

# Effects of Polymer Micelles of Alkylated Polyethylenimines on Generation of Gold Nanoparticles

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Mono- and di-alkylated polyethylenimines (PEI-1R, PEI-2R) were synthesized and used as both reductants, by exploiting the functionality of the polyethylenimine's (PEI) amino groups, and stabilizers able to protect nascent gold nanoparticles generated from hydrogen tetrachloroaurate ( $\text{HAuCl}_4$ ). From TEM images of the stained polymers, it is clear that the polymer micelles are round and well-structured when formed from PEI-2R, fused and less well-structured when formed from PEI-1R, and totally nonstructured when formed from PEI. These findings coincide with the results found by using pyrene as a probe to investigate aggregation behavior, where PEI-2R with a fluorescence intensity ratio ( $I_1/I_3$ ) of 1.48 forms the more closely packed polymer micelles than PEI-1R ( $I_1/I_3 = 1.64$ ) and PEI ( $I_1/I_3 = 1.72$ ). The use of the highly alkylated polymer micelle (PEI-2R) results in the fastest reduction of  $\text{HAuCl}_4$ , and gives the most effective protection to the generated gold nanoparticles. When used at higher polymer concentrations than required for micelle formation, it was found that polymer hydrophobicity was highly influential in directing the nanoparticle's morphology, i.e., the resulting polymer micelles were labeled with perfect and round necklace-like gold nanoparticles when PEI-2R was used, and imperfect and less round gold nanoparticles when PEI-1R was employed. These structures were totally absent when PEI was used. The use of alkylated PEI, being able to act simultaneously as both a reductant and as a very effective protective agent, greatly simplifies the process used for preparing gold nanoparticles.

## Introduction

Interest in colloidal metal nanoparticles protected by polymers is increasing, as these materials offer tremendous options for combining sought-after properties that originate from both the nanoparticles and the polymers.<sup>1–4</sup> Amphiphilic polymers have received special attention, since their amphiphilic character not only provides solubility in polar media, but also allows interactions with metal precursors and the resulting metal colloids. The most valuable feature of polymers containing metal nanoparticles, which distinguishes them from metal colloids prepared in a low-molecular environment, is the possibility of preparing films and coatings. This in turn extends the prospects for additional potential applications.

Polyethylenimine (PEI) is a water-soluble polymer that is widely used in industry.<sup>5</sup> A characteristic of PEI is its ability to form a number of different complexes with metal ions,<sup>6</sup> anionic polyelectrolytes,<sup>7</sup> and surfactants.<sup>8</sup> In our previous work,<sup>9</sup> dumbbell-like water-soluble copolymers synthesized by introducing ethyleneimine groups into both terminals of polyoxypropylenediamine were investigated to study their characteristics, especially their ability to chelate metal ions in nanoparticles. The results indicated that these ABA-type dumbbell-like copolymers with highly branched architectures possessed an excellent ability to chelate metal ions and to prevent nanoparticles from agglomerating. In this study, new alkylated PEIs have been synthesized via a simple one-step addition reaction of the alkyl groups grafted onto one or two terminals of commercially available linear PEI. The strategy of this study was to localize PEI chains to avoid them becoming entangled

with each other by introducing a lipophile to form polymer micelles, so that the metal nanoparticles are generated in the restricted environment of the hydrophilic shell of the polymer micelles. By means of polymer stain, well-structured polymer micelles were observed as the alkyl group composition of the polymer was increased. Interestingly, after introduction of the metal salt, polymer micelles labeled with gold nanoparticles were found for the two alkylated PEIs (PEI-1R, PEI-2R) above their micelle-forming concentrations, but the necklace-like structures were not observed for the nonalkylated PEI. Alkylated PEI serves both as a reducing agent and as a protective agent at the same time, thus enabling gold nanoparticles to be prepared, using a mild one-step process at room temperature.

## Experimental Section

**Materials.** The linear polyethylenimine (PEI,  $M_n = 423$ ) and octyl/decyl glycidyl ether (ODGE, octyl/decyl (v/v) = 2:1) were purchased from Aldrich and were used without further purification. Pyrene (Merck) was purified by recrystallizations from ethanol twice. Anhydrous sodium dihydrogen phosphate (Tedia) and anhydrous disodium hydrogen phosphate (Merck) were used as received.  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (99.9+%) was purchased from Aldrich and used as received. All the aqueous solutions were made up with distilled water, which was deionized in a Millipore Milli-Q water system. Other solvents were reagent grade or were purified by standard methods.

**Methods. Synthesis and Characterization.** Alkyl-grafted PEIs were synthesized by a one-step addition reaction. The average carbon number of the alkyl group of ODGE was determined from the  $^1\text{H}$  NMR spectrum to be 8.7. The stoichiometric amounts of ODGE were added to a 250-mL flask with linear

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PEI (1.75 g) and 120 mL of ethanol under nitrogen atmosphere. The mixture was then heated and stirred at 80 °C for 16 h. The completion of the reaction was monitored by observing the disappearance of the characteristic epoxide absorption peak at 915  $\text{cm}^{-1}$  in the FT-IR spectrum. After the solvent was removed under a reduced pressure, the viscous solution was poured into hexane to precipitate the polymer. Finally, the product was dried at 60 °C for 48 h in a vacuum oven. The potentiometric titration method for determining the total amine values of the polymers was by direct titration with 1:1 2-propanol–ethylene glycol as a solvent, using a Mettler-Toledo DL50 autotitrator.

IR (KBr, pellet) 3365–3287 ( $-\text{NH}_2$  or  $-\text{NH}-$ ), 2956–2826 ( $-\text{CH}_2-$  or  $-\text{CH}_3$ ), 1570 ( $-\text{NH}-$  deformation), and 1109  $\text{cm}^{-1}$  ( $-\text{C}-\text{O}-\text{C}-$  stretching).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm)  $\delta$  1.0–0.8 ( $-\text{CH}_3$ ), 1.2–1.5 ( $-\text{CH}_2-$ ), 2.2–2.7 (m,  $-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-$ ), 3.1–3.6 (m,  $-\text{CH}_2-\text{O}-$  and  $-\text{CHOH}-$ ).

**Fluorescence Measurements.** All fluorescence measurements were conducted by using a fluorescence spectrophotometer (model F-4010, Hitachi, Japan). A stock saturated solution of pyrene was first prepared by introducing solid pyrene into aqueous solution. The water-soluble PEI polymers were dissolved in saturated pyrene solution to prepare 1.0 g/L solution, which were then serially diluted. The intensity ratio of the emission spectrum of pyrene at 374 and 385 nm, which is defined as  $I_1/I_3$ , was measured as a function of polymer concentration. All the solutions for the fluorescence measurements were put in a buffer solution to maintain the pH at 7. For reference,  $I_1/I_3$  values for pyrene in water and *n*-hexane were measured to be 1.86 and 0.58, respectively.

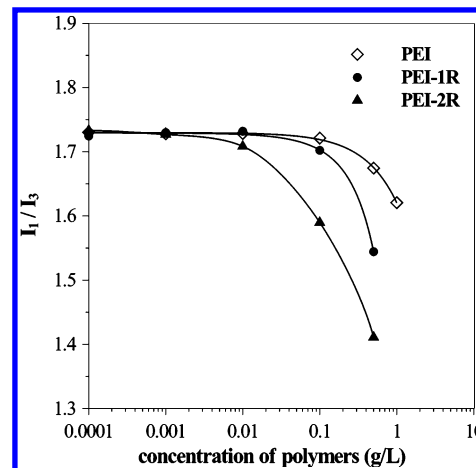
**Colloid Preparation.** Typically, the gold nanoparticles were simply synthesized from a 10 mL aqueous solution containing  $\text{HAuCl}_4$  (fixed at 0.1 mM) and the polymer at 25 °C. Reduction of metal ions was carried out by amino groups of polyethylenimine. After mixing  $\text{HAuCl}_4$  with polyethylenimine samples at a concentration of  $2 \times 10^{-3}$  mol/L of amino groups, that is 0.09 g/L of sample PEI, 0.14 g/L of PEI-1R, and 0.21 g/L of PEI-2R, the solutions gradually changed from colorless to pale-blue or red-violet, indicating that  $\text{Au}^{3+}$  ions began to be reduced into  $\text{Au}^0$ . All glassware was cleaned with concentrated nitric acid.

**Characterization.** Transmission electron microscopy (JEOL JEM 1200-EX electron microscope operated at 80 kV) was used to obtain the particle size, morphology, and particle-size distribution of the metal nanoparticles. The samples were prepared by placing a drop of the colloidal solution on a Formvar/carbon-coated copper grid and allowing the solvent to evaporate. The number-average particle sizes and size distributions were determined based on the measurement of at least 150 particles. UV–vis spectra were recorded with a Beckman Coulter DU 800 spectrophotometer.

## Results and Discussion

The polymers PEI-1R and PEI-2R carry different amounts of lipophilic substituent (R) attached to the terminal amino groups of PEI. The associated identifiers, i.e., 1R and 2R, indicate the number of alkyl chains incorporated per PEI backbone. The course of the reaction to synthesize the polymers was monitored by observing the disappearance of the characteristic epoxide absorption peak at 915  $\text{cm}^{-1}$  in the FT-IR spectrum. The total amine values of the polymers PEI, PEI-1R, and PEI-2R were determined by a potentiometric titration method, and shown to be  $2.14 \times 10^{-2}$ ,  $1.38 \times 10^{-2}$ , and  $9.60 \times 10^{-3}$  mol/g, respectively.

The amino group has been reported to be oxidized to imine in the aqueous phase as alkylamine complexes with metal ions.<sup>10</sup>

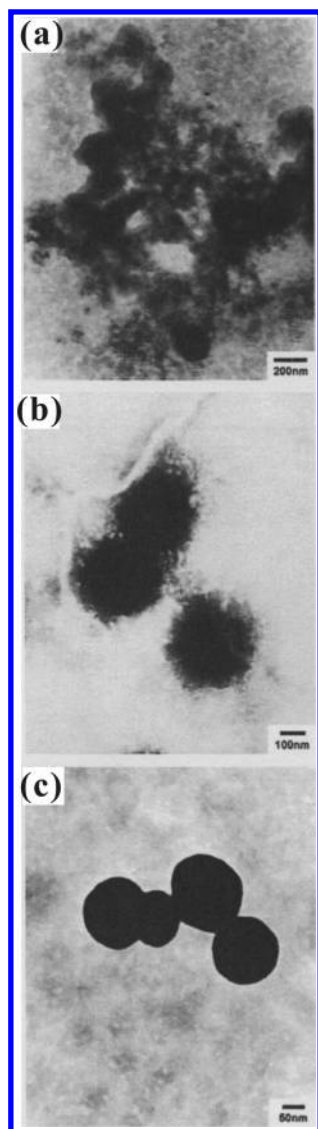


**Figure 1.**  $I_1/I_3$  values in equilibrium as a function of concentration for PEI, PEI-1R, and PEI-2R.

To follow the changes in the polymer accompanying the reduction of  $\text{HAuCl}_4$ , we examined the FT-IR spectra of PEI before and after interaction with the gold salt. The deformation band of  $-\text{NH}-$  in PEI is present at 1570  $\text{cm}^{-1}$  in the FTIR spectrum of the noncomplexed amine; however, it disappears in the spectrum of the corresponding gold-complexed PEI (prepared with a molar ratio of  $\text{N/Au} = 5$ ) after 10 days, which indicates the occurrence of the oxidation of amino groups in PEI by  $\text{Au}^{3+}$ .

Pyrene was used as a probe to investigate the aggregation behavior of the amphiphile polymers. The fluorescence intensity ratio ( $I_1/I_3$ ) of the first peak (at 374 nm) to the third peak (at 385 nm) of pyrene can serve as a measure of the polarity of pyrene's surroundings,<sup>11,12</sup> e.g., the  $I_1/I_3$  value is 0.58 in hexane, and 1.87 in water. Figure 1 shows the variation of  $I_1/I_3$  as a function of the concentration of added polymer, where the aqueous solution is saturated with pyrene. At low polymer concentrations, the value of  $I_1/I_3$  is approximately 1.76 for all three polymers, i.e., close to that of pure water. The  $I_1/I_3$  value begins to decrease gradually at concentrations of about  $5 \times 10^{-1}$ ,  $10^{-1}$ , and  $10^{-2}$  g/L for PEI, PEI-1R, and PEI-2R, respectively, indicating that the polymers start to form aggregates at these concentrations. These  $I_1/I_3$  values obtained for the polymer aggregates can be rationalized by considering the extent of water penetration into the microcavities of the polymers. The polarity of the polymeric environments experienced by the pyrene probe was in the following order: PEI (most polar) > PEI-1R (less polar) > PEI-2R (least polar). This indicates that PEI-2R having a higher level of alkyl group incorporation results in the formation of the most compact structure able to protect the pyrene molecules efficiently from the bulk aqueous phase. At concentrations above  $10^{-1}$  g/L, the  $I_1/I_3$  value of PEI-2R is less than 1.5, indicating that the PEI-2R aggregates are as closely packed as are the commercial nonionic micelles (Triton series), which have comparable  $I_1/I_3$  values of 1.47–1.40.<sup>13</sup> For PEI-1R, the increasing polarity detected can be attributed to a loosening of the polymer micelles as a result of reduced alkyl group incorporation and greater hydration.

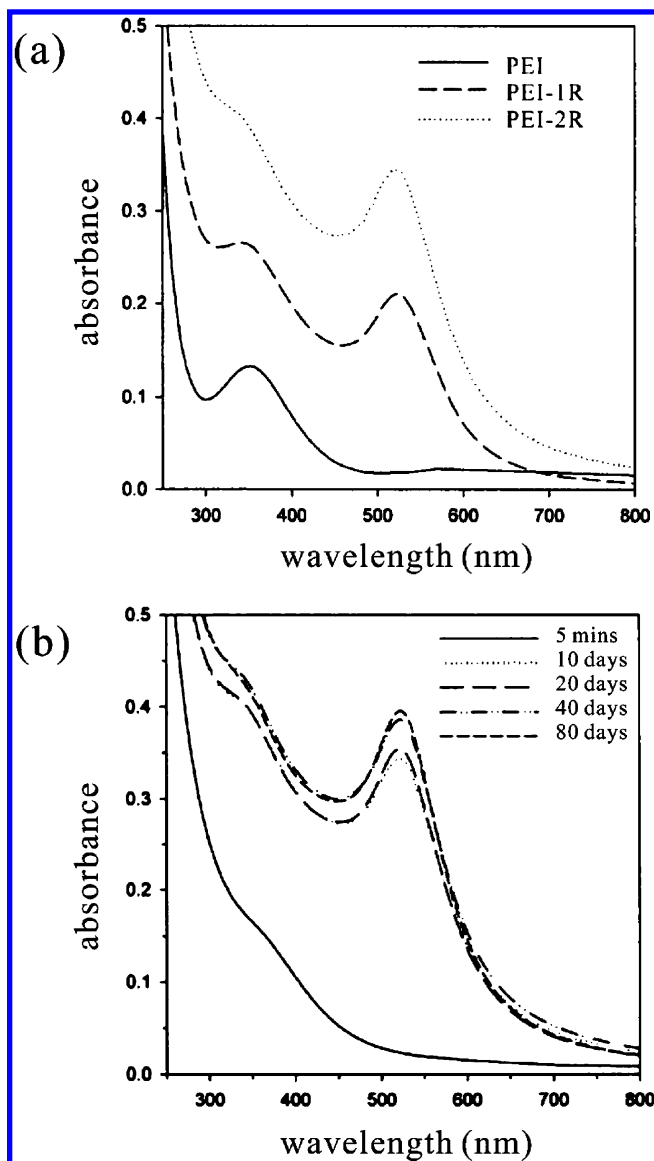
The above discussion relates to the properties of polymer micelles investigated by means of a pyrene probe. The polymer micelles can also be directly observed by microscopy through polymer staining, using phosphotungstic acid (PTA) as a positive stain,<sup>14</sup> to react with the surface functional amino groups on PEI, PEI-1R, and PEI-2R, so that the structure of the polymer micelles can be imaged by TEM. Figure 2 shows the structures of polymers stained with 2% PTA on TEM grids, where the



**Figure 2.** TEM images of PTA staining: (a) PEI, (b) PEI-1R, and (c) PEI-2R. ( $[N] = 2 \times 10^{-3}$  M).

concentration of the amino groups is in each case  $2 \times 10^{-3}$  M, with [PEI], [PEI-1R], and [PEI-2R] being equal to  $9.3 \times 10^{-2}$ ,  $1.5 \times 10^{-1}$ , and  $2.1 \times 10^{-1}$  g/L, respectively. Compared with the rather dynamic structures of PEI, the micelles of PEI-2R are more compact and well-structured with a diameter of about 150 nm, whereas the micelles of PEI-1R are extremely diffuse, and interact with each other. If the TEM micrographs in Figure 2 are compared with  $I_1/I_3$  values for each polymer at the amine concentration of  $2 \times 10^{-3}$  M,  $I_1/I_3$  values of 1.72 (PEI), 1.64 (PEI-1R), and 1.48 (PEI-2R) can be related to the corresponding structures of the polymer aggregates as shown in Figure 2, parts a, b, and c, respectively, i.e., the lower  $I_1/I_3$  ratio results from the well-structured polymer aggregates.

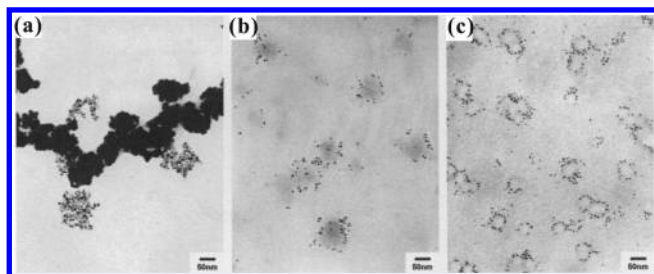
A large number of methods for preparing colloidal metal dispersions involve the presence of polymer during reduction from the metal precursors.<sup>15–19</sup> The polymer template usually serves to both control the particle size and passivate the surface of the nanoparticles against agglomeration. Our previous studies have used polyethylenimine copolymers as protectors for the formation of metal nanoparticles because of the strong coordination between ethylenimine and the metal ion.<sup>9,20</sup> In this study, the alkyl-grafted polyethylenimine aggregates simultaneously act both as protective agents and as reductants in aqueous solution after the addition of  $\text{HAuCl}_4$ , thereby significantly



**Figure 3.** (a) UV-vis spectra of alkylated PEI protected gold nanoparticles with a N/Au molar ratio of 20, after 10 days. (b) UV-vis spectra of PEI-2R protected gold nanoparticles with a N/Au molar ratio of 20, at different time intervals.

simplifying the process for preparing the gold nanoparticles. An aqueous solution of chloroauric acid was simply mixed with the polymers, possessing an amine-functionality, at 25 °C. This procedure spontaneously resulted in the formation of gold nanoparticles without the addition of an extra reducing agent. The gold nanoparticles were synthesized from a polymer solution containing 0.1 mM  $\text{HAuCl}_4$  (an equivalent ratio of amine to  $\text{Au}^{3+}$ , N/Au = 20). The solutions were found to turn from colorless to red-violet for PEI-1R (after 12 h) and PEI-2R (after 8 h), indicating that  $\text{Au}^{3+}$  ions had begun to be reduced to  $\text{Au}^0$ . However, the PEI solution turned pale-blue after more than 20 h. The colloidal solutions of alkylated PEIs showed a plasmon band at 523 nm in the UV-vis spectra (Figure 3a), evidencing the existence of gold nanoparticles.<sup>21</sup> However, for the solution of PEI, the plasmon peak was diminished and gave rise to a very broad shoulder that shifted to higher wavelengths after 10 days. It was also noted that although the self-reduction of gold happened faster for PEI-2R, the complete self-reduction occurred over a period of 40 days (Figure 3b). Compared with alkylated PEIs, the reduction rate for the PEI solution was so slow that the absorption band of  $\text{AuCl}_4^-$  at 362 nm could still



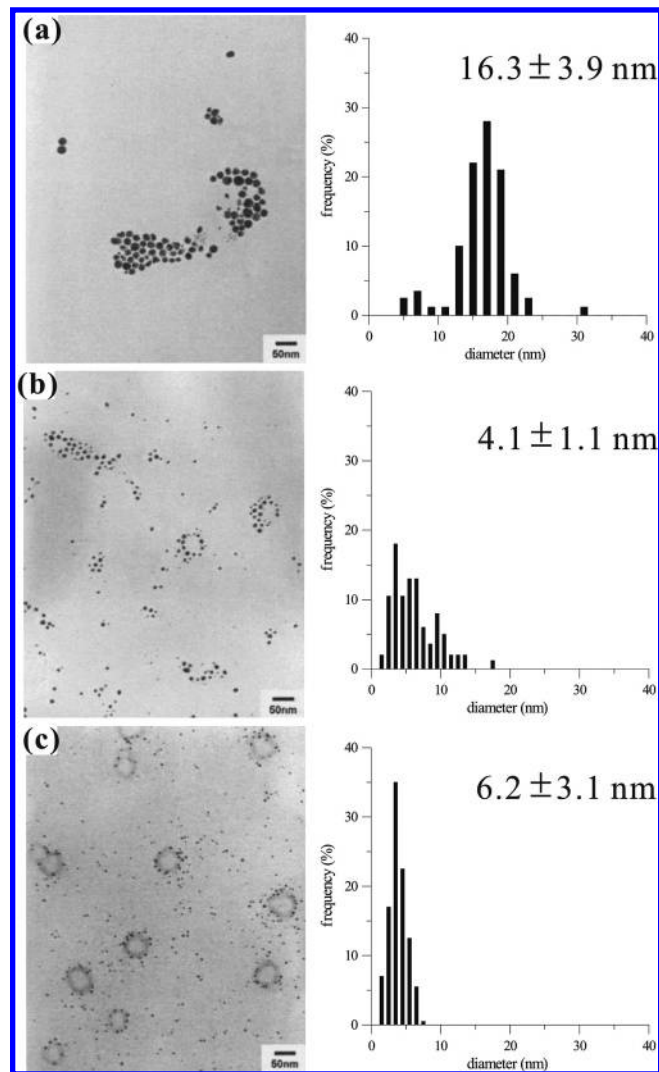


**Figure 4.** TEM images of gold nanoparticles, after 10 days, protected by (a) PEI, (b) PEI-1R, and (c) PEI-2R. N/Au molar ratio = 20.

be detected even after several weeks. We speculate that this phenomenon can be attributed to the high local concentration of ethylenimine units in the polymer aggregates with well-defined structures, where the reduction function of amine-functionalized polymers yields metal nanoparticles without the addition of an extra reducing agent.<sup>22–24</sup> Indeed, very high concentrations of PEI (at polymer concentrations above 0.5 g/L) result in the rapid self-reduction of the gold salt; however, under these conditions the colloids formed were found to sediment immediately.

TEM micrographs for the gold colloids, reduced and stabilized by PEI, PEI-1R, and PEI-2R, were compared with each other as shown in Figure 4(parts a to c). After 10 days, with an equivalent ratio of amine to  $\text{Au}^{3+}$  of 20, serious agglomeration of the PEI solution resulted in a very unstable colloid, in contrast to the red-violet and clear gold dispersions of the alkylated PEIs. In the presence of PEI-1R and PEI-2R, the particle sizes were  $5.2 \pm 2.0$  and  $6.0 \pm 2.9$  nm, respectively. These results indicate that the presence of the alkyl groups protected the gold nanoparticles more effectively during the reduction of  $\text{Au}^{3+}$ . Moreover, it is interesting to observe that gold-decorated polymer micelles were found for alkylated PEIs, and the necklace-like nanostructures for PEI-2R are more obvious than those observed for PEI-1R, as shown in Figure 4, parts b and c. Gold nanoparticles generated by using PEI, PEI-1R, and PEI-2R were compared to the corresponding polymer aggregates. It was found that there exists a close relationship between the structures of nanoparticles and the properties of the polymer aggregates, i.e., PEI chains aggregate together, which results in the coagulation of gold nanoparticles (Figure 4a), whereas the well-structured and less-structured polymer micelles generated with PEI-2R and PEI-1R showed distinct (PEI-2R) and less distinct (PEI-1R) necklace-like nanostructures (Figure 4c,b).

To further identify the effects of the lipophile and the polymer concentrations for the different alkylated PEIs (PEI-1R, PEI-2R) on the formation of nanoparticles, the particle sizes were investigated with different N/Au ratios by varying the polymer concentrations. For PEI-2R with the N/Au ratio higher than 10, red-violet and clear gold dispersions were obtained and the colloids were found to remain stable for more than three months. However, with a molar ratio of N/Au equal to 5, some dark solids precipitated from the red-violet solution after two months, indicating large particle formation at low polymer concentrations. Figure 5 shows the TEM micrographs and the corre-



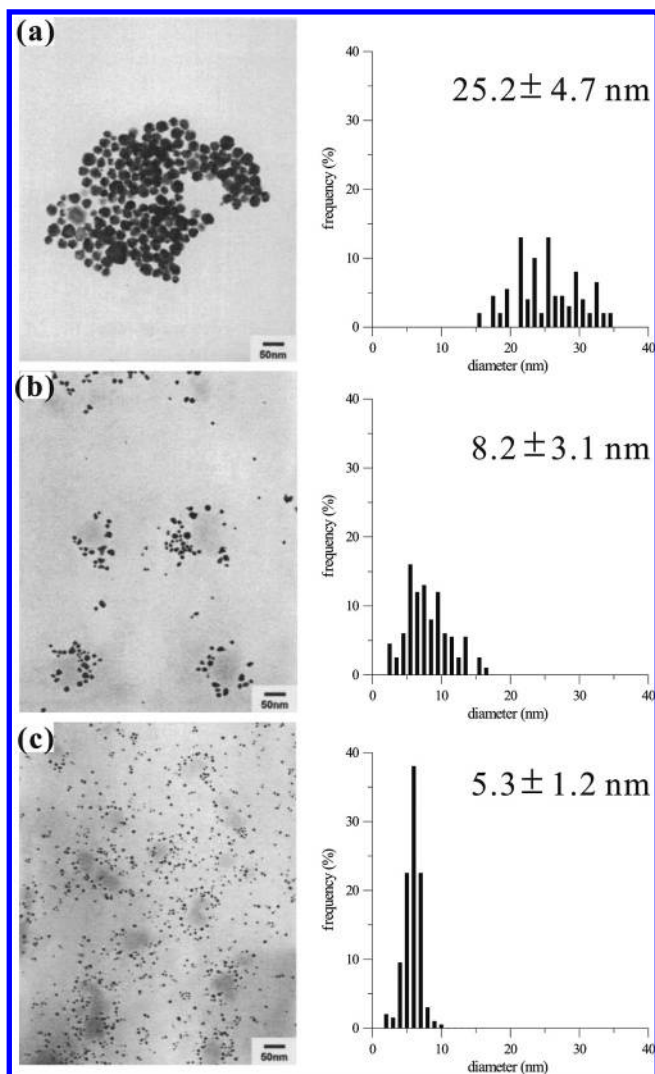
**Figure 5.** TEM micrographs and size distribution histograms of gold nanoparticles, after 20 days, protected by PEI-2R with N/Au molar ratios of (a) 5:1, (b) 10:1, and (c) 20:1.

sponding particle size distribution histograms of gold colloids generated by using PEI-2R after 20 days. With a low polymer concentration, i.e., N/Au equal to 5, the TEM image clearly reveals a large degree of particle agglomeration (Figure 5a). As the molar ratio of N/Au increases to 10 (Figure 5b) or 20 (Figure 5c), the utilized polymer concentration increases to the point where it is above the micelle-forming concentration as shown in Table 1, but the colloidal particle size decreases from 6.2 nm to 4.1 nm. With N/Au ratios of 10 and 20, polymer micelles labeled with gold nanoparticles were found; however, the well-shaped gold-decorated polymer micelles are more often observed for PEI-2R at higher polymer concentrations. This suggests that at low polymer concentrations the diffuse polymer aggregate is less effective in preventing further particle growth and precipitation from the solution. In many cases, the presence of hydrophobic components in the polymer leads to smaller

**TABLE 1**

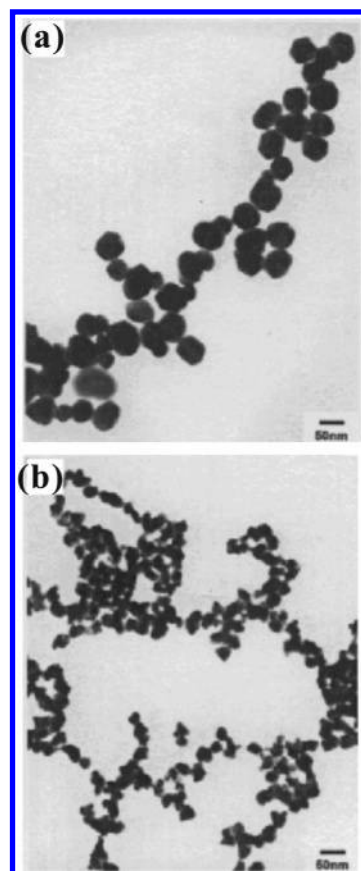
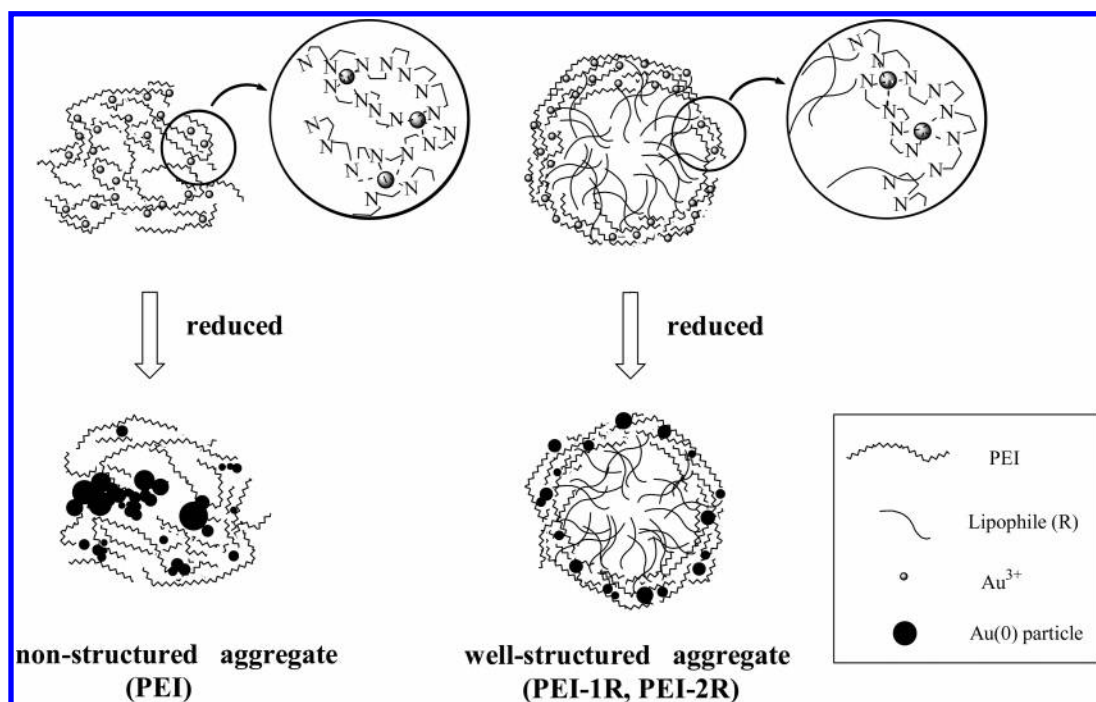
polymer	total amine values <sup>a</sup> (mol/g)	MFC <sup>b</sup>	[polymer] at N/Au = 20 <sup>c</sup>	[polymer] at N/Au = 10 <sup>c</sup>	[polymer] at N/Au = 5 <sup>c</sup>
PEI	$2.14 \times 10^{-2}$	$5.0 \times 10^{-1}$	$9.3 \times 10^{-2}$	$4.7 \times 10^{-2}$	$2.3 \times 10^{-2}$
PEI-1R	$1.38 \times 10^{-2}$	$1.0 \times 10^{-1}$	$1.5 \times 10^{-1}$	$7.3 \times 10^{-2}$	$3.6 \times 10^{-2}$
PEI-2R	$9.60 \times 10^{-3}$	$1.0 \times 10^{-2}$	$2.1 \times 10^{-1}$	$1.0 \times 10^{-1}$	$5.2 \times 10^{-2}$

<sup>a</sup> The amine values were measured by potential titration analysis. <sup>b</sup> Micelle-forming concentration (MFC). <sup>c</sup> The corresponding polymer concentration (g/L) with  $[\text{HAuCl}_4]$  was fixed at  $10^{-4}$  M.



**Figure 6.** TEM micrographs and size distribution histograms of gold nanoparticles, after 20 days, protected by PEI-1R with N/Au molar ratios of (a) 5:1, (b) 10:1, and (c) 20:1.

#### SCHEME 1



**Figure 7.** TEM micrographs of gold nanoparticles, after 20 days, protected by PEI with N/Au molar ratios of (a) 5:1 and (b) 10:1.

particle sizes with narrow size distributions and high colloidal stabilities.<sup>25–27</sup> The formation of gold nanoparticles generated under the protection of the less hydrophobic PEI-1R was observed by TEM as shown in Figure 6. In comparison to PEI-2R, PEI-1R incorporation results in larger particle sizes with the same N/Au ratio. A partial aggregation of the colloidal particles was also observed at low polymer concentration (N/

Au equal to 5). At higher concentrations (N/Au equal to 10 or 20), the gold-decorated polymer micelles for PEI-1R are not as obvious as those observed for PEI-2R.

The hydrophilic PEI has been reported to be used as a protecting agent when preparing gold colloids reduced by sodium borohydride; however, PEI was not found to be able to efficiently stabilize gold particles.<sup>28</sup> In the present study, PEI functions as both a reductant and a stabilizer for gold nanoparticle formation. As shown in Figure 7a,b (with N/Au ratios equal to 5 and 10), the higher PEI content of the solution results in the smaller size of nanoparticles. When compared with alkylated PEIs, it is clear that the particles generated with nonalkylated PEI coagulate to form large particles, since nonalkylated PEI does not protect the gold particles as well as PEI-1R or PEI-2R. At higher polymer concentrations (N/Au = 20), the gold particles precipitate from the PEI solution after 20 days. This can be attributed to the aggregates (as shown in Figure 4a) coagulating, since PEI chains are dynamically translated inside the solution without being localized in the outer shell of the polymer micelle.

After the addition of Au<sup>3+</sup> and following reduction, PEI produces coagulated gold particles, but PEI-1R or PEI-2R results in polymer micelles decorated with gold nanoparticles, as seen in the TEM images of the stained polymers. The solution characteristics and the associated phenomena for PEI and the alkylated PEIs are summarized and interpreted in Scheme 1. The amino groups of ethylenimine, from either PEI or alkylated PEI, coordinate with Au<sup>3+</sup> and protect the resulting Au nanoparticles. However, the ethylenimine chains, which become entangled with the use of PEI, remain confined in the outer shell of the polymer micelles when alkylated PEIs are used. It is much easier for the gold particles in the aggregates of nonalkylated PEI to collide with each other compared with those of alkylated PEIs. Therefore, coagulated gold particles were observed for nonalkylated PEI. In contrast, the confined gold nanoparticles in the presence of PEI-1R or PEI-2R have less possibility to contact with each other. Therefore, the resulting gold nanoparticles are smaller and are localized in the outer shell of the polymer micelles, which gives rise to the necklace-like structures.

## Conclusions

Colloidal gold nanoparticles were synthesized through self-reduction by the amino groups of PEI. In the presence of alkylated PEIs, the higher polymer concentrations result in more closely packed polymer aggregates, and also more stable gold colloidal dispersions. Necklace-like structures of gold nanoparticles were found for PEI-2R above its micelle-forming con-

centration, but were not observed for nonalkylated PEI. Compared with the entangled ethylenimine chains of nonalkylated PEI, the alkylated PEIs confine the amino groups on the outer shell of the polymer micelles and operate as protective agents as well as effective reductants, thereby greatly simplifying the process for preparing gold nanoparticles.

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