

Water-soluble branched copolymers dextran-polyacrylamide and their anionic derivatives as matrices for metal nanoparticles *in situ* synthesis

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Introduction

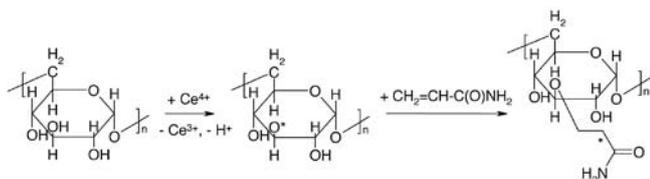
Noble metal nanoparticles (NPs) are becoming increasingly important in a variety of scientific fields as well as their potential applications in catalysis, photographic processes, cosmetics, medicine, biotechnology, etc. [1 ÷ 9]. Properties of nanosystems strongly depend on the morphology, crystal structure, and dimension of nanoparticles. The methods of NPs synthesis determine all these parameters and stability of colloid system as well. Therefore extensive research has gone into developing suitable preparation techniques to form noble metal nanoparticles. Chemical reduction of metal ions into neutral metal clusters is the most extensively investigated method. Polymer matrices have attracted considerable attention as a promising approach for *in situ* synthesis of metal NPs of controlled size and morphology. The internal structure of macromolecules affects both the process of NPs formation and metal colloid stability [4, 5].

Experimental Section

Materials. Dextran ($M_w = 2 \times 10^4$ designated as D20 throughout and $M_w = 7 \times 10^4$ designated as D70 throughout) were purchased from Fluka. Branched copolymers Dextran-*graft*-Polyacrylamide (designated as D20-g-PAA and D70-g-PAA) were synthesized in our laboratory and characterized previously [10, 11]. The sample of linear Polyacrylamide (PAA) was synthesized under the same condition. NaOH from Aldrich was used for alkaline hydrolysis of polymer samples.

Synthesis of polymer matrices. Cerium-ion-induced redox initiation method was used for the synthesis of the branched copolymers D-g-PAA [10]. The average number of grafting sites per backbone molecule (n) depends on the ratio of Ce(IV) concentration to Dextran [10]: $n = \frac{[mol\ Ce(IV)]}{[mol\ Dextran]}$. The amount of monomer acrylamide (AA) was kept the same for both syntheses.

The mechanism of Ce(IV) initiation involves the formation of chelate complex [12], which while decomposing generates free radical sites on the polysaccharide backbone. These active free radicals trigger PAA chains growth in the presence of acrylic monomer. The reaction path is shown below:



0.2 mmol of Dextran (D20 or D70) was dissolved in 100 ml of distilled water. This solution was stirred while removal of the dissolved oxygen was achieved by bubbling a gentle flux of argon for about

20 min. Then Ce(IV)/HNO₃ initiator (0.125 N HNO₃) was injected to obtain $n=5$ for both syntheses. Acrylamide monomer (0.2 mol) was added and the polymerization proceeded under argon atmosphere for 24 h. The synthesized copolymers were precipitated into an excess of acetone, re-dissolved in water and finally freeze-dried. The content of Dextran component in branched copolymers is less than 3 %, thus, their macromolecules have star-like architecture (Tab. 1).

Table 1

Molecular parameters of polymers obtained by SEC-LS

Sample	$M_w \times 10^{-6}$ [g·mol ⁻¹]	R_g , [nm]	Cont _{Dextran} ^a , [%]
D70-g-PAA	2.15	85	3
D20-g-PAA	1.60	67	1
PAA	1.40	68	-

Alkaline hydrolysis of synthesized branched and linear samples was carried out as follows: 2 g of D-g-PAA was dissolved in 200 ml of distilled water then the required amount of NaOH solution was added to it. The mixture was placed in water bath at 50°C. The probes were taken in 30 min and precipitated by acetone. All samples were freeze-dried and kept under vacuum. The anionic derivatives of the polymers are designated as PAA-anionic and D-g-PAA-anionic throughout.

Self-Exclusion Chromatography coupled with light scattering (SEC-LS) was used for polymer samples characterization. SEC analysis was carried out by using a multidetection device consisting of a LC-10AD Shimadzu pump (throughput 0.5 ml·min⁻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.

The degree of conversion of non-ionic samples to ionic form was analyzed using potentiometric titration of hydrolyzed samples and it was close to 30%.

***In situ* Ag nanoparticles synthesis.** The silver nanoparticles (Ag NPs) were synthesized using the polymer matrices such as linear PAA and branched copolymers D-g-PAA in anionic and ionic forms. NaBH₄ was used as a reducing agent.

0.25 ml 0.1M AgNO₃ was added to 5 ml of aqueous solution of polymer (C=0.1 g/dl) and stirred during 20 min. Then 5 ml of 0.1 M NaBH₄ was added. The solution turned dark reddish brown immediately after adding of NaBH₄, thus particle formation was indicated. The stability of obtained nanosystems was being

controlled during 6 months. Second experiment was carried out using 0.3M AgNO₃ and more concentrated polymer solution (C=0.5 g/dl). Absorption spectra were observed in UV-Vis region using Varian Cary 50 Scan UV-Visible Spectrophotometer. Original product solutions were diluted before spectral measurements. The identification of Ag NPs and their size analysis were performed using high-resolution transmission electron microscopy (TEM) and selected area electron diffraction (JEOL (Japan) Jem-1000CXII).

Pd nanocatalyst preparation. The palladium nanoparticles (Pd NPs) were synthesized using the polymer matrices of anionic derivatives of linear PAA and branched copolymers D-g-PAA. Polymers solutions were added to aqueous suspension of ZnO and stirred during 2 h. Then solution of palladium chloride was added and stirred during 3 h. The bittern was kept 10 h at room temperature, then filtered, washed and dried. Pd NPs were obtained by chemical reduction of Pd ions into neutral metal clusters using hydrogen as reductant. The heterogeneous catalysts are designated as Pd-PAA-anionic/ZnO and Pd-D70-g-PAA-anionic/ZnO throughout.

The identification of Pd NPs and their size analysis were performed using high-resolution scanning electron microscopy (JEOL (Japan) JSM-7500).

Catalytic activity of synthesized catalysts was studied in the reaction of 3,7,11-threemethyl-dodecyl-1-ol-3 hydration.

Results and Discussion

In situ synthesis of Ag NPs in polymer matrices resulted in rather stable colloids excepting anionic derivative of PAA. Analysis of microscopy data confirms the obtaining of spherical or roughly spherical Ag NPs with average grain size 20 nm (Fig. 1a) X-Ray diffraction data are in a good agreement with that of face-centered-cubic form of metallic silver (Fig. 1b).

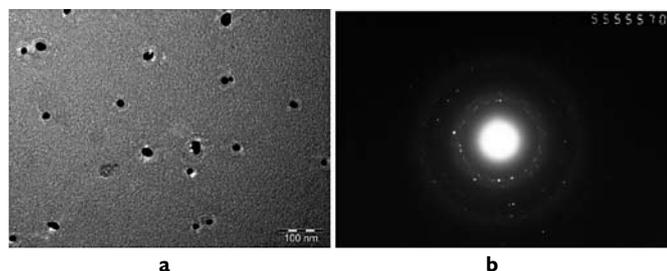


Fig. 1. (a) TEM and (b) diffraction images of the Ag NPs synthesized in D70-g-PAA matrix

The UV-Vis spectrum of silver colloids revealed a surface Plasmon absorption band with a maximum at 400 nm indicating the presence of Ag NPs (Fig. 2, 3).

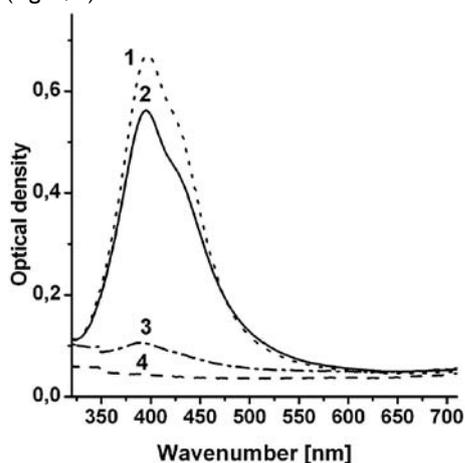


Fig. 2. UV-Vis spectra of Ag NPs synthesized in polymer matrices: 1 – D70-g-PAA, 2 – PAA, 3 – D70-g-PAA-anionic, 4 – PAA-anionic. [AA monomer]/[Ag⁺]=3

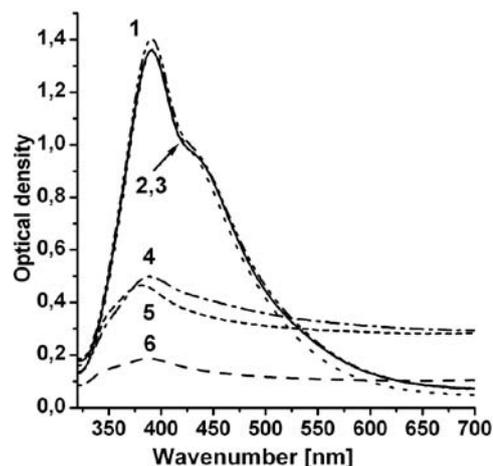


Fig. 3. UV-Vis spectra of Ag NPs synthesized in polymer matrices: 1 – D70-g-PAA, 2 – D20-g-PAA, 3 – PAA, 4 – D70-g-PAA-anionic, 5 – D20-g-PAA-anionic, 6 – PAA-anionic. [AA monomer]/[Ag⁺]=5

The position and shape of the Plasmon absorption depends on the particles size and shape [2]. As all Ag NPs syntheses were carried out under the same conditions only the nature and structure of polymer matrices affect the particle size and morphology.

The analysis of UV-Vis spectroscopy and TEM data shows that for nonionic polymer matrices at lower molar ratio of monomer AA links to Ag⁺ (Fig. 2) the branched polymer is the most efficient. When molar ratio increases the efficiency of linear and branched polymer matrices becomes close (Fig. 3). For anionic linear and branched polymer matrices the maxima of optical density of Ag colloids are rather lower in comparison with nonionic polymers. *In situ* synthesis of AgNPs in anionic matrices the formation of a precipitate was observed. The stable colloid system was not obtained in PAA-anionic polymer matrix at [AA monomer]/[Ag⁺]=3, all Ag particles precipitated.

UV-Vis spectrum for Ag NPs obtained in D70-g-PAA-anionic matrix reveals the shift of absorption maximum to short-wave region indicating formation smaller particles in comparison with polymer matrices D20-g-PAA-anionic (Fig. 3). The branched polymers D70-g-PAA-anionic and D20-g-PAA-anionic have the same number of grafts, but different distance between them [10, 11]. Thus, the internal structure of branched polymers in solution affects the process of Ag NPs formation.

The Ag colloids prepared in the branched polymer matrices were kept at room temperature without precipitate appearance.

Linear and branched anionic polymer matrices were also used for preparation of heterogeneous catalysts Pd-PAA-anionic/ZnO and Pd-D70-g-PAA-anionic/ZnO. TEM images display a granular structure of catalyst surfaces, and Pd particles formed in linear and branched polymer matrices have different size (Fig. 4 a,b). Pd particles have size of 2-10 nm and they are fairly evenly distributed on the surface of the media only when using the branched polymer matrix (Fig. 4b). In the case of Pd/ZnO catalyst grains are much larger; some of them have diameter more than 100 nm and form aggregates.

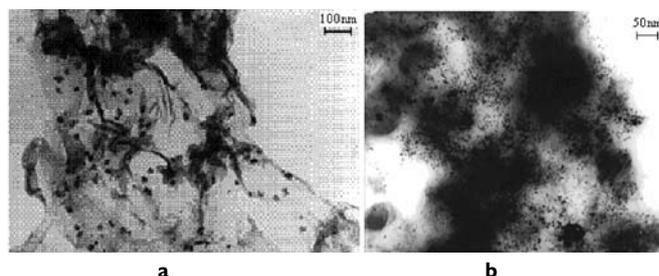


Fig. 4. TEM images of Pd NPs on catalyst surface: (a) Pd-PAA-anionic/ZnO and (b) Pd-D70-g-PAA-anionic/ZnO

The heterogeneous Pd catalysts synthesized in branched polymer matrices Pd-D20-g-PAA-anionic/ZnO and linear Pd-D70-g-PAA-anionic/ZnO one were considerably more active in the reaction of 3,7,11-threemethyl dodecin-1-ol-3 hydration than the catalyst Pd-PAA-anionic/ZnO. The catalysts prepared in branched matrices provide the rate of hydration 7 times higher in comparison with catalyst synthesized in linear PAA.

Conclusions

In situ synthesis of Ag NPs in the solutions of linear PAA and branched polymer D-g-PAA resulted in stable Ag colloids. Ag NPs size and morphology were depended on macromolecular structure of polymer matrices. PAA and D-g-PAA anionic derivatives are less efficient in comparison with nonionic polymer matrices for Ag NPs synthesis, but when it is required to use polyelectrolyte matrices the branched samples are preferable.

Anionic derivatives of linear PAA and branched D-g-PAA matrices were used for Pd nanocatalyst preparation. The efficient heterogeneous catalysts with nanosized Pd particles distributed on the surface of catalyst carriers were synthesized only when branched polymer matrices were only in branched polymer matrices.

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