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Functional Polymers in the Generation of Colloidal Dispersions of Amorphous Selenium

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Received February 11, 1980

ABSTRACT: Stable colloidal dispersions of red, amorphous selenium have been prepared by the reduction of selenious acid in dilute aqueous solutions of hydrazonium polyacrylate. The initially formed particles average 1000–1200 Å in diameter. These particles can be grown by adding hydrazine and selenious acid in a cyclical fashion. Reduction of selenious acid in a control system in which hydrazonium propionate was substituted for the hydrazonium polyacrylate yielded a flocculent precipitate of amorphous selenium. The formation of the stable colloidal dispersion in the presence of the functional polymer can be understood in terms of a locus control formalism, which views the discrete polymer molecules as loci (submicroscopic reaction vessels) to which the reaction is restricted. Stable colloidal dispersions are then obtained because stabilization occurs in the same volume element in which the particle is nucleated. Hydrazonium salts of acrylic acid copolymers and other polyacids can also be utilized in the preparation of stable colloidal selenium dispersions.

Polymer-bound reagents and macromolecular catalysts have been extensively utilized in the synthesis of polypeptides,[1,2] catalysis of acyl transfer,[3] and numerous organic syntheses.[4-7] Most often, these reactions have involved functionalized, cross-linked, styrene–divinylbenzene resins. There are a few instances, however, where soluble macromolecules have been employed.[3,8] In this paper, we report the preparation of stable colloidal dispersions of red amorphous selenium with hydrazine, bound as hydrazonium ion, to soluble polyacids. The range of chemical processes for which macromolecular reagents are useful has thus been expanded to include the formation of colloidal sols.

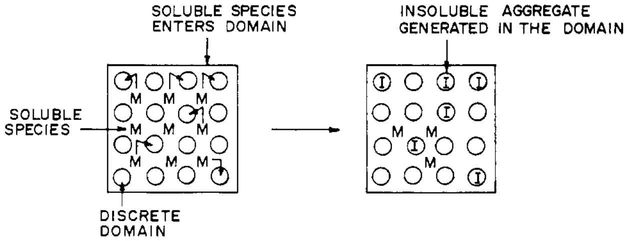
Selenium has been of great importance as a photoconductive material.[9] Accordingly, it is useful to be able to prepare colloidal dispersions of elemental selenium and to control their particle size and size distribution.

Watillon and Dauchot[10] prepared monodisperse selenium particles by an elaborate procedure in which selenious acid was reduced in the presence of colloidal gold sols. The gold particles served as nuclei for the selenium particles. The resultant dispersions were quite dilute, having a volume fraction in selenium of 10^{-5}–10^{-6}.

The reduction of selenious acid with a functionalized polymer is a simple process through which fairly concentrated monodisperse selenium sols can be prepared. A typical dispersion is shown in Figure 1.

We have adopted the term locus control to describe our system in which functional macromolecules in solution act to generate a high concentration of insoluble atoms or molecules in their domain. At the submicron level, a locally supersaturated condition is thus created which effectively restricts particle nucleation to the domain of the polymer molecule. The idea of the locus control formalism is described in Scheme I. If one has a system in which there exists a uniform array of domains (soluble macromolecules, indicated by the circles) dispersed throughout a continuous medium in which there is dissolved a monomeric species M and if M will undergo a reaction leading to the formation of the aggregate insoluble species I in the domain but not in the continuous medium, then one has created a situation in which I must be generated in the locus of the domain. Just such a situation has been created through the binding of hydrazine, as hydrazonium ions, to the domain of polyacids. Thus, when selenious acid is added to a dilute aqueous solution of hydrazonium polyacrylate or hydrazonium polysulfonate, stable colloidal dispersions of red amorphous selenium are obtained. The polymer acts to control the particle size and number because selenium atoms are only generated in the domain of the polymer.

Scheme I
The Locus Control Concept



Experimental Section

A. Materials. Poly(acrylic acid) (Polysciences, Inc., mol wt 250 000, or K & K Laboratories, Inc., 2% aqueous solution) was used as received.

Copoly(styrene–acrylic acid) $(60/40)_M$ was prepared by the free-radical copolymerization of styrene (72.8 g, 0.70 mol) and acrylic acid (48.4 g, 0.70 mol). The polymerization was carried out for 18 h at 70 °C in ethyl acetate (480 mL) and was initiated with benzoyl peroxide (3.38 g, 0.014 mol). The monomers were reagent grade and inhibitors were removed chromatographically prior to polymerization. The polymerization was carried out under Ar in a stirred 1-L, four-necked flask. The reaction mixture was purged with N_2 for 1 h prior to initiation of the polymerization. The polymer was purified by reprecipitation from methanol into water. The acrylic acid content was determined to be 38.7 mol % by titration with 0.1 N sodium hydroxide.

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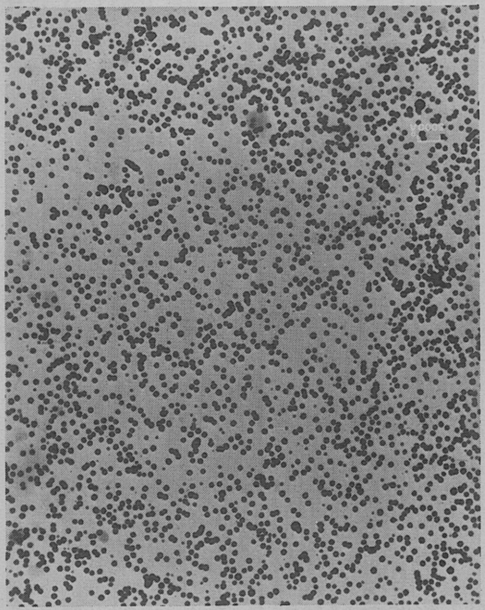

Figure 1. Typical colloidal Se dispersion (magnification 20 000).

Poly[2-(acrylamido)-2-methylpropanesulfonic acid] was prepared by the free-radical polymerization of 97.6 g (0.424 mol) of the sodium salt of 2-(acrylamido)-2-methylpropanesulfonic acid, AMPS (Lubrizol Chemicals). The polymerization was carried out in deionized water (400 mL) and was initiated at 30 °C by the $(NH_4)_2S_2O_8/NaHSO_3$ redox couple (0.00424 mol). The reaction was carried out in a water bath, and the exotherm was held to 35 °C by cooling. The reaction was subsequently heated to 55 °C and was held at 55 °C for 2 h. The polymer was purified by reprecipitation into acetone and a nearly quantitative amount of polymer was isolated. The free acid was regenerated by ion exchange just prior to the preparation of the selenium dispersion (see example 5).

Other materials, including **selenious acid**, **hydrazine hydrate**, and **propionic acid**, were reagent grade and were used as received.

B. Selenium Dispersions. Example 1. Poly(acrylic acid)-Based Dispersion (Single Stage). Deionized water (250 mL) and poly(acrylic acid) (K & K Laboratories, Inc., 59.32 mequiv) were charged into a 500-mL, three-necked round-bottomed flask, equipped with a Teflon paddle stirrer, gas inlet tube, thermometer, graduated addition funnel, and reflux condenser. The solution was purged with Ar and stirred gently for 0.25 h. Hydrazine hydrate (95%, 29.66 mmol) was then added at ambient temperature. Selenious acid (21.33 mmol) in 50 mL of deionized water was added over 0.25 h at ambient temperature, yielding a tomato soup red, stable, colloidal dispersion of amorphous selenium. The size of the particles in the dispersion ranged from 500–1000 Å.

Example 2. Precipitation of Se in the Absence of a Functional Polymer. Deionized water (250 mL) and propionic acid (59.32 mequiv) were charged into a 500 mL, three-necked round-bottomed flask, equipped as in example 1. The solution was purged with Ar and stirred gently for 0.25 h. Hydrazine hydrate (95%, 29.66 mmol) was then added at ambient temperature. Selenious acid (21.33 mmol) in 50 mL of deionized water was added over 0.25 h at ambient temperature. A massive flocculent red-violet precipitate which settled quickly on standing was the product of this reaction. [It should be noted that this reaction is identical with the first example except that propionic acid was substituted for poly(acrylic acid).]

Example 3. Poly(acrylic acid)-Based Dispersion (Multistage). Deionized water (550 mL) was charged into a 1-L four-necked round-bottomed flask, equipped as in example 1. Ten grams (138 mequiv) of poly(acrylic acid) (Polysciences, Inc.) was added to the flask and the system was purged with Ar and stirred gently. The polymer was then partially neutralized with hydrazine hydrate (95%, 69.5 mmol) and stirred for an additional 20 min. A solution of selenious acid (J. T. Baker Chemicals, 95%, 9.63 g, 69.5 mmol) in 280 mL of deionized water was added dropwise at ambient temperature over a 3-h period. A ruddy colloidal dispersion of selenium particles in water was thus obtained. The average size of the selenium particles in the dispersion was 1200 Å (see Figure 2).

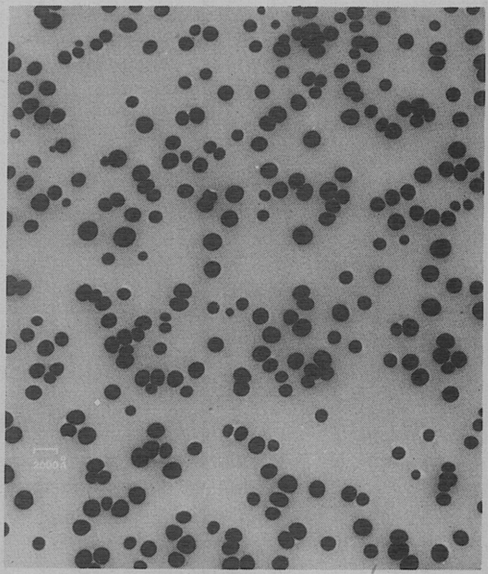

Figure 2. Multistage Se dispersion, stage 1 (magnification 50 000).

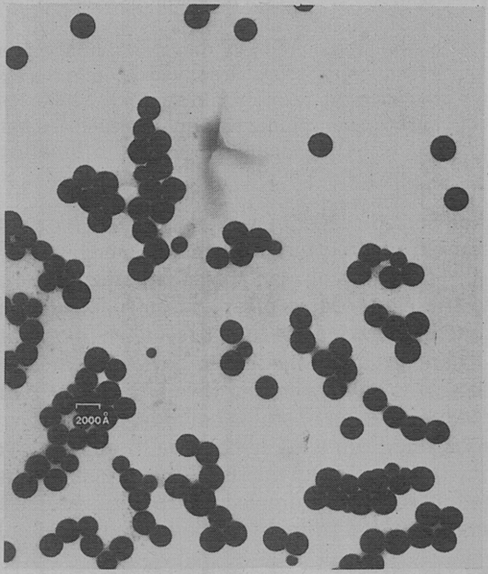

Figure 3. Multistage Se dispersion, stage 4 (magnification 50 000).

Stage Two. Growth of Previously Nucleated Selenium Particles. After the removal of an aliquot of the above dispersion, a second increment of hydrazine and selenious acid was added. With approximately 600 mL of solution remaining in the flask, it was calculated that the volume represented 104 mequiv of poly(acrylic acid). Subsequently, 69.5 mmol of hydrazine hydrate was added, followed by the dropwise addition of 69.5 mmol of selenious acid in 250 mL of deionized water. The dispersion remained stable throughout this procedure while becoming somewhat more reddish. At this point, the average size of the selenium particles had been increased to 1400 Å. The particle number remained unchanged. This staged addition of hydrazine and selenious acid can be continued, further increasing the nonvolatile content of the dispersion and the relative fraction of selenium in the dispersion. Indeed, the staging of this particular dispersion was so continued. In the process, the particles continued to grow and the distribution of size narrowed. Figure 3 shows an electron micrograph after the addition of the fourth stage; the average particle size was 1900 Å.

Example 4. Copoly(styrene–acrylic acid)-Based Dispersion (Single Stage). Deionized water (250 mL), ammonia (4.23 mequiv), and copoly(styrene–acrylic acid) (4 g, 16.92 mequiv) were charged into a 500-mL, four-necked round-bottomed flask, equipped as in example 1. The solution was purged with Ar and stirred gently for 0.25 h. Hydrazine (8.4 mmol) was added at ambient temperature. Selenious acid (8.4 mmol) in 40 mL of deionized water was then added dropwise over 2 h. A tomato soup red colloidal dispersion of selenium particles in water was thus obtained.

Example 5. Poly[2-(acrylamido)-2-methylpropanesulfonic acid]-Based Dispersion (Single Stage). Poly[2-(acrylamido)-2-methylpropanesulfonic acid sodium salt], poly(AMPS, Na salt) (10 g, 48.3 mequiv), and 300 mL of deionized water were charged into a 1-L Erlenmeyer flask. An excess of Dowex 50W-X8 cation-exchange resin in the H^+ form was added and the mixture was slurried for 0.5 h. The ion-exchange resin had been rigorously purified by cycling it from the H^+ to OH^- form and by washing and soaking in methanol and water. The resin beads were removed by filtration through a coarse sintered-glass filter and the filtrate was transferred to a 1-L, four-necked round-bottomed flask, equipped as in example 1. The solution was purged with Ar and stirred gently for about 0.25 h. Hydrazine hydrate (95%, 36.2 mmol) was added at ambient temperature. Selenious acid (36.2 mmol) in 100 mL of deionized water was then added dropwise over about 2 h. A stable, dark red colloidal dispersion of amorphous selenium was thus obtained.

C. Determination of Particle Size. 1. Microscopy. The size of the particles in the various dispersions was determined by transmission electron microscopy (TEM). Samples were prepared for TEM by placing a drop of the dispersion on a carbon-coated microscope grid. Micrographs were taken of representative areas of the grids.

2. Calculation of the Average Particle Diameters $\bar{D}_n$ and $\bar{D}_w$. The diameters of 100 particles on micrographs for each dispersion were measured in two directions. Number-average ($\bar{D}_n$) and weight-average ($\bar{D}_w$) diameters were determined for each dispersion ($\bar{D}_n = \sum_i N_i D_i / \sum_i N_i$, $\bar{D}_w = \sum_i N_i D_i^4 / \sum_i N_i D_i^3$). The ratio of $\bar{D}_w/\bar{D}_n$ gives a numerical measure of the polydispersity of the dispersions.

3. Calculation of Particle Number. The particle number per unit volume, N, was calculated on the basis of the equation $N = 3\nu/(4\pi r^3)$, where ν was the volume fraction of selenium in the nonvolatile fraction and r was the number-average particle radius.

Results

Stable colloidal dispersions of amorphous selenium particles, 250–1500 Å in diameter, are directly obtained by the addition of selenious acid to dilute solutions of hydrazonium polyacrylate. The hydrazine salt is made in situ by adding less than a stoichiometric amount of hydrazine to an aqueous solution of poly(acrylic acid). An amount of H_2SeO_3 equal to the number of moles of bound hydrazine is then added dropwise to directly yield the dispersion.

Example 3 in the Experimental Section details the formation and stagewise growth of a typical selenium dispersion. Scheme II shows our conception of the nucleation and stagewise growth of a single selenium particle in the domain of a given polymer molecule. It is assumed that the solution is sufficiently dilute that each macromolecule can be viewed as discrete and noninteracting. Each polymer molecule is considered to occupy a volume element which is 50–500 Å in diameter, depending on its molecular weight. Each molecule contains n carboxylic acid residues of which $0.75n$ have been neutralized with hydrazine. By virtue of the salt formation, $0.75n$ hydrazonium ions have been restricted to the volume element occupied by the macromolecule. Selenious acid is molecularly dissolved and is at the same concentration in every volume element of the solution. Those selenious acid molecules in the locus of the macromolecule react with the hydrazonium ions, therein generating $0.75n$ selenium atoms. Because of the small size of the domains, only one particle is formed in any given domain. All $0.75n$ selenium atoms generated in a given domain are assumed to condense into a single particle. With the reaction of $0.75n$ hydrazonium ions, the polymer is returned to its initial state and the process can be repeated. In the aqueous solution, the hydrophobic selenium particles remain bound to the polymeric molecules. The dispersion is thus stabilized by both charge and steric effects.

Scheme II
Locus Control Scheme for Nucleation and Growth of Amorphous Selenium Particles

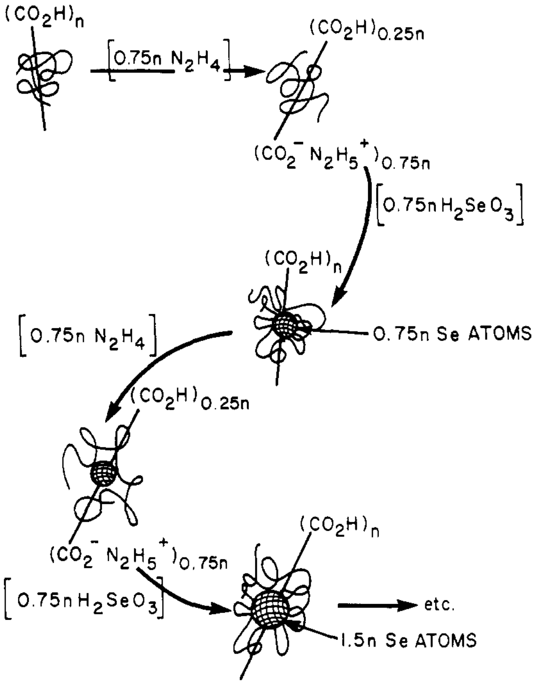

Table I

increment	$\bar{D}_n$, Å	$\bar{D}_w$, Å	$\bar{D}_w/\bar{D}_n$	$10^{-18}N$[a]
1	1250	1358	1.09	8.2
2	1424	1508	1.06	8.1
3	1708	1774	1.04	5.1
4	1924	2030	1.05	3.7

[a] Particle number per unit volume, $N = 3\nu/4\pi r^3$; in units of particles per cm^3.

The incorporation of greater amounts of selenium into the dispersion, via the cyclical addition of hydrazine and selenious acid, is depicted in the bottom half of Scheme II. In example 3, samples of the dispersion were removed at various stages during the cyclical addition of hydrazine and selenious acid. The concentration of selenious acid and hydrazonium ions was stoichiometric and adjustments were made during the cyclical process for polymer which had been removed. The diameter of the particles after the addition of the first increment of hydrazine and selenious acid ranged from 400 to 1800 Å, with an average diameter of about 1200 Å. After the addition of the second increment, the average particle diameter had increased to 1400 Å; the particle number remained unchanged and the distribution narrowed. With the addition of increments three and four, the particles continued to grow and the distribution narrowed further. Table I shows the change in particle size, size distribution, and particle number with the addition of each increment. Figures 2 and 3 show typical electron micrographs of the dispersions. The histograms in Figures 4 and 5 show the distribution of particle size for the first and last increments.

The sizes of the particles in the micrographs were assessed manually and, consequently, only a relatively small

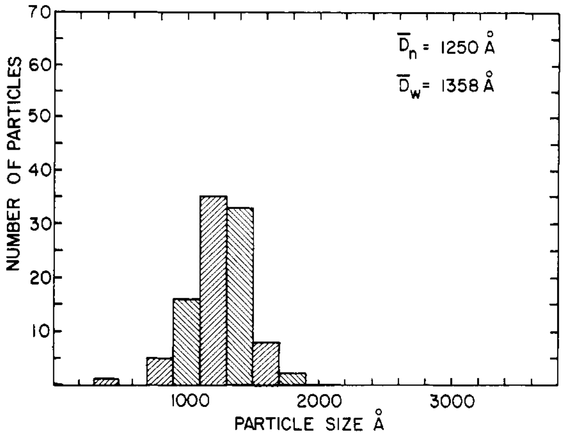

Figure 4. Histogram for particle size distribution of stage 1.

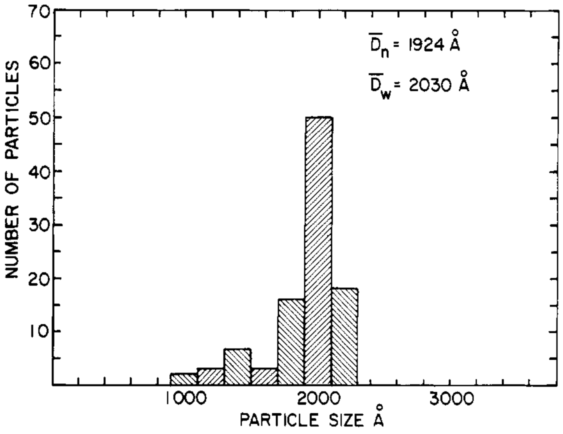

Figure 5. Histogram for particle size distribution of stage 4.

number of particles (100) were measured for each dispersion. The number-average and weight-average particle diameters were calculated as described in the Experimental Section. The particle number remained *essentially* constant during the cyclical addition of the first two increments of hydrazine and selenious acid and decreased only slightly with the addition of increments three and four. This indicates that accretion was minimal and that new nuclei were not being formed in significant number. The particle size distribution was quite narrow initially, and as the particles were grown, the distribution narrowed even further. Because of the narrowness of the distribution, the increased uniformity of increments 2–4 is evidenced more clearly by the micrographs (Figures 2 and 3) and the histograms (Figures 4 and 5) than by the numerical $\bar{D}_w/\bar{D}_n$ ratio. The narrowing of the particle size distribution is indicative of a process in which the smaller particles grow at a faster rate than the larger particles.

Hydrazonium salts of polyacids other than poly(acrylic acid) have been employed as functional domains for the generation and stabilization of colloidal dispersions of selenium. In the Experimental Section, procedures are detailed in which a copolymer of styrene and acrylic acid and a homopolymer of 2-(acrylamido)-2-methylpropanesulfonic acid were used in the preparation of colloidal dispersions of amorphous selenium. The dispersions prepared with poly[2-(acrylamido)-2-methylpropanesulfonic acid] were not as stable over extended periods of time (weeks or months) as those prepared with the agency of hydrazonium polyacrylate.

If one carries out a control reaction in which selenious acid is reduced in an aqueous solution of propionic acid which has been partially neutralized with hydrazine, a massive flocculent precipitate of amorphous selenium is obtained. Given the fact that propionic acid is an appropriate monomeric model compound for the repeat residue in poly(acrylic acid), this experiment demonstrates the necessity of a functional polymer for stabilization of the selenium sol.

Discussion

Amorphous selenium has classically been prepared by chemical reduction from aqueous solution.[11] Commonly, the procedure involves the reduction of an aqueous solution of selenious acid with hydrazine hydrate (eq 1). The

$$H_2SeO_3 + N_2H_4 \rightarrow Se^0 + 3H_2O + N_2$$

reduction is irreversible; it occurs spontaneously on mixing the reagents and the byproducts are innocuous. The reaction is acid catalyzed and the kinetics have recently been described.[12] To bring locus control to bear on the reaction, one has only to bind either of the reactants to a soluble domain. The domain can be either micellar[13] or macromolecular. When the locus is polymeric, the volume element of each macromolecule comprises a microscopic phase different from the solution. This microscopic phase plays a number of roles during particle nucleation and growth. Its primary role is that of a catalyst. Initially, the polymer binds a reagent essential to the reduction of H_2SeO_3. The polymer has not been fully neutralized with hydrazine; thus, the hydrogen ion concentration in the domain of the polymer is higher than that in bulk solution. This is an important feature in light of the fact that the reduction of H_2SeO_3 by hydrazine is acid catalyzed.[12] We have found that the reaction does not proceed when the acid residues are fully neutralized. If it is postulated that selenite and biselenite are not reduced by hydrazine, then this occurrence might be attributed to the dissociation of selenious acid in neutral solution. Binding and acidity thus combine to ensure that Se is generated primarily in the domain of the polymer. The generation of Se atoms in the domain of the polymer can be viewed as being analogous to homogeneous nucleation. However, from a systemic point of view, the domain of the macromolecule is best viewed as a second phase in which the reaction is localized. In this sense, the polymer molecules are heterogeneous nuclei, like the gold nuclei of Watillon and Dauchot.[10] As such, one would expect that the number of selenium particles initially generated would be equal to the number of macromolecules. We have not determined the molecular weight and the molecular weight distribution for our poly(acrylic acids). If, however, for conjecture, we take $\bar{M}_w = 250\,000$ for the poly(acrylic acid) sample of example 3 and if we assume a distribution of 2.5, the number of macromolecules per cm^3 calculates out to be 7.2×10^{17}. This number is not inconsistent with the actual particle number after the addition of the first increment in example 3 (8.2×10^{18} particles/cm^3).

The growth of the Se particles without renucleation might be explained classically in terms of absorption of sol-forming ingredients in a system in which all the stabilizer molecules have been adsorbed on the surface of the already existing particles. However, in our system, the sol-forming and sol-stabilizing ingredients are one and the same. So, all that is required for growth without renucleation is that the functional polymer remain intimately associated with the surface of the particles which were initially nucleated in the polymer's domain. In a sense, the reaction is no more heterogeneous than in the beginning; the only difference after particle nucleation is that the functional polymer is bound to a surface.

The secondary role of the polymer is to stabilize the freshly nucleated particles against accretion and agglomeration. This factor was not considered in the choice of functional polymer for binding of hydrazine and the subject of stabilization will not be dealt with in this paper. However, the fact that poly(acrylic acid) is effective in stabilizing hydrophobic sols, such as Se in water, is understandable in terms of the conventional conception of steric and charge stabilization.[14,15]

Summary

Stable colloidal dispersions of amorphous selenium can be simply prepared with the agency of hydrazonium salts of polyacids. The formation of these dispersions has been rationalized in terms of localization of the selenium-forming reaction in the domain of individual macromolecules. The procedure, which we have termed locus control, allows for the preparation of nearly monodisperse selenium sols in the range of 1000–2000 Å. We believe that this is the first instance in which the utility of polymer-bound reagents in the preparation of colloidal sols has been recognized.

Acknowledgment. We thank Dr. W. H. H. Gunther for his contribution in devising chemistry through which locus control could be applied to the preparation of colloidal dispersions of selenium. We also express our appreciation to K. Johnson for his efforts in obtaining electron micrographs on these dispersions.

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Friction Coefficient of Polymer Molecules in Dilute Solution near the Θ Point. 1. A Rapid Method for Determining Small Differences in Sedimentation Coefficients: Polystyrene in Cyclohexane

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Received September 14, 1979

ABSTRACT: A rapid and accurate method for determining small differences in sedimentation coefficients in the analytical ultracentrifuge is described. The method compares distances traveled by two solvent–solution boundaries in equal periods of time under slightly different conditions of concentration or temperature. Narrow-distribution polystyrenes in the Θ solvent cyclohexane are used for illustration of the method. The following results are obtained: The coefficient of concentration dependence of the reciprocal value of the sedimentation coefficient is $(k_s)_\Theta = (4.1 \pm 0.2) \times 10^{13} s^0 = (0.062 \pm 0.003) M^{1/2}$ mL/g. This value is definitely smaller than the intrinsic viscosity, in contradiction to a theoretical result by Freed. The temperature coefficient of the sedimentation coefficient at infinite dilution is $(\mathrm{d} \ln s^0/\mathrm{d}T)_\Theta = (1.85 \pm 0.03) \times 10^{-2} - (0.87 \mp 0.04) \times 10^{-5} M^{1/2}$ deg^{-1}. For $M \geq 10^5$ the temperature dependence of k_s can be represented by $(\mathrm{d}k_s/\mathrm{d}T)_\Theta = (0.3 \pm 0.1) + (0.87 \mp 0.02) \times 10^{-5} M$ mL g^{-1} deg^{-1}. In addition we found $s_\Theta^0 = (1.51 \pm 0.02) \times 10^{-15} M^{1/2}$ s in accordance with literature data. A comparative discussion is given of the temperature dependence of the expansion factors for differently defined radii of the polymer molecule. Doubts are raised with respect to the reliability of recent first-order perturbation theories for the intrinsic viscosity. The concentration dependence of s will be discussed in a subsequent paper.

Introduction

In the past different results have been obtained with respect to the vanishing or nonvanishing of the concentration dependence of the sedimentation coefficient of random-coil polymers in dilute Θ solutions. We refer to the coefficient $(k_s)_\Theta$ defined by the relation

$$s(c) = s(0)/\{1 + (k_s)_\Theta c\} \qquad (T = \Theta) \tag{1}$$

The early conclusion reached by Cantow[1] about a vanishing concentration dependence for polystyrene (PS) in cyclohexane (CH) at 35 °C was disproved by preponderant experimental evidence in later years.[2-9] Haug and Meyerhoff[10] reported that $(k_s)_\Theta$ is zero for the Θ system poly(dimethylsiloxane) in bromocyclohexane at 28 °C. Llopis et al.[11] did the same with respect to poly(ethyl acrylate) in 1-propanol at 28 °C. Nonvanishing concentration effects were reported for poly(methyl methacrylate) in n-butyl chloride at 35 °C[7] and poly(α-methylstyrene) (PαMS) in CH at 38.2[9] and 39 °C.[12]

Contradictory results were also reached in the theory: Yamakawa[13] ($(k_s)_\Theta = 0$) vs. Pyun and Fixman.[14] Recently (1976) a quite different conclusion was reached by Freed,[15] who claimed that $(k_s)_\Theta$ is equal to the intrinsic viscosity $[\eta]_\Theta$. Experimental data by Kotera and co-workers[9] were

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