Reviews

Wrapping Oligomers and Polymers around Metal Atoms, Metal Clusters, and Metal Colloids

Mark P. Andrews*

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Geoffrey A. Ozin*

Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario M5S 1A1, Canada

Metal atoms deposited into oligomers and polymers can be trapped in the form of organometallic complexes, clusters, and colloids. In this way new varieties of organometallic compounds and composite materials can be made. An account is given of the use of metal atoms as reagents for derivatizing or compounding oligomers and polymers. Applications of the resulting materials in the areas of redox processes, bioseparations, catalysis, magnetic and magnetooptic processes, and nonlinear optics are discussed. Chemical organization of the polymer microenvironment is important for controlling certain aspects of the growth and stabilization of different kinds of particles.

Introduction

Metal atoms and molecular high-temperature species are now well-known to be useful chemical reagents for the synthesis of a diverse group of organometallic and inorganic compounds.[1,2] The technique for making compounds and other materials in this way is variously known as metal vapor synthesis (MVS), vapor synthesis, or metal atom synthesis. In its capacity to make specialty materials from ephemeral fragments of solid-state matter, the MVS methodology is also beginning to declare a unique position for itself alongside the established methods of materials science.[2–5] The apparatus and principles of the technique are closely related to many industrial processes that utilize highly reactive atomic and molecular species[6] to give thin films, metastable materials, alloys, etc., assembling them atom by atom, fragment by fragment. As reported at a recent symposium,[5] new materials prepared by MVS now include unusual metal/zeolite compositions, organic-solvent-soluble ("living") colloids, catalysts, magnetic compounds and structures, and synthetically versatile precursor molecules. Thus some of the strongest electrophiles known have been prepared by Lagow and co-workers. The zerovalent lanthanides produced by Cloke are stimulating new research into the reactivity and electronic structure of f-orbital compounds. If sufficiently volatile, these lan-

thanide molecules may also be useful sources of dopants for semiconductor devices. With MVS Andrews and Lamberti have produced nanoparticle metallic alloys of soluble and insoluble elements.[4] Already these "microalloys" reveal some unusual physical properties (disorder, "missing atom effects") connected both to the manner in which the materials are prepared and to the effects of small particle size.[7,8]

In polymer science, six areas can be identified where metal atoms are recognized for their special role. These areas are (i) the synthesis of organometallic monomers, (ii) monomer polymerization induced by high-temperature vapors, (iii) the preparation of organometallic polymers by *direct reaction of polymers with metal atoms,* (iv) the concatenation of organic molecules by metal atoms to form oligomers, (v) the use of polymers to host metal atom aggregation, and (vi) the preparation and screening of polymerization catalysts.[9]

Impetus for devising methods to affix mononuclear and cluster organometallic complexes to polymer backbones comes from a number of fields. In catalysis it is recognized that "heterogenized" homogeneous organometallic catalysts can offer the advantages of both the hetero- and homogeneous systems.[10] Further motivation for making polymers containing spatially and dimensionally well-defined metal, metal oxide, metal chalcogenide, and semiconductor particles is due to the interest in fabricating *integrated chemical systems* (ICS).[11] An ICS is a composite system containing different components, usually of less than a few micrometers, designed and arranged for specific functions or to carry out specific processes. For example, the pho-

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(2) Andrews, M. P. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y.; Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1987; Vol. 357, p 158.

(3) Ozin, G. A. *CHEMTECH* **1985**, 488.

(4) Andrews, M. P.; Lamberti, V. E. Microalloyed Nanoparticles Formed from Metal Atoms Quench-Condensed in a Rotating Glass Cryostat. Abstract of paper presented at *Mater. Res. Soc. Symp. G: Multicomponent Ultrafine Microstructures*, Boston, Nov. 1988.

(5) New Materials from Metal Vapor Chemistry. Abstracts of proceedings, ACS Symp. Am. Chem. Soc Mtg., Los Angeles, Sept. 1988. Much of this work will be published in forthcoming issues of *Chem. Mater.*

(6) *Thin Films from Free Atoms and Particles*; Klabunde, K. J., Ed.; Academic Press: New York, 1985.

(7) Lowe, W. P.; Andrews, M. P.; MacHarrie, R.; Lamberti, V. E. *Appl. Phys. Lett.*, in press.

(8) Marcus, M.; Lamberti, V. E.; Andrews, M. P. 5th International Conference on X-ray Absorption Fine Structure (XAFS V), Seattle, WA, Aug 1988.

(9) Andrews, M. P. *Encyclopedia of Polymer Engineering and Science*, 2nd ed.; Wiley: New York, 1987; Vol. 9, p 623.

(10) Pittman, C. U., Jr. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pregamon: Oxford, 1982; Vol. 8, p 553.

(11) Bard, A. J. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 1187.

toelectrochemical conversion of solar energy might be used to drive useful chemical reactions. The ICS components (particles, polymer, catalyst materials) are selected for structure, chemical/physical synergy, and organization to determine the overall performance of the system. Andrews and co-workers[12] used MVS to introduce a new method for compartmentalization of molecules and clusters in phase-separated block copolymers. These media are substantially more robust than surfactant, amphiphilic, or detergent micelles.

Although the polymer and composite materials derived from MVS have yet to mature in terms of applications in technology, there are a number of subjacent areas of materials science where the technique is likely to contribute rather uniquely. Examples are magnetic fluid synthesis and the preparation of ferrite composites, nonlinear optical materials, and hydrogen getters. The following sections describe how MVS has contributed to new developments in organometallic polymers and composite materials, as they originate from metal atoms, multimers, and colloids.

Arene-Functionalized Oligomers and Polymers

Once inside a polymer metal atoms can be manipulated selectively only if some way can be found to prevent them from reassembling to give massive particles. This can be done by introducing kinetic barriers to mass transport (freezing) or by forming weakly or strongly bonded complexes between the atom and a substituent on the polymer. To make clusters or stacks of atoms, the polymer must be allowed to intervene in some manner to control cluster growth; but the atom/polymer interaction must not be so strong that cluster formation is prevented. The first successful studies of metal atom diffusion and aggregation in polymers for the purpose of isolating groupings of less than 10 atoms near room temperature evolved from the known small-molecule metal atom chemistry of arenes. This chemistry was elaborated into a cluster chemistry in macromolecules. Thus the phenyl substituent became the workhorse for much of the metal vapor chemistry of polymers. The reasons for this are fairly simple. The reaction of arenes with metal atoms is a low activation energy, simple orbital mixing process that traps the atom between two coplanar phenyl rings. As we shall see, this allows compound formation to compete very effectively with other processes (oxidative addition, abstraction, isomerization), in those instances where the ligand carries potentially reactive substituents such as halogens, oxygen, active hydrogen, monoenes, or dienes. The formally zerovalent π-arene sandwich complexes also form a class of molecules whose electronic structure and chemical reactivity are becoming very well understood.[13] For the most part, the preparation of these compounds via metal atoms seems to be limited only by the ambient pressure in a given reactor, the molecules having been prepared at temperatures ranging from 10 to 273 K. It was Timms who first derived them from reactions between metal atoms and arenes.[14] The interaction of metal atoms with phenyl-substituted siloxane polymers and oligomers was subsequently studied by Timms and Francis.[15] They demonstrated that vapors of Ti, V, Cr, Mo, and W gave bis(arene)metal complexes in which the metal atom acts as a cross-linking or concatenating unit in the siloxane. For

Scheme I

M = Ti, V, Cr, Mo, W.
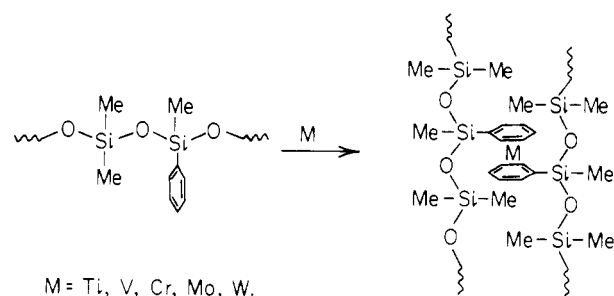
example, early-transition-metal atoms react with the phenyl groups suspended from the backbone silicon linkage of a Dow Corning poly(methylphenyl-*co*-dimethylsiloxane) fluid (DC510).[15] These reactions produce organometal polymers as shown in Scheme I. Experiments are conducted by evaporating metal into 75–100-mL volumes of the polymer, spun as a thin film on the inner surface of an evacuated Pyrex flask. A suitable cryogen is used to maintain a vapor pressure below 10^{-3} Torr. In general, the use of these kinds of liquid media permits chemical reactions between metal atoms and ligands to occur at higher temperatures, where a more favorable competitive balance exists for bis(arene)metal complex formation as compared with metal atom aggregation. Later, Ozin, Huber, and Francis[16] published evidence indicating that these complexes could themselves become targets for nucleating additional metal atoms left circulating in the fluid medium. Their work implied that low nuclearity (n = 2–5) polymer-encapsulated molecules of the metals Ti, V, Cr, and Mo could be grown under carefully defined conditions of temperature and polymer and metal concentration.[17]

From its inception in the late 1960s, MVS has carried through to the 1980s the reputation of requiring high-temperature sources to produce metal vapors and expensive cryogens to trap and investigate reactive intermediates and products.[18] To the contrary, recent research has adequately demonstrated that neither very high nor very low temperature methods are necessary conditions for performing syntheses with metal atoms.[17-22] Thus, running through some of the metal atom research is a theme concerned with ways of generating and stabilizing metal atoms, clusters, and colloids, at or close to room temperature. The concept is a little akin to membrane mimesis in the loose sense of the definition of compartmentalization or organization of guest species in a well-defined manner in a host.[23] The ability to transfer the metal aggregates from the fluid phase, intact to solid supports such as carbon, inorganic oxides and zeolites, emerged as a result of such investigations.[3,17,22,24]

Metal atoms diffusing in liquids containing arenes are most likely captured in an initial event according to

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(13) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

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(21) Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1988**, 707.

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(24) Ozin, G. A.; Nazar, L. F.; Hugues, F. U.S. Patent 4,522,855, 1985.

$$M + L \xrightarrow{k_1} ML \tag{1}$$

$$ML + L \xrightarrow{k_2} ML_2 \tag{2}$$

Step 1 is deemed reasonable in view of the half-sandwich metal arene complexes isolated and characterized in low-temperature matrices.[25] Succeeding steps are assumed to proceed by accretion of metal atoms, one at a time, commencing with the parent ML_2 sites as shown in the following:

$$ML_2 + M \xrightarrow{k_3} M_2L_2 \tag{3}$$

$$M_2L_2 + M \xrightarrow{k_4} M_3L_2 \tag{4}$$
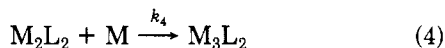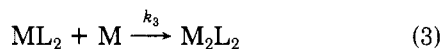
Support for step 3 derives from the outcome of experiments where indication was given that M could add directly to bis(arene)metal complexes to give an M_2L_2 species.[26,27] These liquid-phase addition reactions are postulated to occur at a metal site, preformed in a support medium that contains arene functionalities.[28] The arene substituents thus act as chemical traps for the diffusant and thereby inhibit competing metal atom polymerization reactions of the type

$$M_1 \xrightarrow{M} M_2 \xrightarrow{M} M_3 \xrightarrow{M} \cdots M_{colloid} \tag{5}$$
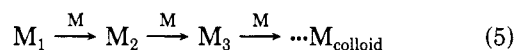
which would otherwise proliferate in a ligand-free medium.

The principle of these reactions has been extended to quantitative depositions of transition-metal atoms into thin, quiescent liquid films of a wide range of arene-containing fluids. These *microscale* thin liquid film experiments form the intermediate link between the cryogenic matrix-isolation experiments and the macroscale experiments conducted at much higher temperatures.[29] The experiments and arguments implicating metal cluster compounds in these arene-containing liquids have been detailed in a series of papers to which the reader is referred.[27,28,30] In brief, single metal atoms react with one or two benzene rings in rare-gas matrices to form the respective half-sandwich $(\eta^6\text{-}C_6H_6)M$ or sandwich complex $(\eta^6\text{-}C_6H_6)_2M$, depending on the relative concentrations of the various components.[25,31] In metal atom reactions with poly(methylphenyl-*co*-dimethylsiloxane), kinetic studies have revealed the existence of $(C_6H_6)_mM_2$ for M = V, Cr, and Mo, where m may be 2.[30] The product distributions depend on the metal concentration. Simple series–parallel competitive kinetic schemes have been given to account for the cluster growth curves for V_n, Cr_n, and Mo_n/DC510 (n = 1–4).[30]

"Molecular alloying" to make the binary AB compound was indicated by experiments involving the simultaneous or sequential deposition of Ti, V, Cr, and Mo into the siloxanes.[16,32,33] Having identified the bis(arene)metal complex as the locus of additional reactivity in the siloxanes, the chemistry was then extended to α,ω-phenyl-

substituted oligo- and polyethers[34] and oligo- and poly-(silastyrene)s.[35]

Although the cryogenic matrix-isolation studies described above do not allow assignment of the ligand stoichiometry of the $(arene)_mM_n$ species, a good case for the assignment could be made by means of some crossover experiments. In these experiments a metal atom A is reacted with a π-arene complex containing a metal atom, B. Among other possible outcomes, the experiment is meant to distinguish simple displacement reactions involving the exchange of A and B. Thus, the outcome of metal atom deposition into low-temperature, methylcyclohexane solutions of $(arene)_2M$ (M = V, Cr) suggested that a metal dimer species forms by direct addition of the metal atom to a preformed $(arene)_2M$ complex.[26] Because neither free arene nor metal atom crossover products were detected in this experiment, the arene stoichiometry suggested was 2. In addition an experiment was designed that demonstrated that $(arene)_2Mo$ dissolved in an unreactive, arene-free liquid polymer could be quantitatively titrated by Mo atoms.[28] The product showed an optical absorption spectrum identical with that obtained by reaction in a variety of phenyl-containing media. Circumstantial evidence for the existence of compounds formulated as $(C_6H_6)_2M_2$ comes also from gas-phase ion–molecule and metal-cluster ion–molecule reactions. Although no definitive structural assignments were reported, species such as $(C_6H_6)_2Cr_2^+$,[29] $(C_6H_6)_2VFe^+$,[36] and $(C_6H_6)_2Pt_n^+$ (where n = 2–6) have been detected.[37] A bis(benzene)dimetal structure, similar to that of the aforementioned $(arene)_2M_2$ clusters formed in the liquid phase, was suggested for the $(C_6H_6)_2VFe^+$ species.

Attempts to isolate crystals of the benzene or toluene complexes containing two metal atoms were frustrated by the extreme thermal instability of the products in the liquid. Similar experiences with these ligands were recorded by Lamanna; however, a product containing two Cr atoms was finally isolated by him when mesitylene was substituted as the ligand.[38] Microscale metal atom reactions similar to those conducted by Ozin et al.[26] gave a product whose electronic absorption is remarkably similar to the liquid-phase spectrum of the axially symmetric dimer recovered from preparative-scale synthesis. Single-crystal X-ray analysis showed that mesitylene (Mes) and chromium in the dimer are arranged in an alternating manner, Mes/Cr/Mes/Cr/Mes. Thus the overall stoichiometry is Mes_3Cr_2, and there is no direct Cr–Cr bond in the solid state. This result and those of Lamanna's microscale experiments would seem to argue, at least for the case of chromium, that both the mechanism of formation and the bonding within the dimer be reconsidered. For reactions with mesitylene one can add to eq 3 the following:

$$ML + ML_2 \xrightarrow{k_{3'}} LMLML \tag{3'}$$

The reaction of Cr with the mesitylene ligand may actually be a special case in which subtle changes in electronic and geometric structure associated with this ligand have come into play, and since no contrary evidence exists for the benzene, toluene, or polymer-bound ligands, the question there remains unresolved. Moreover, the results with

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(35) Ozin, G. A.; Andrews, M. P.; West, R. W. *Inorg. Chem.* **1986**, *25*, 580.

(36) Hettich, R. H.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 6222.

(37) Whetten, R. L.; Cox, D. M.; Trevor, D. J.; Kaldor, A. *Surf. Sci.* **1985**, *156*, 8.

(38) Lamanna, W. M.; Gleason, W. B.; Britton, D. *Organometallics* **1987**, *6*, 1583.

mesitylene/Cr conflict with the results of the crossover study involving toluene or benzene ligands.[26] Crossover experiments with bis(mesitylene)Cr and, say, vanadium, and (arene)Cr(arene′) + vanadium may provide mechanistic details regarding product formation specific to this ligand.

Lamanna's concatenated mesitylene complex represents an important application of MVS to the synthesis of new classes of one-dimensional chains.[39,40] There have been a number of other reports of MVS preparations of organometallic chains linked by the metal atom.[9] Invariably these are marked by low degrees of polymerization. A great deal of effort has been devoted to transition metals to discover general criteria for the design of highly conducting materials. At the moment, the difficulties associated with isolating stacked organometallic chains with a high degree of polymerization appear to be formidable, and their extreme reactivity toward oxygen presently makes them undesirable for most practical applications.

In summary, low nuclearity clusters of metal atoms are stabilized under specific conditions of temperature and metal loading in arene-functionalized polymeric and oligomeric hosts. Critical for the growth and stabilization of species containing more than two atoms are polymers having a high degree of mobility at the reaction temperature, initial coordination of a metal atom to form a stable sandwich complex, and the simultaneous development of a network of chains cross-linked by metal atoms through the formation of these sandwich complexes. Although the lability of these clusters in the liquid medium clearly obviates their direct use as catalysts, these experiments make an important contribution to our understanding of metal atom/polymer interactions. The relevance of this work to the metallization of polymers and adhesion science is manifest.

Organometallic Monomer Synthesis

The reactivities of multiple bonds and the methods for their activation are of great interest for the polymerization of metal-containing monomers.[10] The synthesis of organometallic monomers from olefins via MVS is sometimes complicated by the facile oligomerization or polymerization of the organic compound or the formation of metal-containing oils or intractable solids.[9] Green and co-workers[41] have recently devised an elegant Mo-atom-based preparation of a series of 1,1′-disubstituted bis(η^6-vinylarene)-molybdenum compounds. The monomer was prepared by reaction of vinyl magnesium bromide with bis(η^6-chlorobenzene)Mo. The latter compound was prepared by reaction of atomic Mo with chlorobenzene at 77 K. Note that compound formation with atomic Mo proceeds without reaction with chlorine. Free radical polymerization (azobis(isobutyronitrile)) at 313 K in benzene gave 60–80% conversion to polymer in 36–60 h. Some decomposition of the monomer occurred, meaning that the final macromolecules were not true homopolymers, but copolymers of the organic monomer and the organomolybdenum monomer (ratio 1:5, respectively). The polymers are readily soluble in benzene and are therefore thought to have low molecular weights. In fact the poly-[bis(η^6-allylbenzene)molybdenum(0)] species was found from vapor-phase osmometry to have a number-average degree of polymerization of $\bar{x}_n = 33 \pm 10$. The implication is that
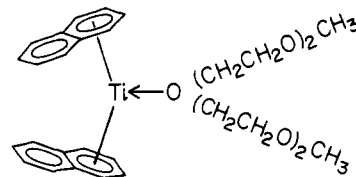
Scheme II

(I)

(II)

(III)
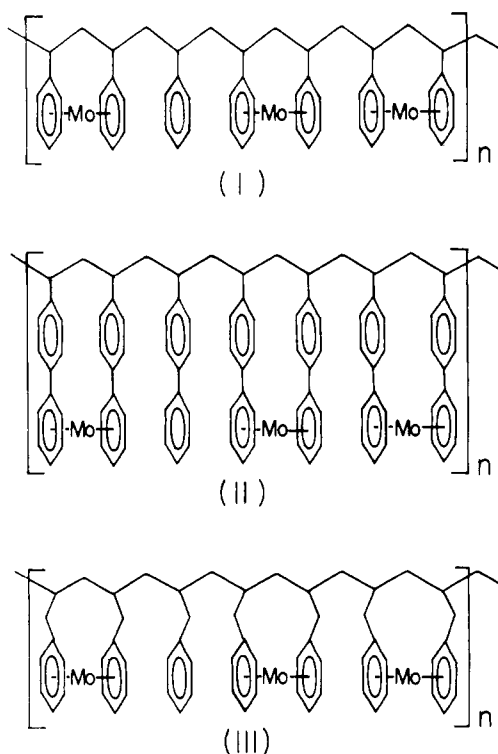
the conformation of the polymer results from an alternating intramolecular–intermolecular propagation step to give structures of the type illustrated in Scheme II. The data reported are consistent with the formulation of a cyclic ladder structure. These polymers warrant further study, for it seems possible that additional metal atoms might be intercalated to give stacked organometallic chains. In this manner, some of the difficulties associated with the isolation of linear stacks longer than the triple-decker isolated by Lamanna might be overcome.

Naphthyl-Functionalized Polymers

This work[42] derives from earlier observations of Francis[43] and co-workers that early-transition-metal atoms form π-arene complexes with polycyclic hydrocarbons. These complexes exhibit properties distinctly different from those of the monocyclic arenes, particularly with respect to ligand displacement.[44] Noteworthy are the reactions of Ti, V, and Cr with naphthalene and selected naphthalene derivatives. The products have been assigned bis(η^6-naphthalene)metal structures on the basis of their optical and NMR spectroscopy. At low temperatures they are stable even in strongly coordinating solvents. On warming above 150 K in tetraglyme, the solvent appears to participate in the coordination sphere of the (η^6-naphthalene)$_2$Ti:

The high reactivity of the (η^6-$C_{10}H_8$)$_2$Ti complex may be compared with that of (η^6-C_6H_6)$_2$Ti, which is stable to tetrahydrofuran below 373 K. The lower Ti–arene bond

(39) Böhm, M. C. *Z. Naturforsch.* **1984**, *39a*, 223; *J. Chem. Phys.* **1984**, *80*, 2704.
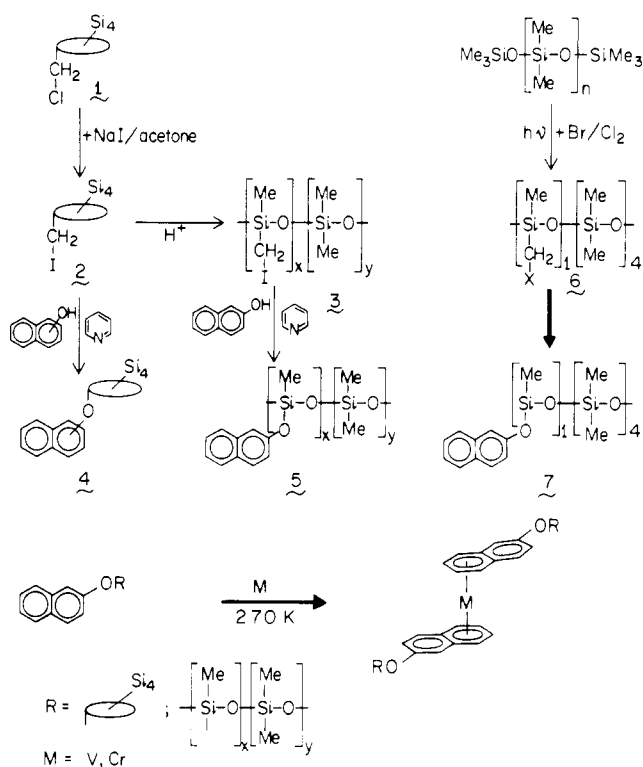
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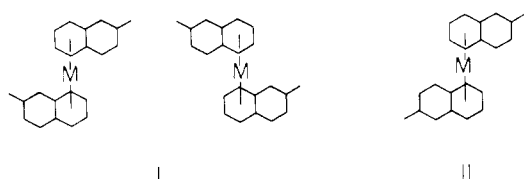
Scheme III

Figure 1. UV–visible spectra obtained after the deposition of metal vapors of Cr, Mo, or W into a thin film of 2 at ≈220 K.[45]

Table I. Infrared Spectra (cm⁻¹) of M(CNR)₆ Macromolecular Complexes Formed from the Reaction of Cr, Mo, W, and V Atoms with Isocyano-Functionalized Polysiloxane

$Cr(CNR)_6$	$Cr(CNR)_6^+$	$Mo(CNR)_6$	$W(CNR)_6$	$V(CNR)_6$
				2112
	2085[b]			
				2056
2010[a]		2010	2010	
1975[a]				
		1960 br		
1950[a]				
			1945 br	

[a] Distorted O_h $Cr(CNR)_6$ macromolecular complex. [b] Air exposure of $Cr(CNR)_6$. $\nu(CN)$ of virgin polymer, 2145 cm⁻¹. Polymer 2 was used for this study.

energy conjectured for naphthalene versus benzene, and/or an η^6–η^4 rearrangement, may be responsible for the greater reactivity of the $(\eta^6\text{-}C_{10}H_8)_2Ti$ derivative, relative to that of $(\eta^6\text{-}C_6H_6)_2Ti$.

A major observation of this study is that a highly reactive titanium–naphthalene complex does exist, which is stable at room temperature. The potential of this molecule to shuttle between η^6–η^6, η^6–η^4, and η^4–η^4 (16-, 14-, and 12-electron states, respectively) confers upon it an extreme electron richness and coordination unsaturation. Ligand-exchange studies of the analogous chromium complex illustrate these unusual features of its reactivity.[44] The Ti species is an attractive candidate for future screening of its catalytic behavior.

To further investigate metal atom reactions with oligomeric and polymeric ligands, Francis and co-workers have devised two synthetic routes to naphthalene-functionalized oligo- and polysiloxanes. These are illustrated in Scheme III. Reactions of V and Cr atoms with these macromolecular ligands yielded anchored bis(arene)metal complexes. Ti attacked the oxygen linking naphthalene to the backbone. Studies of model chromium complexes, revealed that the metal binds only to the unfunctionalized ring in the monosubstituted naphthalenes and that diastereoisomers I and II can be distinguished in the ¹H and

¹³C NMR spectra. The high reactivity of the parent $(\eta^6\text{-}C_{10}H_8)_2M$ complexes toward ligand displacement by CO and RNC was also observed for the polymer-attached and model complexes (Scheme III). The pattern of reactivity,
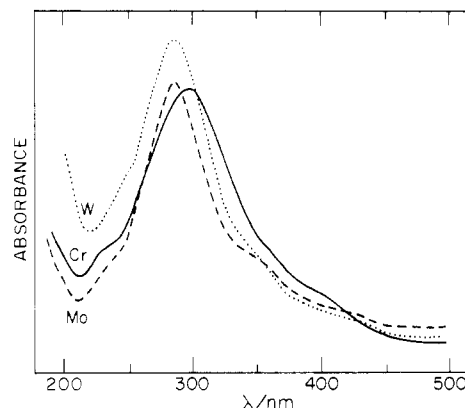
however, appears to be determined by the presence of the polymer backbone. Ti atom attack at oxygen was avoided by using a polymer in which the naphthalene function was attached directly to the silicon atom in the backbone of the siloxane.

Isocyano-Functionalized Polymers

Francis and co-workers extended the metal atom–polymer chemistry to include isocyano-functionalized polysiloxanes.[45] This is significant because the new polymers provide the added versatility to stabilize a range of mononuclear and cluster metal microstructures. The macromolecule 2, first reported by them, is shown in Scheme IV. This work has been extended to linear copolymers 5 and homopolymers 6, also illustrated in Scheme IV.

The isonitrile polymers have been reacted with a number of elements and the products probed on a microscopic scale by infrared and UV–visible spectroscopies. Reaction of Cr, Mo, W, or V vapors with the isocyano-functionalized polysiloxane (denoted 2) gave the polymer-encapsulated $M(CNR)_6$ complexes. Small-molecule analogues were used to argue the vibrational (Table I) and optical (Figure 1) assignments in the polymer-based complexes. For example, the free polymer (CN) stretching mode at 2145 cm⁻¹ is partially replaced by a broad 1950-cm⁻¹ band after reaction between the isocyano group and chromium. Cooling the sample to 77 K resolves the broad band into a group of absorptions positioned at 2010, 1950, and 1975 cm⁻¹. This effect was attributed to a distortion of the idealized O_h symmetry of a $Cr(CNR)_6$ complex by the polymer microenvironment. Air exposure caused irreversible loss

(44) Bush, B. F.; Lynch, V. M.; Lagowski, J. J. *Organometallics* **1987**, *6*, 1267.

(45) Francis, C. G.; Klein, D.; Morand, P. D. *J. Chem. Soc., Chem. Commun.* **1985**, 1142. Francis, C. G.; Morand, P. D.; Radford, P. P. *J. Chem. Soc., Chem. Commun.* **1986**, 211.

Scheme IV
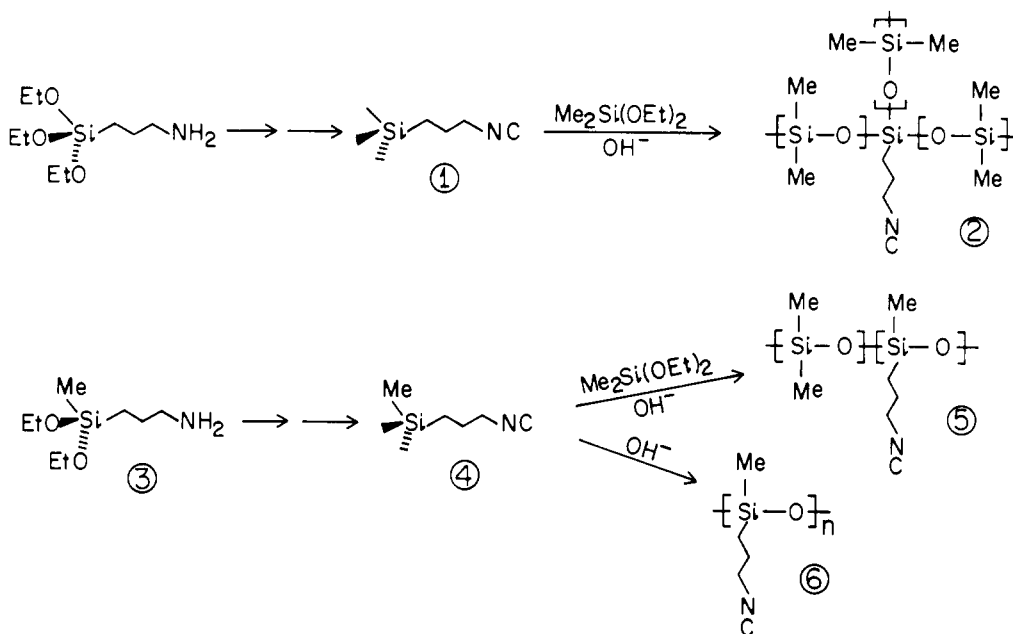
of the intensity of these infrared signatures, and the appearance of a new band at 2085 cm^{-1}, ascribed to the macromolecule-bound [Cr(CNR)$_6$]$^+$ cation. This finding agrees with previous observations for chromium complexes of small-molecule isonitrile ligands. Reactions with Mo and W gave similar results. The electronic spectra of these M(CNR)$_6$ complexes are also in line with the optical properties of the small-molecule counterparts, as well as with accepted assignments of the respective hexacarbonyl complexes. Thus optical excitations in the 200–300-nm region are associated with MLCT transitions, whereas those at lower energies in the range 350–450 nm are ascribed to ligand-field transitions. The reactivity of atomic vanadium toward the isocyano-substituted polysiloxane is rather interesting, especially as binary isonitrile complexes of V are currently unknown. The infrared spectrum of the product shows (CN) stretching modes at 2112 and 2056 cm^{-1}, which indicate terminal isonitrile ligands. The UV–visible spectrum consists of two broad overlapping bands at 322 and 350 nm, with shoulders at 242/265 and 450/560 nm. By comparison with the optical spectroscopy of V(CO)$_6$, an assignment to the V(CNR)$_6$ molecule was suggested. The spectral broadening, compared with the Cr analogues, was attributed to a dynamic Jahn–Teller distortion of the ideal O_h symmetry.

In the case of Fe and Ni atoms, new polymer-encapsulated mononuclear metal isonitrile complexes, M(CNR)$_m$ (where M = Fe, m = 5; M = Ni, m = 4), were obtained. Co atoms yielded the Co$_2$(CNR)$_8$ species directly. The molecular weight of these polymers could be varied systematically. In fact, for Fe atom reactions, the product ratio of Fe(CNR)$_5$ to Fe$_2$(CNR)$_9$ depended on the molecular weight of the polymer (control of bimolecular encounters between metal centers). Thus Fe(CNR)$_5$ alone forms in high molecular weight polymers, whereas Fe-(CNR)$_5$/Fe$_2$(CNR)$_9$ mixtures form in low molecular weight polymers. The corresponding Pd atom reaction produced the Pd$_3$(CNR)$_6$ polymer-supported trinuclear metal isonitrile complex. This compound was characterized by comparison with a small-molecule analogue, Pd$_3$[hexakis(cyclohexylisonitrile)].

The iron system is especially intriguing, as the infrared and UV–visible spectra of the polymer-bound (yellow) mononuclear Fe species convert, on UV photolysis, to
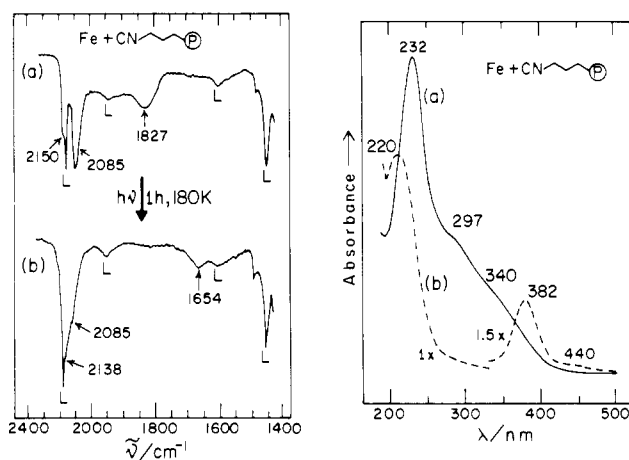
Figure 2. Left: infrared spectra obtained (a) following deposition of Fe atoms into a thin film of **2** at 200 K and (b) after photolysis of the matrix at 180 K (L: bands associated with the polymer). Right: optical spectra obtained (a) after deposition of Fe atoms into a thin film of **2** at 200 K and (b) after photolysis of the matrix at 180 K.[45]

spectra characteristic of the binuclear (orange) species (eq 6). The proposed transformation is depicted in Figure 2.

$$Fe(CNR)_5 \rightarrow Fe_2(CNR)_9 \qquad (6)$$

Again these deductions were founded on reasonable comparisons with small-molecule, isonitrile model complexes, FeL$_5$ and Fe$_2$L$_9$, (where L = CO, CNR). It is thought that encounters between metal centers in this system are allowed because of the higher chain mobility associated with the lower molecular weight of the polysiloxane chosen for this particular study.

Finally, we observe that certain organometallic polymers are also photosensitive. Interesting is the finding that the iron centers, Fe(CNR)$_5$, can be photochemically crosslinked in a process that involves the conversion of FeL$_5$ to Fe$_2$L$_9$.

The successful development of a photoelectrolysis device by Müller-Westerhoff and Nazzal[46] gives strong motivation

(46) Müller-Westerhoff, U. T.; Nazal, A. I. *J. Am. Chem. Soc.* **1984,** *106,* 5381.

to pursue the chemistry of (polymer-supported) bimetallic complexes. Similarly attractive is the use of polymer-bound bimetallic complexes as surface reactants on semiconductor electrodes. Thus it is significant that in the presence of an electron-transfer agent such as ferrocene, the solution-phase or surface-confined Cr and Ni atom isonitrile-functionalized polysiloxanes can be electrochemically oxidized.[47] The cyclic voltammetric responses are consistent with first the electrochemical generation of $Fe(Cp)_2^+$, followed by "chemical" reduction by the metal centers confined in the polymer. In essence, the transfer of electrons from the polymer to the electrode is mediated by the ferrocene acting as an "electron relay". However, for neither the Cr nor the Ni polymer-bound complexes was it possible to achieve direct electrochemical oxidation/reduction at a Pt electrode. It is likely that the lack of electrochemical activity for these elements originates in ohmic resistances across the electrode–polymer interface due to the absence of mobile ionic carriers within the polymer. Support for this reasoning comes from the observation that a model dicationic chromium compound is in fact electroactive. Air oxidation of films of the Cr and Ni isonitrile-functionalized polysiloxanes yield the mono- and dication polymer-bound metal complexes, respectively. Chemical and electrochemical measurements indicate that Ni(0) and Ni(II) species generated in the same polymer matrix ([P]) can react to give the dimeric species [Ni$_2$-(CN–[P])$_8$]$^{2+}$, in a manner presumed to be similar to that in the known solution-phase conproportionation of Ni(0) and Ni(II) complexes of CH_3NC. Conproportionation affords the dimer complex [Ni$_2$(CNMe)$_8$]$^{2+}$. Identification of the dimeric polymer-bound analogue was based on similarities between the infrared and UV–visible spectra of unattached dimer species in solution.

The microscale MVS experiments on the Co and Ni systems have been scaled up in a rotary reactor. The low-viscosity liquid poly(dimethylsiloxane) solvent was used in preparations that were conducted at 270 K. The resulting highly colored, viscous oils gave infrared and UV–visible spectra in good agreement with the corresponding microscale studies. The ^{1}H NMR spectra confirmed that attack by metal atoms at oxygen in the polymer backbone had not occurred.

From this work it is apparent that a broad family of novel transition-metal-containing polymers originates in the metal atom chemistry of isocyano-functionalized polysiloxanes. Isocyano groups attached to the polymer backbone are capable of providing a definable microenvironment for stabilizing mono-, bi-, and trinuclear metal sites.

Cyclopentadiene-Functionalized Polymers

Polymer-bound cyclopentadiene (Cp) is one of the ligands most commonly used for attaching organometallic complexes to polymers. These compounds have been used as hybrid-phase catalysts. As active components in the paint and coatings industries,[48] the ferrocene derivatives are used as stabilizers against photochemical degradation. The ligand yields a wide range of transition-metal compounds having robust metal–cyclopentadienyl bonds, combined with highly reactive metal centers. In addition

(47) Francis, C. G.; Lipero, S.; Morand, P. D.; Morton, P. R.; Nash, J.; Radford, P. P., preprint of paper in press.

(48) *Organometallic Polymers*; Carraher, C. E., Jr., Sheats, J. E., Pittman, C. U., Eds.; Academic Press: New York, 1978. Pittman, C. U. In *Catalysis by Polymer Supported Transition Metal Complexes*; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980. *Metal-Containing Polymeric Systems*, Sheats, J. E., Carraher, C. E., Jr., Pittman, C. U., Eds.; Plenum: New York, 1985, and references cited therein.

Scheme V
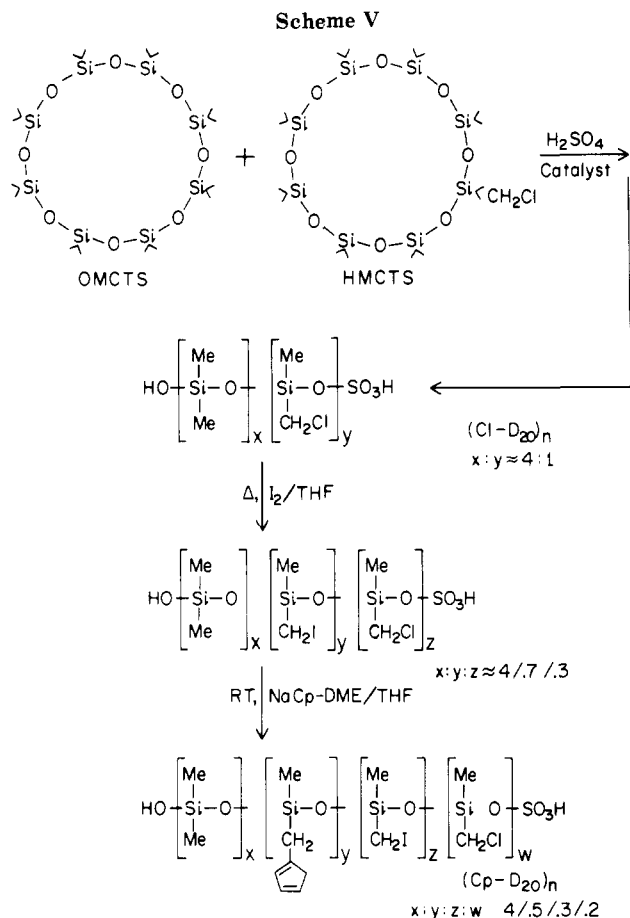
the ferrocene–ferricenium redox couple offers the opportunity to fabricate mixed-valence ferrocene polymers, which have been found to exhibit semiconductivity. The attachment of the ferricenium cation to biocompatible polymers reflects discoveries showing that certain ferricenium salts exhibit cancerostatic properties against Ehrlich ascites murine tumor.[49]

Previous work in this area may be approximately categorized as follows: (a) polymerization of a cyclopentadienyl–organometallic monomer in which the metal complex either forms an integral part of the polymer chain or functions as a pendant species; (b) derivatization of a commercial organic polymer or polymerizable monomer with cyclopentadiene, followed by its conversion to a polymer-bound organometallic complex; (c) modification of commercial rubbers and plastics with cyclopentadiene groups, with interest mainly in generating thermally reversible cross-linked polymer networks.

The feasibility of directly coordinating metal atoms of the Cp groups of a Cp-functionalized polysiloxane has been investigated by Ozin and Nazar.[17,50] They described the synthesis of Cp–siloxane polymers with a variable degree of Cp substitution, either containing the cyclopentadiene ligand attached to the silicon via a methylene linkage or containing the Cp group attached directly to the silicon atom. In the latter class of polymer, a degree of freedom with respect to variation of viscosity and steric hindrance on the polymer backbone was introduced by attaching different alkyl substituents on the silicon chain.

The two methods used to prepare the cyclopentadiene-functionalized siloxane polymers are outlined in
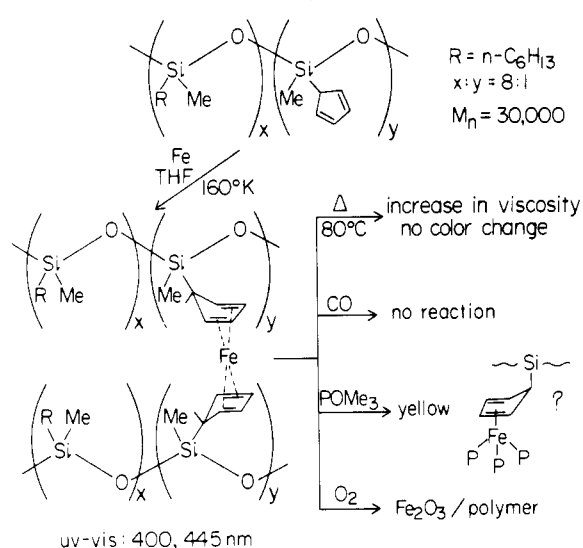
(49) Neuse, E. W. In *Metal-Containing Polymeric Systems*; Sheats, J. E., Carraher, C. E., Jr., Pittman, C. U., Eds.; Plenum: New York, 1985.

(50) Ozin, G. A.; Nazar, L. F., manuscript in preparation. Nazar, L. F. Ph.D. Thesis, University of Toronto, 1987.
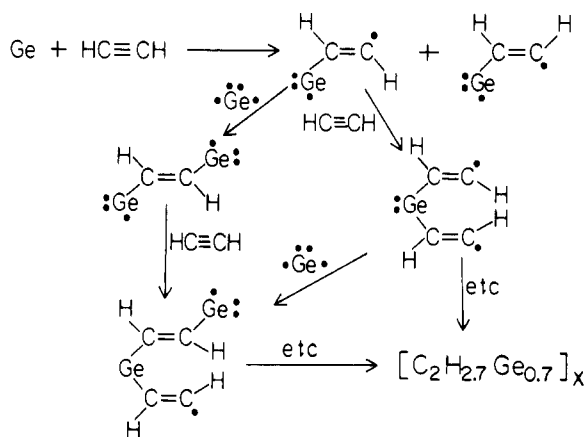
Scheme VI
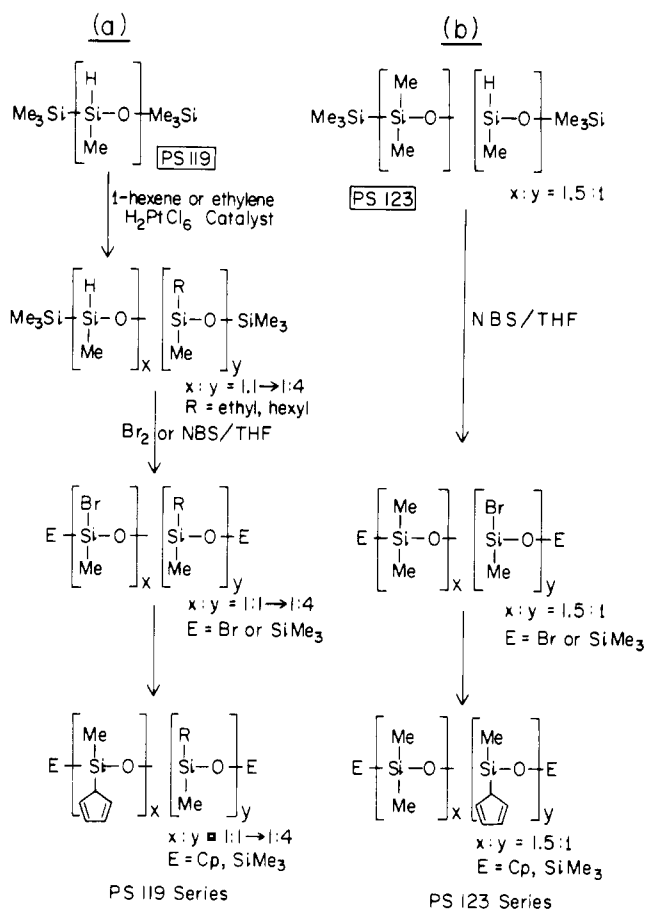
Scheme VII

Scheme VIII

Schemes V and VI. In the design of these polymers, specifically for examining their reactions with metal atoms, two main objectives were established: (i) achieving a compromise on the degree of Cp substitution, such that a satisfactory level of metal bonding could be obtained, while minimizing Diels–Alder condensation of Cp sites; (ii) establishing acceptable molecular weight, viscosity, vapor pressure, chain mobility, and solubility characteristics, to facilitate manipulation of the polymer in a MVS rotary-reactor experiment.

Cp-functionalized polysiloxanes were obtained with Cp substitution levels controllable in the range 10–50%. The molecular weight distributions were quite narrow, and fractions could be obtained in the ranges 4000, 25 000, 50 000, and 110 000. Diels–Alder cross-linking was controlled to times ranging from 2 to 15 h, depending on the Cp loading and the temperature.

The reactivity of these Cp-functionalized polysiloxanes toward Fe, Co, and Ni atoms was demonstrated.[17,50] The polymer-bound iron species was most thoroughly investigated. Iron atom depositions into the polymer were typically conducted in a 50% solution of THF. A summary of the iron atom reaction with one of these polymers is sketched in Scheme VII. These reactions yielded *green* polymers that are stable at room temperature and contain the 16-electron bis(cyclopentadiene)iron(0) moiety appended to the polymer backbone. A model 16-electron *green* monomer, bis((trimethylsilyl)cyclopentadiene)-iron(0), exists that is stable up to about 243 K. It transforms in the presence or absence of O_2, to the corresponding 18-electron *orange* ferrocene derivative. Conversely, reaction of the polymer-bound complex with O_2 yields polymer-entrapped iron oxide rather than a polymer-anchored ferrocene derivative. These differences in

reactivity are thought to be due to kinetic constraints originating in steric effects imposed by the polymer.

MVS of Integral Metal–Acetylene Polymers

Polyacetylenes, in the pure and/or suitably doped state, display interesting electronic transport properties. On this basis Klabunde and Zoellner[51] anticipated that metal atom reactions with acetylene could lead to polyacetylene compositions in which the metal, in an atomic or cluster form, would be incorporated into the polymer. In particular, they set out to determine whether Ge and Sn vapors would polymerize acetylene and simultaneously function as dopants.

Both Ge and Sn atoms react with C_2H_2 at 77 K producing acetylene–metal copolymers having a reproducible stoichiometry, i.e., $(C_2H_{2.7}Ge_{0.72})_x$ and $(C_2H_{2.6}Sn_{0.70})_x$. The metal appears to be incorporated in the M(II) and M(IV) oxidation states. Dopant amounts of 0.36 and 0.35 in Ge or Sn are comparable to those achieved with Li(0.30) and Na(0.21–0.28),[52] but the main-group composites are insulators.

Of the metals V, Cr, Mn, Fe, Co, Ni, Pb, Ge, and Sn, only the latter two yielded the polymeric products. The ^3P electronic ground state of Ge and Sn atoms was thought to be at the origin of this uniqueness, possibly as indicated

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(52) Chung, T.-C.; Feldblum, A.; Heeger, A. J.; MacDiarmid, A. G. *J. Chem. Phys.* 1981, *74*, 5504.
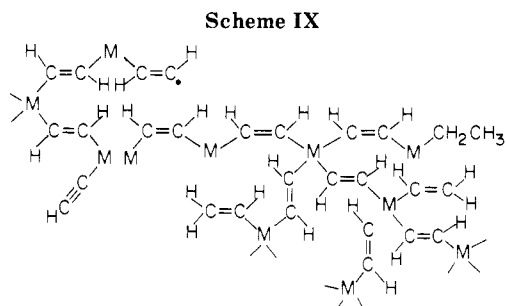
Scheme IX

in Scheme VIII. The compounds $[C_2H_{2.7}Ge_{0.72}]_x$ and $[C_2H_{2.6}Sn_{0.7}]_x$ formed in this way are weakly paramagnetic with about one unpaired electron for every 2×10^4 and 3.5×10^6 carbon atoms, respectively. They oxidize irreversibly in O_2 with loss of paramagnetism and formation of metal oxides. In the case of tin, SnO_2 was identified by Mössbauer spectroscopy, which also established, before exposure to O_2, the presence of Sn(II) and Sn(IV) species, but no sign of α- or β-Sn. On assembling the data of this study, Klabunde and Zoellner[51] concluded that the best average preliminary structure for these polymers may be along the lines depicted in Scheme IX. This is intended to illustrate a high polymer, cross-linked with occasional defects, resulting in trapped radicals and containing C_2H, C_2H_3, and C_2H_5 units.

The discovery that Ge and Sn atoms can simultaneously act as polymerization initiators and polymer dopants with acetylene is both timely and technologically significant as there currently exists considerable interest in organometal polymers and polymer-supported metal clusters for a wide range of applications in materials and catalytic science. For example, new organotin polymers prepared by this technique might be examined for use as oxygen-reactive ion-etch barriers for making resists.

Sodium Atom Induced Anionic Polymerization

Anionic polymerization is initiated by both homogeneous and heterogeneous catalysts. Initiation by alkali-metal atoms[53] contrasts with previous work utilizing metal particles and films, where the kinetics of initiation are complicated by solvated species and adsorption–desorption processes. In the MVS literature there have been no reports of high yield, high molecular weight homopolymer, copolymer, or block copolymer synthesis due to initiation by metal atoms.[9] Past techniques have relied on the 77 K cocondensation of metal atoms and monomer to form solid films on the walls of stationary reactors. The latter technique has all the disadvantages associated with condensed-phase inhomogeneities, restricted mass transport, and complicated meltdown chemistry. Heffner et al. circumvented these problems by using sodium atoms to initiate the anionic polymerization of styrene (Sty), α-methylstyrene, and methyl methacrylate (MMA) in liquid THF solution at 150 K in a spinning glass cryostat.[53] Molecular weights varied from 10^5 to greater than 10^6 depending on reaction conditions. The development of this technique is important in several ways. The use of the reactor provides an easy method for batch, anionic polymerization. Styrene, for example, polymerizes essentially instantaneously on exposure to the sodium vapor. The technique can be straightforwardly extended to make block copolymers. (As a convenient source of living polystyrene, MMA–Sty–MMA triblocks are easily made under the

high-purity conditions of the experiment.) These possess technologically useful properties due to their unique molecular architecture.[54] More generally, the living polymers can be used in active-center (anion to free radical, anion to cation) transformations. These studies are part of a wider effort to use metal atoms to prepare dispersely filled polymer composites. Such composites are of interest in the study of the modification of polymer properties and of the appearance of new properties due to the chemical or physical inclusion of single or aggregated metal centers. We turn to these kinds of materials next.

Metal Atom Reactions in Reactive Polymers: Encapsulated Metal Oxide Colloids

Much has been written about the effects of confining systems that order or phase separate within regions whose characteristic length scales are comparable to various intrinsic scale distances.[23] Interesting effects are anticipated from phased arrays of minute objects. For example, a ferromagnetically ordered state appears for the magnetic moment of dipoles that are distributed in a spatially periodic manner.[55] Ordered arrangements of magnetic dispersants smaller than the wavelength of light can produce magnetooptic effects that depend on the patterning of the magnetic component.[56] When the spatial distribution of the magnetic submaterial is symmetric about the magnetization direction, the entire structure behaves as a uniaxial "crystal" magnetized along the axis of symmetry. For unsymmetrical distributions and structures, elliptically polarized normal modes of light propagate in the direction of magnetization.

Naturally occurring organized states are stimulating paradigms for basing designs of new ordered systems in artificial structures. Certain organic block copolymers can be induced to phase separate into sub-100-Å spheres or lamellae that are periodic over limited distances.[57] To exploit the capacity of these kinds of systems to self-organize, Andrews et al.[12] showed that a phase-separable organic polymer offering two chemically distinct sites of potential reactivity can be converted selectively to a carrier of metal atoms and that the latent reactivity of the metal atom derivative allows it to be modified chemically at low temperature and clustered within the host. Their approach involves the site-specific capture of metal atoms deposited in a vacuum to give isolated, high-energy mononuclear organometallic centers within a polymer film. These centers can be converted at ambient or subambient temperatures (i.e., below the polymer glass transition temperature) to, for example, metal oxide microclusters. A prototypical system involving chromium atoms and their conversion to corundum-type oxide microclusters in arene-functionalized polymer films has been studied.

Atomic chromium was chosen for initial study because of the ease with which it sublimes, as compared with the more vigorous evaporation conditions required to generate atomic Ti, V, Mo, Nb, Ta, or W. This made feasibility studies easier to conduct. Chemical selectivity is ensured because of the facility with which the metal atom yields the sandwich complex. The resulting chromium/polymer system in this instance should be viewed as a dispersion of atoms interacting strongly with the support (phenyl
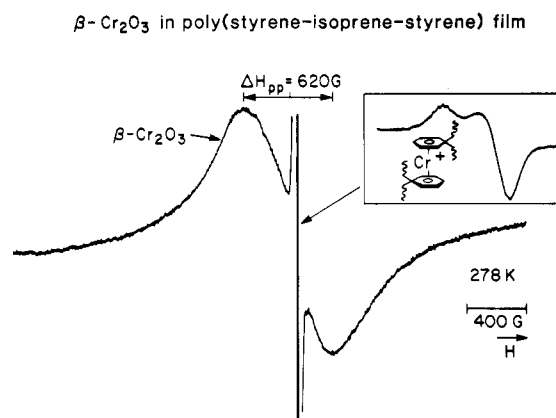
(53) Heffner, S. A.; Andrews, M. P.; Galvin, M. E. *Polym. Commun.* **1988**, *29*, 335.

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β- Cr₂O₃ in poly(styrene-isoprene-styrene) film

Figure 3. Electron paramagnetic resonance signal from minute β-Cr₂O₃ particles in a poly(styrene–isoprene–styrene) film. The spectrum was recorded for the sample maintained 30 °C below the Neel transition temperature of bulk chromia.

substituents) but poised for subsequent conversion in the macromolecular host. The polymer thus carries the latent reactivity of the atom in a high-energy state (with regard to oxidation). Chromium also carries useful spectroscopic information about its location in the macromolecular host. The oxidized, polymer-bound Ph_2Cr^+ complex is paramagnetic and electron paramagnetic resonance (EPR) active at room temperature and below. Cr^+ therefore spin-labels the polymer. Consequently, information can be acquired concerning the degree of dispersion of the chromium atoms in the polymer, their state of aggregation, and local polymer chain dynamics. Last, oxidation under mild conditions (room temperature, 1 atm of air) converts the chromium to clusters of Cr_2O_3 in solid films of the polymer. Bulk Cr_2O_3 is antiferromagnetic below its Neel temperature (308 K); however, minute clusters of the material are paramagnetic and can therefore be detected by EPR spectroscopy.

Thus Cr was deposited into 150 K liquid tetrahydrofuran solutions of a poly(styrene–isoprene–styrene) triblock, spun in vacuo as a thin liquid film on the surface of a rotating glass cryostat. Evidence from EPR spectroscopy showed that the resulting polymer-anchored (inter/intra-chain) bis(arene)Cr sandwich complex is locally mobile in the macroscopically rigid film at room temperature. The Cr atom is discharged from the rings by subsequent reaction with oxygen diffused into the film. Although α-Cr_2O_3 is not EPR active below 308 K, an intense signal was observed at 278 K (Figure 3), which remained largely unchanged when the sample was cooled to 77 K. Cr_2O_3 microclusters are indicated, and these were confirmed to be ≈40 Å by in situ measurements of the oxidation and aggregation process. Confirmation that the microclusters are confined to the phase-separated regions of the polymer is still forthcoming, but evidence for the spatial confinement of the organometallic precursor is definitive. Future efforts might focus on the synthesis of polymers in which the convertible unit is not simultaneously a cross-link and on integrating magnetic and optical processes within the organized submaterial with interfacial and spatially localized chemical transformations.

No experiments have been undertaken yet, but MVS might also be used to produce ferrite/polymer composites. The critical parameter in the design of such composites is the inclusion material. Improvements in the dispersion patterns of ferrite materials whose resonance phenomena highly enhance microwave attenuation are strongly encouraged. MVS, with its ability to provide rapid screening of materials, intimate mixing of components, and access

to novel compositions in a manner that can sidestep the usual thermodynamic constraints, could meet or exceed some of these challenges.

By wrapping polymers around magnetic colloidal particles, new applications for MVS can be found in the biochemical and biomedical sciences. Recent work has shown that endocytic vesicles can be endowed with magnetism by using extremely fine (10–20 nm) ferrite particles coated with biological ligands.[58] The ligands are prepared by coating the particles with bovine serum albumin and then conjugating asialoglycopeptides. High-gradient magnetic separation efficiently captures endosomes and lysosomes containing the specific ligands. Elsewhere we note that monodisperse magnetic polymer particles are employed for immunoassay. These particles must be well-characterized with respect to size and composition. Moreover, the magnetic particle component in these materials must consist of species small enough to show little or no magnetic remanence after having been subjected to magnetic fields. Magnetic remanence otherwise reduces the ease of redispersion of the particles.[59] Particles showing superparamagnetism are clearly desired for this kind of undertaking, and MVS is well disposed to make them.

Metal Atom Reactions in Unreactive Polymers and Oligomers: Encapsulated Metal Colloids

The preparation of metal colloids in organic solutions and polymers can be considered to be a natural outcome of the ability to stabilize metal atoms or clusters in solvating media, as described in the preceding sections for oligomers and polymers. The scientific and technological gains from developing this kind of composite could be rewarding. Some commercially successful magnetic fluids are prepared by thermal and ultraviolet decomposition of metal carbonyls, metal salt reduction, electrolytic deposition, and aerosol methods.[60] The MVS method clearly offers a great deal of flexibility in preparing such materials.

Further importance in the development of ferrofluids is attached to the fact that composites containing both metallic magnetic and *non*magnetic particles show a pronounced magnetic dichroism in the 3-mm wavelength range.[61] Under certain conditions metallic chains of particles can form into grids that will strongly absorb microwave radiation when the chains are parallel to the plane of polarization of the incident radiation. The effect is large enough to be used in principle to develop devices such as polarizers, isolators, attenuators, and modulators in this wavelength range.

Although not explicitly concerned with microwave absorption, the work of Francis and Timms[62] should be regarded for future applications of MVS to magnetic fluid synthesis. They investigated the deposition of Cr, Fe, Co, and Ni atoms into a liquid poly(dimethylsiloxane) (Dow Corning 200). This polymer is the phenyl-free analogue of DC510 described earlier. These kinds of experiments involving unreactive polymers (devoid of ligating func-

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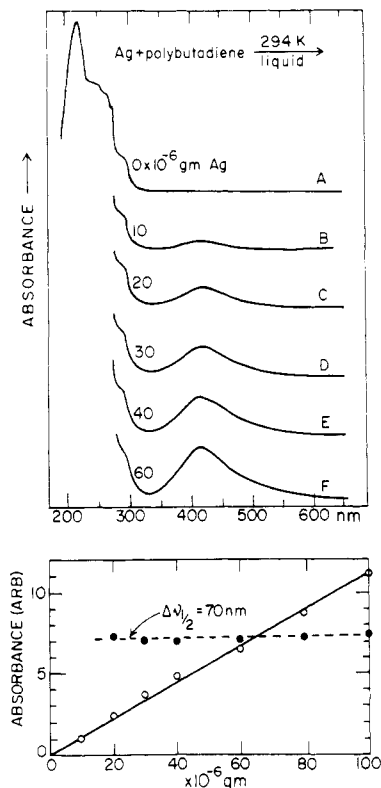
(61) Popplewell, J. P.; Davies, P.; Llewellyn, J. P. *J. Magn. Magn. Mater.* **1987**, *65*, 235. Birch, J. R.; Bentley, C. A.; Llewellyn, J. P. *Electron. Lett.* **1985**, 313.

(62) Francis, C. G. Ph.D. Thesis, University of Bristol, 1978.

tionalities) produce polymer-dispersed metal colloids without any evidence of metal–polymer insertion products. An extension of this approach involves the deposition of iron atoms into liquid poly(phenylmethyl-*co*-dimethyl-siloxane) in a rotary reactor to form polymer-attached bis(arene)iron(0). This compound decomposes at 243 K to give polymer-encapsulated colloidal iron. Air oxidation yields metal oxide agglomerates, possibly within the same polymer environment.[3] Andrews et al.[12] used a variant of this technique to make solid films of superparamagnetic Fe_3O_4 in polystyrene. Recently, the method attracted interest in Japan,[63] where there is an ongoing effort to make, understand, and apply ultrafine particles.[64] Finally, in contrast to Klabunde's[65] catalytically active, small-molecule solvated metal atom dispersed (SMAD) slurries, metal colloid/liquid poly(dimethylsiloxane) slurries are catalytically inactive.

Polymer composites of Pt or Pd produced by MVS can be used to develop polymer-based hydrogen getters. In this conception, ultrafinely dispersed metal in a block copolymer is used in a heterogeneously catalyzed hydrogenation of a reducible (olefin) portion of the polymer. The second component in the polymer block, not reducible, would provide the structural integrity necessary for film formation, pelletization, etc.

The modification of the optical properties of composites is another area that has seen application of MVS. Early work in this area showed that silver atoms deposited into a variety of fluids such as oligomeric olefins, polyolefins, and 2-methyltetrahydrofuran formed colloids.[2] Polymers are often used to stabilize aqueous colloidal suspensions of noble metals. The preparation and stabilization of organosols are somewhat more difficult.[66] The MVS method is particularly well suited for making organosols directly and at low temperatures.[67,68] Andrews and Ozin[67] found that when atomic silver is deposited at carefully controlled rates, in vacuo, into cooled, weakly interacting liquid supports (i.e., polyolefins, oligoolefins, vinyl and siloxane polymers, crown ethers, and low molecular weight ether solvents), silver particles develop with a size distribution, at a fixed temperature, that remains independent of silver loading as judged by optical absorption spectroscopy. Apparently, the rate at which Ag is deposited and diffuses in these media is commensurate with the relaxation time required for solvent monomer, oligomer, or polymer adsorption and/or conformational reorientation to form a protective barrier about a growing particle. The coating prevents the particle from growing beyond a critical dimension. With regard to the optical properties of the particle submaterial, the electron density profile and the breaking of translational symmetry at the particle surface have decisive effects on the linear optical properties of the composite. Optically this manifests itself in the *linear* growth of the surface plasmon absorption (Figure 4) with increasing metal concentration and in the *invariance* of the λ_{max} and bandwidth at half-height $\Delta\nu_{1/2}$. For example, Ag atoms deposited into liquid squalene at 260 K formed colloids on the order of 70 Å in diameter as determined from the optical absorption of the dipolar surface plasmon mode. The particles were stable at 260 K but agglomerated further at room temperature. Nev-

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Figure 4. Growth of the dipolar silver plasmon mode absorption resulting from the quantitative deposition of silver atoms into liquid poly(butadiene) at 294 K. The insert shows a graphical representation of the silver atom concentration dependence of the absorption at the peak maximum and bandwidth.

Scheme X
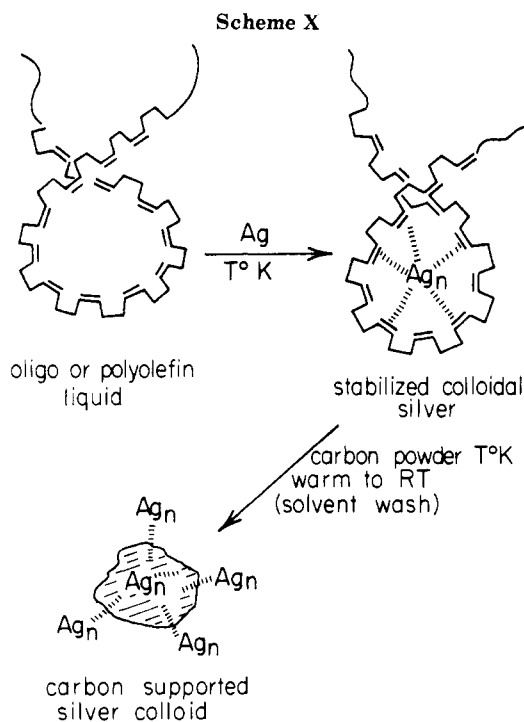
ertheless, colloidal particles in oligomers and polymers show greater stability toward thermally induced aggregation than do the easily desolvated species produced in low molecular weight liquid solvents such as ethers. The manner by which silver and palladium particles grow in these liquid media has been exploited to produce metal–carbon composites suitable for fuel cell electrodes.[67,68] To make these, the solvated metal atom solutions are contacted with various forms of pretreated carbons either

during the metal atom deposition step or subsequent to the formation of the metal particle/solvent mixture. In this way, desolvation of the metal site and deposition of metal atom aggregates on the surface and within the pores of the carbon ensue as depicted in Scheme X. Sub-20-Å, reasonably uniformly dispersed carbon supported metal aggregates have been prepared in this way. Control of both particle size and size distribution depends sensitively on the preparation conditions.

This approach is likely to generate interest in any application requiring ultrafinely divided supported metal particles. For example, $Ag_n°/C$ and $Pd_n°/C$ compositions produced in this way were fabricated into porous oxygen gas electrodes (backed onto porous nickel) for use in an alkaline H_2/O_2 fuel cell.[3,67,68] Both metals catalyzed the reduction of oxygen in concentrated KOH solution. Current densities of 200 and 105 mA cm^{-2} at 0.8 V were obtained for the Pd and Ag carbon electrodes, respectively. The electrodes showed substantial activity out to 1000 mA cm^{-2}.

Klabunde has found that colloidal gold solutions prepared by condensation of the metal with organic solvents give stable liquid suspensions at room temperature.[69] The Au/acetone system consisted of roughly spherical particles 100–300 Å in diameter. In some cases films are formed after stripping the solvent from Pd/acetone and Sn/acetone colloids.[70] The films are semiconducting, with transport properties similar to those of silicon. All of these metal colloids incorporate substantial amounts of organic fragments, making them less attractive as agents for making high-purity films. They are, however, interesting from the viewpoint that some are soluble in organic media.[71] For example, smaller gold particles (10–40 Å) are collected as a fraction soluble in acetone, when gold powders are isolated in perfluorotri-*n*-butylamine. Detailed optical properties of these particles, particularly with regard to the effect of the organic component, have been reported.[71] This discovery could be important to any process requiring polymer/metal composites because it offers the possibility of codispersing polymer and metal in the same organic solvent, thereby facilitating film formation via spin casting, etc. Similarly, living colloids might be dissolved in organic monomers, which are subsequently polymerized. Liebert et al.[72] appear to have been the first to publish results based on the idea of entraining a colloid in a polymer by polymerizing a monomer containing suspended (magnetic) colloidal particles. Use of the "living" colloids from MVS clearly broadens the scope of application of this technique.
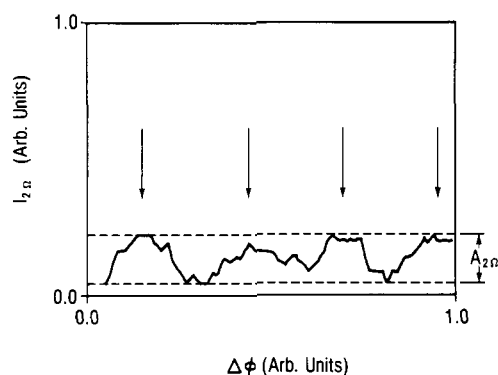
Solid films of polymers containing colloidal metals made by MVS can be cast from solution. The rigid environment fixes the particles in position and thus allows for leisurely spectroscopic examination of the material. Dielectric breakdown and nonlinear optical susceptibility are among the many phenomena in composite media in which nonlinearity plays an important role. In a nonlinear composite, unlike a linear one, the dielectric function (ϵ) depends on the applied electric field. It is now known that the cubic nonlinear dielectric susceptibility of an "effective medium" (metal spheres diluted in a dielectric host) is resonantly enhanced when the dielectric constant of the host and metal spheres obey the condition Re $[\epsilon_{sphere}(\omega)] = -2\epsilon_{host}$.

Figure 5. Electrooptic modulation amplitude as a function of phase difference between the two arms of the interferometer. The arrows show the positions where the modulation efficiency is expected to be a maximum, as determined from the phase-difference dependence of the interferometer without modulation.

This relation defines the dipolar surface plasmon mode in small metallic spheres. Here, both the metal nonlinearity and the dielectric host nonlinearity near the metal inclusions dominate the material response. To date, experiments with metal colloids have been confined to aqueous solutions and a precipitate glass.[73] Further study of the phenomenon, with a view to evaluating its potential in implementing some device ideas, would be helped by immobilizing the particles in a suitable host. Andrews and Kuzyk[74] showed that sub-100-Å microspheres of silver could be grown from silver atoms deposited into 145 K solutions of poly(methyl methacrylate) (PMMA) in THF. Solid films of the composite could be spun in thicknesses ranging from 1 to 1000 μm on conventional substrates. The measurement of the third-order susceptibility uses Mach–Zehnder interferometry, which requires high electric fields to modulate the refractive index of the sample. Since conventional methods for producing silver colloids by chemical reduction generate adventitious charged species, such procedures cannot be used to produce the composites. The intrinsically cleaner metal vapor methodology avoids this problem by giving liquid, silver organosols from which Ag/PMMA composites can be obtained directly. PMMA was selected because it is optically transparent in the region of interest in this experiment, it is commonly used to make optical devices, and it is a macroscopically rigid host suitable for immobilizing the silver particles.

Transmission electron microscopy of films containing 0.045 wt % silver revealed that the microspheres collect into colonies of 200–500 nonoverlapping spheres, some of which exhibit dark bands from twin dislocations and/or stacking faults. The colonies are separated over distances greater than 1000 Å. The mean particle size before processing between indiumtin oxide patterned plates is 79 Å with a standard deviation of 36 Å. After processing above the polymer glass transition temperature (T_g), both the average particle size and also the number density of particles increased. This suggests diffusion and growth of spheres smaller than 20 Å in diameter (not visible under the microscope) when the medium is annealed above T_g.

For the Mach–Zehnder experiment, the film thickness was $d = 6.8 \times 10^{-6}$ m and the light intensity at the detector at twice the modulating frequency ($\Omega = 4.0$ kHz) is shown as a function of phase difference in Figure 5 for a root mean square (rms) modulating voltage of $V_{rms} = 83.4$ V. The arrows show the phase difference where the modu-

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lating efficiencies are expected to be the greatest, as determined from the phase difference dependence of the light output from the interferometer with no modulation.

The measured value of the quadratic electrooptic coefficient of the composite is $s_{1133} = (2.0 \pm 0.5) \times 10^{-22}$ m^2/V^2. A similar measurement of pure PMMA shows that the coefficient is smaller than $s_{1133} = (4.2 \pm 0.5) \times 10^{-23}$ m^2/V^2. The laser wavelength of both measurements was at $\lambda = 633$ nm, located away from the absorption maximum at $\lambda = 435$ nm. Although the enhancement is expected to be much smaller here than for a resonant measurement, the third-order susceptibility of the composite at low levels of loading (0.045 wt % or a volume fraction of 4.5×10^{-4}) was at least 5 times larger than that of undoped PMMA.

The third-order susceptibility calculated from the quadratic electrooptic coefficient is $\chi^{(3)}_{1133} = 1.6 \times 10^{-14}$ esu. Using optical-phase conjugation techniques,[73] a third-order susceptibility, enhanced at the maximum of the plasmon absorption, was determined to be $\chi^{(3)}_{1133} = 2.4 \times 10^{-9}$ esu. The enhancement factor, as determined by the quotient of the phase conjugation measurement and the electrooptic measurement, is 8.5×10^5 when the difference in concentration between the two samples is taken into account. This compares favorably with the predicted enhancement factor of 3.6×10^6.[73] In other words, the third-order susceptibility of the metallic spheres is enhanced roughly 10^6-fold by exciting at the maximum absorption of the dipolar surface plasmon. It is currently thought that the nonlinear response is dominated by the electrons in the metal particles.[74] Composite media such as these may ultimately find use in developing and testing device ideas related to third-order processes important to optical information processing.[73]

Metal Atom Reactions with Hydrocarbon/Surfactant Fluids

An approach that utilizes MVS in conjunction with micelles to mediate reaction chemistry and determine particle dimensions has been described by Timms and co-workers.[75] Their idea is to "wrap" a surfactant layer about a magnetic particle. Like iron, cobalt combines with toluene to give a thermally unstable, formally zerovalent mononuclear bisarenemetal complex.[3,22,73,76] It seems to be possible to control the release of the cobalt atom from the bis(toluene)Co molecule to guide the subsequent nucleation of the atom in the surfactant medium. The method appears to yield ferrofluids with excellent magnetic properties. Preliminary MVS results communicated for Co/toluene/Manoxol OT describe black colloidal suspensions that could be pumped down to a sticky toluene-free mass. The material is reversibly soluble in toluene and in this sense probably has surfactant bound to the surface of the superparamagnetic particles. There is apparently no decomposition of the surfactant. Transmission electron microscopy studies revealed approximately spherical particles with a mean particle diameter of 50 ± 6 Å (cf. the organometallic route, which typically produces 70 ± 10 Å particles[77]). Extended X-ray absorption fine structure spectroscopy revealed cobalt–cobalt interatomic distances similar to those of bulk cobalt. A model for the
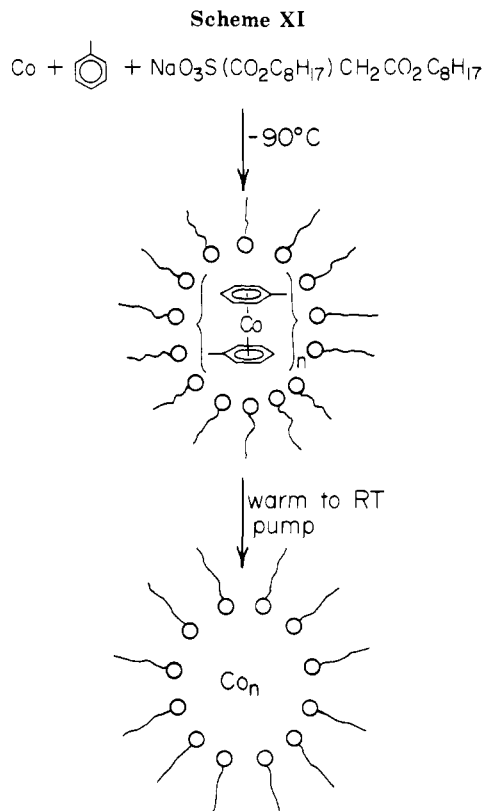
Scheme XI

production, aggregation, and stabilization of these metallic magnetic fluids is represented in Scheme XI.

Marcus and Andrews[78] have used similar procedures to obtain ≈30 Å Co spheres dispersed in a liquid-crystal surfactant, sodium bis(2-ethylhexyl)sulfosuccinate (AOT). Their studies are concerned with the outcome of placing perturbing objects inside an ordering material where the dimensions of the perturbation are comparable to some important length scale. It turns out that the individual cobalt particles are comparable in size to the organized structural component of the spontaneously formed hexagonal phase of pure AOT. This phase consists of cylindrical micelles about 20 Å apart. The cobalt particles tend to assemble into rods about 110 Å long by 30–40 Å wide, but there is no tendency for the rods to align with any columnar structure in the AOT. Optical microscopy and X-ray scattering show that the addition of only 2 vol % of Co particles supresses the hexagonal phase. At lower concentrations, segregation of particles to isotropic regions could be observed as the temperature of the composite was raised to the hexagonal/isotropic two-phase region. It was argued that the particles act as built-in defects which, when sufficient in numbers, "soften" the hexagonal phase enough to allow the proliferation of additional defects, resulting in a runaway softening and melting. Among other things this work may help determine the kinds of conditions required for making robust integrated chemical systems.

Conclusion and Perspective

Metal atoms deposited into oligomers and polymers can be entrained in the form of organometallic complexes, clusters, and colloids. In this manner new varieties of organometallic compounds and composite materials have been made. Applications of these new materials are anticipated in the areas of redox processes, bio separations, catalysis, magnetic and magnetooptic processes, and non-

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linear optics. The distinctively chemical perspective from which MVS has evolved places it in a rather unique position to prepare new "nanocrystalline" and "nanophase" composites[79] that are currently under examination in a

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number of laboratories. Future work would do well to link MVS as a specialized materials methodology to timely and well-conceived applications in these areas. Although more research is needed to develop the full scientific and technological potential of MVS in polymer science, the results of the research reported to date should continue to stimulate activity in this area.

Articles

High-Resolution Electron Microscopy and Image Simulation of TT-, T-, and H-Niobia and Model Silica-Supported Niobium Surface Oxides

J. G. Weissman,[†,§] E. I. Ko,[*,†] P. Wynblatt,[‡] and J. M. Howe[‡]

Department of Chemical Engineering and Department of Metallurgical Engineering and Materials Science, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

The behavior of silica-supported niobium surface oxides during heat treatment was examined by high-resolution transmission electron microscopy (HRTEM). Surface oxides, consisting of between 4 and 50 Å Nb_2O_5 reactively radio-frequency sputter deposited onto 800 Å SiO_2, were calcined at 773 and 873 K for up to 16 h and were so designed to approximate high-surface-area materials suitable for catalytic applications. Also examined was the stability of three known crystalline forms of niobia, TT-, T-, and H-Nb_2O_5. Lattice image simulations were necessary to unequivocally identify the various Nb_2O_5 phases observed. TT- and T-Nb_2O_5 were found to have a nearly identical structure; a structure for TT-Nb_2O_5 is proposed. Besides amorphous monolayers, two major types of crystalline Nb_2O_5 were found on the surface oxide samples: very small crystals corresponding to T-Nb_2O_5, which could not be unambiguously defined by HRTEM in terms of thickness or orientation, and relatively large crystals of H-Nb_2O_5. These findings are discussed in terms of literature results, and a new model for the phase-transition behavior of Nb_2O_5 is presented.

Introduction

One class of industrially important catalytic systems is that of surface oxides, in which one oxide is supported on the surface of a different high-surface-area oxide; their uses include oxidation of olefins and production of unsaturated hydrocarbons.[1,2] The surface oxide can be dispersed over the support in amorphous monolayer or multilayer coverages, or as distinct crystallites, or a combination of these types, depending on the strength of interfacial interaction between the support and the supported oxides and the loading of the surface oxide. There has been an increasing body of evidence (for example, ref 3–6) that points to the importance of such an interaction on the structural and chemical properties of these systems. Our program of studying the catalytic and physical properties of surface oxides has recently led to the preparation of thin films consisting of niobium surface oxides supported on silica (Nb_2O_5–SiO_2), characterized by surface analysis and conventional electron microscopy (TEM).[7,8] The films were prepared in such a way as to mimic their high-surface-area counterparts,[9] so as to obtain structural information on this system.

Our previous results showed that there are important differences between the thin-film and high-surface-area samples toward calcining. Three types of Nb_2O_5 were found to occur on the thin-film samples: I, niobia strongly held to the surface via direct niobium–oxygen–silicon bonds; II, niobia crystallizing under the influence of the surface; III, niobia not interacting with the surface. Types I and II were also found to occur on the high-surface-area samples. Reasons for the appearances of the different types of niobia on different samples are discussed elsewhere and depend on a combination of factors including surface hydroxyl concentration of the silica substrate and reactivity of the Nb_2O_5 precursor.[8,10]

Since the structure of a supported oxide, in this case niobia, is important in understanding its reactivity as well

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*To whom correspondence should be sent.
[†] Department of Chemical Engineering.
[‡] Department of Metallurgical Engineering and Materials Science.
[§] Present address: Texaco, Inc., P.O. Box 509, Beacon, NY 12508.

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