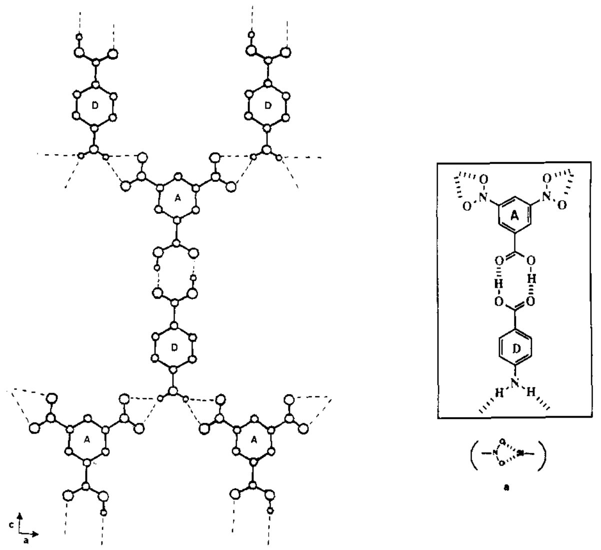

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Figure 2. ORTEP drawing of the hydrogen-bonded aggregate of I, viewed in projection onto the (010) crystal plane. The labels A and D refer to the molecules of 4-aminobenzoic acid and of 3,5-dinitrobenzoic acid, respectively. Hydrogen bonds are indicated by dashed lines. The polar nature of this aggregate is evident since all the nitro groups of A are pointing to the top of the figure and all the amino groups of D are pointing to the bottom. The array is not strictly planar since the interplanar angle between the mean plane of the NO_2 group and the hydrogen to which it is bonded (a) and the plane of the NH_2 group is 39°.

structures with predictable hydrogen-bond patterns. Such predictable patterns can be used to control various aspects of a crystal packing pattern, including the centric or acentric nature of the whole crystal or of subsets of the crystal. By choosing molecules that self-associate by hydrogen bonding into acentric aggregates, the resulting three-dimensional packing pattern is often biased to be acentric also,[15] so this method provides a useful alternative to chiral substitution[16] or inclusion in chiral clathrates[17] for preparing acentric nonlinear optical materials.

Acknowledgment. We are grateful to Professor Doyle Britton, University of Minnesota, for crystallographic assistance and helpful discussions of this work. We thank Nathan Frink, University of Minnesota, for making goniometric measurements. Dr. Robert Twieg and Dr. Herbert Looser from IBM, San Jose, CA, are acknowledged for assistance with second harmonic measurements. Financial support was provided by the Office of Naval Research (N00014-86-K-0660).

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(15) Etter, M. C.; Frankenbach, G. M., unpublished results.

(16) Twieg, R.; Azema, A.; Jain, K.; Cheng, Y. Y. *Chem. Phys. Lett.* **1982**, *92*, 208–211.

(17) Wang, Y.; Eaton, D. F. *Chem. Phys. Lett.* **1985**, *120*, 441–444.

Nonaqueous Perfluorocarbon-Derived Gold Colloids. Clustering of Metal Atoms in Fluorocarbon Media. 1

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Received August 15, 1988

Recently, we reported the successful preparation of colloidal gold[2] and palladium[3] in nonaqueous media by a process of atom clustering in excess organic solvent at low temperature. The metal atom vapor synthesis technique and apparatus have been described elsewhere.[4] By using polar organic solvents, this method yielded stable purple and black sols with gold and palladium, respectively. On the basis of this success, we have been studying the clustering of Au atoms in fluorocarbon media. Au/perfluorocarbon sols might be expected to possess unique properties imparted by the low chemical reactivity, polarity, and surface tension associated with perfluorocarbon solvents. Indeed, our initial findings show that very small gold particles can be prepared that exhibit quite unusual properties regarding aggregation. Initial studies of these unique materials are reported herein.

Au atoms have been codeposited with excess perfluorocarbon solvent vapor at 77 K. Perfluorotri-*n*-butylamine (PFTA) was most often used. The frozen matrix was light brown and yellow, became darker brown with warming, and was dark brown–black at room temperature. The resulting mixture was not a solution but rather a slurry in which the colored material settled. Nevertheless, it was found that the residue could be dispersed in polar organic solvents yielding brown, cola-colored solutions.

The recovery and dispersion of the particles could be accomplished in two ways. The PFTA, in which the particles are not "soluble", was removed by vacuum filtration, and the new solvent (acetone or ethanol, for example) introduced to dissolve the filter cake and form the brown solution. Alternatively, the Au particles were transferred from the slurry into the polar organic phase by solvent extraction, the PFTA being immiscible with most familiar solvents.

These PFTA-derived Au particles are quite selective with regard to dispersion in different solvents. For example, they could be dissolved in light aliphatic alcohols, ketones, aldehydes, and tetrahydrofuran (THF). They dissolved in, as well as reacted with, pyridine and its derivatives. The particles were insoluble in hydrocarbons, diethyl ether, and water. The ability to dissolve in most polar organics, but not in water, suggests a donor–acceptor interaction that requires the solvent to be a better Lewis base than water. This correlation between solvent functionality and the ability to dissolve the colloidal particles finds a parallel in the earlier work,[2] in which stable colloids were developed only when the codeposited solvent was a polar organic.

Transmission electron microscopy (TEM) studies[5] revealed that Au atoms had initially clustered to form roughly spherical particles ranging from 1 to 2 nm in diameter along with some larger aggregates; aging in solution for periods ranging from a few days to a few weeks led to further aggregation to form stable colloidal particles in the 2–10-nm range (Figure 1). Analysis of histogram data with a log probability graph yielded a straight line to indicate the distribution is log normal. The median size was found to be 3.4 nm with a geometric standard deviation of 1.5. Unlike the sols produced by the earlier method of direct Au/acetone codeposition in which the individual particles

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(1) Department of Physics.

(2) (a) Lin, S.-T.; Franklin, M. T.; Klabunde, K. J. *Langmuir* **1986**, *2*, 259. (b) Franklin, M. T.; Klabunde, K. J. In *High Energy Processes in Organometallic Chemistry*; Suslick, K. S., Ed.; ACS Symposium Series. No. 333; American Chemical Society: Washington, D.C., 1986; pp 246–259.

(3) Cardenas-Trivino, G.; Klabunde, K. J.; Dale, E. B. *Langmuir* **1987**, *3*, 986.

(4) (a) Klabunde, K. J. *Acc. Chem. Res.* **1975**, *8*, 393. (b) Klabunde, K. J.; Timms, P. L.; Skell, P. S.; Ittel, S. *Inorg. Synth.* **1979**, *19*, 59.

(5) TEM samples were prepared placing a drop of solution on a carbon-coated Cu grid; the solvent was allowed to evaporate.

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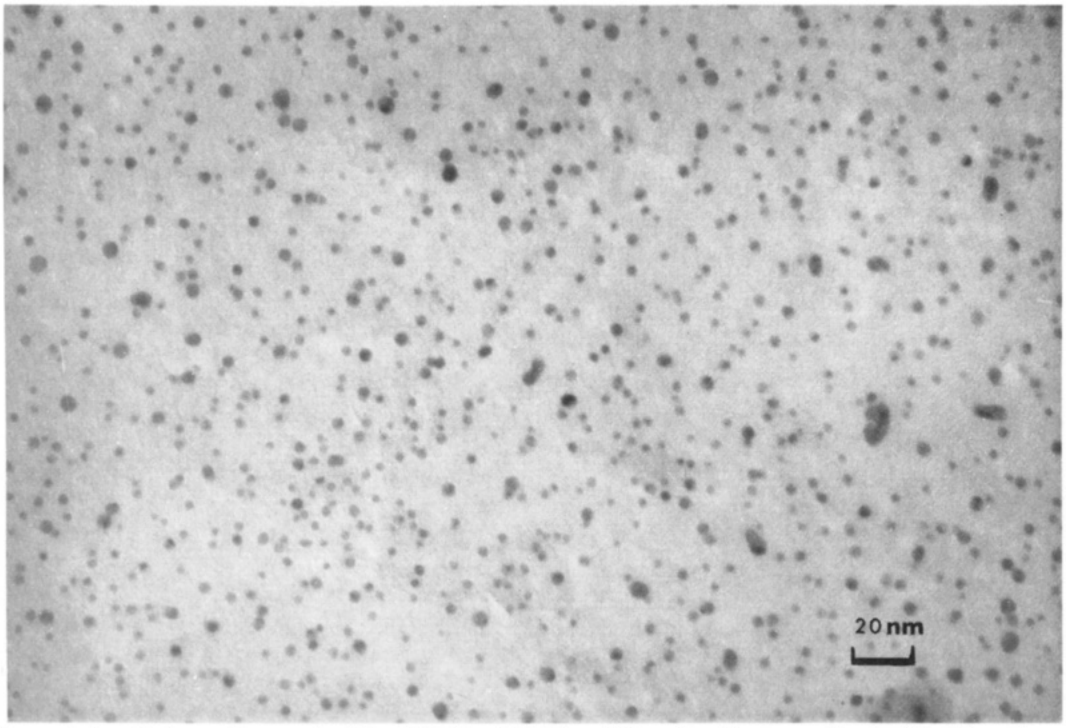

Figure 1. Transmission electron micrograph of Au/PFTA colloidal particles after they were dissolved in ethanol.

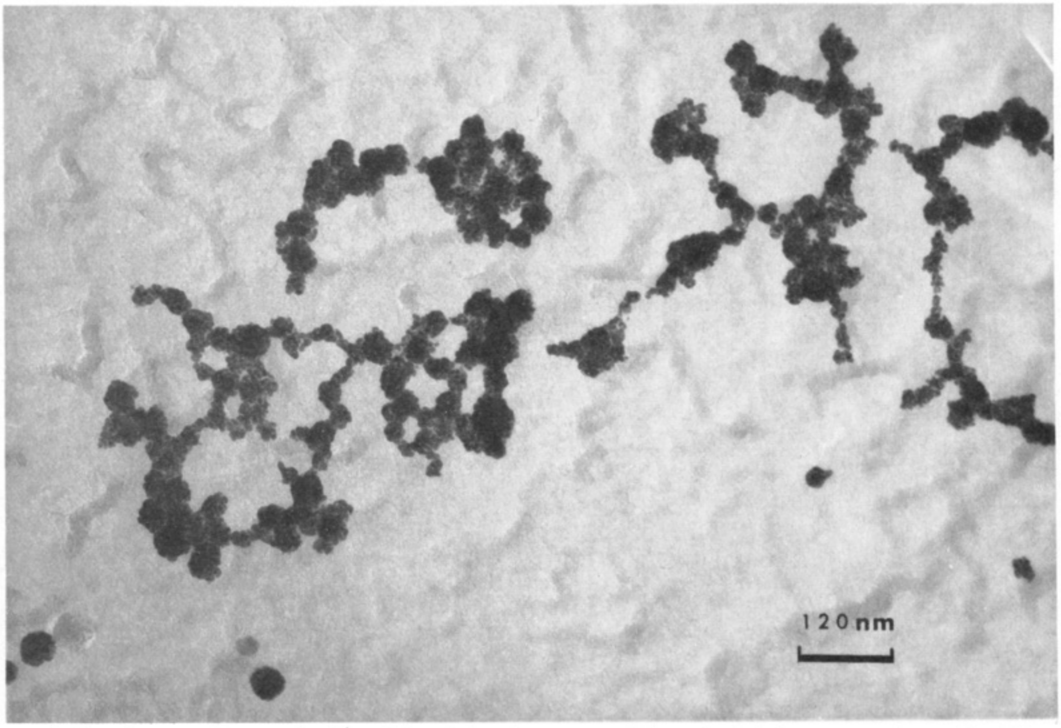

Figure 2. Transmission electron micrograph of a pyridine-induced aggregate. The spherical clusters are the result of the second growth stage and are further aggregating as ramified structures at the onset of the third stage. Note the monomer components (as in Figure 1) of the spherical clusters.

appeared to be weakly bound or chained together,[2] the PFTA-derived particles, as seen in Figure 1, do not associate and seem to repel each other. Freshly prepared solutions of the particles did not exhibit a well-defined plasmon absorption maximum in the visible spectrum; rather there was a steady increase in absorbance extending from 700 to about 250 nm. With age, usually several days to a few weeks, a weak maximum developed at about 480 nm; this gradually became more defined, moved to longer wavelengths, and finally stabilized at 501–504 nm, coincident with the aforementioned changes observed by using TEM. The reason for the differences in the rate of growth and stabilization among various samples, particularly as monitored by daily acquisition of the UV–visible spectrum, is not yet understood. It does, however, appear to be solvent-dependent with the development requiring only a few days in acetone or ethanol but as long as 50 days in the case of THF. This plasmon maximum is significantly lower in wavelength than those observed in the 525–570-nm range in the case of the previous nonaqueous colloids[2] and suggests a much smaller particle size. Photon correlation spectroscopy (PCS) studies have also shown that dissolved Au/PFTA particles are smaller, having hydrodynamic radii of ~7–20 nm.[6] (The sizing of particles by PCS is strongly weighted toward the largest particles present, by the relationship

$$I(r) \propto r^6$$

where I is the intensity of the scattered light and r is the radius of a particle.[7])

Another interesting feature of these Au/PFTA particles is that after dispersion in a solvent they can be deposited as a gold-appearing film or powder, allowed to dry, and then be redissolved. The particles are both lyophilic (solvent loving) and lyoselective. They also possess some of the properties of very large ligand-stabilized molecular clusters, and preliminary EXAFS and XRD measurements indicate that they consist of a metal core. Thus, fluorocarbon moieties, detected by GC-MS analysis of bromination and pyrolysis products, evidently exist as ligands coordinated only to surface metal atoms. The evidence suggests a colloid/cluster duality in the properties of these particles. A few recent accounts of large metal clusters bearing peripheral ligands or coatings have been reported by other workers,[8–10] and in this context we find parallels between those and the present Au/PFTA particles.[11]

The Au/PFTA colloids, both dissolved and undissolved, undergo reactions with various additives. In solution, this usually leads to coagulation, floculation, and precipitation of the particles. Addition of any ionic substance (HCl, NaI, KBr, $HgCl_2$) immediately brought this about, as did I_2. Bromination of the Au/PFTA solid resulted in the evolution of perfluoroalkyl bromides. When tertiary phosphines were allowed to react with the particles, precipitation was observed; however, after 2 days the solid material had redissolved and the mixture was colorless. Removal of the solvent left a white Au–phosphine complex that has not yet been fully characterized. The reactivity of the particles appears to parallel that of organogold(I) compounds.[11]

IR, XPS, pyrolysis/GC-MS, and ^{19}F NMR studies revealed the presence of a perfluorocarbon moiety strongly associated with the colloidal particles before and after being dissolved in acetone. Elemental analysis of Au/PFTA powder, recovered from acetone and thoroughly dried, yielded the formula $Au_{17}C_{20}H_{30}F_{26}N$ (O_7 by balance). The N/F ratio in this formula is nearly the same as in PFTA; thus, there is apparently one molecule of PFTA, not necessarily intact, for every 17 Au atoms. The excess carbon, all of the hydrogen, and the assumed oxygen are probably due to coordinated acetone residues. Determination of the Au/fluorocarbon interaction has been difficult, and efforts to elucidate are continuing.

Of particular importance in this work is the study of the kinetics and morphology of aggregation. Pyridine added in very small amounts induces a controlled rate of aggregation that can be monitored by PCS, TEM, and changes in plasmon absorbance. Early qualitative results reveal three stages of growth: (1) fast aggregation (amalgamation) of solvated atoms to spherical colloidal monomers, (2) pyridine-induced monomer aggregation (without amalgamation) to compact spherical clusters, and (3) aggregation of these clusters to larger, noncompact or ramified structures. Figure 2 shows the micrograph of a sample taken near the end of the second stage and the beginning of the third stage. Note the resistance of the monomer particles to merge or amalgamate together. The concept of reversibility, i.e., fragmentation of aggregates, is currently being investigated. Ongoing work in this area focuses on the development of this system as a model to which other aggregation phenomena may be compared, for example, in the synthesis of new magnetic particles in our laboratories. The surface chemistry of the colloid particles is also being explored.

Acknowledgment. The support of the 3M Co. and partial support by the National Science Foundation–Materials Chemistry and the Office of Naval Research is acknowledged with gratitude. We thank Drs. Fred Behr and Richard Howells for providing PFTA samples.

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[6] The early growth stage that was observed by using microscopy and visible spectroscopy has not yet been as successfully monitored with PCS. This was primarily due to difficulties associated with intense absorbance of the 488-nm laser line. It is anticipated that by use of the 633-nm line of a He–Ne laser absorbance by the sample will be minimized in future experiments.

[7] Taylor, T. W.; Scrivner, S. M.; Sorensen, C. M.; Merklin, J. F. *Appl. Opt.* **1985**, *24*, 3713.

[8] Schmid, G.; Klein, N.; Korste, L.; Kreibig, U.; Schönauer, D. *Polyhedron* **1988**, *7*, 605, and references therein.

[9] Vargaftik, M. N.; Zagorodnikov, V. P.; Stolyarov, I. P.; Moiseev, I. I.; Likholobov, V. A.; Kochubey, D. I.; Chuvilin, A. L.; Zaikovsky, V. I.; Zamaraev, K. I.f Timofeeva, G. I. *J. Chem. Soc., Chem. Commun.* **1985**, 937.

[10] Bradley, J. S.; Hill, E.; Leonowicz, M. E.; Witzke, H. *J. Mol. Catal.* **1987**, *41*, 59.

[11] Puddephatt, R. J. *The Chemistry of Gold*; Elsevier: New York, 1978; pp 98–156, and references therein.

Radiation Cross-Linking of Poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene]: Effect on Solid-State Ionic Conductivity

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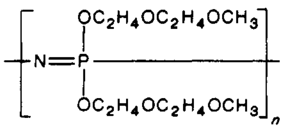
Received October 7, 1988

At the present time great interest exists in solid electrolyte systems for possible use in high-energy-density batteries.[1,2] The polyphosphazene poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (I) shows excellent promise as a solid electrolyte host when dissolved $LiCF_3SO_3$ is used as the charge carrier.[3–6] Although this system shows



$$\left[\,N{=}\overset{\displaystyle OC_2H_4OC_2H_4OCH_3}{\underset{\displaystyle OC_2H_4OC_2H_4OCH_3}{P}}\,\right]_n$$

I, $n \cong 15\,000$

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[1] Armand, M. B.; Chabagno, J. M.; Duclot, M. J. In *Fast Ion Transport in Solids*; Vashista, P., Mundy, J. N., Shennoy, G. D., Eds.; North-Holland: New York, 1979; p 131.

[2] Shriver, D. F.; Farrington, G. C. *Chem. Eng. News* **1985**, *63* (20), 20.

[3] Blonsky, P. M.; Shriver, D. F.; Austin, P. E.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.

[4] Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *Solid State Ionics* **1986**, *18/19*, 258.

[5] Allcock, H. R.; Austin, P. E.; Neenan, T. X.; Sisko, J. T.; Blonsky, P. M.; Shriver, D. F. *Macromolecules* **1986**, *19*, 1508.

0897-4756/89/2801-0014$01.50/0