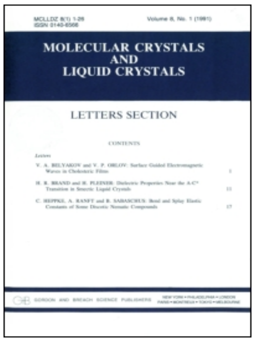

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Green route synthesis of nanosilver into polyelectrolyte solutions at high pH value

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ABSTRACT
Formation and properties of Ag sols fabricated in aqueous solutions of linear and branched polyelectrolyte matrices using ascorbic acid and hydrogen as reductant was studied at pH = 12. Alkaline medium was used to prove the difference of the AgNPs nucleus onto carboxylate and carbamide groups of polymer matrix. The structure of the host polymer affects the process of AgNPs formation in aqueous solution. It was proved the difference in the nucleation process for nanoparticles formation in carbamide and carboxylate groups. The aggregation of both types of AgNPs leads to forming of polydispersed polygonal nanoparticles in sols synthesized with both reductants.

KEYWORDS
Branched polymer; polyelectrolyte; nanoparticle; silver; hydrogen; ascorbic acid

1. Introduction

The synthesis of nanoparticles has been extensively studied mainly owing to their advantageous applications [1–6]. Nanosilver uses an antimicrobial agent; home water purification systems, medical devices, cosmetics, etc. Besides their antimicrobial features, silver nanoparticles exhibit strong optical features making the nanoparticles suitable for biological sensing and imaging. The properties of nanomaterials strongly depend upon the size and morphology of nanoparticles, their interactions with stabilizers and surrounding media. Various chemical reduction systems as sodium borohydride, hydrazine, ascorbic acid have been used to wet synthesize of silver nanoparticles [8, 9]. However the green route synthesis of nanoparticles opens a new gateway for the production of silver nanoparticles (AgNPs), which are non-toxic and can be use for biomedical application [10–12]. Due to the high reactivity and agglomeration ability of AgNPs, their colloidal solutions often are not stable. Chemical reduction of silver salt in polymer matrix is the most prominent technique for synthesis of stable silver sols. Recentry we have proved the efficiency of using branched polymers dextran-graft -polyacrylamide as matrices for the formation of silver NPs and their stabilization. For sol preparation we used sodium borohydride, hydrazine, and glucose as reductant [9, 13–14].

In this paper we focuses on the formation and properties of Ag sols synthesized in linear and branched polyelectrolyte matrices using ascorbic acid and hydrogen as reductant.

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Absence of toxic products of reaction were the main reasons to use its as a reduction agent. pH = 12 was used to mediate the difference of the nucleus of the silver nanoparticles onto carboxylate and carbamide groups of polymer matrix.

2. Experimental

2.1. Materials

Polyacrylamide (PAA) and branched copolymer Dextran-graft-Polyacrylamide (D-g-PAA) in anionic form were used as polymer matrices for in-situ synthesis of Ag sols. Synthesis, characterization and alkaline hydrolysis of nascent non-charged polymers and their anionic derivatives were described in [15, 16]. For nascent star-like polymer the PAA chains were grafter to Dextran core with $Mw = 7 \times 10^4$. According to the synthesis condition a theoretical number of grafts in copolymers was equal to 5 and 20, the copolymers were designed as D-g-PAA5 and D-g-PAA20 correspondingly. For comparative experiments the linear PAA was synthesized.

The non-charged branched and linear samples were saponified during 30 min using NaOH in order to obtain polyelectrolytes, referred as D-g-PAA5(PE), D-g-PAA20(PE) and PAA(PE). During alkaline hydrolysis the $-CONH_2$ groups of PAA chains were converted to the $-COONa$ groups.

The hydrolyzed samples were precipitated into an excess of aceton, dissolved in bi-distillated water, then freeze-dried and kept under vacuum for preventing them from further hydrolysis.

Silver Sol Synthesis. Ag sols were synthesized into aqueous solution of linear and branched polymer matrices. The polymer solutions were prepared in double-distilled deionized water and had pH = 7÷7,3 just after polymer dissolving. The pH = 12 was created by adding 0.2 ml of ammonia water solution (30%). 2 ml 0.1 M AgNO3 was added to 5 ml of aqueous solution of polymer (C = 0.1 g/l). This mixture was stirred during 20 min and heated to 60°C.

Ascorbic acid or hydrogen were used as a reducing agent. For ascorbic acid: 0.15 ml of 0.01 M ascorbic acid was added to polymer solution with Ag^+ precursor under continuous stirring. For the hydrogen: the polymer solution with precursor was purged with hydrogen during 30 min. It turned reddish brown, thus the formation of AgNPs was indicated.

2.2. Experimental methods

Characterization of polymer matrices

Size-exclusion chromatography (SEC). SEC analysis was carried out by using a multidetection device consisting of a LC-10AD Shimadzu pump (throughput 0.5 ml·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 NaNO3 was used as eluent.

Potentiometric titration was performed for determination of conversion degree of amide groups into carboxylate ones during alkaline hydrolysis using a pHmeter pH-340 Economic Expres (St. Petersburg, Russia). HCl (0.2 N) and NaOH (0.2 N) were used as titrants. The concentration of the aqueous polymer solutions was 2.10^{-3} g.cm-3 Polymer solutions were titrated successively with HCl up to pH = 2 and then with NaOH up to pH = 12. Previously, fine blank titrations (titration of non-hydrolyzed polymer) were made. The measurements

Table 1. Molecular parameters of polymer matrices.

Sample	$M_w \times 10^{-6}$	R_g,nm	M_w/M_n	A, %
D-g-PAA5	2.15	85	1.72	35
D-g-PAA20	1.43	64	1.98	37
PAA	1.40	68	2.40	28

were performed at T = 25°C under nitrogen. The absorption of OH^- anions was calculated through the analysis of the titration curves and the limits of the corresponding values were used to determine the conversion degrees of carbamide groups into carboxylate ones (A, %).

The molecular parameters of synthesized uncharged polymer matrices and their conversion degree to anionic form after hydrolysis are shown in the Table 1.

Characterization of silver sols

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

Transmission electron microscopy (TEM). Transmission electron microscopy (TEM) images were registered with CM12 microscope (FEI, Netherlands) equipped with a Megaview SIS Camera. Image analysis was carried out using the open source software ImageJ. Diameter values (d) were estimated from area values (S) according to the formula: $d = 2\sqrt{(S/\pi)}$. Over a dozen TEM images were processed for size distribution analysis in order to obtain reliable data.

3. Results and discussion

The theoretical and experimental works demonstrate that branched polymer systems are more compact as compared with their linear analogs [15], have more rigid internal structure and higher local concentration of functional groups in comparison with linear macromolecules of the same chemical nature. Such structure peculiarities gives advantages to use branched polymer as matrices for stable nanosystems fabrication [15].

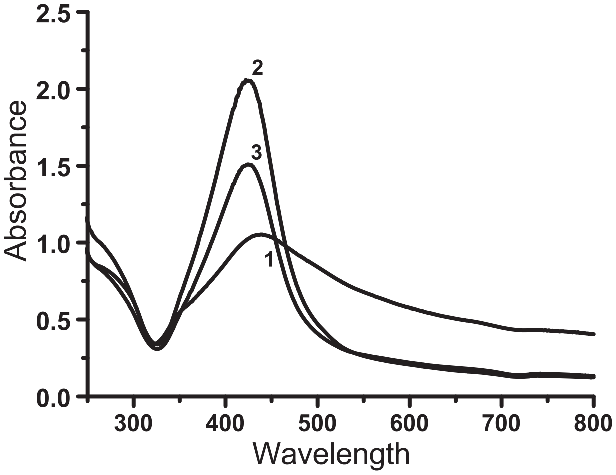

Figure 1. Absorbance spectra of silver sols synthesized into polyelectrolyte polymer matrices: 1- PAA(PE); 2-D-g-PAA5(PE); 3-D-g-PAA20(PE) (just after synthesis).

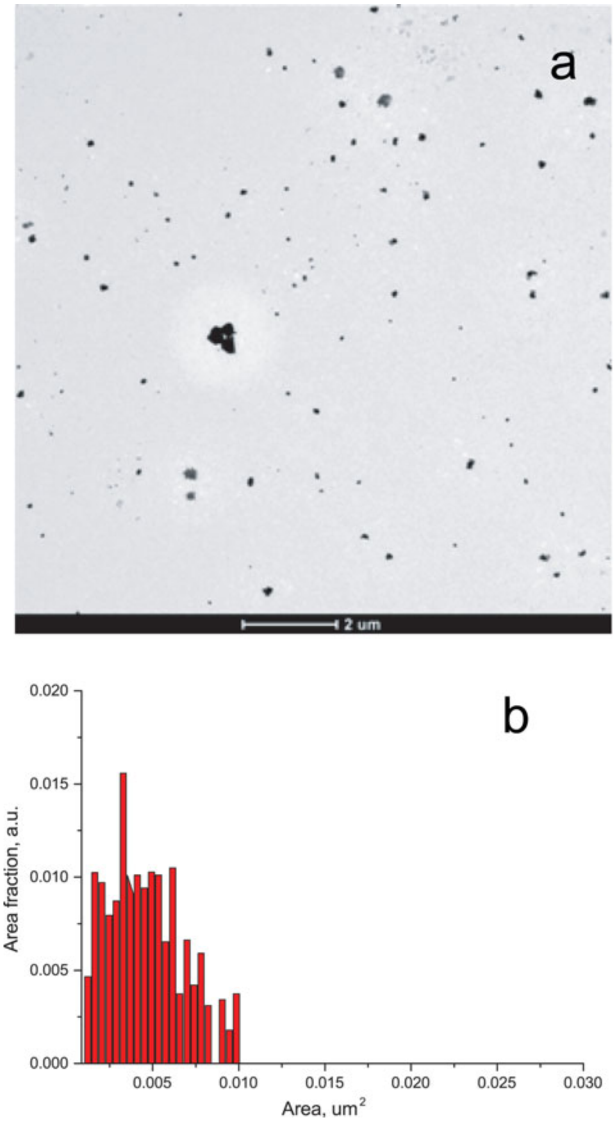

Figure 2. TEM images (a) and size distribution histogram (b) of silver sols synthesized into D-g-PAA5(PE) matrix (3 days after synthesis).

In our previous research [17] it was proved that grafted chains in branched polymers Dextran-graft-Polyacrylamide even in nonionic form have worm-like or mushroom conformation that is far from random coil. For all hydrolyzed D-g-PAA$_n$ (PE) the grafted chains are extremely straightened therefore their conformation cannot be changed when solution dilutes [16]. Saponified Dextran-graft-Polyacrylamide contains two types of functional groups: carbamide and carboxylate ones. The pH value of the solutions was equal to ~7–7,3 after dissolving PAA(PE) and D-g-PAA(PE) samples in bi-distilled water. Thus, carboxylate groups of polymer were partially hydrolyzed in such conditions. The nucleation process after reductant addition should differ for silver ions interacting with carbamide or carboxylate moiety. At $pH = 12$ all carboxylate groups are completely dissociated, and therefore are in COO^- form. Thus, polymer matrices contain both $CONH_2$ groups and COO– groups.

Silver sols synthesized using ascorbic acid as reductant

Sols formation was registered in both linear and branched polymer matrices. Plasmon bands are much narrower in shape for nanoparticles synthesized in solution of branched polymers, but the position of maximum remains comparable for all nanosystems (Figure 1). The absorption maxima of silver sols obtained in branched matrices are registered at 425 nm, are narrower than for linear matrices with maximum at 440 nm. The blue shift of maximum position testifies the formation of smaller Ag nanoparticles in branched polyelectrolytes in comparison with linear one. The absorbance in the range of 300 nm for all spectra (Figure 1) can correspond to small AgNPs of 2–4 nm in size or Ag^+ ions. Taking in account an excess of reducing agent it can be concluded that this peak deals with the presence in sols only the silver particles less than 4 nm in size.

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. Obviously the nucleation process should differ for nanoparticles formed on carbamide and carboxylate groups of polymer matrix. Carboxylate groups bearing silver ions promote the formation of very small AgNPs in comparison with nanoparticles formed on carbamide groups. On the other hand, the rigid macromolecular structure restricts moving out the small NPs formed. For that cause NP aggregation of both type of AgNPs leading to forming polydispersed in size and polygonal in shape nanoparticles. It was confirmed by TEM (Figure 2). One can summarize that alkaline medium promotes both yield and aggregation of NPs. The branched polymer D-g-PAA5 (PE) was more efficient than D-g-PAA20(PE). Thus, for in-situ synthesis of nanoparticles in polymer template the optimal branched structure exists. Sols synthesized in linear polyelectrolyte solution was not stable, some precipitation process was observed just after synthesis.

Silver sols synthesized using hydrogen as reductant

The well expressed SPR maxima for sols synthesized using hydrogen as reductant was observed and its internsity was depended on polymer matrix type (Figure 3). The peak at the range of 440–450 nm is dedicated to particles of 75–100 nm in size [18, 19]. The shoulder

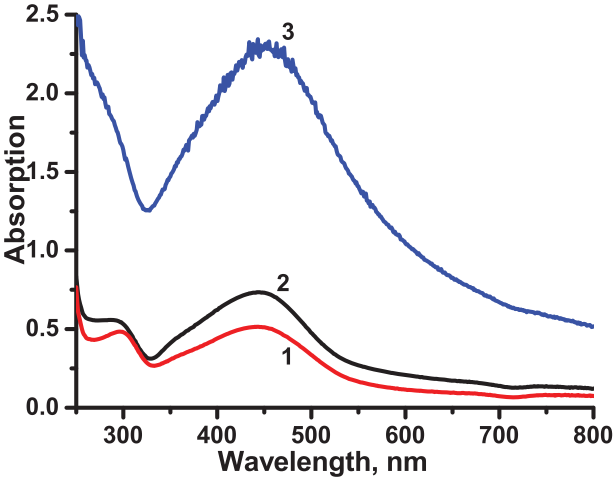

Figure 3. UV-visible spectra of AgNPs synthesized in polyelectrolyte matrices: 1 – PAA(PE), 2- D-g-PAA5(PE), 3 - D-g-PAA20(PE) (just after synthesis).

existence points the increasing of scattering contribution to the value of absorption with the growth of particle size, at it has been proved by David D. Evanoff et al. [21]. Optical density at peak maxima as a function of concentration and size of AgNPs indicates the highest ability of D-g-PAA20 (PE) to stabilize colloidal system with higher content of silver component in comparison with nanosystems synthesized in D-g-PAA5 (PE) and PAA(PE). This conclusion concerning effect of polymer matrix on the sols formation is in agreement with the data for nanosystems synthesis using ascorbic acid as reductant.

Spectroscopy data has been confirmed by TEM (Figure 4; a, b). Nanosystems consist multi-branched asymmetric particles (Figure 4; a) with linear size 50-100 nm (take into account the complicated shape of nanoparticles the area distribution of nanoparticles in TEM image was analyzed (Figure 4, b).

TEM images of silver sols synthesized using hydrogen revealed their high polydispersity (Figure 4, a–b). We observe clearly the presence of AgNPs aggregates of complicated shape. The image statistical treatment confirms their higher average diameter and polydispersity of AgNPs synthesized in polyelectrolyte matrices using hydrogen (Figure 4, b) in comparison with the systems described above.

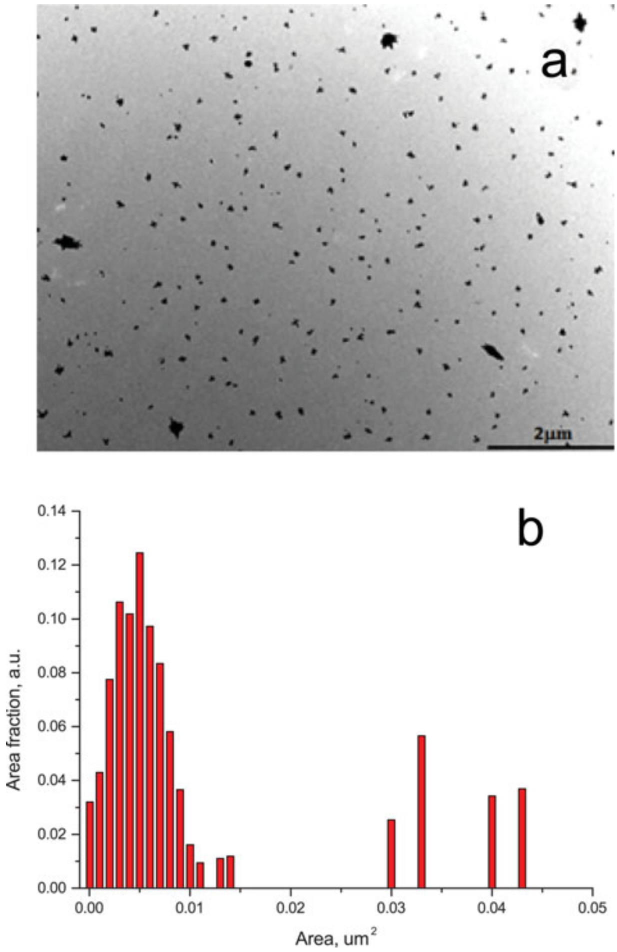

Figure 4. Small-scale TEM image (a) and size distribution histogram (b) for silver sol synthesized into D-g-PAA5(PE) (3 days after synthesis).

At pH = 12 a stable system was not obtained into PAA(PE) template. Some precipitation of Ag particles was observed just after synthesis. That can explain low intensity of absorption band in Figure 1 (curve 1); Figure 3 (curve 1). On the contrary, the nanosystems synthesized in branched polyelectrolyte matrices were stable.

4. Conclusions

The internal structure of the host polymer affects the process of Ag NPs formation in aqueous solution. Branched polyelectrolyte polymer matrices are much more efficient for silver colloid synthesis and stabilization of NPs in comparison with linear one at pH = 12. It was proved that the nucleation process differs for nanoparticles formation on carbamide and carboxylate groups of polymer matrix. Carboxylate groups bearing silver ions promote the formation of very small AgNPs in comparison with nanoparticles formed on carbamide groups. The aggregation of both type of AgNPs leads to formation of polydispersed in size and polygonal in shape nanoparticles. Thus, alkaline medium promotes both yield and aggregation of NPs.

At pH = 12 a stable system was not obtained into PAA(PE) template. Some precipitation of Ag particles was observed just after synthesis, however the nanosystems synthesized in branched polyelectrolyte matrices were stable.

References

[1] Rodríguez-León, Ericka, Iñiguez-Palomare, Ramón, Elena Navarro, Rosa, Herrera-Urbina, Ronaldo, Tánori, Judith, Iñiguez-Palomares, Claudia and Maldonado, Amir. (2013). *Nanoscale Research Letters*, *8*, 318.

[2] Jiang, D., Xie, J., Chen, M., Li, D. Zhu, J., & Qin, H. (2011). *Journal of Alloys and Compounds*, *509*, 1975–1979.

[3] Kabashin, A.V., Delaporte, P., Pereira, A., Grojo, D., Torres, R., Sarnet, T., & Sentis, M. (2005). *Nanoscale Research Letters*, *5*, 454–463.

[4] Iravani, S., Korbekandi, H., Mirmohammadi, S. V., & Zolfaghari, B. (2014). *Res Pharm Sci.*, *9*(6), 385–406.

[5] Kora, AJ, Sashidhar, RB, & Arunachalam, J. (2010). *Carbohydrate Polymers*, *82*, 670–679.

[6] Vilchis-Nestor, AR, Sánchez-Mendieta, V, Camacho-López, MA, Gómez-Espinosa, RM, Camacho-López, M. A., & Arenas-Alatorre, J (2008). *Materials Letters*, *62*, 3103–3105.

[7] T.Liu, D. Li, Yang, D., & Jiang, M. (2011). *Materials letters*, *65*, 628–631.

[8] Chekin, F., & Ghasemi, S. (2014). *Bull. Mater. Sci.*, *37*, (6), 1433–1437.

[9] Chumachenko, V., Kutsevol, N., Rawiso, M., Schmutz, M., & Blanck, C. (2014). *Nanoscale Research Letters*, *9*, 164.

[10] Sadeghi, B., & Meskinfam, M. (2012). *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *97*, 326–328.

[11] Singhal, G., Bhavesh, R., Kasariya, K., Sharma, A. R., & Singh, R. P.. (2011). *J Nanopart Res.*, *13*, 2981–2988.

[12] Kora, A. J., Sashidhar, R. B., & Arunachalam, J.. (2010). *Carbohydrate Polymers*, *82*, 670–679.

[13] Kutsevol, N. V., Chumachenko, V. A., Rawiso, M,., Shkodich, V. F., & Stoyanov, O. V. (2015). *Journal of structural chemistry*, *V.56*(5), 1016–1023.

[14] Kutsevol, N., Chumachenko, V., Rawiso, M., & Shyichuk, A. (2016). *Micro & Nano letters*, *22*, 1–4.

[15] Kutsevol, N., Bezugla, T., Bezuglyi, M., & Rawiso, M. (2012). *Macromol. Symp.*, *V.317–318*(1), 82–90.

[16] Kutsevol, N., Bezuglyi, M., Rawiso, M., & Bezugla, T. (2014). *Macromol. Symp.*, *335*, 12–16.

[17] Peña-Rodríguez, O., González Pérez, P. P., & Pal, U. (2011). *Int. J. Spectroscopy, article ID 583743*, *10*.

[18] Kutsevol, N., Guenet, J. M., Melnyk, N., Sarazin, D., & Rochas, C. (2006). *Polymer*, *47*, 2061–2068.

[19] Bulavin, L. eonid., Kutsevol, N. ataliya., Chumachenko, V. asyl., Soloviov, D. mytro., Kuklin, A. lexander., & Marinin, A. ndriy.. (2016). *Nanoscale Research Letters*, *11*, 35.

[20] Bhui, Dipak Kumar, Bar, H. arekrishna., Sarkar, P. riyanka., Sahoo, Gobinda Prasad, De, Sankar Prasad, & Misra, A. jay.. (2009). *Journal of Molecular Liquids*, *145*, 33–37.

[21] Evanoff, D. D. Jr., & Chumanov, G. (2004). *J. Phys. Chem. B.*, *108*(37), 13957–13962.