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COLLOIDAL SILVER NANOPARTICLES PROTECTED BY WATER-SOLUBLE NONIONIC POLYMERS AND “SOFT” POLYACIDS

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ABSTRACT

Stable silver colloids were prepared by the *in situ* reduction of silver nitrate $AgNO_3$ in the presence of various protective poly-

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mers. Several nonionic polymers and polyacids, and one anionic polyelectrolyte were investigated for their ability to stabilize such silver colloids. UV-vis spectroscopy was employed to characterize the colloidally-stable silver samples, and the particle sizes, size distributions, and particle shapes were determined by transmission electron microscopy. The interactions among the silver precursors and colloids, and the polymeric matrices can have an influence on the nanoparticle features, the optical properties, and the long-term colloidal stability of the colloid dispersions.

INTRODUCTION

Nanosized, colloidal metal nanoparticles protected by polymers are known and have been technologically used for a very long time. New interest in these materials emerged, however, since they can be especially useful for many technological applications, due to the metal nanosizes and the related novel size effects and properties. Thus, interesting optical, catalytic, magnetic, and electronic properties can be expected from such nanometal-polymer composite materials [1-24].

Silver nanoparticles in the nanometer size-regime and protected by a polymeric matrix can find uses in many fields. Like gold, nanosized silver particles exhibit interesting optical properties. Depending on the particle size, shape, and agglomeration silver colloids can show a range of colors from the typical yellow, to orange, brown, and violet. Another important application for silver colloids is in catalysis: silver nanoparticles can be used as electron-transfer and storage [25-28] or oxidation catalysts [29, 30].

For many of these applications, the selection of the protective polymer matrix is crucial since it can ideally fulfill several functions. For instance, the polymer can influence the particle sizes and morphologies during the *in situ* preparation of the metal colloids, or it can also prevent the deactivation and destabilization of the metal colloids during storage and use.

A very important factor is the large influence the polymer has on the technological applicability of these metal-polymer systems. For instance, the selection of the protective polymer with its special properties such as surrounding the nanometal can be extremely important with respect to the modification of the catalytic and optical properties of the entire metal-polymer system. Therefore, it is important to investigate a broad variety of protective polymers for their ability to stabilize such metal colloids. Several types of polymers are of interest, and two groups are described below:

(1) Water-soluble homopolymers and random copolymers possessing a hydrophobic backbone to interact with the metal colloid surface, and hydrophilic side groups to interact with the polar dispersion medium, are often used for the stabilization of metal colloids [3]. For these flexible polymers the stabilization of the metal colloid is based on steric effects [1, 31].

(2) Polyelectrolytes are another interesting group since they combine both steric and electrostatic stabilization (that is, *electrosteric stabilization*), which can be of great importance for the long-term stabilization of metal colloids. Furthermore, they are interesting for a variety of technological applications, such as catalysis, since they can create an electrostatic environment surrounding the nanoparticles. In addition, polyelectrolytes can provide strong interactions with various metal precursor ions by the formation of ion pairs. Such interactions have already been shown advantageous for obtaining small particle sizes with narrow size distributions [21, 23].

For the present investigations several representatives of the polymer types described above were investigated for their ability to stabilize colloidal silver nanoparticles. Specifically, an anionic sulfonate polyelectrolyte and three polyacids (which are partially deprotonated in aqueous medium) were chosen, along with a selection of nonionic, water-soluble polymers for comparison. Two types of polyacids were employed, namely polysulfonic acids and one polyphosphonic acid, incorporating the “soft”, that is, easily-polarizable sulfur and phosphorus atoms. Such soft atoms can be expected to interact well with other soft species, such as Ag° or Ag^+ ions. The desired silver colloids were prepared from silver nitrate $AgNO_3$ precursor by *in situ* reduction with potassium borohydride KBH_4 in aqueous medium. In this case the precursor species is cationic, namely the Ag^+ aquo-complex. This should result in effects on the ionic interactions of the silver precursor ions with the polymer, the resulting nanoparticle features, and the colloidal stability of the samples for the different polymeric matrices involved. The particle sizes, shapes, and size distributions of the colloidal dispersions were investigated by transmission electron microscopy (TEM), and UV-vis spectroscopy was employed for additional characterization. The choice of the type of the protective polymer can have a large influence on the nanoparticle features, the optical properties, and the colloidal stability of the samples.

EXPERIMENTAL

Chemicals and Reagents

Silver nitrate ($AgNO_3$) and potassium borohydride (KBH_4) were obtained from Aldrich. The nonionic polymers and polyacids/polyelectrolyte were purchased from Aldrich and Polysciences. Table 1 lists the polymers employed, along with their origin and molecular weight.

Colloid Preparations

All glassware was cleaned with concentrated nitric acid before use. An aqueous solution of an excess of KBH_4 was prepared just before use and rapidly

TABLE 1. Origin and Molecular Weight of the Protective Polymers

Polymer	Company	Molecular Weight [a]
Nonionic polymers:		
Poly(N-vinyl-2-pyrrolidone-co-vinyl acetate) 60:40 (mol.)	Aldrich	$M_W \sim 50{,}000$
Poly(2-ethyl-2-oxazoline)	Aldrich	$M_W \sim 500{,}000$
Poly(N-vinyl-2-pyrrolidone)	Aldrich	$M_W \sim 360{,}000$
Poly(ethylene oxide)	Aldrich	$M_W \sim 900{,}000$
Polyacids and anionic polyelectrolyte:		
Poly(styrene sulfonic acid)	Polysciences	Not available
Poly(2-acrylamido-2-methyl-1-propane-sulfonic acid)	Aldrich	$M_W \sim 2{,}000{,}000$
Poly(vinyl phosphonic acid)	Polysciences	high
Poly(sodium, 4-styrene sulfonate)	Aldrich	$M_W \sim 70{,}000$

[a] M_W: weight-average molecular weight.

added to the stirred aqueous solutions containing $AgNO_3$ (6.8×10^{-4} M) and the polymers or the polyelectrolyte in a mass ratio of polymer:silver = 25:1. The reduction of the silver precursor could be observed immediately by the change of color from colorless to yellow.

Characterization

Transmission electron micrographs were taken with a JEOL-100 CX II transmission electron microscope (operating at an accelerating voltage of 80 kV) in order to obtain the sizes, shapes, and size distributions of the silver nanoparticles. The samples were prepared by placing a drop of the colloidal dispersion on a formvar/carbon-coated copper grid (placed onto a filter paper to remove excess solvent) and letting the solvent evaporate. The particle sizes were measured with a comparator, and the number-average particle sizes and size distributions were determined based on the measurement of 100-250 particles. The UV-vis spectra were recorded with a Milton Roy Spectronic 3000 Array instrument (10 mm pathlength quartz cuvettes) in the range 250 to 600 nm.

RESULTS AND DISCUSSION

Table 2 summarizes the results obtained by TEM, that is, the number-average particle size (and standard deviation) and the observed particle features for the silver colloids protected by the various nonionic polymers, polyacids, and the anionic polyelectrolyte. Similarly, Table 3 shows the respective UV-vis spectroscopic data obtained after the reduction, along with the color of the samples.

Nonionic Protective Polymers

For the nonionic polymers poly(N-vinyl-2-pyrrolidone-co-vinyl acetate) and poly(2-ethyl-2-oxazoline) stable silver colloids with average particle diameters below 10 nm were obtained. It is known that a higher hydrophobic character of the protective polymers is advantageous [3]. Less hydrophobic polymers, such as poly(ethylene oxide) of comparable molecular weight, resulted in poorly-stabilized samples, and the formation of precipitates occurred within a few days.

Poly(N-vinyl-2-pyrrolidone) (PVP) homopolymer is known and used as an efficient stabilizer for many metal colloids [1, 3, 4]. However, while the use of poly(N-vinyl-2-pyrrolidone-co-vinyl acetate) and poly(2-ethyl-2-oxazoline)

TABLE 2. Transmission Electron Microscopy Results for Silver Colloids

Polymer	Average Particle Size (nm) (Std.Dev.)	Particle Features
Nonionic polymers:		
Poly(N-vinyl-2-pyrrolidone-co-vinyl acetate) 60:40 (mol.)	6.7 (2.4)	Spherical, separate
Poly(2-ethyl-2-oxazoline)	2.9 (2.6)	Spherical, separate
Polyacids and anionic polyelectrolyte:		
Poly(styrene sulfonic acid)	7.3 (6.4)	a)
Poly(2-acrylamido-2-methyl-1-propane-sulfonic acid)	5.8 (2.7)	a)
Poly(vinyl phosphonic acid)	4.7 (7.6)	b)
Poly(sodium, 4-styrene sulfonate)	3.6 (4.4)	a)

a) Very small, spherical particles, coexisting with fewer larger, spherical ones.

b) Mostly spherical, separate particles, coexisting with fewer oval-shaped and close-to-spherical ones.

resulted in well-stabilized silver colloids, which could be stored for several months, less stable colloidal dispersions were obtained for PVP. This is in agreement with results obtained by Henglein [32] where PVP was also found to be a less efficient stabilizer for silver colloids in water than in ethanol, in comparison to other investigated polymers, such as polyethyleneimine. The results obtained here show that suitable random copolymers of PVP could be very effective for the long-term stabilization of colloidal silver nanoparticles. Specifically, an improved effect was observed for the poly(N-vinyl-2-pyrrolidone-co-vinyl acetate) copolymer investigated here, which resulted in well-stabilized silver col-

TABLE 3. UV-vis Spectroscopic Data for Silver Colloids Reduced by $KKBH_4$

Polymer	**Color**	**λ_{max} (nm)**	**FWHM (nm)**
Nonionic polymers:			
Poly(N-vinyl-2-pyrrolidone-co-vinyl acetate) 60:40 (mol.)	Yellow	401.7	82
Poly(2-ethyl-2-oxazoline)	Dark orange	415.7	86
Polyacids and anionic polyelectrolyte:			
Poly(styrene sulfonic acid)	Deep yellow	396.7	49
Poly(2-acrylamido-2-methyl-1-propane sulfonic acid)	Light yellow	396.3	42
Poly(vinyl phosphonic acid)	Yellow	404.2	74
Poly(sodium, 4-styrene sulfonate)	Orange	381.3	45

loids even for a long storage time of several months. The introduction of the vinyl acetate component apparently contributed to this benefit.

The TEM micrographs reveal largely spherical particles for poly(N-vinyl-2-pyrrolidone-co-vinyl acetate) and poly(2-ethyl-2-oxazoline), and Figure 1 shows a representative example for silver nanoparticles protected by poly(2-ethyl-2-oxazoline).

The results from the UV-vis spectroscopic investigations are listed in Table 3. The samples show a plasmon absorption band around 400-415 nm and a minimum near 320 nm, which is typically found for colloidal silver nanoparticles [33, 34]. The full bandwidths at half-maximum (FWHM) are about 85 nm for these nonionic protective polymers. A representative example for the UV-vis spectra is shown in Figure 2, for silver nanoparticles protected by poly(N-vinyl-2-pyrrolidone-co-vinyl acetate).

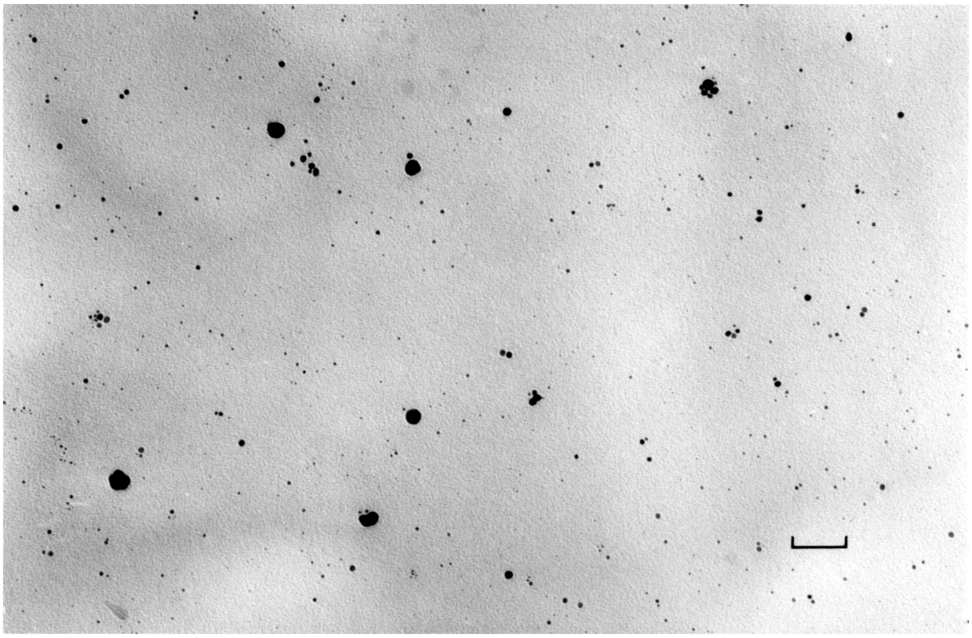

Figure 1. TEM micrograph of silver nanoparticles reduced from $AgNO_3$ by KBH_4 in the presence of poly(2-ethyl-2-oxazoline), average molecular weight M_w 500,000, (bar = 85 nm).

The dispersions remained yellow and were colloidally stable for several months, with no precipitation being observed. However, since the reductions were performed in aqueous solutions in air it has to be expected that the silver nanoparticles were partially oxidized on their surface during very long storage times, due to the sensitivity of the colloidal silver nanoparticles to oxygen in air [32].

Polyacids and Anionic Polyelectrolyte

The stabilizing effect of polycarboxylic acids for silver colloids has already been described in the literature, and is known to give long colloidal stability even in the presence of air [34-36]. This protective function of polycarboxylates has been ascribed to certain ligand properties towards various silver clusters [34]. Similarly, negatively charged monolayer surfaces (for instance, from phosphate or carboxylate acids) turned out to be necessary for the electro-

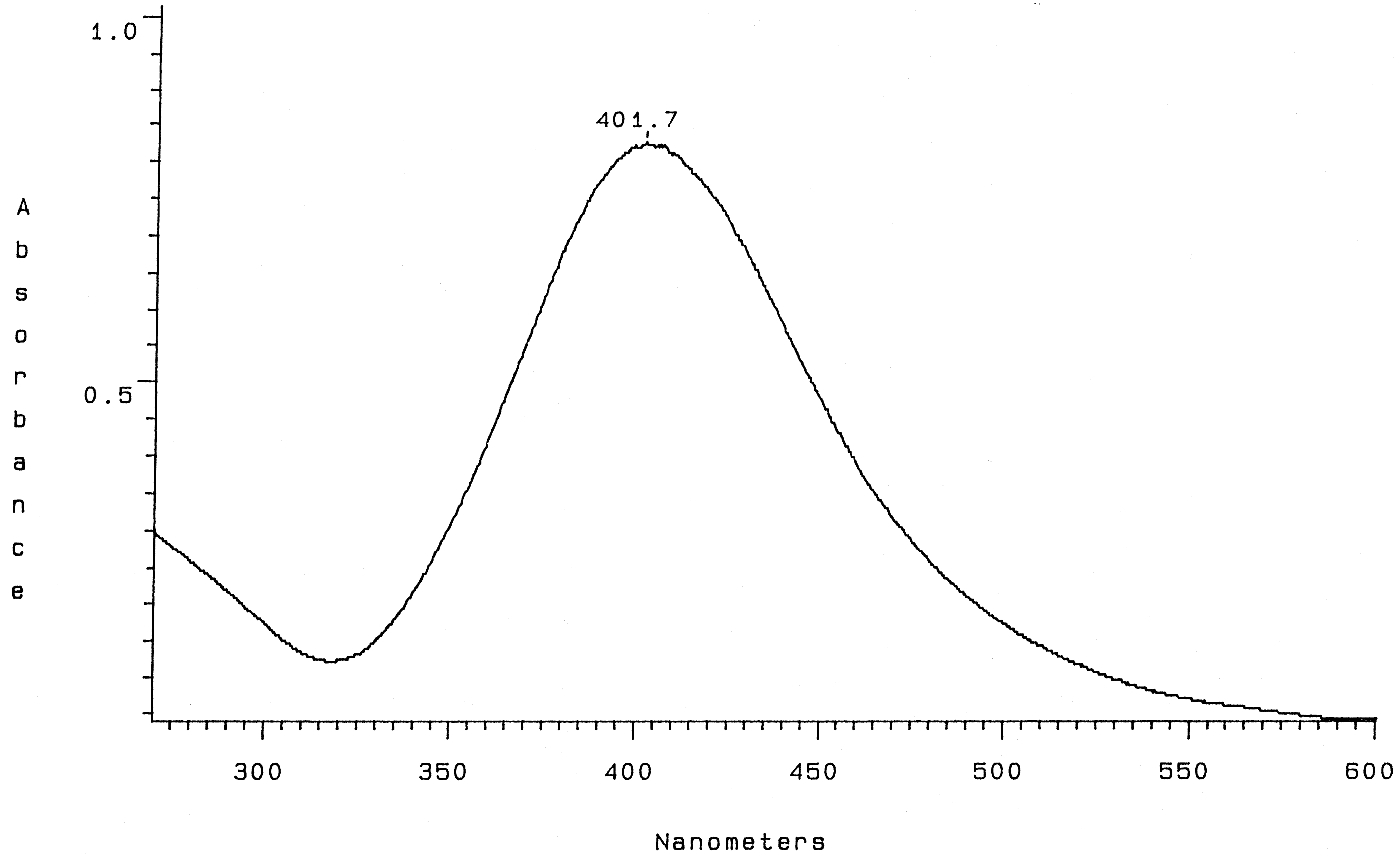

Figure 2. UV-vis spectrum for silver nanoparticles protected by poly(N-vinyl-2-pyrrolidone-co-vinyl acetate).

chemical generation of silver particles. They apparently provide "binding sites" for the silver ions Ag^+ [26, 37]. Finally, the presence of polyphosphate has been shown to provide a stabilizing effect for silver colloids [38].

For these investigations, polyacids incorporating soft atoms, such as sulfur and phosphorus, have been selected for study. According to the Pearson concept for soft and hard ions and atoms [39], it can be expected that such soft atoms can interact well with soft silver species, such as Ag^+ and Ag°. In water these polyacids are partially deprotonated, offering binding sites by ion pair formation with the Ag^+ precursor ions. In addition, ion exchange between the protons H^+ and the silver ions Ag^+ will easily occur. For this reason, one anionic polyelectrolyte, namely poly(sodium, 4-styrene sulfonate), incorporating the "soft" sulfonate group was selected. This polyelectrolyte contains the sodium cation Na^+ as counterion, which can be easily exchanged by the Ag^+ precursor ion.

As can be seen from Table 2, all investigated samples resulted in stable colloids with particle diameters below 10 nm. They did not show any precipitation even after storage in air and in the dark for several months. Usually, small spherical silver nanoparticles, coexisting with a few larger ones were observed for these samples. A representative TEM micrograph for silver nanoparticles protected by poly(2-acrylamido-2-methyl-1-propane sulfonic acid) is shown in Figure 3.

In contrast to the other polyacids and the anionic polyelectrolyte investigated, the poly(2-acrylamido-2-methyl-1-propane sulfonic acid) sample turned from yellow to colorless during a longer storage period of several months. This is an indication for complex formation of the silver species with the polymer, probably due to the amido groups being present in this polymer. A similar exception was found in the use of poly(methacrylamidopropyltrimethyl ammonium chloride), which resulted in less-stabilized silver colloids accompanied by the decolorization of the dispersion. This was in strong contrast to that of other cationic polyelectrolytes investigated [40].

The UV-vis spectra also show typical plasmon absorption bands for silver colloids, located at around 380-405 nm. Figure 4 shows the UV-vis spectra for an example, namely, silver colloids protected by poly(styrene sulfonic acid). The bandwidths are smaller than for the samples prepared in the presence of the nonionic polymers, and the absorption maxima are shifted towards shorter wavelengths ("blue shift"), especially for the poly(sulfonic acid) samples. Such blue shifts are typical for the sorption of nucleophilic species on the surface of colloidal silver particles [41], resulting in the accumulation of electrons and the polarization of the silver nanoparticles [41]. Blue shifts could be also due to

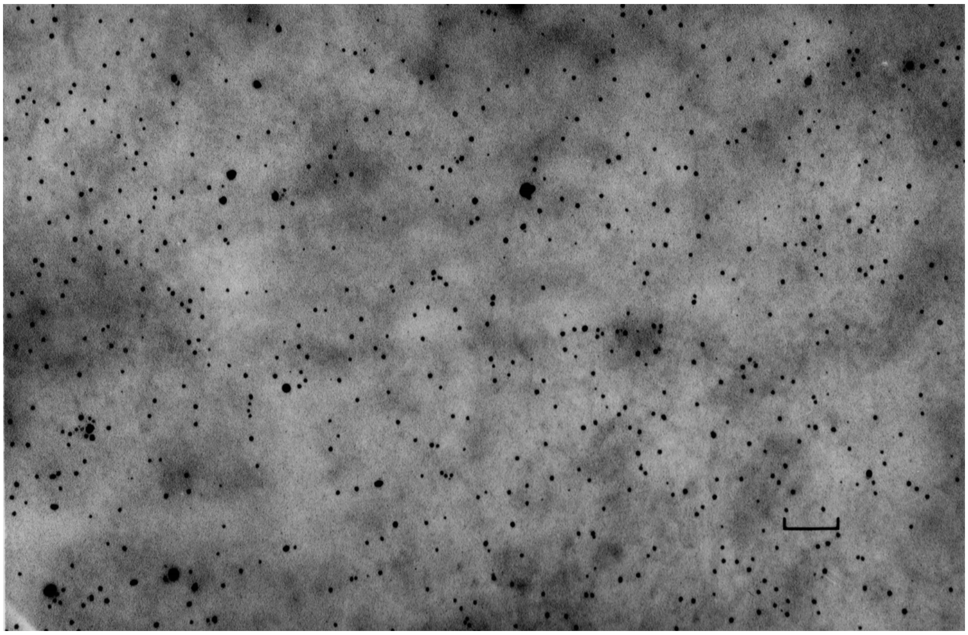

Figure 3. TEM micrograph of silver nanoparticles reduced from $AgNO_3$ by KBH_4 in the presence of poly(2-acrylamido-2-methyl-1-propane sulfonic acid), (bar = 112 nm).

smaller particle sizes; however, in this case they would also be accompanied by an increase in bandwidth. Since smaller bandwidths are found here for the freshly prepared samples, the main effect stems from the interaction of the anionic polymer species with the silver colloid surface. Also, the TEM results show that the average particle diameters are not significantly smaller for the samples using the polyacids than for the ones employing the nonionic polymers. Therefore, the blue shifts are an indication for strong interactions between these protective polymers and the silver colloids.

The blue shift and narrowing of the full width at half maximum (FWHM) is less pronounced for the poly(vinyl phosphonic acid), indicating a weaker interaction and electron transfer than for the poly(sulfonic acid) species. This could be due to a less soft character of the phosphorous in comparison to sulfur, and a different "ligand quality" towards the silver species (Ag^+ or silver clusters). Further investigations with a series of different polyacids should be interesting for clarifying a possible interpretation in terms of the "soft/hard-principle".

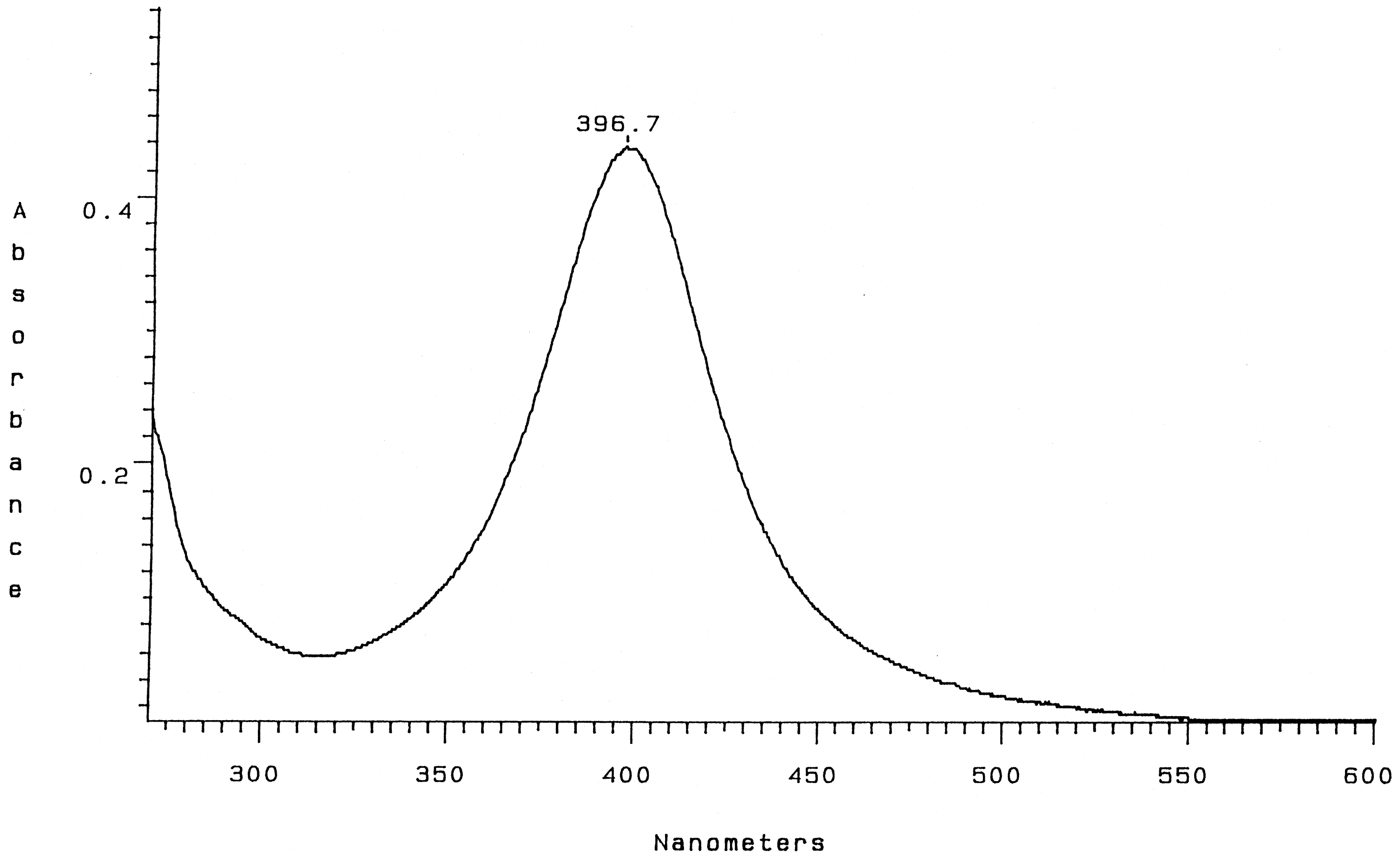

Figure 4. UV-vis spectrum for silver nanoparticles protected by poly(styrene sulfonic acid).

CONCLUSION

Several nonionic polymers and “soft” polyacids were found to be suitable as efficient stabilizers for silver colloids, and particle sizes below 10 nm could be obtained in many cases. The choice of the protective polymer has an influence on the optical properties of the resulting polymer-metal system. The polyacids incorporating soft atoms, especially sulfur, show strong interactions with the silver colloid surface (as can be seen from the UV-vis spectroscopic shifts), indicating electron transfer with the silver colloid surface. This could also result in protection from oxidation, at least for a certain amount of time.

Future research should involve the investigation of an extended series of polyacids and anionic polyelectrolytes, including carboxylic acid types, to compare the interactions between soft-atom and hard-atom polyacids with silver colloid surfaces.

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