

Block copolymer-mediated synthesis of silver nanoparticles from silver ions in aqueous media

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Abstract

We report here on the silver (Ag) nanoparticle synthesis in aqueous solutions of poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) block copolymers in the absence of any additional agents. In particular, we examined the effect of reaction temperature, molecular weight of PEO-PPO block copolymer and PEO-PPO block copolymer concentration on the reduction of silver ions (Ag^+) and the resulting formation of Ag nanoparticles in aqueous PEO-PPO block copolymer solutions. We found that Ag nanoparticles were formed from aqueous silver nitrate (AgNO_3) solutions containing PEO-PPO block copolymer above 100°C . This is most likely due to the dehydration of Ag^+ caused by thermal motion of water molecules in higher-temperature aqueous solution at high vapor pressure. We also found that the formation of Ag nanoparticles in aqueous PEO-PPO block copolymers with larger molecular weight and with increase in the concentration of PEO-PPO block copolymer in aqueous solutions.

Keywords: Silver nanoparticle, Poly(ethylene oxide)-poly(propylene oxide) block copolymer, Silver nitrate, Silver ion reduction, Reaction temperature, Hydration, Dehydration.

1. Introduction

Nanometer-sized metal particles (metal nanoparticles) are attracting significant attention in the last couple of decades because of their unique properties that are distinct from bulk metal and their wide applications in chemistry, physics and biology fields [1-21]. The physical and chemical properties of metal nanoparticles depend strongly on the size, shape and assembly of metal nanoparticles. Therefore, it is still important and challenging task to develop the controllable synthesis of metal nanoparticles with different sizes, shapes and assemblies. There are a number of reports on the controlling size and shape of metal nanoparticles in wet chemistry. For example, the size, shape and assembly of gold nanoparticles are controlled by judicious combination of the capping agents (e.g., alkylthiols, surfactants and polymers) and reducing agents (e.g., NaBH₄, hydrazine and ascorbic acid). Furthermore, the block copolymer- and supramolecule-mediated synthesis of gold nanoparticles has been developed because the block copolymers and supramolecules can display dual function: the reducing function for metal ions and capping (stabilizing) function for metal nanoparticles formed [22-32]. Silver (Ag) nanoparticles are synthesized through the citrate reduction, silver mirror reaction, polyol process, seed-mediated growth and light-mediated synthesis [19]. We have also developed a facile and efficient synthetic method of gold and silver nanoparticles from reduction of tetrachloroaurate(III) ions ([AuCl₄]⁻) and silver ions (Ag⁺) in solutions of poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) block copolymers, respectively (named as block copolymer-mediated synthetic method) [33-42]. In this method, gold nanoparticles are formed in both aqueous and formamide solutions of PEO-PPO block copolymers in the temperature range of 4-100 °C. On the other hand, Ag nanoparticles are formed from silver nitrate (AgNO₃) formamide solutions of PEO-PPO block copolymer at 100 °C but not from aqueous AgNO₃ solutions of PEO-PPO block copolymers at 100 °C for 24 h [37, 38]. Then, we explore the

synthesis of Ag nanoparticles directly from aqueous AgNO₃ solutions of PEO-PPO block copolymers in the absence of any additional agents. The development of synthetic methodology of other metal nanoparticles from gold nanoparticles in aqueous media should provide further opportunities of the block copolymer-mediated synthesis of metal nanoparticles.

In the present work, we examine the effect of reaction temperature, molecular weight of PEO-PPO block copolymer and PEO-PPO block copolymer concentration on the reduction of silver ions (Ag⁺) and the resulting formation of Ag nanoparticles in aqueous solutions of PEO-PPO block copolymers. Different from other studies on the Ag nanoparticle synthesis using PEO-PPO block copolymers[43-49], the methodology that we present here aims at the direct synthesis of Ag nanoparticles from Ag⁺ in aqueous PEO-PPO block copolymer solutions in the absence of any additives but not from [Ag(NH₃)₂]⁺ [43-45], not in the lyotropic liquid crystal phase (that is formed in high concentration of PEO-PPO block copolymers) [46] and not in the presence of additives such as reducing agents [47-49].

2. Experimental

2.1. Ag Nanoparticle Synthesis

Silver (Ag) nanoparticles were prepared by mixing a 20×10^{-3} mol L⁻¹ silver nitrate (AgNO₃; 99.999+ %, Aldrich) aqueous (18.2 MΩ cm, Millipore-filtered water) solution (0.25 mL) with aqueous solutions (25 mL) containing poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) block copolymer (H(OCH₂CH₂)_x(OCH₂(CH₃)CH)_y(OCH₂CH₂)_xOH; Pluronic, BASF Corp.) or poly(ethylene oxide) (PEO) homopolymer (H(OCH₂CH₂)_xOH; Sigma-Aldrich) in 50 mL container of a Teflon-lined stainless steel autoclave. The PEO-PPO block copolymers that we considered for Ag nanoparticle synthesis in this work are Pluronic P103, Pluronic F68, Pluronic F88, Pluronic F127 and Pluronic F108 [34]. For comparison purposes, a PEO

homopolymer (PEG8000, Sigma-Aldrich) was applied for Ag nanoparticle synthesis. Properties of the PEO-PPO block copolymers and a PEO homopolymer considered here are listed in **Table 1**. The various polymers allow us to examine the effects of metal ion reduction activity (due to block copolymer overall chain length and/or PEO block length) and polymer adsorption, colloidal stabilization (due to block copolymer overall chain length and hydrophobicity) and presence of block copolymer micelles on the formation and structure of Ag nanoparticles. The Ag^+ concentration following mixing (at the start of the reaction) was $2.0 \times 10^{-4} \text{ mol L}^{-1}$. The polymer concentrations reported here are those of the polymer solution prior to mixing with the metal ion solution (the polymer concentration in the reaction medium was 1.0 % lower than that before mixing). In order to examine the effect of reaction temperature on Ag nanoparticle formation, following agitation by vortex mixer for ~10 sec, the solutions were left standing in temperature range of 5-140 °C for 24 h in 50 mL container of a Teflon-lined stainless steel autoclave for the reaction to be completed. For comparison purposes, diamminesilver(I) ions ($[\text{Ag}(\text{NH}_3)_2]^+$) was tested as a silver precursor for Ag nanoparticle synthesis in aqueous PEO-PPO block copolymer solutions in temperature range of 5-140 °C for 24 h.

2.2. Characterization

The formation of Ag nanoparticles was monitored by observing changes in the absorption spectra centered at ~410 nm originating from the Surface Plasmon Resonance (SPR) of Ag nanoparticles [50] using a UV-visible spectrophotometer (V-630, JASCO Corporation) at room temperature. The size and shape of the obtained Ag nanoparticles were determined by a transmission electron microscope (TEM) (JEM-2010, JEOL Ltd.) in conventional transmission mode using 200 kV. The preparation of the TEM samples involved several steps of dilution with water and concentration via centrifugation in order to remove excess block copolymer.

Formation of Ag nanoparticles was also confirmed from X-ray diffraction pattern measured with powder X-ray diffraction (XRD) system (RINT-2200V PC, RIGAKU).

3. Proposed Mechanism on Silver Ion Reduction by PEO-PPO Block Copolymers in Aqueous Solutions

In order to achieve the direct synthesis of Ag nanoparticles from reduction of Ag^+ by PEO-PPO block copolymers in aqueous solutions, we first consider the mechanism of Ag^+ reduction by PEO-PPO block copolymers. On the basis of information reported for the reduction of metal ions by PEO-type surfactants [1, 2], PEO homopolymer [51, 52] and PEO-containing polymers [22-24] and our previous work [33-42], three possible mechanisms of metal ion reduction by PEO-PPO block copolymers are proposed as described below (a, b and c). We believe that the mechanism (c) is the most responsible for metal ion reduction in PEO-PPO block copolymer systems.

(a) Alcohol (hydroxyl) functionality of a PEO-PPO block copolymer molecule for metal ion reduction [1, 3].

Alcohols are very often used as reducing agents for the synthesis of metal nanoparticles [1, 3, 19]. However, in our experiments, the reduction of Ag^+ ions and Ag nanoparticle formation are not observed in aqueous solutions containing alcohols (e.g., methanol, ethanol, 1-propanol, 2-propanol, ethylene glycol and glycerol) at concentrations that are consistent with the PEO-PPO block copolymer concentration range used in our work.

(b) Oxidizing and reducing function of hydroperoxides (ROCOOH) formed from polyethers such as PEO-PPO block copolymers upon reaction with oxygen from the air [1, 2, 24]

It is reported that the hydroperoxides formed from oxidation of the surfactant most likely were responsible for metal ion reduction. We tested the formation of Ag nanoparticles with

PEO-PPO block copolymers (e.g., EO₆PO₂₂EO₆, Pluronic L44) having PEO block length comparable to that of the reported PEO-type surfactants [1, 2], and found that Ag⁺ reduction and Ag nanoparticle formation were not observed. So, this effect is significantly small even if PEO-PPO block copolymers were forming hydroperoxides in air-saturated water. If hydroperoxides formed from PEO-PPO block copolymers facilitate metal ion reduction, the effect of PEO block length does not need to be considered because oxidation of polyether occurs only at endgroup of polymer. Namely, the formation of hydroperoxides cannot explain the effects of block copolymer molecular weight (block length).

(c) Reduction of bound Ag⁺ ions with cavities (pseudocrown ether structure) [53-61] through oxidation of the oxyethylene and oxypropylene segments by the metal center [51].

Poly(ethylene oxide) (PEO) forms a conformation similar to crown ethers (pseudocrown ether structure) by binding with metal ions in aqueous solution due to the ion-dipole interactions between the metal ions and the electron lone pairs of the ethylene oxide linkages [53-56]. The cyclization of PEO with metal ions requires longer (> EO₇) PEO chains [53, 54]. The strength of the attraction is afforded by the interaction of several oxygen atoms in the PEO chain with one ion [53, 54, 59]. This mechanism can explain the effect of PEO chain length on the metal ion reduction. This mechanism can explain reasonably our experimental results; in particular, effects of block copolymer block length (molecular weight) so that we believe that this process primary works for metal ion reduction in PEO-PPO block copolymer systems.

4. Results and Discussion

4.1. Ag Nanoparticle Formation in Aqueous PEO-PPO Block Copolymer Solutions

Silver (Ag) nanoparticles are formed from silver nitrate (AgNO₃) formamide solutions of PEO-PPO block copolymers at 100 °C but not from aqueous solutions at 100 °C (the reaction

period for 24 h) [37, 38]. Indeed, we confirmed that no remarkable absorption band originating from SPR of Ag nanoparticles was observed in every aqueous solution of PEO-PPO block copolymers that we examined in this work in the temperature range of 5-100 °C (see **Figure 1**). This indicates that Ag nanoparticles were not formed in aqueous PEO-PPO block copolymer solutions in the temperature range of 5-100 °C. Then, we tested the Ag nanoparticle synthesis above 100 °C in 10 wt% PEO-PPO block copolymer aqueous solutions. In the temperature at 120 and 140 °C, the absorption band centered at ~410 nm originating from SPR of Ag nanoparticles was observed in aqueous solutions of Pluronic F88, Pluronic F127 and Pluronic F108 but not in aqueous solutions of Pluronic F68 and Pluronic P103 (see **Figure 1** and upper panel of **Figure 2**). This indicates that Ag nanoparticles were formed in aqueous Pluronic F88, Pluronic F127 and Pluronic F108 solutions at 120 and 140 °C but not in aqueous Pluronic F68 and Pluronic P103 solutions. TEM observation revealed the formation of spherical, plate-like and rod-like Ag nanoparticles at 120 °C in aqueous solutions of Pluronic F88, Pluronic F127 and Pluronic F108 (see **Figure 3**). The X-ray diffraction measurement confirmed the formation of Ag nanoparticles but not Ag₂O nanoparticles (see **Figure 4**). The peaks observed in XRD patterns shown in **Figure 4** are assigned to (111), (200), (220) and (311) facets of silver. Note here that Ag nanoparticles were not formed from aqueous AgNO₃ solution in the absence of PEO-PPO block copolymers even after heating at 120 and 140 °C for 24 h. No noticeable absorption band was observed in aqueous AgNO₃ solution after heating at 120 and 140 °C for 24 h (see bottom panel of **Figure 1** and upper panel of **Figure 5**). This indicates that the reduction of Ag⁺ in aqueous PEO-PPO block copolymer solutions above 100 °C is not caused by hydrothermal reaction due to the high-temperature aqueous solutions at higher vapor pressure. We also revealed that the increase in the polymer concentration promoted the Ag⁺ reduction and Ag nanoparticle formation. Absorbance centered at ~410 nm originating from SPR of Ag

nanoparticles increased with increasing the polymer concentration (see **Figure 5**). These results support that the Ag^+ reduction in aqueous solutions is attributed to the reducing function of PEO-PPO block copolymers. Furthermore, we confirmed that Ag nanoparticles were not formed by mixing of an aqueous AgNO_3 solution with a hydrothermal-treated aqueous solution of PEO-PPO block copolymer (the result is not presented here).

4.2. Connection between Reaction Temperature and Ag Nanoparticle Formation in Aqueous PEO-PPO Block Copolymer Solutions

Now we realized that the formation of Ag nanoparticles in aqueous PEO-PPO block copolymer solutions required higher temperature than 100 °C. So, let us consider here the mechanism on the formation of Ag nanoparticles from Ag^+ above 100 °C in aqueous PEO-PPO block copolymer solutions by comparison between $[\text{Ag}(\text{NH}_3)_2]^+$ and Ag^+ as silver precursor ions. In the case of Ag nanoparticle synthesis from $[\text{Ag}(\text{NH}_3)_2]^+$ in aqueous PEO-PPO block copolymer solutions, Ag nanoparticles are formed at ambient temperature [43-45]. We also confirmed the Ag nanoparticle formation from $[\text{Ag}(\text{NH}_3)_2]^+$ in aqueous PEO-PPO block copolymer solutions in the whole range of 5-140 °C in the absence of any additional agents. Typically, the magnitude of metal ion reduction is defined in terms of redox potential of metal ions. Namely, metal ions with higher redox potential should be reduced easily. However, in fact, Ag^+ with higher redox potential (= 0.799 V_{NHE} at 25 °C) than $[\text{Ag}(\text{NH}_3)_2]^+$ (= 0.373 V_{NHE} at 25 °C) is not reduced in aqueous PEO-PPO block copolymer solutions at ambient temperature while $[\text{Ag}(\text{NH}_3)_2]^+$ with lower redox potential than Ag^+ is easily reduced at ambient temperature in aqueous PEO-PPO block copolymer solutions. This suggests that the Ag^+ reduction and the resulting formation of Ag nanoparticles in aqueous PEO-PPO block copolymer solutions is not related to the redox potential of silver precursor. Then, we consider that the Ag^+ reduction and

the resulting formation of Ag nanoparticles in aqueous PEO-PPO block copolymer solutions are attributed to the hydration of Ag^+ in aqueous solutions. Namely, the hydration of Ag^+ by water molecules in aqueous solutions would prevent the interaction between Ag^+ and PEO-PPO block copolymers in aqueous solutions (see **Figure 6**). So, if the hydrated water molecules around Ag^+ were removed, Ag^+ could interact with PEO-PPO block copolymers directly, and Ag^+ should be reduced by PEO-PPO block copolymers in aqueous solutions (see **Figure 6**). In general, smaller ions are more hydrated compared to larger ions. For example, Ag^+ is hydrated by 4 water molecules, while $\text{Ag}(\text{NH}_3)_2^+$ is hydrated by 2.8 water molecules because the size of Ag^+ is smaller than that of $[\text{Ag}(\text{NH}_3)_2]^+$. Thus, the incorporation of Ag^+ into the pseudo-crown ether structures of the PEO-PPO block copolymers would be prevented significantly due to the hydration compared with that of $\text{Ag}(\text{NH}_3)_2^+$. Namely, the thermal motion of water molecules around Ag^+ enhanced by heating (above 100 °C) would be required for removal of hydrated water from Ag^+ . We also considered another possible mechanism on the Ag nanoparticle formation in aqueous solutions above 100 °C. Typically, the hydrothermal treatment with high temperature and high vapor pressure leads to the increase in the basicity of water. So, PEO-PPO block copolymers would be oxidized due to the increased basicity of water above 100 °C, and consequently Ag^+ would be reduced to form Ag nanoparticles by the oxidation of PEO-PPO block copolymers. However, if the Ag^+ reduction by PEO-PPO block copolymers above 100 °C were promoted by the increased basicity of water by hydrothermal treatment, Ag nanoparticles must be formed in every PEO-PPO block copolymers and PEO homopolymer that we examined in this work at high temperature. Namely, molecular weight effect on the Ag nanoparticle formation from Ag^+ (as seen in **Figure 2**) should not be observed in PEO-PPO block copolymer system, if the increased basicity of water by hydrothermal treatment was main contributor to the Ag nanoparticle formation in PEO-PPO block copolymer system. Indeed, the

formation of Ag nanoparticles from $\text{Ag}(\text{NH}_3)_2^+$ in PEO-PPO block copolymer system was independent on the molecular weight of PEO-PPO block copolymer and temperature. Thus, the Ag^+ reduction and Ag nanoparticle formation through the complexation of Ag^+ with PEO-PPO block copolymers above 100 °C would be attributed to the dehydration of water molecules from Ag^+ in the high-temperature aqueous solutions at higher vapor pressure.

4.3. Connection between Molecular Weight of PEO-PPO Block Copolymer and Ag Nanoparticle Formation in Aqueous PEO-PPO Block Copolymer Solutions

We also noticed that the absorbance centered at ~410 nm originating from SPR of Ag nanoparticles plotted as a function of molecular weight of PEO-PPO block copolymer dramatically increased above 10,000 g mol^{-1} molecular weight of PEO-PPO block copolymer (see bottom panel of **Figure 2**). This means that Ag nanoparticle formation in aqueous PEO-PPO block copolymer solutions requires PEO-PPO block copolymers with higher molecular weight than 10,000 g mol^{-1} . As described in section 3, the metal ion reduction by PEO-PPO block copolymers in aqueous solutions is caused by the formation of pseudocrown ether structures (cavities) with metal ions [33, 34, 51, 53-56]. Reduction of bound metal ions proceeds via oxidation of the polymer by the metal center [33, 34, 51]. In particular, the level of hydration (swelling) and polymer loops of PEO-PPO block copolymers are related to the initial reduction process (complexation of PEO-PPO block copolymers with metal ions) [34]. Since longer chain (larger molecular weight) of PEO-PPO block copolymers provide a number of loop structures which act as reaction sites, Ag^+ would be reduced more significantly with longer chain (larger molecular weight) of PEO-PPO block copolymers.

4.4. Connection between Micelles Formation and Ag Nanoparticle Formation in Aqueous

PEO-PPO Block Copolymer Solutions

Finally, let us discuss the role of micelles on the Ag^+ reduction and Ag nanoparticle formation because PEO-PPO block copolymers form micelles due to the amphiphilic character afforded from hydrophilic PEO block and hydrophobic PPO block. In order to elucidate the role of micelles on the on Ag^+ reduction and Ag nanoparticle formation, we tested the Ag nanoparticle synthesis in aqueous solutions of PEO homopolymer (PEG8000). In fact, Ag nanoparticles were not formed in aqueous solutions of PEO homopolymer in the same experimental condition with PEO-PPO block copolymer system (the result is not shown here). This indicates that the reduction activity of PEO homopolymer for Ag^+ in aqueous solutions is lower than that of PEO-PPO block copolymers. This is consistent with Au nanoparticle synthesis in PEO homopolymer system. Au nanoparticles were formed at 2 days after reaction initiation [33, 34]. Longenberger and Mill have also reported that Ag nanoparticle formation required 20 days for reaction completion in aqueous solutions of PEO homopolymer [51]. This indicates that the PPO block in the PEO-PPO block copolymer plays an important role for promotion of metal ion reduction. Then, we consider the contribution of micelles to the Ag^+ reduction and the resulting Ag nanoparticle formation. However, our findings suggest that the micelles themselves seem to be not related directly to cavity formation, because Pluronic F88 having higher critical micellization concentration (cmc) is most effective for Ag nanoparticle formation in the Pluronic P103, F68, F88, F127 and F108. **In the contrast**, block copolymer networks (e.g., cyclization and crosslinking) seem to be related to reaction activity (cavity formation). In our previous work reported in reference [34], the kinetic experiments and analysis reveal that concentration of block copolymer participating into $[\text{AuCl}_4]^-$ reduction at early stage increases with block copolymer concentration for Pluronic F127 and F108 systems while decreases for Pluronic P103 and P105 systems. We believe that the difference is most

likely due to the balance between cyclization and crosslinking of block copolymers initially formed. Higher cyclization and lower crosslinking induce more effective complexation of polymer with ions while lower cyclization and higher crosslinking induce less complexation of polymer with ions [62]. Degree of polymer crosslinking would increase with increase in block copolymer concentration so that the rate constant would decrease with increase in block copolymer concentration. Longer chain polymers such as Pluronic F88, F127 and F108 should be cyclized so that reduction of Ag^+ would be enhanced with block copolymer concentration. On the other hand, the lower activity of Pluronic P103 and F68 for Ag^+ reduction is most likely due to less cyclization of block copolymer because of shorter polymer chains. So, we consider that PEO blocks contribute to metal ion reduction more significantly than PPO blocks at early stage of metal ion reduction because of hydrophobicity of PPO blocks. Instead, PPO blocks induce the adsorption of block copolymers on the metal clusters and/or particles formed, and enhance the metal ion reduction by both PEO and PPO blocks (metal formation) on the surfaces. Furthermore, the adsorption function of PPO blocks improves colloidal stabilization and growth of metal nanoparticles.

5. Conclusions

Silver (Ag) nanoparticles were formed directly from aqueous silver nitrate (AgNO_3) solutions of PEO-PPO block copolymers above 100 °C. This is most likely attributed to the dehydration of water molecules from Ag^+ by thermal motion of water molecules by high temperature and high vapor pressure. The dehydrated Ag^+ would interact more significantly with PEO-PPO block copolymers, and hence, Ag^+ would be reduced by PEO-PPO block copolymers in aqueous solutions. Furthermore, we found that PEO-PPO block copolymers with longer chain (larger molecular weight) are more reactive with Ag^+ . Also higher

concentration of PEO-PPO block copolymers enhanced Ag^+ reduction and Ag nanoparticle formation. These are most likely due to larger number of looping which act as reaction site afforded from longer chain (larger molecular weight) PEO-PPO block copolymers.

The formation mechanism of Ag nanoparticles in aqueous solutions of PEO-PPO block copolymers presents a range of possibilities for further development. The self-assembled structures afforded by amphiphilic polymers can be exploited as one-, two- and three-dimensional templates for hybrid metal/polymer ordered materials. We are currently exploring the self-formation and -organization of metal nanoparticles on solid particles such as silica particles and polymer particles in solutions. The tunability of block copolymer self-assembly on the solid particles should be an asset to the above.

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Table 1. Properties of the PEO-PPO block copolymers $(EO_xPO_yEO)_x$ and PEO homopolymer (EO_x) used in this study [34]

Pluronic	Molecular weight	PEO wt%	PPO block mol. weight	PEO block mol. weight	cmc (mM) (25 °C)	Nominal formula
P103	4950	30	3465	1485	0.141	EO ₁₇ PO ₆₀ EO ₁₇
F68	8400	80	1680	6720	320.5	EO ₇₆ PO ₂₉ EO ₇₆
F88	11400	80	2280	9120	11.51	EO ₁₀₃ PO ₃₉ EO ₁₀₃
F127	12600	70	3780	8820	0.555	EO ₁₀₀ PO ₆₅ EO ₁₀₀
F108	14600	80	2920	11680	3.082	EO ₁₃₂ PO ₅₀ EO ₁₃₂
PEO	8000	100	0	8000	-	EO ₁₈₁

cmc: critical micellization concentration

Figure captions

Figure 1. (Upper panel) Absorption spectra recorded at 24 h after mixing an aqueous AgNO_3 solution (0.2 mM) with aqueous Pluronic F88 solution (10 wt%) at different reaction temperatures: -1, 5, 25, 40, 60 80, 100, 120 and 140 °C. (Bottom panel) Absorbance centered at ~410 nm originating from SPR of silver nanoparticles recorded at 24 h after mixing an aqueous AgNO_3 solution (0.2 mM) with an aqueous PEO-PPO block copolymer solution (10 wt%) : (\square) Pluronic P103, (\triangle) Pluronic F68, (\bullet) Pluronic F88, (\blacktriangle) Pluronic F127 and (\blacklozenge) Pluronic F108, plotted as a function of reaction temperature. Also shown are (\circ) absorbances at 410 nm of aqueous AgNO_3 solution left standing at 5, 25, 40, 60 80, 100, 120 and 140 °C for 24 h, as control experiments.

Figure 2. (Upper panel) Absorption spectra recorded at 24 h after mixing an aqueous AgNO_3 solution (0.2 mM) with aqueous PEO-PPO block copolymers solution (10 wt%) at 120 °C. (Bottom panel) Absorbance centered at ~410 nm originating from SPR of Ag nanoparticles recorded at 24 h after mixing an aqueous AgNO_3 solution (0.2 mM) with an aqueous PEO-PPO block copolymer solution (10 wt%) at (\circ) 100 °C, (\bullet) 120 °C and (\square) 140 °C plotted as a function of molecular weight of PEO-PPO block copolymer.

Figure 3. TEM images of Ag nanoparticles synthesized in 10 wt% PEO-PPO block copolymer aqueous solutions at 120 °C: (top images) Pluronic F88, (middle images) Pluronic F127 and (bottom images) Pluronic F108.

Figure 4. X-ray diffraction patterns of Ag nanoparticles synthesized in 10 wt% PEO-PPO

block copolymer aqueous solutions at 120 °C: (top panel) Pluronic F88, (middle panel) Pluronic F127 and (bottom panel) Pluronic F108.

Figure 5. (Upper panel) Absorption spectra recorded at 24 h after mixing an aqueous AgNO₃ solution (0.2 mM) with aqueous Pluronic F88 solution with different concentrations: 0, 1.0, 5.0, 10, 15 and 20 wt% at 120 °C. (Bottom panel) Absorbance centered at ~410 nm originating from SPR of Ag nanoparticles recorded at 24 h after mixing an aqueous AgNO₃ solution (0.2 mM) with an aqueous PEO-PPO block copolymer solution at 120 °C: (□) Pluronic P103, (△) Pluronic F68, (●) Pluronic F88, (▲) Pluronic F127 and (◆) Pluronic F108, plotted as a function of block copolymer concentration.

Figure 6. Schematic illustration of Ag nanoparticle formation from Ag⁺ in an aqueous PEO-PPO block copolymer solution above 100 °C.

Figure 1. Sakai et al.

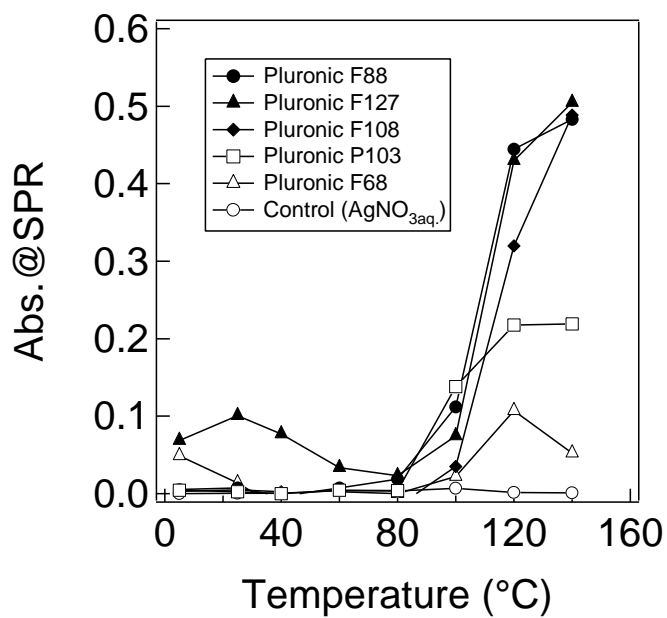
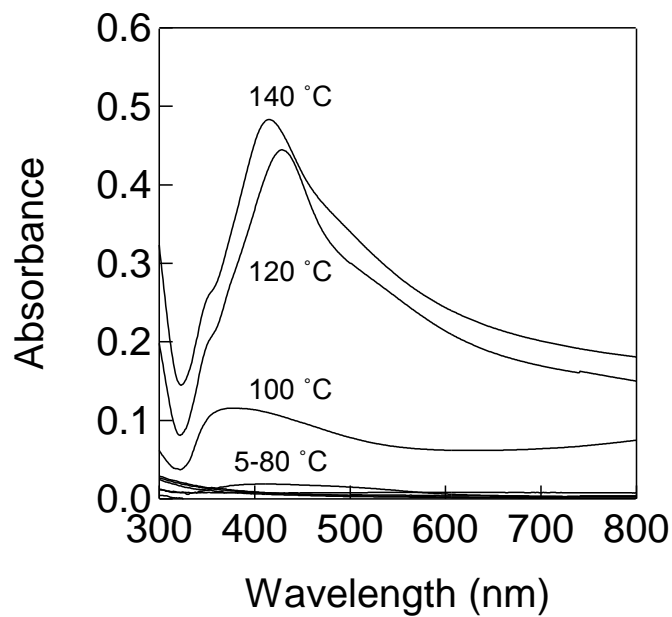


Figure 2. Sakai et al.

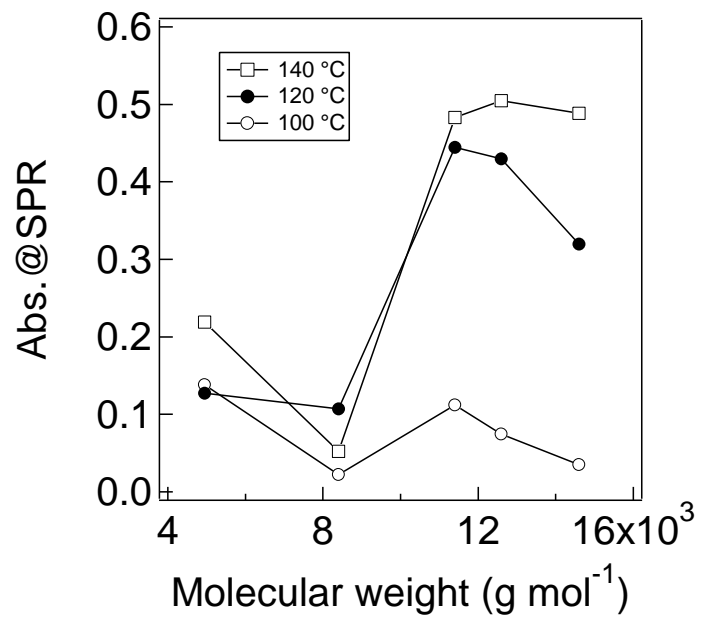
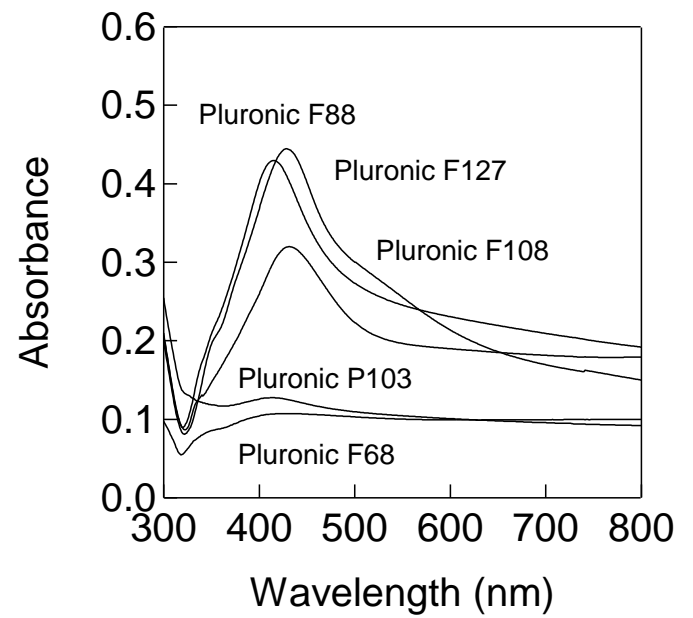
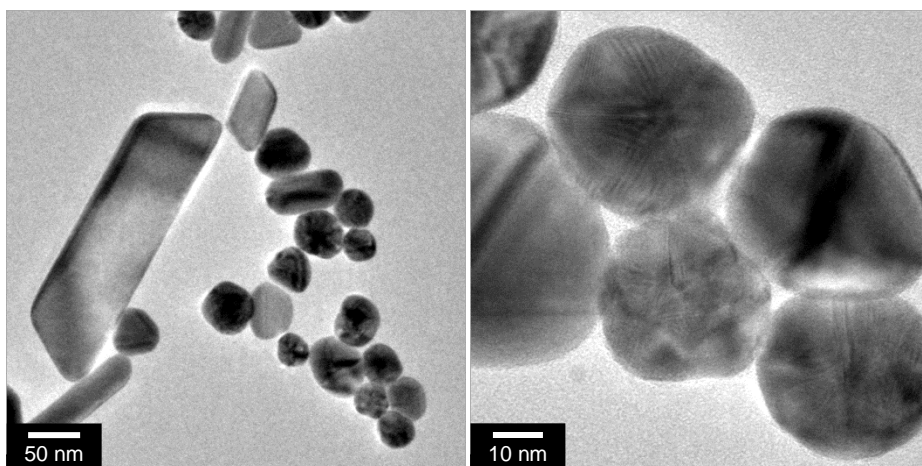
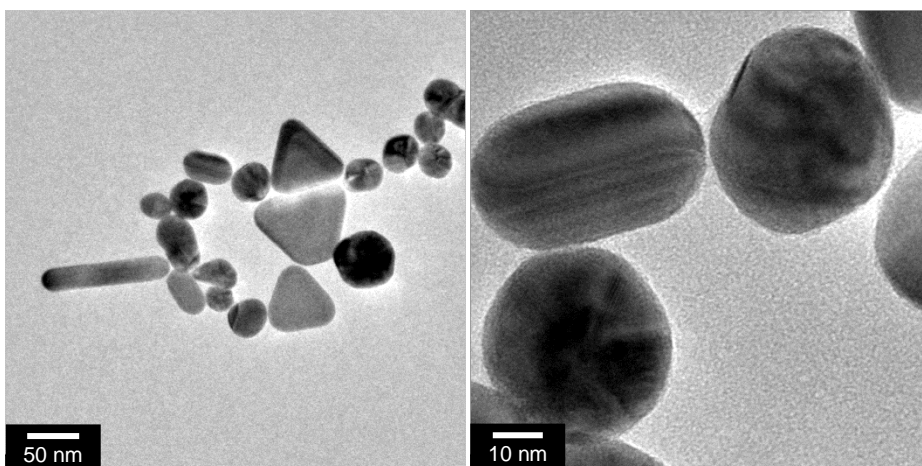


Figure 3. Sakai et al.

10 wt% Pluronic F88_{aq.} at 120 °C



10 wt% Pluronic F127_{aq.} at 120 °C



10 wt% Pluronic F108_{aq.} at 120 °C

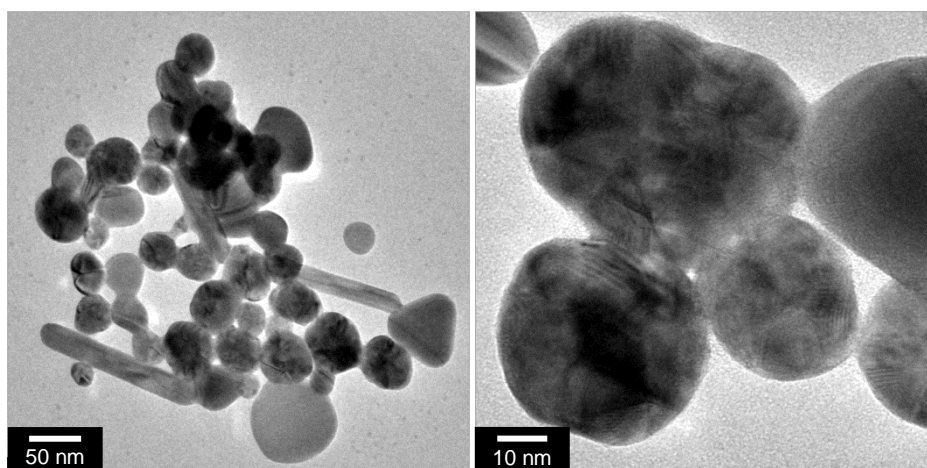


Figure 4. Sakai et al.

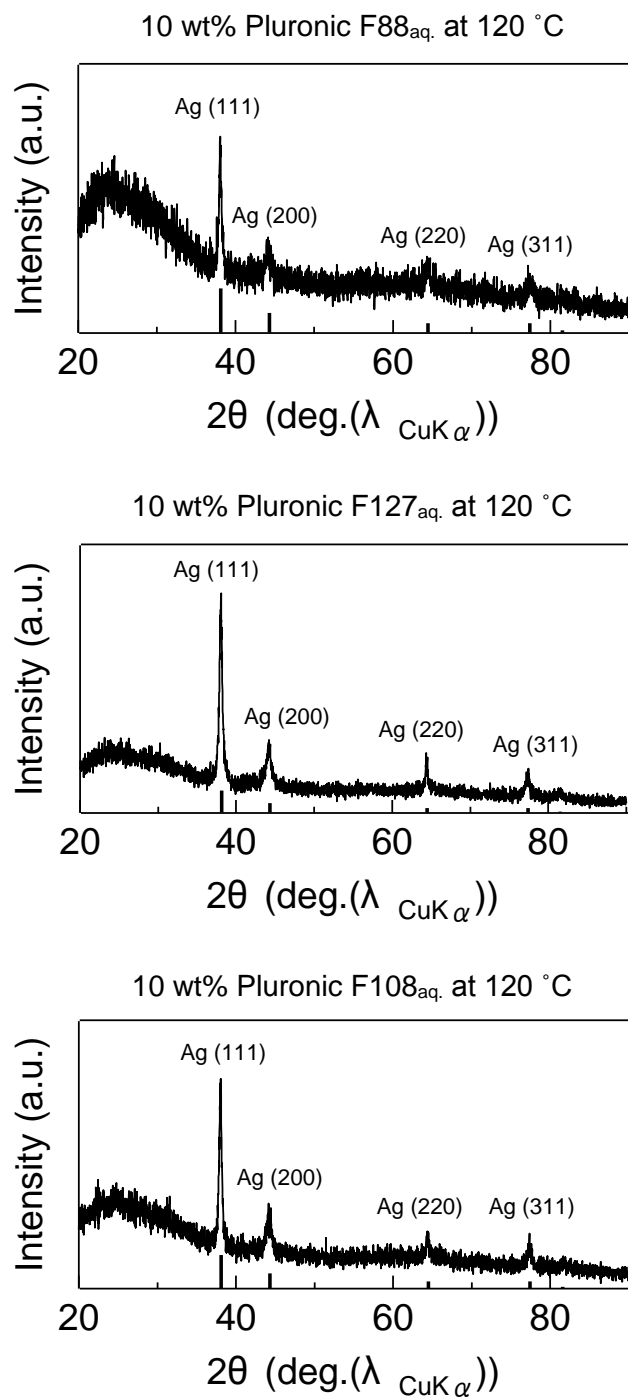


Figure 5. Sakai et al.

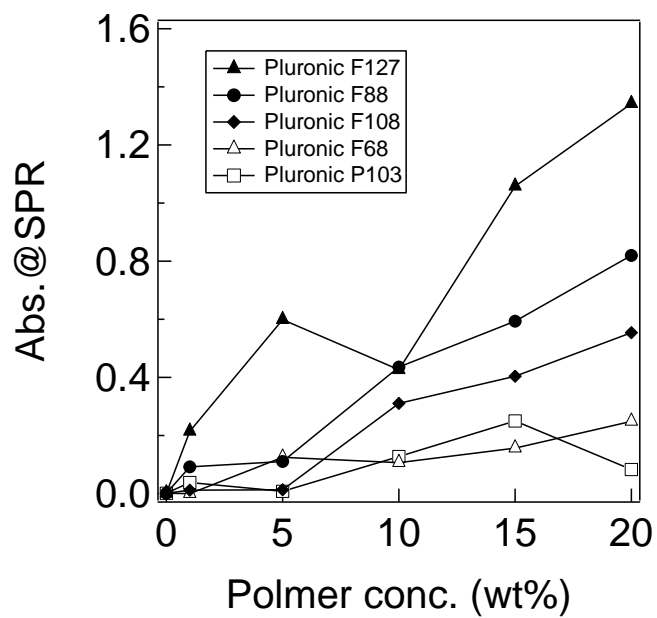
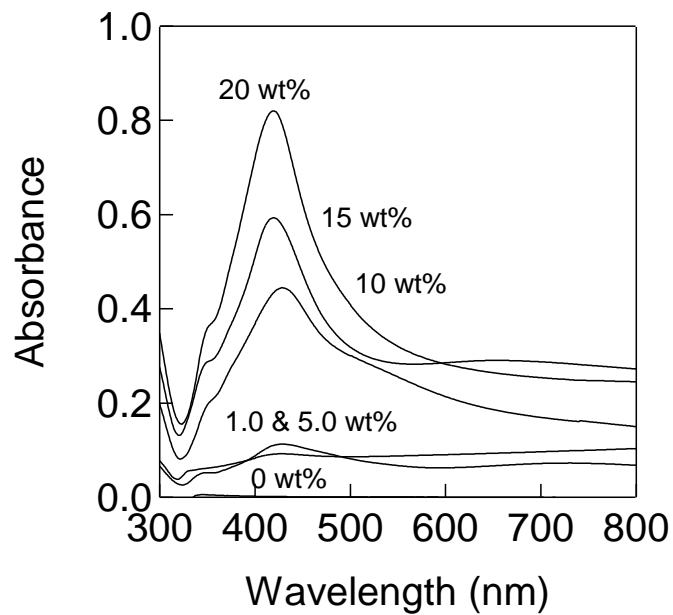


Figure 6. Sakai et al.

