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Formation of Plasma Polymer Thin Films Containing Reactive Metal Chelate Sites

J. M. Skelly,[1a] N. C. Morosoff,*[1b] V. T. Stannett,[1c] and A. L. Crumbliss*[1a]

The Department of Chemistry, Duke University, Durham, North Carolina 27708; The Department of Chemical Engineering and Graduate Center for Materials Research, University of Missouri—Rolla, Rolla, Missouri 65401; and the Camille Dreyfus Laboratory, Research Triangle Institute, PO Box 12194, Research Triangle Park, North Carolina 27709

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We report here the successful incorporation of chemically active Co^{2+} and Ni^{2+} centers into plasma polymer thin films. Metal center incorporation was accomplished by simultaneous plasma polymerization of sublimed Co^{2+} or Ni^{2+} complexes with gaseous "comonomers" or Ar. The metal complexes include *N,N'*-bis(salicylidene)-1,2-phenylenediaminecobalt(II) (CoSalophen), *N,N'*-bis(salicylidene)ethylenediaminecobalt(II) (CoSalen), *N,N'*-bis(3-fluorosalicylidene)ethylenediaminecobalt(II) (CoFluomine), *meso*-tetraphenylporphyrinatocobalt(II) (CoTPP), *meso*-tetraphenylporphine (TPP), and *meso*-tetraphenylporphyrinatonickel(II) (NiTPP). Modification to the metal complex structure was observed by IR and UV–vis spectroscopies. IR spectra of plasma polymer films containing the Schiff's base complexes, prepared using Ar as a carrier gas, contained a band at 2190 cm^{-1}, which can be attributed to nitrile group formation, and would necessarily result from destruction of the Co^{2+} inner coordination sphere. This type of bond cleavage was eliminated by the use of polymerizable "comonomers" instead of Ar. IR spectra of CoFluomine films exposed to pyridine vapor indicate that pyridine is chemically bound within the films. Gravimetric analysis of the CoFluomine films revealed that the pyridine is bound in a 1:1 Co:pyridine ratio, suggested that the metal center remains chemically active. IR spectra of plasma polymer films containing the porphyrin complexes contain evidence for modification to the phenyl and pyrrole rings, indicating that the complexes may be attached to the plasma polymer matrix at these sites. UV–vis spectra of plasma polymer films containing CoTPP contain a band at 610 nm which may be due to chlorin formation, which is consistent with pyrrole ring substitution. Plasma polymer film solubility in toluene was used to estimate the extent of cross-linking within the films. Solubility was found to generally increase with increased concentration of complex in the films. This is discussed in terms of increased deposition rate and decreased glow discharge pressure during synthesis of films with higher metal chelate content.

Introduction

As a part of our overall program of synthesizing and characterizing metal-containing plasma polymers[2] we have been investigating the incorporation of cobalt(II) chelates into plasma polymer thin films. Specifically, we are interested in determining the experimental parameters that allow three fundamental conditions to be met: (1) minimal destruction of metal chelates by the plasma; (2) accessibility of metal centers within the plasma polymer to small molecules (ligands); (3) retention of chemical reactivity of the metal center. It has been demonstrated that preservation of the essential features of monomer structure is possible while depositing a plasma polymer if the monomer molecule undergoes a minimal interaction with the plasma.[2g,h,3] Typically, this is accomplished by the use of low power levels, high pressures (to minimize the density of high-genergy electrons), and high flow rates (to minimize residence time in the plasma).

The retention of monomer structure has been reported for the plasma polymerization of copper phthalocyanine (CuPc)[3] and for nickel and lead phthalocyanines (NiPc and PbPc, respectively.[4] CuPc rapidly sublimed through an Ar plasma has a high degree of structure retention as evidenced by UV–vis spectroscopy.[3] The material formed from the polymerization demonstrated chemical and electrical properties associated with monomeric CuPc, such as the reduction of solvated viologens under visible light, yet was insoluble in both pyridine and concentrated sulfuric acid, which are good solvents for monomeric CuPc. NiPc and PbPc were sublimed into a plasma without the reported use of additional carrier gases.[4] The resulting films showed excellent retention of chelate structure according to FTIR and UV–vis spectroscopies. NiPc and PbPc films deposited onto electrode surfaces demonstrated

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(1) (a) Duke University. (b) University of Missouri—Rolla. (c) Research Triangle Institute.

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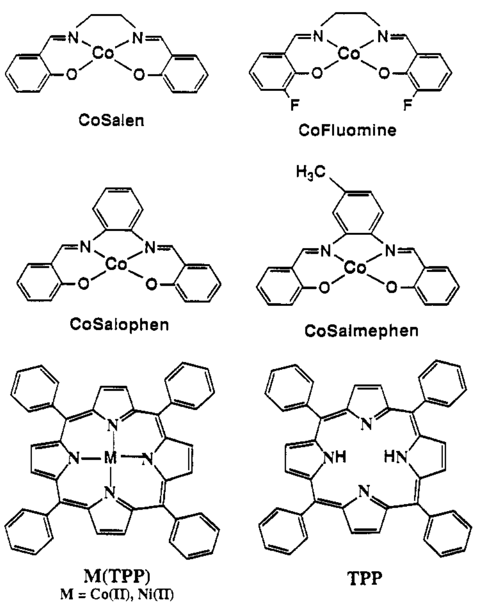

Figure 1. Structures of transition metal (Ni(II), Co(II)) complexes prepared as sublimed films and incorporated into plasma polymer thin films.

excellent sensitivity to NO_2 at ppm concentrations in air,[4] and electron diffraction patterns obtained from transmission electron microscopy did not show any crystalline structure. The reaction of Ni and Pb centers with NO_2 implies that these sites are directly accessible to gases diffusing through the film. In addition, work in this laboratory[2i,j] has shown that Ni incorporated into plasma polymer films will react with CO and NO gases to form $Ni(CO)_xL_y$ and $Ni(NO)_xL_y$ complexes. These reactions also imply the accessibility of the metal centers to permeant molecules.

We report here the incorporation of nickel(II) and several cobalt(II) chelates (shown in Figure 1) into plasma polymer thin films using either an Ar plasma or a polymerizable carrier gas ("comonomer"). Both types of plasma polymer films are composed of a plasma polymer network (matrix) incorporating the metal chelates. In the case of the Ar plasma, the plasma polymer matrix is composed solely of metal chelate fragments. In films prepared using a "comonomer", it is likely that the plasma polymer matrix consists mostly of reacted comonomer fragments. Our techniques described here permit the preparation of new plasma polymer thin-film materials with metal sites which maintain the inner coordination shell structure of the parent chelate monomer. This means that, in principle, plasma polymer thin films can be prepared with metal sites in a controlled chemical environment and with a specific reactivity.

Experimental Section

Materials. The complexes *meso*-tetraphenylporphyrinatocobalt(II) (CoTPP; λ_{max} = 409 and 523 nm), *meso*-tetraphenylporphine (TPP; λ_{max} = 415 nm), and *meso*-tetraphenylporphyrinatonickel(II) (NiTPP) were used as purchased from Strem Chemical Co. Cobaltous acetate tetrahydrate was used as obtained from Fisher Chemical Co. *o*-Phenylenediamine and 3-fluorosalicylaldehyde were used as purchased from Aldrich Chemical Co. Ethylenediamine was used as obtained from Eastman Chemical Co. Salicylaldehyde, pyridine, and 1-methylimidazole (1-MeIm) were purchased from Aldrich Chemical Co. and distilled prior to use. O_2, N_2, Ar, and *trans*-2-butene (99.0%) were purchased from Linde Industrial Gases and used without further purification. NaCl crystals were purchased from International Crystal Laboratories.

N,N'-Bis(salicylidene)-1,2-phenylenediaminecobalt(II) (CoSalophen), *N,N'*-bis(salicylidene)-3,4-diaminotoluenecobalt(II) (CoSalmephen), *N,N'*-bis(salicylidene)ethylenediaminecobalt(II) (CoSalen), and *N,N'*-bis(3-fluorosalicylidene)ethylenediaminecobalt(II) (CoFluomine) were synthesized by a variation of published methods.[5] CoSalen and CoSalophen monohydrate were also purchased from Aldrich Chemical Co. and used as obtained. Metal chelates were characterized by IR spectroscopy and purity was determined by elemental analysis. CoSalophen: % Calcd: C, 64.35; H, 3.78; N, 7.51. % Found: C, 64.30; H, 3.84; N, 7.33. CoSalmephen: % Calcd: C, 65.12; H, 4.16; N, 7.23. % Found: C, 65.06; H, 3.92; N, 7.53. CoSalen: % Calcd: C, 59.09; H, 4.34; N, 8.61. % Found: C, 58.92; H, 4.49; N, 8.60. CoFluomine: % Calcd: C, 53.20; H, 3.32; N, 7.75. % Found: C, 52.52; H, 3.24; N, 7.65. ν_{CF} = 1232 cm^{-1}.

Methods and Equipment. Thin-film preparations were carried out in a continuous flow, inductively coupled plasma reaction chamber described earlier.[2g,h] The bottom of the chamber was sealed to an aluminum base plate by means of an O-ring. A tantalum heating boat inside the reactor was connected to two copper wire terminals which passed through two ports in the base plate. Current to the copper terminals was regulated using a variable transformer. Two threaded ceramic plugs insulated the copper terminals from the base plate and a series of Swagelok and Cajon-ultratorr fittings provided a vacuum tight seal around the terminals. A molybdenum shield could be moved over the heating boat to prevent sublimation into the plasma and thereby provide precise deposition times.

Equipment used for plasma generation was a Tegal 300-W rf generator, operating at 13.56 MHz, with a matching network and a Bird Electronics Model 4410 wattmeter. Infrared spectra were obtained directly from the polymer films using an Analect FX-6200 FTIR spectrophotometer. UV–vis spectra were measured directly from the polymer films using a Beckman ACTA III spectrophotometer. Pressures in the plasma reactor and in the receiving side (low-pressure side) of the permeation manifold were measured using MKS Baratron differential pressure transducers with 1- and 10-Torr pressure ranges, respectively. Pressures in the high-pressure side of the permeation manifold were measured using a mercury manometer. Gravimetric analyses were performed using a Cahn 2000 thermostated controlled-atmosphere electrobalance.

Plasma polymer thin films were prepared as follows. The metal complex was added to the heating boat (ca. 100 mg of metal chelate) and the reactor was sealed and evacuated. The Schiff's base chelates (CoSalen, CoSalophen, CoSalmephen, CoFluomine) were mixed with cobalt powder prior to adding to the heating boat which was covered with a molybdenum shield (4:1 w/w, cobalt:complex). After the reactor had reached a constant base pressure (ca. 1 mTorr) the comonomer or Ar was introduced at the desired flow rate (0.5–0.6 cm^3/min), followed by the heating of the complex in the tantalum heating boat. Both current and potential through the tantalum heating boat were monitored during polymerization and could be used to regulate the sublimation rate of the metal complex. Metal chelate loading was controlled by varying the delivery rate of metal chelate to the plasma by means of the power input to the heating boat. This, in turn, was controlled by means of a variable transformer; the voltage and current to the boat were measured. The percent weight loading of metal chelate was measured directly in the film as described below. Reactor pressures were maintained between 2 and 20 mTorr to permit adequate deposition rates of the metal complexes onto a substrate 6 cm from the boat. When the desired sublimation rate (e.g., 1 μg/(cm^2 min); the desired sublimation rate depends on the desired film loading) of the sample was achieved, the rf power supply was turned on (2–8 W rf power), initiating a glow discharge (plasma). The molybdenum shield was then removed, allowing the cobalt chelate to sublime into the plasma. The cobalt chelate plasma polymer was allowed to deposit for several minutes (15–20 min). The amount of plasma

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polymer deposited ranged from 20 to 100 μg/cm^2. After the deposition period (15–20 min), the molybdenum shield was moved over the heating boat again and the plasma generator was turned off. Film samples prepared by the above method are referred to as plasma polymer films, while those prepared similarly but without plasma interaction and a comonomer or Ar are referred to as sublimed films. Plasma polymer and sublimed films were deposited onto NaCl windows and glass slides to obtain all FTIR and UV–vis spectra, respectively, by transmission. Films were also deposited onto Al foil substrates in order to measure mass thickness gravimetrically. IR absorbances for CoSalophen (748 cm^{-1}), CoSalmephen (748 cm^{-1}), CoSalen (1530 cm^{-1}), CoFluomine (1319 cm^{-1}), CoTPP (749 cm^{-1}), NiTPP (749 cm^{-1}), and H_2TPP (749 cm^{-1}) were plotted as a function of sublimed film *mass thickness* (μg/cm^2). These plots were used to determine the percent of complex in plasma polymer films according to the following equation:

$$(h_l/m_s)/l_l \times 100 = \text{wt }\%$$

where m_s is the slope from the appropriate plot of IR absorbance as a function of sublimed film mass thickness in cm/(μg cm^{-2}), h_l is the height of the corresponding IR absorbance from the spectrum of the plasma polymer film in cm (7.6 cm/absorbance unit), and l_l is the mass thickness of the plasma polymer layer in μg/cm^2. The weight percent is the ratio of the *effective* mass thickness for the complex in the film, to the mass thickness of the entire plasma polymer layer. Therefore, the percentage of metal complex, in all plasma polymer films reported here, is expressed as a weight percent.

Results and Discussion

The cobalt chelates shown in Figure 1 were selected for several structural characteristics. The chelates are stable under ambient conditions, which allows for synthesis without concern for special handling of the plasma polymer films. In addition, the rate of metal dissociation from the chelates is insignificant. Peripheral groups on the ligands (see Figure 1) serve as possible activation sites in the plasma, which may provide binding sites to the plasma polymer matrix under less harsh plasma conditions. Also, aromatic rings in the ligand structure promote retention of structure during polymerization.[2g]

Schiff's Base Complexes Plasma Polymerized in an Ar Plasma. Initially, plasma polymer films were prepared using Ar to support the plasma rather than using a polymerizable "comonomer". Modification to the metal chelate structure was monitored through IR spectrsocopy. Spectra of CoSalophen and CoSalmephen films prepared in a continuous Ar plasma contained several differences from IR spectra of the corresponding sublimed films (films prepared without plasma interaction). Most notable is the appearance of two new bands at 2920 and 1377 cm^{-1} which are believed to be indicative of new methyl group stretching and deformation vibrations[6] not present in the original compound. This indicates partial destruction of the complexes by the plasma, since new methyl groups would necessarily be formed from fragmented metal complex molecules in films produced using Ar plasmas. The new bands at 2920 and 1377 cm^{-1} tend to be more pronounced for plasma polymer films produced at higher plasma powers (10–30 W). However, at very high plasma powers (>30 W) IR spectra exhibited a large degree of broadening and blending of all bands in the spectrum, indicative of extensive modification and destruction of the metal chelate by the plasma.

Infrared spectra of the above plasma polymers contained another new band at 2190 cm^{-1}, which is also more pronounced for plasma polymer films produced at higher plasma powers (>10 W). This band is consistent with the C–N stretching frequency of a nitrile group and is common in plasma polymers produced from monomers containing nitrogen atoms, such as vinylpyridine.[6] In the case of the Schiff's base complexes, the only site available to produce a nitrile group is the imine moiety. Bond cleavage to produce the nitrile group would most easily occur at either the *N*-phenyl bond (in the case of CoSalophen and CoSalmephen) or the ethylene bridge (in the case of CoSalen and CoFluomine). Such a bond cleavage would likely cause the loss of the metal chelate's square planar geometry.

Work in our laboratory[2g,h] has shown that CoSalen incorporated into plasma polymer films will retain its inner coordination shell when the films are prepared using a pulsed Ar plasma technique. A pulsed plasma utilized an on/off (t_{on}/t_{off}) duty cycle for the RF power supply. The pulsed plasma conditions used for CoSalen are as follows: t_{on} = 6 ms, t_{off} = 55 ms, rf power = 5 W; CoSalen sublimation rate = 4.8 μg/(cm^2 min), 17% CoSalen (w/w); mass thickness = 55.10 μg/cm^2. CoSalen, when incorporated into a plasma polymer film prepared in a pulsed Ar plasma, was found[2g,h] to form microcrystalline domains and to retain its inner coordination sphere, as is evident from its O_2 binding abilities. Crystalline CoSalen is known to bind O_2 reversibly.[5] O_2 binding in the plasma polymer films was indicated by the appearance of a band at 1271 cm^{-1} in IR spectra measured under O_2 without prior exposure to pyridine vapor. The band was not present in spectra measured under N_2 and is consistent with an O–O stretching frequency for O_2 bound to CoSalen.[7]

Plasma Polymer Films Prepared Using Comonomers. As an alternative to Ar, polymerizable carrier gases (*trans*-2-butene, ethylene, cyclooctene, hexamethyldisilazane, hexamethyldisiloxane) were used to support the plasma during metal chelate polymerization. Infrared spectra of metal complex plasma polymer films prepared using hexamethyldilazane and hexamethyldisiloxane were similar to spectra of films prepared with the metal complexes and hydrocarbon comonomers. However, they also displayed new bands at 1250, 1021, 914, and 834 cm^{-1}. The IR spectra of pure hexamethyldisilazane plasma polymer films (no metal complex) also displayed these same bands, and they are attributed to Si-containing groups in the polymer. The large number and strong absorbances of these bands made IR characterization of these films quite difficult, since they obscurred many of the metal complex bands. Therefore, results presented in this work will be limited to films prepared using hydrocarbon comonomers. Most data reported here were collected using the *trans*-2-butene comonomer, which has vary weak IR absorbances in the regions where metal complex loading was measured.

The simultaneous deposition of the metal chelates with a plasma-polymerized "comonomer" allows for the use of continuous rf power. When plasma polymer films were formed using these "comonomers" a much more pronounced increase in band intensity at 2920 and 1377 cm^{-1} (attributable to methyl group deformation) was observed in IR spectra of the films, when compared to similar films prepared using Ar plasma. This apparently larger degree of methyl group formation in these plasma polymers stems from the use of the polymerizable gases. The polymer-

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(7) Murry, K. S.; van der Bergen, A.; Kennedy, B. J.; West, B. O. *Aust. J. Chem.* **1986**, *39*, 1479.

izable gases support the plasma during the synthesis of these films and provide the bulk of molecular fragments in the plasma, as well as the material for the plasma polymer matrix. Also, for these films, IR band formation at 2190 cm^{-1} was very small or absent entirely for powers as high as 7 W, indicating that bond cleavage near the imine moieties has been eliminated by use of polymerizable carrier gases, and that the inner coordination sphere chelate structure is maintained.

CoSalen plasma polymers, prepared by the above method, have been shown[2g,h] to retain the reversible O_2 binding ability of the CoSalen monomer, indicating the retention of the metal chelate inner coordination sphere. CoSalen plasma polymers were produced using cyclooctene (cyclooctene flow rate = 0.20 cm^3/min, 17% CoSalen (w/w), mass thickness = 55.10 μg/cm^2, CoSalen sublimation rate = 4.8 μg/(cm^2 min), rf power = 5 W continuous power). Upon exposure to pyridine vapor (48 h) and subsequently O_2 (2 h), IR spectra of the CoSalen/cyclooctene plasma polymer films contained new bands at 1145 and 1127 cm^{-1}, which disappeared upon purging with N_2. These two bands have been attributed to O–O IR stretching frequencies for O_2 coordinated to cobalt.[7]

CoSalen has also been successfully incorporated into *trans*-2-butene plasma polymers without loss of chemical activity of the metal center, such as O_2 binding.[2g,h] CoSalen/*trans*-2-butene plasma polymer films (rf power = 5 W continuous, CoSalen sublimation rate = 2.8 μg/(cm^2 min), *trans*-2-butene flow rate = 0.51 cm^3/min, 47% CoSalen (w/w), mass thickness = 141.06 μg/cm^2) were exposed to pyridine vapor (30 min) and subsequently O_2 (1 h). Infrared spectra measured in O_2 contained a new band at 1134 cm^{-1}, which has been attributed to an O–O stretching frequency for cobalt bound O_2.

CoFluomine was found to maintain its inner coordination sphere when incorporated into *trans*-2-butene plasma polymer thin films, as was evident from their ability to bind to the axial ligand, pyridine, as the monomeric parent compound does. CoFluomine/*trans*-2-butene plasma polymer films exposed to pyridine vapor in Ar exhibited a 22% weight increase, consistent with a 1:1 (Co:pyridine) ratio. Infrared spectra of CoFluomine plasma polymer films exposed to pyridine vapor in Ar contained several differences from films that were not exposed. Most notable is the shift in position of the band at 1232 cm^{-1}. This IR band, as well as those associated with pyridine, remained after 24 h of purging with Ar. The gravimetric analysis and IR data are consistent with the conclusion that pyridine is chemically bound within the polymer at the cobalt sites.

After exposure to pyridine, further exposure of CoFluomine/*trans*-2-butene plasma polymer films to O_2 caused no additional weight gain. Apparently, the cobalt center remains accessible to pyridine, but modification to the ligand structure has diminished or eliminated the reversible O_2 binding abilities associated with the parent compound.[5]

Structural changes to the CoFluomine structure are evident from IR spectra. The most notable difference between spectra of CoFluomine/*trans*-2-butene plasma polymers and those of CoFluomine sublimed films is the dramatic decrease in intensity in the band at 1232 cm^{-1} (Figure 2) which is present in spectral of the sublimed film. The change was observed for plasma polymers formed over a range of several plasma powers (2–10 W). This band is consistent with a C–F stretching frequency, and its decrease upon plasma polymerization indicates the cleavage of a significant number of the fluorine–carbon bonds, which may be expected for fluorinated hydrocarbons.[8]

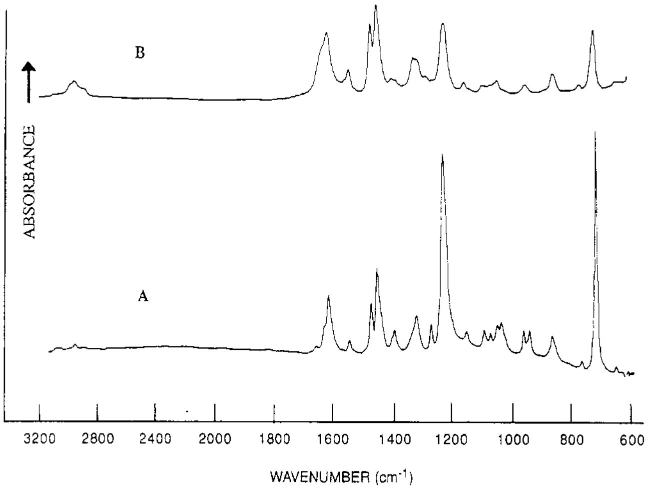

Figure 2. FTIR absorbance spectra of CoFluomine prepared as (A) a sublimed film (mass thickness = 91.75 μg/cm^2, measured under Ar, 1 atm) and (B) a plasma polymer film (mass thickness = 63.16 μg/cm^2, deposition rate = 5.26 μg/(cm^{2}min), *trans*-2-butene flow rate = 1.16 cm^3/min, rf power = 3.0 W, P_g = 14 mTorr, P_m = 8.6 mTorr, 57% CoFluomine (w/w)). Note the dramatic decrease in the band at 1232 cm^{-1} relative to bands near 1500 cm^{-1}.

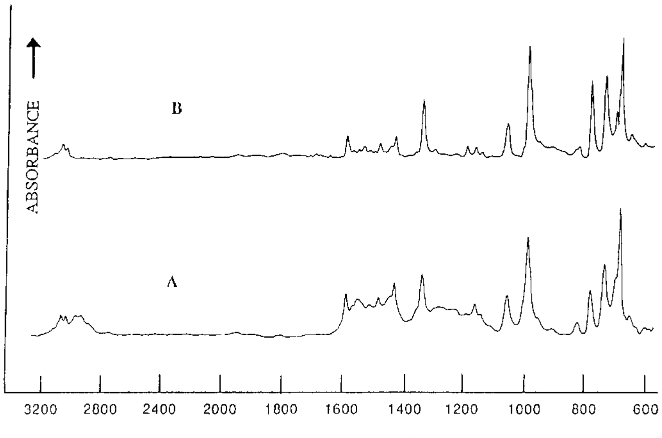

Figure 3. FTIR absorbance spectra. (A) CoTPP/*trans*-2-butene plasma polymer film (mass thickness = 47.11 μg/cm^2, deposition rate = 3.1 μg/(cm^{2}min), rf power = 2.0 W, flow rate = 0.59 cm^3/min, P_m = 6.2 mTorr, P_g = 13.0 mTorr, 63% CoTPP (w/w)). (B) CoTPP sublimed film (mass thickness = 75.27 μg/cm^2).

Porphyrin Complexes. CoTPP was found to maintain its structure upon incorporation into plasma polymer films. Compared to those of CoTPP sublimed films, IR spectra of plasma polymer films (made with ethylene or *trans*-2-butene) contained new broad bands at 1300 and 1500 cm^{-1} and a larger band at 2920 cm^{-1} (see Figure 3). However, these bands are attributed to the plasma polymer matrix as described above for the plasma polymers containing Schiff's base complexes. The band at 2190 cm^{-1}, seen in IR spectra to Schiff's base complex plasma polymers, was not observed in spectra of CoTPP plasma polymer films, even those prepared at 10 W rf power. This

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(8) d'Agostino, R. In *Plasma Deposition, Treatment, and Etching of Polymers*; d'Agostino, R., Ed.; Academic Press: New York, 1990; p 95.

indicates that there is no formation of nitrile groups and therefore no C–N bond cleavage at the pyrrole nitrogen atoms. This suggests that the porphyrin complex is much more robust in the plasma than the Schiff's base complexes.

A minimal amount of substitution to the CoTPP phenyl rings may be present in the plasma polymer, as indicated by the changes in band intensities near 700 cm^{-1}, which have been assigned to phenyl ring deformation.[9] Also, some substitution has occurred on the pyrrole rings as evidenced by the slight decrease in intensity of the band at 1000 cm^{-1}, which has been assigned as a combination of the C–H rock (pyrrole) and C_β–C_β stretch (pyrrole) frequencies[9,10] (C_β refers to the outermost carbon atoms of the pyrrole ring, i.e., β position to the pyrrole nitrogen). Substitution at the pyrrole rings implies that the porphyrin may be bound to the plasma polymer matrix through these sites.

UV–vis spectra of CoTPP plasma polymer films indicate that the Co center is in the 2+ state, since the λ_{max} values match those of CoTPP benzene solutions, as well as literature reports.[11,12] UV–vis spectra of CoTPP/*trans*-2-butene plasma polymers on glass slides exhibited λ_{max} values of 408, 526, and 612 nm. The band at 612 nm can be attributed to cobalt chlorin complexes within the polymer film.[13] This is consistent with the IR evidence for pyrrole ring substitution, since the chlorin structure is a porphyrin macrocycle with a partially reduced pyrrole ring.[13]

We have previously demonstrated that plasma polymer films containing CoTPP may bind O_2 reversibly,[14] which further indicates that the CoTPP macrocycle structure and particularly the Co^{2+} inner coordination sphere are maintained upon incorporation into plasma polymer films. When films were exposed to 1-methylimidazole (1-MeIm) vapor in Ar and then subsequently exposed to O_2, IR spectra exhibit an absorption band at 1100 cm^{-1}, which is not present in spectra of sublimed films or 1-MeIm alone.[14] We have attributed this band to an O–O stretching frequency[15–17] of cobalt bound O_2. In addition, UV–vis spectral changes associated with similar treatment of CoTPP plasma polymer films is also consistent with reversible O_2 binding. When the films were exposed to 1-MeIm vapor in N_2, and subsequently O_2, the band at 526 nm in the UV–vis spectrum reversibly shifted to 528 nm (1-MeIm in N_2) and then to 547 nm (O_2). This change was reversed by heating the sample under N_2 at 130 °C.

For comparison, the nonmetalated porphyrin, H_2TPP, was incorporated into *trans*-2-butene plasma polymer films. Modification to the TPP structure by the plasma was examined using infrared spectroscopy and several differences were found between spectra of H_2TPP/*trans*-2-butene plasma polymer films and those of H_2TPP prepared as sublimed films. A band appearing at 3310 cm^{-1} (N–H stretch) in spectra of H_2TPP sublimed films has been replaced in H_2TPP/*trans*-2-butene plasma polymer films by a large broad band centered near 3400 cm^{-1} (see Figure 4), indicating substitution on the rings containing the N–H groups which are present in the free ligand, H_2TPP. In addition, the bands at 962 cm^{-1} (C–H(pyrrole) rock)[18] and 1470 cm^{-1} (C=N stretch)[18] have significantly decreased in intensity relative to other bands (e.g., 748 cm^{-1}), indicating substitution at the pyrrole rings. The band at 1348 cm^{-1}, present in spectra of sublimed films of H_2TPP, is no longer distinguishable in the IR spectrum of the plasma polymer film; this is indicative of pyrrole[18,19] or phenyl ring[19] substitution. These spectral changes suggest significant modification to the pyrrole ring in H_2TPP during plasma polymerization and therefore binding of the porphyrin to the polymer matrix is likely to be occurring at these sites. Spectra of H_2TPP plasma polymer films did not contain a band at 2190 cm^{-1} (as seen in the case of Schiff's base plasma polymers prepared in Ar), indicating that the modification is not extensive enough to form nitrile groups, which would necessarily involve pyrrole ring opening.

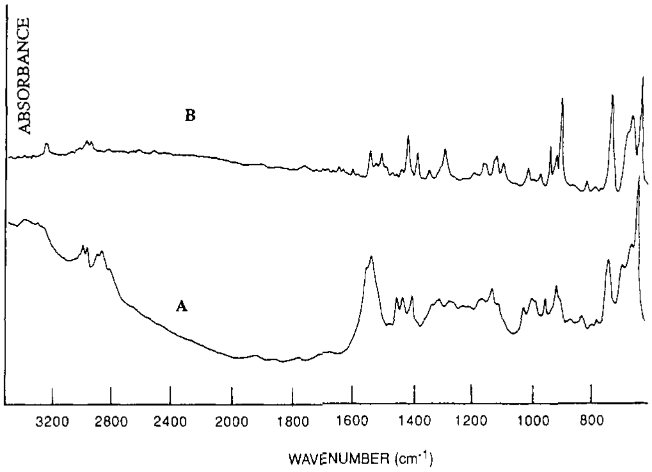

Figure 4. FTIR absorbance spectra of H_2TPP deposited as (A) a TPP/*trans*-2-butene plasma polymer (mass thickness = 74.44 μg/cm^2, deposition rate = 6.7 μg/(cm^{2}min), flow rate = 0.54 cm^3/min, rf power = 7.0 W, P_m = 6.9 mTorr, P_g = 6.0 mTorr, 31% TPP (w/w)) and (B) a sublimed film (mass thickness = 24.28 μg/cm^2).

In addition to the above comparison to H_2TPP, a metalated porphyrin, NiTPP, was also incorporated into a plasma polymer film. NiTPP is not known to bind axial ligands such as O_2 and 1-MeIm and was used here to eliminate misleading spectral anomalies associated with metal chelate plasma polymer incorporation that may be misinterpreted as O_2 or axial base binding. IR spectra of plasma polymer films containing NiTPP were nearly identical to those containing CoTPP, due to their similar structures. Modification to the NiTPP structure was similar to that described above for CoTPP. No spectral evidence for axial base or O_2 binding was observed for films containing NiTPP.

Glow Discharge Pressure and Thin-Film Solubility. Plasma parameters during deposition and changes therein in response to changes in operating variables can

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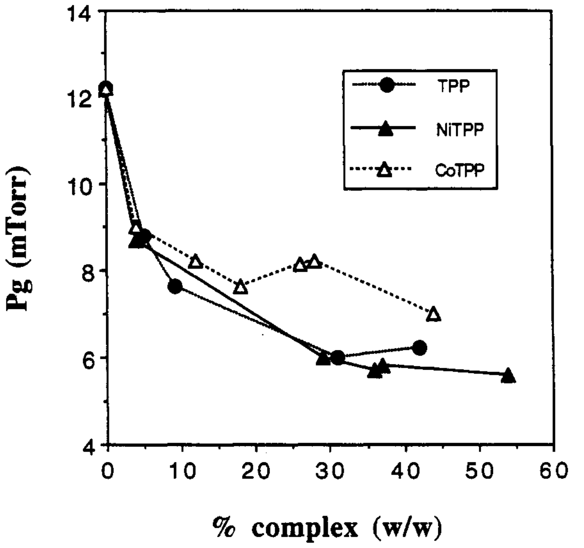

Figure 5. Plot of reactor pressure during glow discharge, P_g, as a function of percent metal complex (film loading) in *trans*-2-butene plasma polymer films (P_m = 6.7 mTorr, rf power = 7.0 W, flow rate = 0.55 cm^3/min, mass thickness approximately 70.00 μg/cm^2).

provide information regarding intermediates in the plasma deposition process. One such parameter is the steady state pressure in the glow discharge, P_g (attained within 20 s of plasma initiation),[20] which was found to decrease with increasing percent complex loading (w/w) in the film (see Figure 5). The glow discharge pressure was highest when no complex was being polymerized (12.2 mTorr) and decreased rapidly with successively higher loaded films, i.e., with successively higher delivery rate of metal chelate to the plasma, eventually reaching about 7.0 mTorr for a film with 44% CoTPP (w/w). Even lower values of P_g were registered for high delivery rates of TPP and NiTPP. The pressure of the monomer without plasma, P_m, was kept constant for all of these polymerizations, at approximately 6.7 mTorr.

The lower values of P_g observed for plasma polymer films prepared with higher metal complex loadings provided information concerning the process of polymerization. The gas phase of the plasma (supported by a comonomer) contains reactive species such as radicals and ions.[21] Presumably, on sublimation of metal complexes into the gas phase and the plasma, the reactive species may bond to suitable sites on the porphyrin ring, such as double bonds, which may have been activated by the plasma in the gas phase or on the film surface.[21] As the concentration of metal complex in the gas phase and on the surface is increased (for increasingly higher loaded films) a greater portion of the fragments is removed from the gas phase and P_g begins to decrease. Consequently, the deposition rate for the higher loaded films is greater due to the larger number of fragments being deposited from the gas phase, as well as the increased amount of porphyrin being sublimed. Figure 6 illustrates how the deposition rate of plasma polymer increases with higher film loading (note that the deposition rate reaches a maximum near a loading of 25% CoTPP). Eventually, P_g reaches a minimum value where the porphyrin concentration in the gas phase and surface is high enough to remove fragments at the same rate that they are produced. In Figure 5, this minimum is reached near a loading of 25% metal complex. Increasing the sublimation rate of the porphyrin past this minimum value will result in the deposition of increasing amounts of porphyrin which do not react with gaseous monomer fragments.

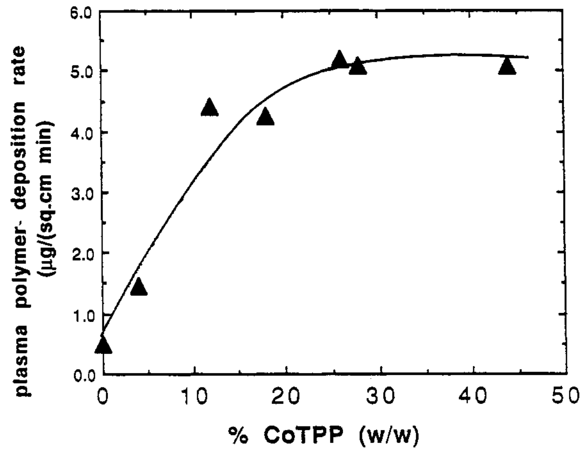

Figure 6. Plot of plasma polymer deposition rate for CoTPP/*trans*-2butene plasma polymer films as a function of percent CoTPP loading (w/w) (rf power = 7.0 W, flow rate = 0.55 cm^3/min, mass thickness is approximately 70.00 μg/cm^2).

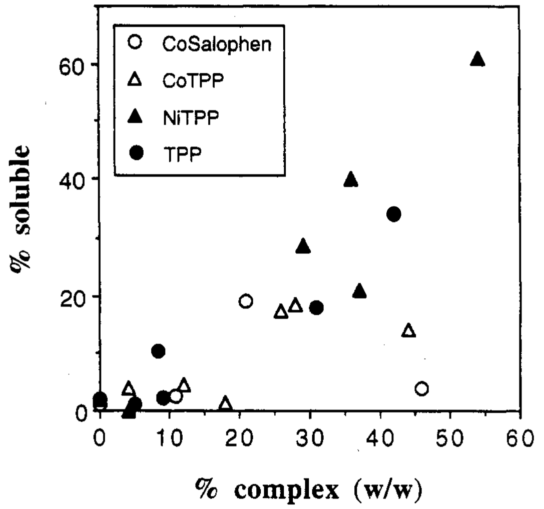

Figure 7. Plot of metal complex/*trans*-2-butene plasma polymer percent solubility in toluene as a function of percent metal complex film loading (*rf* power = 7.0 W, flow rate = 0.55 cm^3/min, mass thickness approximately 70.00 μg/cm^2).

Solubility data for the plasma polymer films are consistent with the above description for higher loaded films. For CoSalophen, CoTPP, NiTPP, and H_2TPP plasma polymer films, solubility of the films was found to generally increase with increasing percent (w/w) metal complex loading in the film (see Figure 7). This is expected if at higher sublimation rates the chelate: (1) is covered quickly due to higher deposition rates, thereby limiting its exposure to plasma at the surface; (2) experiences only a limited degree of interaction with the plasma in the gas phase. The picture that emerges is of a cross-linked matrix (formed from *trans*-2-butene fragments) with some chemical bonds between the matrix and the metal complex moieties. Chemical bonds between metal complex molecules are unlikely. Therefore, as the matrix is diluted and contiguity between metal complex molecules becomes more probable, solubility increases. At a percolation

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threshold for the metal complex phase, a jump in solubility is expected, as seen in Figure 7 near loadings of 25% metal complex. This picture is confirmed by the data presented in Figure 6 and gas-permeability results reported elsewhere.[22] In the latter a discontinuity in the plot of gas permeation versus CoTPP percent loading is found, also at a loading of 25%.[22]

Conclusions

The above evidence indicates that structural integrity, chemical activity, and chemical accessibility can be maintained when the metal complexes described above are incorporated into plasma polymer films. Structural integrity can be promoted by the use of polymerizable carrier gases or "comonomers". The use of a comonomer was found to eliminate the formation of nitrile groups as evidenced by IR spectra of the plasma polymer films. In addition, the use of low rf powers (below 5 W for Schiff's base complexes and below 10 W for porphyrin complexes) decreases the degree of modification to the ligand structure during polymerization. In the case of CoFluomine, however, a significant number of C–F bonds were cleaved during polymerization. Cobalt centers were found to be chemically active and accessible for the complexes incorporated. Electron pair donors which can act as axial ligands, such as pyridine and 1-MeIm, will bind to cobalt centers as indicated by gravimetric analysis and UV–vis and IR spectroscopies.

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