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Metal Vapor Synthesis of Organometal Polymers and Polymer-Supported Metal Clusters

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ABSTRACT

Metal vapor chemistry has matured from being merely a curiosity and is now established as a viable synthetic technique. Recently the method has been applied to the formation of organometallic polymers and polymer-supported metal clusters. The purpose of this chapter is to provide a short review of the initial studies in the field. The synthesis of organometallic polymers is described via either formation of the organometallic polymer precursor or the reaction of metal vapor with a preformed polymer and the two techniques are compared with respect to the chemical and physical properties of the products. The generation of polymer-stabilized small metal clusters at ambient temperatures, by the deposition of a metal vapor into fluid polymer, thin films, is then discussed with particular reference to the combination of matrix-scale and macrosynthetic metal vapor synthesis. Some thoughts regarding the mode of stabilization of metal clusters are also presented. Finally, a brief description of the formation, by evaporation techniques, of metal particle-polymer interactions is included to indicate other types of experiment which may be used.

INTRODUCTION

Although the two fields of cryochemistry and organometallic polymer chemistry have been studied widely [1,2], only recently has some attempt been made to apply metal vapor synthesis to the formation of organometallic polymers and polymer-supported cluster species.

Two basic approaches to the functionalization of polymers by means of metal-containing species have been used:

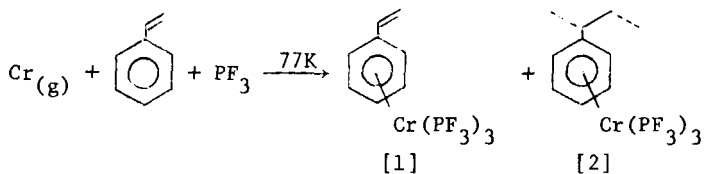
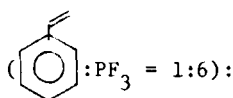
- 1) formation via interaction of a monomer with metal vapor, followed by polymerization of the organometallic polymer precursor, and
- 2) formation by the interaction of a polymer with metal vapor.

In addition, several workers have employed polymers as supports upon which to deposit metal vapors in order to study metal clusters and clustering processes.

We have divided this chapter into three sections corresponding to these methodologies, but we have also subdivided the second topic in order to distinguish between organometallic polymers and polymer-supported metal clusters.

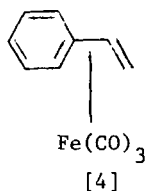
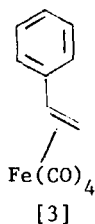
FORMATION OF METAL-CONTAINING POLYMERS
VIA INTERACTION OF A MONOMER WITH METAL VAPOR

The use of metal vapor synthesis to produce organometallic polymers can be considered really to have begun with the work of Middleton [3]. He observed an involatile, cream-colored material as a product in the cocondensation of chromium vapor with styrene and trifluorophosphine. I.r. spectra, supported by ^{19}F n.m.r. spectra, showed that the product consists of a mixture of [1] and [2]. A direct synthesis of bis(styrene)chromium was found to be unsuccessful, the only product being a black, waxy material, the



i.r. spectrum of which resembles that of polystyrene.

Subsequently, Blackborow reported the cocondensation of iron with styrene at 77K [4]. The only product is polystyrene. However, on warming the condensate from 77K in an atmosphere of CO, compounds [3] and [4], as well as iron pentacarbonyl, are formed:



Similarly, cocondensation of chromium with styrene produces polystyrene [5], but there is intractable material present in which chromium is bound to polystyrene. This was identified by its mass spectrum which contained peaks due to $(\text{C}_8\text{H}_8)_n\text{H}_m\text{Cr}$, where $n = 2$, $m = 0$ and $n = 3-5$, $m = 4$. Warming the cocondensate from 77K in an atmosphere of CO or PF₃ leads to the formation of small amounts of $(\eta^6\text{-C}_6\text{H}_5\text{CH=CH}_2)\text{CrL}_3$ (where $L = \text{CO}$ or PF_3), plus a non-crystallizable oil, identified by its ¹H n.m.r., i.r. and mass spectra as an analog of [2]. From its oily nature and low molecular weight (M.Wt. = 860 in benzene) it is obvious that the polymerization has occurred only to a limited extent.

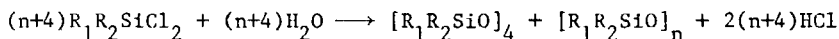
Cocondensation of nickel with styrene in a toluene matrix at 77K [5] yields red-brown crystals which appear to be tris(styrene)-

nickel, in which nickel is presumably coordinated to the side chain of each styrene molecule. The compound is thermally unstable, decomposing above 253K. The product of decomposition must be the nickel-polystyrene adduct obtained by Klabunde and coworkers [6] from the nickel-styrene cocondensation. This was reported to be an air-stable, black solid which is soluble in toluene and acts as a selective, homogeneous hydrogenation catalyst. Analogous materials were obtained from the reaction of nickel vapor with tetrafluoroethylene.

Lagowski [7] has shown that nickel atoms react with propyne and pent-2-yne at 77K to yield various organic oligomers as well as a black, nickel-containing species which independently oligomerizes alkynes to form arene and cyclooctatetraene derivatives. Interestingly, iron atoms were found to react with pent-2-yne to yield a symmetric tetramer as the sole hydrocarbon product.

In the previous reactions, the aim of producing an organometallic polymer precursor was defeated by the facile polymerization of the alkene or alkyne under the conditions of the metal vapor process. Some other approaches have been taken in an effort to produce a more controlled polymerization process.

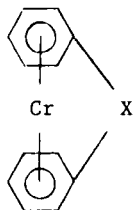
Hydrolysis of dichlorosilanes constitutes a major route to organopolysiloxanes, via an initial reaction of the type:



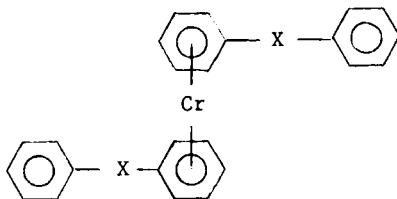
An alternative mode of formation is via rearrangement of the Si-O bonds in some alkoxy-silanes [8]. With this in mind, reaction of chromium vapor with $PhMeSiCl_2$ or $PhSi(OC_2H_5)_3$ at 140K was performed, using methylcyclohexane as a diluent in a rotary solution reactor [10] to give the corresponding bis(η^6 -arene)chromium complexes. However, in neither case does the complexed silane subsequently give the desired polymer.

A different route to organometallic polymers may occur where the formation of the organometallic unit R_1-M-R_2 , during the metal

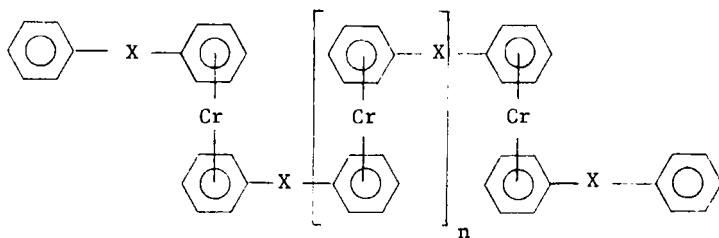
vapor reaction, constitutes a chain propagation step. Examples of this process are the cocondensation of chromium vapor with 1,4-diphenylbutane [11] and the solution reaction of chromium or vanadium vapor with the fluid 1,1,3,3-tetraphenyl-1,2,2,3-tetramethyltrisiloxane [10]. As well as the corresponding cyclophanes [5]



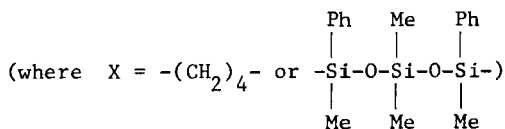
[5]



[6]



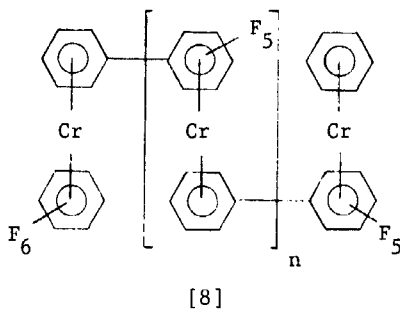
[7]



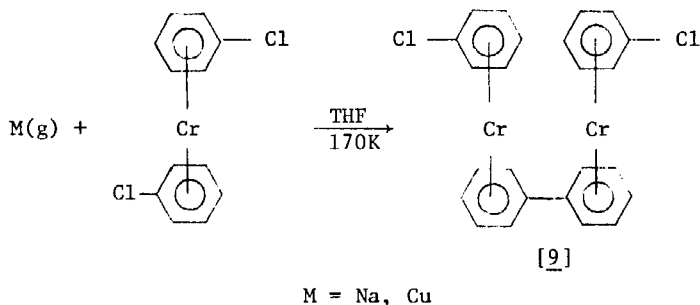
and simple bis(arene)metal complexes [6], ladder polymers [7] may be obtained, although the value of n is unknown.

McGlinchey [12] has also shown that $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\eta^6\text{-C}_6\text{F}_6)$, prepared by the cocondensation of chromium vapor with a mixture of C_6H_6 and C_6F_6 , reacts with Me_3SnLi to give oligomers [8] in which a link of the type $\text{C}_6\text{F}_5\text{-C}_6\text{H}_5$ is formed.

The ability of sodium or copper atoms to abstract halogen



from coordinated aryl halides enables organometallic units to be coupled, as in the following reaction reported by Timms [13]:



The interest in this latter type of system presumably stems from the electro-conducting properties of some organometallic polymers such as poly(ferrocenylene) [14].

REACTIONS OF METAL VAPORS WITH POLYMERS

The development of the rotary solution reactor by Timms [15] played an important part in facilitating the use of polymers as ligands in metal vapor synthesis (Figure 1A). The fact that a polymeric ligand cannot be volatilized into the reactor under co-condensation conditions means that it is difficult to obtain an

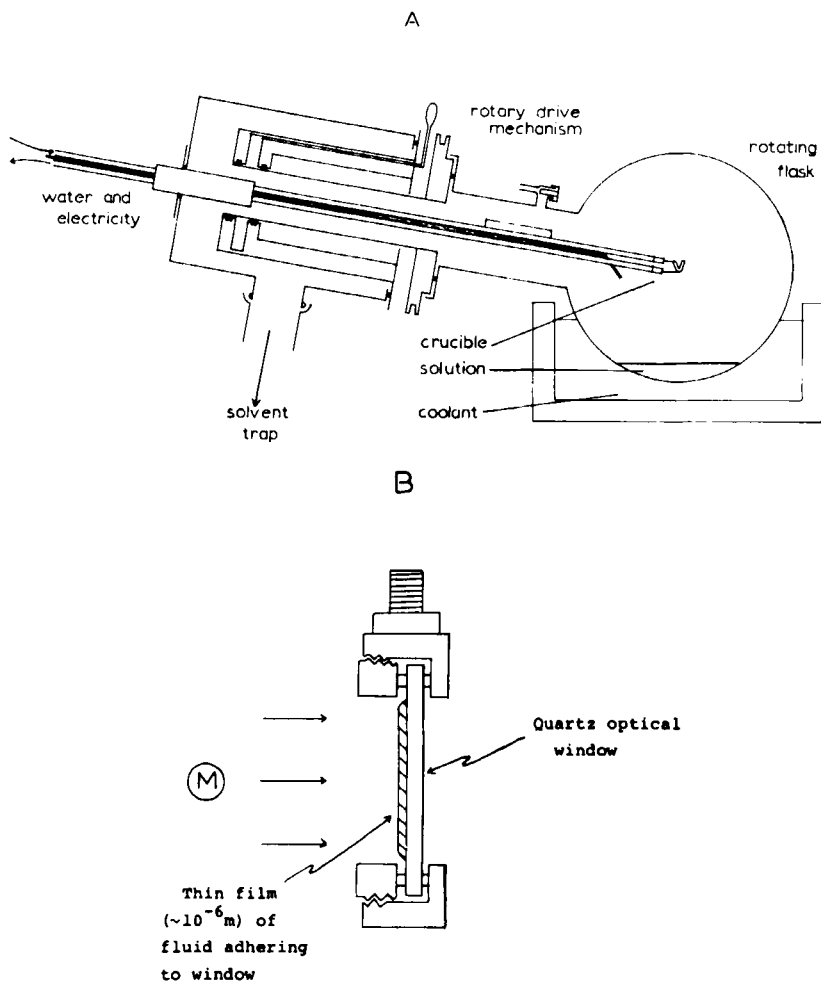


FIG. 1. Schematics of (A) the metal vapor rotary reactor [15] and (B) the metal vapor fluid matrix method [16].

efficient reaction between metal vapor and a polymer. However, using the solution technique, organometallic polymers can be prepared directly by reaction with the metal vapor.

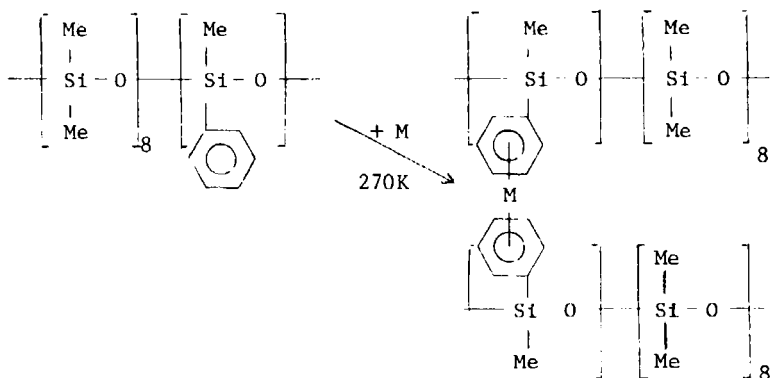
The extension of this principle to polymer-supported metal cluster species was achieved as a result of the development of the

Fluid Matrix Technique [16] (a modification of the spectroscopic method of Blyholder [17]). In this procedure a liquid polymer film is formed on a spectroscopic window and metal vapor is deposited into the film (Figure 1B). Spectroscopic observation of the matrix at various stages during the reaction provides a means for monitoring the course of the reaction.

(a) Formation of Organometallic Polymers

The polymers reported as ligands in metal vapor synthesis [9,10] may be divided into three types: polysiloxanes, poly(phenylethers) and polystyrenes.

The polysiloxanes investigated are commercially available fluids made by Dow Corning, designated DC510, DC550 and DC556. The poly(methylphenylsiloxane) DC510 possesses a number average molecular weight of 3300, with a ratio of phenyl to methyl substituents of 1:17. The metal vapors of Ti, V, Cr, Mo and W react with DC510 at 270K to give colored, air-sensitive fluids which were shown to contain η^6 -arene-metal species [10]. However, metal vapors of Mn, Fe, Co and Ni give only metal slurries.



[10]

As the concentration of bis(arene)metal species is increased, a corresponding increase in viscosity of the fluid occurs. Using the chromium system as an example, the variation of viscosity with arene-complexation was measured (Figure 2). The graph shows

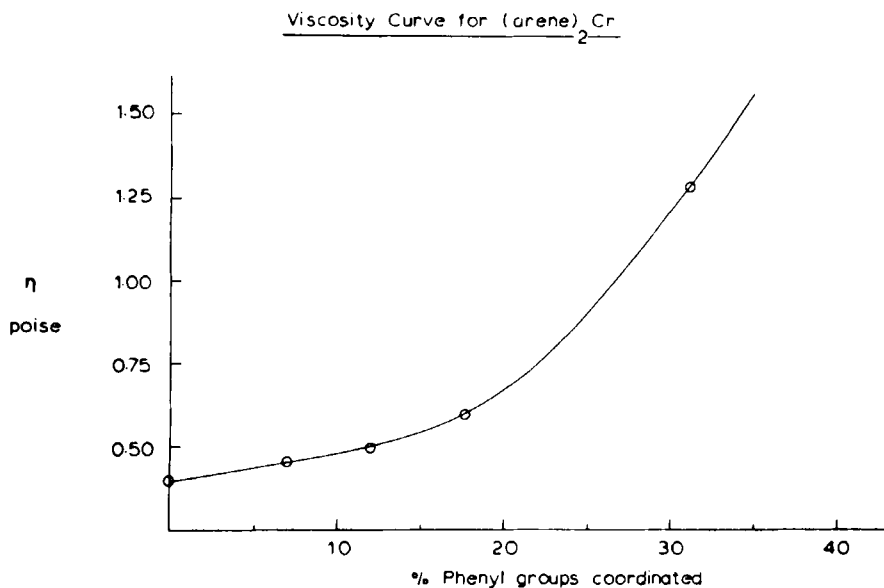


FIG. 2. Variation of viscosity with arene complexation in the Cr/DC510 system [10].

that at low metal loading (<20%) the viscosity increases slowly but at higher loadings a rapid increase in viscosity occurs.

It was observed that for low metal loadings, conversion of metal to complex is essentially quantitative but decreases until, at about 40% phenyl group coordination, it is no longer possible to coordinate more metal. Interestingly, this limit to the uptake of chromium coincides with a high and rapidly rising viscosity for the polymer. Similarly, reaction of chromium vapor with DC550 [a poly(methylphenylsiloxane) with a viscosity of 1.25 poise] leads to a poor yield of bis(arene)chromium and the presence of large metal aggregates.

As was mentioned previously, the products are very air-sensitive but, with the chromium-containing fluid, oxidation to (arene)₂Cr(I) is followed by hydrolysis of the phenyl-silicon

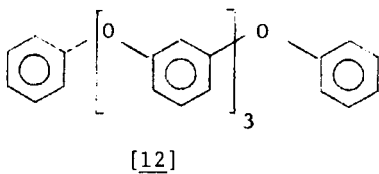
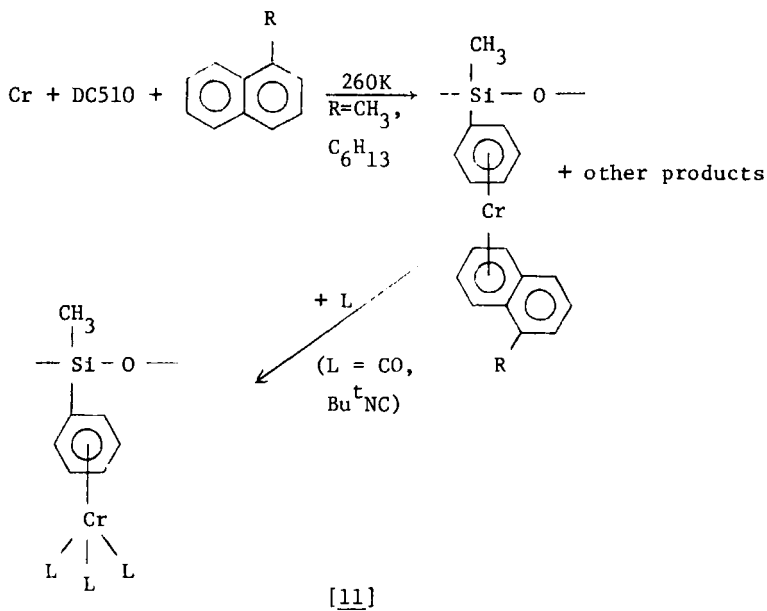
bond to yield bis(benzene)chromium(I). Cleavage of the bond occurs as well in the zerovalent metal state with methanol but the rate of reaction is greatly reduced. The changes in reactivity are attributed to an increased polarization of the carbon-silicon bond in the former case, favoring nucleophilic attack at silicon.

Treating the Cr/DC510 system with 7,7,8,8-tetracyanoquinodimethane (TCNQ) yields a clear, green fluid containing a species of formula $[(\text{arene})_2 \text{Cr}]^+[(\text{TCNQ})_2]^-$. Conductivity measurements showed that the new fluid possesses a specific conductivity of $1.87 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$, compared with a value of $2 \times 10^{-16} \text{ ohm}^{-1} \text{ cm}^{-1}$ for an uncomplexed polysiloxane [10]. It is difficult to imagine any long-range order in this polymeric fluid so that an increase of $\sim 10^{10} \text{ ohm}^{-1} \text{ cm}^{-1}$, attributed to the $[(\text{arene})_2 \text{Cr}]^+[(\text{TCNQ})_2]^-$, is quite appreciable.

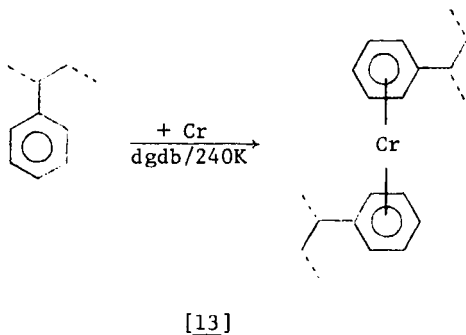
It was also demonstrated [10] that it is possible to form various derivatives of DC510 by simple ligand displacement reactions from mixed naphthalene/DC510 sandwich complexes. These were formed by reaction of chromium atoms with a mixture of an alkylnaphthalene (R = methyl, hexyl) and DC510. The naphthalene is then easily displaced by CO or Bu^tNC , affording the corresponding $[\text{Cr}(\text{DC510})(\text{CO})_3]$ and $[\text{Cr}(\text{DC510})(\text{Bu}^t\text{NC})_3]$ complexes as shown below [11].

The DC556 fluid possesses -OH substituents in addition to the phenyl and methyl substituents. However, Cr atoms appeared only to react with the phenyl groups rather than forming a complex of the type $\text{Cr}^{\text{III}}(\text{OSiR}_3)_3$.

The second class of polymers investigated was a poly(phenyl-ether), Santovac 5, with structure [12]. Reaction at 300K with chromium or vanadium vapors yields the corresponding bis(arene)-metal complexes [10].



Finally, solid polystyrene (M.Wt. ca. 25,000) and poly(p-Bu^t-styrene) were able to be used as ligands in the synthesis of bis-(arene)chromium complexes as shown below:



Diethylene glycol dibutylether was used as the diluent to obtain a 3% w/v solution which was reacted with metal at 230K [10]. The use of polymeric solids as ligands does create some problems, however. It is very difficult to obtain unreactive solvents which are able to maintain the complexed polymer in solution while possessing a low vapor pressure in order for the metal vapor reaction to be carried out.

(b) Formation of Polymer-Supported Metal Clusters

The manipulation of metal atom recombination reactions under cryochemical conditions has been widely used to produce metal clusters and cluster complexes [18,19,20]. Until recently [16], however, there has been no procedure in the open literature for stabilizing these cluster species for subsequent testing as real, working catalysts. By extending the metal vapor-poly(methylphenylsiloxane) work, described in the previous section, to lower temperatures and higher metal concentration, with in situ spectroscopic monitoring of product formation, it has been possible to obtain some interesting results concerning metal cluster growth and stabilization in liquid, polymeric media in the temperature range 210-290K. In this section we will concentrate on the unimetallic vanadium-poly(methylphenylsiloxane) system [21] and its extension to bimetal and trimetal vapor-polymer reactions [22].

(i) Unimetallic Systems. As mentioned earlier, the metal vapors of Ti, V, Cr, Mo and W react with DC510 at 270K in a metal vapor rotary reactor to give the respective polymer-anchored bis(arene)metal complex. In the case of the V/DC510 system, the strongest band observed in the optical spectrum occurs at 324 nm and corresponds to a metal(d)-to-ring(π^*) charge transfer excitation of the polymer-supported bis(arene)vanadium complex.

The V vapor-fluid matrix experiment [21] involved low metal deposition rate ($\leq 10^{-8}$ mol min $^{-1}$) into a thin film (roughly 10^{-6} m) of DC510 adhering to a quartz window (diameter 1 cm) under vacuum at 250K. As well as the intense MLCT band at 324 nm, the

growth of a new absorption at 453 nm (Figure 3a) was observed. The growth characteristics of these two bands as a function of vanadium loading are illustrated in Figure 3b. Significant points to note under conditions of comparatively low metal loading are (i) the absence of broad optical absorptions in the 200-300 nm region associated with bulk electronic excitations of colloidal vanadium (note that the reaction of V vapor with a polymethylsiloxane DC200, or a paraffin oil, gives only a broad absorption in this region) and (ii) the absence of any absorptions in the region 200-700 nm associated with species other than those emerging at 324 nm and 453 nm, when conducted at temperatures $\geq 250\text{K}$.

Under conditions of higher vanadium loading, the growth of a broad, underlying absorption in the region of 230-240 nm was observed (Figure 3a: E), close to that associated with colloidal vanadium generated in DC200 (Figure 3a: F). The product distribution for equivalent metal loadings, normalized with respect to polymer-anchored bis(arene)vanadium, in the V/DC510 reaction, as a function of the temperature of deposition in the range 210-270K, is shown in Figure 4. It can be seen that formation of the bis(arene)vanadium species is favored in the range 250K, while formation of the other species becomes more important at both higher and lower temperatures in the region 210-270K. The origin of the V_{colloid} absorption, however, appears to be different in the 210K and 270K extremes; namely, rapid metal aggregation in the surface layers of the film for the more rigid polymer at the lower temperature end and colloidal metal formation within the film for the more mobile polymer at the higher temperature end. In addition, when the reaction was performed at 210K (Figure 5), two new species were produced, absorbing at 550 nm and 635 nm.

Collecting together the data from the V/DC510 system (as well as a series of similar observations for Ti, Cr and Mo vapors condensed with DC510 and Santovac 5 [21]) and by analogy with the optical data for V_2 and V_3 trapped in solid argon at 10-12K [23], the most probable explanation for the bands in the visible region

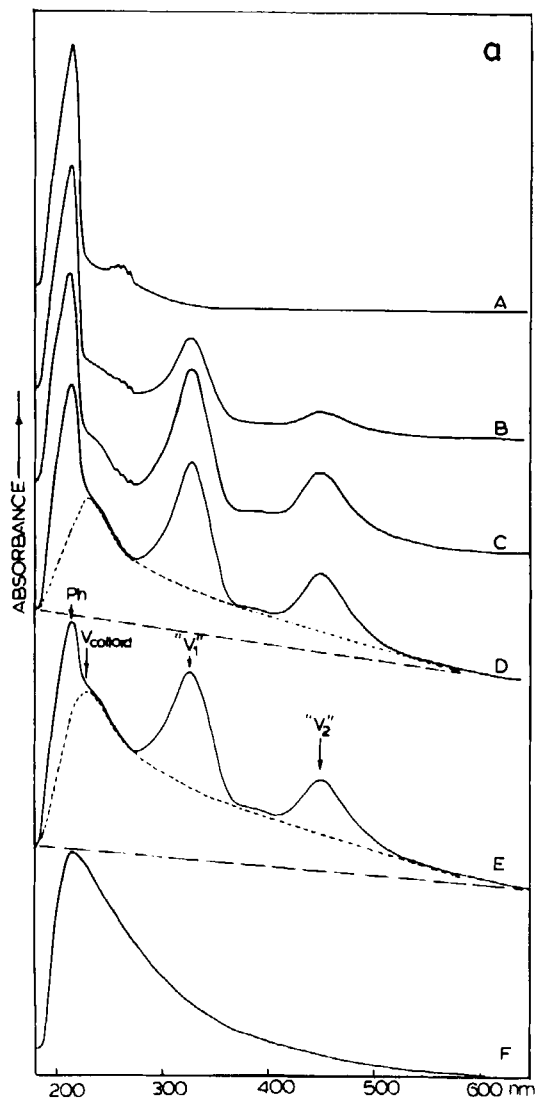


FIGURE 3.

of the V/DC510 spectrum is that they are primarily associated with metal-localized excitations in very small, polymer-stabilized vanadium clusters, with nuclearities in the range $n = 2-4$. A graph of the energies for these transitions as a function of the

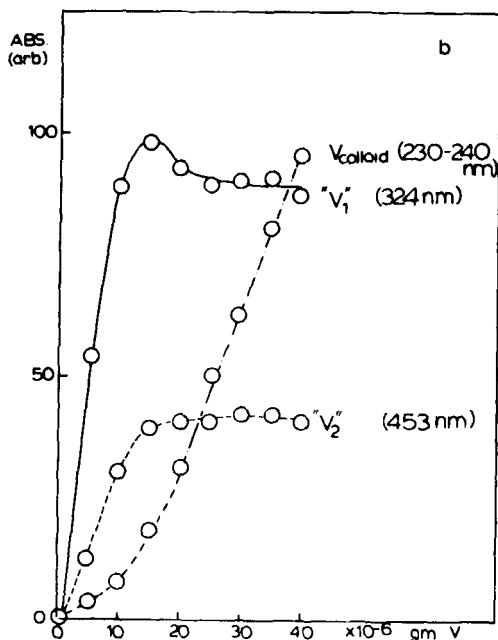


FIG. 3a. (A-E) Ultraviolet-visible spectra of the products formed with increasing loading of V vapor into DC510 deposited at 250K and (F) the spectrum of colloidal vanadium generated in DC200. 3b. Graphical representation of the growth-decay behavior of species labelled V_1 , V_2 and V_{colloid} in Figure 3a, as a function of vanadium loading into DC510.

reciprocal of the suggested metal nuclearity (Figure 6) displays a monotonic correlation, as would be expected for the HOMO-LUMO band gap with increasing cluster size. Similar effects have been observed for Mo_n ($n = 2, 3, 4, 5$) in DC510 [24].

Current thoughts concerning probable modes of cluster growth and stabilization in a polymer (or oligomer) are shown in Figure 7. This scheme is intended to illustrate an initial chain-propagation step and/or cross-linking process involving single metal atoms complexed to two arene rings. These can then act as metal nucleation centers for subsequent cluster growth, either 'unsolvated' (Figure 7, III) or stabilized by oxygen groups or arene rings on

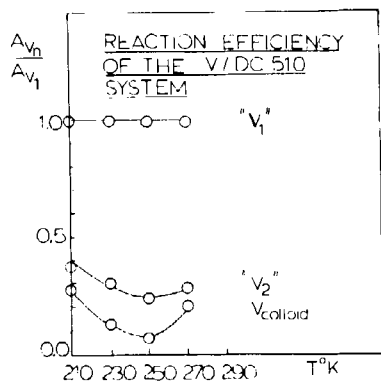


FIG. 4. Product distribution for equivalent V loadings, normalized with respect to polymer-anchored bis(arene)vanadium, in the DC510 reaction, as a function of the temperature of deposition in the range 210-270K [21].

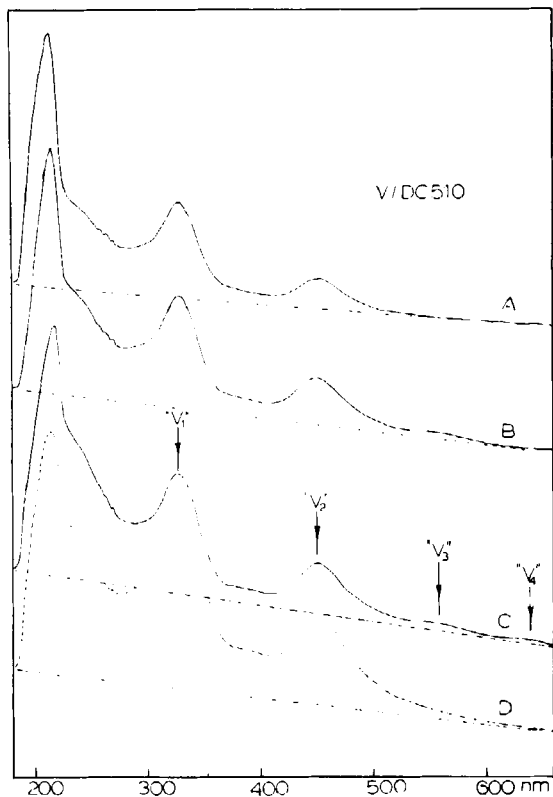


FIG. 5. Ultraviolet-visible spectra of the products formed with increasing loading of V vapor into DC510 at 210K.

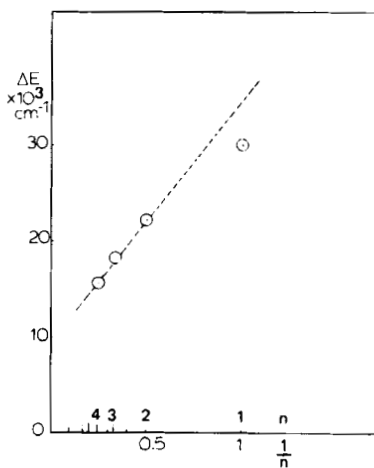


FIG. 6. Graphical representation of the transition energies observed for the DC510-stabilized V_n species as a function of n^{-1} (see text for details).

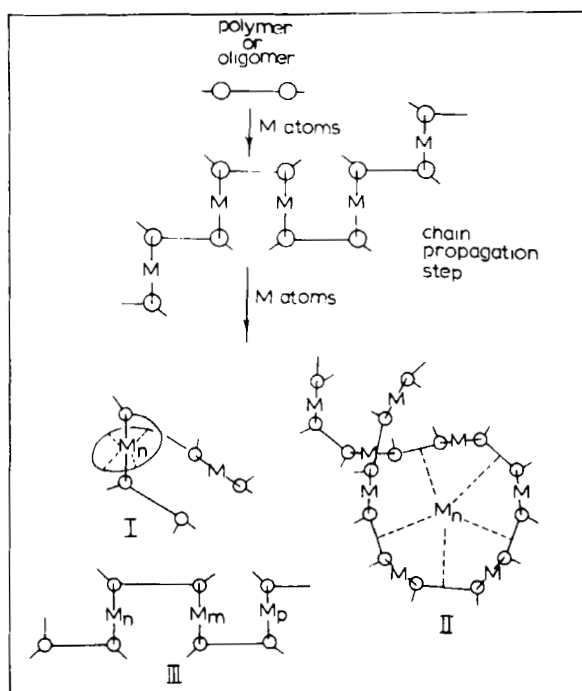
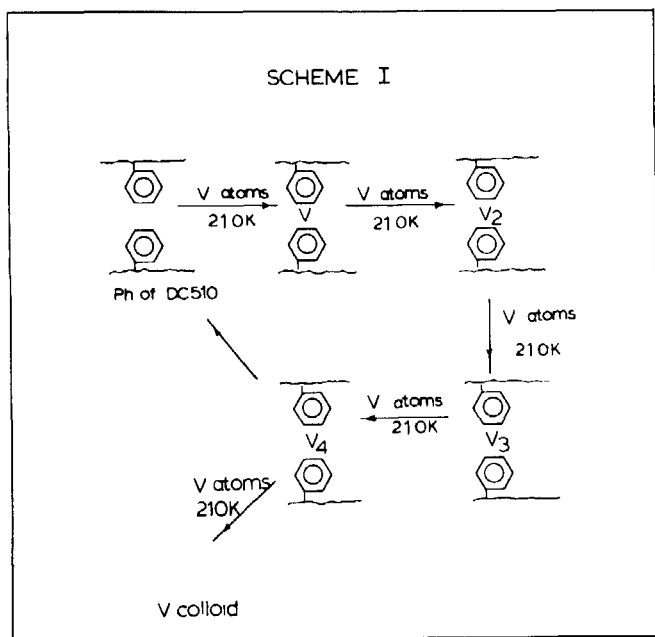


FIG. 7. Schematic of possible modes of cluster growth and stabilization in a functionalized polymer (or oligomer).

the polymer (Figure 7, I). An alternative mode of cluster stabilization involves physical entrapment within a high-viscosity organometal polymer network (Figure 7, II).

From a preliminary kinetic analysis [25] of the growth decay behavior of the metal cluster species in the DC510 system, a scheme is currently envisaged in which M_n are formed in a series of sequential nucleation events and stabilized by interaction of each metal atom with at least one phenyl group on the polymer chain (see Scheme I, below):



As the metal cluster develops, the metal-arene interaction diminishes in strength (*cf.* chemisorbed benzene on metal surfaces) until at a critical cluster size (e.g., Ti: $n = 2$; V: $n = 4$; Cr: $n = 3$; Mo: $n = 5$) the arene(s) is released from the cluster, allowing further aggregation of the metal into a size regime which is capable of displaying broad optical absorptions characteristic of

colloidal metal. Expulsion of the metal clusters from their solvation shells can also be achieved by raising the temperature of the polymer to around room temperature, the outcome usually being rapid metal agglomeration to higher-nuclearity, bulk-like clusters. Additional experimental support for the existence of polymer-stabilized metal clusters has very recently emerged from some preliminary laser Raman measurements on the vanadium and chromium DC510 systems [25]. The spectra display a number of very intense Raman lines in the region $260\text{--}100\text{ cm}^{-1}$ which are most probably associated with metal-metal stretching modes of very low-nuclearity vanadium clusters.

A point of special significance is illustrated in Figure 8 which demonstrates the feasibility of generating and studying

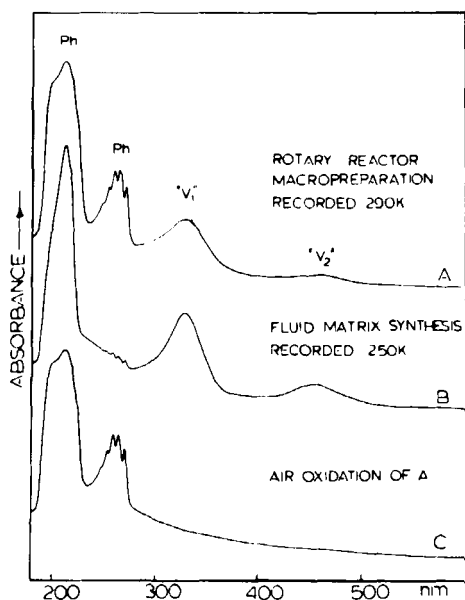


FIG. 8. Comparison of product formation in the V/DC510 system, (A) using a macroscale rotary reactor, (B) using the fluid matrix technique and (C) the air oxidation of the sample shown in (A) [21].

polymer-supported, mononuclear and cluster systems by way of both rotary reactor and matrix spectroscopic metal vapor-liquid polymer techniques [21]. Similar results have recently been obtained for the Mo/DC510 system [24].

(ii) Multimetallic Systems. It has been demonstrated that organo multimetallic polymers containing mononuclear and/or cluster metal sites can be readily generated by the metal vapor-fluid matrix technique [16,21,22]. In this brief discussion we will focus attention on the V/Cr/DC510 and Ti/V/Cr/DC510 combinations, using the MLCT transitions of the bisarene complexes (318, 324 and 355 nm for the Cr, V and Ti/DC510 systems respectively) and the metal-localized excitations of polymer-stabilized dichromium (402 nm) and divanadium (453 nm) as spectroscopic probes of the extent and site of metal attachment.

The initial deposition of Cr vapor into DC510 at 250K is shown in Figure 9 and is seen to display the MLCT band of polymer-supported bis(arene)chromium at 318 nm as well as polymer-

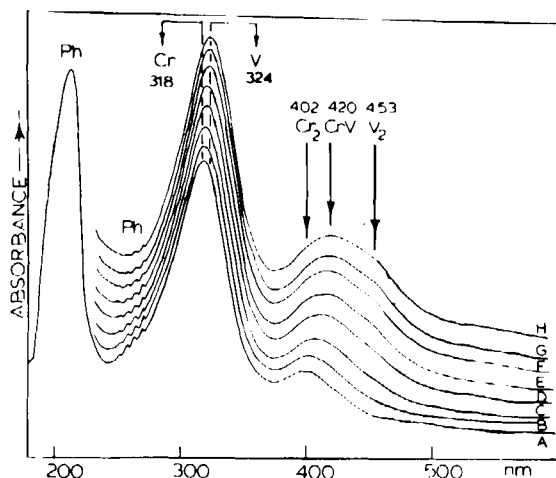
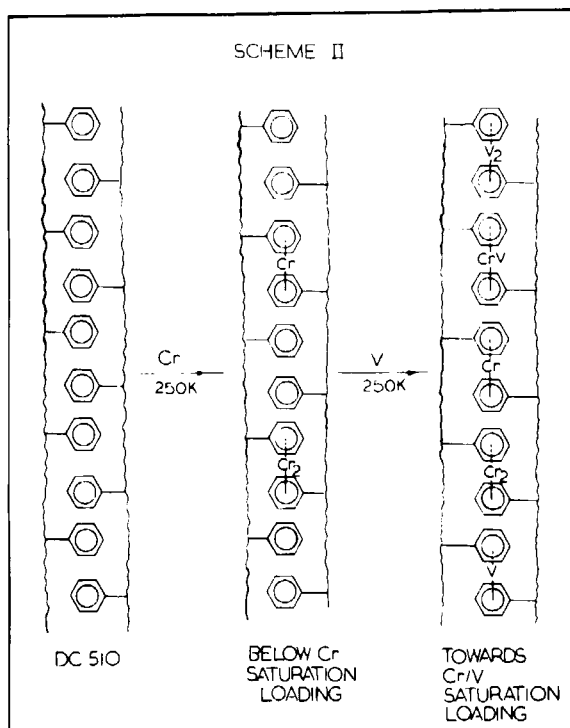


FIG. 9. The ultraviolet-visible spectra of the products of (A) a Cr vapor deposition into a film of DC510 at 250K, followed by (B-H) roughly equal increments of V vapor [22].

stabilized dichromium at 402 nm. Subsequent depositions of V into the DC510 at 250K, close to the saturation loading, are depicted in Figure 9B-9H and show a small spectral shift of the original 318 nm band to 324 nm, corresponding to the growth of the polymer-anchored bis(arene)vanadium complex. Concomitant with this growth in the MLCT region is the broadening and shifting of the polymer-stabilized dichromium band at 402 nm to eventually yield a structured band with maxima at 402, 420 and 453 nm, the latter being associated with the previously identified divanadium absorption. The new absorption, at energies intermediate between those of Cr_2 and V_2 absorptions, can be ascribed to the polymer-stabilized, bimetallic cluster CrV [22]. This is in keeping with the observation of averaged metal-localized excitation energies in heterobinuclear cluster carbonyl complexes [26] and heteronuclear diatomic clusters [33].

A possible explanation of the way in which the chromium and vanadium vapors interact with the DC510 under the conditions outlined above is illustrated in Scheme II.

Figures 10a and 10b illustrate the progress of sequentially depositing Cr/V/Ti or Cr/Ti/V respectively into a thin film of DC510 adhering to a quartz optical window held at 250K. The deposition of approximately 2×10^{-6} gm of chromium into the DC510 leads to the appearance of the characteristic 318 nm absorption of polymer-anchored bis(arene)chromium (Figure 10a: A) together with a small amount of the polymer-stabilized dichromium species. Addition of a roughly equal increment of vanadium causes further growth of the MLCT absorption assigned to bis(arene)chromium but with a noticeable red shift of the peak maximum to 324 nm (Figure 10a: B), the wavelength of anchored bis(arene)vanadium [16,21]. Deposition of a roughly equal increment of titanium into the polymer film (Figure 10a: C and D) causes additional growth in the MLCT region but with a new peak at 355 nm, depicting the generation of polymer-attached bis(arene)titanium [16]. In an attempt to obtain clearer spectroscopic resolution of the bis(arene)chromium and vanadium sites, similar trimetal vapor



depositions were conducted using the deposition order Cr/Ti/V. An illustrative spectral trace is shown in Figure 10b. Following the sequential Cr/Ti deposition (Figure 10b: B), the coexistence of bis(arene)chromium and titanium on the polymer is easily discerned by the MLCT bands at 318 and 355 nm respectively. Further deposition of V clearly defines the continued growth in the MLCT region but with a new maximum at 324 nm (Figure 10b: C and D).

MISCELLANEOUS REACTIONS OF METAL VAPORS WITH POLYMERS

The previous section (b(II)) described how metal vapor-polymer interactions, occurring within a fluid polymer, could lead to a small, well-defined metal cluster species. Another group of

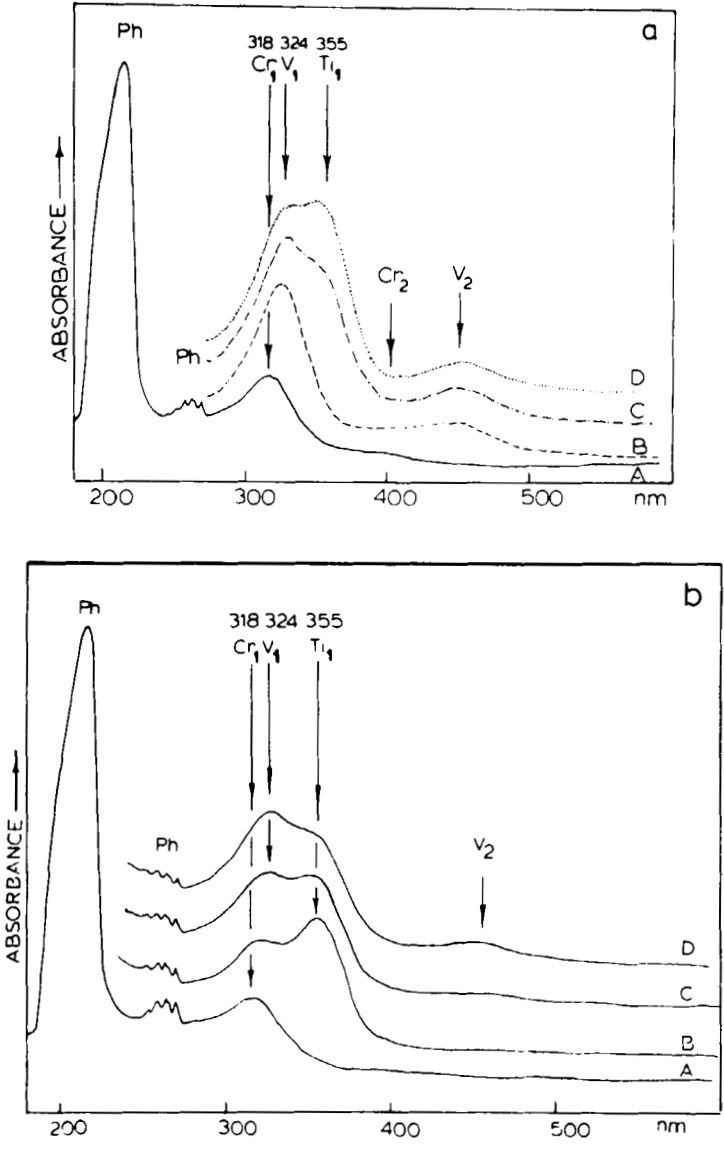


FIG. 10a. Ultraviolet-visible spectra of a thin film of DC510 at 250K following deposition of (A) Cr, (B) V, (C) Ti and (D) Ti vapors in increments of approximately 2×10^{-6} gm [22].

10b. Essentially the same conditions as Figure 10a except that the metal vapor deposition sequence follows the order (A) Cr, (B) Ti, (C) V and (D) V [22].

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workers [27,28] has shown that small metal particles, with mean sizes in the region below 10 nm, can be grown on the surface of a polysiloxane oil. The apparatus consists of a rotating disc and furnace assembly mounted within a vacuum chamber. Oil is supplied at the center of the disc and flows outward due to the centrifugal force, allowing metal vapor to interact with a continuously replenished film of oil.

In the experiments reported, metal vapors of Al [27] or Fe [28] were produced at a rate of $\sim 8 \text{ mmol min}^{-1}$ and deposited on the surface of the polysiloxane to give extremely fine particles. In the Fe-polymer system, concentration of the metal-polymer suspension under air resulted in the isolation of mainly Fe_3O_4 particles with average diameter of about 2.5 nm. Magnetic measurements showed that these particles exhibit superparamagnetism, but that the magnetic interaction between particles is quite small as a result of their dispersion in the fluid.

In contrast, Burkstrand reported a series of experiments in which copper vapor was deposited onto the surface of a solid polystyrene [29,30] or polyvinylalcohol [31] film. The chemical interactions taking place on the surface were monitored by x-ray photoemission spectroscopy. With polystyrene, using low copper coverages (< 0.01 monolayer), the copper $2p_{3/2}$ core electron binding energy is 1.5 eV less than the value for bulk copper, indicative of a copper atom in a region of high electron density. This could be a surface complex such as bis(arene)copper. At higher copper coverages, the core lineshape showed the presence of a new peak attributed to isolated small clusters of copper atoms. When the polystyrene was pretreated with an oxygen plasma process [30], generating carbon-oxygen bonds on the surface, subsequent deposition of copper vapor resulted in the formation of a copper-oxygen-polymer complex. This showed increased adhesion of the deposited metal films onto the polymer.

An alternative route for the production of thin films of polymer-containing metal has been reported by Boonthanom and White

[32]. Evaporation of copper and cocondensation with organic fragments, such as those produced by heating polyethylene, gave films (thickness ~ 90 nm) consisting of polyethylene containing small clusters of copper atoms. Annealing at 493K in air converted the Cu to Cu_2O with accompanying loss of the polymer. This resulted in the production of small "islands" of cuprous oxide, separated by ~ 10 nm, for which the conductivity characteristics were treated as a model of the conductivity in bulk copper.

CONCLUSIONS

In summary, the formation of metal-containing polymers via interaction of metal vapor with a monomer is complicated often by the lack of control of polymerization of the polymer precursor during the metal vapor process. It seems likely that the most profitable studies in this area will come from an approach similar to those of Timms [13] and McGlinchey [12].

Another way of alleviating this problem is the use of a pre-formed polymer as a ligand. Some of the advantages of this approach are shown from the early observations in the fields of liquid-phase organometal polymers and polymer-supported metal clusters, *viz.* (i) the experiments can be performed at either a macrosynthetic or matrix spectroscopic scale of operation, (ii) the experiments can be entirely conducted at or close to room temperature, (iii) the resulting organometal polymers and polymer-stabilized metal cluster compositions are homogeneous liquids (the term "homogenized-heterogeneous catalysts" may turn out to be an appropriate description for the latter) which have reasonable stabilities at room temperature, and (iv) the methodology is easily extended to bimetallic and trimetallic combinations.

Although solid polymers present some difficulties as ligands in metal vapor synthesis, a combination of the standard solution methods of metal vapor chemistry and the techniques of thin-film

technology should facilitate development of this area of research in the future.

The use of metal vapor synthesis in collaboration with polymer chemistry is still a novel field, but the tremendous possibilities which exist for such techniques suggest that the future is extremely promising.

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