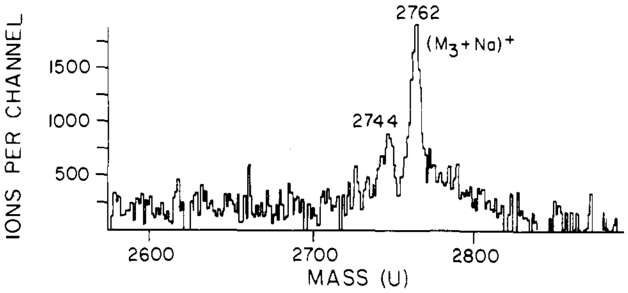

Figure 2. ^{252}Cf plasma desorption positive ion mass spectrum of *N*-acetylperhydropalytoxin, T = 54 000 s.

N-acetylpalytoxin in the same mass region. A prominent peak was observed at M = 2746 u and a smaller peak at 2730 u. Again, no peaks were observed above M = 2900 u. The mass increase of 42 u for the *N*-acetyl derivitive is consistent with the addition of an *N*-acetyl group to palytoxin. If these ions comprise the intact molecule, they are most likely adducts of the form $(M + Na)^+$. To test this, we performed a second experiment on the *N*-acetylpalytoxin where a thin film of the material was electrosprayed over a layer of CsI. When the double layer is activated by a fission fragment, Cs^+ ions are released from the bottom layer, rapidly diffuse through the fission track, percolate through the molecules in the upper layer, and have some probability of forming ion-dipole complexes of the form $(M + Cs)^+$. The result of this experiment is shown in Figure 1c. An additional peak at M = 2856 u is now observed whose mass is 110 u higher than the primary peak. This is precisely the (Cs − Na) mass difference. Thus, the identification of the peaks in the previous spectra as $(M + Na)^+$ adducts is verified. Although the possibility cannot be ruled out that these are fragment ions of a larger molecule, it seems unlikely that this is the case. There is no evidence of higher mass peaks down to the level of 5% of the intensity of the peaks observed. The molecule undoubtedly has multiple sites where an alkali metal ion could attach and the probability is very small that fragmentation would yield a single Na^+-containing fragment with a unique mass independent of the Na-attachment site. From the results of four independent measurements, the molecular weight of the $(M + Na)^+$ adduct of *N*-acetylpalytoxin is 2746.1 ± 0.35 u. The molecular weight of *N*-acetylpalytoxin is, therefore, 2723.1 ± 0.35 u (M_2) and palytoxin, 2681.1 ± 0.35 u (M_1). Since the ^{13}C satellites were not resolved, these masses are isotopically averaged values (C = 12.011 u).[11]

The positive ion spectrum of *N*-acetylperhydropalytoxin is shown in Figure 2. A significant peak is observed at M = 2762 and a smaller peak at 2744 u. Assigning the more intense peak to the type $(M + Na)^+$ gives M = 2739.4 ± 0.4 u (M_3). The mass increase as a result of hydrogenation of *N*-acetylpalytoxin is 16.3 ± 0.6 u suggesting that the parent molecule contains eight double bonds. In all of these samples, there is evidence of a second component of palytoxin with a mass 16–18 u lower than the principal component.[12]

Acknowledgments. We acknowledge the contributions of C. J. McNeal and Dr. S. Hosozawa to these experiments. This work was supported by the National Institutes of Health (GM-26096) (R.D.M.).

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(11) New results recently obtained from chemical degradation and elemental analysis show that the most plausible molecule formula of palytoxin is $C_{121}H_{207-209}N_3O_{61}$.
(12) We have also observed this by means of high pressure TLC and LC.

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Electrically Conductive Polyimide Films Containing Palladium Coordination Complexes

Sir:

Polymers which conduct an electric current have received considerable attention in the recent chemical literature. Although a few polymeric systems such as $(SN)_x$,[1] polyacetylene,[2] and poly(*p*-phenylene)[3] have conducting properties when complexed with electron donors or accepters, the majority do not. The incorporation of conductive fillers into insulative polymers is one of the most common methods for imparting electrical conductivity. To date these fillers have been at rather high concentrations and primarily particulate in nature such as metal and carbon fibers.[4] The doping of polymers with dissolved metal salts for this purpose has received little attention. Success has been marginal where this technique has been applied (e.g., little enhancement in both surface and volume electrical conductivity).[5-8] It should be noted, however, that 20 years ago there was a brief report[9] regarding the incorporation of bis(acetylacetonato)copper(II) into a polyimide which resulted in a significant decrease in volume electrical resistivity (~10^{12} Ω cm). No other reports of this study have appeared in the open literature. We communicate a significant success in this area by reporting the production of palladium-containing polyimide films which exhibit surface and volume resistivities approximately ten orders of magnitude lower than that measured for the polymer alone.

The polyimide precursors selected for this study were 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (BTDA, I) and 4,4′-oxydianiline (ODA, II). Best results were

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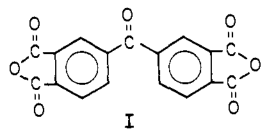
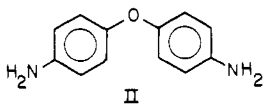
Table I. Palladium Containing BTDA-ODA-Polymer Films

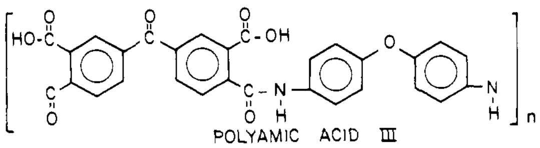
films	volume resistivity, Ω cm	surface resistivity, Ω	metal content, %
polymer + Li_2PdCl_4	6.1×10^{10}	4.5×10^{7} (side 1) 8.2×10^{10} (side 2)	0.17 Li 5.33 Pd
polymer + $Pd[S(CH_3)_2]_2Cl_2$	3.3×10^{10}	very low (unmeasurable)	0.23 S 7.02 Pd
polymer + Na_2PdCl_4	2.3×10^{15}	$>10^{16}$	1.36 Na 4.69 Pd
polymer alone	$\sim1.0 \times 10^{17}$	$\sim1.0 \times 10^{17}$	



I
BTDA



II
ODA



POLYAMIC ACID III

observed when lithium tetrachloropalladate(II) (Li_2PdCl_4) or bis(dimethyl sulfide)dichloropalladium(II) {$Pd[S(CH_3)_2]_2Cl_2$} served as the source of metal. The synthetic procedure employing Li_2PdCl_4 involved (1) formation of the polyamic acid from the monomers (20% solids) in *N,N*-dimethylacetamide (DMAC), (2) addition of metal species to the polyamic acid (III) in a 1:4 mol ratio, (3) fabrication of a thin film of the "palladium-polyamic acid complex" by casting on a plate glass surface, and (4) thermal imidization (300 °C) to the "palladium-polyimide complex" film. An "in situ" method whereby polymerization was carried out in the presence of $Pd[S(CH_3)_2]_2Cl_2$ proved more satisfactory in this case. Excellent quality, red-brown, flexible films were reproducibly made with these two coordination complexes. In the case of $Pd[S(CH_3)_2]_2Cl_2$, the side of the film exposed to the atmosphere possessed a definite metallic appearance. A large number of additional palladium materials were investigated in this study, such as Pd metal, $Pd(NH_3)_2Cl_2$, $Pd(acac)_2$, K_2PdCl_4, Na_2PdCl_4, and $PdCl_2$, but none had a significant effect on electrical conductivity except Na_2PdCl_4 and $PdCl_2$. With $PdCl_2$, high quality, good conducting films were not reproducible. The addition of Na_2PdCl_4 gave excellent appearing films but enhanced the conductivity of the polymer by only two orders of magnitude. The failure of these additives to improve polymer electrical conductivity is probably due to insufficient solubility of these palladium salts in DMAC and/or the DMAC-polyamic acid solution. This phenomenon likely results from the production of "islands" of palladium throughout the polymer framework rather than uniformly distributed palladium.

Table I lists the dramatically lowered volume and surface resistivities achieved by the addition of Li_2PdCl_4 and $Pd[S(CH_3)_2]_2Cl_2$ to the polyimide and the experimentally measured metal content for various films. Since the dimethyl sulfide adduct yielded similar results, the presence of lithium does not appear to be crucial for a resistivity decrease. This is a significant finding since Sarbolouki[10] has recently reported the production of polyimide films with excellent antistatic properties by low level loading with lithium salts. No conductivity data, however, was reported for this hydroscopic film. To date the minimum volume resitivity we have been able to attain has been 10^{10} Ω cm. There appears to be an optimum palladium content in these films because increasing the palladium concentration above ~5% results in no further resistivity lowering. For example, several Li_2PdCl_4 containing films were cast which differed in concentration of palladium. The volume resistivity of each film with its measured palladium content follows: 2.31%, $\sim10^{15}$ Ω cm; 4.72%, $\sim10^{10}$ Ω cm; 8.76%, $\sim10^{9}$ Ω cm.

Table II. XPS Data for Palladium-Containing BTDA-ODA-Polymer Films

substance	Pd $3d_{5/2}$, eV	Pd $3d_{3/2}$, eV
polymer + Li_2PdCl_4	335.2	340.2
polymer + $Pd[(CH_3)_2]_2Cl_2$	334.7	340.9
polymer + $PdCl_2$	334.3	339.5
polymer + Na_2PdCl_4	336.2	341.6
Pd metal	335.2	340.8
$PdCl_2$	337.3	342.6

Surface resistivity measurements also yielded lower values which depended on the side of the film being monitored, especially in the Li_2PdCl_4 case. The side of the film exposed to the atmosphere (side 1) during the thermal imidization gave consistently lower values than the side next to the glass (side 2). This observation suggests either some sintering of the metal surface has occurred and/or the presence of a thin insulative glass coating appears on the film surface. The appearance of an etched surface on the glass after removal of the polyimide film supports the latter contention. With $Pd[S(CH_3)_2]_2Cl_2$, which possessed a highly metallic appearance, surface resistivities were so low that the instrument used to conduct the ASTM method of test (D257-66) overloaded at electrification voltages as low as 10 V regardless of the side of the film being measured.

The employment of X-ray photolectron spectroscopy X-ray (PES) has proven invaluable in understanding these results. The measured X-ray PES Pd $3d_{5/2,3/2}$ binding energies indicate that palladium has been reduced to the elemental state in the conducting polyimides (Table II). In fact, even with nonconducting palladium containing films (i.e., $PdCl_2$ and Na_2PdCl_4) appreciable reduction has occurred. Although $PdCl_2$ containing films show no hint of Pd(II), the binding energies of palladium in Na_2PdCl_4 films show a significant amount of Pd(II) on the surface (Figure 1). The inadequate reduction of Na_2PdCl_4 coupled with the lower solubility of both $PdCl_2$ and Na_2PdCl_4 in DMAC, no doubt, accounts for the poor resistivity results (Table I) here. It is interesting to note that little if any chlorine, sulfur, and lithium are detectable by X-ray PES in films prepared with Li_2PdCl_4 or $Pd[S(CH_3)_2]_2Cl_2$. This no doubt reflects the low concentration of these elements in the polyimide as determined via elemental analysis (Table I). Thermal imidization apparently removes these elements as volatile components.

Less satisfactory insulative palladium containing films have also been examined via X-ray PES. The results of this study illustrate the usefulness of the X-ray PES technique in this area of research and points-out some potential problems which must be dealt with in preparing conductive polyimides by the addition of metal ions. With certain films silicon has been detected on the surface (Si $2P_{1/2,3/2}$). In other cases the metal has either not been detected or is nonuniformly distributed over the film surface. X-ray PES also provides some rationale as to why palladium concentrations >5% do not lower further the re-

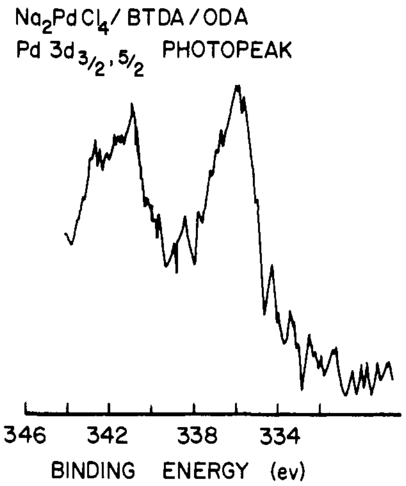


Figure 1. X-ray photoelectron spectrum (Pd $3d_{3/2,5/2}$) of Na_2PdCl_4 containing polyimide film.

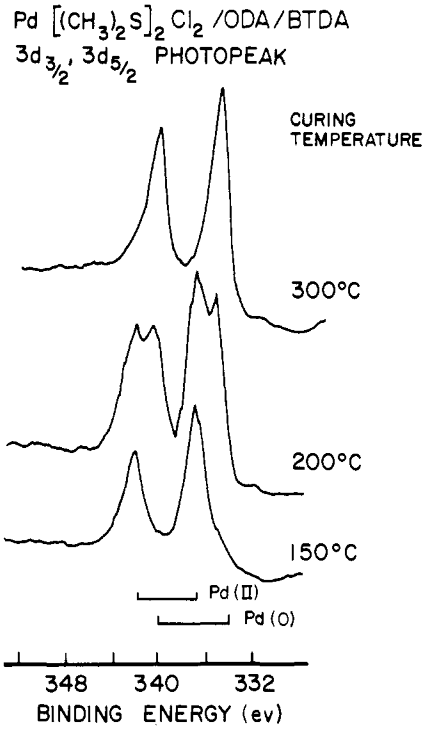


Figure 2. X-ray photoelectron spectrum (Pd $3d_{3/2,5/2}$) of $Pd[S(CH_3)_2]_2Cl_2$ containing polyimide film after curing at various temperatures.

sistivity of Li_2PdCl_4 containing films. After 3-h curing, the XPS spectrum clearly shows evidence for Pd(II) and Pd(0) on the surface. In other words for the higher palladium content complete reduction is not accomplished. Longer heating periods result in more complete reduction but with some polymer degradation.

We have attempted to determine the temperature at which metal reduction takes place within the polyimide-metal complex matrix. We have determined, using infrared spectroscopy, that the BTDA-ODA-polyamic acid "cures" to the polyimide at temperatures below 200 °C. Several samples containing palladium salts which had been "cured" at various temperatures were examined by XPS to determine the oxidation state of the metal. These results clearly indicate that metal reduction takes place above 200 °C in the case of Li_2PdCl_4, and at a somewhat lower temperature in the case of $Pd[S(CH_3)_2]_2Cl_2$ (Figure 2) and apparently has no connection with polyimide formation.

The results described in this preliminary report are unique for palladium at this point. Extension of this study to highly soluble platinum, silver, and gold coordination complexes has not resulted in highly conducting films even though X-ray PES data suggest that reduction to the elemental state has occurred during the curing process. The metal specificity described here regarding the modificiation of polymer film conductivity is reminiscent of the aluminum ion specific enhancement of high temperature adhesive properties of certain polyimides.[11] Certainly other polymer properties should be modifiable with the right choice of metal ion.

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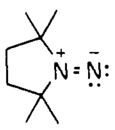
Synthesis and Direct Spectroscopic Observation of *N*-(2,2,5,5-Tetramethylpyrrolidyl)nitrene. Comparison of Five- and Six-Membered Cyclic 1,1-Dialkyldiazenes

Sir:

We report the synthesis, infrared and electronic spectra, and the kinetics of the thermal decomposition of *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene (**1**). Because the six-membered ring 1,1-diazene **2** has been characterized,[1] these results allow some estimate of the importance of structure on the spectral properties and kinetic behavior of 1,1-dialkyldiazenes.[2] In addition, the first approximate heat of formation of a 1,1-diazene from experiment is provided.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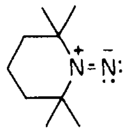
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Addition of *tert*-butyl hypochlorite (*t*-BuOCl)[3] to a stirred solution of 1-amino-2,2,5,5-tetramethylpyrrolidine (**3**)[4] and triethylamine (Et_3N) in anhydrous diethyl ether at −78 °C