Protection Effects of Hydrophile-Grafted Silicone Copolymers on the Formation of Colloidal Silver Nanoparticles

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Received: August 29, 2003; In Final Form: December 31, 2003

Silicone copolymers with varying weight percents of hydrophilic groups with or without charge were used as protectors to stabilize the silver nanoparticles prepared by chemical reduction of Ag$^+$ ion with sodium borohydride NaBH$_4$, and the effects of hydrophobic moiety and hydrophile on protection were investigated. UV−vis spectroscopy was employed to characterize the silver colloids, and transmission electron microscopy (TEM) was used to determine the metal particle sizes and morphologies. The silicone copolymer can effectively protect the formation of silver nanoparticle with sufficiently high concentration of polymer. It was found the high hydrophobic content rather than hydrophilic content results in better protection to nanoparticles. The results strongly suggest that the silicone copolymer of SHE cannot effectively protect the silver nanoparticle if its hydrophile cannot interact with metal ion or nanoparticles as it is positive-charged.

Introduction

Interest in colloidal metal nanoparticles protected by polymers is increasing, since these materials offer tremendous options for combining properties stemming from both the inorganic components and the polymers.[1−6] Amphiphilic polymers have received special attention, since the amphiphilic character not only provides solubility in polar media, but also allows interactions with metal precursors and the resulting metal colloids. It has been shown that in many cases the presence of hydrophobic components in the polymer leads to smaller particle sizes with narrow size distributions and high colloidal stability.[7−9] However, good interactions of the polymer with the metal precursor and the resulting metal colloid, for instance, by complex or ion-pair formation are equally important.[10,11] Polysiloxane shows tremendous hydrophobicity compared to the usual long-chain hydrocarbons or polymer skeletons and has been used as hydrophobic groups for a wide range of applications.[12,13] If the polysiloxane is equipped with an appropriate hydrophile which can interact with metal ions or metal paparticles, then this amphiphilic silicone copolymer would be very effective to act as a protector for the formation of metal nanoparticles.

Our previous studies have used polyethyleneiminated copolymers as protectors for the formation of metal nanoparticles because of the strong coordination between ethylenenimine and metal ions.[14,15] This study examined silicone copolymers with different pendant hydrophilic groups such as diethanol tertiary amine (SHE, nonionic) and triethyl quaternary amine (SQE, cationic) for their abilities to stabilize silver colloids, where the amino units on hydrophile complex with metal ions were used to separate the ions,[7] and the high hydrophobic character of polymer backbone, poly(dimethylsiloxane) (PDMS), can effectively provide the steric hindrance to protect the resultant metal nanoparticles. The properties of silver colloid resulting from the interactions of silver precursor salt and silver particles with these silicone copolymers were investigated and compared using UV−vis spectroscopy and TEM. The effects of different

preparation conditions of nanoparticles also were studied, including the mass ratio of stabilizer to silver, the content of the hydrophilic and hydrophobic groups, and the pH value of the system. In the cases with protonated SHE and charged SQE copolymers, electrostatic interaction was also found to be involved and profoundly influenced the nanoparticle features and colloidal stabilities.

Experimental Section

Materials. Poly(methylhydrogensiloxane) (DC1107), octamethylcyclotetrasiloxane (D4), hexamethyldisiloxane (DC200), and platinum divinyltetramethyl disiloxane (Pt catalyst) were obtained from Dow Corning. Allyl glycidyl ether (Acros), sulfuric acid (Merck), diethanolamine (Lancaster), and triethylamine (Merck) were used as received. Silver nitrae (AgNO$_3$) and sodium borohydride (NaBH$_4$) were purchased from Acros and Lancaster. All other chemicals were reagent grade and used as received.

Methods. *Synthesis and Characterization of Hydrophilic-Grafted Polysiloxane.* The synthesis of hydrophilic-grafted polysiloxane is a three-step process. All the copolymers were synthesized as stabilizers (Scheme 1) following the same procedures and conditions as described in detail in our previous work.[16,17]

SCHEME 1: The Structures of Hydrophile-Grafted Silicone Copolymers

SHE copolymer
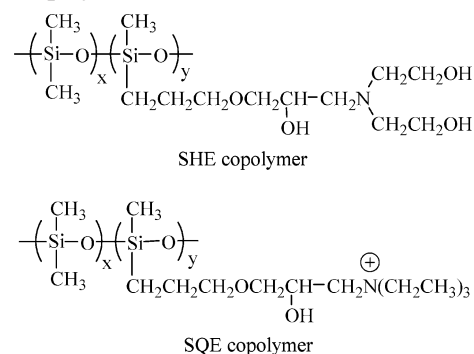
SQE copolymer

Step 1. Synthesis of Siloxane Copolymer. Siloxanes DC1107, D4, and DC200 were reacted using sulfuric acid as a catalyst,

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TABLE 1: Symbols and Compositions of Hydrophile-Grafted Polysiloxanes with Varying wt % of Hydrophile

copolymer	wt % of DC1107	wt % of D4	wt % of DC200	M_n of SG copolymer[a]	EEW of SG copolymer[b]	hydrophile content[b] (mol%)	hydrophilic moiety[c] (mol/g)	hydrophobic moiety[d] (mol/g)
SHE40	40	55	5	7012	259.4	46.5	2.71×10^{-3}	3.28×10^{-3}
SHE60	60	35	5	6770	207.7	68.5	3.14×10^{-3}	1.69×10^{-3}
SHE80	80	15	5	6479	190.4	82.0	3.40×10^{-3}	6.89×10^{-4}
SQE60	60	35	5	6770	207.7	68.5	4.81×10^{-3}	1.72×10^{-3}

[a] The average molecular weight was measured by gel permeation chromatography analysis. [b] The EEW and the ratio of the mole percent of epoxy content were determined by the method described in our previous study.[17] [c] Hydrophilic moiety: $-N(CH_2CH_2OH)_2$ or $-N^+(CH_2CH_3)_3$. [d] Hydrophobic moiety: poly(dimethylsiloxane).

at a temperature of 45 °C under nitrogen to obtain a viscous transparent liquid product, poly(dimethylsiloxane−methylhydrogensiloxane) (SH) copolymer.

Step 2. Synthesis of Siloxane Copolymer Derivative. Using platinum as a catalyst, siloxane copolymer (SH) was reacted with an overdose of allyl glycidyl ether in dry toluene, at a temperature of 75 °C under nitrogen to obtain the SG copolymer. The number-average molecular weight M_n of SG copolymer was determined by GPC (Waters 510 high-pressure liquid chromatography pump with a Waters 410 differential refractometer). Polystyrene and THF (HPLC grade) were used as standard and mobile phases (flow rate: 1 mL/min), respectively. The M_n and molar content of SG copolymers are shown in Table 1. From the definition of epoxy equivalent weight (EEW), the weight of an epoxy compound containing 1 mole of epoxy group, the ratio of the number of dimethylsiloxane units to that of epoxysiloxane units (*m:n*) can be calculated from the following equations:

$$n = \frac{M_n \text{ of SG}}{\text{EEW of SG}}$$

$$m = \frac{M_n - (n \times 158)}{74}$$

where 158 and 74 are the unit weight of dimethylsiloxane and epoxysiloxane, respectively.[17] Thus, the mole percent of epoxy content ($n/(m + n) \times 100\%$) for the silicone copolymers can be obtained.

Step 3. Synthesis of Nonionic/Cationic Hydrophilic-Grafted Silicone Copolymer. The SG copolymer was reacted further with excess diethanolamine or triethylamine in ethanol at 70 °C to obtain SHE and SQE copolymer, respectively. However, as the hydrophilic group of polysiloxane derives from the DC1107, the hydrophilic degree increases with increasing the weight percent of the DC1107. Thus, adjusting the stoichiometry of DC1107 and D_4 in the reaction mixture, we can vary the active reaction sites for the entry of hydrophilic moieties. The hydrophilic-grafted polysiloxanes SHE40, SHE60, and SHE80 were synthesized by the three-step reaction using the siloxanes DC1107/(D4+DC200) with various wt % to be 40/60, 60/40, and 80/20, respectively. Table 1 shows the composition of hydrophile-grafted polysiloxanes with varying percentages of hydrophilic groups.

Colloid Preparation. A defined amount of silicone copolymer and AgNO$_3$ were first dissolved in ethanol. The pH was adjusted with diluted NaOH or nitric acid. The resulting solution was stirring for 15 min. An aqueous solution of an excess of NaBH$_4$ was freshly prepared and rapidly added to the stirred solution containing AgNO$_3$ (5×10^{-4} M) and the silicone copolymer. All glassware was cleaned with concentrated nitric acid before used.

TABLE 2: Transmission Electron Microscopy Results for Silver Colloids Reduced by NaBH$_4$

no.	silicone copolymer	mass ratio	N/Ag[a]	PDMS/Ag[b]	pH value[c]	average particle diameter (nm)
1	SHE60	125/1	42.5/1	22.8/1	9.2	5.5 ± 2.0
2	SHE60	75/1	25.5/1	13.5/1	9.3	5.8 ± 2.3
3	SHE60	25/1	8.5/1	4.5/1	9.3	5.6 ± 2.5
4	SHE60	15/1	5.1/1	2.7/1	9.2	d
5	SHE60	5/1	1.7/1	0.9/1	9.1	d
6	SHE40	25/1	7.3/1	8.8/1	9.2	4.1 ± 1.8
7	SHE80	25/1	9.2/1	1.9/1	9.2	7.1 ± 2.8^e
8	SHE60	25/1	8.5/1	4.5/1	10.4	4.4 ± 2.1
9	SHE60	25/1	8.5/1	4.5/1	7.6	11.1 ± 6.9
10	SHE60	25/1	8.5/1	4.5/1	5.5	f
11	SQE60	25/1	8.5/1	4.6/1	9.2	d

[a] The molar ratio of hydrophilic moiety to silver. [b] The molar ratio of hydrophobic moiety to silver. [c] Adjusted by adding diluted NaOH or nitric acid. [d] Large multi-particle aggregates. [e] Average particle size and standard deviation for the particles excluding the coexisting large aggregates. [f] Aggregates consisting of large particles.

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 on the basis of the measurement of at least 100 particles. UV−vis spectra were recorded with a Beckamn Coulter DU 800 spectrophotometer (10 mm path length quartz cuvettes).

Results and Discussion

Silicone copolymers with various hydrophilic group weight percentages and different pendant hydrophilic groups were investigated for their ability to stabilize colloidal silver nanoparticles, and their effects on the nanoparticle features and colloidal stabilization. Several silver colloids were prepared according to the preparation conditions listed in Table 2. Average diameters and standard deviations determined by TEM are also given. The effects of different preparation conditions were studied, including the mass ratios of stabilizer to silver, the content of the hydrophilic and hydrophobic groups, the system pH, and the type of grafted hydrophiles. Colloidal silver nanoparticles stabilized by silicone copolymers have average diameters down to 5 nm, varying with preparation conditions. The colloidal stability depends largely on the particle sizes, that is, the silver colloids incorporating the particles larger than 20 nm showed precipitation in a few hours or days, whereas the colloids with smaller particles remained stable for several months.
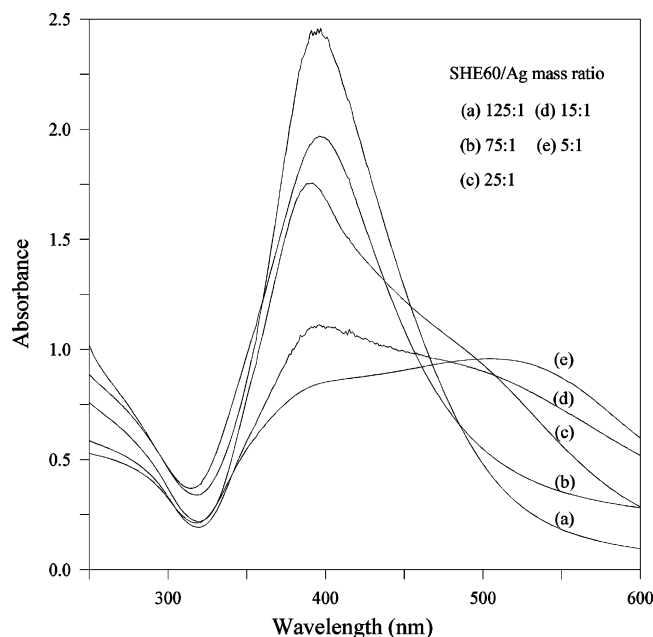
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Figure 1. UV−vis spectra for silver nanoparticles protected by SHE60 copolymer with the SHE60/Ag mass ratio of (a) 125:1, (b) 75:1, (c) 25:1, (d) 15:1, (e) 5:1.

Figure 2. TEM micrographs and size distribution histograms of silver nanoparticles protected by SHE60 copolymer with the SHE60/Ag mass ratio of (a) 125:1, (b) 75:1, (c) 25:1, (d) 15:1, (e) 5:1.

With the mass ratio of SHE60/Ag higher than 25, dark-yellow clear silver dispersions were obtained, and remained colloidally stable for several months.However, some dark brown solids precipitated from solution within hours when the mass ratio of SHE60 to $AgNO_3$ was less than 15. Figure 1 shows the UV−vis spectra for silver nanopartices taken immediately following the reduction by $NaBH_4$. For the samples with mass ratios of polymer/metal = 125:1 and 75:1 (plots a and b in Figure 1), a peak was observed at about 400 nm, along with a minimum around 320 nm, both of which are typical for nanosized silver colloids. The intense peak at 400 nm results from absorption by surface plasmas in the silver nanoparticles.[18] The UV−vis spectrum for the sample with mass ratio = 25:1 (plot c) reveals that the 400 nm peak decreases and gives rise to a shoulder shifted to higher wavelengths that imparts a perceptible reddish tint to the solution. This spectral trend continues with the further decreasing of the SHE60/Ag mass ratio to 15:1 and 5:1 (plot d and plot e). Red-shifts of the plasmon peak upon aggregation of metal nanoparticles can be interpreted by Mie theory and have been the subject of recent calculations by Schatz and co-workers.[19−21] TEM observations support the assignment of the red-shifted peak to aggregate species. Figure 2 shows the TEM micrographs and the corresponding particle size distribution histograms of silver colloids. When the mass ratio of SHE60 to Ag decreases from 125, 75, to 25, the colloidal particle size does not change remarkably. Also, within this range, no obvious aggregation has been observed. However, when the SHE60/Ag mass ratio is less than 15, the TEM image reveals a significant change in particle features. Figure 2e shows the TEM image, which clearly reveals large, multi-particle aggregates. It suggests that at low polymer concentration the protective polymer layer is less effectively built-up around the silver particles to prevent further particle collision, thus the particles coagulate to form large aggregates and precipitate from the solution. The formation of the large aggregates in Figure 2e indicates the occurrence of absorption after 400 nm, as shown in the plot e of Figure 1. These analytical results demonstrate that protective polymers with higher SHE60/Ag mass ratio, that is, higher N/Ag ratio and higher PDMS/Ag ratio stabilize the nanoparticles better.
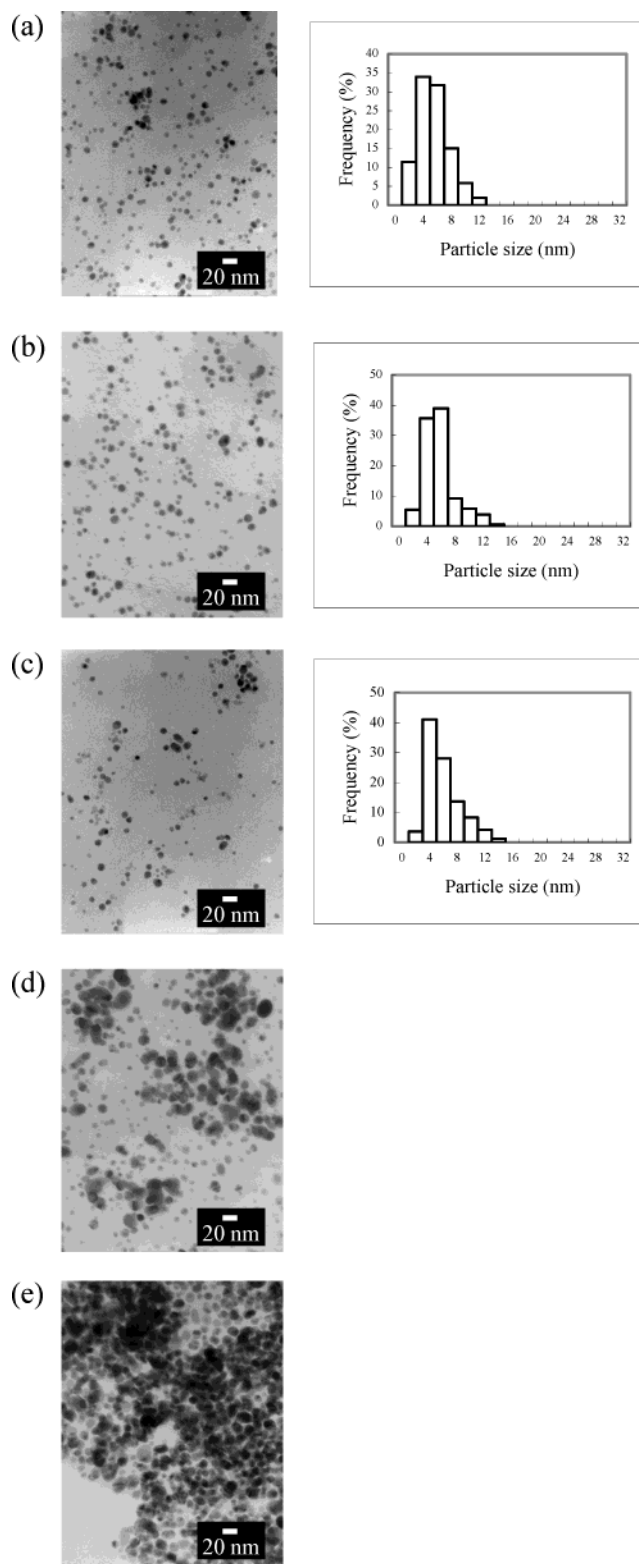
These protecting effects can be derived from either hydrophobic or hydrophilic moieties.

The protective polymer has to provide functional groups to interact with the metal precursor and the resulting metal colloid to obtain small and stable metal colloids. In this study, the functional groups are the hydrophile of diethanolamine. As shown in Table 1, it is expectable that the number-average
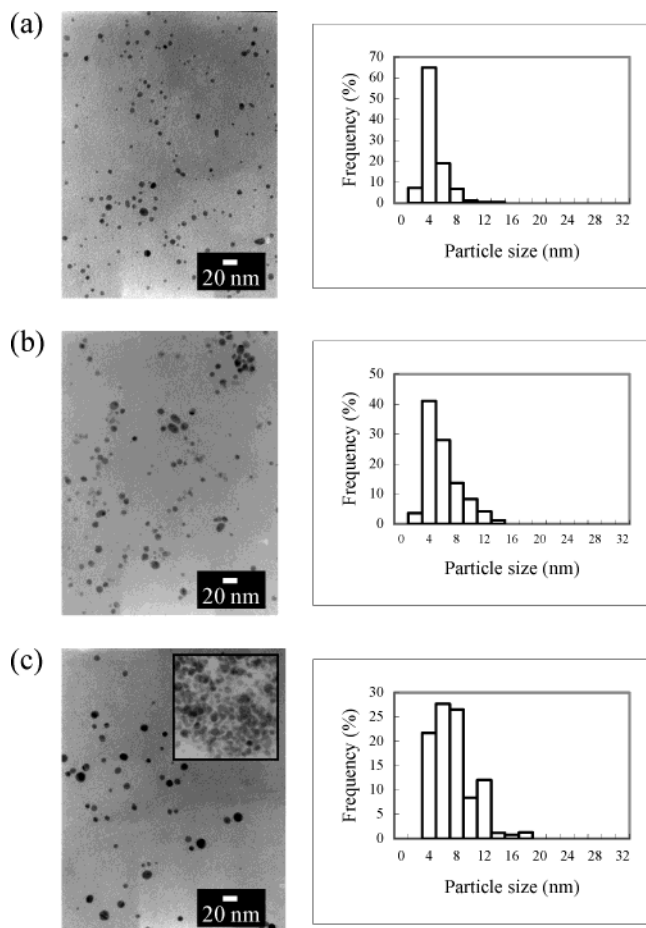
Figure 3. TEM micrographs and size distribution histograms of silver nanoparticles protected by (a) SHE40, (b) SHE60, (c) SHE80 copolymer with the SHE/Ag mass ratio of 25:1.
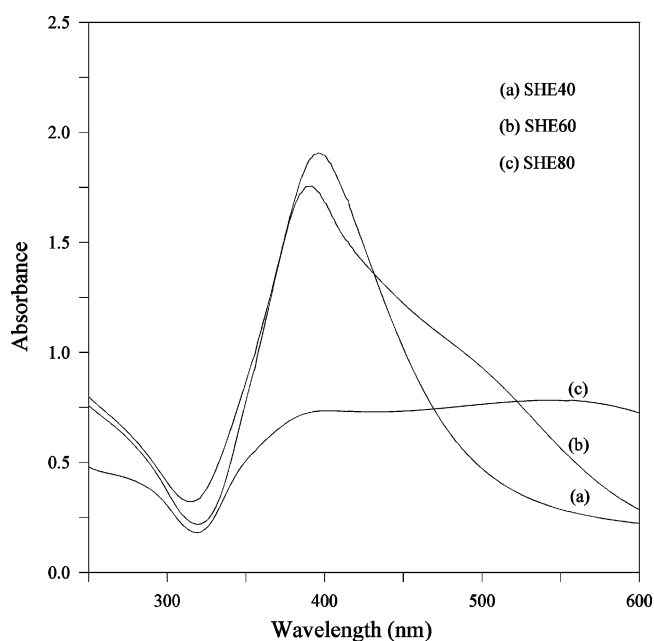

Figure 4. UV−vis spectra for silver nanoparticles protected by (a) SHE40, (b) SHE60, (c) SHE80 copolymer with the mass ratio of 25:1.

Figure 5. TEM micrographs of silver nanoparticles protected by SHE60 copolymer at (a) pH 10.4, (b) pH 9.3, (c) pH 7.6, and (d) pH 5.5.

molecular weights of SHE40, SHE60, and SHE80 are similar since the molecular weights of their corresponding precursor SG copolym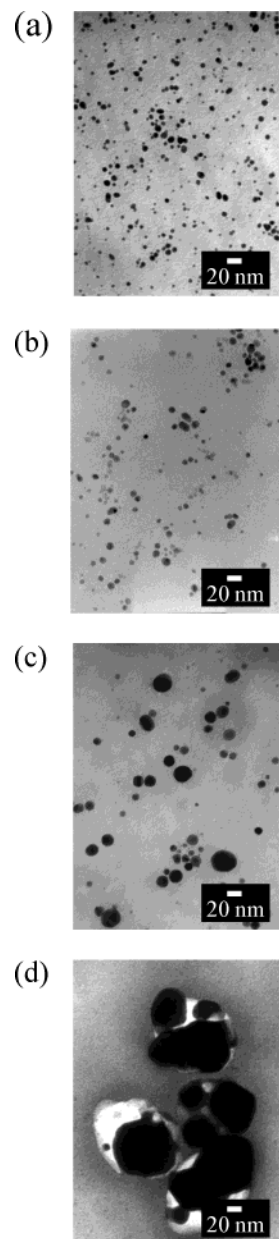er are comparable. The content of the hydrophiles of SHE copolymers with the comparable molecular weights thus can be expected to be an important influence on the particle size and distribution. The nonionic SHE copolymers containing different content of the amino units were used as protective polymers with the mass ratio SHE copolymer/Ag fixed at 25. More hydrophile-content per polymer was found to result in larger particle sizes and broader size distributions of the colloidal Ag nanoparticles, that is, for SHE40, small nanoparticles with narrow distribution (4.1 ± 1.8 nm) were obtained (Figure 3a); for SHE80, many particles coagulate together (see inset in Figure 3c), while for SHE60, the particles are in between. From the corresponding UV−vis spectra (Figure 4), the obvious red-shifted absorption at 500 nm−600 nm further demonstrates the existence of large aggregates for SHE80. For SHE40, SHE60, and SHE80, the molar ratio of N/Ag is 7.3, 8.5, and 9.2, respectively. Although the molar ratio of N/Ag is highest for SHE80, the values display little difference. These results indicate that, when the molar ratio of N/Ag is 7.3−9.2, the particle size
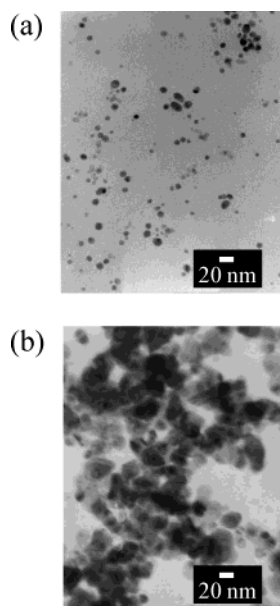
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Figure 6. TEM micrographs of silver nanoparticles protected by (a) SHE60 copolymer, (b) SQE60 copolymer with the mass ratio of 25:1.

is not influenced mainly by the hydrophile content but rather by the hydrophobic moiety of polymer, parallel to many cases in which the presence of hydrophobic components in the polymer leads to smaller particle sizes with narrow size distribution and high colloidal stability.[7-9]

Alkylamines[22,23] and polyallylamine[15] have been used as stabilizers to prepare silver nanoparticles, since the amino groups can coordinate with metal ions and interact with the reduced metal nanoparticles via the unpaired electron on nitrogen. Therefore the role of the hydrophile of SHE60 in protection can be investigated by varying the pH value to obtain different ratios of (tertiary amine)/(quaternary amine). At higher pH (pH = 10.4 and 9.3), the average diameter of the prepared silver particles is about 4-5 nm with a narrow size distribution (Figure 5a and 5b), which is much smaller than for silver colloids prepared below pH 7.6 (Figure 5c), and serious aggregation of

the colloidal particles occurs at pH 5.5 (Figure 5d). Thus, it can be concluded that the lower pH of the precursor solution results in the larger average diameter of the silver colloids. In this study, a series of pH values of SHE60 solutions given different additions of HCl was determined by potential meter, and the degrees of protonation of the tertiary amine in SHE60 under different pH were calculated from the titration curve as 0, 0.1, 3.8, and 78.9%, respectively, for pH = 10.4, 9.3, 7.6, and 5.5. Obviously, the lower pH results in higher content of positively charged amine in SHE, interrupting the interaction between the polymer and metal ions, and causing the beginning of agglomeration and the much larger particle size, contrasting with the use of nonionic polymer as protective matrix. The reduction of $AgNO_3$ by borohydrides involves the initial formation of Ag^+ or Ag_4^{2+} cation,[7,24,25] and thus, the electrostatic repulsion between the positive silver ions and the positively charged polymer side groups should prevent initial interactions, similar to the observation that polyelectrolytes have resulted in less stable dispersions and larger particle sizes for same charge precursors.[9]

To further identify the interaction phenomena with metal ions for the SHE60 with high protonation at low pH, a comparable silicone copolymer SQE60 with cationic hydrophile is synthesized. The TEM micrograph for the silver colloid stabilized by cationic SQE60, as shown in Figure 6b, is compared with that protected by nonionic SHE60 as shown in Figure 6a, and serious agglomeration was noted for cationic SQE60, resulting in a very unstable colloid in contrast to SHE, for which yellow-orange and clear silver dispersions were stable for several months. The results from Figures 5 and 6 strongly suggest that the silicone copolymer of SHE cannot effectively protect the silver nanoparticle if its hydrophile cannot interact with silver ion or nanoparticles as it is positive-charged.

The silicone copolymers exert a significant effect on the size and size distribution of the silver particles. Based on the results of Figures 1-6, Scheme 2 illustrates the functions of SHE in protecting silver nanoparticles. Before reduction, SHE separates the silver ions by chelating with the ions through the interactions between the unpaired electrons on the nitrogen of hydrophile of diethanolamine in SHE. Meanwhile, following reduction,

SCHEME 2: Formation of Colloidal Silver Nanoparticles under Non-charged and Positive-charged Silicone Copolymers

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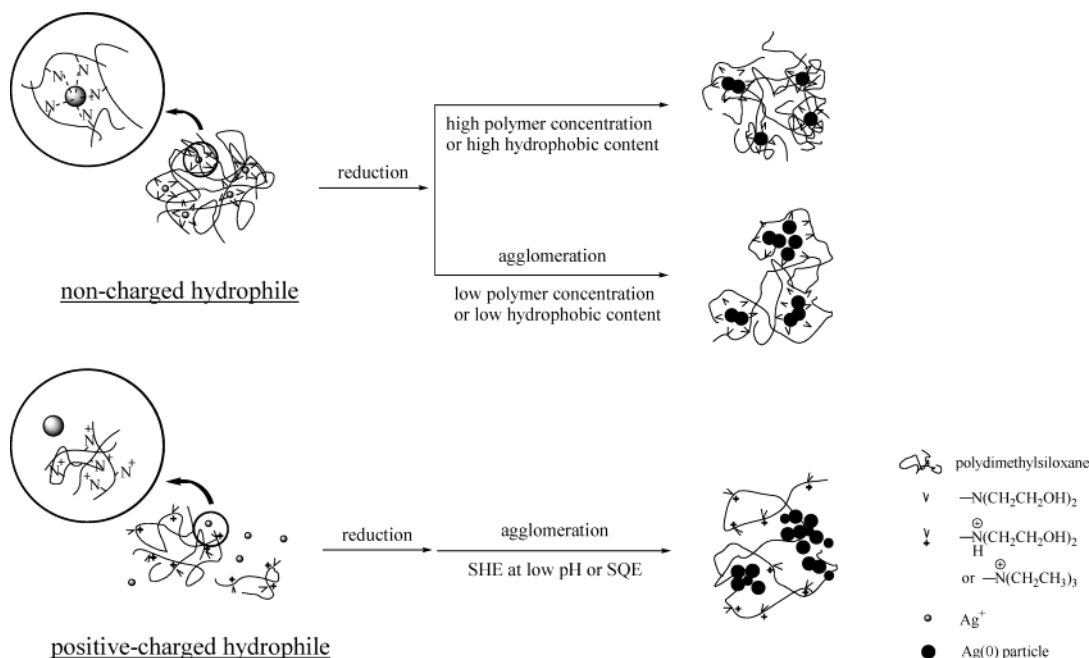
SHE provide steric hindrance to prevent the approach and aggregation of the metal particles, since the hydrophobic segments of SHE adsorb on the metal surface by means of the coordination between the hydrophile and metal particles. Small and uniform silver nanoparticles have been obtained in the presence of SHE40, which contains more hydrophobic segments and thus offers better interaction with the metal surface to build a well-structured protective polymer layer. In case of SHE at low pH or SQHE, the initially poor interactions between cationic hydrophile of silicone copolymer and silver ion due to electrostatic repulsion cause the beginning of agglomeration and much larger particle size. This phenomenon strongly suggests that the silicone copolymer can effectively protect the silver nanoparticles only if its hydrophobic moiety content is sufficient to provide steric hindrance, and its hydrophile can interact with metallic ions before reduction.

Conclusions

Colloidal silver nanoparticles were synthesized in ethanol by the chemical reduction of Ag^+ ion with $NaBH_4$ under the protection of hydrophile-grafted silicone copolymers. Protective polymers with higher SHE60/Ag mass ratio stabilize the nanoparticles better. With the molar ratio of N/Ag being 7.3−9.2, the particle size is not influenced mainly by the hydrophile-content but rather is dominated by the hydrophobic moiety of the polymer. The lower pH of the precursor solution results in the larger average diameter of silver colloids, and serious agglomeration also was observed for cationic SQE60, strongly suggesting that the silicone copolymer of SHE can effectively protect the silver nanoparticle only if its hydrophile can interact with metal ion or nanoparticles.

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