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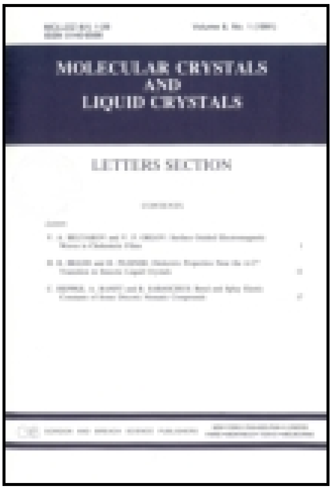

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Synthesis of Silver Nanoparticles in Star-Like Dextran-Graft-Polyacrylamide Matrices

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Synthesis of Silver Nanoparticles in Star-Like Dextran-Graft-Polyacrylamide Matrices

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*Branched copolymers Dextran-*graft*-Polyacrylamide (D-*g*-PAA) with star-like architecture of macromolecules and linear Polyacrylamide (PAA) were used for* in situ *synthesis of Ag nanoparticles. Aqueous silver colloids were characterized by UV-vis spectroscopy, TEM and dynamic light scattering. The internal structure of polymer matrices in solution affects the Ag nanoparticle formation and stability of colloid systems. Branched structure of D-*g*-PAA macromolecules provides obtaining of stable silver colloids even at high temperature when linear PAA matrix is not efficient.*

Keywords silver nanoparticles; branched polymers; polyacrylamide; polymer matrices

1. Introduction

Silver nanomaterials are the subject of focused researches due to their unusually enhanced physicochemical properties and biological activities compared to the bulk parent materials. Silver nanoparticles (Ag NPs) are becoming increasingly important in a variety of scientific fields. Their actual and potential applications include catalysis, photographic processes, cosmetics, medicine, biotechnology, etc. [1–10].

Properties of nanosystems strongly depend on the morphology, crystal structure, and dimension of nanoparticles. The predominant salt precursors, reducing and stabilizing agents as well as conditions of the synthesis processes determine the characteristics of Ag NPs and disperse system as a whole. Chemical reduction of metal ions into neutral metal clusters in suitable polymer solution is a promising approach of Ag NPs formation. Polymer matrix has to play crucial role in protection metal particles from aggregation. Chemical nature and internal structure of macromolecules seem to effect the formation of metal particles in solution.

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Table 1. Molecular parameters of polymers determined by SEC-LS

Sample	$M_w \times 10^{-6}$ g·mol^{-1}	R_g nm	$R_g{}^2/M_w \times 10^{21}$ m^2·mol·g^{-1}	$Cont_{Dex}$ %
D-*g*-PAA5	2.15	85	3.36	3.3
D-*g*-PAA20	1.43	64	2.85	4.9
PAA	1.40	68	—	—

LS, light scattering; SEC, size-exclusion chromatography.

2. Experimental

Materials

Silver nitrate ($AgNO_3$) and sodium borohydride ($NaBH_4$) were purchased from Aldrich. Acrylamide (AA) obtained from Aldrich was twice re-crystallized from chloroform and dried under vacuum at room temperature for 24 h. Dextran with molecular weight $M_w = 7\times10^4$ from Fluka and Cerium (IV) ammonium nitrate (CAN) from Aldrich were used without further purification. Distilled water was used for preparation of all solution and colloids.

Polymer Matrices

Branched copolymers Dextran-*graft*-polyacrylamide (D-*g*-PAA) with Dextran backbone ($M_w = 70\ 000$) and Polyacrylamide grafts as well as linear Polyacrylamide (PAA) were synthesized in our laboratory [11,12]. Grafting PAA chains to Dextran backbone was carried out by "grafting from" method and CAN was used as initiator of radical polymerization. The synthesis of branched copolymer D-*g*-PAA was described in details in [13].

According to the synthesis condition the theoretical numbers of grafts in synthesized copolymers were 5 (D-*g*-PAA5) or 20 (D-*g*-PAA20). Since the content of Dextran component in D-*g*-PAA is small (Table 1), the structure of macromolecules is star-like.

The value $R_g{}^2/M_w$ was calculated for assessment of the compactness of branched copolymers in solution. D-*g*-PAA5 macromolecules were revealed to be less compact than D-*g*-PAA20 ones (Table 1).

In situ ***Ag Nanoparticle Synthesis***

Ag NPs were synthesized in polymer matrices D-*g*-PAA5, D-*g*-PAA20 and linear PAA. Rather strong reducing agent $NaBH_4$ was used. The syntheses were carried out at 0, 20 and 80°C.

10 ml of aqueous solution containing 0.0005 g of D-g-PAA and 0.051 g $AgNO_3$ was stirred during 20 min and 5 ml of 0.1 M $NaBH_4$ was added. The solution turned dark reddish brown immediately after adding of $NaBH_4$, thus particle formation was indicated. The stability of nanosystems obtained was being controlled during 6 months.

Ag Nanoparticles Characterization

The identification of Ag NPs and their size analysis were performed using high-resolution transmission electron microscopy (TEM) and selected area electron diffraction (JEOL

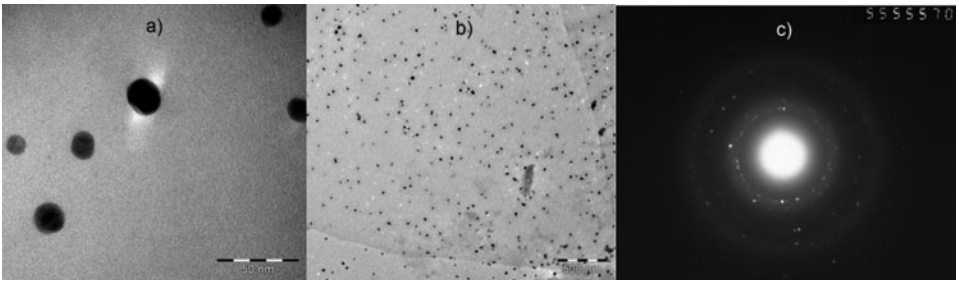

Figure 1. TEM **(a, b)** and diffraction **(c)** images of Ag NPs synthesized in D-*g*-PAA5 matrix.

(Japan) Jem-1000CXII). Particle size distribution was calculated by digitizing the TEM image with Image Tool, from which the average size and standard deviation of Ag nanoparticles were generated.

Absorption spectra were observed in UV-vis region using Varian Cary 50 Scan UV-Visible Spectrophotometer. Original product solutions were diluted before spectral measurements.

Dynamic light scattering experiments were carried out using An ALV5000 autocorrelator (ALV, Langen, Germany). A Spectra Physics 2020-2W argon ion laser ($\lambda = 514.5$ nm) acts as the coherent light source. The normalized autocorrelation functions of the intensity of the light scattered by the particles are measured at a scattering angle $\theta = 40^\circ$ and 140° and are analyzed using the CONTIN software.

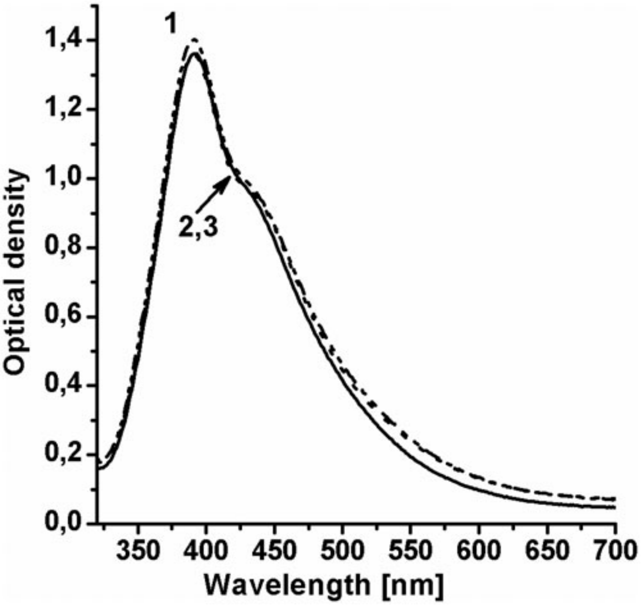

Figure 2. UV-Vis spectra of Ag NPs synthesized at 20°C in polymer matrices: 1 – D-*g*-PAA5; 2- D-*g*-PAA20 and 3 – PAA.

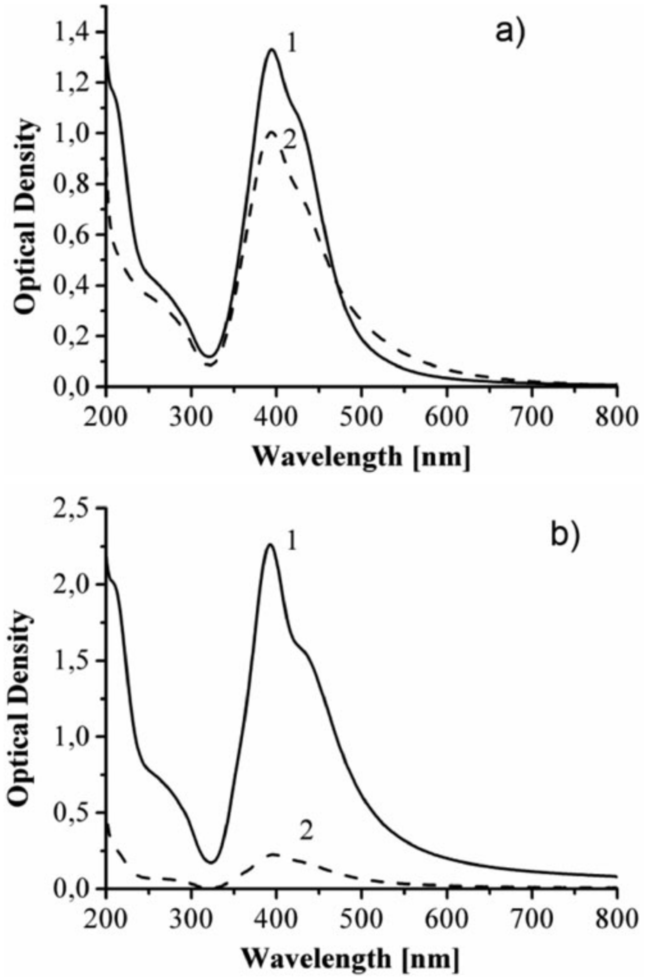

Figure 3. UV-vis spectra of Ag NPs synthesized in polymer matrices: 1 – D-*g*-PAA5, 2.

3. Results and Discussion

In situ synthesis of Ag NPs in D-*g*-PAA and PAA polymer matrices resulted in rather stable silver colloids. Analysis of microscopy data confirms the obtaining of spherical or roughly spherical Ag NPs with average grain size 10–20 nm (Fig. 1 a,b). Electron diffraction data are in a good agreement with that of face-centered-cubic form of metallic silver (Fig. 1c).

The UV-vis spectra of silver colloids revealed a surface Plasmon resonance band with a maximum about 400 nm indicating the presence of Ag NPs (Figs. 2–3). The shape and position of Plasmon curve depend on the particles size and fashion [2]. The maxima on UV-Vis spectra correlate with nanoparticles size obtained from TEM.

Linear PAA is known to be suitable matrix for Ag NPs in aqueous medium [9,13]. In addition to its role as a stabilizer for Ag colloids, the amino groups of PAA can form complexes with Ag^+ in the solution to substantially reducing the reduction rate, leading to the formation of undistorted shape of particles. PAA macromolecules take a random coil conformation in solution that is typical for linear macromolecules. The internal structure

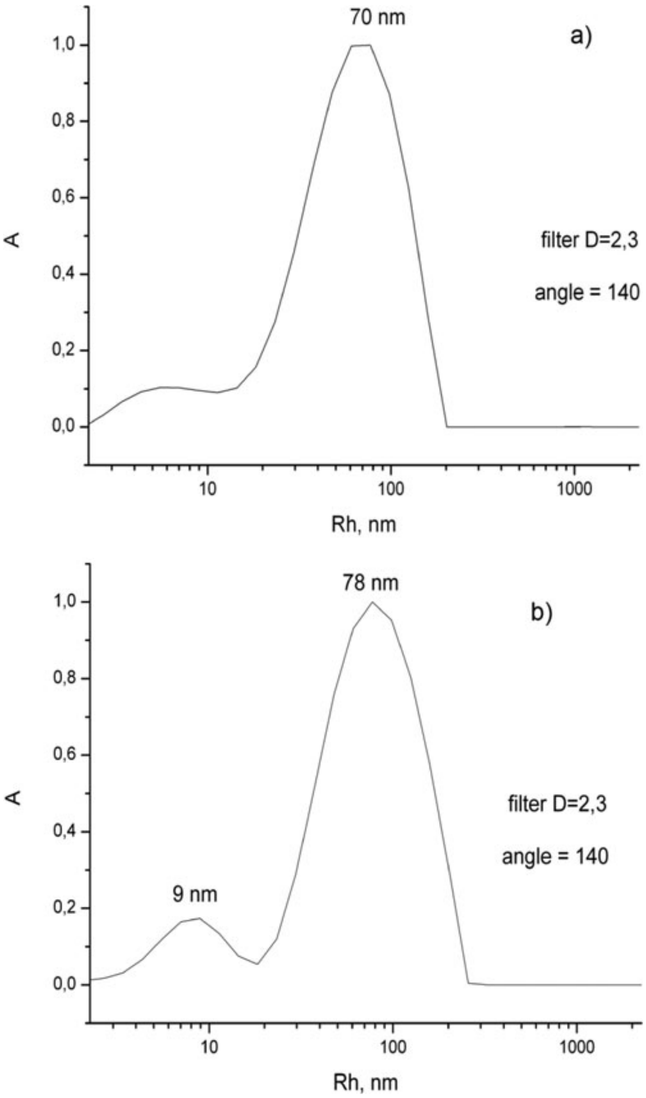

Figure 4. DLS measurements for AgNPs synthesized in linear PAA (**a**) and branched D-g-PAA5 (**b**) polymer matrices at 80°C.

of branched D-*g*-PAA copolymers is determined by the architecture of macromolecules. These copolymers are star-like polymer structures with small Dextran core and rather long PAA arms. So, the internal structure of polymers is supposed to affect some properties of colloids obtained in their presence.

UV-vis spectra of Ag colloids synthesized at 20°C (Fig. 2) show the maxima of absorption at 395 nm for all matrices, but the influence of the temperature of synthesis is different for colloid samples obtained in linear and branched polymer matrices (Fig. 3 a,b). The maximum position correlates with nanoparticles size calculated from TEM investigations.

Increase of synthesis temperature leads to decreasing of absorbance for system Ag/PAA (Fig. 3b). Ag NPs synthesized at 80°C in linear PAA are unstable, some precipitation just

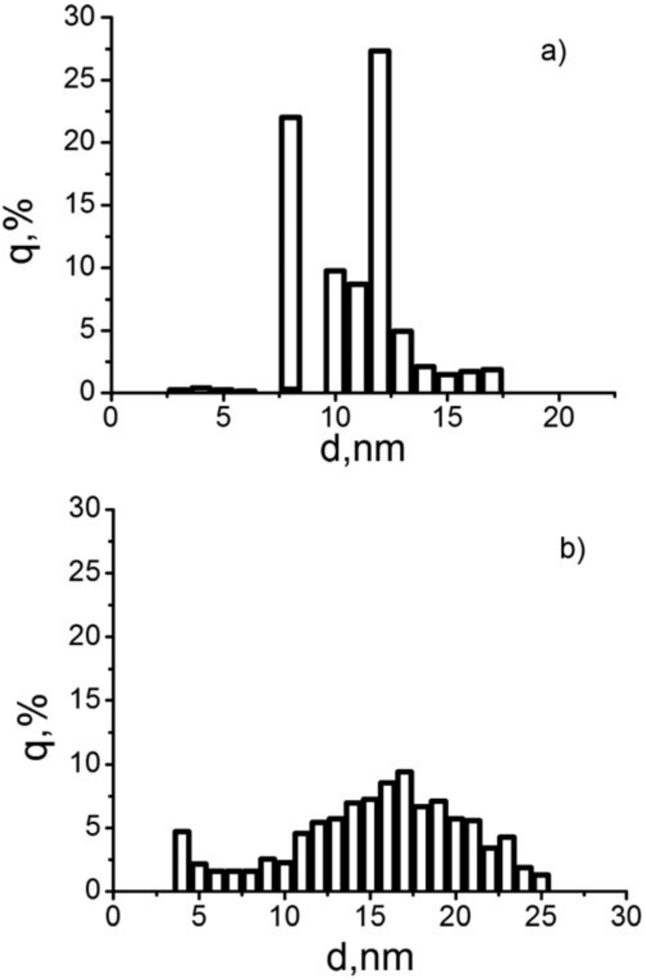

Figure 5. Size distribution histograms of the Ag NPs prepared from the solution of D-*g*-PAA20 at 80°C. Fresh-prepared Ag colloid (a) and after 6 moths (b).

after synthesis is observed. On the contrary, temperature rise of Ag NPs synthesis in star-like D-g-PAA matrices conditions increasing of absorbance for system Ag/D-g-PAA that indicates a higher concentration of Ag NPs in solution.

The analysis of UV-vis spectroscopy and TEM data shows that branched polymers D-*g*-PAA are the more efficient for synthesis and stabilization of Ag NPs water dispersions in comparison with linear PAA.

Dynamic light scattering analysis confirmed the differences in particle size distribution of Ag NPs for colloids obtained at 80°C in PAA and D-*g*-PAA matrices (Fig. 4) More intensive peaks corresponds to polymer molecules and less ones to silver NPs.

The Ag colloids prepared in the branched polymer matrices were kept at room temperature without precipitation in 6 months.

Ag NPs *in situ* syntheses under described condition always gave the nanoparticles with bimodal size distribution (Fig. 5a). The histograms keep these characteristics for colloids, which were maintained for 6 months (Fig. 5b).

The template role of the host polymer for the *in situ* synthesis of nanoparticles consists in improvement of the nanoparticle dispersion inside the polymer matrix and also in prevention of the aggregate formation. The internal structure of polymers in solution affects the process of Ag NPs formation at different temperatures.

4. Conclusions

Synthesis Ag NPs in D-*g*-PAA and PAA polymer matrices resulted in rather stable colloids with nanoparticles of 10–20 nm in size. The internal structure of polymers in solution affects the process of Ag NPs formation at different temperatures. Branched polymer matrix D-*g*-PAA allows obtaining stable silver colloids even at high temperature when the linear PAA matrix is not efficient.

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