CONDUCTIVE POLYMERS

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CONDUCTIVE POLYMERS

Edited by

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PREFACE

Those who recognize that our modern life style is dependent, to a large extent, on the use of organic polymers as thermal and electrical insulators, may be surprised to learn that specific plastics may also be used as conductors of electricity. In addition to demonstrating the versatility of polymers, this use as conductors will lead to developments which were not possible with other available materials of construction.

This is a new field which is growing rapidly because of intensive research and developmental efforts by many different industrial, governmental and university investigators. Many of these researchers reported advances in this art at a symposium on conductive polymers sponsored by the American Chemical Society's Division of Organic Coatings and Plastics Chemistry held at the Second Chemical Congress of the North American Continent at Las Vegas, in August 1980. The proceedings of this timely symposium are presented in this book.

The editor wishes to take this opportunity to express his gratitude to the authors who contributed to this book and to the ACS Organic Coatings and Plastics Division for sponsoring this effort.

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CONTENTS

New Horizons in Conductive Polymers 1
Raymond B. Seymour

Synthesis and Characterization of Conductive Palladium Containing Polyimide Films 7
T.L. Wohlford, J. Schaff, L.T. Taylor, T.A. Furtsch, E. Khor, and A.K. St. Clair

Conductive Polymeric Composites from Short Conductive Fibers 23
Donald M. Bigg and E. Joseph Bradbury

Metalloplastics - High Conductivity Materials 39
D.E. Davenport

Plastics as Current and Heat Conductors 49
Robert M. Simon

Synthesis and Characterization of Metallo-Organic Conducting Materials with Tetraazannulenes 57
William E. Hatfield

Electrical and Physical Properties of Thin Films Containing Charged Microgel Polymers 71
Donald A. Upson and Gerald A. Campbell

Electrical Properties of Group IV B Metallocene Polyoximes 77
Charles E. Carraher, Jr., Raymond J. Linville, Tushar A. Manek, Howard S. Blaxall, J. Richard Taylor, and Larry P. Torre

Electric Conductivities of Poly(Vinyl Ketone)s Reacted with Phosphoryl Chloride 85
Takeshi Ogawa, Ruben Cedeño, Tito E. Herrera, Benjamin Almaráz, and Motomichi Inoue

Unusual Charge Transfer at a Photoconductor-Copolymer Interface: Its Role in a Novel Particle Migration Microfilm 95
Jack Y. Josefowicz and Chung C. Yang

Highly Conducting Poly(p-phenylene) via Solid-State Polymerization of Oligomers 115
L.W. Shacklette, H. Eckhardt, R.R. Chance, G.G. Miller, D.M. Ivory, and R.H. Baughman

Conducting Complexes of a Processible Polymer: Poly(p-phenylene Sulfide) 125
R.R. Chance, L.W. Shacklette, H. Eckhardt, J.M. Sowa, R.L. Elsenbaumer, D.M. Ivory, G.G. Miller, and R.H. Baughman

Macromolecular Metals and Semiconductors: A Comparative Study 137
R.H. Baughman, J.L. Brédas, R.R. Chance, H. Eckhardt, R.L. Elsenbaumer, D.M. Ivory, G.G. Miller, A.F. Preiziosi, and L.W. Schacklette

Electrosynthesis and Study of Conducting Polymeric Films 149
A.F. Diaz, K.K. Kanazawa, J.I. Castillo, and J.A. Logan

Dependence of Polymer Electronic Structure on Molecular Architecture: Polyacetylenes, Polyphenylenes and Polythienylene 155
C.B. Duke and A. Paton

The Effect of Structural Variables on the Conductivity of Iodine Doped Polyacetylene 171
Walter Deits, Peter Cukor, and Michael Rubner

Studies in Conducting Polymers 183
G.W. Wnek, J. Capistran, J.C.W. Chien, L.C. Dickinson, R. Gable, R. Gooding, K. Gourley, F.E. Karasz, C.P. Lillya, and K.-D. Yao

Cofacial Assembly of Metallomacrocycles: A Molecular Engineering Approach to Electrically Conductive Polymers 209
Carl W. Dirk, Karl F. Schoch, Jr., and Tobin J. Marks

Utilization of Polyacetylene, $(CH)_x$, in the Fabrication of Rechargeable Batteries 227
Paul J. Nigrey, David MacInnes, Jr., David P. Nairns, Alan G. MacDiarmid, and Alan J. Heeger

Index 235

NEW HORIZONS IN CONDUCTIVE POLYMERS

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One of the distinguishing features among materials, classified by the ancients as animal, vegetable or mineral, was the ability to serve as conductors of heat. The animal and vegetable classes were covalently-bonded organic compounds which were characterized by their inability to conduct heat. After the discovery of electricity, these compounds were also found to be nonconductors of electrical current, and hence they could be used as insulators for both heat and electricity.

In contrast, the minerals, or at least the metals in this classification, were excellent conductors of heat and electricity. Much of our modern industrial progress has been based on the use of metals, such as copper, aluminum, silver and mercury, as conductors and of organic polymers, such as polyethylene and polystyrene, as insulators.

That nonmetallic materials could store electrostatic electricity was recognized by Thales of Miletus at least 2500 years ago. He demonstrated that amber became charged by rubbing and, of course, the term electricity was coined from the Greek word elektron, meaning amber. Gilbert expanded this concept and charged a series of nonconductors by this rubbing technique or electrification in 1600 A.D.

Otto van Gueriche developed a machine for the production of static electricity by rubbing a ball of sulfur. Since most classical organic polymers, i.e., elastomers or rubbers, fibers and plastics like amber, are also nonconductors, they store electrostatic charges. This phenomenon accounts for the attraction of dust by plastic articles such as blow-molded bottles, the accumulation of electrical charges in carpets in dry weather and radio-frequency and electromagnetic interference (RFI, EMI) of plastic structures.

The tendency for polymers to store electrostatic charges was overcome in the past by the addition of carbon black or acetylene black to natural rubber and metallic powders to plastics and by the blending of metallic fibers or metal-coated fibers with organic fibers.[1] Polymeric composites that were fair conductors of heat and electricity were produced by adding larger amounts of conductive materials to elastomers and plastics.[2-5]

More recent investigations on the effect of metals and salt additives on conductivity by Taylor, short conductive fibers by Bigg, metallized glass fibers (metalloplastics) by Davenport and metal alloy high aspect ratio flakes by Simon are described in chapters in this book.

Macrocyclic tetrazannulene complexes with metallic ions, such as Ni^{2+} and Pd^{2+}, are also good conductors.[6] The synthesis and properties of these organic conductors are described in a subsequent chapter by Hatfield.

Cationic and anionic charged microgel polymers, group IV B metallocene polyoximes and metallic salts of ionomers[7] also provide conductivity in polymeric systems. The first two systems are described in chapters by Upson and Carraher.

Polymers produced by the quenching of sulfur nitride vapor are also conductive. These polymers, which have a ceiling temperature of 145°C, vary in color from dark blue to golden depending on the method used for their preparation.[8,9]

Onnes discovered that mercury was a superconductor some 70 years ago, and more recently Jerome and Beckgaard have reported the superconductivity of ditetramethyltetrathioselenofulvalene hexafluorophosphate $(TMTSF)_2PF_6$. This organic compound has a zero resistance when subjected to high pressure at 0.9K.[10]

It was observed in 1950 that β-carotene, which has an orange color related to the presence of 11 conjugated bonds, exhibits semiconductive and photoconductive properties.[11] It was also noted in the early 1950's and 1960's that polyacetylene[12] and polyphenylacetylene[13] were semiconductors. Newer developments in these polymeric semiconductors are discussed in subsequent chapters.

It had also been observed previously that the rate of thermal dehydrochlorination of polyvinyl chloride could be monitored by noting the formation of colored products and that this discoloration was related to the production of a conjugated polyene structure.[14]

Comparable colored polyenes were also obtained by the thermal dehydration of polyvinyl alcohol, the thermal dehydrocyanation of polyacrylonitrile and by the Ziegler-Natta type polymerization of

1,6-heptadiyne.[15] More information on the electronic structure and spacial and electronic relationships of extended electron systems is provided in a chapter by Marks.

While polyacetylene is the most widely investigated conductive polyene,[16] many other polymers with delocalized π electrons have been studied. Considerable information on the synthesis and properties of polyacetylenes is provided in chapters by MacDiarmid, Gibson, Deits, Karasz, Wnek, Chien and co-workers.

Other related conductive polymeric systems are the polyimides,[17] poly-N-vinylcarbazole,[18] polyphenylene,[19] polypyrrole,[20,21] N,N-(1,4-phenylene-dimethylidene) bis (3-ethynylaniline),[22] and polyphenylene sulfide. Additional information on the conductivity of polyimides, polypyrroles and polyphenylene sulfide is provided in chapters by Taylor, Diaz, Baughman, Chance, Shacklette and Clarke. Information on the conductivity of the reaction products of polyvinyl ketones with phosphoryl chloride and across the interface between selenium and polystyrene-polymethyl methacrylate is provided by Ogawa and Josefowicz.

Polyvinylidene fluoride and polyvinyl fluoride have piezoelectric properties and polyvinyl chloride and polyacrylonitrile have ferroelectric properties. Thus, these polymers may be used as transducers.[23]

The potential usefulness of conductive polymers has been increased dramatically by the discovery that the electrical conductivity could be increased by several orders of magnitude by "doping," i.e., the addition of electron acceptors (p-type) such as iodine or arsenic pentafluoride[24] and by the addition of electron donors (n-type), such as sodium or sodium naphthalide.[25] The effect of this "doping" technique[26] on the conductivity of polyacetylenes, polyphenylene and polyphenylene sulfide are also discussed in subsequent chapters in this book.

At the present time, the most extensive technological application of conductive polymers is in the electrophotographic industry. For example, polymers which are nonconductors in the dark, can conduct current when exposed to light.[27] Both p- and n-type materials are being produced by "doping" and specific polymers are being used as photo- and piezo-conductors.[28] In addition to the conductive potentials for polymers, such as polyacetylene, or polydiacetylene also has potential applications. It changes color during conformational transitions to different processes.[29]

MacDiarmid and Heeger, who are co-authors of a chapter in this book, have already demonstrated that thin sheets of "doped" polyacetylene can convert sunlight to electricity and hence have potential for use as solar converters as well as for batteries.

Perhaps the most promising prediction of things to come from conductive polymers is summed up in the statement of Nobel laureate John R. Schreiffer who states, "This is the hottest thing in modern physics."

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SYNTHESIS AND CHARACTERIZATION OF CONDUCTIVE PALLADIUM CONTAINING POLYIMIDE FILMS

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INTRODUCTION

The doping of neutral polymers with dissolved metal salts or metal complexes for the purpose of imparting electrical conductivity to the polymer has received little attention. In the few instances where this technique has been applied enhancement of conductivity has been marginal. Angelo[1] initially reported in a patent the synthetic procedure for the addition of metal ions to numerous types of polyimides. Few properties of the films which he cast are available from the patent. However, the electrical properties at room temperature of a film derived from 4,4'-diaminodiphenylmethane, pyromellitic dianhydride and bis(acetylacetonato)-copper(II) were given as follows: percent copper, 3.0%; dielectric constant, 3.6%; dissipation factor, 0.004-0.01; volume resistivity, 8×10^{12} ohm-cm. The measured resistivity represented a 5-6 orders of magnitude enhancement over the polymer alone. Further patents or published work in this area are not available.[2]

Superior antistatic properties have been reported[3] for a newly available soluble polyimide (DAPI-Polyimide) film to which had been added a low level of either $LiNO_3$ or LiCl. Film physical properties and smoothness remained unchanged except that electrical resistance was sharply lowered. Conductivity was increased approximately 2000% over the standard unfilled polyimide. These lithium doped films were observed to be slightly hygroscopic which may account for the reduced resistivity.

A series of metal salts having poly(alkylbenzimidazoles) as the parent ligand have been synthesized.[4] Values for the electrical resistivity did not significantly change upon doping the

polymer with either $CrCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ or $Ni(C_2H_3O_2)_2 \cdot 4H_2O$. In contrast treatment of the polymer with HCl thereby forming the polymer conjugate acid changed the volume resistivity from 10^{13} ohm-cm to 10^6 ohm-cm. X-ray photoelectron spectra of the core levels of nitrogen and metal suggested the formation of polybenzimidazole-metal complexes.

The surface electrical conductivity of films of poly(vinyl-alcohol)-Cu(II) and poly(acrylamide)-Cu(II) complexes has been shown[5,6] to increase by spreading an acetone solution of iodine over the film surface. After iodine treatment a whitish substance identified as γ-CuI appears on the film surface. The strongly adhering γ-CuI is believed to be responsible for the enhanced electrical conductivity.

Glassy polymers have been produced from[7] solutions of $Ca(NCS)_2$ and the polymer derived from Bisphenol A and epichlorohydrin. Increased electrical conductivity was found to result from salt incorporated into the polymer. Surface and volume resistivities for the polymer alone were $1x10^{15}$ ohm and $5x10^{13}$ ohm-cm; whereas, for "phenoxy" polymer with 13% $Ca(NCS)_2$ by weight the values were $1x10^{10}$ ohm and $4x10^{10}$ ohm-cm. The decrease in resistivity was attributed to the high equilibrium water content accompanying calcium ion addition.

In our laboratory the doping of polyimides with metallic species has been demonstrated to (1) increase the softening temperature, (2) increase high temperature adhesive properties, and (3) change the polymer decomposition temperature.[8] We wish to report here the synthesis and characterization of a series of palladium-filled polyimide films many of which exhibit significantly lowered surface and volume resistivities. A preliminary communication on one of these polyimide films has recently appeared.[9]

EXPERIMENTAL

Materials - Pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) were obtained from commerical sources and purified by sublimation at 215°C at less than 1 torr, melting point 497°K and 558°K respectively. Oxydianiline (ODA) and 3,3'-diaminobenzophenone (DABP) were obtained from commercial sources and purified by recrystallization.[10] 3,3'-Diaminodiphenylcarbinol (DADPC) was prepared by reduction of DABP. Equimolar quantities of 3,3'-DABP and sodium borohydride were dissolved in diglyme. Small amounts of ethanol and water were added to serve as proton sources for the reaction. The DABP solution was allowed to stir for approximately 20 hours. 6M HCl was added slowly and the pH was adjusted to 6-7. The solution was then extracted with brine and THF. The organic layers were removed by flash evaporation and a waxy yellow compound was obtained. The wax was dissolved in water and recrystallized. The resulting

3,3'-DADPC was very pure with a melting point of 125°C as determined by differential thermal analysis at 5°C/min. (lit. value is 125°C). An infrared spectrum of the product showed a strong -OH peak at 3550 cm^{-1}. The monomer was thus considered to be polymer grade. N,N-Dimethylacetamide (DMAC) was obtained from Burdick and Jackson and used as received. The solvent was reagent grade, distilled in glass and packed under N_2. Lithium tetrachloropalladate(II) (Li_2PdCl_4) was prepared by a previously reported procedure.[11] Dichlorobis (dimethylsulfide)palladium(II), ($Pd(S(CH_3)_2)_2Cl_2$), was synthesized by slightly modifying a reported[12] procedure for the analogous platinum complex. All other chemicals were of reagent grade or equivalent and were obtained from commercial sources.

Polymerization - Polymerizations were carried-out in solutions containing 20% solids (w/w) by adding diamine (0.004 mole) and DMAC to a flask flushed with dry nitrogen. The appropriate dianhydride (0.004 mole) was then added as a solid in a single portion and the solution was stirred at room temperature for 30-36 hours. At this point the appropriate metal complex (0.001 mole) was added directly or added as a solution in a minimum amount of DMAC to the polyamic acid-DMAC solution. In most cases polymerization conducted *in situ* with the appropriate metal complex gave similar results. Polymer-metal complex solutions were refrigerated until cast.

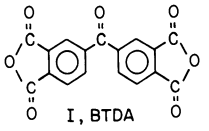
Preparation of Films - Polyamic acid-metal complex solutions were poured onto soda-lime glass plates. Solutions were spread using a doctor blade with a 8-16 mil gap to ensure a final film thickness of approximately 1 mil. Films of the polyamic acid-metal complex were dried in static air at 60°C for two hours. Imidization was thermally achieved by heating in a forced air oven 1 hour each at 100°, 200° and 300°C. A specially constructed aluminum box was employed for imidization in an anerobic environment. Polyimide-metal complex films were removed from the glass plate by soaking several hours in warm water.

Characterization - Thermal mechanical analyses (TMA) were performed on films in static air at a 5°C/min temperature program on an E.I. DuPont Model 990 Thermomechanical Analyzer. Thermogravimetric analyses (TGA) were obtained on films at 2°C/min. in static air. Surface and volume resistivities were measured following the standard ASTM method of test for electrical resistance of insulating materials (D 257-66) employing a Keithley voltage supply, electrometer and four-point probe. X-ray photoelectron spectra (XPS) were obtained on a DuPont 650B spectrometer equipped with a Mg anode (Mg K_α=1253.6ev) target. The binding energies of all electrons were measured relative to the instrumental background carbon ($1s_{1/2}$) photopeaks taken to have a value of 284.0 ev. Scanning electron microscopy was performed with an AMR 900 Scanning Electron Microscope utilizing an EDAX 707A X-Ray Analyzer. Graphite was vapor deposited onto the film surface prior to analysis.

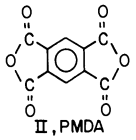
RESULTS AND DISCUSSION

Palladium-filled polyimide films have been prepared using the following dianhydride-diamine pairs: BTDA + ODA, BTDA + DABP, BTDA + DADPC, PMDA + ODA, PMDA + DABP and PMDA + DADPC (Structures I-V). A number of palladium additives were screened many of which proved unacceptable because of insufficient solubility in DMAC or in the polymer-DMAC solution. While good quality films could be produced with slightly soluble $PdCl_2$ and Na_2PdCl_4 and even dispersed palladium metal, only minor modifications could be realized in polymer properties. In many of these cases non-uniform features in the film were apparent. Best results todate have been obtained with Li_2PdCl_4 and $Pd(S(CH_3)_2)_2Cl_2$ as additives. Reasonably good quality, dark red-brown films have been fabricated for the six monomer pairs noted below.

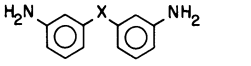
The synthetic procedure involved formation of the polyamic acid, VI, in DMAC, intimate mixing of the palladium complex and polyamic acid, and thermal imidization in air to the palladium-filled polyimide film. An alternate *in situ* method whereby polymerization to the polyamic acid was performed in the presence of



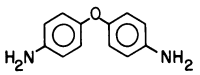
I, BTDA



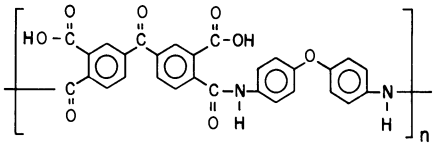
II, PMDA



III, DABP (X = C=O)
IV, DADPC (X = CH-OH)



V, ODA



VI, POLYAMIC ACID

the palladium complex also proved satisfactory. The films, as removed from the glass plate, many times possessed noticeably different surfaces depending upon whether the film had been exposed to the glass or to the air during the imidization procedure. This difference was very noticeable for the two $Pd(S(CH_3)_2)_2Cl_2$ containing films BTDA + ODA and BTDA + DABP. While the glass side had a dark red-brown appearance, the air-side possessed a definite silvery, metallic appearance. Re-heating of these films after removal from the glass plate caused the glass-side to also metallize. The metallic looking surfaces could not be produced with either PMDA, DADPC or Li_2PdCl_4 containing films. The presence of oxygen during the imidization process appears crucial, since BTDA + ODA and BTDA + DABP doped with $Pd(S(CH_3)_2)_2Cl_2$ do not give rise to metallic surfaces when cured in either a dry N_2, Ar, N_2/H_2 or moist Ar atmosphere.

Regardless of the additive, monomer pair or curing atmosphere, the films are essentially static free, moisture free and relatively thermally stable. The PMDA derived polymers yielded more brittle films which is not surprising due to their rigid chemical structure and high modulus. However, the technique of casting thinner films produced greater film flexibility.

Thermomechanical (TMA) and thermogravimetric (TGA) data have been obtained on most of the films. Table I lists the apparent polymer decomposition temperatures from TGA for polymer alone and palladium-filled films. Thermal stability is reduced by approximately 25% for Li_2PdCl_4 films and approximately 40% for $Pd(S(CH_3)_2)_2Cl_2$ films except for DADPC films where the two complexes yielded similar data. Data on films cured in nitrogen were about the same within experimental error. It is unclear why the sulfur containing additive gives rise to a less thermally stable film since the monomer-additive mole ratio was always 4:1. The effect of the two palladium complexes on the apparent glass transition temperature from TMA was not as significant except again for the BTDA + DADPC + $Pd(S(CH_3)_2)_2Cl_2$ film which showed an 84°C rise. In general, the AGT was unchanged or increased. The Li_2PdCl_4 was least deleterious in modifying the highly desirable thermal and mechanical properties of the BTDA + ODA and BTDA + DABP polyimides. Naively one might attribute these results to the apparently higher experimentally determined palladium content in the $Pd(S(CH_3)_2)_2Cl_2$ films. Since the two palladium complexes are of comparable molecular weight and all filled polyimides are prepared employing a 4:1 mole ratio the % Pd should not appreciably differ. Calculated % Pd for the filled BTDA polyimides range from 4.5-5.2%. The Li_2PdCl_4 films yield %Pd in the 4-5% range. This is reasonable since we have only subtracted the water of imidization in our %Pd calculation. Elemental analyses suggest that a significant amount of Li and Cl has been lost during the curing process which could account for the

TABLE I

THERMOGRAVIMETRIC AND THERMOMECHANICAL DATA FOR PALLADIUM-FILLED POLYIMIDES

Film	PDT[a]	AGT[b]	%Pd
BTDA + ODA	540	286	-
BTDA + ODA + Li_2PdCl_4	411(392)[c]	336(326)	4.8(4.2)
BTDA + ODA + $Pd(S(CH_3)_2)_2Cl_2$	317(351)	317[d](357)[d]	7.9(5.0)
BTDA + DABP	570	257	-
BTDA + DABP + Li_2PdCl_4	410(403)	278(252)	5.0(4.89)
BTDA + DABP + $Pd(S(CH_3)_2)_2Cl_2$	320(372)	253(258)	6.3(5.00)
BTDA + DADPC	547	307	-
BTDA + DADPC + Li_2PdCl_4	375(432)	299(270)	4.54(4.57)
BTDA + DADPC + $Pd(S(CH_3)_2)_2Cl_2$	377(350)	391[d](361)[d]	4.96(4.81)
PMDA + ODA	580	405	-
PMDA + ODA + Li_2PdCl_4	-	-	-
PMDA + ODA + $Pd(S(CH_3)_2)_2Cl_2$	340(360)	401[d](394)[d]	5.86(6.41)
PMDA + DABP	-	321	-
PMDA + DABP + Li_2PdCl_4	-	-	-
PMDA + DABP + $Pd(S(CH_3)_2)_2Cl_2$	- (360)	- (390)[d]	- (5.99)
PMDA + DADPC	580	340	-
PMDA + DADPC + Li_2PdCl_4	393(396)	371[d](346)	- (5.79)
PMDA + DADPC + $Pd(S(CH_3)_2)_2Cl_2$	353(355)	393[d](385)	5.30(5.24)

[a]Polymer decomposition temperature (°C)

[b]Apparent glass transition temperature (°C)

[c]Numbers in parenthesis correspond to data on polymers cured in nitrogen

[d]With decomposition

lower than calculated values. The situation regarding $Pd(S(CH_3)_2)_2Cl_2$ is difficult to explain since many of these films show %Pd > 5.2%. A more heterogeneous film is one obvious rationalization for these data; while significant polymer decomposition may have occurred during curing since the PDT for these polymers are just above 300°C.

The primary purpose for this study was to ascertain if palladium-filled polyimides exhibited lower resistivities than unfilled polyimides. Table II outlines these results. For BTDA derived films, four different combinations of dianhydride, diamine and additive yielded dramatically lowered resistivities. With PMDA only one combination was successful even though all good quality films were prepared in an identical manner. Surprisingly Li_2PdCl_4 gave a lowered resistivity value with BTDA + DADPC; while, $Pd(S(CH_3)_2)_2Cl_2$ with the same monomer pair exhibited a polymer-alone resistivity value. The results with BTDA + DABP, however, were reversed. Both additives with BTDA + ODA gave conductive films. The metallic surface on one side displayed by the two conductive $Pd(S(CH_3)_2)_2Cl_2$ films, no doubt, reduces resistivity ($<10^5$ ohm-cm). An exact measurement could not be made with our resistivity measuring device. The sulfur-containing additive with BTDA + DADPC and all PMDA films, on the other hand, gave no metallic surface and no resistivity lowering. The metallic surface is apparently not a necessity for improving conductivity, since some Li_2PdCl_4 films are conductive and none show a metallic surface. Although as Table II attests, resistivities are higher for Li_2PdCl_4.

The results on curing the films in a non-oxygenated atmosphere are equally interesting, Table III. No metallic surfaces are produced with $Pd(S(CH_3)_2)_2Cl_2$ as an additive and no resistivity lowering is observed. The presence of dioxygen seems crucial in this regard. Moist argon and forming gas (N_2/H_2) give the same unchanged results. A nitrogen curing atmosphere, however, does not change the resistivity results appreciably from the air-cured, conductive Li_2PdCl_4 films. Compare Tables II and III. It is significant that in each case, with Li_2PdCl_4, the resistivity values are always one to three orders of magnitude higher for nitrogen cured films. We, therefore, believe that dioxygen is crucial for production of the most conductive films, however, the chemistry of the two additives during the imidization process may be subtly different.

X-ray photoelectron spectroscopy (XPS) has proven valuable in studying some of these palladium-filled polyimides. Measured XPS binding energies (Pd $3d_{5/2,3/2}$) indicate that an appreciable amount of palladium has been reduced to the elemental state in most films. In other words, during the imidization process reduction of palladium has occurred. In general, those films which have lowered resistivities exhibit the most surface reduced palladium with the exception of BTDA + DADPC + Li_2PdCl_4. Differences between air and glass for the conductive films are very apparent here again,