

Smart Silver Nanoparticles from Nanoreactors made by Invertible Polyesters

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ABSTRACT

We developed a simple way to prepare smart silver nanoparticles that are well dispersible in both polar and nonpolar media. The synthesis was performed using solutions of an invertible amphiphilic polyester made via a polycondensation reaction of sebacic acid and poly(ethylene glycol). Reduction, formation of silver nanoparticles, and their stabilization occur in the polyester micellar domains (nanoreactors) that are formed in the reaction medium.

Comparison of XRD experimental data shows that microphase separation of polyester units resulting in subsequent large range ordering occurs by change of the polyester concentration. The shape and size of the domains depend on the polyester concentration and the ratio between the lipophilic and hydrophilic constituents in the macromolecule as well as on solvent (reaction medium) polarity.

Keywords: smart nanoparticles, polymeric nanoreactors.

1 INTRODUCTION

Size- and shape- control of nanoparticles has generated essential interest due to potential applications in optics, electronics, magnetic media, and catalysis [1]. A number of methods for preparing silver colloids include chemical reduction with or without stabilizing polymers [2] and reduction in reverse micelles [3]. The concept of a nanoreactors for the development of nanoparticles has been explored recently, for example in [4, 5]. Polymers may be used as steric stabilizers and also as a means to control nanoparticle growth and interparticle spacing [6].

2 EXPERIMENTAL

The invertible amphiphilic polyester ($M_w = 22,600$ g/mol) is synthesized via a polycondensation reaction of sebacic acid and poly(ethylene glycol) with a molecular weight of 300 g/mol [7]. The polycondensation was carried out in a boiling toluene solution in the presence of sulfuric acid as a catalyst. The molecular weight of the polyester was estimated via static light scattering in acetone at 25 °C at a fixed angle of 173° using a Malvern Nano ZS instrument equipped with a He-Ne laser. For the synthesis of silver colloids, $Ag(NH_3)_2OH$ solution containing about 0.3 g/mL of Ag^+ ions was added to the polyester solution in

benzene. A solution of 0.2 g of sodium hydroxide in 1.0 mL of water was added to a solution of 0.12 g of silver nitrate in water to give a brown precipitate of silver oxide. The polyester concentration was 5 and 25 mM. The resulting mixture was stirred at room temperature. Soon after the addition of the silver precursor to the polyester solution, silver nanoparticles started to form. Their formation manifested by a yellow coloration of the solution. It is well known that formation of Ag colloids may be monitored by observing changes in the absorption spectra using UV-Vis spectroscopy.

Developed silver nanoparticles were characterized using UV-Vis spectroscopy, dynamic light scattering (DLS), and scanning electron microscopy (SEM). Polyester solutions of various concentrations were analyzed by means of X-ray diffraction measurements (XRD) before the synthesis of silver nanoparticles. Wide-angle and small-angle X-ray scattering curves were recorded by a Phillips X-ray diffractometer (Cu- K_α radiation monochromatized by an Ni filter). The optical absorption spectra of the samples were recorded on a Cary Varian 100 UV-Vis spectrophotometer over the wavelength range from 350 to 800 nm. The particle size distribution was measured by dynamic light scattering (DLS) at 25 °C at a fixed angle of 173° using a Malvern Nano ZS instrument equipped with a He-Ne laser. The size and shape of the obtained silver colloids were confirmed by scanning electron microscopy (FESEM, LEO 1530 microscope). For the formation of a silver particulate layer and SEM investigations we used dip-coating equipment operated with a step motor. Dispersions of the synthesized silver colloids for UV-Vis spectroscopy, DLS and SEM measurements were prepared by diluting the resultant reactive mixture with toluene or acetone.

3 RESULTS AND DISCUSSIONS

Changes in optical density were used to follow formation of silver nanoparticles in time. We studied Ag^+ reduction adding silver precursor to, respectively, 5 mM and 25 mM polyester solutions. We observed that a rapid reaction starts immediately after mixing the reagents. Characteristic absorption bands (indicated after the dispersion of the nanoparticle samples when toluene was the dispersion medium) (Fig.1, plots 1,2) appeared in UV-Vis spectroscopy measurements after only 4 hours of the reaction. Similar absorption bands were observed when dispersion was performed in acetone (Fig.1, plots 3,4). No changes in the maximum wavelength of the absorption

bands have been observed with the increase in polyester concentration from 5 to 25 mM in toluene and acetone.

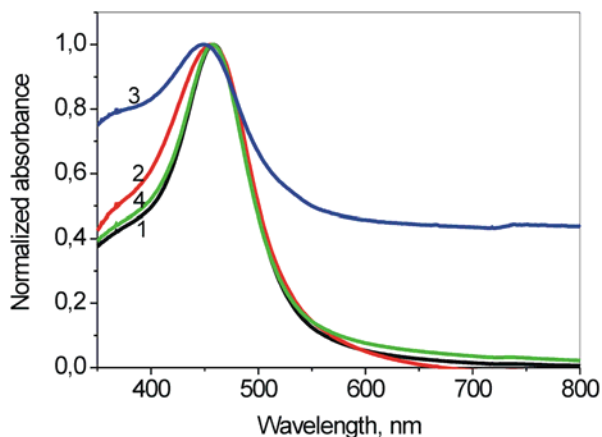


Figure 1 UV-Vis spectra of prepared amphiphilic silver nanoparticles dispersed in toluene (1,2) and acetone (3,4) (polyester concentration 5mM — 1,3, 25 mM — 2,4).

The presented results show that the formation of the silver nanoparticles occurs after the addition of the precursor solution to the concentrated solutions of the invertible amphiphilic polyester. The nanoparticle development is controlled by the concentration of the polyester. We observed that the absorption band on the spectra became wider, indicating a possible slight aggregation of silver nanoparticles. The resultant silver nanoparticles are well-dispersible in both polar and nonpolar media. Figure 2 presents DLS data that show the particle size distribution of the resultant nanosilver dispersed after the synthesis in acetone and toluene. The plots indicate that the size distribution of the developed silver nanoparticles is narrow in both polar and nonpolar dispersion media. The normalized volume density plots show a maximum at about 8 nm for the measurements performed in acetone and at about 12 nm for the measurements carried out in toluene. The measured size of the developed nanoparticles is in good agreement with the size of polyester architectures reported recently [7].

A morphological study of the synthesized silver nanoparticles has been done using SEM. Figure 3 shows the SEM micrograph of the nanoparticles dispersed in toluene after the synthesis. For the SEM measurements, developed silver colloids were diluted with toluene, and a thin film was fabricated using the dip-coating technique. The picture indicates that the size distribution of the silver nanoparticles is very narrow. The average diameter of the nanoparticles is approximately 12 nm. Therefore, the diameter of the silver nanoparticles measured by SEM confirms the results of the DLS measurements.

Polyester solutions of various concentrations were analyzed by wide-angle X-ray scattering. The WAXS curve of 5 mM polyester solution (Figure 4) in benzene is typical for a semicrystalline polymer with several sharp diffraction

peaks superposed on a broad amorphous halo. The degree of crystallinity (X_{cr}) has been found to be about 45%. The mean size of the crystallites (D) was estimated and found to be 27 nm.

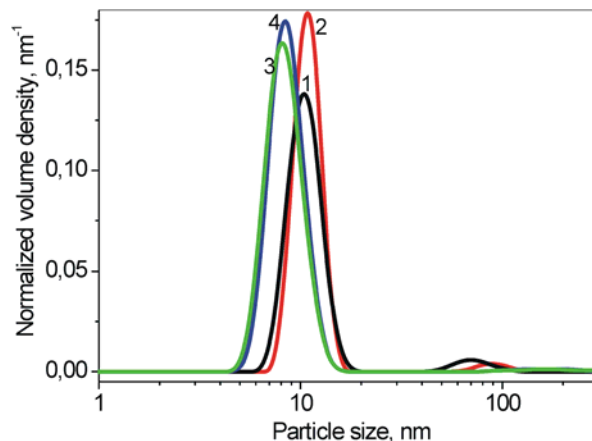


Figure 2 The size distribution of prepared amphiphilic silver nanoparticles dispersed in toluene (1,2) and acetone (3,4) (polyester concentration 5mM — 1,3, 25 mM — 2,4).

The macromolecules of the amphiphilic polyester contain alternately distributed lipophilic and hydrophilic units. They tend to form stable invertible micelles in solvents of various polarity. It is known that concentrated block copolymer solutions form domain structures with a certain size and shape. This process depends on the size of hydrophilic (here, poly(ethylene glycol) (PEG)) and hydrophobic (here, polymethylene) fragments. X-ray diffraction patterns recorded from the various concentrations of the polyester solution reasonably confirmed the presence of ordered domains made from the amphiphilic macromolecules. The ordering of polyester domains is obviously related to the polymer concentration in the solution.

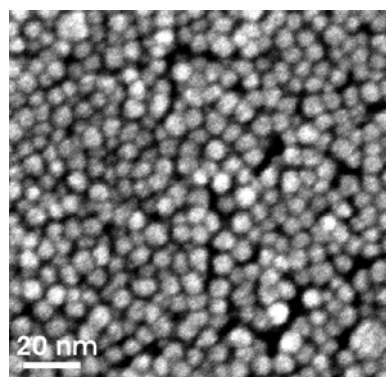


Figure 3 SEM micrograph of prepared in polyester nanoreactors (polyester concentration 25 mM) silver.

We suggest that the mobility of polymer fragments increases by dissolving of the polyester in benzene. Comparison of WAXS experimental data shows that microphase separation of polyester units resulting in subsequent large range ordering occurs. Incompatible hydrophilic and hydrophobic constituents of the polyester form micellar domains that may be considered as nanoreactors for the formation of silver nanoparticles.

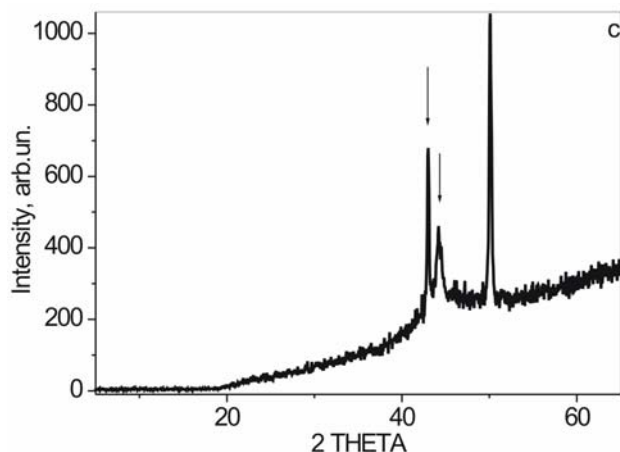
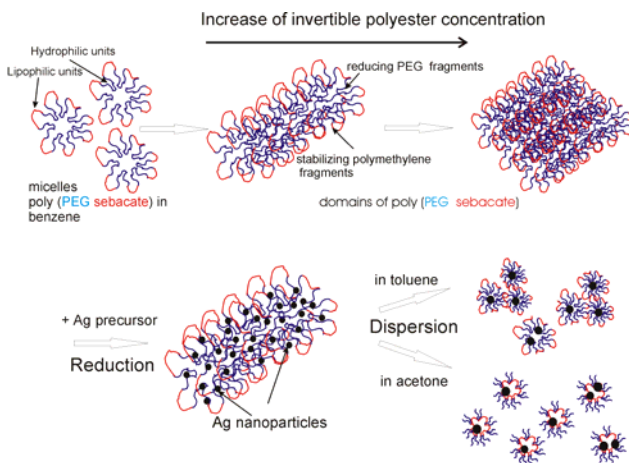


Figure 4 X-ray diffraction patterns for 5 mM polyester concentration in benzene.

It is known that poly(ethylene glycol) chains form a spiral structure in bulk. It consists of seven monomer units distributed along two convolutions with an interval of 1,93 nm. The macromolecule conformation remains stable in a concentrated polymer solution. It was found that metal complexes initially bound to pseudo crown ether structures of the poly(ethylene glycols) are reduced by the macromolecules.



Scheme 1 Formation of silver nanoparticles in polyester nanoreactors.

The invertible polyester micelles form ordered cylindrical associates with changing polyester concentration. The

associates transform into the lamellar phase with further increases in the polyester concentration.

We believe that the reduction of silver ions from the precursor $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ occurs in PEG cavities formed from the hydrophilic constituent of the invertible amphiphilic polyester (as shown in Scheme 1). Simultaneous stabilization takes place by the fragments of the invertible polyester chains. Further study of the reduction mechanism and kinetics of nanoparticles formation is in progress.

3 CONCLUSIONS

We developed a simple way to prepare uniform amphiphilic silver nanoparticles in concentrated solutions of an invertible polyester. Polymeric micellar domains serve as stable confined nanoreactors and simultaneously act as nanoparticle stabilizers. The silver complex is trapped in the polymeric nanoreactors and is reduced by their hydrophilic poly(ethylene glycol) branches. Due to the invertible properties of the polyester, the developed silver nanocolloids are amphiphilic and form stable colloidal solutions in both polar and nonpolar dispersion media. Controlled packing of nanoparticles is achieved by self-organization of the stabilized clusters on casting from a solution. We foresee that this technique can be extended for the preparation of a variety of metal nanoparticles under appropriate conditions.

4 REFERENCES

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