

# Single-Step Synthesis and Stabilization of Metal Nanoparticles in Aqueous Pluronic Block Copolymer Solutions at Ambient Temperature

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A single-step synthesis of gold nanoparticles with an average diameter of  $\sim 10$  nm from hydrogen tetrachloroaurate(III) hydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) has been achieved in air-saturated aqueous solutions that contain poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) block copolymers but not any other reducing agent. These amphiphilic block copolymers act as both reductants and colloidal stabilizers and prove very efficient in both functions. The formation of gold nanoparticles is controlled by the overall molecular weight and relative block length of the block copolymer. The synthesis procedure reported here is environmentally benign and economic, as it involves the minimum possible number of components: it uses water as the solvent, it uses commercially available polymers, it proceeds fast to completion, and it results in a “ready-to-use” product.

## Introduction

Metal nanoparticles such as nanospheres,<sup>1</sup> nanorods,<sup>2,3</sup> nanocubes,<sup>4</sup> nanoplates,<sup>5,6</sup> nanotetrapods,<sup>7</sup> and nanoprisms<sup>8</sup> are attracting significant attention because of their size-dependent optical, magnetic, electronic, and catalytic properties.<sup>9–14</sup> For example, gold nanoparticles exhibit intense photoluminescence only when their sizes are much smaller than a certain value ( $\sim 5$  nm in diameter).<sup>9</sup> The development of simple and versatile methods for the preparation of nanoparticles in a size- or shape-selected and -controlled manner is an important and challenging task.<sup>1–8,15,16</sup> In addition, utilization of nontoxic chemicals, environmentally benign solvents, and renewable materials are emerging issues that merit important consideration in a synthetic strategy.<sup>17</sup>

The preparation of metal nanoparticles in solution most commonly involves the chemical reduction of metal ions. Surfactant-stabilized reverse micellar (“water-in-oil”) systems have been used as nanoreactors for the chemical reduction of metal ions in organic solvents.<sup>16,18–20</sup> In aqueous solutions,<sup>17,21–27</sup> metal nanoparticles have been typically produced from the chemical reduction of metal ions by reducing agents dissolved in water; such reduction takes place in the presence of water-soluble polymer or surfactant and with the aid of externally supplied energy such as heating,<sup>17</sup> photoirradiation,<sup>21</sup> or ultrasound irradiation.<sup>22</sup> These methods allow for control of the size and concentration of the dispersed particles.<sup>21,22,26,27</sup> However, concerns and problems remain, such as the use of organic solvents, the byproducts from the reducing agent, the multiple steps required, and the high concentration of protective agent needed to attain colloidal stability of the nanoparticles.<sup>23</sup> In an aim to address some of these problems, a single-step synthesis of gold nanoparticles in aqueous solutions has been proposed using poly(ethylene oxide),<sup>24</sup> diamine-terminated poly(ethylene oxide),<sup>25</sup> amine-functionalized, third-generation poly(propyleneimine) dendrimers,<sup>26</sup> or  $\alpha$ -biotinyl-PEG-*block*-[poly(2-(*N,N*-dimethylamino)ethyl methacrylate)] (PEG: poly(ethylene glycol)).<sup>27</sup> Still, these recently reported

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**Table 1. Properties of the Pluronic Block Copolymers Used in This Study<sup>28</sup>**

Pluronic	mol wt	PEO wt %	PPO block mol wt	PEO block mol wt	cmc <sup>a</sup> /mM (25 °C)	nominal formula
L64	2900	40	1740	1160	26.31	(EO) <sub>13</sub> (PO) <sub>30</sub> (EO) <sub>13</sub>
P65	3400	50	1700	1700	38.22	(EO) <sub>19</sub> (PO) <sub>29</sub> (EO) <sub>19</sub>
P84	4200	40	2520	1680	6.190	(EO) <sub>19</sub> (PO) <sub>43</sub> (EO) <sub>19</sub>
P103	4950	30	3465	1485	0.141	(EO) <sub>17</sub> (PO) <sub>60</sub> (EO) <sub>17</sub>
P104	5900	40	3540	2360	0.508	(EO) <sub>27</sub> (PO) <sub>61</sub> (EO) <sub>27</sub>
P105	6500	50	3250	3250	0.461	(EO) <sub>37</sub> (PO) <sub>56</sub> (EO) <sub>37</sub>
P123	5750	30	4025	1725	0.052	(EO) <sub>19</sub> (PO) <sub>69</sub> (EO) <sub>19</sub>
F127	12600	70	3780	8820	0.555	(EO) <sub>100</sub> (PO) <sub>65</sub> (EO) <sub>100</sub>
PEO homopolymer	6000	100	0	6000		(EO) <sub>136</sub>

<sup>a</sup> cmc: critical micellization concentration.

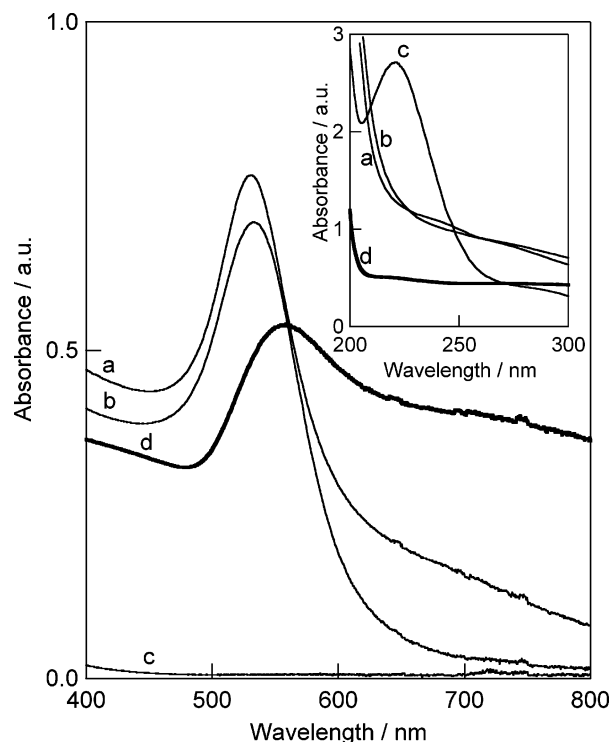
single-step methods require the utilization of polymers that may be “exotic”, a high concentration of protective agent for colloidal stability, and/or a high temperature.<sup>25–27</sup>

In the present work, we report the single-step synthesis and stabilization of gold nanoparticles from hydrogen tetrachloroaurate(III) hydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O) in air-saturated aqueous poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) block copolymer (Pluronic) solutions at ambient temperature. In addition to acting as reductants, PEO–PPO–PEO block copolymers, even at low concentrations, proved very efficient in stabilizing the colloidal dispersion of the resulting gold nanoparticles. The synthesis method presented here is environmentally benign, since it involves water and polymers that are not only nontoxic but also approved for pharmaceutical use. It is also economical, as it proceeds fast to completion and results in a “ready-to-use” product. Moreover, variation of the block copolymer molecular characteristics and the relative concentration of the reactants allows for tunability of particle properties.

### Experimental Section

Gold nanoparticles were prepared by simply mixing an aqueous  $2 \times 10^{-3}$  mol L<sup>-1</sup> hydrogen tetrachloroaurate(III) hydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O; 99.9+%, Aldrich) solution with an aqueous PEO homopolymer (PEG6000, Fluka Biochemika) solution or an aqueous PEO–PPO–PEO block copolymer (Pluronic L64, P65, P84, P103, P104, P105, P123, or F127, BASF Corp.) solution so that the final AuCl<sub>4</sub><sup>-</sup> concentration was  $2 \times 10^{-4}$  mol L<sup>-1</sup>. The polymer concentrations reported here are those of the aqueous polymer solution prior to mixing with the HAuCl<sub>4</sub> solution. The mixing ratio was such that the final polymer concentration was 10% lower than that before mixing. Following agitation by a vortex mixer for ~10 s, the solutions were left standing at  $25 \pm 1$  °C for 2 h for the reaction to proceed (note: the absorbance spectra remained almost unchanged after 2 h, indicating completion of the reaction). The Pluronic PEO–PPO–PEO block copolymers considered in this study were selected in order to examine the effects of molecular weight and the PEO/PPO block ratio on the synthesis of gold nanoparticles and their colloidal stabilization. The properties of the polymers used here are listed in Table 1.<sup>28</sup>

The reduction of AuCl<sub>4</sub><sup>-</sup> and the formation of gold nanoparticles were monitored by observing changes in the absorption spectra centered at ~220 nm for the gold(III) chloride solutions<sup>22</sup> and those centered at ~540 nm originating from the surface plasmon of the gold nanoparticles<sup>3</sup> using a UV–visible spectrometer (GENESYS 6, Thermo Spectronic). The size and shape of the obtained gold nanoparticles were determined by a transmission electron microscope (JEM-100CX, JEOL Ltd., ×100 000) in the conventional transmission mode using 80 keV. The size distributions of the gold nanoparticles synthesized were obtained by measuring the diameter of more than 500 particles viewed in the micrographs.

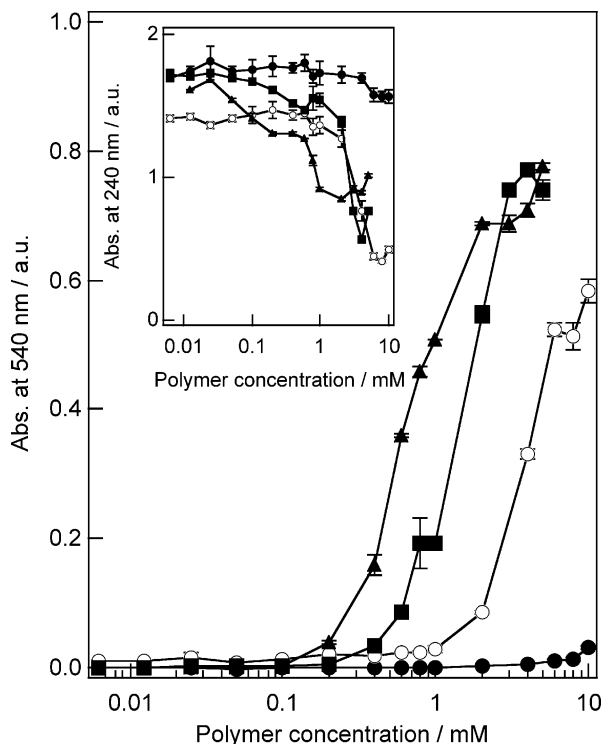


**Figure 1.** Absorbance spectra recorded at 2 h after mixing an aqueous AuCl<sub>4</sub><sup>-</sup> ion solution and a 5.0 mM aqueous (a) Pluronic P103 or (b) Pluronic F127 block copolymer solution. Also shown for comparison are absorbance spectra at (c) 2 h and (d) 2 days after mixing an aqueous AuCl<sub>4</sub><sup>-</sup> ion solution and a 5.0 mM aqueous PEO homopolymer solution, with the PEO molecular weight intermediate to those of Pluronic P103 and F127.

### Results and Discussion

Figure 1 shows absorbance spectra obtained at 2 h after mixing an aqueous AuCl<sub>4</sub><sup>-</sup> ion solution and a 5.0 mM aqueous Pluronic P103 or F127 block copolymer solution. Also shown for comparison purposes are absorbance spectra recorded at 2 h and at 2 days after mixing an aqueous AuCl<sub>4</sub><sup>-</sup> ion solution and a 5.0 mM aqueous PEO homopolymer solution (the PEO molecular weight was selected to be intermediate to those of Pluronic P103 and F127). The absorption band centered at ~220 nm that originates from the gold(III) chloride solutions<sup>22</sup> and the band centered at ~540 nm that originates from the surface plasmon of the gold nanoparticles<sup>3</sup> were monitored. At 2 h after the initiation of the reaction, the absorption band centered at ~540 nm (due to gold nanoparticles) was prominent in both Pluronic P103- and Pluronic F127-containing solutions but was not observed at all in the PEO homopolymer solution. Correspondingly, the absorption band centered at 220 nm (due to AuCl<sub>4</sub><sup>-</sup> ions) was pronounced after 2 h in the aqueous PEO homopolymer solution but not in the case of aqueous Pluronic P103 and

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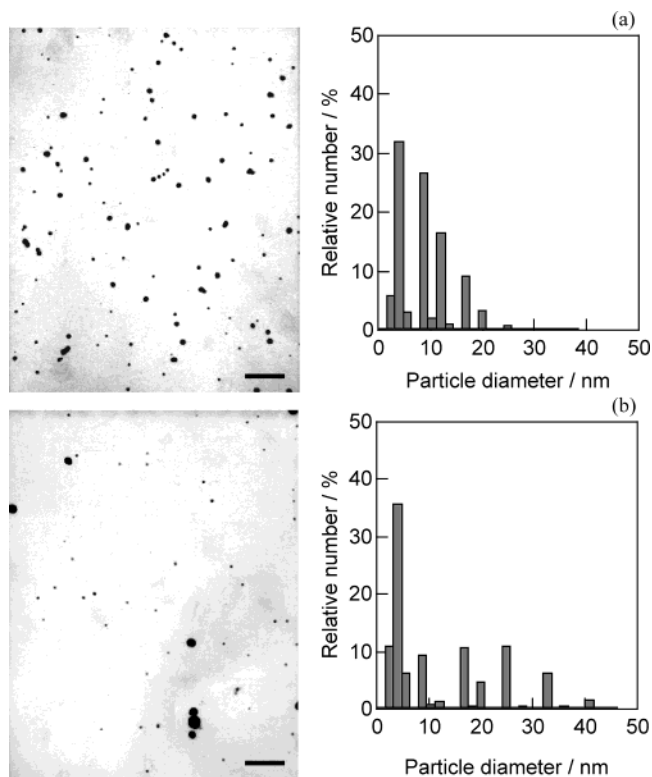


**Figure 2.** Absorbance at  $\sim 540$  nm at 2 h after mixing an aqueous  $\text{AuCl}_4^-$  ion solution and an aqueous (■) Pluronic P103 or (▲) Pluronic F127 block copolymer solution plotted as a function of polymer concentration. Also shown are absorbances at  $\sim 540$  nm at (●) 2 h and (○) 2 days after mixing an aqueous  $\text{AuCl}_4^-$  ion solution and an aqueous PEO homopolymer solution. The inset shows absorbances at 240 nm for the same systems and conditions plotted as a function of polymer concentration.

F127 block copolymer solutions. It took  $\sim 2$  days for gold nanoparticles to form in the PEO-homopolymer-containing system (as evidenced by the absorption increase at  $\sim 540$  nm and the decrease at 220 nm).

It is notable that the gold nanoparticles thus produced in aqueous Pluronic block copolymer solutions are highly stable even at low polymer concentrations ( $\text{AuCl}_4^-/\text{Pluronic}$  block copolymer molar ratio  $\sim 1/10$ ) and show no signs of aggregation and precipitation even after 8 months of being left standing at ambient temperature. On the contrary, precipitation of gold nanoparticles occurred after only 2 days when we synthesized them using the PEO homopolymer as the reductant/stabilizer. The high absorbance observed at longer wavelengths in aqueous PEO solution at  $\sim 2$  days after mixing (see Figure 1) indicates that gold nanoparticles form aggregates and precipitate.<sup>29</sup> The colloidal stabilization of gold nanoparticles by Pluronic block copolymers is most likely due to their amphiphilic character and their ability to form micelles in solution and/or on the surface of particles.<sup>30</sup> It becomes evident from the above that PEO-PPO-PEO amphiphilic block copolymers confer a distinct advantage over the PEO homopolymer both as reaction media and as stabilizers.

The effect of polymer concentration on the  $\text{AuCl}_4^-$  ion reduction and nanoparticle formation is shown in Figure 2. At 2 h after the initiation of the reaction, the absorption centered at 240 nm (due to  $\text{AuCl}_4^-$  ions) was high and independent of the PEO homopolymer concentration,



**Figure 3.** Electron micrographs and size distributions of gold nanoparticles produced in (a) Pluronic P103 and (b) Pluronic F127 block copolymer solutions. The Pluronic concentration is 1.0 mM. The scale bar represents 100 nm.

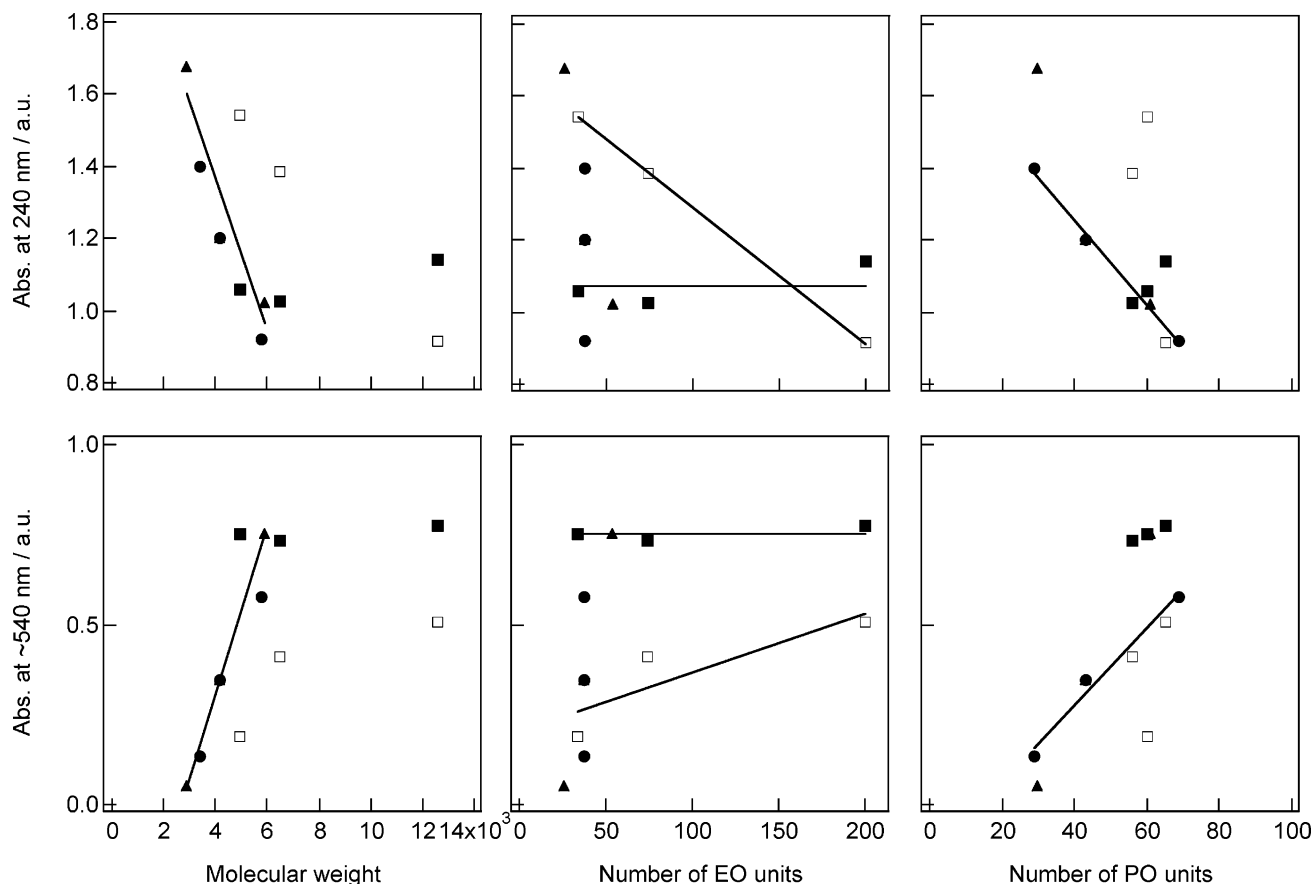
while the absorbance decreased with an increase in the Pluronic P103 or F127 block copolymer concentration gradually until 1.0 mM and then more abruptly. The absorbance at  $\sim 540$  nm (due to gold nanoparticles) started to increase from  $\sim 0.1$  mM Pluronic, while a small increase in the absorbance at  $\sim 540$  nm was observed only above 6.0 mM PEO after 2 h (see Figure 2). At  $\sim 2$  days after mixing, the absorbances at 240 nm decreased compared to those recorded at 2 h. The absorbance of the PEO system at 240 nm decreased drastically above  $\sim 2.0$  mM PEO; correspondingly, the absorbance at  $\sim 540$  nm increased (see Figure 2).

Figure 3 shows typical transmission electron micrographs and size distributions of the gold nanoparticles obtained in 1.0 mM Pluronic block copolymer solutions. Spherical nanoparticles with number-average diameters of 8.3 nm (standard deviation, 4.8 nm) and 11.3 nm (standard deviation, 10.0 nm) were observed in the aqueous Pluronic P103 and F127 solutions, respectively. No particles with a diameter above  $\sim 20$  nm were observed in the P103 system, whereas particles with diameters of up to 40 nm were observed in the F127 system. The particle sizes reported here are lower than the sizes obtained by Longenberger et al.<sup>24</sup> in aqueous PEO homopolymer solutions or by Iwamoto et al.<sup>25</sup> in aqueous diamine-terminated PEO solution. The average diameter of gold nanoparticles produced in amine-functionalized, third-generation poly(propyleneimine) dendrimer solutions varied from 4 to 33 nm depending on the initial molar ratio of polymer and metal ion.<sup>26</sup>

After establishing the facile synthesis of spherical nanoparticles in aqueous PEO-PPO-PEO block copolymer media, we turn our attention to how the synthesis depends on the block copolymer characteristics. To examine the relative contribution of the molecular weight and the PEO and PPO block length on the reduction of the

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**Figure 4.** Absorbances at 240 and  $\sim 540$  nm at 2 h after mixing an aqueous  $\text{AuCl}_4^-$  ion solution and 5.0 mM aqueous PEO–PPO–PEO block copolymer solutions plotted against the block copolymer molecular weight, number of EO units, and number of PO units: (▲) Pluronic L64, P84, and P104 with 40% PEO; (■) Pluronic P103, P105, and F127 having a PPO block with a MW of  $\sim 3500$  g/mol; (●) Pluronic P65, P84, and P123 having a PEO block with a MW of  $\sim 1700$  g/mol. Also shown are absorbances obtained for (□) Pluronic P103, P105, and F127 when these block copolymers had been added at a 1.0 mM concentration.

$\text{AuCl}_4^-$  ions and the formation of gold nanoparticles, we present in Figure 4 absorbances at 240 and  $\sim 540$  nm at 2 h after mixing an aqueous  $\text{AuCl}_4^-$  solution with aqueous PEO–PPO–PEO block copolymer solutions plotted as a function of the block copolymer molecular weight, number of EO units, and number of PO units. The block copolymers that we considered allow us to assess the effect of the overall polymer molecular weight at a fixed PEO/PPO ratio (L64, P84, and P104 all with 40% PEO), the effect of the PEO block length at a constant PPO block length (P103, P105, and F127 all having a PPO block with a molecular weight (MW) of  $\sim 3500$  g/mol), and the effect of the PPO block length (P65, P84, and P123 all having a PEO block with a MW of  $\sim 1700$  g/mol). Investigations of polymer molecular characteristics on the formation of colloidal particles such as the one reported here are scarce.<sup>23,31</sup> Bronstein et al. have investigated polymer effects on the formation of gold nanoparticles in organic media using polystyrene-poly-4-vinylpyridine (PS-*b*-P4VP) having various PS and P4VP block lengths.<sup>20</sup> In aqueous systems, the effects of the metal ion/stabilizer mixing ratio, reaction temperature, reaction time, and energy amount in the system upon the formation of colloidal particles have been typically considered.<sup>23,31</sup>

The effect of the overall molecular weight of the block copolymer can be discerned by comparing Pluronic L64, P84, and P104 with a fixed PEO/PPO ratio. As seen from the left-hand-side panels in Figure 4, the absorbance at 240 nm (due to reduction) decreased linearly and that at

$\sim 540$  nm (due to nanoparticle formation) increased with increasing polymer molecular weight.

Comparison of Pluronic P103, P105, and F127 having a PPO block with a MW of  $\sim 3500$  g/mol allows us to probe the effect of the PEO block length on the reduction of  $\text{AuCl}_4^-$  ions and the formation of gold nanoparticles. The absorbances at 240 and  $\sim 540$  nm were almost constant (see the center panels in Figure 4), which seems to indicate that variation of the PEO block length does not influence the reduction of  $\text{AuCl}_4^-$  ions and the formation of gold nanoparticles. We believe that this is most likely due to the complete reduction of 0.2 mM  $\text{AuCl}_4^-$  ions so that the absorbances at 240 and  $\sim 540$  nm were saturated at 5.0 mM Pluronic; this can be discerned in Figure 2, where the rate of absorbance change decreases at higher polymer concentrations. To clarify this point, we also present in Figure 4 data obtained from 1.0 mM Pluronic P103, P105, and F127. These absorbances changed linearly with an increase in the PEO block length (see the center panels in Figure 4), indicating that PEO does have an effect.

The effect of the PPO block length on the reduction of  $\text{AuCl}_4^-$  ions and the formation of gold nanoparticles was obtained from the examination of Pluronic P65, P84, and P123 having a PEO block with a MW of  $\sim 1700$  g/mol. As seen in the right-hand-side panels in Figure 4, the absorbance at 240 nm decreased linearly and that at  $\sim 540$  nm increased with an increasing block copolymer PPO length.

Let us compare our findings with the presumed mechanism for the reduction of  $\text{AuCl}_4^-$  ions and the formation of gold nanoparticles in the presence of PEO polymers:<sup>24</sup>

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(1)  $\text{AuCl}_4^-$  ions bind to pseudocrown ether structures (cavities) that are formed from PEO coils.<sup>32</sup>

(2) The bound  $\text{AuCl}_4^-$  ions are reduced via the oxidation of PEO by the metal center.

(3) This resulting Au(I) species then migrates to other cavities where the equilibrium  $3\text{Au(I)} \leftrightarrow 2\text{Au} + \text{Au(III)}$  occurs.

(4) The metal atoms coalesce to form clusters, which then grow to yield small metal particles.

Since step 2 is enhanced by the formation of cavities, the particle formation process becomes more efficient with an increasing number of cavities.<sup>24</sup> The number of cavities increases with the PEO polymer molecular weight and concentration.<sup>24</sup>

The above mechanism is consistent with the observed increase in the reaction activity with an increase in the molecular weight, PEO block length (see Figure 4), and/or concentration (see Figure 2) of the Pluronic block copolymer. Moreover, our findings indicate that the PPO block also contributes to the reaction activity (see Figure 4). On the basis of the observed immiscibility between the PPO homopolymer and metal ion aqueous solutions, it has been suggested<sup>33</sup> that PPO blocks can not directly contribute to the reduction of metal ions but can help enhance the reactivity of the PEO blocks with metal ions. We believe that there is sufficient hydration of PPO segments in the PEO–PPO–PEO block copolymer media<sup>34</sup> to allow direct interaction between metal ions and PO. We certainly find the reaction activity of Pluronic PEO–PPO–PEO block copolymers to be much higher than that of the PEO homopolymer even when the PEO–PPO–PEO block copolymer molecular weight is smaller than that of the PEO homopolymer (comparison between the PEO homopolymer and Pluronic P103 in Figures 1 and 2). To clarify the relative contributions of the PEO and PPO blocks to the reduction of  $\text{AuCl}_4^-$  ions, we are pursuing an investigation that uses various PEO–PPO–PEO block copolymers and different metal ions and we are carrying out a kinetics investigation of  $\text{AuCl}_4^-$  reduction at the initial reaction stage.

### Conclusions

The synthesis of gold nanoparticles with a diameter of  $\sim 10$  nm has been achieved at ambient temperature by

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simply mixing an aqueous hydrogen tetrachloroaurate-(III) hydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) solution with an aqueous Pluronic PEO–PPO–PEO block copolymer solution. The block copolymer molecular weight and PEO and PPO block lengths controlled the reaction activity of the block copolymer with  $\text{AuCl}_4^-$  ions. The reaction activity of the PEO–PPO–PEO block copolymers was much higher than that of the PEO homopolymer even when the PEO–PPO–PEO block copolymer molecular weight was smaller than that of the PEO homopolymer. Moreover, the metal nanoparticles produced in aqueous PEO–PPO–PEO block copolymer solutions are much more dispersible and stable than those produced in the aqueous PEO homopolymer solution. The colloidal stabilization of gold nanoparticles by PEO–PPO–PEO block copolymers is most likely due to their amphiphilic character and their ability to form micelles in solution and/or on the surface of particles.<sup>30</sup> The synthesis method presented here is environmentally benign and economical, since it only involves water and commercially available polymers and proceeds fast to completion.

The utilization of PEO–PPO–PEO block copolymers in the synthesis of metal nanoparticles presents a range of possibilities for further development. The self-assembled structures afforded by amphiphilic block copolymers<sup>35</sup> can be exploited as nanocontainers, as three-dimensional templates for hybrid metal/polymer ordered monomaterials, and as anchors (when present on surfaces) for surface modification with metal. The tunability of block copolymer self-assembly in selective solvents<sup>36,37</sup> should be an asset to the above. We are currently exploring aqueous amphiphilic block copolymer solutions for the synthesis of other metal nanoparticles. We are also correlating the particle size and formation kinetics to the reaction conditions and mechanism.

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