

Research Article

Gold Nanoparticles Size Design and Control by Poly(*N,N'*-diethylaminoethyl methacrylate)

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Poly(*N,N'*-diethylaminoethyl methacrylate) (PDEAEM) with different molecular weights was used to stabilize gold nanoparticles (AuNPs) obtained by *in situ* reduction of tetrachloroauric acid using citrates under acidic conditions and in organic/alcoholic medium. The influence of the pH value on gold nanoparticle size in the presence of PDEAEM was investigated. Results show that the pH of the reacting mixture has a dramatic effect on the size, polydispersity, and morphology of the resulting AuNPs. Moreover, the size of the nanoparticles (NPs) may be modified by changing the solution's pH or by changing the solvent type. Electron microscope images showed that the sizes of AuNPs coated with PDEAEM were not sensitive to the variation of the polymer molecular weight in the range between 9000 and 29300 g/mol; however their aggregation behavior depended strongly on the polymer molecular weight as revealed by dynamic light scattering studies. AuNPs stabilized with PDEAEM (AuNP@PDEAEM) are stable in water at acidic pH and in organic polar solvents.

1. Introduction

Polymers possessing nonionic, anionic, cationic, and amphiphilic nature have been shown to exhibit a great potential to be used as stabilizers or protecting agents as well as reducing agents in the preparation of polymer/metal NPs [1–3]. Polyvinyl alcohol, polyethylene glycol, and polyvinylpyrrolidone have been the most widely used [4–8]. Meanwhile, poly(2-vinylpyridine) and poly(ethyleneimine) possessing coordination ability with metals through the nitrogen have been also used as stabilizers for metal colloids [9, 10]. Polymers possessing tertiary amine groups in their structure such as poly(*N,N'*-dimethylaminoethyl methacrylate) (PDMAEM) and poly(*N,N'*-diethylaminoethyl methacrylate) (PDEAEM) are also suitable as stabilizing/reducing

agents for the preparation of metallic NPs [3, 11–15]. Several reports used linear and star PDMAEM for the preparation of gold and silver NPs. In all these cases, the formation of the NPs is carried out in neutral and basic aqueous solutions, whereas no AgNPs were formed in acid solutions (pH < 7) because PDMAEM exhibited the reducing property only when the pH of aqueous solution was above 7 [16]. Meanwhile, PDEAEM (pK_a between 7.0 and 7.3) is a water insoluble polymer under nonacidic conditions [17]. This cationic polymer is less used than PDMAEM in the preparation of metallic NPs; nevertheless, PDEAEM is a pH-sensitive polymer envisioned for controlled release purposes [18–20]. In addition, due to this partial hydrophobicity, PDEAEM self-assembles in a complex way [21] and has been shown to be a good candidate for nanotemplate formation including AuNPs [22].

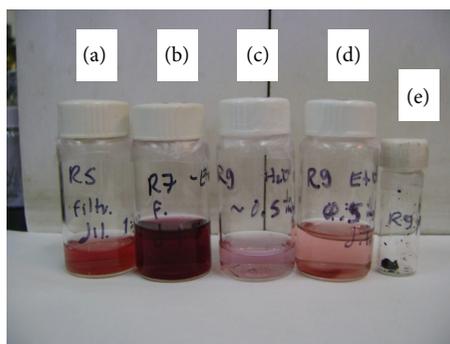


FIGURE 1: Images of AuNP synthesis: (a) synthesized at pH 4 (diluted), (b) synthesized in *p*-dioxane/water (undiluted), (c) synthesized in isopropanol, redissolved in water, (d) synthesized in isopropanol, redissolved in ethanol, and (e) isolated AuNP@PDEAEM synthesized in isopropanol.

Therefore, in this study the preparation of AuNPs using PDEAEM as a stabilizing agent is reported. Reactions were carried out at different acidic pH values and in organic solvents, aiming to control the gold nanoparticle size and morphology, since it is well known that the precise control of particle shape, size, and colloidal stability is essential for applications of AuNPs [23–25]. The shape control in AuNP synthesis is usually achieved by the seed-mediated growth; however there are reports on the addition of salts, polymers, and the usage of specific natural reducing agents that favors the formation of nonspherical morphologies [26].

2. Experimental Section

2.1. Materials. Tetrachloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Aldrich, 99%), tribasic sodium citrate, 4,4-azobis(4-cyanovaleric acid), and *p*-dioxane were purchased from Sigma-Aldrich and used as received. *N,N*-Diethylaminoethyl methacrylate (DEAEM, Sigma-Aldrich) was distilled under reduced pressure before use. The following chemicals were provided by FERMONT México and used as received: dichloromethane (DCM), tetrahydrofuran (THF), diethyl ether, ethanol, isopropanol, sodium hydroxide, and concentrated hydrochloric acid. 4-Cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid, the chain transfer agent (CTA), was prepared according to a general procedure described in the literature by Thang et al. [27].

2.2. Synthesis of PDEAEM Polymers. PDEAEM polymers in different molecular weights were prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization using a trithiocarbonate chain transfer agent (CTA). The synthetic conditions were adapted from the report of Ponce-Vargas et al. [28]. One example is described: A mixture of DEAEM (10.8 mmol), CTA (0.20 mmol), and ACVA (0.025 mmol) was dissolved in 6 mL of *p*-dioxane and transferred to an ampoule containing a magnetic stir bar. Oxygen was removed using three cycles of freeze-vacuum-thaw, and the ampoule was sealed with flame. Polymerization was performed at 70°C for 24 h under magnetic stirring.

Purification was performed by precipitating in an excess of petroleum ether followed by dissolving in dichloromethane and precipitating again with petroleum ether. This procedure was repeated two times and the polymer product dried in vacuum overnight. The polymer was obtained with the following characteristics: $M_n = 9000$ g/mol, $\mathcal{D} = 1.18$, where M_n is number average molecular weight and $\mathcal{D} = M_w/M_n$ is the dispersity. By adjusting the ratio of DEAEM to CTA to ACVA two additional polymers with the following characteristics were obtained: $M_n = 24500$ g/mol, $\mathcal{D} = 1.31$ and $M_n = 29300$ g/mol, $\mathcal{D} = 1.10$. For the preparation of a PDEAEM polymer without having a trithiocarbonate moiety, the same synthetic methodology was used, with the exception that the CTA was not used. By this conventional free radical polymerization a polymer product with the following characteristics was obtained: $M_n = 18000$ g/mol, $\mathcal{D} = 1.97$.

2.3. Preparation of AuNPs Stabilized by PDEAEM. The well-known Frens method for AuNPs synthesis using citrate [29] was modified in the following way: an aqueous PDEAEM solution was prepared by dissolving 40 mg of polymer in 40 mL of water in a flask. The pH of the mixture was adjusted by addition of diluted HCl or NaOH (0.01 N). After adjusting the pH of the solution, the polymer solution was stirred for additional 4 h. Afterwards, HAuCl_4 (10 mg, 0.024 mmol) was added into the polymer solution under stirring. Then, the solution was heated for 30 min at 60°C. Afterwards, an aqueous tribasic sodium citrate solution (2 mL, $C = 10$ mg/mL) was added dropwise to the flask. Within 4 min the solution turned wine-red, indicating the formation of AuNPs. After 2 h, the reaction was removed from the heating and allowed to cool to room temperature. For isolation of the gold nanoparticles/PDEAEM nanocomposites (AuNPs@PDEAEM), the dispersion was filtered off using a syringe filter of 0.2 microns. Then water was evaporated up to 1 mL residue using a rotary evaporator. Afterwards, 10 mL of water having a pH of 10 was added and the AuNPs@PDEAEM precipitates. The product was centrifuged at 3000 rpm, the aqueous supernatant discarded, and the AuNP@PDEAEM dried for 24 h in a vacuum oven at 40°C.

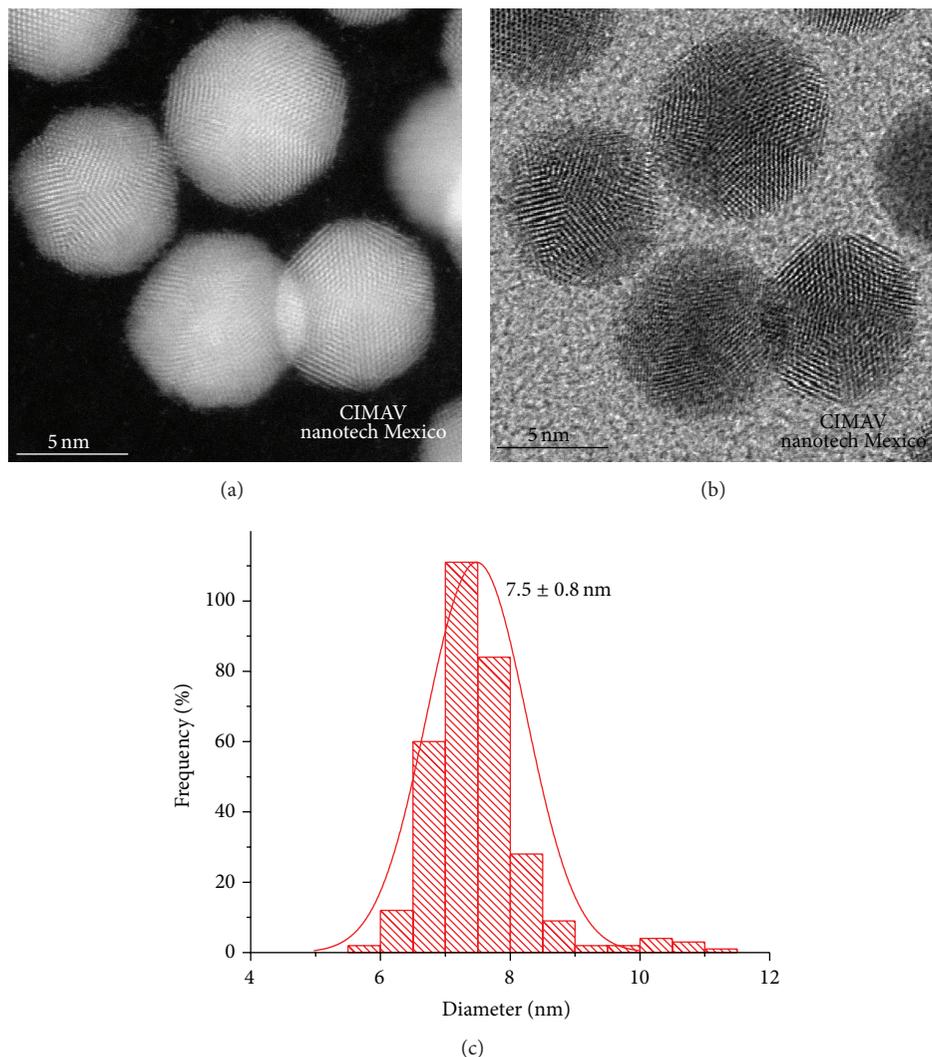


FIGURE 2: Representative HAADF and BF STEM images ((a), (b)) and the corresponding diameter distribution histograms (c) of coated AuNPs@PDEAEM prepared at pH 4.8 (reaction 3).

In the cases where organic/alcoholic solvents were used (*p*-dioxane, ethanol, and isopropanol) the synthetic strategy was modified in the following way: water was changed for the organic/alcoholic solvent with the exception of the aqueous sodium citrate solution. Purification was achieved by evaporating the solvent followed by addition of 10 mL of water having a pH of 10. AuNPs@PDEAEM were isolated as described above. Images from the obtained AuNPs dispersions, dilutions, and isolated AuNP@PDEAEM can be seen in Figure 1.

2.4. Characterizations. Electron microscope micrographs were acquired by analytical transmission electron microscope models JEOL100 C and JEM2200FS. The latter equipment has probe Cs corrected and most of the images were acquired in the scanning transmission electron microscopy

(STEM) mode, using a bright field (BF) and a high angle annular dark field (HAADF) detector; both microscopes worked at 200 kV. Samples were prepared by dispersing a small quantity of AuNPs@PDEAEM in isopropanol under sonication. A drop of that solution was poured into a 400-mesh lacy carbon copper grid followed by drying in air at room temperature. Diameter distribution histograms were constructed by counting AuNPs one by one from STEM images. Dynamic light scattering (DLS) measurements were carried out on AuNPs@PDEAEM dispersions at 25°C using a Malvern Instruments Zetasizer Nano NS (DTS 1060). The instrument is equipped with a green laser (532 nm). DLS experiments were performed at the scattering angle of 173° (backscattering) and it was stabilized for 10 min before data collection. The dispersions were filtered through 0.45 μm nylon membrane filter before analysis. The volume-average

hydrodynamic diameter (D_h) and polydispersity index (PDI) were calculated using Malvern Instruments dispersion technology software, based on CONTIN analysis and Stokes-Einstein equation for spheres as usual. UV-Vis spectra from various AuNP's dispersions were recorded by using a UV-Vis Varian Cary 100 Spectrophotometer at room temperature, for the measurement of the surface plasmon band of the AuNPs.

3. Results and Discussion

3.1. Synthesis of Coated AuNPs Prepared at pH 4.8 with PDEAEM Chains of Different Molecular Weight. Due to the hydrophobicity of PDEAEM in neutral or basic aqueous solution, we explored the synthesis of AuNPs at low pH values. In acidic conditions PDEAEM polymer chains are protonated and therefore fully water soluble. First, the possible effects of different molecular weights of PDEAEM in the size of the AuNPs were studied. The coated particles were prepared at pH 4.8 with a mass ratio of PDEAEM/ HAuCl_4 (3.75 : 1). Linear PDEAEM chains with $M_n = 9000, 18000,$ and 24500 g/mol were used to coat AuNPs. Table 1 (reactions 2, 3, and 4, resp.) shows size measurements from electron images for AuNPs where the values are $4.9 \pm 0.9, 7.5 \pm 0.8,$ and 4.4 ± 1.4 nm, respectively. The results of this study show that there is only a small influence of the molecular weight of PDEAEM chains in the size of the obtained nanoparticles. PDEAEM chains of 9000 g/mol and of 24500 g/mol are efficient to stabilize and control the size of the AuNPs. Figure 2 shows a typical STEM image (a, b) and related histogram (c) of the nanoparticles prepared in reaction 3.

UV-Vis spectra of the coated nanoparticle solutions in different pH's values were recorded and they are shown in Figure 3.

As can be seen, the maximum of the surface plasmon wavelength of reactions 2, 3, and 4 is located at $520\text{--}521$ nm. The most notable feature in these three reactions is the decrease in the maximum absorbance value for reaction 2 performed using a PDEAEM of 9000 g/mol. From these plots it can be concluded that synthesis of coated nanoparticles is accomplished well at mild acidic media ($3 < \text{pH} < 4.8$).

3.2. Study of the Effect of pH on the Size of AuNPs Obtained in Presence of PDEAEM. Table 1 shows that the size of nanoparticles prepared in reactions 3 and 6 using PDEAEM of 18000 g/mol could be controlled by changing the pH value of the media resulting in an increase in the particle size. The size of the nanoparticles clearly increases from 7.5 ± 0.8 nm (reaction 3, Figure 2) to 15 ± 1.8 nm (reaction 6, Figure 4) as the pH is decreased from 4.8 to 3 with a noticeable increase in the size distribution. It is worth noting that when the synthesis is carried out at pH 3 , a noticeable proportion of nanoparticles as polyhedrons were found (see Figure 4(c)), while for the synthesis at pH 4.8 (reaction 3) only spherical shapes were observed.

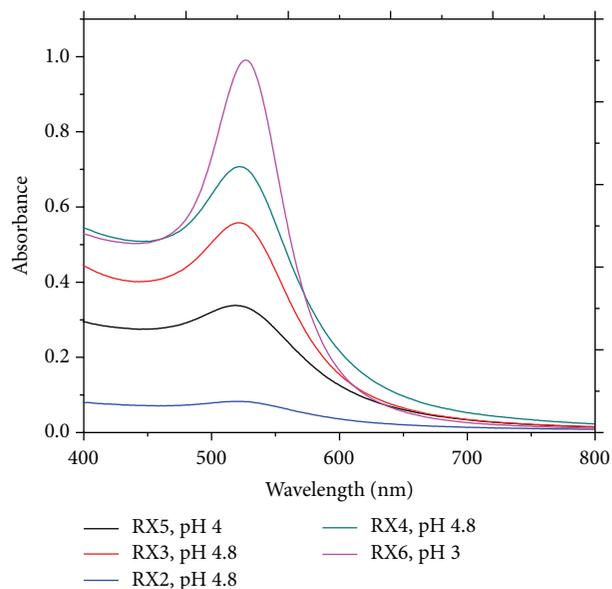


FIGURE 3: UV-Vis spectra of several PDEAEM-AuNPs prepared in aqueous acidic conditions: (RX2) pH 4.8 PDEAEM 9000 ; (RX3) pH 4.8 PDEAEM 18000 ; (RX4) pH 4.8 PDEAEM 24500 ; (RX5) pH 4 PDEAEM 29300 ; (RX6) pH 3 PDEAEM 18000 .

The AuNP dispersion, distribution of sizes, and morphologies are shown in Figure 4. Bright field STEM image (Figure 4(a)) shows a good dispersion (no agglomeration); this image at low magnification confirms a uniform distribution of sizes. The statistical measurement values were plotted in Figure 4(b), showing ~ 2 nm standard deviation value. However the images at higher magnification show rectangular, triangular, and other polygonal shapes for each NP; it can be noticed that all of them have the same diameter controlled according to the pH precursor solution value (synthesis conditions). These shapes may result from the effect of the HCL added to decrease the pH, since it has been reported that HCL promotes the growth of nanoparticles with preferential directions [30]. Some reports show that when nanoparticles are synthesized using citrate at pH lower than 3 , slight aggregation takes place; but in our case the nanoparticles are quite stable due to the protection given by the PDEAEM.

Figure 5 shows the DLS measurement of the AuNPs@PDEAEM dispersions in water reported as volume-average hydrodynamic diameters (D_h). As it can be seen, D_h of 13 and 19 nm for reactions 3 and 4, respectively, were measured. A dramatic increase in D_h to 110 nm for reaction 2 was observed. The only difference between reactions 2, 3, and 4 is the molecular weight of the PDEAEM polymer used during the synthesis. Probably, short chain polymer coatings (9000 g/mol) are not enough to effectively shield the NPs from each other. Parts of the NPs remained uncoated, and polymeric bridging between NPs is taking place, which

TABLE 1: Synthesis results of AuNPs prepared at different reaction conditions.

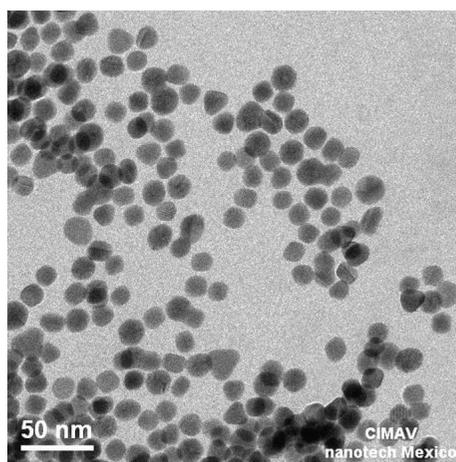
Reaction (RX)	Polymer	M_n^a in g/mol (D^b)	Solvent	pH	Ratio polymer : Au (mg/mg)	λ_{\max}^c (nm)	D_h^d (nm)	D_{STEM}^e (nm)
1	None	—	Water	7	4 : 1	543	19	—
2	PDEAEM	9000 (1.18)	Water	4.8	3.75 : 1	520	110	4.9 ± 0.9
3	PDEAEM	18000 (1.97)	Water	4.8	3.75 : 1	520	13	7.5 ± 0.8
4	PDEAEM	24500 (1.31)	Water	4.8	3.75 : 1	521	19	4.4 ± 1.4
5	PDEAEM	29300 (1.1)	Water	4	4 : 1	519	21	4.4 ± 0.9
6	PDEAEM	18000 (1.97)	Water	3	3.75 : 1	526	27	15 ± 1.8
7	PDEAEM	29300 (1.1)	Dioxane : water (15 : 1)	—	4 : 1	526	—	10.1 ± 1.1
8	PDEAEM	18000 (1.97)	Ethanol	—	3.75 : 1	521	72	4.6 ± 1.5
9	PDEAEM	18000 (1.97)	Isopropanol	—	3.75 : 1	531	569	3.5 ± 1.0

^a M_n is the number average molecular weight; ^b $D = M_w/M_n$ is the dispersity in molecular weight.

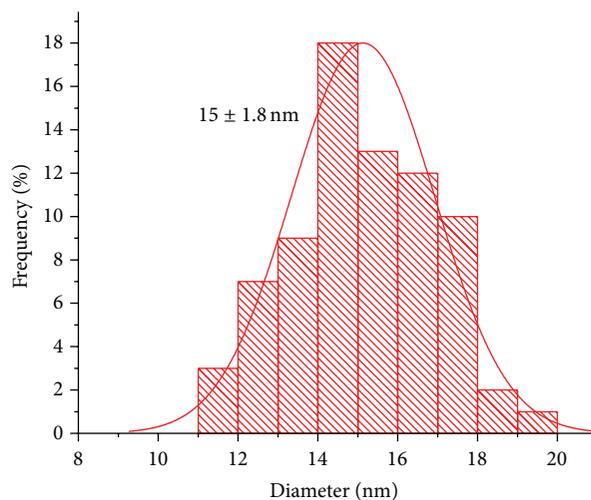
^c λ_{\max} is the maximum of the surface plasmon resonance peak.

^d D_h is the hydrodynamic diameter of AuNPs@PDEAEM.

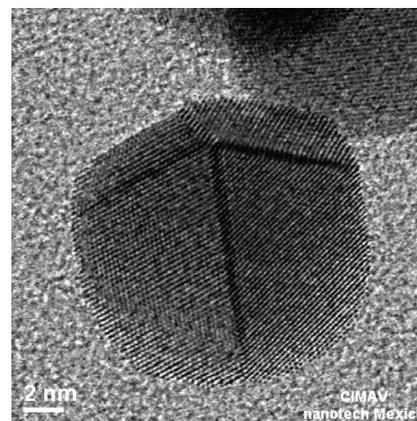
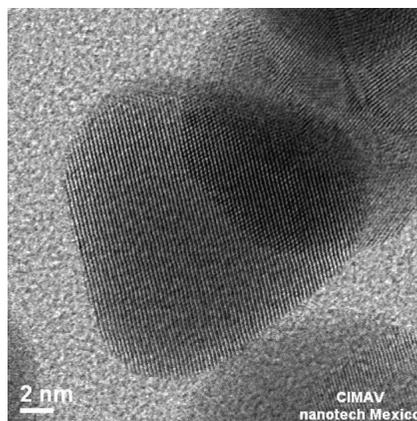
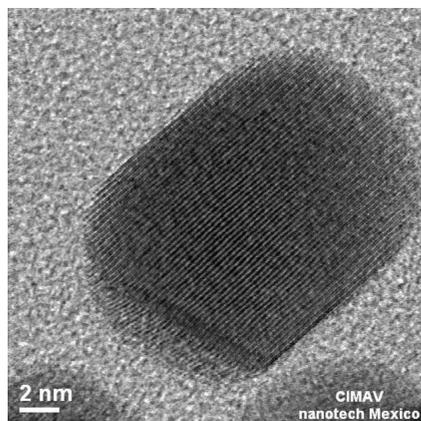
^e D_{STEM} is the average diameter of AuNPs by scanning transmission electron microscopy (STEM).



(a)



(b)



(c)

FIGURE 4: BF STEM images (a) at low magnification, (b) size distribution histogram, and (c) AuNPs morphologies prepared at pH 3 (reaction 6).

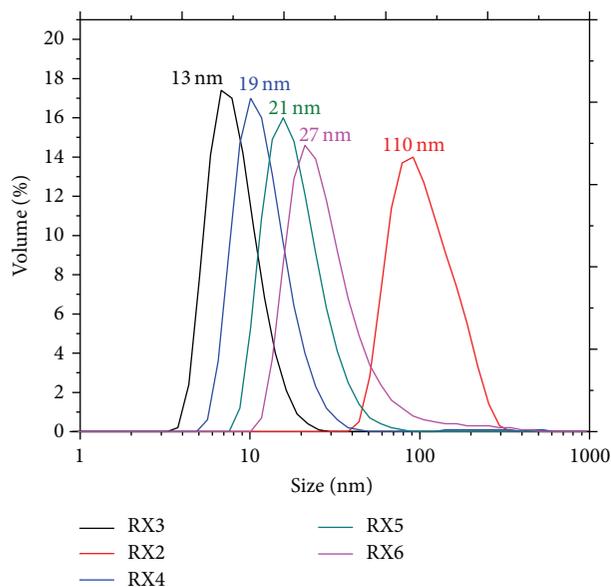


FIGURE 5: Size distribution measured by DLS of PDEAEM-AuNPs prepared in acidic aqueous conditions: (RX2) pH 4.8 PDEAEM 9000; (RX3) pH 4.8 PDEAEM 18000; (RX4) pH 4.8 PDEAEM 24500; (RX5) pH 4 PDEAEM 29300; (RX6) pH 3 PDEAEM 18000.

favors the formation of larger aggregates. While PDEAEM of 9000 g/mol do not stabilize well 5 nm AuNPs (reaction 2), 4.4 nm AuNPs are well stabilized using almost 3 times larger PDEAEM (reaction 4). AuNPs of 15 nm coated with PDEAEM of 18000 g/mol at pH 3 show D_h of 27 nm (reaction 6), demonstrating a good stabilization and no AuNP to AuNP bridging. This is because at this pH PDEAEM has a higher ionization degree than at pH 4.8, enough to hinder aggregation due to electrostatic repulsion imparted by the PDEAEM chains. The size of the obtained AuNPs does not change much with the molecular weight of the polymer used as already discussed before (see Table 1; reactions 2, 3, and 4). So, the main effect of different molecular weights of PDEAEM used in the AuNPs synthesis is the stabilization of AuNPs dispersions: larger molecular weight prevents aggregation and lower molecular weight does not (Figure 6); nevertheless precipitation of AuNPs was not present.

3.3. Proposed Mechanism of Gold Nanoparticles Formation.

Many studies report in the literature on the use of polymers as reducing agents in the formation of AuNPs particularly the use of polymers containing amino groups which possess the ability to reduce Au^{3+} cations to form AuNPs without any additional reducing agents [9, 10]. PDEAEM is an ionizable polymer in which tertiary amine groups can be protonated by decreasing the pH of its polymer solution. Accordingly, in acidic aqueous solution the nitrogen atoms of PDEAEM could not donate lone pair electrons to Au ions; therefore *in situ* reduction is not possible here and the addition of an external reducing agent is absolutely necessary. In this work,

the role of PDEAEM as a stabilizing agent is crucial for the control of the size of AuNPs.

The mechanism of AuNPs formation begins with strong interaction between PDEAEM and Au^{3+} cations. Appropriate groups in PDEAEM (carbonyl groups and nitrogen having the electron pair available) absorb Au ions (see Figures 7(a) and 7(b)). The seeds thus formed serve as nucleation centers for forming gold nanoparticles when the citrate ions were added (Figure 7(c)). After addition of citrate, reduced Au atoms start to grow from the nuclei to form the nanoparticles (Figures 7(d) and 7(e)). PDEAEM chains used in this work bear a trithiocarbonate moiety at one end of the chain. Duwez et al. [31] showed that dithioesters or trithiocarbonates can be directly chemisorbed on gold substrates and are sufficient to stabilize the particles in suitable solvents (water or DMF). We believe that this situation also positively influences the results of this work.

3.4. AuNPs Prepared in the Presence of PDEAEM in Organic/Alcoholic Media.

The effect of some organic solvents in the preparation of AuNPs was also studied. Figure 8 shows STEM and TEM images for AuNPs synthesized in ethanol (a) and isopropanol (b), respectively (see Table 1, reactions 8 and 9, resp.). Both reactions were carried out using the same PDEAEM of 18000 g/mol. The average AuNPs sizes obtained were 4.6 ± 1.5 nm and 3.5 ± 1 nm, respectively.

It was tested if ethanol and isopropanol acted as reducing agents under the reaction conditions used in this study (stirring for 2 h at 60°C); the results showed no change in the color of the solution indicating lack of nanoparticle formation up to 2 h. When we carried out the reaction of formation of nanoparticles in the presence of PDEAEM and ethanol or isopropanol (no reducing agent added) there was also no reaction after 1 day. Figure 9 shows absorbance spectra obtained from PDEAEM coated AuNPs synthesized and measured in organic media. As can be seen, the maximum of surface plasmon wavelength is shifted from 521 nm to 531 nm when medium was changed from ethanol to isopropanol.

Remarkable difference in the intensity of absorption was also observed in these reactions, which is usually associated with the nanoparticle concentration in the medium. If we compare the data in Table 1 (last two rows) from DLS studies, we understand that AuNPs prepared in isopropanol with PDEAEM aggregates form a half micrometer bunch of AuNPs increasing the local concentration of AuNPs, resulting in a high intensity of surface plasmon and a shift to a higher surface plasmon wavelength maximum, which is usually associated with bigger AuNP sizes. It is clear that the dispersibility of AuNPs@PDEAEM in isopropanol is not as good as in ethanol, while in water it depends strongly on pH value.

4. Conclusions

Protonated PDEAEM solutions can be employed to prepare high-quality gold nanoparticles in aqueous media using

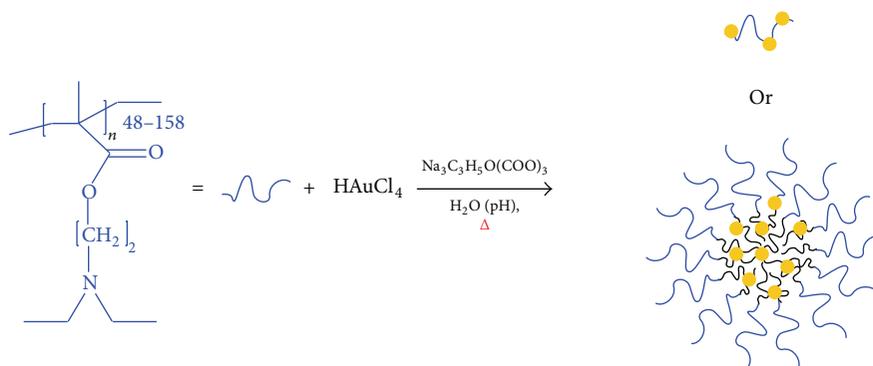


FIGURE 6: Scheme showing synthesis and self-aggregation of AuNPs@PDEAEM.

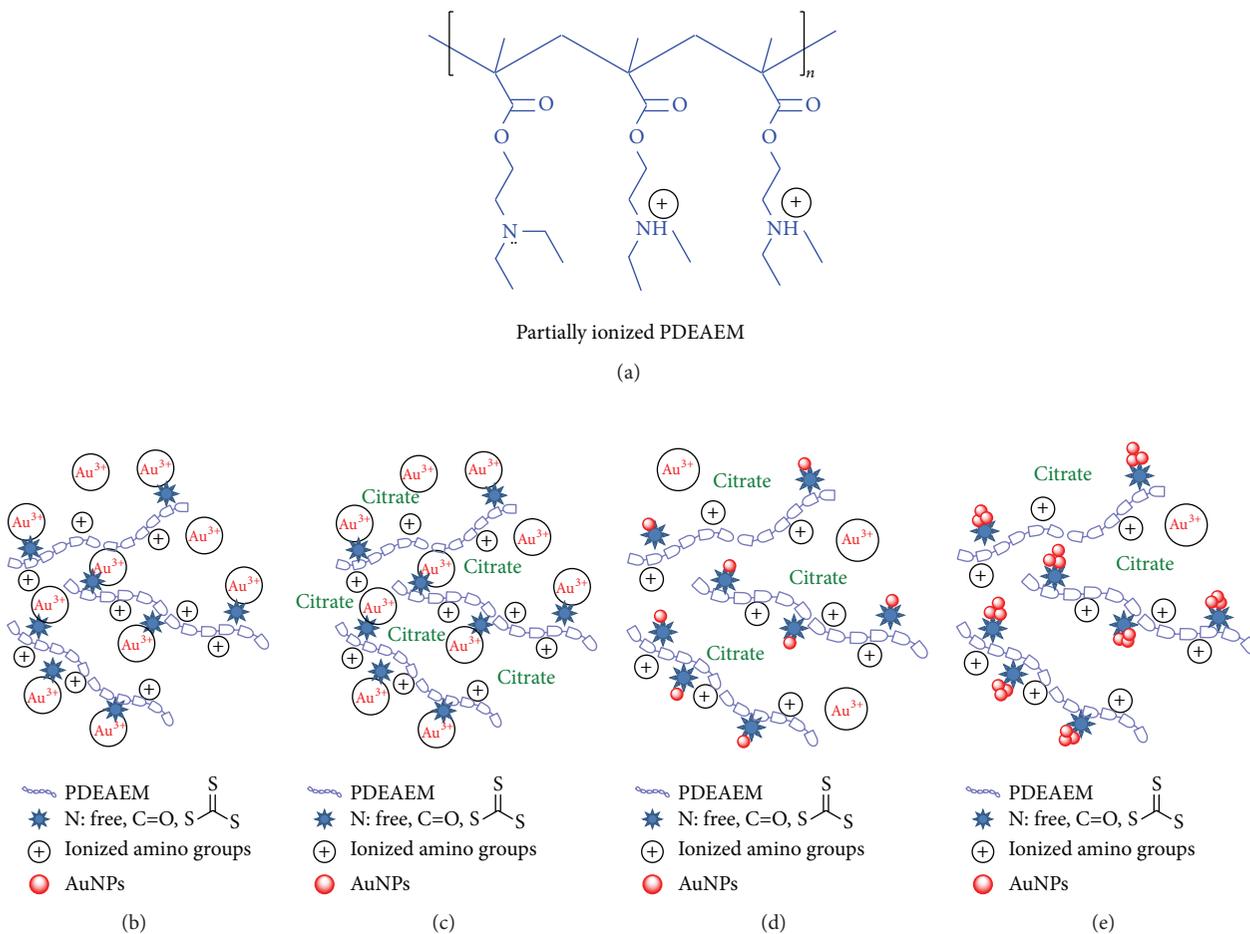


FIGURE 7: Proposed mechanism of AuNPs formation by using acidic aqueous PDEAEM solutions.

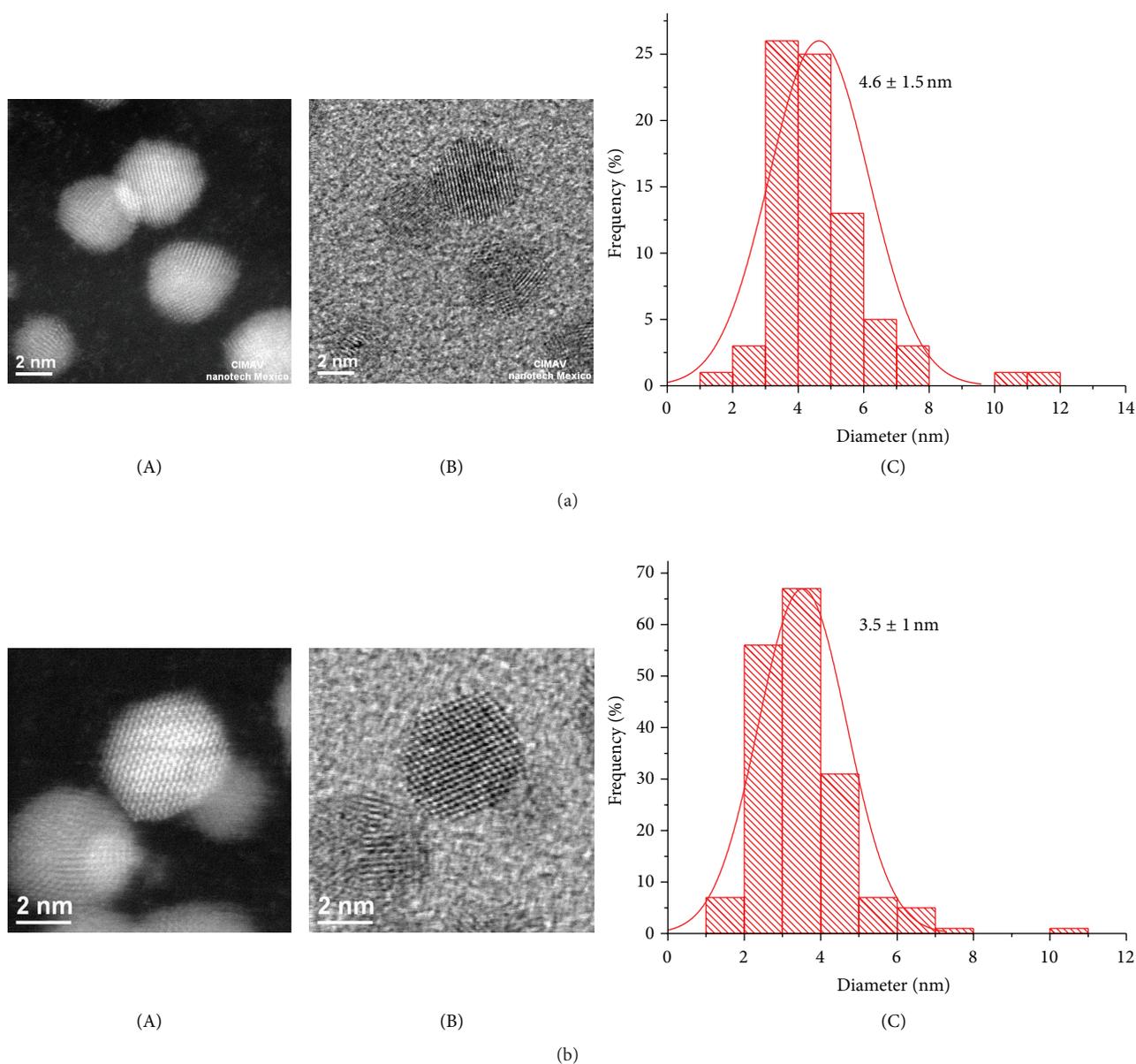


FIGURE 8: (a) HAADF and BF STEM images ((A), (B)) and the size distribution histogram of AuNPs (C) prepared with PDEAEM in ethanol ((a), reaction 8) and in isopropanol ((b), reaction 9).

citrates as reducing agents. The average size can be controlled varying the pH value. Stable AuNPs in organic/alcoholic solvents can also be prepared using PDEAEM. The sizes of formed AuNPs can be varied from 3.5 nm up to 15 nm, with narrow size distributions just by changing the solvent conditions. In addition, the stability and self-assembly of AuNPs@PDEAEM were assessed by DLS. Results show that aggregation of AuNPs to sizes of 100 to 500 nm is a result of small size PDEAEM (9000 g/mol) at pH 4.8 (slight acidic conditions) and also in the presence of a not very polar alcoholic solvent (isopropanol). Higher molecular weight PDEAEM

(29300 g/mol) resulted in AuNPs@PDEAEM diameters of 219 nm, while the single AuNPs retain their size (4-5 nm). Independently of AuNPs size and hydrodynamic diameters of the AuNPs@PDEAEM micellar composites, the prepared AuNPs coated with PDEAEM were stable in acidic water and alcohols.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

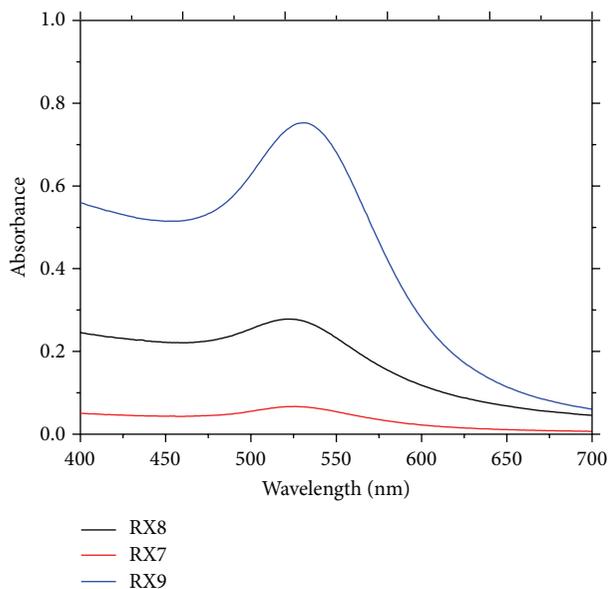


FIGURE 9: UV-Vis spectra of several PDEAEM-AuNPs prepared in organic solvent conditions: (RX7) dioxane/water; (RX8) ethanol; (RX9) isopropanol.

Acknowledgments

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