

Silver Colloid Synthesis in Linear and Branched Anionic Polymer Matrices by Using Ascorbic Acid as Reductant

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Silver colloids were synthesized in linear and branched anionic polymer matrices at different pH reducing by ascorbic acid. The template role of the host polymers in anionic form was studied at pH = 7 and pH = 12. Linear Polyacrylamide and star-like copolymers Dextran-*graft*-Polyacrylamide after alkaline hydrolysis were used as matrices. Silver colloids were studied by UV-Vis spectrophotometry just after synthesis and in 3 months. It is shown that branched polymer matrices are more efficient in comparison with linear one for *in situ* silver nanoparticle synthesis. The pH value affects the process of formation was investigated.

Keywords: Silver Nanoparticles, Polyacrylamide, Branched Polymer, Ascorbic acid.

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1. INTRODUCTION

At nanoscale, silver exhibits unique physical, chemical and biological properties, which are required for several practical applications, such as wound healing, water disinfection, biological and chemical sensing, nonlinear optics, catalysis etc. Due to the high reactivity and agglomeration ability of Ag nanoparticles (NPs), their colloidal solutions are not stable in time. [1] Thus, it is necessary to investigate new efficient methods of Ag NPs synthesis and stabilization.

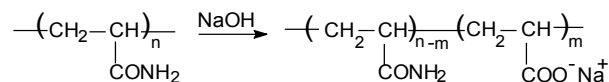
There is an array of routes to obtain Ag colloids. Among them the chemical reduction of silver salt in polymer matrix is the most prominent technique for *in situ* Ag NPs synthesis. The nature of reduction agent, pH and temperature conditions, nature and structure of polymer matrix significantly affect the process of NPs formation and could control their shape, size and size distribution. [2] The present study focuses on the formation and properties of Ag colloids synthesized by reduction of silver nitrate dispersed in anionic linear and branched polyacrylamide matrices. Absence of toxic products of reaction and biocompatibility of ascorbic acid were the main reasons to use it as a reduction agent. Variation of the reactivity of ascorbic acid with pH was effective to mediate the reduction rate of the silver precursor and the number of the nucleus of the silver nanoparticles. [3]

2. EXPERIMENTAL

2.1 Materials

Silver nitrate (AgNO₃) and ascorbic acid were purchased from Aldrich. As polymer matrices the linear Polyacrylamide (PAA) and branched copolymer Dextran-*graft*-Polyacrylamide (D-*g*-PAA) were used. All polymers were in anionic form. Their synthesis, characterization and alkaline hydrolysis of initial non-charged polymers were described in details previously [4]. For

synthesis we used Dextran with molecular weight $M_w = 7 \times 10^4$ (Fluka) and Acrylamide (Aldrich). Cerium (IV) ammonium nitrate (Aldrich) was used as initiator of radical polymerization. According to the synthesis condition a theoretical number of grafts in branched copolymer was equal to 5 (D-*g*-PAA5) and 20 (D-*g*-PAA20). The synthesized branched and linear samples were saponified. During alkaline hydrolysis the -CONH₂ groups of PAA chains are converted to the -COONa groups according to:



All solutions for further investigations were prepared in double-distilled deionized water.

2.2 Silver Colloid Synthesis

Ag NPs were synthesized in aqueous solution of linear and branched polymer matrices at 60 °C at pH = 7 and pH = 12. Ascorbic acid was used as a reducing agent. Molar ratio of AA monomer to silver ions was equal to 7.

2 ml 0.1M AgNO₃ was added to 5 ml of aqueous solution of polymer ($C = 0.1$ g/l). The pH value was created by adding 0.2 ml of ammonia water solution (30 %). This mixture was stirred during 20 min and heated to 60°C. Then 0.15 ml of 0.01 M ascorbic acid was added. The solution turned yellow immediately after adding of the reduction agent. The stability of obtained nanosystems has been controlled during 2 months.

2.3 Experimental Methods

Characterization of polymer matrices.

Size-exclusion chromatography. SEC analysis was carried out by using a multidetection device consisting

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of a LC-10AD Shimadzu pump (throughput $0.5 \text{ ml} \cdot \text{mn}^{-1}$), an automatic injector WISP 717+ from WATERS, 3 coupled 30 cm-Shodex OH-pak columns (803HQ, 804HQ, 806HQ), a multi-angle light scattering detector DAWN F from WYATT Technology, a differential refractometer R410 from WATERS. Distilled water containing 0.1 M NaNO_3 was used as eluent.

Potentiometric titration was performed for determination of conversion degree of amide groups into carboxylate ones during alkaline hydrolysis [4].

Characterization of silver nanoparticles.

UV-Vis spectrophotometry. UV-Vis spectra were recorded using Varian Cary 50 Scan UV-Visible Spectrophotometer. Original silver colloids were diluted before spectral measurements.

3. RESULTS AND DISCUSSION

The molecular parameters of synthesized uncharged polymer matrices are shown in Table 1.

Table 1 – Molecular parameters of polymers determined by SEC

Sample	$M_w \times 10^{-6}$ [g·mol ⁻¹]	R_g [nm]	M_w / M_n
D-g-PAA5	2.15	85	1.72
D-g-PAA20	1.43	64	1.98
PAA	1.40	68	2.40

According to high values of M_w and R_g for branched copolymers and also taking into account the low content of polysaccharide component in copolymer (less than 6 %) we can assume that these copolymers are star-like ones. Hydrolysis degrees (α) for all polymers used were close to 30 % (Table 2).

Table 2 – Degree of conversion of D-g-PAA n and PAA samples during hydrolysis

Sample	$\alpha, \%$
Time of hydrolysis, min	30
D-g-PAA5	37
D-g-PAA20	35
PAA	28

The extremely extended structure of branched macromolecules in anionic form (after hydrolysis) was confirmed by viscosimetry. It's known that reduced viscosity of polyelectrolyte solution increases in very dilute regime due to unwrapping of charged polymer chains. In our previous work [5] it was shown that grafted chains in branched polymers even in non ionic form have worm-like or mushroom conformation that is far from random coil. For all hydrolyzed D-g-PAA n the PAA chains are extremely straightened therefore their conformation cannot be changed when solution dilutes [4]. It explained the absence of polyelectrolyte effect with dilution on the dependence of reduced viscosity (Fig. 1).

Linear and branched polymer matrices used as templates for silver colloids synthesis differed in the internal polymer structure which determined the local concentration of functional groups on PAA chains. The local concentration of functional group is higher in branched polymers in comparison with linear one due to their internal structure peculiarities.

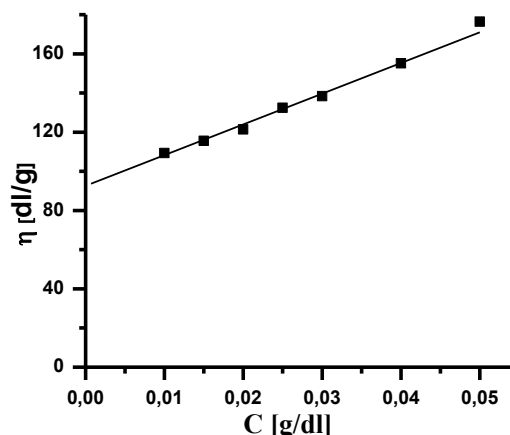


Fig. 1 – Dependence of reduced viscosity on polymer concentration for D-g-PAA5 in anionic form in salt free solution

The stable colloids were obtained as a result of *in situ* synthesis of Ag NPs in polymer matrices at pH = 7 and pH = 12 (Fig. 2-4). The UV-Vis spectra of synthesized colloids revealed a surface Plasmon resonance absorption with a maximum at 400-450 nm. The position, shape and intensity of the Plasmon resonance absorption depend on the silver particle size, their concentration and NPs size distribution [6]. The pH value of the reaction affects the size and shape evolution of resulting silver NPs. At pH = 7 the broad bands of absorption were observed only in branched polymer matrices. In linear template the stable silver colloid was not obtained.

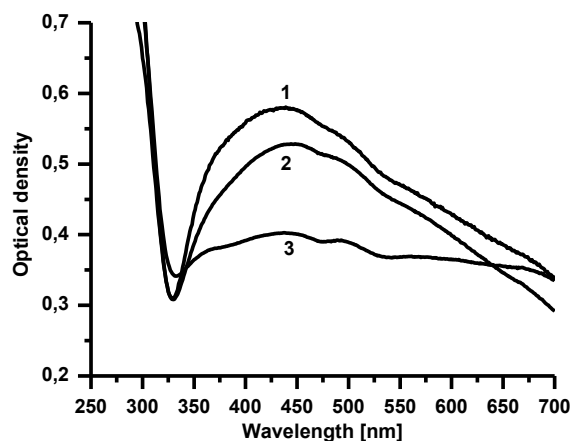


Fig. 2 – UV-Vis spectra of Ag NPs synthesized in D-g-PAA5 (1), D-g-PAA20 (2) and PAA (3). pH = 7

The increase of pH up to 12 led to formation of colloids in all polymer matrices. More narrow and intensive Plasmon resonance absorption with the same position of the maximum as at pH = 7 were observed. But, it was evident that the branched polymer matrices were more efficient than linear one. The absorption maxima of silver colloids obtained in branched matrices were observed at 425 nm, were more narrow than for linear matrices with maximum at 440 nm.

At both pH the branched polymer matrices allowed to obtain stable nanosystems with more intensive Plasmon resonance absorption maxima in comparison with linear PAA. The branched polymer D-g-PAA5 was

more efficient than D-g-PAA20. Thus, for in-situ synthesis of nanoparticles in polymer template the optimal branched structure exists.

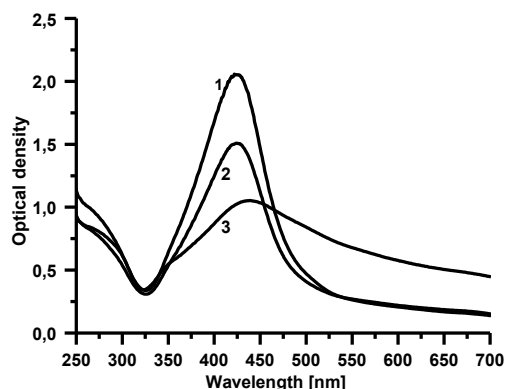


Fig. 3 – UV-Vis spectra of Ag NPs synthesized in D-g-PAA5 (1), D-g-PAA20 (2) and PAA (3). pH = 12

Obviously, the formation of silver nanoparticles carries out more efficiently on the carboxylate groups of polymer matrices. Should be noted that all polymer used had approximately 30 % of carboxylate groups and 70 % of acrylamide groups on PAA chains. At pH = 12 all carboxylate groups are completely dissociated and it can lead to the most efficient capturing of silver ions before reduction process.

Aging effect of the silver colloids was studied during 3 months after colloid synthesis in branched and linear polymer matrices (Fig. 4, 5).

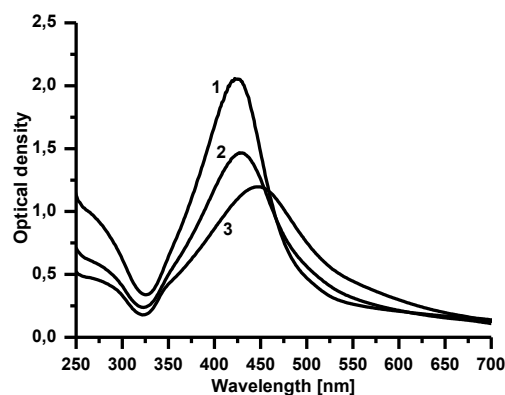


Fig. 4 – UV-Vis spectra of Ag NPs synthesized in D-g-PAA5 at pH = 12 after synthesis (1), in 3 days (2), in 2 months (3)

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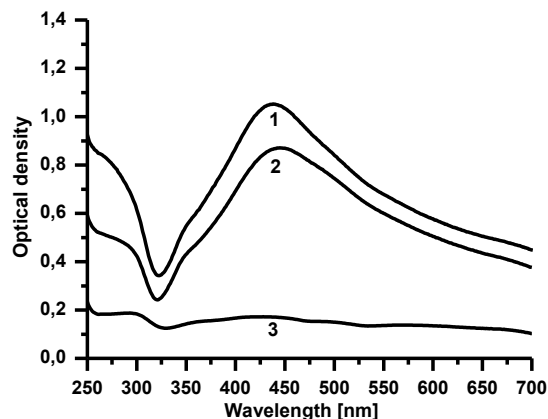


Fig. 5 – UV-Vis spectra of Ag NPs synthesized in PAA at pH = 12 after synthesis (1), in 3 days (2), in 3 months (3)

The red-shift of maxima of surface Plasmon resonance bands and the decreasing of the bands intensity were observed for nanosystems synthesized in all polymer templates. Obviously it was caused by size increasing of the particles as well as their partial sedimentation. In 3 month complete sedimentation was observed for colloid obtained in linear polymer matrix. Therefore, branched matrices enhance stability of the system in comparison with linear one.

4. CONCLUSIONS

The internal structure of the host polymer affects the process of Ag NPs formation in aqueous solution. Branched polymer matrices are much more efficient for *in situ* silver colloid synthesis and stabilization of NPs in comparison with linear one at pH = 7 and pH = 12. The high value of pH is more appropriate for the reduction process by using ascorbic acid for obtaining of silver colloids in anionic polymer matrices. At pH = 12 all carboxylate groups of anionic polymer matrix are completely dissociated and it lead to the most efficient capturing of silver ions before reduction process.

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