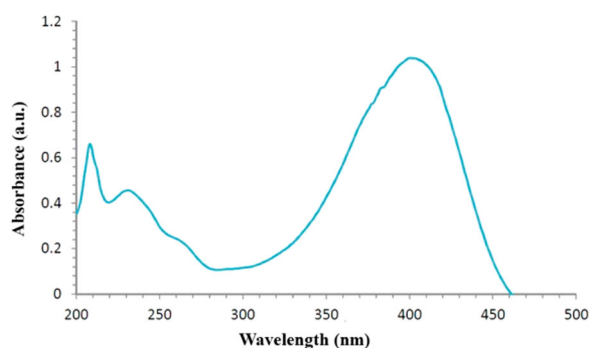
In order to investigate the potential of the Ag NPs for the reduction of 4-nitrophenol (4-NP), the catalytic



**Figure 1.**  $^1\text{H}$  NMR spectra of (a) POX polymers, POX-PCL copolymers(b) in  $\text{CDCl}_3$ , and POX-PCL copolymers in  $\text{D}_2\text{O}$ .

reaction was monitored by UV/Vis spectrometer using an excess of  $\text{NaBH}_4$  (9, 22). Because there is only one product, 4-aminophenol, and the extent of reaction can

be followed by measuring the change in UV/Vis absorbance at 400 and 300 nm (29, 30). For comparison, in the absence of Ag NPs, first, 0.005 mol/L 4-NP solution

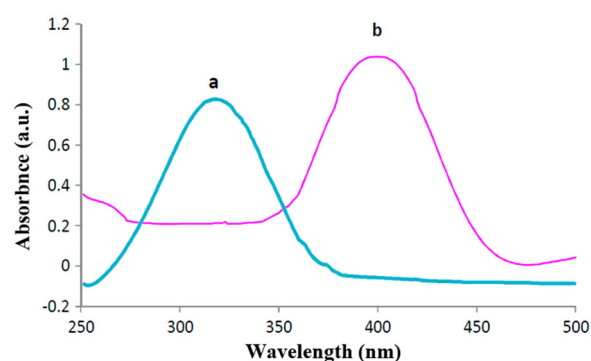


**Figure 2.** UV/Vis absorption spectra for the Ag NPs prepared on POX-PCL copolymer.

was prepared and monitored for the change of absorption. The light yellow aqueous 4-NP solution shows absorption at about 317 nm (a) in Figure 4. After the addition of  $\text{NaBH}_4$  solution, the absorption maximum shifts to 400 nm (b) due to the formation of the 4-nitrophenolate in the alkaline condition, with a color change from light yellow to bright yellow. Moreover, the maximum absorption is no change over times after adding superfluous  $\text{NaBH}_4$  solution, which confirms that the reduction reaction does not proceed by aqueous  $\text{NaBH}_4$  solution (29).

According to the UV/Vis spectrum in Figure 5, after the addition of Ag NPs as catalyst, the absorbance peak at 400 nm significantly decreased with time and a new peak at 300 nm corresponding to 4-aminophenol gradually developed within 12 min. Without the addition of catalyst, the absorbance kept unaltered and the reduction process would not proceed. This shift of peak indicated that the Ag NPs catalyzed the reduction reaction (9, 22).

Figure 6 shows a linear correlation between  $\ln(A)$  and reaction time at 295 K, indicating that the 4-NP reduction is a pseudo-first order. The apparent rate constant ( $k$ ) at



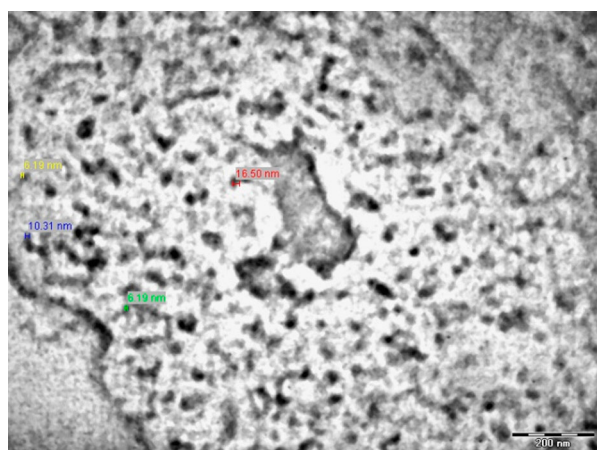
**Figure 4.** UV/Vis spectra of (a) 4-NP before and after adding  $\text{NaBH}_4$  solution.

295 K was calculated from the slope to be  $2.12 \times 10^{-3} \text{ s}^{-1}$ . This value obtained for 4-NP reduction is comparable to the previous findings in the literature for the Ag NPs (31).

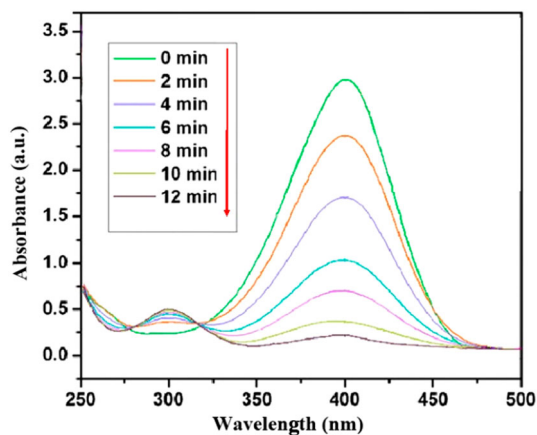
## Experimental design

### Chemicals and apparatus

Chemical reagents in high purity were purchased from Merck and Sigma. All materials were of commercial reagent grade. UV/Vis spectra from various Ag NPs solutions for the measurement of the surface Plasmon band of the Ag NPs were recorded by Micro plate Spectrophotometer System (SPECTRA max PLUS384) at room temperature. The particle size and morphology were investigated by a JEOL JEM-2010 transmission electron microscope on an accelerating voltage of 200 kV. Dynamic light scattering experiments were performed with commercially available equipment (Zetasizer Nano from Malvern) with a 4-mW He-Ne laser (633 nm wavelength) and a fixed

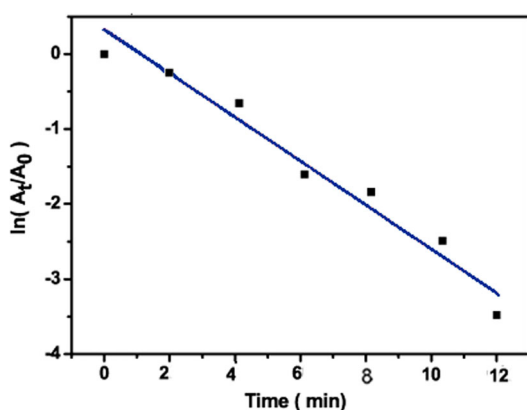


**Figure 3.** TEM image of Ag NPs stabilized by polymeric micelles.



**Figure 5.** Time base UV/Vis spectra monitoring 4-NP reduction catalyzed by Ag NPs.





**Figure 6.** The relationships of  $\ln(A_t/A_0)$  versus reaction time.

detector angle of  $173^\circ$ . The molecular weight distributions were determined by size exclusion chromatography (Agilent 1100) using a PSS GRAL 100 Å column connected to a differential refractometer, with an RI detector with  $\text{CHCl}_3$  as mobile phase at  $25^\circ\text{C}$ . Polystyrene standard samples were used for calibration. GC-Mass experiments were recorded using a Shimadzu GCMS-QP 505 A with DB5 column.

### Preparation of POX

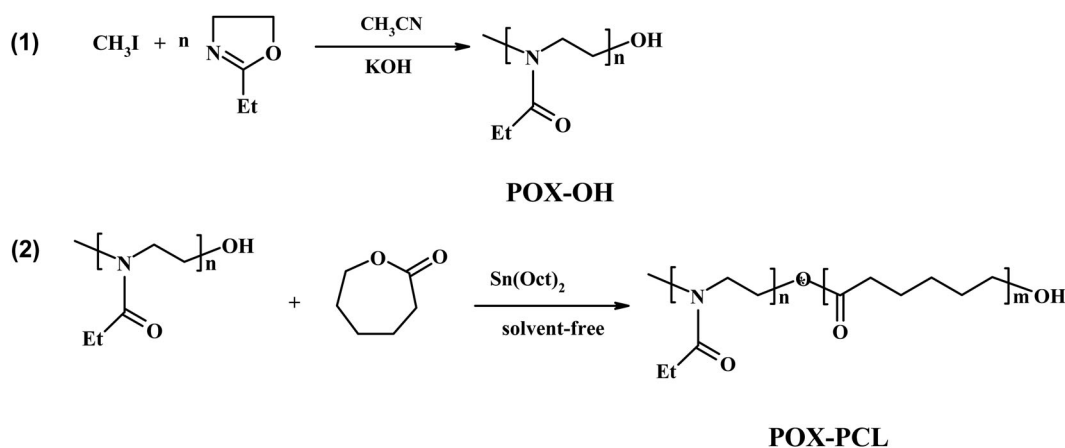
POX were prepared by cationic polymerization according to the procedure reported elsewhere (27). In brief, to 30 mL of dried acetonitrile, 2.6 mL ( $25.6 \times 10^{-3}$  mol) of 2-ethyloxazoline was introduced, and 0.1 mL ( $1.6 \times 10^{-3}$  mol) of iodomethane was added. After stirring for 72 h, at  $110^\circ\text{C}$ , the polymerization was stopped by pouring methanolic KOH into the reaction mixture at room temperature. The POX was purified by precipitation in diethyl ether and then dried under vacuum at  $50^\circ\text{C}$  for 1 h. The yield of reaction was 85%.

### Preparation of Poly(2-ethyl-2-oxazoline)-poly( $\epsilon$ -caprolactone) diblock copolymers (POX-PCL) copolymers

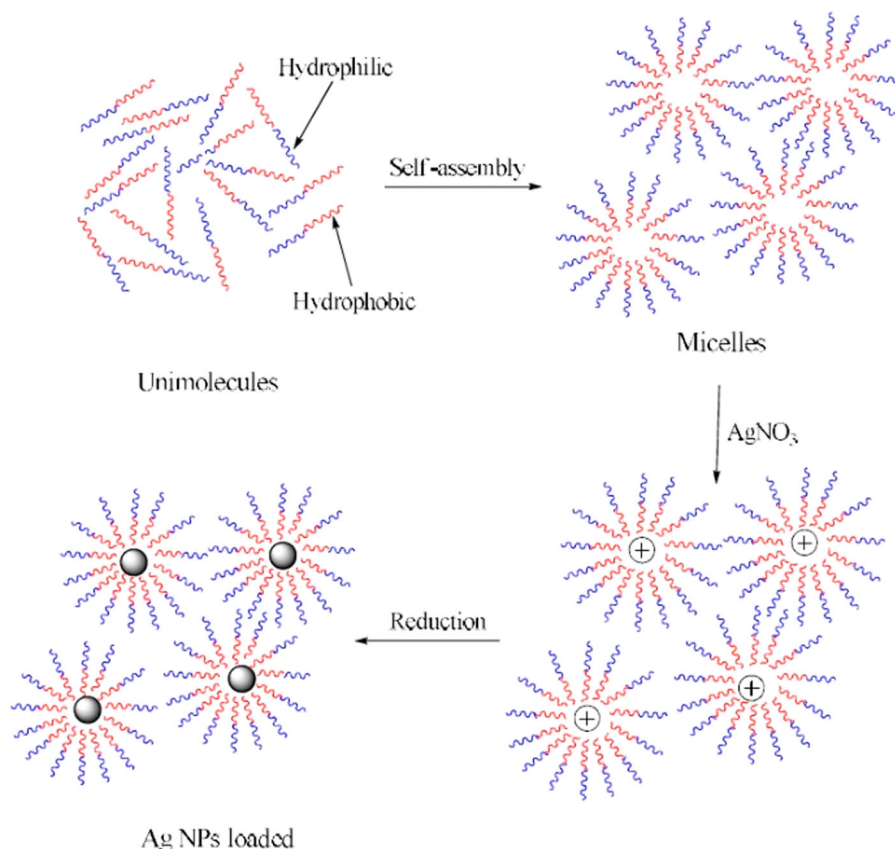
About 1 mL of  $\text{Sn}(\text{Oct})_2$  in toluene ( $1 \times 10^{-3}$  M) was added to a polymerization ampule equipped with a magnetic stirrer and vacuum inlet. Toluene was evaporated under vacuum at  $60^\circ\text{C}$  for 30 min. About 1.33 mL of  $\epsilon$ -caprolactone and 1.42 g POX as the macroinitiator were added to the polymerization ampule and it was left under vacuum for 1 h at  $60^\circ\text{C}$ . The polymerization ampule was sealed and it was stirred at  $120^\circ\text{C}$  for 12 h. Then it was cooled and the ampule contents were dissolved in chloroform. The solution was filtered and product was precipitated in diethylether (Scheme 2). The yield of reaction was 90%.

### Formation of Ag NPs via using (POX-PCL) copolymers

The preparation of the Ag NPs via coordination reduction process is outlined below (shown in Scheme 2). The micelles as a nanoreactor were prepared by the addition of water to the copolymer solution in an acetone–water system. The amphiphilic copolymer (100 mg) was first dissolved in acetone (5 mL) to give a 20 mg/mL of copolymer solution. Then 50 mL ultrapure water was added dropwise under stirring for about 5 h, and the mixture was continually stirred overnight to form stable micelles. After that, residual acetone was eliminated under reduced pressure at room temperature. To fabricate the copolymer-stabilized Ag NPs, 0.1 mL of  $\text{AgNO}_3$  (0.1 M) solution was added to 10 mL of micelle solution of POX-PCL copolymer (2 mg/mL).  $\text{NaBH}_4$  was quickly added to the solution under stirring for 0.5 h. Thereafter, the resulting Ag NPs were dialyzed against ultrapure



**Scheme 1.** The fabrication of Ag NPs stabilized by POX-PCL copolymer.



**Scheme 2.** Synthesis of POX-PCL diblock copolymers.

water for 2 days (MWCO 12,000–14,000) to remove extra  $\text{NaBH}_4$ .

### Catalytic reduction of *p*-nitrophenol

To evaluate the catalytic performance of the synthesized Ag NPs-loaded copolymer catalyst, the catalytic reduction technique was carried out in a standard quartz cell with a 1 cm path length and about 4 mL volume. 0.3 mL of  $\text{NaBH}_4$  (0.1 M) was mixed with a given amount of Ag NPs and a portion of ultrapure water, keeping the final concentration of  $\text{NaBH}_4$  at 10 mM. Immediately after the addition of 30  $\mu\text{L}$  of *p*-nitrophenol (0.01 M) the UV/Vis absorption spectra were recorded by a UV-vis spectrometer at certain time interval in a scanning range of 250–500 nm at 20°C at time interval of 1 min.

### Conclusions

In the present study, we demonstrated a successful preparation of Ag NPs using polymeric micelles. The amphiphilic copolymer, containing POX and PCL segments, could self-assemble into micelles which served as support for the Ag NPs fabrication in selective solvents.

Ag NPs exhibited good catalytic activity for 4-NP reduction to 4-aminophenol in the presence of  $\text{NaBH}_4$  in aqueous solution.

### Disclosure statement

No potential conflict of interest was reported by the authors.

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