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Inorganic Chemistry

Communications

Polymer-Trapped Semiconductor Particles

Sir:

A significant portion of organic chemistry deals with material (e.g. butadiene, benzene, coronene) that may be considered kinetically stable fragments of bulk graphite. Inorganic fragments of solid-state material are much less extant and most of these are encumbered with stabilizing ligands that overshadow the properties of the inorganic cluster. Nevertheless, elegant physical studies have been carried out on ephemeral fragments of solid-state compounds prepared in the gas phase,[1,2] in low-temperature matrices,[3,4] or as colloids.[5-7] These show that properties change dramatically when the particle size is reduced below the average hole–electron distance (about 15 nm in PbS). The mechanical properties and kinetic instability of these preparations leave everything to be desired from a material or device viewpoint. We have examined other preparative methods, metathesis in microemulsion, gas–solid reactions on high surface area silica, synthesis within the channels of perfluorocarbon sulfonic acid membranes,[8] and generation of semiconductor particles within polymer films. Ethylene–15% methacrylic acid copolymer (E-MAA) proved to be an excellent matrix, providing good mechanical and optical properties and conferring high kinetic stability on nanometer-sized semiconductor particles.

E-MAA is milled with a metal acetate or acetylacetonate at 160 °C (acetic acid or acetylacetone distills out) to give a (partially) neutralized ionomer.[9] The exact morphology of this material has not been established, but phase-separated polar clusters about 5 nm diameter in a polyethylene matrix is a generally accepted structure.[10,11]

For our purposes, we view the ionomer as a microemulsion wherein the metal cations are dissolved in the polar clusters. (The carboxylate groups of the copolymer are the anions.) Optically clear films can be pressed from these ionomers with metal cation concentrations up to 1 M. Mixing ionomer with metal-free E-MAA (repressing several times to achieve homogeneity) gives films of lower metal concentration just like dilution of a conventional solution. E-MAA films are essentially transparent between 240 and 3000 nm.

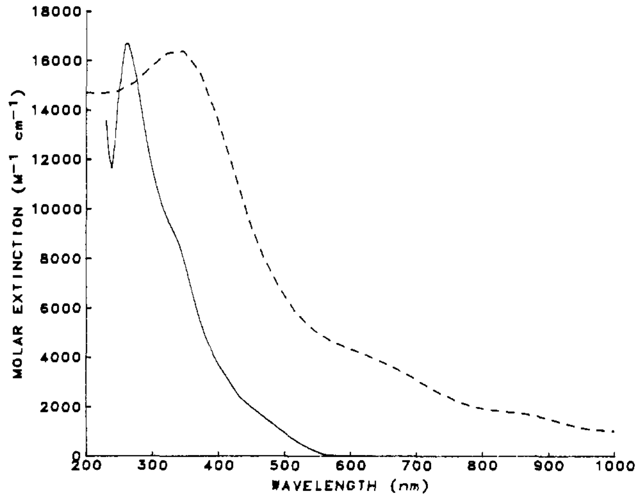

Figure 1. Absorption spectra of 0.01 M PbS in E-MAA (solid curve) and bulk PbS[12] (broken curve). M = mol/L.

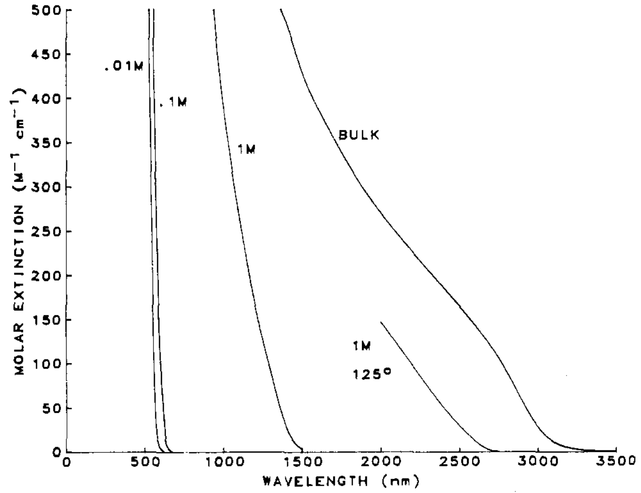

Figure 2. Absorption spectra of 0.01, 0.1, and 1 M PbS in E-MAA prepared at 25 °C, 1 M PbS in E-MAA prepared at 125 °C (average size 12.5 nm), and bulk PbS.[12]

E-MAA films 30–300 μm thick containing 0.0005–1 M Pb^{2+} (1 M Pb ~ 20 wt % Pb) were exposed to 1 atm H_2S at 25 °C for at least 2 h. The final colors for films were yellow, orange, red, brown, or black with increasing concentration of Pb. Films initially containing 1 M Pb^{2+} exhibited these colors in sequence within a minute. Absorption spectra were measured directly on the films with an E-MAA reference and converted to molar extinction, ε, in units of M^{-1} cm^{-1}, given in Figures 1 and 2, including bulk PbS[12] for comparison.

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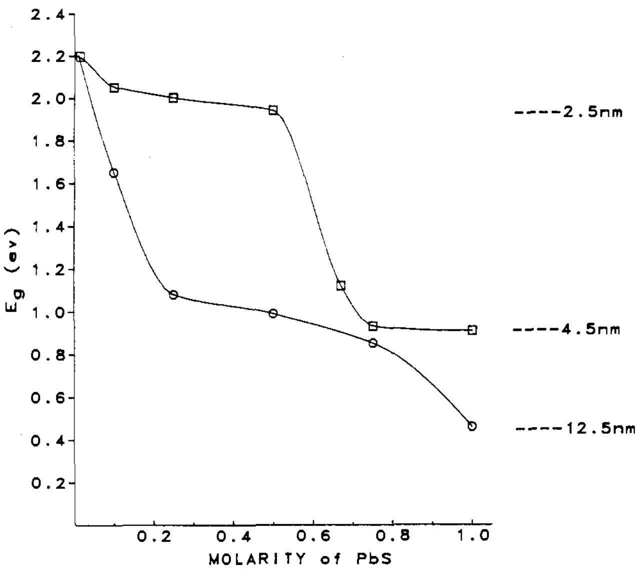

Figure 3. Band gap energy, in eV, of PbS as a function of concentration of PbS in E-MAA (M) and corresponding particle diameter. PbS was prepared at 25 (squares) and 125 °C (circles).

X-ray diffraction characteristic of PbS could be obtained for concentrations above 0.3 M PbS in E-MAA directly on the films. Line broadening of the peaks was converted to particle size by using the Scherrer–Jones equation.[13] Band gaps were obtained by extrapolating the square root of the molar extinction to zero.[14] Figure 3 shows the relationship of concentration, band gap, and particle size for PbS made in E-MAA at 25 and at 125 °C.

Beer's law is strongly disobeyed from 1 M to 0.01 M PbS, particularly in the visible region, but the molar extinction does not change below 0.01 M. The average number of cations per cluster, n, is given by

$$n = VNC$$

where V is the volume of a cluster in liters, N is Avogadro's number, and C is the cation concentration in moles per liter of polymer. (The density of metal-free copolymer is 0.94 g/mL.) Assuming the cluster size is 5 nm diameter (6×10^{-23} L) or smaller, at 0.01 M concentration there is statistically less than one Pb per cluster, suggesting that the limiting spectrum is that of monomeric PbS. Further support comes from a comparison with the spectrum of gaseous PbS[15,16] at 1200 °C and the spectrum of PbS vapor trapped in an argon matrix[17] at 11 K.

It appears that, at 25 °C, the PbS particle size is determined by the initial loading of Pb^{2+} within each cluster,[18] but at 125 °C there is migration and aggregation within the polymer. This is more clearly seen when a film containing 0.34 M PbS prepared at 25 °C is heated to 125 °C. The film changes from orange to black as the particle size goes from 2.5 to 4.5 nm. It is of interest that 1 M PbS made at 25 °C does not change its color (black), band gap (0.91 eV) or size (4.5 nm) on heating to 125 °C, whereas PbS made at 125 °C is iridescent and has a particle size of 12.5 nm. Cross sections of the film prepared at 125 °C show a number of layers of PbS aggregates parallel to the film surface of variable thickness near 1 μm, with variable spacings of tens of micrometers, which is undoubtedly the Liesegang ring phenomenon,[19] but with the usual centimeter spacing and millimeter thickness in aqueous media reduced to micrometer size because of the much higher viscosity of the E-MAA copolymer.[20]

Table I. Band Gaps of Dilute and Bulk Semiconductors

	band gap, eV	
	dilute	bulk
PbSe	1.9	0.25
ZnS	4.7	3.5
ZnSe	3.5	2.6
CdS	3.1	2.5

We found the activation energy of aggregation of 0.25 M PbS (<2.5 nm PbS → 4.5 nm PbS) in E-MAA to be 76 kcal. This coincides with an estimate for the energy of flow of the E-MAA copolymer. Extrapolation of the half-lives for aggregation at 150, 125, and 100 °C gives a half-life at 25 °C of 10^5 years. Direct measurements of 0.1–1 M PbS in E-MAA show no change in absorption spectra when the samples are allowed to stand for 1 year in laboratory air or when they are immersed in water, methylene chloride, or hexane. A sample of 0.01 M PbS in E-MAA showed no aggregation in 1 year but a 50% loss in concentration. This might be due to oxidation to $PbSO_4$ or loss of H_2S to re-form Pb^{2+}.

The samples prepared at 25 °C show very little light-scattering despite the large difference in refractive index between the PbS and the copolymer because the particle size is much smaller than the wavelength of light. On the other hand, the iridescent PbS produced at 125 °C is a reprise of the oil film on water, but with a much larger refractive index difference for the PbS micro-Liesegang rings in the E-MAA matrix.

Comparable results are obtained for other semiconductors. The band gaps of some dilute semiconductors in E-MAA are compared with their bulk values in Table I.

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Registry No. E–MAA, 25053-53-6; E–MAA (lead salt), 66593-08-6; H_2S, 7783-06-4; PbS, 1314-87-0; lead acetate, 301-04-2; lead acetylacetonate, 15282-88-9.

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