Cryochemical synthesis of silver organosols in methyl acrylate

Boris M. Sergeev,*[a] Gleb B. Sergeev,[a] Yen J. Lee,[a] Andrei N. Prusov[b] and Vladimir A. Polyakov[c]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation.*
E-mail: gbs@cryo.chem.msu.su
[b] *A. N. Belozersky Institute of Physicochemical Biology, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation. Fax: +7 095 939 3181*
[c] *D. I. Mendeleev Russian Chemico-Technological University, 125047 Moscow, Russian Federation*

Joint condensation of silver vapour and methyl acrylate under vacuum onto a surface cooled with liquid nitrogen, followed by heating of the resulting co-condensate to room temperature, leads to partial polymerisation of the methyl acrylate and formation of highly stable organosols containing up to ~0.5 mg ml^{-1} of silver; the size of the metal particles does not exceed 15 nm.

Metal organosols are convenient objects both for the investigation of the physicochemical properties of metallic nano-sized particles and for the preparation of metal-containing polymers,[1] supported metallic catalysts[2] and metallic coatings.[2,3] Some unusual properties of metallic nano-sized particles and their precursors, atoms and small clusters, in particular, their high reactivity and tendency for aggregation,[2] hamper the preparation of highly concentrated metal-containing disperse systems, with a narrow size distribution of particles. The use of unsaturated organic compounds as disperse systems might be promising as a solution to this problem.[4] In this case, there is no need to introduce additional compounds such as surfactants into the system, because stabilisation can be achieved due to the more efficient interaction of the surface metal atoms with the monomer molecules. The ability of a series of monomers, for example, *p*-xylene, to undergo low-temperature polymerisation in the solid phase opens the way for a direct cryochemical synthesis of metal-polymer nano-sized composites.[5,6]

In this paper, we present the results obtained during the preparation of stable silver organosols in methyl acrylate by semi-preparative cryochemistry. Silver and methyl acrylate were chosen as objects for the study, because the state of small silver particles in organosols can be monitored by optical spectroscopy[7,8] and because it was of interest to prepare metal-containing polymers of the acrylic series.

Organosols were obtained by low-temperature co-condensation of silver and methyl acrylate vapour at a pressure of 10^{-3} to 10^{-4} Torr on the interior surface of a glass reactor, immersed into a Dewar vessel with liquid nitrogen, and subsequent melting of the co-condensate by heating the reactor to room temperature.[2,9] The content of the metal in the organosols was determined by atomic emission spectroscopy with an inductively coupled plasma. The silver was vaporised from a quartz crucible heated with a tungsten coil. The methyl acrylate to be vaporised was maintained at –35 °C to –40 °C. This procedure permits changing the concentration of the metal in the co-condensate by varying the rates of vaporisation of the components. When the silver content increases, the colour of the co-condensate changes from pale-yellow to dark-brown. When methyl acrylate is removed from the resulting organosol formed after melting of the co-condensate, a transparent dark-brown rubber-like film, readily soluble in acetone and chloroform, is left at the bottom of the reactor. The fact that the ^{1}H NMR spectrum recorded after dissolution of this film in $CDCl_3$ contains no signals typical of the $CH_2{=}CH$ group protons (δ ~6 ppm) indicates in our opinion that the methyl acrylate has polymerised during the cryochemical experiment. To estimate the yield of the polymer, a polymerisation inhibitor – the stable 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO, 10^{-3} M) – was added to the organosol just after melting. The remaining monomer was then removed by re-freezing into a tube cooled by liquid nitrogen and the difference between the volumes of the evaporated and recovered methyl acrylate was determined. According to the estimates, the degree of conversion of methyl acrylate under the experimental conditions was 1–2 vol.%. A similar result has been obtained by comparing the integral intensities of the signals corresponding to the CH_3 groups in the ^{1}H NMR spectra of solutions of the organosol in $CDCl_3$ with the intensities of the same signals in the spectra of solutions of the silver-containing polymer in $CDCl_3$. In the control experiments on one-component condensation of methyl acrylate (without metal in the heated crucible), the conditions of which were strictly identical to those of the joint condensation of the monomer with silver, we could not detect any substantial amounts of the polymer. This important result indicates that in this case, as in the case of polymerisation of acrylic acid that occurred with a yield of 30 to 50 vol.% only under conditions of joint condensation with silver,[10] polymerisation of methyl acrylate is initiated by atoms or nano-sized particles of silver rather than by emission of the heated metal vaporiser.

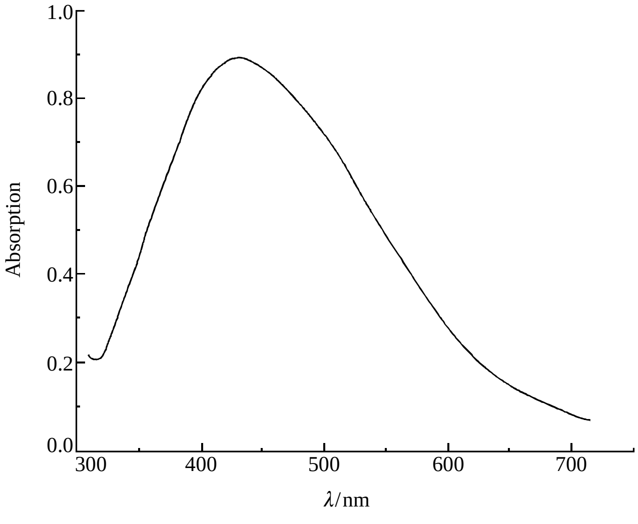

Figure 1 Absorption spectrum of the organosol of silver in methyl acrylate. Silver content 0.45 mg ml^{-1}; optical length of the cell 0.5 mm.

Figure 1 presents a typical absorption spectrum of the organosol obtained after melting of the co-condensate. The observed absorption band with a maximum at 400 nm is characteristic of spherical particles of colloidal silver ≤ 20 nm in diameter.[7] The position of the absorption band in the spectrum of the organosol is consistent with the results of transmission electron microscopy shown in Figure 2. The resulting photomicrographs indicate that the organosol contains silver particles with sizes not exceeding 15 nm. The absorption spectra in acetone of the silver-containing polymer isolated from the organosol and photomicrographs of the particles present in it are similar to those shown in Figures 1 and 2. According to the optical spectrometry data, all the systems obtained are resistant toward aggregation over a period of months.

In our opinion, the aggregative stability of these sols is due to silver-induced polymerisation of methyl acrylate.

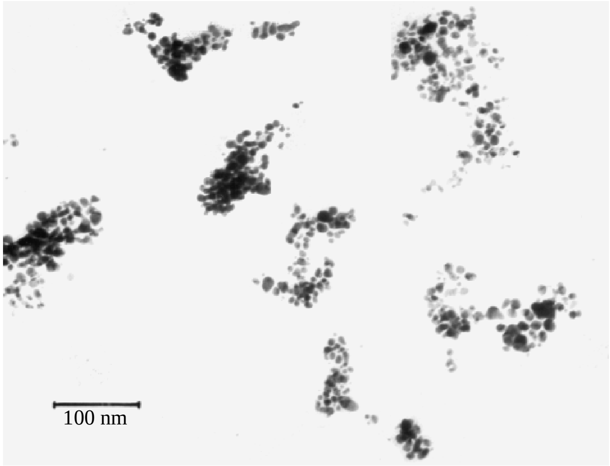

Figure 2 Photomicrograph of silver in the Ag/methyl acrylate organosol.

Apparently, the macromolecules arising in the polymerisation are bound fairly strongly to silver thus forming a shell preventing the aggregation of nano-sized particles. It is also quite likely that, while initiating the polymerisation of methyl acrylate, silver particles acquire an electric charge that ensures an electrostatic contribution to the stabilisation of the sols.

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