

Time-Resolved Investigation of Early Processes in the Reduction of Ag^+ on Polyacrylate in Aqueous Solution

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Aqueous solutions of AgClO_4 (4×10^{-4} to 10^{-2} M) and sodium polyacrylate (0.1 M, mean chain length of 30) are exposed to a pulse of high-energy radiation, and the changes in optical absorption are recorded in the time range from microseconds to seconds. The reduction of Ag^+ by the hydrated electron is slowed by the polyanion, whereas the subsequent reaction of Ag^0 with Ag^+ is practically not affected. Polymer-bound Ag_2^+ has two absorption bands (310 and 440 nm). The formation of Ag_3^{2+} in the reaction of Ag_2^+ with Ag^+ is strongly retarded by the polyanion; it occurs in an interchain process at low Ag^+ concentrations and probably also as an intrachain process at higher ones. Polymer-bound Ag_3^{2+} has a broad UV absorption tailing into the visible. At longer times after the pulse (up to seconds), bimolecular interchain processes take place in which colored complexes are formed, which at first contain a small number of silver atoms and an approximately equal number of Ag^+ ions, and are stabilized by the polyanion chains.

Introduction

In the preceding paper,¹ the early steps of the γ -radiolytic reduction of silver ions in aqueous polyacrylate solution were investigated. The Ag^+ ions are strongly adsorbed on the polymer chains when polyacrylate is present in substantial excess. The reduction occurs through the hydrated electrons that are formed in the radiolysis of the aqueous solvent. Silver atoms are formed, which then are complexed by Ag^+ ions, and subsequently, oligomeric clusters appear through coalescence processes. The affinity of some clusters to the polymer is so great that they form stable complexes with polyacrylate of practically infinite lifetime. These complexes are colored rose, green, or blue depending on the size of the clusters. They can be observed spectrophotometrically in the early stages of silver ion reduction, i.e., when less than about 30% of the Ag^+ ions are reduced. At higher degrees of reduction, the complexes, which are composed of roughly an equal number of silver atoms and ions, are further reduced, and larger clusters and finally metallic nanoparticles consisting of thousands of atoms are present.

In the present paper, pulse radiolysis is used to study time-resolved the very early steps that lead to the colored complexes. A solution of AgClO_4 and sodium polyacrylate is exposed to a short pulse of high-energy radiation, and the changes in absorption are recorded after the pulse in the 10^{-7} s to seconds range. Only a small fraction of the silver ions is reduced during the pulse. A similar study has previously been made by other authors.² The results obtained in the present study are different, since those authors missed some very early events. This difference is probably due to the fact that they used silver sulfate as the silver source; the sulfate ion strongly complexes silver clusters and thus accelerates their coalescence.³

Pulse radiolysis has previously been used to study the atom-to-metal transition of silver in the absence of a stabilizing

polymer.⁴ Naturally, the time-resolved observation of particle growth is of great interest to colloid chemistry. For the reader who compares our particle growth experiments with chemically initiated particle growth, we should point out a significant difference. In a pulse experiment, reduction takes place only during the pulse, and particle growth is solely due to coalescence processes. On the other hand, nuclei are generally generated in a chemical reduction, and larger particles are formed to a large extent via further reduction on the surface of the nuclei.

Experimental Section

The high-energy electrons (3.8 MeV) were produced in a Van de Graaff generator. The pulse length was 200 ns. The apparatus and computer software have previously been described.⁵ The concentration of the hydrated electrons that were generated in the pulse was determined from the absorption change at 700 nm, knowing the absorption coefficient of e_{aq}^- ($1.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and its radiation chemical yield (2.7 electrons per 100 eV absorbed radiation energy). Electron concentrations of 1.0×10^{-6} to 2.5×10^{-5} M were generated. In the presentation of the data, "specific absorbances" in $\text{mol}^{-1} \text{ L cm}^{-1}$ ($\text{M}^{-1} \text{ cm}^{-1}$) are given; the observed absorbance changes were divided by the concentration of the generated electrons and the thickness of the optical cell.

The solutions were deaerated by bubbling with pure argon prior to irradiation. Sodium polyacrylate 2100, PANa, was purchased from Fluka; the mean chain length is 30 (according to the commercial producer). The concentration of the polymer is given in base-mol/L, if not stated otherwise. The polyacrylate to Ag^+ concentration ratio was so high that practically all silver ions were bound to the polymer chains (see Figure 1 of the preceding paper).

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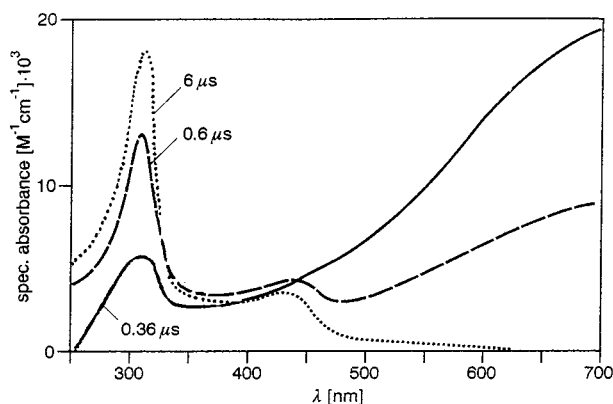
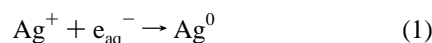


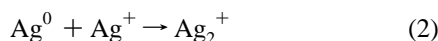
Figure 1. Absorption spectrum at various times (in the microsecond range) after the pulse. Solution is 4.0×10^{-4} M AgClO_4 , 0.10 PANa, 0.5 M 2-propanol. Concentration of hydrated electrons generated is 1.0×10^{-6} M.

Results

Figure 1 shows the absorption spectrum at various times after the pulse (up to $6.0 \mu\text{s}$). The solution contained 4.0×10^{-4} M Ag^+ and 0.1 M polyacrylate. It also contained 0.5 M 2-propanol to scavenge the hydroxyl radicals that are formed in the radiolysis of the aqueous solvent. Shortly after the pulse, the spectrum is dominated by the 700 nm absorption of the hydrated electron, although weak absorptions at 310 and 440 nm are also present on the UV tail of the broad absorption band of e_{aq}^- . The 700 nm absorption decays rapidly, and the absorption bands at 310 and 440 nm grow. The last two bands belong to the same species, since they develop at the same rate. The decay of the 700 nm absorption follows pseudo-first-order kinetics. A rate constant of the reaction



of $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ was obtained. This value is smaller than the value of $4.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which was observed for the reaction in the absence of polyacrylate.⁴ The Ag^0 atom formed in reaction 1 is very short-lived in the presence of Ag^+ ions, since it reacts according to



Free Ag_2^+ absorbs only at 310 nm.^{6,4} The absorption band 440 nm in Figure 1 is attributed to the interaction of the Ag_2^+ with polyacrylate.

The absorption spectrum at longer times after the pulse (up to $250 \mu\text{s}$) is shown in Figure 2. As the 310 nm absorption of Ag_2^+ disappears, a broad absorption ranging over the whole wavelength range and with a weak maximum in the 350–400 nm region is built up. Note also that only an unstructured tail of the absorption extends into the visible (i.e., there is not yet an absorption maximum of a colored complex). Figure 3 shows the temporal absorbance changes at different wavelengths. The kinetic curves reach a plateau at about $250 \mu\text{s}$.

Both the decay of the Ag_2^+ absorption and the buildup of the new absorptions are accelerated by Ag^+ ions. In the experiment of Figure 4, the kinetic curves at 500 nm are shown for different Ag^+ concentrations. One can see that the buildup of the 500 nm absorption becomes faster with increasing Ag^+ concentration. Similar curves at 420 nm were also recorded. Note that the specific absorbance in Figure 4 after $250 \mu\text{s}$, i.e., when the plateau is reached, is greater the higher the Ag^+ concentration (although the same amount of reducing electrons had been

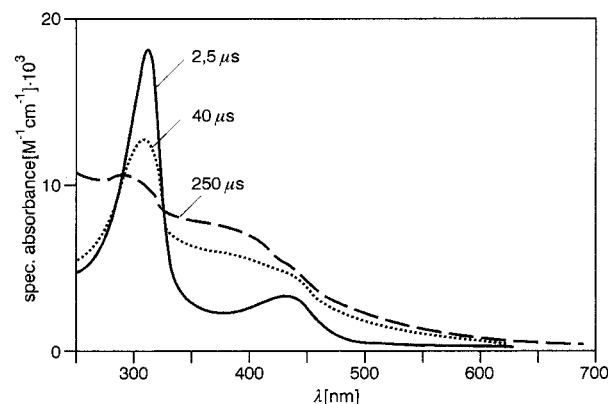


Figure 2. Absorption spectrum at longer times (up to $250 \mu\text{s}$). Solution is as in Figure 1.

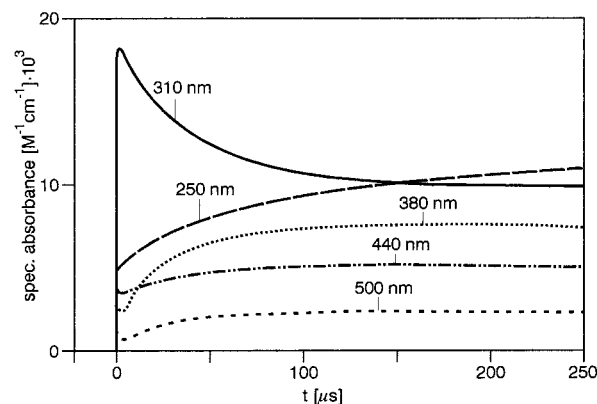


Figure 3. Kinetic curves at various wavelengths. The decay of Ag_2^+ at 310 nm essentially occurs simultaneously with the buildup of the absorptions at longer wavelengths. Solution is as in Figure 1.

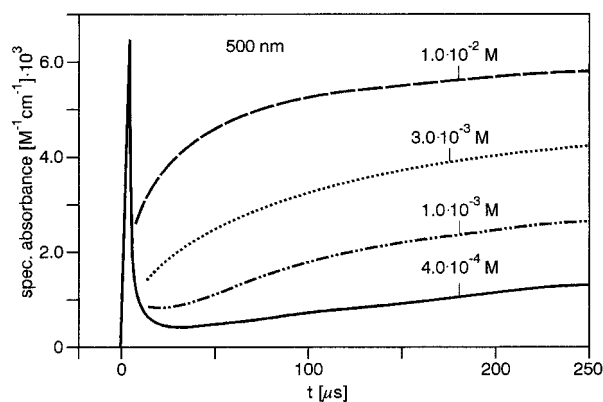


Figure 4. Kinetic curves at 500 nm. PANa concentration is as in Figure 1, but Ag^+ concentrations are different. The peak in the very beginning is due to the hydrated electron, and the minimum in the lower curves is due to the last traces of e_{aq}^- . Note the different ordinate scales in a comparison with Figures 1–3.

generated). Figure 5 shows the temporal changes in the absorption spectrum at the highest Ag^+ concentration of 10^{-2} M. The product now has a more pronounced absorption maximum in the 350–400 nm region than at the lower Ag^+ concentration in the experiment of Figure 2.

Figure 6 is a double-logarithmic plot of the half-life time of the buildup of the 500 nm absorption (from Figure 4) vs the Ag^+ concentration. It can be seen that the half-life time decreases with increasing silver ion concentration. The rate of the process involved does not depend on the dose, since the curves in Figure 4 did not change when stronger electron concentrations were generated in the pulse. Figure 6 also

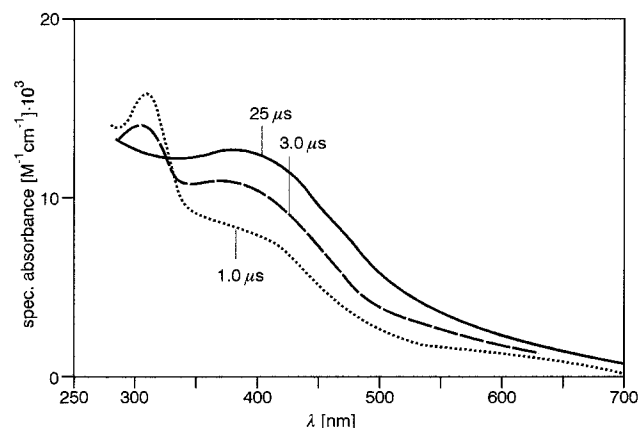


Figure 5. Absorption spectrum at different times. $[\text{AgClO}_4] = 1.0 \times 10^{-2} \text{ M}$.

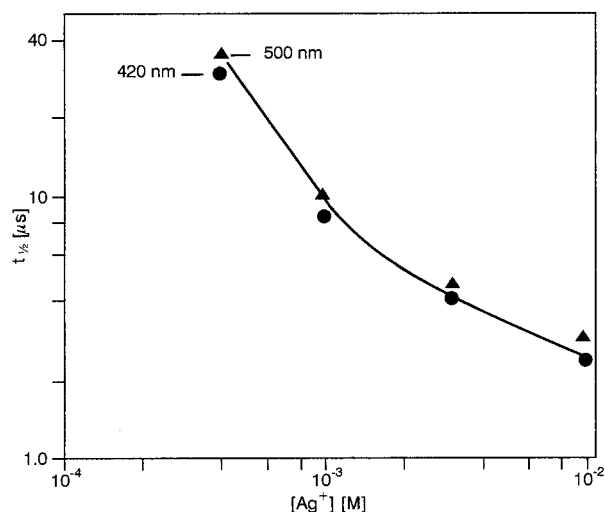
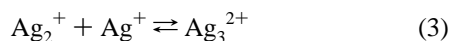


Figure 6. Half-life time of the buildup of the 420 and 500 nm absorptions (from Figure 4) as a function of the Ag^+ concentration. In a comparison with Figures 1–3, note the different ordinate scale.

contains measurements at 420 nm. It should also be mentioned that the 310 nm absorption decayed faster with increasing Ag^+ concentration. All these observations indicate a reaction of Ag_2^+ with Ag^+ :



The rate constant, as derived from the slope of the curve in Figure 6 at Ag^+ ion concentrations below 10^{-3} M is $6.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Reaction 3 has previously been observed in solutions that did not contain the polymer.⁷ The rate constant was found to be $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ under these conditions, i.e., very much higher than in the presence of the polymer, and the equilibrium lay on the right-hand side. Polymer-bound Ag_3^{2+} and Ag_2^+ have absorptions at longer wavelengths that the free species do not possess.

For $[\text{Ag}^+] < 10^{-3} \text{ M}$, the slope of the curve in Figure 6 is close to 1.0, as expected for a pseudo-first-order reaction. However, at the higher silver ion concentrations, where the half-life time amounts to only a few microseconds, the slope becomes smaller. This is the range where intrachain reactions are expected to occur (see below).

At times much longer than shown in Figures 3 and 4, a new process occurs. The broad absorption of polymer-bound Ag_3^{2+} decays at long wavelengths, and a stronger UV absorption band

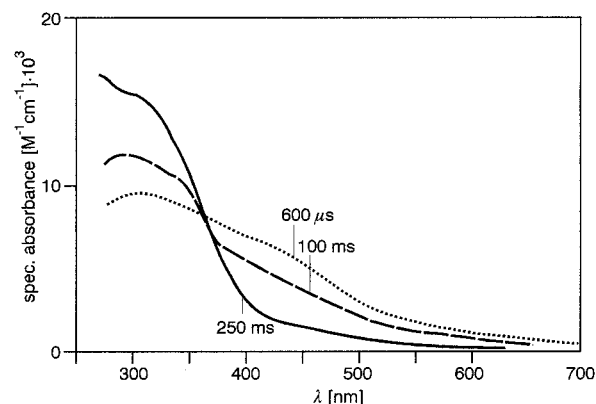


Figure 7. Absorption spectrum at long times up to 0.25 s. Solution is $1.0 \times 10^{-3} \text{ M AgClO}_4$, 0.10 M PANa, 1 M 2-propanol. Initial hydrated electron concentration is $2.8 \times 10^{-6} \text{ M}$.

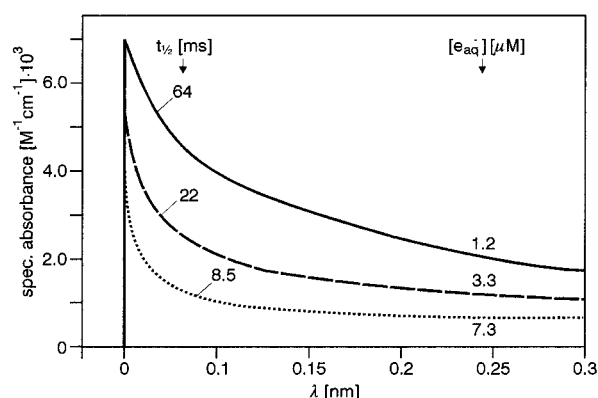


Figure 8. Kinetic curves at 450 nm up to 0.25 s at various doses. The initial hydrated electron concentrations and half-life times of the kinetic curves are also given. Solution is as in Figure 6.

is built up simultaneously. This can be seen in Figure 7, where the absorption spectrum is shown up to 0.25 s. An isosbestic point at 365 nm indicates the transformation from one species into another. This transformation is a second-order process, which can be recognized from Figure 8, where the kinetic curves at 450 nm are shown for various pulse doses (expressed as initial hydrated electron concentrations). The half-life time (indicated on the curves) is proportional to the reciprocal dose. One concludes that the Ag_3^{2+} and Ag_2^+ species undergo reactions with each other, the product absorbing more weakly above 365 nm and more strongly at shorter wavelengths. Whereas Ag_3^{2+} is a species with an odd number of valence electrons, the product is the first species with an even electron number. It could be a dimeric silver, which is complexed by one or two Ag^+ ions and strongly interacts with the anion groups of the polymer.

Using doses, which produce hydrated electron concentrations of a few $\mu\text{mol/L}$ (as in Figures 1–8), does not lead to further changes within milliseconds to seconds; i.e., the complexed dimeric silver species is the last product of reduction that can be observed in the time range available in the pulse experiments. However, when about 10 times stronger pulses are applied, the above second-order processes are much faster and one observes a final buildup of an absorption band with a maximum at 480 nm within seconds. At the higher dose, the next generation of bimolecular cluster reactions takes place, which lead to larger clusters. Figure 9 shows the 480 nm buildup. A similar absorption band appears in the γ -irradiation at the lowest doses (compare with Figure 2a in the preceding paper). From the time-resolved data, this band is attributed to a condensation of the

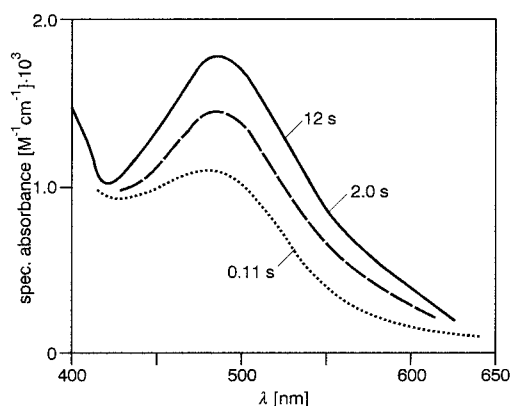


Figure 9. Absorption spectrum at different times (up to 12 s) of a solution that was irradiated with a stronger pulse. Solution is 1.0×10^{-3} M AgClO_4 , 0.10 PANa, 1 M 2-propanol. Initial electron concentration is 2×10^{-5} M.

dimeric silver complexes to form larger complexes consisting of about four silver atoms and an approximately equal number of silver ions.

In the preceding paper, experiments on the reduction of Ag^+ in the presence of an oligomeric carboxylate substituent, $^-\text{OOC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COO}^-$, were also reported, which showed that no colored intermediate complexes were formed. Pulse radiolysis of a solution containing 0.05 M of the oligomeric carboxylate revealed that all reactions occur as in the absence of the additive but with a very much higher rate. The oligomeric carboxylate has no complexing power for intermediate silver clusters but accelerates all growth processes, similar to what had been observed for sulfate anions.³ It was already concluded in the preceding paper that a high density of carboxylate groups along a polymer chain is required to form the colored complexes. Carboxylate groups on small molecules do not stabilize silver clusters, even when they are present in the same overall concentration as in polyacrylate solution.

Discussion

Polyacrylate very strongly retards the growth of silver clusters. In fact, when the reduction of silver ions occurs by continuous γ -irradiation, as described in the preceding paper, the first observed products are complexes of oligomeric silver clusters with the polyanion, which have an absorption maximum in the visible. The pulse radiolysis experiments show that several steps ranging from microseconds to seconds are necessary to build up a colored complex. It is interesting to compare the very early steps with those occurring in the reduction of Ag^+ in the absence of the polyanion.

In the absence of the polyanion, reaction 1 occurs with $k = 4.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. In the presence of 0.1 M polyacrylate, the specific rate is substantially smaller ($1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). In the experiment of Figure 1, the Ag^+ concentration (4.0×10^{-4} M) was very much smaller than the polyacrylate concentration. Under these circumstances, the attachment/detachment equilibrium



lies strongly on the right-hand side; i.e., a very large fraction of the Ag^+ ions are bound to the polyanion (see Figure 1 of the preceding paper). The concentration of the latter is $^{0.1/30} = 3 \times 10^{-3}$ M macromolecules/L. Thus, practically only one Ag^+ ion

is attached to a chain, and many chains even do not carry an Ag^+ ion. Reaction 1 of the hydrated electron is slowed because of the repulsive action of the negatively charged polymer chain that carries a reacting Ag^+ ion. The silver atom formed in reaction 1 detaches easily from the chain and undergoes reaction with an Ag^+ ion on another chain, without an electrostatic repulsion being operative. Thus, reaction 2 is practically not retarded by the presence of the polyanion. As a consequence, reaction 1 is the slowest process that determines the rate of the overall formation of Ag_2^+ . In addition, the silver atom, Ag^0 , does not accumulate substantially between formation (eq 1) and consumption (eq 2), the result being that its intermediate absorption at 360 nm is not detected. In the absence of polyacrylate, reaction 1 is much faster than reaction 2, and the absorption of Ag^0 can be seen.^{4,6}

The PA^- -bound Ag_2^+ ion exhibits the absorption band at 310 nm that is known for the free ion in aqueous solution. In addition, it also has a band at 440 nm (6 μs in Figure 1). We explain this band by a charge transfer: $\text{PA}^- \rightarrow \text{Ag}^+$.

The absorption bands of Ag_2^+PA^- disappear according to a first-order rate law, the rate of disappearance becoming greater with increasing Ag^+ concentration (Figure 6). Thus, reaction 3 is postulated, which has also been detected in the absence of the polyanion.⁷ This reaction is very strongly retarded by the polymer. At an Ag^+ concentration of 4.0×10^{-4} M, for example, the reaction requires about 0.9 μs in the absence of the polymer but 30 μs in its presence. At $[\text{Ag}^+] = 4.0 \times 10^{-4}$ M, the reaction $\text{Ag}_2^+ + \text{Ag}^+ \rightarrow \text{Ag}_3^{2+}$ occurs as an "interchain" process: a chain that carries an Ag_2^+ ion picks up an Ag^+ ion from another chain. This could occur via the free Ag^+ ions in the equilibrium of eq 4 or in the transfer of an Ag^+ ion from one chain to the other during a close encounter. Both events are expected to be slow because of the low concentration of free Ag^+ ions or because of the electrostatic repulsion between two chains. With increasing Ag^+ concentration, more and more chains carry an Ag^+ ion. At the highest Ag^+ ion of 1.0×10^{-2} M used, each chain carries three Ag^+ ions on average. Under these circumstances, the reaction $\text{Ag}_2^+ + \text{Ag}^+ \rightarrow \text{Ag}_3^{2+}$ can also occur as an "intrachain" process. An additional complication arises when polyacrylate is present: the equilibrium of eq 3 lies more strongly on the left side than in the absence of polyacrylate (Figure 4). Thus, Ag_2^+ and Ag_3^{2+} are present in comparable abundancies, which would explain the unusually broad absorption spectrum (250 μs in Figure 2) of the product of the reaction between Ag_2^+ and Ag^+ , and the difference in the spectra at different Ag^+ concentrations (Figures 2 and 5). The broadening of absorption bands could also be due to the existence of different cluster binding sites on the polyanion; different sites may possess differently protonated carboxyl groups in the neighborhood of an attached cluster.

One finally has to state that, in the time range available in the pulse experiment (up to 1 min), the blue clusters (absorption maximum at about 600 nm) that are described in the preceding paper do not appear. These clusters are conceived to be longer silver-silver ion chains on polyacrylate, which are formed when smaller clusters (absorbing at 480 nm) condense. These condensation processes are too slow to be detected in a pulse experiment. The 480 nm cluster has previously been thought to be $\text{PA}^- - \text{Ag}_4^{2+}$.⁸ On the basis of the present findings, a larger structure consisting of about four atoms and an about equal number of Ag^+ ions has to be postulated. Since the cluster, which absorbs around 600 nm, is formed by some condensation and partial reduction of the 480 nm cluster (see preceding paper),

one has to postulate a structure of the 600 nm species of even more than about eight atoms and ions.

Final Remarks

The present pulse radiolysis study complements observations on the radiolytic and chemical reduction of silver ions on polyacrylate chains.¹ It is shown how strongly the elementary processes in the growth of small particles are affected by a polymer, and the findings are thus important for colloid chemistry in all. We have just qualitatively touched here the interesting question of elementary inter- and intrachain reactions. More quantitative studies should be carried out on this aspect, such as on the dependence of the kinetic curves on the chain length of PANa and over a wide concentration range of the polymer. They would require more sophisticated samples of polyacrylate than were available in the present work, i.e., monodisperse samples over a wide range of chain lengths.

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