Reduction of Ag$^+$ on Polyacrylate Chains in Aqueous Solution

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Silver ions are reduced in aqueous solutions that contain sodium polyacrylate or partly carboxylated polyacrylamide or glutaric acid. The reducing agent is the hydrated electron (generated γ-radiolytically) or hydrogen. Complexes of small silver clusters with the polyelectrolyte are formed in the early stages of reduction, the color of the solutions varying from rose to green or blue depending on the size of the complexed silver clusters. In the case of 10% carboxylated polyacrylamide, large colored complexes are not formed, which indicates that a high carboxylate density along the polymer chain is necessary for their formation. The complexes are stable toward heat (100 °C) and oxygen. In the later stages of reduction, the long-wavelength absorptions of the silver−polyacrylate complexes disappear. The UV absorption bands of a magic cluster (probably Ag$_9^+$) are present during a short time interval, until the plasmon absorption band of metallic nanoparticles develops at 380 nm. The colored clusters react with ammonia and cyanide to form large silver particles through the intermediate stage of the magic cluster.

Introduction

Intermediate clusters consisting of a small number of atoms are often observed when silver ions are reduced in aqueous solution in the presence of a polyanion such as sodium polyphosphate[1] or sodium polyacrylate.[2,3] The clusters are stabilized on the polymer chains by interacting with the functional groups of the polymers, the Coulomb repulsion between the chains preventing the clusters from coming easily into close contact. These stabilized clusters can live for hours and days; one can therefore carry out many chemical reactions with them.[3,4] They have absorption bands in the visible and UV, which enables one to follow their formation and disappearance by simple spectrophotometric measurements.

The clusters formed in the presence of polyacrylate are of special interest. In the first stages of Ag$^+$ reduction, the solution acquires a rose or blue color, and the species that produce these colors are unreactive to oxygen. Upon further reduction, these colors gradually disappear and the 380 nm plasmon band of nanometer-sized metallic silver particles finally appears.[3,5−7] The rose species was tentatively attributed to an Ag$_4^{2+}$PA$^-$ complex[3] and the blue species to a larger Ag$_{m+n}^{m+}$PA$^-$ complex.[5,6] Most recently, the scanning tunneling micrograph of a solution of the blue species was interpreted as showing clusters consisting of seven or eight silver atoms.[8] In the present paper, a few new observations are reported on the development of the colored clusters in solution, and we also offer a confirmative view about the nature of the species that was seen in the STM study of ref 8.

Experimental Section

The solutions were in glass vessels, which were deaerated by evacuation or bubbling with argon. The vessel carried a
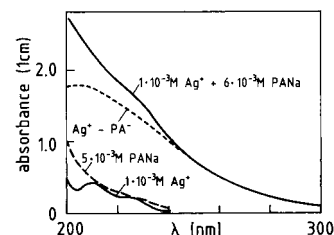

Figure 1. Absorption spectra of solutions containing AgClO$_4$ or PANa or both solutes.

sidearm with an optical cuvette to allow spectrophotometric measurements without bringing the solution into contact with air. γ-Irradiations were carried out in the field of a ^{60}Co source.

Sodium polyacrylate, PANa (MW: 2100), was purchased from Fluka. In some experiments, polyacrylamide (PAA) containing carboxylate groups was used as the complexing reagent; samples with 10% (PAA-10) and 70% (PAA-70) carboxylate content were obtained from Acros Organics. Sodium glutarate, NaOOC−CH$_2$−CH$_2$−CH$_2$−COONa, was used as an "oligomeric substituent" of polyacrylate. Note that the density of adjacent carboxylate groups along the chain of these stabilizers decreases in the sequence PANa, PAA-70, PAA-10, and glutarate. Polymer concentrations are given in base-mol/L, M.

The reducing reagent is the hydrated electron that is formed in the radiolysis of the aqueous solvent. The solutions also contained 2-propanol to scavenge the hydroxyl radicals that are generated simultaneously.

Results

Figure 1 shows the spectrum of a solution containing 1.0 × 10^{-3} M AgClO$_4$ and 6.0 × 10^{-3} M sodium polyacrylate (PANa). This spectrum may be compared to the spectra of the single

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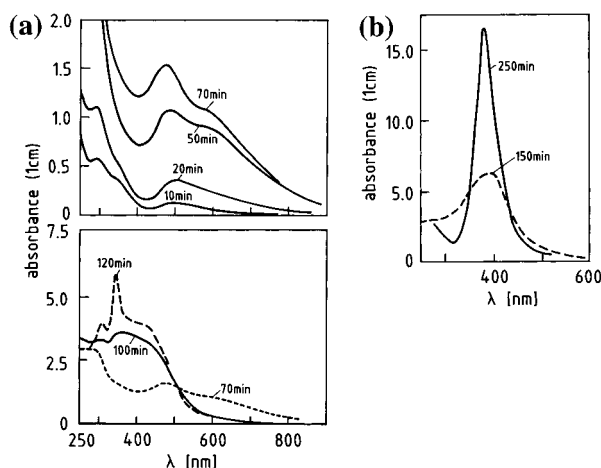* To whom correspondence should be directed.

Figure 2. (a) Absorption spectrum at various times of γ-irradiation of a solution containing 1.0×10^{-3} M AgClO$_4$, 0.1 M PANa, and 0.5 M propanol-2. Note the different ordinate scales. (b) Absorption spectrum at longer irradiation times. Solution as in Figure 2a

components in Figure 1. It can be seen that the absorption maxima of the free silver ion at 210 and 226 nm have disappeared. It is concluded that practically all the Ag$^+$ ions are complexed by the anion groups of the polyelectrolyte. The spectrum of 5.0×10^{-3} M polyacrylate was subtracted from the spectrum of the mixture; this difference spectrum is also shown in the figure and attributed to the Ag$^+$$-PA^-$ complex itself. In the following reduction experiments a high polymer-to-silver ratio was chosen to make sure that practically all silver ions were complexed, i.e., that the reduction of Ag$^+$ occurred on the polymer matrix.

Parts a and b of Figure 2 show the optical spectrum of a solution containing 1.0×10^{-3} M AgClO$_4$, 0.1 M PANa, and 0.5 M 2-propanol at various times of γ-irradiation. The dose rate was 5.6×10^2 Gy/h. After 10 min, the solution had a rose color, absorption maxima are present at 290 and 480 nm, and a weak shoulder is seen at 350 nm. At longer irradiation times, an intense blue color develops; the 350 nm shoulder is no more observed, and a strong absorption over the whole visible range is present (upper part of figure). At still longer times (lower part), the long-wavelength absorption disappears (>500 nm), and for a short time interval two rather sharp bands at 310 and 345 nm are present until the well-known plasmon absorption band of metallic silver particles at 380 nm is finally produced (Figure 2b). At the dose rate applied, 2×10^{-4} M hydrated electrons are generated per hour. To reduce 1.0×10^{-3} M Ag$^+$, about 5 h of irradiation are required (see spectrum at 250 min in Figure 2b). Thus, a lot of excess silver ions are still present at the shorter times shown in Figure 2a, where the spectra of the oligomeric precursors are present.

Colored species were also formed in the early stages of irradiation when the PANa concentration was decreased down to 0.01 M; the colors observed were rose, green, or blue depending on the polymer concentration. All the colored solutions were transparent without any opalescence. Similar effects have in principle been observed by Mostafavi et al.[5,8,9] The important observation in the present investigation is the detection of the intermediate absorption bands at 310 and 345 nm. These bands are known to belong to a "magic" silver cluster of special stability, which is positively charged and contains an even number of valence electrons. The structure of Ag$_9$$^+$ has been attributed to this species,[10,11] although it cannot be distinguished from the structure of Ag$_8$$^{2+}$.[12] Its absorption spectrum resembles the spectra of Ag$_8$ and Ag$_9$ in an argon
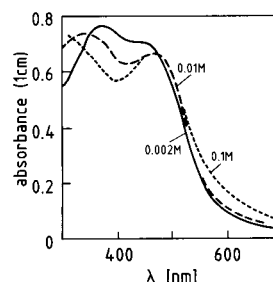

Figure 3. Absorption spectrum of an irradiated solution containing 1.0×10^{-3} M AgClO$_4$, 0.1 M 2-propanol, and various concentrations of PAA-10, with 20 min γ-irradiation.

matrix at low temperature.[13] This cluster is also formed when polyphosphate is the stabilizer (where it absorbs at slightly shorter wavelengths),[3] and it has even been observed with a lifetime of minutes in solutions that did not contain any stabilizer.[11] One has to conclude from the observations in Figure 2 that the various colored species that are formed in the very early stages of reduction are the precursors of Ag$_9$$^+$.

The same effects as in Figure 2 were observed when 0.01 M PAA-70 was used as a stabilizer.

However, with PAA-10 solutions up to 0.1 M the blue absorption in the beginning of irradiation was not produced, although the rose color appeared for a short time period. Figure 3 shows typical spectra of solutions containing 1.0×10^{-3} M Ag$^+$, 0.1 M 2-propanol, and PAA-10 in various concentrations. One can see that the 480 nm band that produces the rose color is present at all three polymer concentrations. In addition, the 380 nm band of metallic particles is present. At longer irradiation times (not shown in Figure 3), the 380 nm band grew strongly and the 480 nm band disappeared. When 0.05 M glutarate was present as stabilizer, no rose or blue coloring at all took place under γ-irradiation. A yellow color developed immediately, and the absorption spectrum contained the 380 nm plasmon band of large colloidal silver particles. Thse findings show that the formation of the long-lived rose and blue silver$-$acrylate complexes strongly depends on the density of adjacent carboxylate groups along the stabilizer chain.

The blue absorption of the complexes is also produced when the reduction of the Ag$^+$ ions is brought about by hydrogen. In the experiment of Figure 4, a solution of 1.0×10^{-3} M AgClO$_4$, 0.1 M PANa, and 1.0×10^{-3} M NaOH was kept under a hydrogen atmosphere and the spectrum recorded at various times. In the absence of the polyelectrolyte, H$_2$ does not reduce the silver ion at ambient temperature. However, the reaction takes place, as can be seen from the changes in the absorption spectrum (Figure 4a). In the beginning, the bands at 480 nm and then around 600 nm develop, which later on decrease in intensity, as new bands at shorter wavelengths appear. The reduction is much slower than in the γ-experiment of Figure 2; after 40 h in Figure 4b, an intermediate stage is reached, where maxima at 420 and 345 nm are seen. At much longer times (not shown in Figure 4), the 380 nm band of metallic silver is present.

The blue complexes are very stable. Exposure to air does not lead to any reoxidation. Heating of a solution for 1 h at 100 °C resulted only in a 10 nm blue shift of the absorption band at long wavelengths without a decrease in the intensity of the band.

The silver$-$polyelectrolyte complexes formed in the early stages of reduction undergo thermal changes upon aging.[5,6] Figure 5 shows a typical example. It can be seen that the absorption maximum is red-shifted upon long-time aging. The
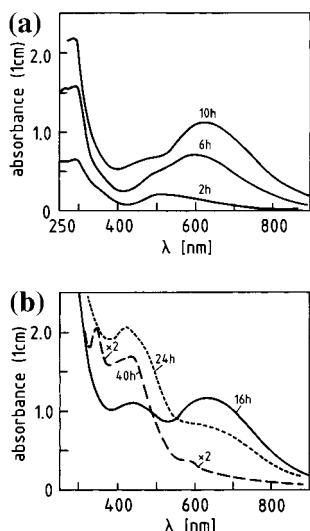
(a)

(b)

Figure 4. (a) Absorption spectrum at various times of reduction by hydrogen. Solution is 1.0×10^{-4} M AgClO$_4$, 0.1 M PANa, 1.0×10^{-3} M NaOH. (b) Absorption spectrum at longer times of H$_2$ reduction. Solution is as in part a.
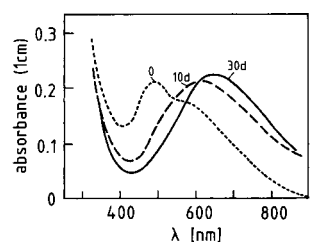

Figure 5. Absorption spectrum (0) of a solution (Figure 2) after 50 min γ-irradiation and after two periods of aging.
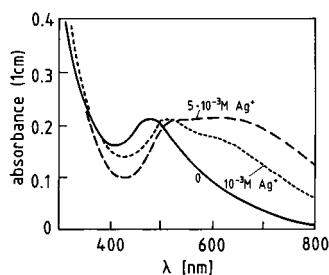

Figure 6. Spectrum of slightly reduced solution before (0) and after two additions of AgClO$_4$. Solution is 2.0×10^{-4} M AgClO4, 0.01 M PANa, 0.1 M 2-propanol, with γ-irradiation of 10 min.

absorption spectrum of complexes is also changed when silver salt is added to the solution. This is demonstrated by Figure 6, where the spectra after partial Ag$^+$ reduction and after two subsequent additions of AgClO$_4$ are shown. The absorption band is immediately shifted to longer wavelengths when the Ag$^+$ concentration is increased.

The colored complexes are reactive toward nucleophilic reagents. In the experiment of Figure 7, 0.1 M ammonia was added to a solution containing blue complexes. The long-wavelength absorption disappeared immediately, and a spectrum was observed that contained the 310 and 345 nm absorption bands of Ag$_9^+$ as well as a band at 420 nm. The latter is attributed to larger metallic particles; it is well-known that larger or agglomerated silver particles have their absorption maximum at a wavelength substantially longer than 380 nm. Addition of 1.0×10^{-3} M KCN had a similar effect; the long-wavelength absorption disappeared, and the solution contained the plasmon band of larger silver particles at 420 nm.
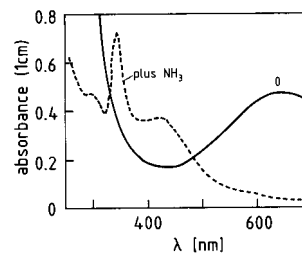

Figure 7. Spectrum of a solution containing silver–polyacrlate complexes before (0) and after the addition of 0.1 M ammonia. Solution is 1.0×10^{-3} M AgClO$_4$, 0.01 M PANa, and 0.1 M 2-propanol.

Discussion

It is shown here that early reduction products of silver are stabilized on polyacrylate chains. The very first product in the reduction of Ag$^+$ by the hydrated electron is the silver atom.[14] It rapidly reacts with an Ag$^+$ ion to produce the cluster Ag$_2^+$. These reactions must occur on the polymer chains in the present experiments, since all the Ag$^+$ ions are bound to the polymer. In the absence of polymer, Ag$_2^+$ produces Ag$_4^{2+}$ in a bimolecular reaction. Ag$_4^{2+}$ then builds up Ag$_9^+$, which lives for minutes until larger metallic silver particles are formed.[10,11] In the presence of 0.1 M polyelectrolyte, these various reactions are affected, since the intermediates are more or less stabilized by interacting with the anion groups of the polyelectrolyte. In fact, their lifetime is so much increased that they can be detected by conventional spectrophotometry. In the following pulse radiolysis paper, some information is obtained about the rates of these very early processes in the presence of polyacrylate. A previous pulse radiolysis experiment on the action of polyphosphate as stabilizer had already shown that certain processes are very strongly retarded.[15]

The exact structure of the colored complexes is not known. These complexes are present at a stage of reduction when a lot of nonreduced silver ions still are present (Figure 2a). It is therefore plausible that the complexes contain reduced and nonreduced silver; the rose complex was earlier thought to be the Ag$_4^{2+}$–PA$^-$ species.[3] The blue complexes are larger species, which are possibly formed by condensation of smaller complexes along the polymer chain. Mostafavi et al.[6,8] speak of spherical clusters consisting of a small number of silver atoms and silver ions, (Ag$_{4+m}$)$^{m+}$, which are complexed by the carboxylate groups of the polyelectrolyte. Our experiments with partly carboxylated polyacrylamide allow us to discuss the complexing phenomenon in more detail. When PAA-70 is used as the complexing agent, all colored clusters from rose to blue are formed as with PANa. However, in the presence of PAA-10, the blue species are not formed, not even under conditions where the overall concentration of carboxylate groups is the same as for PANa. In PAA-10, several carboxylate groups are rarely adjacent to each other along the polymer chain. We have to conclude that the stable blue complexes are formed only when the carboxylate groups have a high density along the chain. Or in other words, adjacent carboxylate groups are involved in the formation of the blue complexes. It could be that one is dealing with a linear chain of silver atoms and a roughly equal number of silver ions along the polyelectrolyte matrix, the positive charges being more or less delocalized along the chain and the position of the absorption maximum depending on the length of the chain. The optical transition involved is possibly an acrylate $\rightarrow$ silver charge transfer. In fact, the distance of 2.5 Å between two adjacent carboxylates in an aligned segment of the polymer is close to the distance of 2.6–2.8 Å between the

silver atoms in typical silver clusters.[16] The effect of a large excess of Ag^+ ions (Figure 6) is explained by an increase in chain length due to the condensation of rose clusters along the chain to buildup the blue ones.

Upon further reduction, the colored clusters break apart because of the fact that they contain less positive charges. This is why Ag_9^+, i.e., a smaller cluster, is seen as an intermediate stage to the formation of large colloidal particles.

It was not yet possible to produce the blue complexes in a concentration high enough for the application of physical structure-detection methods such as X-ray scattering. A silver atom chain can hardly be expected to be seen in the electron microscope. However, a cluster consisting of about eight silver atoms has been seen in the STM study of dried samples of the blue clusters. It was thought to be the result of the complete reduction of the blue precursor $(Ag_{m+4})^{m+}$.[8] The cluster observed *in the STM* is probably related to the magic cluster (Ag_9^+ or Ag_8^{2+}) observed in the present study as a result of the partial reduction of the initial blue clusters *in solution*.

The fact that Ag^+ is reduced by H_2 in the presence of PANa appears remarkable, since this reduction does not occur at ambient temperature in the absence of the polyelectrolyte. The great stabilization of the reduction product must be the reason for the ease of the reduction. One cannot expect that free silver atoms (whose redox potential is -1.8 V^{17}) are first formed as in the reduction by hydrated electrons. We propose that an H_2 molecule transfers two electrons to two silver ions, which are bound near the polyelectrolyte chain, to yield a small complex as the first reaction product, which then grows by additional reduction of adjacent Ag^+ ions.

The complexes are very sensitive toward reagents that strongly interact with silver ions, such as Cl^-,[5,6] ammonia, and cyanide. The removal of the positive charges in the complexes leads to the detachment from the polymer. Similarly, prolonged reduction destabilizes the complexes, and the destabilized silver aggregates can then coalesce to yield larger metallic silver particles. Under the conditions of our present experiments, these growth processes are relatively slow. The 310 and 345 nm absorptions of Ag_9^+ are seen in an intermediate time range until larger metallic particles are present.

Summary

It is shown that the rose and blue silver−polyacrylate complexes are the first reduction products of silver ions in the presence of polyacrylate. The "magic" cluster Ag_9^+ (or Ag_8^{2+}) is formed in the reduction of the colored complexes before larger silver particles are finally formed that possess the typical plasmon absorption band of this metal. A resonance-charge-transfer chain structure of the complexes at the polymer matrix is proposed as well as a mechanism for the reduction of Ag^+ by H_2 on polyacrylate chains.

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