Cryochemical synthesis and properties of silver nanoparticle dispersions stabilised by poly(2-dimethylaminoethyl methacrylate)

Boris M. Sergeev,*[a] Viktor A. Kasaikin,[a] Ekaterina A. Litmanovich,[a] Gleb B. Sergeev[a] and Andrei N. Prusov[b]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation.*
E-mail: bms@cryo.chem.msu.su
[b] *A. N. Belozersky Institute of Physico-chemical Biology, M. V. Lomonosov Moscow State University, 119899 Moscow,*
Russian Federation. Fax: +7 095 939 3181

A cryochemical synthesis of silver nanoparticles stabilised by poly(2-dimethylaminoethyl methacrylate) (poly-DMAEMA) has been performed; it has been found using optical spectroscopy, dynamic light scattering and electron microscopy that silver sols prepared with these nanoparticles in water, acetone and toluene are sterically stabilised by macromolecular poly-DMAEMA layers formed at the surface of nanoparticles, and the thickness of these layers depends on the nature of the solvent.

The cryochemical synthesis of nanoparticles includes simultaneous evaporation of a metal and a volatile component, for example, an organic monomer, 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(2-dimethylaminoethyl methacrylate) (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, stabilised by this polymer in the course of the cryochemical synthesis of the Ag–DMAEMA system, in water, acetone and toluene and to examine the sols by optical absorption spectroscopy, transmission electron microscopy (TEM) and dynamic light scattering.

The procedures used for the cryochemical synthesis of Ag–DMAEMA organic dispersions and for the 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 polymerization in the test system is of particular interest and does not enter into the scope of this work.

The stability of an Ag–DMAEMA organic dispersion obtained at the molar ratio Ag:DMAEMA $\approx$ 1:4000 in the co-condensate was examined by optical absorption spectroscopy (Figure 1). It can be seen that the surface plasmon band of small isolated spherical silver particles[3,4] in the spectrum of the freshly prepared Ag–DMAEMA organosol (Figure 1, curve *1*) was broadened and insignificantly shifted towards the short-wave region three days after, and a long-wave shoulder appeared (curve *2*). These spectral changes are indicative of the formation of an amount of silver nanoparticle aggregates in the test organosol.[4–6] The fact that the spectrum remained almost unchanged over a month (Figure 1, curve *3*) indicates that the sol is highly stable at room temperature.

Table 1 Characteristics of silver sols stabilised by poly-DMAEMA in water, acetone and toluene according to dynamic light scattering data.

Dispersion medium	R_m/nm	R_1/nm	R_2/nm
water	179.2±33.7	53.3	323.5
acetone	80.8±3.7	18.5	111.9
toluene	125.6±27.7	19.8	183.9

A solid silver-containing poly-DMAEMA film was formed after the removal of DMAEMA from the initial organic dispersion under vacuum. Silver sols in solvents of different polarity can be prepared by dispersing this film in water, acetone and toluene. Because the spectra of these sols (Figure 2) are similar to those shown in Figure 1 (curves *2* and *3*), we can conclude that drying of the organic dispersion was also accompanied by partial aggregation.

The state of poly-DMAEMA layers that stabilise the nanoparticles in water, acetone and toluene was examined by dynamic light scattering. The measurements were performed on an ALV-5 scattered laser light goniometer (Germany) at an angle of 90°. A He–Ne laser (25 mW, λ = 633 nm) was used as the light source. The mean radii R_m of light-scattering particles in sols (Table 1) were calculated by the method of cumulants.[7] Afterwards, the particle size distribution of sols as determined by analysing the autocorrelation functions $G(\tau)$ of scattered-light intensity fluctuations using the Tikhonov regularisation procedure[8] with an accuracy of 25% or better. The size-distribution functions of all examined sols showed two distinct modes differing in translation diffusion coefficients. As an example, Figure *3* (points) shows the experimental function $G(\tau)$ obtained by examining an aqueous sol at an aquisition time

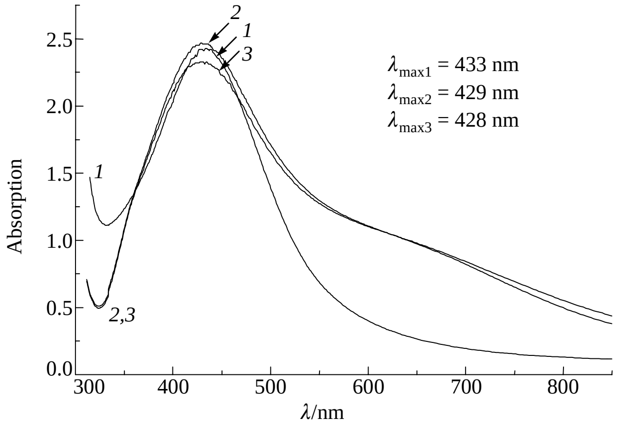

Figure 1 Absorption spectra of an Ag–DMAEMA organic dispersion, measured (*1*) after completion of the cryochemical synthesis and (*2*) 3 or (*3*) 30 days later. Optical path length, 2 mm.

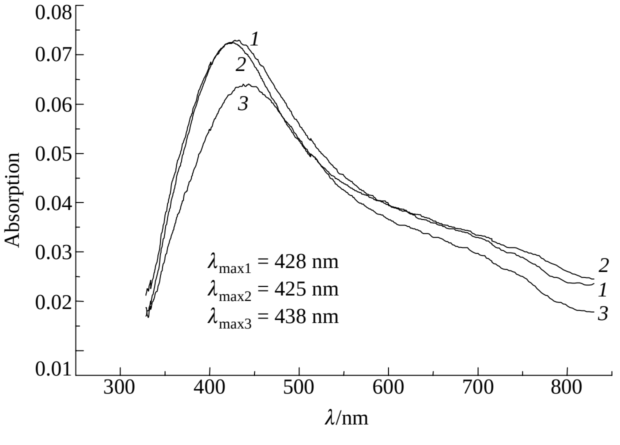

Figure 2 Absorption spectra of sols prepared by dispersing 3 mg portions of dry silver-containing poly-DMAEMA in 6 ml portions of (*1*) water, (*2*) acetone and (*3*) toluene. Optical path length, 2 mm.

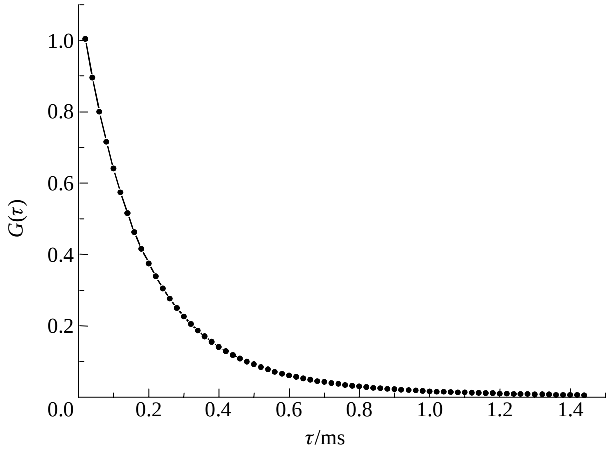

Figure 3 A typical plot of the autocorrelation function of intensity fluctuations of light scattered by silver nanoparticles stabilised by poly-DMAEMA in water.

of 25 min (the signal-to-noise ratio was higher than 15). This function is adequately approximated by the sum of two exponentials (Figure 3, curve). This means that the size distribution of the light-scattering particles is bimodal. In our opinion, this bimodality indicates that both individual silver nanoparticles and their aggregates are present in the sols. 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 the Stokes–Einstein equation.

It can be seen in Table 1 that the R_1 and R_2 values exceed the size of even the largest silver particles (~25–30 nm), which was found by TEM (Figure 4). The reason is that the radius of an equivalent hydrodynamic sphere that corresponds to a light-scattering particle is the sum of the radius of the 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.

Thus, the cryochemical synthesis of nanoparticles in the Ag–DMAEMA system allowed us to prepare silver dispersions (sols) stabilised by poly-DMAEMA in different media. A set of data obtained by optical spectroscopy, TEM and light scattering suggests that 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).

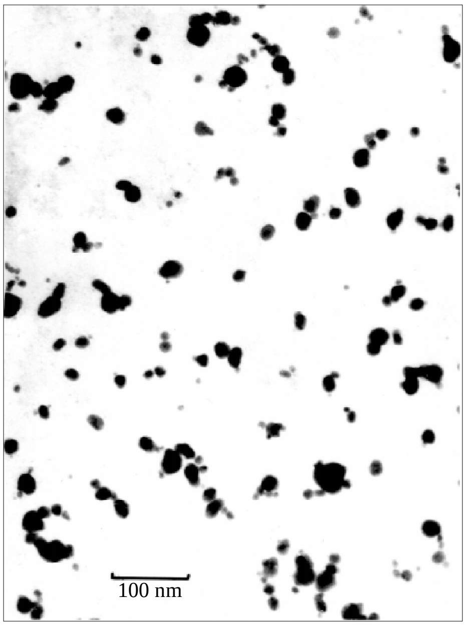

Figure 4 Photomicrograph of silver particles in an Ag–DMAEMA organic dispersion freshly prepared by the cryochemical synthesis.

This work was supported by the Russian Foundation for Basic Research (grant no. 96-03-33970).

References

1 K. J. Klabunde, *Free Atoms, Clusters and Nanoscale Particles*, Academic Press, New York, 1994.
2 B. M. Sergeev, G. B. Sergeev, Y. J. Lee, A. N. Prusov and V. A. Polyakov, *Mendeleev Commun.*, 1997, 151.
3 P. Mulvaney, *Langmuir*, 1996, **12**, 788.
4 U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters*, Springer, Berlin, 1995.
5 U. Kreibig, *Z. Phys. D: At., Mol. Clusters*, 1986, **3**, 239.
6 M. Sastry, N. Lala, V. Patil, S. P. Chavan and A. G. Chittiboyina, *Langmuir*, 1998, **14**, 4138.
7 D. E. Koppel, *J. Chem. Phys.*, 1972, **57**, 4814.
8 A. N. Tikhonov and A. A. Arsenin, *Metody resheniya nekorrektno postavlennykh zadach* (*Procedures for solving ill-posed problems*), Nauka, Moscow, 1979, p. 279 (in Russian).

Received: 30th November 1998; Com. 98/1407 (8/09473J)