MACROMOLECULAR CHEMISTRY
AND POLYMERIC MATERIALS

Specific Features of Interaction of Polyacrylic and Polymethacrylic Acids with Nanoparticles of Amorphous Selenium

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Abstract—A study was made of formation of selenium nanoparticles in water from reduction of sodium selenite with ascorbic acid in the presence of polyacrylic and polymethacrylic acids.

It is well known that nanoparticles of zero-valence metals and nonmetals, with their specific structural features and high surface energy, exhibit abnormal physicochemical properties because of the scale effect of matter [1]. Of special interest are nanoparticles of selenium, a chemical element with unique photoelectric, semiconducting, catalytic, and biological properties and X-ray sensitivity.

Ligand-free nanoparticles are metastable and tend to rapidly aggregate in aqueous solutions. Therefore, they are usually stabilized by water-soluble polymers whose interaction with nanoparticles yields nanostructures of various morphologies [2]. However, the nature of this interaction in formation of nanoparticles in aqueous solutions of polymers still remains to be elucidated.

This work was aimed at elucidating the nature of the above-mentioned interactions and their role in polymer stabilization of selenium nanoparticles (nano-Se^0). To this end, we studied for the first time formation of nano-Se^0 particles in the presence of synthetic polymers differing in the hydrophylic–lipophilic balance. Also, we carried out optical studies of the morphological characteristics of the nanostructures being formed.

EXPERIMENTAL

We studied nano-Se^0 nanoparticles prepared by reducing selenious acid (SA) with ascorbic acid, with and without polymer additions.

As polymeric stabilizers of nano-Se^0 served synthetic polymers, polyacrylic acid (PAA) and poly-methacrylic acid (PMAA), with molecular weights M_w of 27×10^6 and 25×10^3, respectively. This choice was dictated by close structures and Kuhn segment sizes of these polymers, of which only PMAA has side hydrophobic methyl groups [3].

The ionic selenium species SeO_3^{2-} was reduced at the selenium concentration in solution of 0.01 wt % and the polymer-to-selenium mass ratio of 9 : 1 (i.e., under exhaustive saturation of the adsorption capacity of nanoparticles, as revealed for other selenium–polymer nanostructures [4]).

Using the method of flow birefringence [5], we estimated the molecular dispersity of the solutions of the adsorbates being formed, based on analysis of the gradient dependence of the birefringence Δn. Specifically, we studied the birefringence versus the gradient of the rotor rotation rate g and the polymer concentration c at a fixed selenium concentration of 0.01 wt %. We used titanium dynamooptometer with a 4-cm-high internal rotor and the rotor–stator slit width of 0.03 cm. The solutions for birefringence measurements were kept at a constant temperature of 21°C to prevent variations of their viscosities and optical distortions due to the temperature gradient. The measuring facility was calibrated against 2-phenylethanol having a significant birefringence ($\Delta n/g = 17 \times 10^{-12}$), as well as against the polystyrene–bromoform system. The intrinsic birefringence $[n] = \lim_{g \to 0, c \to 0}(\Delta n/gc\eta_0)$ (η_0 is the viscosity of the solvent) was measured accurately to within 10%. The measurements were carried out at $g < g_k$, where g_k is the rate gradient corresponding to the onset of flow turbulence.

The experimentally determined intrinsic birefringence $[n]$ in a general case ($dn/dc \neq 0$, where dn/dc is the increment of the refractive index of the solution, estimated for PAA–Se^0–H$_2$O and PMAA–Se^0–H$_2$O systems at 0.245 and 0.165, respectively) has three components: $[n] = [n]_e + [n]_{fs} + [n]_f$, where $[n]_e$ is the intrinsic anisotropy; $[n]_{fs}$, microform effect; and $[n]_f$, macroform effect [5]. The full segment anisotropy $[n]_{fs} + [n]_e$ is determined by the equilibrium rigidity A of the polymer chain and by the structure of the polymer unit, and $[n]_f$ is related to the shape asymmetry parameter p of the macromolecule (particle) as

$$[n]_f = [(n_s^2 + 2)/3]^2 [M_w (dn/dc)^2 f(p)]/(30\pi R T n_s)$$

$$= \text{const}\, M_w (dn/dc)^2 f(p), \tag{1}$$

where M_w is the molecular weight of the adsorbate macromolecule; n_s, refractive index of the solvent; T, absolute temperature; R, universal gas constant; and $f(p)$, tabulated function of the ratio of the axes of a rigid (impermeable by the solvent) ellipsoid approximating the particle [5].

Relationship (1) is valid both for isolated macromolecule and nanostructure; all what is needed of a particle is to be impermeable by the solvent. Thus, for high-molecular-weight flexible-chain and moderately rigid-chain polymers ($A < 5$ nm), having minor optical anisotropy and low-molecular-weight units, the intrinsic birefringence can be fitted by the approximation $[n] \approx [n]_f$, which allows the parameter p to be estimated directly from the experimentally measured birefringence [5].

Using the elastic (static) light scattering method [6], we estimated M_w and the root-mean-square inertia radii R_g of the polymers and nanostructures, as well as their affinity for solvent, water (from the second virial coefficient A_2). Based on the ratio of the parameters M_w for poly acids and nanostructures they form, we determined the number of the macromolecules adsorbed on the nano-Se^0 surface. The reduced intensity of light scattering by solutions R_0 was measured on a Fica photogoniodiffusometer. The wavelength of the incident, vertically polarized, light was 546.1 nm. The measurements were carried out at light scattering angles θ within 30°–150°. The solutions and solvents were purified by centrifugation at 15×10^3 rpm for 1–1.5 h. The refractive index increment dn/dc was determined from the refractive indices measured on an IRF-23 instrument.

The experimental light scattering data were processed by the Zimm method, by double extrapolation ($c \to 0$, $\theta \to 0$) of the plots of Kc/R_θ vs. $\sin^2(\theta/2) + kc$ (K is the calibration constant, and k, numerical constant).

We determined the average hydrodynamic particle sizes R_H by quasielastic (dynamic) light scattering method [7]. Based on the experimental R_g-to-R_H ratio for the nanostructures, we estimated the parameter ρ^* characterizing the conformation of the nanostructure [8–11].

The optical component of the facility for measuring the dynamic light scattering comprised an ALV-SP (Germany) goniometer (a Spectra-Physics He–Ne laser with a wavelength $\lambda = 632.8$ nm, power ca. 20 mV, as light source). The correlation function of the scattered light intensity was obtained on a 288-channel Photo Cor-FC correlator (Anteks Closed Joint-Stock Company, Russia). Data processing was carried out by standard methods of cumulants and Tikhonov regularization, using appropriate software.

According to the static light scattering data, the parameter M_w remains unchanged ($M_w = 27 \times 10^7$) in going from the PAA–H$_2$O to PAA–Se^0–H$_2$O system, i.e., in the presence of PAA, no nanostructure is formed. For the PMAA–Se^0–H$_2$O system, M_w was estimated at 1.5×10^8, i.e., it increased by a factor of 4300 relative to free PMAA macromolecules. This unambiguously suggests the deciding importance of hydrophobic interactions between macromolecules and nano-Se^0 in formation of nanostructures.

The second virial coefficient A_2 for the PMAA–Se^0–H$_2$O system is equal to zero, which suggests an ideal thermodynamic quality of the solution. For the PAA–Se^0–H$_2$O system, A_2 is negative, namely, -0.8×10^{-4} cm^3 mol g^{-2}, which suggests a bad thermodynamic quality of the solution. Thus, adsorption of macroions on nano-Se^0 improves the thermodynamic quality of the solution.

The parameter R_H for nano-Se^0 particles obtained without polymeric stabilizer was estimated at 170 nm. The particle size of the PMAA–Se^0 adsorbate, estimated by dynamic and static light scattering methods, is much smaller (root-mean-square inertia radius $R_g = 90$ nm and mean hydrodynamic radius $R_H = 90$ nm). The parameter $\rho^* = R_g/R_H$ is equal to unity, which suggests virtually ideal spherical shape of the particles of the adsorbate being formed [8–11].

To determine the radius of the selenium particles occurring in the core of the nanostructure, we lyophilically dried an aqueous solution of PMAA–Se^0,

and the resulting dry pelletized product was examined by small-angle X-ray scattering. We estimated the radius of the spherical Se^0 particles at 15 nm, which is by an order of magnitude smaller than that of selenium particles obtained without polymeric stabilizer. Thus, the nano-Se^0 particles in aqueous solutions have a ca. 75-nm-thick polymer shell.

Optical studies of the PAA and PMAA macromolecules showed that, in the nonionized state, these are Gaussian globules with the asymmetry parameter $p \sim 2$ [12].

Calculation of the parameter p in the $[n] \sim [n]_f$ approximation for the PAA–Se^0–H_2O and PMAA–Se^0–H_2O systems yielded, respectively, $p \sim 1$ (spherical conformation) and $p \sim 2$ (which is inconsistent with the value of the parameter p^*, corresponding to the spherical conformation of the nanostructure) [5]. Also, the fact that the reduced optical anisotropy for the PMAA–Se^0–H_2O system is independent of the concentration (Fig. 1) suggests that the parameter p tends to unity, i.e., that the nanostructure is spherical [5]. The fact that hybrid nanostructures formed by macromolecules and nanoparticles have a spherical shape, even in the case of such a rigid macromolecule as DNA [13], suggests that the $[n] \sim [n]_f$ approximation is invalid for the PMAA–Se^0–H_2O system. Evidently, in this case a significant contribution to the optical anisotropy comes from an effect similar to the microshape effect for an isolated macromolecule (Lyubina [12] showed that the intrinsic optical anisotropy even for PMAA with its high degree of ionization is negligible). This is supported by the fact that the $\Delta n = f(g)$ curves (Fig. 2) for the PMAA–Se^0–H_2O system reach saturation. This suggests an increase in the rigidity of the PMAA macromolecules owing to hydrophobic interactions. Thus, hydrophobic interactions of nonpolar fragments of the macromolecules with one another and with nano-Se^0 constitute the major driving force of adsorption.

In the case of PAA, no nanostructure is formed, and the conformation of the macroions changes, in contrast to nonionic hydrophilic polymers such as polyacrylamide [4]. This is presumably due to dipole–dipole interactions of PAA with selenium nanoparticles.

We showed that selenium nanoparticles are adsorption matrices suitable for accommodating in high local concentrations anionic polyelectrolytes containing hydrophobic methyl groups in the side chains. Our results can be applied to molecular designing of new materials with desired properties.

$(\Delta n/d\eta_0 c)_{g \to 0} \times 10^8$
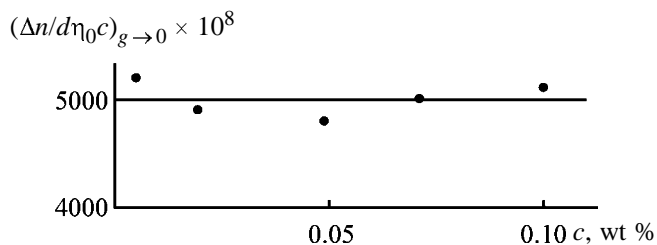
Fig. 1. $(\Delta n/g\eta_0 c)_{g \to 0}$–$c$ dependence for the PMAA–Se^0–H_2O system. (Δn) Dimensionless birefringence of the polymer; (g) flow rate gradient, s^{-1}; (η_0) viscosity of the solvent, cm s g^{-1}; and (c) concentration of the polymer.
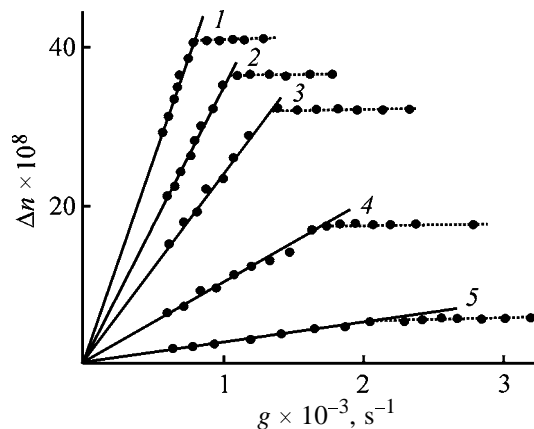
Fig. 2. Variation of the birefringence Δn with the flow rate gradient g for the PMAA–Se^0–H_2O system. c_{PMAA}, wt %: (*1*) 0.1, (*2*) 0.071, (*3*) 0.049, (*4*) 0.0195, and (*5*) 0.0048.

CONCLUSIONS

(1) Reduction of sodium selenite with ascorbic acid in an aqueous solution of polymethacrylic acid yielded spherical nano-Se^0 particles with a size of ca. 15 nm.

(2) Molecular-optical studies showed that the polymethacrylic acid macromolecules adsorbed on nano-Se^0 form an ultra-high-molecular-weight (MW = 150×10^6) spherical nanostructure with a size of ca. 90 nm, comprising over 4000 densely packed macromolecules.

(3) The PMAA–Se^0–H_2O system exhibits an induced conformational transition of polyacrylic acid from a Gaussian globule to a sphere.

(4) The hydrophobic interactions of the macromolecules with nano-Se^0 play the deciding role in their adsorption on nanoparticles.

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