of room-temperature isotropic ionic melts as solvents for electronic spectroscopy has recently been demonstrated.[14]

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Colloidal Metal Particles Dispersed in Monomeric and Polymeric Styrene and Methyl Methacrylate

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Introduction

As Kay has stated, "the physical and chemical behavior of small metal clusters in dielectric thin-film matrices is of considerable interest both from a fundamental and potential applications point of view".[1] Thus, Kay and co-workers have reported interesting properties of gold clusters in fluorocarbons polymer composite films, which were prepared by plasma methods.[1,2] Andrews and Ozin[3] have also reported broad, fundamental studies of metal atoms and clusters in liquid polymeric materials, and Wright[4] has reported interesting synthetic approaches to the synthesis of polymer-trapped metal clusters based on atom agglomeration in organic monomers.

In this communication we report a synthetic approach to preparing metal clusters trapped in solid, organic polymers based on our earlier work involving the preparation of colloidal metals in nonaqueous solvents.[5-7] This method, which involves deposition of metal vapor (atoms) with low-temperature organic solvents followed by controlled/limited atom accretion, is wide in scope and can be employed with a variety of metals and solvents. It allows fairly large-scale preparation of such colloidal solutions, which are of great interest in colloid chemistry, film formation processes, and other areas.[8-11]

Table I. Polymerization Studies of Au-Styrene Compared with Styrene Alone

styrene or Au-Styrene (mL)	mol % AIBN added	yield of polystyrene, %	mol wt of polystyrene^{a}	color
styrene (10)	0.1	2.0	128000	white
styrene (10)	0.2	2.3	83000	white
styrene (10)	0.5	4.2	65000	white
styrene (10)	1.0	6.2	47000	white
Au-styrene (10)^{b,d}	0.1	2.1	53000	light purple
Au-styrene (10)^{b,d}	0.2	3.2	50000	light purple
Au-styrene (10)^{b,d}	0.5	6.2	24000	white
Au-styrene (10)^{b,d}	1.0	7.3	21000	white
Au-styrene (10)^{c,d}	0.1	2.2	72000	purple
Au-styrene (10)^{c,d}	0.2	6.6	41000	purple
Au-styrene (10)^{c,d}	0.5	11.0	32000	purple
Au-styrene (10)^{c,d}	1.0	16.6	22000	purple

^{a} These are relative molecular weights since we used viscosimetry (in benzene at 25 °C); the Kuhn equation is most applicable for linear polymers only, and these may not be linear. ^{b} 1.09×10^{-3} M in gold. ^{c} 1.5×10^{-3} M in gold. ^{d} Very light loadings of Au were used for the studies reported in this table. Much higher loadings, such as 9×10^{-2} M, were possible, giving darker purple colloid solutions.

Results and Discussion

Three approaches to preparing these cluster-polymer composites have been employed:

(1) Codeposition of Metal Atoms with Styrene (or Methyl Methacrylate) Vapor at −196 °C. A typical metal vapor reaction[12,13] where 0.9 g of gold vapor was codeposited with 53 mL of liquid styrene (as a vapor) at −196 °C over 2 h yielded a deep purple matrix. On warming, a purple liquid was formed that was stable at room temperature for several days. Transmission electron microscope (TEM) measurements indicated gold particle sizes ranging from 7 to 15 nm, which are similar to colloids we have prepared in acetone, isopropyl alcohol, and other solvents.[5-7]

(2) Deposition of Metal Atoms into Liquid Styrene or Methyl Methacrylate. With utilization of a rotating metal vapor reactor[14] where liquid monomer (30 mL) was held at −78 °C, metal vapor (e.g., 0.4 g of gold) was evaporated, and the atoms were immersed in the liquid. In this case with Au, a purple liquid was again obtained, and on isolation this colloidal dispersion was very stable at room temperature. TEM again indicated particle sizes from 7 to 15 nm.

(3) Deposition of Metal Atoms into Dissolved Polymer. Again with utilization of a rotating metal atom reactor, 5 g of polystyrene was dissolved in 50 mL of toluene, giving a viscous liquid. Gold atoms (0.05 g) were deposited into this liquid at −78 °C; after warming to room temperature, the toluene solvent was evaporated, leaving a purple solid. Microtoming to 70 nm followed by TEM studies showed particle sizes from 7 to 15 nm.

Polymerization Studies. Colloidal solutions of the cluster monomers were polymerized by conventional means. Thus, AIBN was added to aliquots (all manipulations were carried out under pure N_2), followed by heating to 65 °C for 3 h. Methanol was added to precipitate the polymer, which was filtered off, washed, and dried under vacuum.

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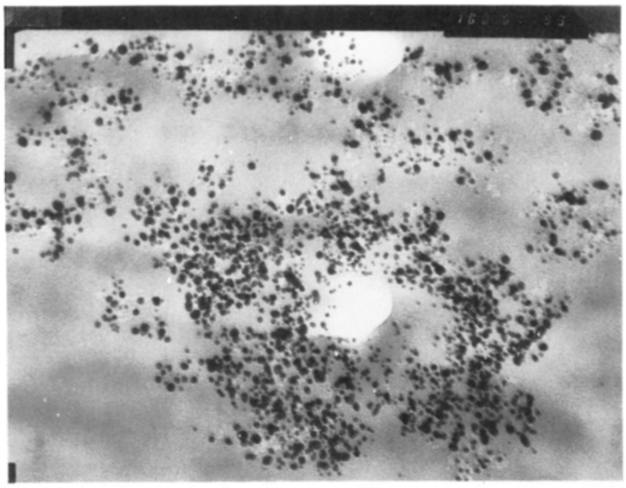


Figure 1. Transmission electron micrograph of gold particles dispersed in polystyrene. These were formed by gold atom accretion in cold liquid styrene followed by AIBN-initiated polymerization. Particle sizes = 7–15 nm.

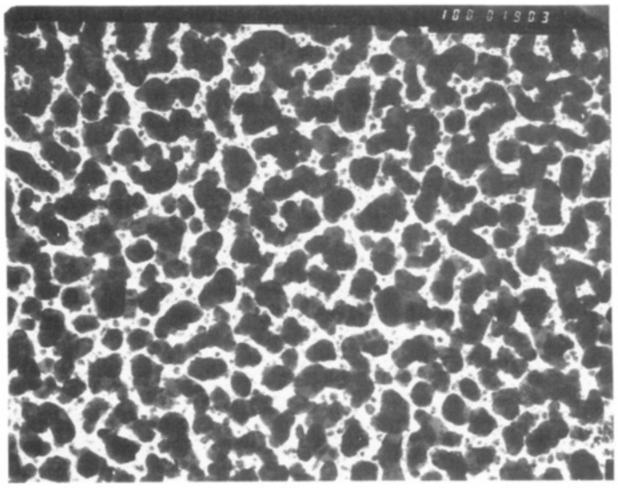


Figure 2. Transmission electron micrograph of gold particles formed by evaporating gold onto a carbon-coated copper grid in the metal atom reactor in the presence of styrene liquid at the bottom of the rotating reactor. Particle size = 40–100 nm.

A series of experiments were carried out where the amount of Au–styrene was held constant and AIBN concentration was varied. Table I summarizes reaction conditions and resultant molecular weights. Control experiments with styrene alone are included.

It is interesting to note that lower molecular weights were found when gold clusters were present. We believe this is due to scavanging of free radicals by the particles as has been demonstrated earlier in related photochemical work by Henglein and co-workers.[15,16] In spite of this, kinetic parameters do not seem to change. Linear plots are obtained when the molecular weight is plotted against $[\mathrm{AIBN}]^{-1/2}$ both for pure styrene and for gold-doped styrene. In other words, typical polymerization behavior was observed, where higher concentration of AIBN causes the initiation of more polymerization chains and so lower molecular weights.

These metal-doped polymers appear very homogeneous. For gold, light purple to deep purple transparent solids were obtained. For palladium, various shades of gray were obtained.

By microtoming the polymers to thickness of about 70 nm, good TEM photographs were obtainable; for example, see Figure 1. These studies showed that particle size did not change during the polymerization. However, the TEM photos show what the naked eye could not—there are definite regions where metal clusters accumulate, and on this scale the samples are obviously not homogeneously dispersed.

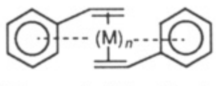
Why should the metal particles agglomerate in regions? This is clearly not the case in the liquid colloidal solutions. Nor is it the case when metal vapor is directly impinged on the carbon film. We showed this by inserting carbon-coated copper grids inside the metal atom reactor about 5 cm from the crucible, and while some of the metal, gold in this case, reached the cold liquid styrene, a small amount reached these grids first. Figure 2 shows the resultant surface clusters that formed. Islands of gold first formed followed by their eventual coalescence into a film. X-ray studies demonstrated the normal crystalline nature of these gold particles.

So during the polymerization process the gold clusters tend to weakly agglomerate until solidification eventually traps them. The clusters do not amalgamate together into larger particles but simply weakly mingle together.

Table II. Particle Sizes and Appearance of Cu, Ag, Pd, and Au Colloids

		particle size range and appearance in	
metal	solvent	liquid monomer	polymer
Ag	styrene	6–11 nm, black	6–11 nm, black
	methyl methacrylate	6–11 nm, black	6–11 nm, black
Pd	styrene	1–2 nm, black	1–2 nm, black
	methyl methacrylate	1–2 nm, black	1–2 nm, black
Au	styrene	7–15 nm, purple	7–15 nm, purple
	methyl methacrylate	7–15 nm, purple	7–15 nm, purple

We should point out another new feature of this work: this is the first time that relatively nonpolar organic solvent (styrene) has been found to allow formation and stabilization of metal colloids. In other cases, polar, oxygenated solvents such as acetone, methyl ethyl ketone, isopropyl alcohol, DMSO, and similar materials were necessary. This stabilizing feature may be due to the ligating action of the unsaturated bonds in styrene, perhaps as shown here:



The importance of this special ligating/solvating effect was further appreciated when we realized that gold particles in liquid styrene did not exhibit an electrophilic mobility as they do in the more polar solvents.[7] Thus, the particles are not charged. Another possible stabilization mechanism should also be considered, however. It may be that the deposited metal atoms initiate some polymerization directly, which could lead to covalently attached low molecular weight polystyrene chains (perhaps a Au(I)–polystyrene bond). We have observed this phenomenon before with nickel atoms as have Blackborow and co-workers with chromium atoms.[17,18] At this time we cannot differentiate between this possibility and that of a pure ligating-solvating effect.

Comparison of Metals. We have studied gold most extensively, followed by palladium. Both metals formed stable colloids in styrene and methyl methacrylate. We have also made preliminary studies of copper and silver.

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The silver colloid did not flocculate over 2–3 days at room temperature; it was stable up to 1 week if kept at 5 °C in the dark. The palladium colloids in these organic monomers were smaller in particle size and more uniform compared with gold and silver. Particle sizes obtained for the various metals are shown in Table II.

Acknowledgment. The support of 3M Corporation and the National Science Foundation through the Materials Chemistry Initiative and the Latin American collaborative research program is acknowledged with gratitude.

Registry No. PMMA, 9011-14-7; Cu, 7440-50-8; Ag, 7440-22-4; Au, 7440-57-5; Pd, 7440-05-3; styrene, 100-42-5; polystyrene, 9003-53-6; methyl methacrylate, 80-62-6.

Cryptate Effects on Sodium-Conducting Phosphazene Polyelectrolytes

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Solvent-free polymer–salt complexes have attracted wide interest because of their potential applications as electrolytes in electrochemical devices.[1,2] The mechanism of charge transport in this class of ion conductors has been partially elucidated,[3,4] but the mobility of both cations and anions complicates the interpretation and reduces the performance of the electrolyte in electrochemical devices. To solve this problem, single-ion-conducting polymeric electrolytes have been synthesized very recently.[5] For example, we have reported the synthesis of both cation (Na^+) and anion (I^-, Br^-, and Cl^-) conducting phosphazene polyelectrolytes.[6,7] Only one type of mobile ion is present in these new polyelectrolytes, so fundamental studies of the factors that influence ion transport are greatly simplified. In the present research, we have studied the influence of cation size on mobility by a comparison of Na^+ with the much larger Na^+ cryptand complexes. The [2.2.2] cryptand ligand $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$ used in this study forms highly stable complexes with alkali-metal ions, in which the cation is contained within the ligand cavity.[8] In a previous study,[9] it was observed that the addition of a crown ether to a polymer–salt complex increases the ionic conductivity, but it is unclear whether this arises from increased mobility of cations, anions, or both.

Table I. Conductivities and Glass Transition Temperatures of $[NP\{O(C_2H_4O)_{7.22}CH_3\}_{1.90}$-$(OC_2H_4SO_3Na)_{0.10}([2.2.2])cryptand)_x]_n$

x	σ, cm^{-1} S 30 °C	σ, cm^{-1} S 80 °C	T_g, K
0	7.2×10^{-7}	2.9×10^{-6}	206
0.05	2.4×10^{-6}	1.4×10^{-5}	204
0.10	3.2×10^{-6}	1.9×10^{-5}	208
0.20	2.8×10^{-6}	1.8×10^{-5}	206

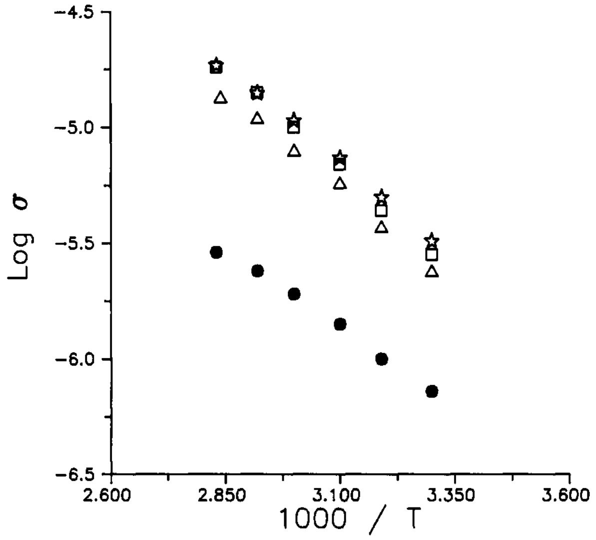

Figure 1. Arrhenius plot of the conductivity of $[Np\{O(C_2H_4O)_{7.22}CH_3\}_{1.90}(OC_2H_4SO_3Na)_{0.10}([2.2.2]cryptand)_x]_n$: ☆, $x = 0.10$; △, $x = 0.05$; □, $x = 0.20$; ●, $x = 0$.

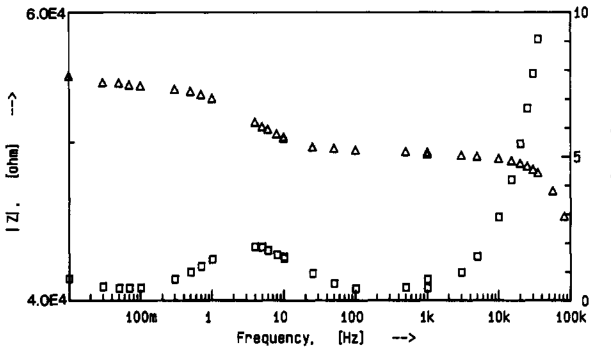

Figure 2. Bode plot of $[NP\{O(C_2H_4O)_{7.22}CH_3\}_{1.90}$-$(OC_2H_4SO_3Na)_{0.10}[2.2.2]cryptand)]_{0.10}]_n$ at 25 °C: □, phase angle; △, impedance. Cell geometric factor: $l/a = 0.113$ cm^{-1}.

Details of the synthesis of $[NP\{O(C_2H_4O)_{7.22}CH_3\}_{1.90}$-$(OC_2H_4SO_3Na)_{0.10}]_n$ (1) were described previously.[6,7] The complexes $[NP\{O(C_2H_4O)_{7.22}CH_3\}_{1.90}(OC_2H_4SO_3Na)_{0.10}$-$([2.2.2]cryptand)_x]_n$, $x = 0.05$, 0.10, and 0.20, were prepared by the combination of 1 and [2.2.2] cryptand in acetonitrile followed by solvent removal under vacuum. The resulting polymers were further dried under high vacuum and then stored in dry nitrogen-filled glovebox.

The glass transition temperatures of the polyelectrolytes were evaluated from differential scanning calorimetry measurements. T_g values are listed in Table I. The addition of cryptand has negligible influence on T_g. This may in part be due to the low ionic concentration in these polyelectrolytes.

One set of conductivity measurements was carried out with ac impedance spectroscopy in the frequency range 10

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