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Triallylphosphine Plasma Polymerization and Reaction of the Product with Volatile Transition Metal Compounds

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SYNOPSIS

The plasma polymerization of triallylphosphine in order to form a crosslinked polymer thin film is described. The plasma polymer thin film has been characterized and shown to contain a high proportion of C=C and P groups conserved from the monomer. The accessibility of the phosphine groups has been demonstrated by reaction with O₂, NO, Ni(CO)₄, and Fe(CO)₅. Reaction with O₂ and NO results in a P=O moiety formation. Reaction with the gaseous metal carbonyls results in fixation of the metal via complexation by the P groups as a result of exchange with CO ligand(s). This illustrates the utility of a ligand donor group containing plasma polymer as an avenue for the formation of a single phase transition metal containing plasma polymer.

INTRODUCTION

Plasma polymers are known to be of irregular structure and they are highly crosslinked. In recent years, there has been considerable interest in metal containing plasma polymers. However, work reported until the present has focused almost exclusively on the production of films containing metal particles as discrete entities or as semicontinuous phases; these films are described as plasma polymer/metal composites.¹⁻³ Optical and electrical applications have been suggested for such composites.

In contrast, the focus of this work is the preparation of plasma polymers in which individual transition metal atoms are complexed by functional groups, which are a part of the plasma polymer network.⁴ In the ideal case, such a film will exist as a single phase. The chemical activity of such metal atoms will be modulated by the ligand(s) to which the metal atom is bound. Electrochemical and cat-

alytic applications are some of the possible uses for such films.

Several experimental approaches can be employed to make such metal containing plasma polymer films. These include:

1. Plasma polymerization of volatile organometallic compounds,
2. Formation of plasma polymers containing ligand groups followed by subsequent reaction with transition metal containing compounds from solution or the gas phase, and
3. Simultaneous plasma polymerization and metal evaporation.

The first approach has been employed in our previous work. Examples include the plasma polymerization of Fe(CO)₅ + C₂ hydrocarbons⁵⁻⁷ and η⁵-cyclopentadienyldicarbonylcobalt(I).⁸ The resulting films have been characterized by a variety of techniques, including ESCA, infrared and Mössbauer spectroscopies, electron microscopy, and cyclic voltammetry. The picture that emerges is one of films that include soluble metal complex oligomers, metal atoms bound to functional groups on the plasma polymer, and metal oxide granules. The relative populations of these species are influenced by reaction conditions. In particular, the ratio of soluble

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to insoluble species decreases with decreasing ratio of volatile organometallic compound to hydrocarbon in the monomer mixture and with increasing W/FM ($W = RF$ power, $F =$ Monomer flow rate, and $M =$ Monomer molecular weight).⁶ Such soluble species include the organometallic cluster tris [η^5 -cyclopentadienylmonocarbonylcobalt(I)] produced in the plasma reaction of $\text{Co}(\eta^5\text{-cp})(\text{CO})_2$ ($\text{cp} =$ cyclopentadienyl ligand).⁸ $\text{Fe}(\text{CO})_5 + \text{C}_2$ hydrocarbon plasma polymers are electrical insulators, but in the form of a perforated or discontinuous coating they can induce the electrochemical deposition of mixed valence metal cyanide compounds with zeolitic properties.⁹⁻¹³ These compounds include Prussian blue⁹⁻¹² and a ruthenium analog.¹³

The second approach to the preparation of metal containing plasma polymer films, as outlined above, was used to obtain the results described in this article. Here we report the preparation of a metal containing plasma polymer by first plasma polymerizing a monomer containing a heteroatom capable of metal coordination, and then exposing the resulting thin film to a volatile organometallic compound with readily exchangeable ligands. In a subsequent article¹⁴ we describe the utilization of the third approach to the preparation of a metal containing plasma polymer by polymerization of a monomer containing a potentially metal coordinating heteroatom in the presence of a metal vapor. These three preparative methods are conducive to the integration of a wide variety of transition metal species within a plasma polymer film.

EXPERIMENTAL

Materials

Triallylphosphine (TAP) was purchased from Strem Chemical Company. After transfer under a N_2 atmosphere, TAP was stored in a closed container connected to the vacuum system at -78°C and was warmed to room temperature ($22\text{--}25^\circ\text{C}$) for plasma polymerizations. Ironpentacarbonyl, $\text{Fe}(\text{CO})_5$, was purchased from Aldrich Chemical Company and was treated identically. The purity of reagents was measured by the % gas condensable, at -78°C for $\text{Fe}(\text{CO})_5$ and at -196°C for TAP. Acceptable purities (99.8% condensibility for $\text{Fe}(\text{CO})_5$ and 97% for TAP) were obtained by repeated freeze/pump/thaw cycles (using a dry ice/acetone bath for $\text{Fe}(\text{CO})_5$ and liquid N_2 for TAP). $\text{Ni}(\text{CO})_4$ was used as obtained from Strem Chemical Company.

The gases, NO , O_2 (National Welders Supply Company Inc.), and CO (Airco Inc.) were used as obtained. Aluminum foil (purified) was obtained from J. T. Baker Chemical Company, while the glass coverslips were purchased from Fisher Scientific.

Methods

Plasma polymers were formed using the inductively coupled reactor (Fig. 1) previously described.¹⁵ The glow discharge was generated using an r.f. transmitter (Heathkit model DX60B). The output was fed into a linear amplifier (Heathkit SB-200) with

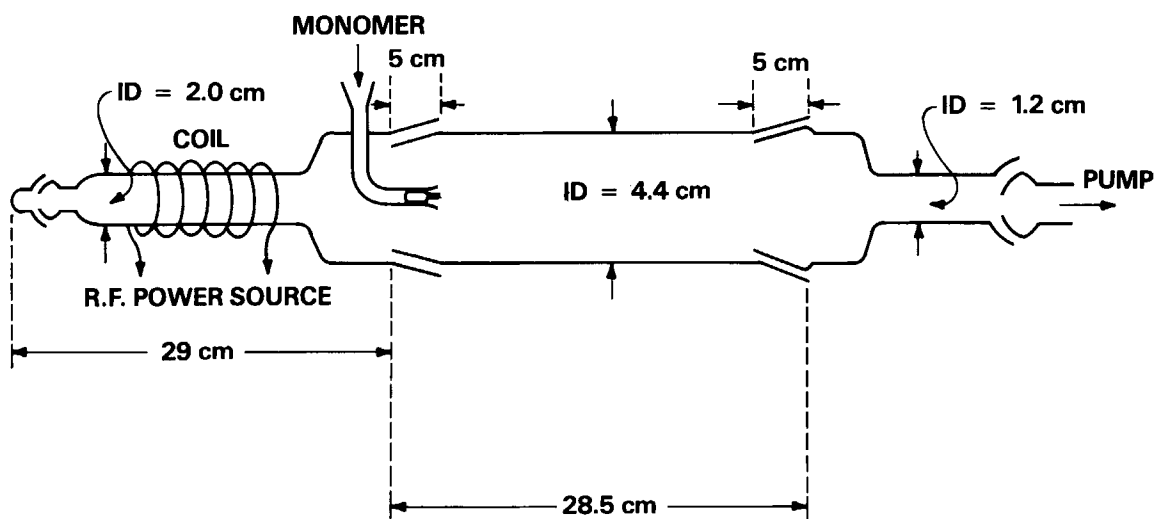


Figure 1 Reaction chamber for the synthesis of TAPPP prepared and handled in the absence of air. Samples for coating were placed at the bottom of the reactor at 0, 4, 8, and 12 cm from the monomer inlet.

a 500 W capacity. The amplifier output was connected to the r.f. coil through a tunable matching network. A Bendix r.f. power meter (model 262, 0.5–225 MHz) was used to measure the r.f. power. The r.f. power supply operated at 13.56 MHz and delivered continuously variable output power from 0 to 200 W. The tuning circuit was adjusted so that the reflected power was maintained at a minimum.

Triallylphosphine Plasma Polymer (TAPPP) Production

Triallylphosphine plasma polymers (TAPPP) were prepared by evacuating the reactor to 1 mtorr and then introducing the TAP at a flow rate of 0.014 to 0.023 cm³ (STP)/min, as measured by the rate of pressure change into a known closed volume. The equilibrium pressure, p_m , reached for the condition where pumping rate = feed rate, was 4–6 mtorr. The minimum power needed to maintain the glow discharge (8–15 Watts) was employed and resulted in a plasma pressure, p_g , of 3–6 mtorr. Pressure was monitored for the entire reaction using a MKS differential pressure transducer. Plasma polymerization lasted between 20 and 60 min, depending on the desired deposition thickness of the TAPPP, which was determined gravimetrically.

Mass Gain of Films

Experiments measuring the mass gain of films of TAPPP, when exposed to reactive gases (O₂, NO, and Fe(CO)₅), were performed using an Inficon Model XTM deposition rate monitor, which employed a quartz piezoelectric crystal. The mass of the film was monitored continuously during the addition and removal of the gases by means of a chart recorder.

Spectroscopic Characterization of Plasma Polymers

Infrared spectra were obtained using either the transmission or the attenuated total reflection (ATR) technique and an Analect Instruments FX 6200 spectrometer. The plasma polymers were deposited either onto aluminum foil, which was pressed against a 45° KRS-5 internal reflection element, or onto NaCl or KBr crystals. Spectral characterization of plasma polymer films, before and after reaction with O₂, NO, Fe(CO)₅, and Ni(CO)₄, was based on at least six replicate spectra. All absorption bands used for characterization were reproducibly obtained at precisely the same position for each replicate experiment.

ESCA spectra were obtained after exposure to air using a Physical Electronics Phi Model 548 ESCA spectrometer, equipped with Mg K-alpha X-ray source, equipped with a model 15–255 precision electron energy analyzer. Plasma polymer was deposited on aluminum foil blanks. A correction for charging was made by reference to the major contributor to the C 1s line at 284.6 eV. The relative amount of each element was obtained from the ESCA signal using sensitivity factors supplied by the instrument manufacturer and a computer program.¹⁶

Elemental Analysis of TAPPP Film

TAPPP was coated on glass cover slips over a period of 2.5 h at 8–10 Watts of r.f. power. The material was removed for elemental analysis by scraping it from the cover slips with a razor blade. The resultant powder was submitted to M–H–W Laboratories for elemental analysis after exposure to air.

Reactions of TAPPP with Various Gases

The reactor system used is shown in Figure 1. This reactor allowed the transfer of samples from the vacuum line to a glove bag without exposure to air. The reactivity of the TAPPP film to gases was determined gravimetrically and spectroscopically. Gravimetric determinations were carried out on TAPPP films deposited on a quartz piezoelectric crystal (deposition rate monitor) as a function of time of exposure. Infrared spectra, obtained for plasma polymer coated on aluminum foil or NaCl, were used to identify the nature of chemical reactions. Exposure of the TAPPP film to gases was always preceded by evacuation of the reaction chamber until constant mass was observed using the deposition rate monitor, indicating complete desorption of volatile components (monomer and oligomer).

The reactant gases, CO, O₂, and NO, were maintained at a pressure of approximately 160 torr (0.21 atm). Duration of treatment was 1–2 days for O₂ and 40 min for all other reactants. The system was then evacuated so that the extent of reaction could be determined.

In order to minimize exposure of plasma polymer films to the atmosphere, films of plasma polymer, deposited on Al foil and then reacted with gasses, were removed from the reactor and were pressed against the ATR internal reflection element in an N₂ filled glove bag. The ATR mount was then rapidly transferred to the N₂ purged FTIR spectrometer.

Ni(CO)₄ was introduced into the reaction cham-

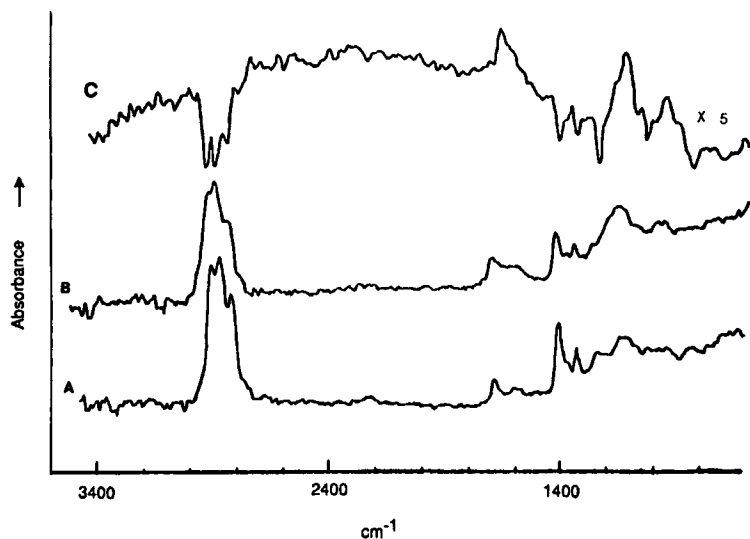


Figure 2 IR-ATR spectra of TAPPP for: (A) Inert atmosphere, (B) After 48 h in air, and (C) Difference spectrum (5× vertical expansion after subtraction of original spectrum A from original spectrum B) obtained by subtracting spectrum A from spectrum B. Samples were coated on aluminum foil substrates 2 cm from monomer inlet at approximately 50 $\mu\text{g}/\text{cm}^2$ using plasma polymerization conditions described in line 1, Table I.

ber immediately after deposition of TAPPP and without exposure to air or light. A pressure of 30 torr $\text{Ni}(\text{CO})_4$ was maintained. After 40 min, the system was opened to a cold trap at liquid N_2 temperature. The pressure of the system exposed to the trap was recorded and then the system was opened to the vacuum pump. After the base pressure was reestablished, the system was flushed four times with approximately 50 torr of N_2 gas. After flushing with N_2 , the reactor was isolated from the vacuum pump and N_2 gas was added to 1 atm pressure. The reactor was then removed from the vacuum line and sealed, while a positive N_2 flow ran through the reactor. The sealed reactor was placed in a glove bag filled with N_2 . In the glove bag, the samples were removed from the reactor and placed either in an ATR cell for IR analysis, or stored in a desiccator for ESCA analysis.

$\text{Fe}(\text{CO})_5$ was also introduced into the reactor after the TAPPP was deposited. Five torr of $\text{Fe}(\text{CO})_5$ was utilized with an exposure duration of 60 min. The $\text{Fe}(\text{CO})_5$ was removed by trapping at liquid N_2 temperatures with pumping.

RESULTS

Triallylphosphine Plasma Polymer Preparation

The triallylphosphine plasma polymer (TAPPP), which was used for chemical characterization as described below, was formed upon exposure of the TAP monomer to a radio frequency discharge of 8–15 watts. These conditions led to a generally reproducible deposition rate and composition for the TAPPP films. The bands in the IR spectra, shown in Figure 2(A), are similar to those found for the

Table I Reaction Conditions for TAP Plasma Polymerization^a

Flow Rate (cm^3/min)	Power (Watts)	Deposition Rate ($\mu\text{g cm}^{-2} \text{min}^{-1}$) Distance from Monomer Inlet (cm)					
		0	2	4	6	8	10
0.16	10	0.82	1.19	1.05	1.07	0.90	0.85
0.15	20		1.44	0.83	1.05	0.74	0.92
0.15	50	0.81	1.18	1.01	0.96	1.23	0.85

^a $p_m = 14$ mtorr; $p_z = 7$ mtorr.

monomer,¹⁷ indicating that both phosphine and C=C functional groups are present in the plasma polymer film. The reproducible deposition rate is not surprising, given the insensitivity of this quantity to RF power (see Table I).

Elemental analysis of TAPPP yielded the empirical formula $C_{8.02}H_{13.3}P_{1.00}O_{1.02}$. ESCA analysis of the surface of the TAPPP film, along with the assumption that the C/H ratio is the same as obtained by elemental analysis, yielded the result $C_{9.15}H_{15.2}P_{1.0}O_{5.20}$. These results suggest that the triallylphosphine monomer ($C_9H_{15}P$) structure is generally maintained, and that under aerobic conditions, the P atom is free to combine with oxygen to form a phosphine oxide.

TAPPP Solubility and Adhesion

TAPPP is insoluble in a variety of solvents, including water, ethanol, dichloromethane, toluene, and concentrated nitric acid. This is a strong indication that the plasma polymer is crosslinked, since the monomer is soluble in dichloromethane and toluene.

TAPPP demonstrated excellent adhesion to Al foil, as demonstrated by the Scotch Tape test. No TAPPP was removed from the Al foil by the tape.

Reaction of TAPPP with O₂

TAPPP films ($15.11 \mu\text{g}/\text{cm}^2$ and $27.97 \mu\text{g}/\text{cm}^2$) exhibited an average irreversible mass gain of 21.5% over a 2-day period when exposed to O₂ at 160 torr and 22–25°C. The conditions of exposure were an O₂ pressure of 160 torr at room temperature (22–25°C). The TAPPP film was characterized by IR spectroscopy before and after exposure to air. Figure 2 shows the original spectrum (A), obtained after only 10 sec exposure to air during transfer to the

Table II IR Spectrum of Triallylphosphine Plasma Polymer after Exposure to Air

Band (cm ⁻¹)	Assignment ^{17,25}
2941	C—H (Stretch)
2925	C—H (Stretch)
2857	C—H (Stretch)
1700	C=O (Stretch)
1650	C=C (Stretch)
1453	C—H ₂ (Stretch)
1435	C—H ₃ (Bend)
1375	C—H ₃ (Bend)
1280	C—P (Symmetric Deformation)
1160	Vinyl CH ₂ , P=O (Bend, Stretch)

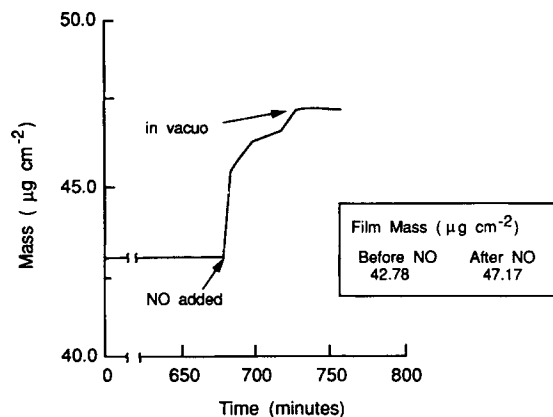


Figure 3 Plot of the mass of a typical TAPPP sample exposed to NO. The sample was prepared using the reactor shown in Figure 1. Conditions: $P_{\text{NO}} = 160$ torr, Temperature = 22–25°C.

FTIR spectrometer, the spectrum obtained from the same film after 48 h exposure to air (B), and the difference spectrum (C). The sample was prepared at a position 2 cm from the monomer inlet under the conditions of Table I, line 1. The IR absorption bands, observed in the spectra, are summarized in Table II along with probable assignments for the chemical groups that give rise to each band. Decreases in certain bands, such as hydrocarbon absorptions at 2941, 2925, and 2857 cm^{-1} , are an artifact caused by loss of plasma polymer film by adhesion to the internal reflection element after acquisition of the first spectrum. The observed increase in absorption at 1700 and 1160 cm^{-1} is attributed to the formation of C=O and P=O moieties, respectively, by reaction with oxygen. The formation of C=O moieties is well known for plasma polymers and is attributed to the reaction of free radicals with oxygen.^{18–24} The formation of the P=O moiety implies the presence of phosphine groups in the plasma polymer prior to reaction with oxygen. All spectra were obtained by FTIR-ATR, the depth of penetration being greater than the thickness of the films being analyzed. Spectra are thus roughly equivalent to those that would be obtained by transmission for the same films. As expected, films prepared by exposure to pure O₂, as for the mass gain studies, exhibit spectra identical to that in Figure 2(B).

The mass gain data and IR spectra (where the depth of penetration exceeds the film thickness) suggest that the O₂ reaction is spread throughout the bulk of the film. The ESCA results and elemental analysis cited above yields the empirical formula $C_{9.15}H_{15.2}P_{1.0}O_{5.20}$ for a TAPPP film exposed to ambient air. The 21.5% average mass increase on ex-

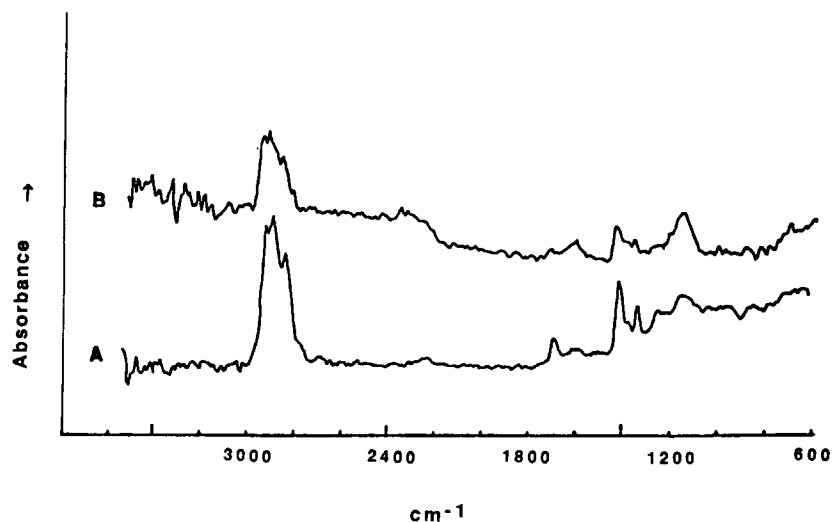


Figure 4 IR-ATR spectra of TAPPP: (A) Inert atmosphere, and (B) Exposed to 160 torr NO for 40 min. Sample was coated on aluminum foil at $50 \mu\text{g}/\text{cm}^2$.

posure to oxygen implies a molecular formula of $\text{C}_{9.15}\text{H}_{15.2}\text{P}_{1.0}\text{O}_{2.0}$. Clearly, this result precludes the reaction of oxygen with only the top 50–100 Å of the films. The same conclusion is obtained as well from the correspondence in relative mass increase [$21.5 (\pm 0.5) \%$] for the two films, which differ in thickness by a factor of two.

Reaction of TAPPP with NO

The result of NO exposure to the TAPPP film parallels the result of exposing the film to oxygen. That result is an irreversible mass gain and two new absorption bands in the IR absorption spectrum. Exposure to NO under the conditions outlined in the Experimental Section results in a 10.3% irreversible mass gain. A plot of the mass of a typical film, as a function of exposure time to NO, is shown in Figure 3. These data are similar in appearance to those obtained for TAPPP exposure to O_2 .

Infrared spectra, obtained before and after exposure to NO, are shown in Figure 4(A) and 4(B), respectively. An increase in the intensity of bands at 1630 and 1160 cm^{-1} is observed, corresponding to the formation of $\text{C}=\text{O}$ and $\text{P}=\text{O}$ groups, respectively. Reaction with NO to produce these $\text{X}=\text{O}$ ($\text{X}=\text{P}, \text{C}$) moieties is supported by several reports in the literature.^{26–32} The oxidation of phosphorus, using NO as the oxidizing agent, proceeds when the basicity and steric factors are favorable. A molecular formula of $\text{C}_{9.15}\text{P}_{1.0}\text{H}_{15.2}\text{O}_{1.0}$ is implied for the oxidized film by the % mass increase observed. Again, this result implies reaction throughout the bulk of the film.

TAPPP Reaction with CO

The reaction of TAPPP with CO differs from the reaction with NO and O_2 in that the irreversible mass gain is considerably smaller and no oxidation of the phosphine group is observed. An average irreversible mass gain of 3.8% is observed for TAPPP films exposed to CO, as shown in Table III. The absolute mass gain is independent of film thickness, suggesting that the mass gain is diffusion controlled.

Infrared absorption spectra were obtained for TAPPP before and after exposure to CO. There was no oxidation of the phosphine group, as indicated by the absence of the absorption band at 1160 cm^{-1} . There were no additional absorption bands observed in the carbonyl region between 2300 and 1700 cm^{-1} , which indicates no significant CO interaction with the bulk of the film. The only change observed is the growth of a weak broad absorption band at 1600 cm^{-1} . Mass gain data may be used to calculate the stoichiometry of the CO adduct as $\text{C}_{9.15}\text{P}_{1.0}\text{H}_{15.2}(\text{CO})_{0.16}$.

Reaction of TAPPP with $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$

After deposition of a known amount of TAPPP, $\text{Ni}(\text{CO})_4$ was introduced into the reactor at a pressure of 30 torr and the reactor was sealed. A constant pressure was observed over the 40–60 min duration of the experiment. Unreacted $\text{Ni}(\text{CO})_4$ was collected by opening a valve to an evacuated trap, cooled by liquid N_2 . A pressure of 7 torr remained in the reaction chamber and trap, indicating the presence of a noncondensable gas. This gas was assumed to be

Table III Results of Reaction of TAPPP Films with CO

Deposition Rate ^a $\mu\text{g}/\text{min cm}^2$	Mass of Film, $\mu\text{g}/\text{cm}^2$			Mass Gain	
	Original	P _{Co} ^b	Final ^c	Net	%
1.04	13.60	14.60	13.99	+ .39	+ 2.9
0.71	8.30	8.95	8.70	+ .40	+ 4.8

^a The deposition rate and mass change are monitored using the Au coated piezoelectric crystal.

^b The maximum mass observed when 160 torr of CO was exposed to the TAPPP film for 40 min.

^c The final mass after CO was removed from the reactor, and a constant mass was observed for 20 min.

CO, produced by a ligand substitution reaction of the $\text{Ni}(\text{CO})_4$ and/or introduced with the $\text{Ni}(\text{CO})_4$. The mass of the TAPPP film was not monitored when exposed to $\text{Ni}(\text{CO})_4$.

In a typical experiment, 2×10^{-4} mol of "phosphine" in a TAPPP thin film were exposed to 2×10^{-3} mol of $\text{Ni}(\text{CO})_4$. The latter amount was calculated from the ideal gas law, assuming 100% purity, although a significant fraction of the pressure in the reactor may be due to dissociated CO. The moles of CO present after the reaction of $\text{Ni}(\text{CO})_4$ with TAPPP were calculated to be 4×10^{-4} , based on the noncondensable gas pressure. This example illustrates that the TAPPP film was exposed to a molar excess of $\text{Ni}(\text{CO})_4$ ($\text{Ni}(\text{CO})_4/\text{P} = \text{ca } 10$) and that only a slight excess of CO ($\text{CO}/\text{P} = \text{ca } 2$) was present after removal of $\text{Ni}(\text{CO})_4$.

Thin films of TAPPP, exposed to $\text{Ni}(\text{CO})_4$, were examined to determine the extent of nickel-phosphorus interaction. A positive nickel spot test was obtained using concentrated HNO_3 to remove the polymer from the glass substrate; sodium dimethylglyoxime salt was used as a complexing agent. The ESCA spectra also show the presence of Ni after the exposure to $\text{Ni}(\text{CO})_4$. These data are presented elsewhere.¹⁴ These results suggest that reaction of the TAP plasma polymer with $\text{Ni}(\text{CO})_4$ resulted in thin films with Ni complex on the surface; the amount of free CO generated as described above suggests that the Ni complex is to be found throughout the bulk of the film as well.

Bands in the carbonyl region of the IR spectrum appear at 2048, 1990, and 1942 cm^{-1} after exposure to $\text{Ni}(\text{CO})_4$ (see Fig. 5). These IR absorption bands are caused by the product of a ligand substitution reaction at Ni. Recent experiments exposing phosphorus modified surfaces to $\text{Ni}(\text{CO})_4$ report almost identical CO stretching frequencies, which were assigned to the mono- and disubstituted complexes, $\text{R}_3\text{PNi}(\text{CO})_3$ and $(\text{R}_3\text{P})_2\text{Ni}(\text{CO})_2$,^{33,34} where PR_3 is a phosphine donor ligand.

Ironpentacarbonyl vapor was also reacted with the TAPPP under the conditions given in the Experimental Section. Weight gain and IR spectra, analogous to the $\text{Ni}(\text{CO})_4$ experiments, were obtained. Weight gain results were erratic, occasionally resulting in a weight loss. This poor reproducibility is attributed to the lower substitution lability for $\text{Fe}(\text{CO})_5$ relative to $\text{Ni}(\text{CO})_4$.³⁵ Figure 6 is an IR absorption spectrum for a TAPPP film whose mass increased from $37.75 \mu\text{g cm}^{-2}$ to $40.29 \mu\text{g cm}^{-2}$ after exposure to $\text{Fe}(\text{CO})_5$ at 5 torr for 60 min, followed by evacuation for 48 h. The estimated stoichiometry for the film is $\text{C}_{9.15}\text{P}_{1.0}\text{H}_{15.2}(\text{Fe}(\text{CO})_4)_{0.025}$. Three IR absorption bands, which do not appear in spectra of TAPPP prepared in an inert atmosphere, appear in the carbonyl region at 1985, 1932, and 1863 cm^{-1} . The three new carbonyl IR absorption bands are not the same as the carbonyl stretching frequencies reported for $\text{Fe}(\text{CO})_5$ or $\text{Fe}_2(\text{CO})_9$.^{36,37} This implies that the new stretching frequencies were observed because of the presence of a phosphine substituted

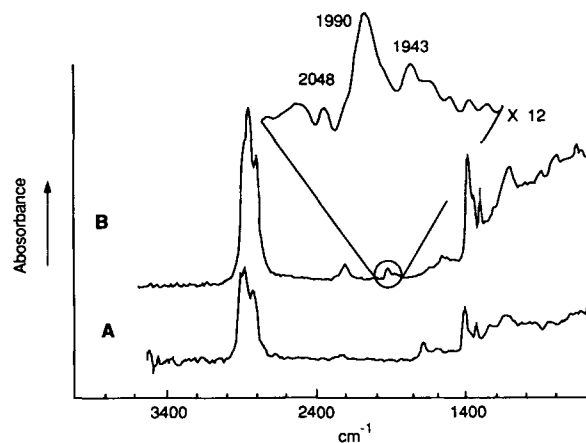


Figure 5 IR-ATR spectrum of (A) TAPPP and (B) TAPPP exposed to 30 torr $\text{Ni}(\text{CO})_4$ for 40 min. TAPPP film loading was approximately $60 \mu\text{g}/\text{cm}^2$ on an aluminum foil substrate.

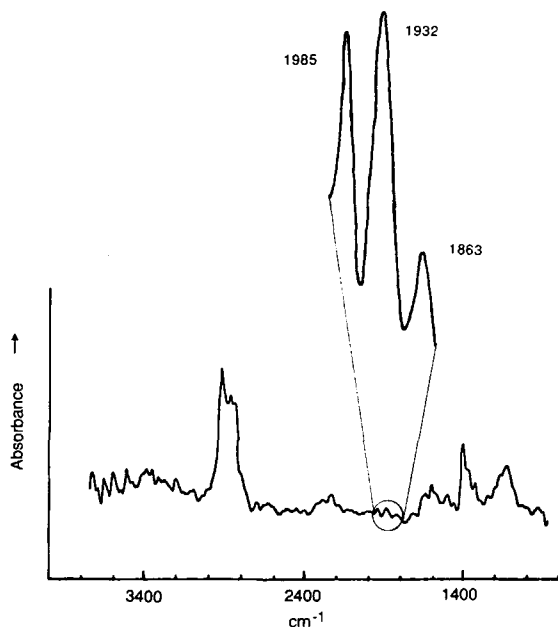


Figure 6 IR-ATR spectrum of TAPPP exposed to 5 torr $\text{Fe}(\text{CO})_5$ for 60 min. TAPPP film loading was approximately $60 \mu\text{g}/\text{cm}^2$.

ironcarbonyl. The CO stretching frequencies observed in the IR spectrum are consistent with the CO stretching frequencies observed for other phosphine substituted compounds of the formula, $\text{Fe}(\text{CO})_4\text{PR}_3$, where PR_3 is a phosphine ligand.³⁸ Although results obtained with $\text{Fe}(\text{CO})_5$ were not as reproducible as with $\text{Ni}(\text{CO})_4$, they do confirm the availability of phosphine coordinating sites in TAPPP and the generality of reacting gaseous metal complexes with plasma polymer films containing ligating atoms in the preparation of metal containing plasma polymers.

DISCUSSION

The results presented above have demonstrated that a plasma polymer, containing reactive phosphine groups, can be formed by exposing TAP to a glow discharge. The accessibility of the phosphine groups has been demonstrated by changes in the infrared spectra after exposure to O_2 , NO , $\text{Ni}(\text{CO})_4$, and $\text{Fe}(\text{CO})_5$. Moreover, ESCA spectra for TAPPP reacted with $\text{Ni}(\text{CO})_4$, presented elsewhere,¹⁴ confirm this interpretation.

The nature of the plasma polymer, as indicated by characterization of the plasma polymerization process and direct examination of the film, is described first, followed by an analysis of the polymer's reactivity with gases.

TAP Plasma Polymerization

The parameter W/F is frequently used to characterize the conditions under which plasma polymerization is carried out.^{6,7} The results reported above were obtained for $W/F = 430$ to 810 MJ/mol . Under these conditions, an insoluble, unoriented thin film is obtained. The level of crosslinking is high enough to prevent solubility of the film, yet low enough to permit diffusion of small molecules through the plasma polymer matrix.

TAP is converted to plasma polymer fairly completely and evenly over the surface of the reactor (see Table I). Over 50% by mass of the reactant monomer is accounted for in the plasma polymer deposited within 15 cm from the monomer inlet. This deposition yield, as well as the infrared spectroscopic data discussed below, suggests the prospect that the plasma polymer can be deposited with preservation of a large proportion of the two monomer functional groups, $\text{C}=\text{C}$ and the P heteroatom.

In addition to the deposition rate, the plasma polymerization process can be described by a comparison of the pressure of the system before glow discharge, p_m , and during glow discharge, p_g . The value of p_g is lower than p_m for TAPPP formation. This observation is in agreement with the observed rapid deposition of plasma polymer. The combination of the conditions of rapid deposition, high yield, and $p_g < p_m$, suggests that the chemical moieties of the monomer are largely conserved in the plasma polymer.

The amount of $\text{C}=\text{C}$ and phosphorus incorporated in the TAPPP is studied with varied success by IR absorption spectroscopy. The partial preservation of the $\text{C}=\text{C}$ moiety in TAPPP is indicated by the presence of the absorption band at 1160 cm^{-1} in IR spectra of TAPPP obtained from samples handled in inert atmospheres. This corresponds to the TAP monomer vibrational mode caused by the $\text{C}=\text{C}$ bend, which has been assigned to an IR absorption band at 1160 cm^{-1} .^{17,25} Phosphorus-carbon stretching bands are routinely observed at 1280 cm^{-1} .²⁵ The IR spectrum of the plasma polymer of TAP shows some absorption band in this region, but they are weak, as is also the case for the monomer.¹⁷

Reaction of TAPPP with Gases

Reaction of TAPPP with diatomic gases indicated reaction with O_2 and NO , but not with CO . Extensive irreversible mass gain was observed upon reaction of TAPPP with both O_2 and NO . The IR absorption

spectra and mass gains are consistent with the oxidation of film-bound phosphorus, upon exposure to O_2 or NO , to form $P=O$ groups. This result establishes the presence, before the reaction, of phosphine groups in the plasma polymer. TAPPP films also show some small, irreversible mass gain upon exposure to CO , which is probably the result of CO adsorbed on the film.

The reactions of TAPPP with $Fe(CO)_5(g)$ and $Ni(CO)_4(g)$ proceed by a different chemical mechanism than with O_2 , NO , or CO . The reaction of the TAPPP film with $Ni(CO)_4$ clearly involves complexation of the phosphine moiety with Ni . The reaction differs significantly from previously studied surface- $Ni(CO)_4$ interactions, where such reactions did not occur. For example, Parkyns³⁸ and Bjorklund and Burwell³⁹ examined the reaction and decomposition of $Ni(CO)_4$ on silica and alumina surfaces by means of IR spectroscopy. It was concluded that the $Ni(CO)_4$ lost all four CO ligands, which effectively formed islands of nickel metal aggregates with CO absorbed on the surface. Although some of the Ni was oxidized by surface hydroxyl groups, some metallic $Ni(O)$ remained as indicated by formation of $Ni(CO)_4$, without concurrent CO_2 generation, upon exposure of the supported Ni to CO .

The use of derivatized surfaces to promote a uniform dispersion of Ni has also been recently studied. The most common modification is the phosphination of polystyrene crosslinked with 2% divinylbenzene.⁴⁰ These phosphinated surfaces coordinate $Ni(O)$ complexes through the use of phosphine ligands. In theory, since the Ni coordinates to a ligand, which is uniformly dispersed throughout the polymer, the Ni is also dispersed uniformly. The bound phosphine ligands were varied to allow the formation of Ni complexes coordinated to one or two phosphine ligands. The temperatures for decarbonylation of the $Ni(CO)_{4-n}(\text{phosphine})_n$ complexes were measured by observing the liberation of CO as a function of temperature. The CO was liberated at $150^\circ C$ for monosubstituted and $200^\circ C$ for disubstituted Ni complexes. The metal carbonyl phosphine complex was reformed upon exposure of the decarbonylated complex to CO gas. The IR spectra for the mono- and disubstituted compounds indicated a symmetry lower than T_d , since two bands were observed. The bands indicated that the decomposition product of the reaction of $Ni(CO)_4$, and the surface [i.e., $Ni(CO)_{4-n}(\text{phosphine})_n$] was reformed.

These results allow a broad interpretation of the reaction of $Ni(CO)_4$ with the TAPPP surface and its subsequent reaction upon exposure to oxygen in the atmosphere. There are three steps that occur in

the reaction of $Ni(CO)_4$ with TAPPP. First, the $Ni(CO)_4$ undergoes a substitution reaction with a phosphine ligand displacing a carbonyl ligand. Second, the substituted $Ni(CO)_3(\text{phosphine})$ is decarbonylated over time by thermal decomposition or oxidation of the nickel, and third, the nickel is oxidized by oxygen upon exposure to ambient air. Evidence to support this three-step process is summarized below.

The $Ni(CO)_4$ substitution reaction is suggested by observation of noncondensable CO remaining in the reaction chamber after exposure of TAPPP to $Ni(CO)_4$. The noncondensable CO pressure is equivalent to that resulting from 4.0×10^{-4} mol of CO , and is observed after reaction of $Ni(CO)_4$ with approximately 2.0×10^{-4} mol of P in TAPPP. Unfortunately, a portion of this CO is present (in unknown concentration) in the $Ni(CO)_4$ as introduced, thereby precluding quantitative conclusions regarding Ni loading of the TAPPP film and the degree of substitution of $Ni(CO)_4$. Such information can be obtained, however, from ESCA and FTIR data. ESCA results, presented in detail elsewhere,¹⁴ demonstrate that there is one Ni atom per 3 phosphorus atoms at the surface of the preparation. The IR spectrum (Fig. 5) obtained for these samples immediately following the reaction shows that both mono- and disubstituted nickel phosphine carbonyl species are formed. The bands at 2048 and 1990 cm^{-1} indicate a monosubstituted nickel carbonyl while the bands at 1943 , and the lower portion of the band at 1990 cm^{-1} point to the presence of disubstituted nickel carbonyl species.⁴¹ These carbonyl bands are subsequently lost upon exposure to air over a period of 24 to 48 hrs. This loss in carbonyl bands corresponds to the decarbonylation of the substituted nickel carbonyl compound which occurs as the nickel is oxidized from $Ni(O)$ to $Ni(II)$. Such oxidation is also indicated by the ESCA analysis.¹⁴

The oxidation of the nickel compound can occur by reaction with atmospheric O_2 or via a more complex route involving the plasma polymer. This mechanism is suggested by previous work with $Ni(CO)_4$ on support surfaces.^{38,39,41,42} Recall that $Ni(CO)_4$ is decarbonylated upon exposure to alumina at room temperatures. The last carbonyl ligand requires some heat applied to the compound before it is totally removed. This heat is necessary, in theory, to mobilize surface hydroxyl groups which oxidize the zero valent nickel. It appears that a similar mechanism is acting in the TAPPP. It is well established that plasma polymers have a significant concentration of unreacted radicals in the film after glow discharge.¹⁸⁻²⁴ The presence of radical groups

in the TAPPP is implied by the rapid and permanent mass gain of the polymer films when exposed to oxygen. The film radicals will also react with atmospheric oxygen. This produces a high surface concentration of oxidizing species on the plasma polymer surface. These oxidizing species can then oxidize nickel that is bound to the phosphine groups in the plasma polymer, which results in decarbonylation. The decarbonylation is not indicative of the breaking of the nickel phosphine bond. The synthesis of Ni(II) phosphine complexes is well documented⁴³ and Ni(II) complexes have been formed with polymer supports with phosphine ligands.⁴⁴

CONCLUSIONS

An insoluble triallylphosphine plasma polymer (TAPPP) is formed by introduction of triallylphosphine (TAP) into a glow discharge. The plasma polymer contains a high concentration of C=C and reactive phosphine groups. The latter groups have been shown to react with O₂ and NO to form the phosphine oxide moiety, and with Ni(CO)₄ and Fe(CO)₅ to form the respective phosphine-metal carbonyl complex. In such complexes, Ni and Fe are bound to the plasma polymer network via coordination to phosphorus.

The demonstrated permeability of this phosphine group, containing plasma polymer to reactive transition metal compounds implies that TAPPP can be a precursor to a variety of metal-TAPPP complexes prepared by impregnation and simultaneous complexation.

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