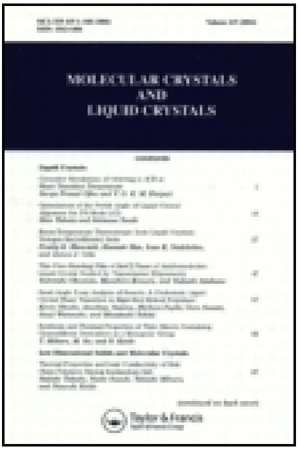

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Low-Temperature Synthesis and Properties of Silver Nanoparticles Stabilised by Acrylic Polymers

Boris M. Sergeev [a], Gleb B. Sergeev [a], Viktor A. Kasaikin [a], Ekaterina A. Litmanovich [a] & Andrej N. Prusov [a]

[a] Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow, 119899, Russia

To cite this article: Boris M. Sergeev, Gleb B. Sergeev, Viktor A. Kasaikin, Ekaterina A. Litmanovich & Andrej N. Prusov (2001): Low-Temperature Synthesis and Properties of Silver Nanoparticles Stabilised by Acrylic Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 356:1, 121-129

To link to this article: http://dx.doi.org/10.1080/10587250108023692

Mol. Cryst. and Liq. Cryst., 2001, Vol. 356, pp. 121-129
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Low-Temperature Synthesis and Properties of Silver Nanoparticles Stabilised by Acrylic Polymers

BORIS M. SERGEEV, GLEB B. SERGEEV, VIKTOR A. KASAIKIN,
EKATERINA A. LITMANOVICH and ANDREJ N. PRUSOV

*Department of Chemistry, M.V. Lomonosov Moscow State University,
Moscow 119899, Russia*

A cryochemical synthesis of silver nanoparticles stablised by poly(2-dimethylaminoethyl methacrylate) has been performed. It has been shown that precursors which do not possess optical properties of colloidal silver are present in the freshly prepared organodispersion of silver in 2-(dimethylamino)ethyl methacrylate (DMAEMA) on the early stages of nanoparticle growth. Sols prepared with cryochemically synthesised silver nanoparticles in water, acetone, and toluene were found to be sterically stabilised by macromolecular poly-DMAEMA layers formed at the surface of the nanoparticles. Dynamic light scattering data show that the thickness of these layers depends on the nature of the solvent.

Keywords: metal nanoparticles; cryochemistry; stabilisation of colloids

INTRODUCTION

The cryochemical synthesis of nanoparticles includes simultaneous evaporation of metal and volatile component, for example, an organic monomer, such as DMAEMA, followed by co-condensation of the vapours onto a cold surface of the vacuum

reactor [1]. Previously, stable silver organosols in the presence of methyl acrylate and poly(methyl acrylate) films containing metal particles of sizes not exceeding 15 nm were prepared [2]. In this study, we decided on poly-DMAEMA as a polymer stabiliser for silver nanoparticles. In contrast to poly(methyl acrylate), poly-DMAEMA is soluble in solvents different in polarity. This fact made it possible to disperse the nanoparticles, *in situ* stabilised by this polymer in the course of the cryochemical synthesis, in water, acetone and toluene and to examine the sols by optical absorption spectroscopy, dynamic light scattering and transmission electron microscopy (TEM).

EXPERIMENTAL

The procedures used for the cryochemical synthesis of Ag-DMAEMA organodispersions and for evaluation of the DMAEMA conversion into poly-DMAEMA were analogous to those described earlier [2]. We found that the conversion was 1.7-1.9% and remained unchanged as the Ag:DMAEMA molar ratio increased from 1:4000 to 1:1000. The mechanism of DMAEMA polymerisation in the test system is of particular interest and does not enter into the scope of this work.

Dynamic light scattering measurments were performed on an ALV-5 scattered laser light goniometer (Germany) at an angle 90°. An He-Ne laser (25 mW, 633 nm) was used as the light source.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of the organodispersion formed upon melting of solid co-condensate prepared at low (<1:4000) silver to DMAEMA molar ratio. Just after completon of melting the resulting solution is colourless. Surface plasmon absorption band characteristic of silver nanoparticles [3, 4] starts to develop only after 30-40 min of ageing the melt at 15°C. Thus, during this period dielectric (optical) properties of silver, which is present in the test system differ strongly from those of colloidal metal. Figure 2 shows that for the first 5 h after melting surface plasmon absorption band grows and narrows, while its position does not change. Later on further growth and narrowing of the band are accompanied by its blue shift from 453 nm to 420 nm. TEM micrographs show that on this stage 5-12 nm isolated particles and an amount of their aggregates are present in the system.

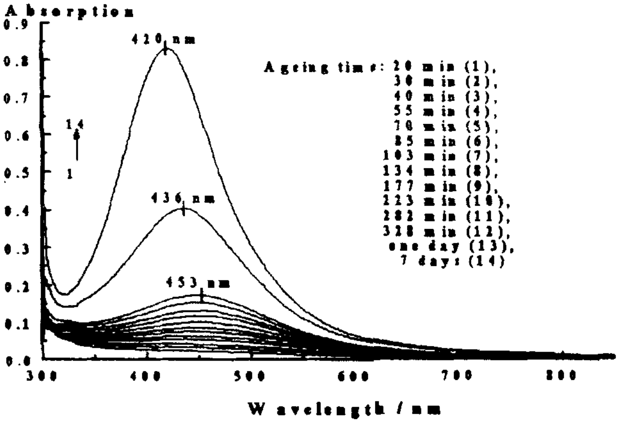

FIGURE 1 Temporal evolution of the absorption spectra of cryochemically prepared silver-DMAEMA co-condensate melt.

Dynamic light scattering examination (see Figure 3) shows that (i) the splitting of the broad diffusion coefficients distribution into two modes coincides in time with the development of absorption at 453 nm, and (ii) the blue shift of the band is accompanied by the appearance of relatively fast diffusing light scattering particles.

A set of data allows us to suppose that formation of silver nanoparticles in the Ag-DMAEMA system proceeds via some

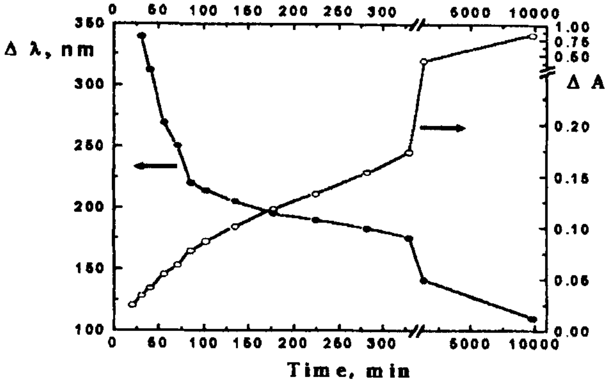

FIGURE 2 Changes in surface plasmon absorption band intensity (Δ A) and width (Δ λ) upon ageing of the cryochemically prepared silver organosol in DMAEMA.

principal stages. Melting of a low-temperature co-condensate is accompanied by partial polymerisation of DMAEMA and agglomeration of silver atoms and oligomeric clusters initially isolated in solid matrix of DMAEMA at 77 K yielding polymer-coated primary particles disposed towards rapid flocculation. Broad diffusion coefficients distribution of light scattering particles may be indicative of large variety of flock's sizes and shapes. Because intensity of the surface plasmon band (Δ A) is proportional to R (Δ A~R) while the band width Δ λ ~ R^{-1} [3,4], the low absorption in the visible range or extremely large bandwidth may be due to small particle size. Another possible cause may be associated with the presence in the test system of small clusters (<1-2 nm) not posessing electronic structure of bulk silver and absorbing light in UV [5].

Since portion of surface, valence unsaturated metal atoms in the flocculated primary particles is high, they agglomerate yielding silver nanoparticles. Formation and growth of the latters are accompanied by appearing in spectra distinct characteristic band at 453 nm (see Figure 1), increase of its intensity Δ A and decrease of the width Δ λ (see Figure 2). Lorentzian shape and fixed position of this band argue that silver nanoparticles are spherical and non-aggregated [3]. The initially broad diffusion coefficients distribution splits into two modes in ~100 min after melting of the co-condensate giving rise to relatively fast diffusing fraction (see Figure 3). Break up of the aggregates (flocks) is, in our opinion, promoted by their loosening upon nanoparticles growth due to substantial decrease of specific area and surface energy.

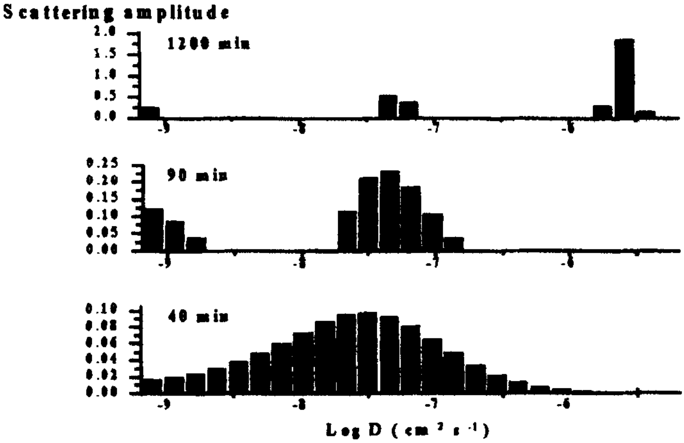

FIGURE 3 Temporal evolution of the translational diffusion coefficients distribution of the light scattering particles in the cryochemically prepared silver-DMAEMA organosol.

Since position of the surface plasmon absorption band depends on the effective dielectric function of the medium which, in turn, is a function of particles volume fraction [3], the observed blue shift at t > 5 h (see Figure 1) may be explained in agreement with our model by loosening of aggregates in the course of nanoparticles growth.

The stability of an Ag-DMAEMA organodispersion obtained at the Ag to DMAEMA molar ratio in co-condensate more than 1:4000 was examined by optical absorption spectroscopy (see Figure 4). It can be seen (curve 1) that in this case the surface plasmon absorption band of small isolated spherical silver particles is already present in the spectrum of the freshly prepared co-condensate melt. This band broadened with time and insignificantly shifted towards the short wavelength

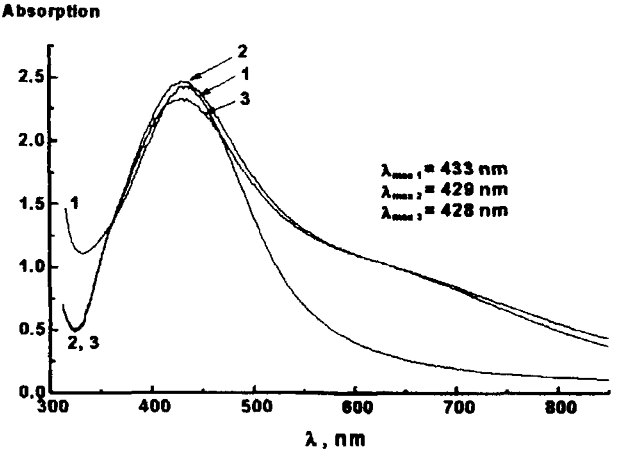

FIGURE 4 Absorption spectra of the silver-2-DMAEMA organosol, measured (1) after completion of the co-condensate melting and (2) 3 or (3) 30 days later. Molar ratio Ag : DMAEMA ~ 1 : 4000, optical path length 2 mm.

region three days after, and long wavelength shoulder appeared (curve 2). These spectral changes are indicative of the formation of an amount of silver nanoparticles aggregates in the test organosol [3]. The fact that the spectrum remained unchanged over a month (see Figure 4, curve 3) indicates that the sol is highly stable at room temperature.

A solid silver-containing poly-DMAEMA film was formed after the removal of unreacted DMAEMA from the initial organodispersion under vacuum. Silver sols in solvents of different polarity can be prepared by dispersing of this film in water, acetone, and toluene. Because the spectra of these sols (see Figure 5) are similar to those shown in figure 4 (curves 2, 3), we can conclude that drying of the organodispersion was also accompanied by partial aggregation of polymer-stabilised nanoparticles.

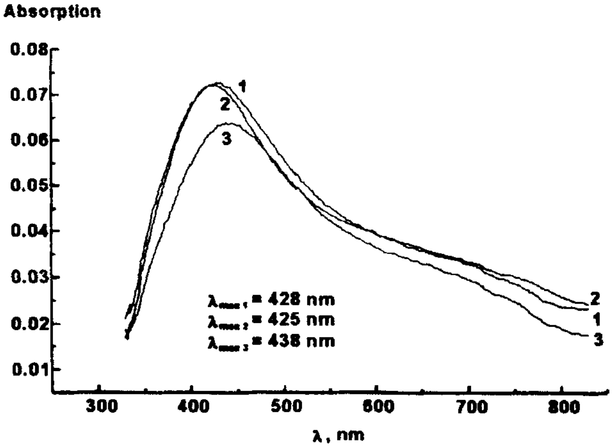

FIGURE 5 Absorption spectra of the silver solsprepared by dispersing of dry silver-containing poly-DMAEMA film in water (1), acetone (2), and toluene (3). Optical path length 2 mm.

The state of poly-DMAEMA layers that stabilise the nanoparticles in water, acetone, and toluene was examined by dynamic light scattering. The mean radii of light scattering particles in the sols (see Table 1) were calculated by the method of cumulants [6]. Afterwards, the particle size distributions in sols were determined by analising the autocorrelation functions of scattered light intensity fluctuations using the Tikhonov's regularisation procedure with accuracy not worse than 25%. Size-distribution functions of all examined sols show two distinct modes differing in translational diffusion coefficients. It means that the size distribution of the light scattering particles is bimodal. In our opinion, this bimodality indicates that both individual silver particles and their aggregates are present in the sols.

TABLE 1 Properties of silver sols sterically stabilised by poly-DMAEMA in water, acetone, and toluene.

Dispersion medium	Mean diffusion coefficient, $D/10^8 cm^2 s^{-1}$	Mean radius, R/nm	Isolated particles, R/nm	Aggregated particles, R/nm
Water	1.23±0.06	179.2±9.4	53.3±14.4	323.5±79.3
Acetone	8.22±0.09	80.8±0.9	18.5±2.1	111.9±11.5
Toluene	3.06±0.15	125.6±6.4	19.8±5.9	183.9±22.0

Table 1 summarises the radii R_1 and R_2 of equivalent hydrodynamic spheres corresponding to each diffusional mode, namely individual particles and their aggregates, respectively. These values were calculated by Stokes-Einstein equation. It is worth to note that the R_1 and R_2 values exceed the size of even the largest silver particles (~25-30 nm), which were found by TEM. The reason is that the radius of an equivalent hydrodynamic sphere that correspond to a light-scattering particle is the sum of the radius of metal core and the thickness of the polymer adsorption layer, which depends on the nature of the solvent. It can be seen in Table 1 that, in an aqueous solution, the radius R_1 of individual particles is more than two times greater than the particle size in acetone and toluene. In our opinion, the difference is due to the fact that, in aqueous media, poly-DMAEMA chains (which contain hydrated and partially protonated amino groups)

bonded to the surface of silver nanoparticles form a more bulky layer than that in acetone and toluene, and this bulky layer sterically stabilises silver nanoparticles.

CONCLUSIONS

Thus, the cryochemical synthesis of the Ag-DMAEMA system allowed us to observe nanoparticles growth and to prepare silver dispersions (sols) stabilised by poly-DMAEMA in different media. A set of data obtained by optical spectroscopy, TEM and dynamic light scattering suggest that at relatively high metal content both individual silver nanoparticles sterically stabilised by macromolecules and their aggregates are present in the sols. The optical and aggregative properties of the sols indicate that the thickness of the layer that stabilises the nanoparticles depends on the nature of the solvent (dispersion medium).

Acknowledgments
This work was supported by RFBR grant no. 99-03-32206.

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