PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 1, 01PCN17(3pp) (2012)

In Situ Synthesis of Silver Nanoparticles in Linear and Branched Polymer Matrices

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(Received 15 June 2012; published online 22 August 2012)

Silver nanoparticles were synthesized in linear and branched polymer matrices at different temperatures. The template role of the host linear Polyacrylamide and star-like copolymer Dextran-*graft*-Polyacrylamide for *in situ* synthesis of nanoparticles was studied by TEM, UV-Vis spectrophotometry and Dynamic light scattering. It was shown that the internal structure of polymers in solution drastically affects the process of Ag NPs formation. Branched polymer matrix allows to obtain a stable silver colloid even at high temperature when the linear PAA matrix is not efficient.

Keywords: Silver Nanoparticles, Polyacrylamide, Branched Polymer.

PACS number: 82.35.Np

1. INTRODUCTION

Silver nanoparticles (Ag NPs) have attracted significant attention due to their unique optical, thermal and electrical properties as well as potential biomedical application. However, the high reactivity of Ag NPs raises difficulties in developing stable silver colloidal solutions. The nanoparticles rapidly undergo to agglomeration, therefore it is urgently to search the manufacturing methods of Ag NPs having good storage stability.

The most extensively investigated route for developing Ag NPs is chemical method where silver salt in polymer matrix solution is reduced by reducing agents [1]. The nature and structure of the polymer matrices affect the shape and size of the particles [1]. Obviously, the internal structure of macromolecule should affect the process of nanoparticle formation. The present study is scoped on silver nanoparticle *in situ* generation using branched and linear Polyacrylamide matrices. The branched polymer structures demonstrate an improvement of ordering phenomenon, so such systems can differ in functionalities from their linear analogues [2, 3].

2. EXPERIMENTAL

2.1 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 $M_w = 7\times10^4$ was purchased from Fluka. Cerium (IV) ammonium nitrate (CAN) from Aldrich was used as initiator of radical polymerization of polymer matrices.

The syntheses of linear PAA and branched copolymer D-*g*-PAA were described in details previously [4]. According to the synthesis condition a theoretical number of grafts in branched copolymer was equal to 5.

PAA and D-*g*-PAA samples were freeze-dried and kept under vacuum. Double-distilled deionised water was used for solutions preparation.

2.2 *In situ* generating of silver nanoparticles

Ag NPs were synthesized using linear and branched polymer matrices at 20, 40 and 80°C. $NaBH_4$ was used as a reducing agent. Molar ratio of AA monomer to silver ions was equal to 5.

0.25 ml 0.3M $AgNO_3$ was added to 5 ml of aqueous solution of polymer (C = 0.5 g/l) and stirred during 20 min. Then 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 obtained nanosystems was being controlled during 12 months.

2.3 Experimental methods

Characterization of polymer matrices.

Size-exclusion chromatography. 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 0.1M $NaNO_3$ was used as eluent.

Characteriozation 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.

Dynamic light scattering (DLS). The particle size measurement was carried out using An ALV5000 autocorrelator (ALV, Langen, Germany). A Spectra Physics 2020-2W argon ion laser ($\lambda = 514.5$ nm) acts as the co-

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herent light source. The normalized autocorrelation functions of the intensity of the light scattered by the particles are measured at a scattering angle $\theta = 40°$ and 140° and are analyzed using the CONTIN software.

Transmission electron microscopy (TEM). 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). The samples were prepared by spraying diluted dispersion onto carbon-coated copper grids and were analyzed.

3. RESULTS AND DISCUSSION

The molecular parameters of synthesized 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}]	M_w/M_n	R_g [nm]
D-*g*-PAA	2.15	1.72	85
PAA	1.40	2.40	68

Branched D-*g*-PAA copolymer has a low content of polysaccharide component (~ 3%). It is star-like copolymer with Dextran core and Polyacrylamide corona [4]. Linear PAA has random coil conformation is solution. Thus, two polymers having similar chemical nature, but different internal molecular structure were used as matrices for Ag NPs preparation. The stable dark reddish brown colloids were obtained as a result of *in situ* synthesis of Ag NPs. Microscopy data show the formation of spherical or roughly spherical Ag NPs with grain size 10 – 20 nm (Fig. 1). X-Ray diffraction data confirm the face-centered-cubic form of Ag NPs.

The position and shape of the Plasmon absorption depends on the particle size [1]. The temperature of Ag NPs synthesis affects the properties of colloidal silver system. For linear PAA the intensity of absorption decreases for colloids obtained at higher temperatures (Fig. 2). Ag NPs synthesized at 80 ºC in PAA were unstable, some precipitation just after synthesis was observed.

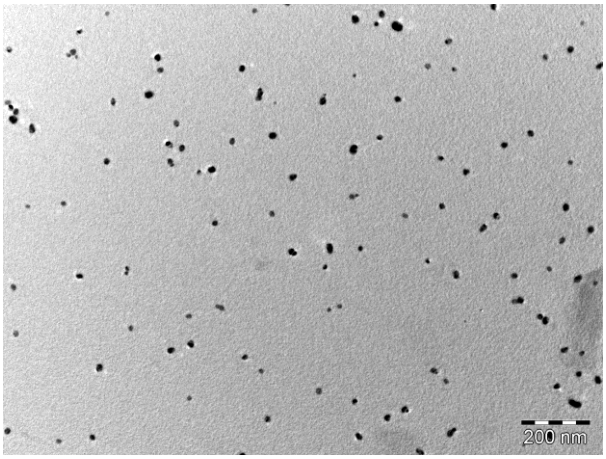

Fig. 1 – TEM image of the Ag NPs synthesized in D-*g*-PAA matrix at 20°C

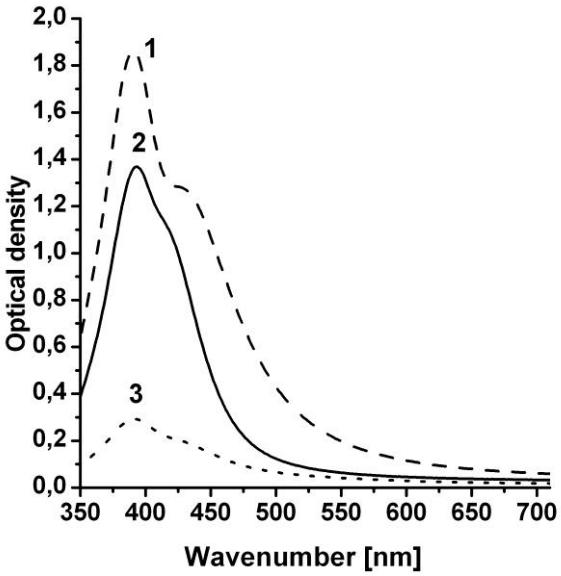

Fig. 2 – UV-Vis spectra of Ag NPs synthesized in PAA matrix at 20 (1), 40 (2) and 80°C (3)

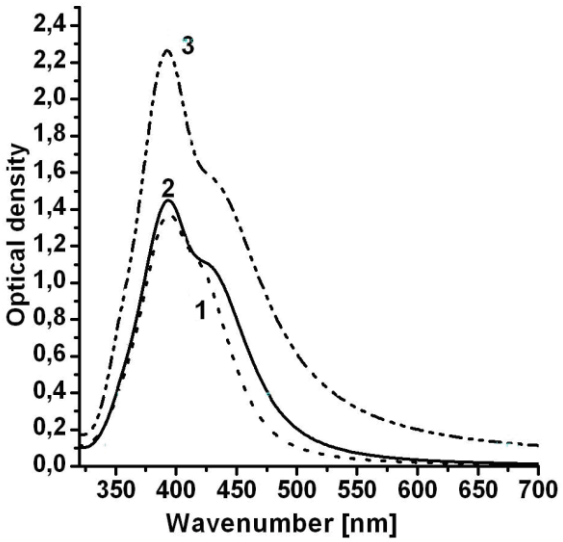

Fig. 3 – UV-Vis spectra of Ag NPs synthesized in D-*g*-PAA matrix at 20 (1), 40 (2) and 80°C (3)

On contrary, for branched polymer matrices the increasing of synthesis temperature leads to absorption increasing (Fig. 3) and all colloid systems are stable (without any precipitation). For both polymer matrices the appearance of shoulder on absorption curve in long-wave range was registered, but for branched polymer matrices the shoulder becomes more distinct for colloids obtained at higher temperatures. This phenomenon can be a result of increasing the amount of larger particles in colloid solution.

DLS analysis confirms the differences in particle size distribution of Ag NPs for colloids obtained at 80 °C in PAA and D-*g*-PAA matrices (Fig. 4).

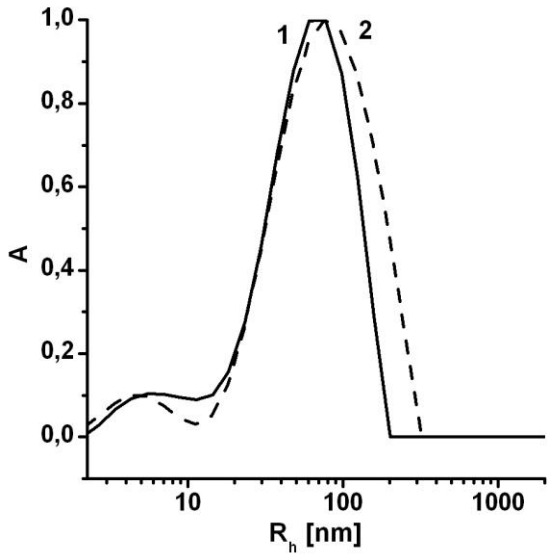

Fig. 4 – DLS size distribution for silver colloids synthesized in PAA (1) and D-*g*-PAA (2) matrices at 80°C.

Ag NPs present a peak centered at 6 and 9 nm for PAA and D-*g*-PAA matrices correspondingly. However, the peak for colloid obtained in PAA is rather smoothed. The intensive peaks centered at 70 and 78 nm refer to hydrodynamic radii of PAA and D-*g*-PAA macromolecules. These results are in good agreement with the SEC data for polymer matrices (Table 1).

The Ag colloids prepared in the branched polymer matrix D-*g*-PAA were stable at room temperature without precipitation during one year.

4. CONCLUSION

The internal structure of polymers in solution affects the process of Ag NPs formation at different temperatures. The template role of the host D-*g*-PAA for the *in situ* synthesis of nanoparticles consists in improvement of the nanoparticle dispersion inside the polymer matrix and also in prevention of the aggregates formation. Branched polymer matrix allows to obtain a stable silver colloid even at high temperature when the linear PAA matrix is not efficient.

AKNOWLEDGEMENTS

This investigation was funded by NATO Grant CB.NUKR.CLG 98424.

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