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Controlled Formation of Ag Nanoparticles by Means of Long-Chain Sodium Polyacrylates in Dilute Solution

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Abstract: A new tool is presented to control formation of Ag nanoparticles. Small amounts of silver ions were added to dilute solutions of long-chain sodium polyacrylates (NaPA). Four NaPA samples covering a molar mass regime of 97 kD $\leq M_w \leq$ 650 kD have been used. With amounts of added Ag^+ as low as 1−2% of the COO^- groups of the polyanionic chains, significant changes could already be induced in the NaPA coils with 650 kD. If the NaPA concentration was kept below 0.1 g/L, the coils with 650 kD exhibited a significant coil shrinking in stable solutions. At larger NaPA concentrations, addition of Ag^+ initiates an aggregation of the polyacrylate coils toward compact structures. Coil shrinking and aggregation was revealed by means of time-resolved static light scattering. If exposed to UV-radiation, small Ag particles formed within the shrunken anionic polyacrylate coils. The Ag nanoparticles were identified by means of an enhanced light scattering and a characteristic plasmon absorption band around 410 nm. No such Ag particle formation could be observed even at 5 times larger concentrations of Ag^+ and NaPA if the two smallest polyacrylate samples have been used under otherwise equal conditions. This molar mass sensitive response of NaPA to Ag^+-addition suggests an interesting phenomenon: if the coil size of the NaPa chains, which act as Ag^+ collectors, is large enough, local Ag^+ concentration in these coil-shaped Ag^+ containers exceeds a critical value, and irradiation with UV generates Ag nanoparticles.

Introduction

Silver nanoparticles are interesting candidates for applications in catalysis, photochemistry, and electronics.[1−3] Production is predominantly performed from aqueous solutions of Ag^+ salts via chemical reduction or by exposure to UV or γ-radiation.[1,3] Addition of surfactants or water-soluble polymers may control particle growth and stabilize intermediates. One of the most frequently applied additives for irradiative[4−9] and chemical[10] reduction is the sodium salt of poly(acrylic acid) (NaPA). Belloni et al.[4] and Henglein et al.[5] first showed the capability of NaPA to stabilize intermediate Ag_n^{m+} clusters[4,5] and described conditions necessary to form Ag nanoparticles.[5]

Reduction by means of irradiation with electromagnetic waves proceeds via the generation of solvated electrons.[4,5,11] The process could be supported by the addition of 2-propanol or acetone, which act as radical scavenger and reductant.[4,5,11] Various procedures based on irradiative reduction in aqueous solution are strikingly simple.[8,12,13] Kubal[8] irradiated aqueous solutions of $AgNO_3$ in the presence of anionic polymethylmethacrylate chains and observed size dispersity of the hydrosols varying with the type and duration of the radiation.[8] Zhang et al. illuminated ethanolic $AgNO_3$ solutions in the presence of polypropyleneoxide−polyethyleneoxide−polypropyleneoxide triblock copolymers by means of ambient light.[12] Shin et al.[13] used polyvinylpyrrolidone (PVP) to stabilize Ag nanoparticles generated by γ-irradiation. They compared various molecular weight samples of PVP and revealed a decrease of the Ag-particle size with increasing PVP concentration and with decreasing PVP molar mass.[13] In another approach, which does not use irradiation but which is equally simple, Hoppe et al.[14] achieved Ag nanoparticle formation by heating an aqueous solution of PVP. They described the change in size distribution and shape as a function of the concentration ratio of PVP to Ag^+. It is these simple procedures on which the present account will focus.

Our system comprises dilute aqueous solutions of NaPA at neutral pH with sub-stoichiometric amounts of $AgNO_3$. Ag-particle formation is induced by exposing the solutions to UV-

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Table 1. Light Scattering Parameters of the NaPA Samples under Consideration

sample	M_w/kD	R_g/nm	A_2/10^6 mol·L/g
Paa85k	97	19	15
Paa165k	149	31.7	8.2
PA500k	453	74.7	6.3
PA800k	650	114.3	3.9

light. As an important new aspect, the present work uses sodium salts of PA with averaged molar masses larger than 80 kD. Four NaPA samples covering a molar mass regime of 97 kD $< M_w < 650$ kD have been investigated. This exceeds considerably the values of all samples used so far,[4–7] which have mass values of 10 kD.

With the present investigation, we demonstrate for the first time that Ag-particle formation can be controlled by means of variation of the molar mass of NaPA. At the same time, we provide insight on the single chain behavior of the anionic PA while Ag-particle formation takes place. This success has been achieved by characterization of the dilute NaPA solutions with various amounts of Ag^+ ions prior to and after exposure to UV-light. Characterization was performed by means of time-resolved static light scattering (TR-SLS) and UV−vis spectroscopy. In each sample, an inert salt level of 0.01*n* NO_3^- screened intermolecular electrostatic repulsions among NaPA chains and facilitated interpretation of the scattering data in terms of single chain behavior. The results open up interesting perspectives on new routes to nanostructered silver material.

Experimental Section

Materials. Four samples of sodium polyacrylate with different molecular weights were used. The molecular parameters were determined by static light scattering in aqueous 0.01*n* NaCl and are summarized in Table 1. The lower molecular weight samples paa85k and paa165k were purchased from PolySciences Europe, Eppelheim, FRG. The samples with the two highest molecular weights, PA500k and PA800k, were from PSS, Mainz, FRG. $AgNO_3$ and $NaNO_3$ with a purity >99% from Fluka (Buchs) were applied as is. Bi-distilled water was generated with a conductivity below 0.1 μS/cm.

Sample Preparation. All solutions were prepared with bi-distilled water. Prior to use, the bi-distilled water was degassed by exposing it to ultrasound for 2 h and subsequently to a gentle stream of argon for 2 h. All solvents and solutions were kept under an atmosphere of argon. Three different solutions were prepared: (1) an aqueous solution of 0.01*n* $NaNO_3$ was used as solvent; (2) the silver ions were prepared as an aqueous 0.64 mM solution of $AgNO_3$, which was 0.01*n* in NO_3^- by means of 0.00936 M $NaNO_3$; and (3) NaPA was dissolved in an 0.01*n* $NaNO_3$ solution (solution (1)) at concentrations of 0.12 and 0.24 g/L. The final solutions were prepared by combining 5 mL of (3) with $n\cdot 0.1$ mL of (2) and $(5-n\cdot 0.1)$mL of (1), resulting in NaPA concentrations of 0.06 g/L (0.64 mM monomers) and 0.12 g/L (1.28 mM monomers), respectively, and various Ag^+ concentrations. Selected values for $n =$ 1, 2, 4, 5, and 10 led to Ag^+/COO^- ratios of 0.01, 0.02, 0.05, and 0.1, respectively. To each Ag^+ concentration, an additional solution was generated as a reference solution. Reference solutions had the same Ag^+ and NO_3^- contents as the corresponding final solutions but did not contain NaPA chains. Solutions with Ag^+ ions were kept in the dark until they were used. The solutions were investigated by static light scattering and by UV−vis spectroscopy. Formation of Ag nanoparticles was initiated by exposing each sample to a UV-lamp (Dr. Hönle 400F) for 2 min. The lamp operated with a cutoff filter for wavelengths smaller than 320 nm. Samples were placed in a cubelike box in front of the lamp, 20 cm apart, resulting in a power density of 5 mW/cm^2.

Static Light Scattering. Solutions were filtered into cylindrical quartz cuvettes with an outer diameter of 2 cm (Hellma, Müllheim, FRG). Filtration was performed with Millex-GS, CA filters (Millipore) having a pore width of 0.22 μm. Solutions that contained Ag^+ ions were characterized prior to and after exposure to UV-light. Static light scattering experiments are performed with a home-built goniometer equipped with a He−Ne laser as light source. The laser operates at a wavelength of 633 nm. The instrument allows one to simultaneously record scattering intensities at 18 fixed angles. Recording an angular-dependent curve takes 2 ms, thus enabling time-resolved experiments.[15] Each scattering curve was based on 1000 recordings requiring 2 s. The time interval for the start of two succeeding curves was 20 s. The measuring temperature was 25 °C.

The light scattered by dilute polymer chains is expressed in terms of the Rayleigh ratio ΔR_θ as a function of the NaPA concentration c in g/L and the momentum transfer q. In the limit of dilute solution and small momentum transfer, a linear approximation according to Zimm becomes valid,[16] whereby the second virial coefficient A_2 considers deviations from ideal solution behavior.

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{M_w}\left[1 + \frac{R_g}{3}q^2\right] + 2A_2c \tag{1}$$

In the present work, scattering depends in a complex way on the ratio of Ag^+ ions and COO^- groups, and a simple extrapolation procedure to $c = 0$ becomes impossible. Hence, the scattering curves were approximated according to the angular-dependent part of eq 1,

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{M_w(\text{apparent})}\left[1 + \frac{R_g(\text{apparent})}{3}q^2\right] \tag{2}$$

which renders the extracted weight averaged molar mass M_w and the *z*-averaged radius of gyration R_g to apparent values of the NaPA chains. In eqs 1 and 2, K is the contrast factor of NaPA in aqueous solution. Contrast factor K and the momentum transfer q have been calculated with 1.333 as refractive index of the aqueous solvent. For the refractive index increment of NaPA, a value of 0.171 mL/g, originally determined in aqueous 0.01*n* NaCl, has been used.[17] For particles with an apparent size smaller than 30 nm, values for M_w and R_g were extracted from fits of eq 2 to the complete scattering curves. Parameters for larger particles were established by using the first seven scattering angles corresponding to a *q*-regime of $5.92 \times 10^{-3} \le q \le 2.51 \times 10^{-2}$. Berry plots[18] to the first seven scattering angles have been applied for the solutions that exhibited aggregation. Experiments under all conditions have been reproduced.

UV−Vis Spectroscopy. UV−vis spectra of aqueous NaPA solutions containing Ag^+ were recorded with a Lambda 19 spectrometer (Perkin-Elmer). QS-cuvettes with a path length of 5 cm have been used.

Results and Discussion

The major aspects of the present findings shall be outlined by a detailed description of the results from two representative NaPA samples (paa165k and PA800k), which differ considerably in their molar mass.

In a first series of experiments, sample PA800k (650 kD) was investigated at a concentration of 0.06 g/L. If expressed in monomer concentration, this corresponds to 0.64 mM. Two different Ag^+-contents, 6.4 and 12.8 μM, have been applied with this NaPA concentration. These two silver contents amount only to 1% or 2% of the carboxylate functions. Results are

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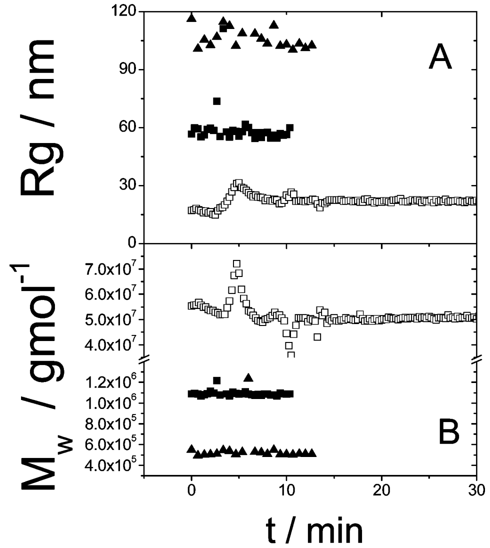

Figure 1. Apparent radii of gyration (A) and apparent molar mass values (B) at variable time *t* for sample PA800k at [NaPA] = 0.64 mM and $[NO_3^-]$ = 0.01*n*. Sample PA800k has a molar mass of 650 kD. The symbols denote: measurement without $[Ag^+]$ (▲); measurement with $[Ag^+] = 6.4$ μM before exposure to UV-light (■); measurement with $[Ag^+] = 6.4$ μM after exposure to UV-light (□).

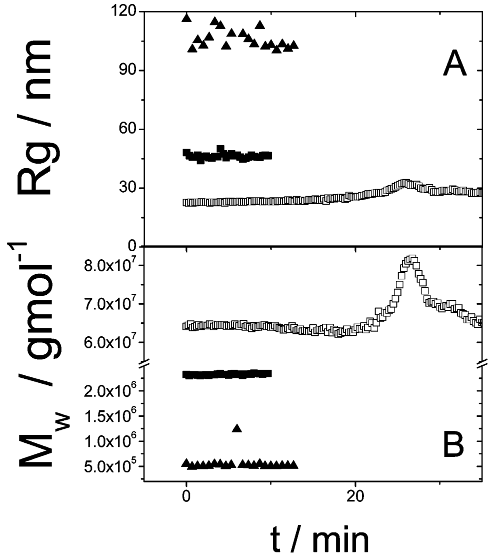

Figure 2. Apparent radii of gyration (A) and apparent molar mass values (B) at variable time *t* for sample PA800k at [NaPA] = 0.64 mM and $[NO_3^-]$ = 0.01*n*. Sample PA800k has a molar mass of 650 kD. The symbols denote: measurement without $[Ag^+]$ (▲); measurement with $[Ag^+] = 12.8$ μM before exposure to UV-light (■); measurement with $[Ag^+] = 12.8$ μM after exposure to UV-light (□).

summarized in Figures 1 and 2. The apparent molecular weight M_w and radius of gyration R_g in the absence of silver ions are 500 kD and 100 nm, respectively. Because of the fact that the NaPA solution is extremely dilute, these values are close to the real values. Characterization of the sample under the same conditions but with Ag^+ ions exhibits slight changes already prior to exposure to UV-light. The apparent molecular weight increases to 1100 kD in the case of $[Ag^+] = 6.4$ μM and to 2350 kD at the higher Ag^+ content of 12.8 μM. The increase of the apparent molar mass by a factor of 2.2 and 4.7 may be caused by two superimposing effects. (i) Scattering data that are influenced by excluded volume effects obey eq 1. If a concentration series for such a system is not accessible, data have to be fitted with eq 2. This inevitably results in M_w and R_g values that are smaller than the true values. A diminishing excluded volume effect reduces the influence of the $2A_2c$ term and brings the apparent values for M_w and R_g from eq 2 closer to the true values. (ii) The shrinking coils incorporate silver ions. These incorporated heavy metal ions modify the overall refractivity of the particles and hence its scattering contrast. Also, a slight aggregation cannot be ruled out completely but is of minor relevance as will be outlined below.

The changes in apparent molar mass values are accompanied by changes in particle size. The apparent radius of gyration decreases to 57 and 46 nm, respectively. This excludes a large degree of aggregation and indicates a considerable shrinking of the coil dimensions. Although a shrinking of the coil dimensions is expected from earlier viscosity experiments,[19] its extent is surprisingly large. For the alkaline earth cations, almost stoichiometric amounts of cations are necessary to shrink the NaPA chains to similar extents.[20,21] In the case of alkaline earth cations, the driving force is considered to be a neutralization of the chains, which liberates solvating water molecules.[22,23] In the light of the extremely small amount of Ag^+ per COO^-, a similar mechanism can be ruled out for the present system. As outlined already by Strauss and Begala,[19] two-coordinate argentous ion complexes may cause intramolecular cross-linking through bridging. Such an Ag-complex formation, identified as chelating bidentate, has been recently found by means of IR spectroscopy on sodium polymethacrylate brushes.[24]

An effect that is even more striking occurs after exposure of the sample to UV-light. The apparent molar mass of the polymers increases further by more than an order of magnitude, whereas the dimensions shrink by more than $^1/_2$ in both cases. A few Ag^+ ions are hardly capable of forcing as many as 10 NaPA chains into a small, condensed particle, and we discard aggregation as the major cause for the increase of the apparent molar mass. Rather, an electronic effect may cause these drastic changes in the scattering intensity. A partial reduction of silver ions produces silver clusters, which assemble as clouds of silver clusters within the coils. The dimensions of these clouds have the same order of magnitude as the size of their hosting coils, whereby the absolute value could easily be smaller by a factor of 0.5. The increase of the molar mass is explained by the strong scattering contribution of the silver clusters. Deviations of this strong scattering from the Rayleigh−Debye−Gans (RDG) approximation are considered to be negligible for the following reason. Clouds of small isolated Ag clusters or Ag nanoparticles are formed within the coils. Although the size of these clouds lies in the same order of magnitude as the size of the hosting coils, it is not this size but the size of the single Ag nanoparticles that determines the extent of deviations from RDG approximation. Yet, the isolated particles are likely to be smaller than 1 nm because of the low abundance of Ag^+ cations (1−10 Ag^+ per 100 COO^-).

Independent support of the hypothesis of Ag nanoparticle formation is presented by the onset of an absorption band of the samples exposed to UV-light. As is shown in Figure 3, this

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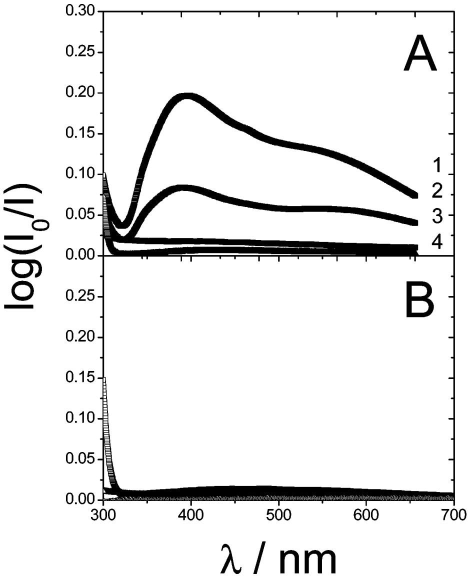

Figure 3. UV−vis spectra of the same aqueous solutions of NaPA in the presence of Ag$^+$ as investigated by SLS in Figures 1, 2, 4, and 5. Part A from top to bottom: spectra of PA800k at [NaPA] = 0.64 mM and [NO$_3^-$] = 0.01*n* with [Ag$^+$] = 12.8 μM after exposure to UV-light (1); with [Ag$^+$] = 6.4 μM after exposure to UV-light (2); with [Ag$^+$] = 6.4 μM before exposure to UV-light (3); reference sample without NaPA and with [Ag$^+$] = 6.4 μM after exposure to UV-light (4). Part B: spectra of paa165k at [NaPA] = 0.64 mM and [NO$_3^-$] = 0.01*n* with [Ag$^+$] = 32 μM after exposure to UV-light; with [Ag$^+$] = 6.4 μM after exposure to UV-light; reference sample without NaPA and with [Ag$^+$] = 32 μM after exposure to UV-light. The three curves are indistinguishable.

absorption band is not detectable in the samples prior to exposure. It lies in the range of 410 nm, typical for the plasmon resonance band of silver particles. An additional experiment with twice the concentrations of NaPA and Ag$^+$ exhibited already aggregation directly after addition of the Ag$^+$ ions and shall be discussed later. It is of utmost importance in this context, that exposure of a pure AgNO$_3$ solution to UV-light for 2 min did not result in a formation of silver nanoparticles even if [Ag$^+$] = 32 μM. Hence, it is the anionic PA coils that collect Ag$^+$ cations by means of their electrostatic potential leading to local excess concentrations of Ag cations, which form the prerequisite of Ag nanoparticle formation.

To demonstrate the impact of molecular weight, the same experiments were performed with sample paa165k having a molar mass of only 149 kD. In one experiment, an NaPA concentration of 0.06 g/L was used together with a silver content of [Ag$^+$] = 6.4 μM. This corresponds to the same conditions applied for sample PA800k where [Ag$^+$]/[COO$^-$] = 0.01. As can be seen from Figure 4, addition of silver ions and successive exposure to UV-light neither has an effect on the apparent molar mass nor on the apparent size of the PA chains. Increase of the concentrations of the silver ions by a factor of 5 does not significantly change any of the polymer size parameters (Figure 5), neither does a 5-fold concentration of both components (not shown here). Also, exposure to UV-light has no observable effect. The anionic coils of sample paa165k are much smaller than those of the sample PA800k. Apparently, the former fail to generate local excess concentrations of Ag$^+$ cations large enough to initiate Ag nanoparticles.

As in the case of the higher molar mass sample, further insight is obtained from a look at the UV−vis spectra (Figure 3). The sample at low concentration of the NaPA and Ag$^+$ does not show absorption at the regime where a plasmon band is expected.

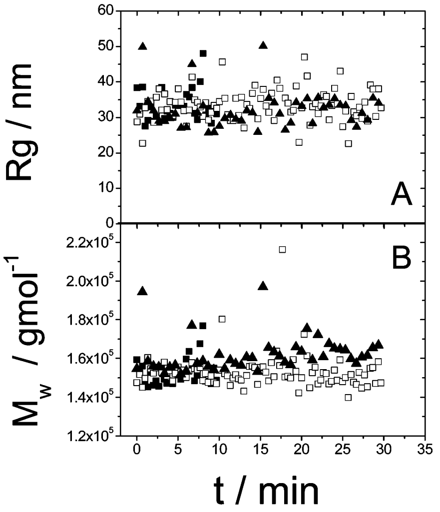

Figure 4. Apparent radii of gyration (A) and apparent molar mass values (B) at variable time *t* for sample paa165k at [NaPA] = 0.64 mM and [NO$_3^-$] = 0.01*n*. Sample paa165k has a molar mass of 149 kD. The symbols denote: measurement without [Ag$^+$] (▲); measurement with [Ag$^+$] = 6.4 μM before exposure to UV-light (■); measurement with [Ag$^+$] = 6.4 μM after exposure to UV-light (□).

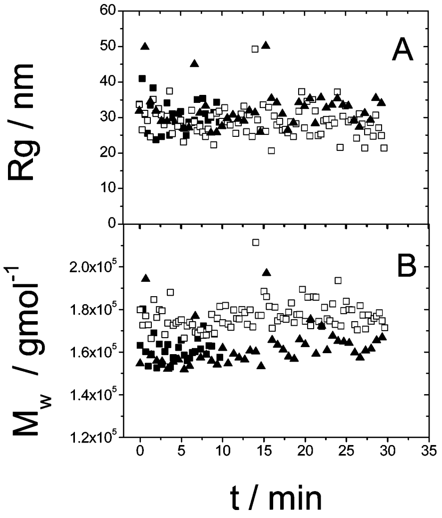

Figure 5. Apparent radii of gyration (A) and apparent molar mass values (B) at variable time *t* for sample paa165k at [NaPA] = 0.64 mM and [NO$_3^-$] = 0.01*n*. Sample paa165k has a molar mass of 149 kD. The symbols denote: measurement without [Ag$^+$] (▲); measurement with [Ag$^+$] = 32 μM before exposure to UV-light (■); measurement with [Ag$^+$] = 32 μM after exposure to UV-light (□).

The trends observed with the NaPA samples with 149 kD (paa165k) and 650 kD (PA800K) are confirmed and supplemented by the results from two additional samples represented in more detail in the Supporting Information. The additional samples have molar mass values of 97 kD (paa85k) and 453 kD (PA500k), respectively. As expected, addition of Ag$^+$ ions to an NaPA solution with a molar mass of 97 kD has no effect on the size and apparent molar mass of the anionic PA coils, nor does a successive irradiation with UV-light generate any Ag nanoparticles. At a molar mass of 453 kD, the PA coils exhibit for the first time the characteristic features of Ag nanoparticle formation. Remarkably, the Ag$^+$ concentration required to initiate Ag nanoparticle formation has to be at least

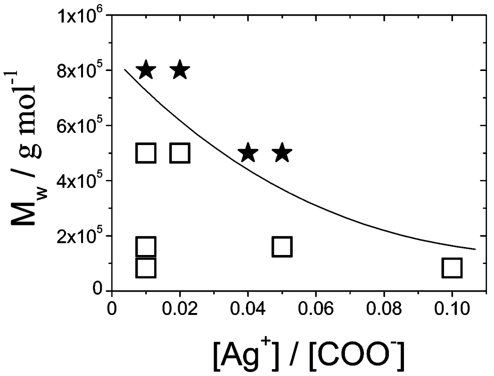

Figure 6. Overview on the Ag nanoparticle formation at an NaPA concentration of 0.64 mM determined by SLS. The ordinate represents the molar mass of the NaPA samples and the abscissa the Ag^+ cations per COO-residues from NaPA applied. The symbols denote particle formation as indicated by SLS (*) and particle formation not observed (□). The line serves as a guide to the eye.

2 times larger than that in the case of the 650kD sample. Thus, the behavior of the sample with $M_w = 453$ kD was comparable to the one with 650 kD, except for the fact that it reveals a further interesting detail of the particle formation. Only if the Ag^+ concentration exceeds a certain critical level can Ag particle formation be initiated at all with a given PA sample. It is this critical value that depends on the molar mass of the PA sample. An overview on the onset of Ag nanoparticle formation at a constant NaPA concentration of 0.06 g/L corresponding to 0.64 mM is given by means of Figure 6. In this figure, the regime where particles are formed is indicated by means of an M_w versus $[Ag^+]$ diagram.

Finally, we would like to draw attention to the aggregation observed with the high molecular weight sample PA800k in the presence of Ag^+. Aggregation was observed for this sample if the concentrations of Ag^+ and NaPA were twice as large as the respective concentrations applied in Figure 1. Apparently, the increase of the NaPA and Ag^+ concentration at constant $[Ag^+]/[COO^-] = 0.01$ increases the likelihood for intermolecular contacts and intermolecular bridging due to bidentate Ag complexes. Figure 7 represents the evolution of molar mass and particle size as a function of time. Correlating these two quantities results in a power law

$$R_g \approx M^a$$

with an exponent of $a = 0.42$, which is slightly smaller than the one expected for unperturbed coils. The difference is considered to be significant and indicates an enhanced compactness of the aggregating NaPA chains. Similar findings were published by Wu et al.,[25] who found exponents of $0.46 < a < 0.48$ for Ca^{2+}-induced aggregation of partially hydrolyzed poly(acrylamide).

Further insight is provided by a closer look at the particle scattering factor

$$P(q) = \frac{\Delta R_\theta(q)}{\Delta R_\theta(q = 0)}$$

of the aggregates. Figure 8 represents a small selection of experimental curves, recorded at different aggregation times.

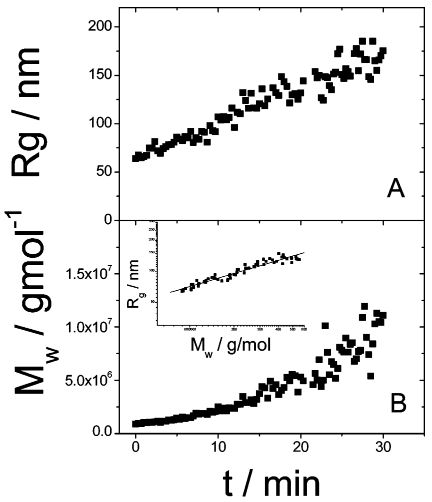

Figure 7. Apparent radii of gyration (A) and apparent molar mass values (B) at variable time t for sample PA800k at [NaPA] = 1.28 mM, $[Ag^+] = 12.8$ μM, and $[NO_3^-] = 0.01n$. Sample PA800k has a molar mass of 650 kD. The inlet indicates power law behavior of the apparent radii of gyration versus apparent molar mass with an exponent of 0.42.

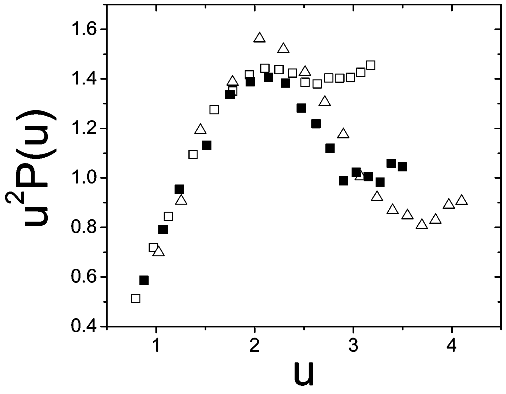

Figure 8. Selected scattering curves from the aggregation run shown in Figure 6 represented as normalized Kratky representations. Normalized variable is $u = R_g{\cdot}q$. The symbols denote (□) $t = 16.33$ min; (■) $t = 26.25$ min; (△) $t = 33.75$ min.

The Kratky plot is chosen because this type of plot exhibits a maximum for compact particles. Typical representatives of compact polymer chains are starlike or nonrandomly branched polymer chains.[26] In fact, the curves show features similar to those of theoretical curves of branched structures, whereby the ratio of the maximum divided by the height of the succeeding plateau is characteristic for the number of arms (starlike branched) or the number of branching points (nonrandomly branched). In line with this correlation, an increase of this ratio indicates an increase of the degree of branching.

Summary

While aiming at a revelation of the impact of Ag^+ ions on the size and structure of large NaPA chains in dilute solution, similar to earlier work on the respective influence of alkaline earth cations,[20,21] we stepped over an interesting phenomenon. First, the amount of Ag^+ required to cause instability of the dissolved NaPA chains with a molar mass of 650 kD is orders of magnitude smaller than in the case of alkaline earth cations.[20] One Ag^+ ion per 100 COO^- residues of the NaPA coils causes

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already a shrinking of the coil dimensions by a factor of 2. Solutions of these shrunken NaPA coils were stable.

Stable solutions of the two largest NaPA samples, with a few percent of the COO^- groups decorated with Ag^+, exhibit an interesting photochemical effect. Illumination of the respective aqueous solutions by UV-light generates Ag nanoparticles, incorporated in and protected by the shrunken NaPA coils. The particles are identified by an increased scattering signal and by the appearance of a plasmon absorption band at 410 nm. Initiation of Ag nanoparticle formation by UV-light depends on a subtle interplay of the Ag^+ and NaPA concentrations and on the molecular weight of the NaPA sample. At a given polymer concentration, the Ag^+ content has to exceed a certain value to initiate the process. The propensity to support Ag nanoparticle formation decreases with decreasing molar mass of the NaPA coils. If the molar mass of the added NaPA chains is as small as 149 kD or if the NaPA chains are totally absent, Ag nanoparticle formation cannot be initiated by UV-light under present conditions. These findings suggest that locally high Ag^+ concentrations are a prerequisite for the initiation of particle formation. This can be achieved by anionic polyacrylate chains if their degree of polymerization is large enough.

Formation of Ag nanoparticles interferes with aggregation if the concentration of the NaPA is large enough. This could be verified by means of the sample with the largest molecular weight where the overlap concentration is the lowest.

Finally, attention shall be focused on an important impact provided by the use of NaPA as aids to form Ag nanoparticles. Polyacrylates are extremely suitable to build variable molecular architectures[27] and to assemble into controlled supramolecular structures with organized polyacrylate domains.[28] The resulting supramolecular structures offer new routes to organize Ag nanoparticles into tailor-made spatial distributions once a critical Ag^+ concentration is exceeded in the polyacyrlate domains.

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Supporting Information Available: Description of results from light scattering experiments on two NaPA samples with molecular weights of 97 and 453 kD, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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