MODIFICATION OF POLYIMIDE FILMS VIA TIN COMPLEX INCORPORATION,

by

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MASTER OF SCIENCE

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CHEMISTRY

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Blacksburg, Virginia
This thesis is dedicated to my parents,
Ruth and Burton Ezzell
ACKNOWLEDGEMENTS

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Chapter I

INTRODUCTION

The discovery that polymers can be made to conduct electricity is generally agreed to be "one of the more remarkable materials-research events of recent years". The development of conductive polymers from originally insulating materials such as polyacetylene, poly(phenylene oxide) and poly(phenylene sulfide) has led to extensive current research efforts. Numerous polymer systems have been investigated with the goal of transforming the materials' electrical properties from insulative to semiconductive or metallic.

Several approaches are currently employed to modify the electrical properties of polymers. One of the more recently developed methods involves doping of the polymer via incorporation of molecular species such as AsF₅ or I₂, in order to form charge-transfer complexes with the polymer, or to interact with the polymer in some other way to form charge carriers. In these systems the polymer backbone actually participates in the conduction process leading to the term "intrinsic conductor". Polyacetylene has been the most studied of the intrinsic conductors. Polyacetylene's electrically conductive (\(\rho=10^{-3}\) ohm-cm) films have been the subject of intensive experimental and theoretical studies. Poly(phenylene oxide) and poly(phenylene sulfide) are intrinsic conductors of more recent interest. These "synthetic metals" are of high commercial interest due to their potential for displacing metals from current applications. Advantages of conductive polymers over metals include: lighter weight, lower cost, and higher
energy storage capability. These intrinsically conductive polymers are expected by many to have uses as storage batteries, wire and cable sheathing, and as electromagnetically shielded housings for electronic equipment. These products are speculated to be responsible, by 1987, for a 1.2 to 1.5 billion dollar market (600 million pounds of polymer at $2.00-$2.50 lb.).

Intrinsically conductive polymer systems are not without their drawbacks. Polyacetylene, after doping to a high level of conductivity, is found to be no longer air stable. It is also very hydrolytically unstable. This makes the material suitable only for anaerobic conditions free of moisture. Poly(phenylene sulfide) and poly(phenylene oxide) are air stable, but they too are rapidly hydrolyzed under ambient conditions. Mechanical properties of these materials often fall short of what is required for specific applications. Polyacetylene is quite brittle and unprocessable after doping to high conductivity. Poly(phenylene sulfide) is much more processable, but not as conductive as polyacetylene. Work is underway to improve the environmental durability, mechanical properties, and processability of these polymers.

Another approach to conductive polymers has been the incorporation of conductive species ("fillers") into the polymer matrix. In this case the polymer maintains its insulative properties and conduction occurs through the electrical contact of the filler materials. These materials are therefore termed "extrinsic conductors". Examples of commonly used conductive fillers are carbon black, metal flakes, and carbon fibers. Resistivities of $10^{10}$ to $10^{1}$ ohm-cm are obtainable via
the judicial use of conductive fillers. Enhancement of the polymers' mechanical properties is sometimes realized as well. The conductivity of filled polymers is dependent upon:

(i) Conductivity of the filler.

(ii) Volume or weight fraction of the filler.

(iii) Shape of the filler particles.

(iv) Wettability of the filler by the polymer matrix.

Conductivity is highly dependent upon the degree of contact between filler particles. Fibers have been found to allow a higher conductivity than particles of the same weight loading due to their increased contact area. A filler content of 10-40 weight % is generally used. Typically many decades of resistivity are spanned between 10 and 40 weight % of filler loading. A 10^13 ohm-cm change is reported to be common. The thermal conductivity of polymers is also enhanced via the addition of conductive fillers. The polymer system to be made conductive is chosen with the particular mechanical properties of the application in mind. Many commercial polymers have been so modified. Conductive composites are marketed commercially and used for applications requiring static-free materials, materials as electromagnetic shielding, and for applications requiring electrical resistivities of about 10^1 ohm-cm or greater.

A somewhat successful approach in making conductive polymeric materials involves the use of metal complexes as additives to polymers. Polyimide systems were selected for this modification with the goal of obtaining an electrically conductive material with the
elevated temperature properties and environmental stability of polyimide. This technique involves dissolving the metal complex in the polyamic acid solution, fabrication of the material as a film, and thermal curing to 300°C in order to (i) allow imidization of the polyamic acid to the desired polyimide and (ii) alter the metal complex to a conductive state either thermally or by reaction with the polymer, solvent or other species. Surface conductive polyimide films have been reported by this method via the use of palladium¹³ and silver¹⁴ complexes as additives. Extensive study of the Pd-derived film revealed that a tightly bound surface layer of Pd(0) was responsible for the film conductivity.¹³ Surface migration of the complex followed by reduction produced the conductive Pd layer. Thermal stability of the polyimide was compromised, however, in that the polymer decomposition temperature dropped from 540° to 317°C.¹³ Lithium¹⁵ and copper¹⁷ complexes have been examined as polymer additives in some detail. No reduction took place but hydrolysis/dehydration of the metal, coupled with its migration to the polymer surface was apparent. Other metals briefly surveyed include iron, chromium, manganese, aluminum, calcium, cobalt and magnesium.¹⁶

One previous study briefly examined SnCl₂·2H₂O as an additive to polyimide.¹⁶ Thermal properties of the material indicated tin incorporation had a minimal effect on polyimide thermal stability. Surface electrical resistivity was measured to be 10¹⁰ ohm for one tin-containing polyimide.¹⁸ These results provided the impetus for the present study. A variety of tin complexes were chosen for incorporation
into two polyimide systems. The materials were fabricated and studied as films. The electrical and thermal properties of these materials have been characterized. A number of analytical techniques have been employed to evaluate the chemical fate of the tin species after incorporation into polyimide.

The ultimate goal of this study was the development of thermally stable, surface conductive polyimide films via tin-complex incorporation. Tin compounds were selected to serve as precursors to semiconductive or conductive species which would be retained by the polyimide matrix and thus modify its electrical properties. These materials could have aerospace applications where nonstatic or conductive films with good elevated temperature properties are required.
Chapter II

HISTORICAL

This chapter is meant to be a brief introduction into three topics of concern to this research: tin-containing polymers, polyimides, and metal-ion containing polyimides. This is by no means a complete review of these topics but it is presented to show some of the diverse previous work in tin-containing polymers, and to demonstrate the chemistry of polyimides and metal complex-modified polyimides.

A. Tin Incorporation into Polymers

Tin-containing polymers have consisted primarily of systems where the tin atom is bound to the polymer, either in the main chain or as a pendant group. These have always been in the form of organotin polymers, where the tin atom is bound to at least one carbon atom. Less work has been done concerning systems where the tin species is merely an additive.

Polymers with tin functionalities were first synthesized with the aim of mimicking the commercially successful silicone polymers. It was postulated that organotin polymers would have the same low-friction and elevated temperature properties of the silicones. However, research revealed that most organotin polymers were difficult to synthesize relative to the silicones, and that they had inferior thermal properties.19

More recently, the primary interest in organotin polymers has been in their use as biocidal agents. Trialkyltin halides were found to be
good biocidal compounds, and therefore have been added to paint formulations for use where antifungal and germicidal properties were required. Tin compounds were favored for these applications (e.g., to prevent fouling by marine life on ships' hulls) since they (i) were found to be active at ppb concentrations and (ii) are eventually degraded by the environment to harmless tin oxides. It was discerned that tin additives were leached rather quickly from these protective coatings, requiring frequent repainting in order to maintain the required biocidal properties. An interest in organotin polymers was developed when it was discovered that when bound to a polymer chain, the release rate of the tin biocide could be controlled over a much longer period of time. This is generally accomplished by binding the tin biocidal species to the polymer via an ester linkage, which slowly hydrolyzes to release the toxin at a low but adequate concentration.\textsuperscript{20}

The current preferred route to synthesizing polymers containing a tin species as a pendant group is the reaction of a linear polymer system having a reactive functional group with a tin complex. A monofunctional tin complex gives a linear polymer system while a difunctional tin monomer yields a crosslinked system. For example, reaction of the sodium salt of poly(acrylic acid) with a trialkyltin halide yields the polymer shown:\textsuperscript{21}

\[
-\{\text{C-C}_n\}_n- \\
|  \text{C=0} \\
|  |  \text{O} \\
|  |  |  \text{Sn-R}_3
\]
The sodium salt of poly(vinylalcohol) and a trialkyltin halide yield:

\[
\begin{array}{c}
\text{O} \\
\text{Sn-R}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{n} \\
\end{array}
\]

\[
\text{C-C} \\
\text{n}
\]

Reaction of poly(ethyleneimine) with a trialkyltin halide likewise yields:

\[
\begin{array}{c}
\text{Sn-R}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{n} \\
\end{array}
\]

\[
\begin{array}{c}
\text{C-N} \\
\end{array}
\]

The previous three reactions are performed via an interfacial technique at ambient temperature. The polymer (or its salt) is dissolved in an aqueous phase and reacted with the tin halide dissolved in an immiscible organic phase. Problems have arisen with this technique. Unexplainably, only a few tin compounds have been found to react with some functional polymers. For example, tri-n-butyltin chloride reacts with the sodium salt of poly(vinyl alcohol) but the corresponding tri-n-propyltin compound does not. The reaction of alkyltin halides with functional polymers has been found to be far from quantitative.21

Some polymer properties have been dramatically improved via incorporation of pendant tin species. The tri-n-butyltin modified poly(vinyl acrylate) resulted in a weight loss of only 12% at 850°C in both air and N₂. Poly(ethylene imine) modified with the same complex yielded a polymer with enhanced thermal stability, semiconductive properties (105-1011 ohm-cm bulk resistivity), hydrolytic stability, and
biocidal activity at a concentration of 40 ppb.21

Organotin polymers with the tin species contained in the polymer backbone have also been prepared by the interfacial techniques previously described. Direct reaction techniques (sodium salts of diacids with organotin dihalides) have been used as well to make organotin polyesters:22

\[
\begin{align*}
\text{R} & \quad \text{O} & \quad \text{O} \\
\text{Sn-O-C-(CR_2)_x-C-O} & \quad \text{R}
\end{align*}
\]

Various interfacial reaction techniques have produced organotin polyethers,22

\[
\begin{align*}
\text{R} & \quad \text{Sn-O-(CR_2)_x-O} & \quad \text{R}
\end{align*}
\]

and organotin polyimines.23

\[
\begin{align*}
\text{R} & \quad \text{Sn-NH-(CR_2)_x-NH} & \quad \text{R}
\end{align*}
\]

At present, organotin polymers containing pendant tin species are of more interest than the tin-backbone polymers. The incorporation of tin species into the polymer "mainchain" generally results in materials with poor thermal and mechanical properties. Pendant-tin
incorporation maintains the mechanical properties of the original mainchain polymer along with, in some cases, enhancement of thermal stability. Thermal and mechanical properties of pendant-tin containing polymers have been improved even more by crosslinking the systems after tin-incorporation.24

Synthesis of novel tin-containing polyimides have been reported in which the tin species is located in the polyimide mainchain.25 The key to obtaining these polymers is synthesis of a tin-containing diamine monomer, di(n-butyl)tin-di(p-aminobenzoate), Figure 1. Block copolymers were synthesized with this monomer and either para or meta-phenylene diamine reacted with pyromellitic dianhydride. The tin-containing monomer was substituted for 10-50 mole % of either the M-PDA or P-PDA (as shown in Figure 2).

Intrinsic viscosities were found to decrease with increasing tin-diamine content. Low basicity of the tin monomer (due to the ester functions) was speculated to be responsible for a lower conversion. TGA analysis revealed a 20% weight loss between 402 and 469°C and a 60% weight loss at > 600°C. Thermo-oxidative instability of the butyl side groups and ester linkages was believed to be responsible for the weight loss at lower temperature. Electrical properties of these tin-containing polyimides were not evaluated.25

An interesting application of tin-containing polymers was found for 25-30 mol % tributyltin methacrylate/methyl methacrylate copolymers. By casting thin films from dipole orienting ketone solvents, or by subjecting the polymer to a high voltage electric field above Tg thereby
Figure 1. A Tin-Containing Diamine Monomer
Figure 2. Reaction of Tin Containing Diamine.
orienting the polymer dipoles. The oriented polymer was then found to be both piezo- and pyroelectrically active. Non-oriented polymers did not possess these qualities.26

A very novel tin-containing polymer system is derived from tin(IV) phthalocyanines. The monomer used is the dihydroxide shown in Figure 3. Condensation of this species via sublimation yields covalently linked (via Sn-O bonds) ordered assemblies. The degree of polymerization has been found to be 100 or more. Partial oxidation of the tin nuclei with \( I_2 \) gave these materials semiconductive properties. Conductivity of tin phthalocyanines is one dimensional and occurs through the ligand. A resistivity of 2x10^4 ohm-cm at 300°C was reported for these polymers after iodine doping. They are hydrolytically and thermally stable and highly inert to chemical attack. It is possible to recover them intact after dissolving in concentrated H_2SO_4.27

Problems with tin phthalocyanines include a difficult synthesis and more difficulty in control of doping. These materials have interesting properties, but they have been overshadowed by their silicon analogs, which have greater conductivities by a factor of 10^5. A shorter bond distance (Si-O vs. Sn-O) which allows better ligand-metal overlap is thought to be the cause.27

Tin complexes employed as additives to polymers rather than functionally linked to polymers have at present only one major application: (i.e., stabilizers to poly(vinyl chloride) (PVC)). PVC is not processable without these stabilizers due to its rapid dehydrochlorination at the processing temperature (\( \sim 180^\circ C \)). Severe
Figure 3. A Tin-Containing Metalloocene Monomer.
darkening and loss of polymer mechanical properties result. This also may be induced by light. The tin compounds employed as stabilizers have been organotins, usually of \( \text{R}_2\text{Sn}(\text{XR'})_2 \) formulation where \( \text{R} = \text{alkyl} \) (C2-C8) and \( \text{X} = \) oxygen or sulfur bound to long alkane residues having alkene, anhydride, acid, ester and other functionalities. Stabilizers are selected by empirical methods. Different degradation routes exist for PVC and one particular tin compounds is often a better inhibitor for one degradation mechanism than another. Compounds are selected with the final product use in mind (i.e., whether thermal or photolytic resistance is to be optimized).\(^\text{28}\)

Inhibition of dechloroalkylation of PVC is speculated to occur via several routes. The tin species can exchange chlorine atoms with reactive chlorine from the polymer, thereby inhibiting initiations of the dehydrochlorination reaction. The tin species may also serve as a chain transfer agent to stop radical chain reactions from occurring in the PVC. Finally the tin species may react with HCl as shown:

\[
\text{R}_2\text{SnX}_2 + 2\text{HCl} \rightarrow \text{R}_2\text{SnCl}_2 + 2\text{XH}
\]

where \( \text{X} \) is an ester, ether, or mercaptan species. Such a reaction will absorb HCl and prevent HCl from further degrading the polymer.\(^\text{28}\)

PVC stabilization via tin-complex addition is at the present time a highly developed art. Development of more insight into the processes involved has been hampered due to the complicated nature of PVC degradation.\(^\text{27}\)
B. Polyimides

Polyimides are polymers containing the imide linkage as seen in the following structure:

Polyimides are well known for their elevated temperature thermal properties. They are the oldest known thermally stable polymers and are among the most widely marketed today. Polyimide properties are dependent upon the nature of the polymer backbone (aliphatic, aromatic, hydrogen content, etc.). Highly aromatic polyimide backbones are more commonly employed than aliphatic. Properties of highly-aromatic-backbone polyimides are similar and are summarized in Table I.

Polyimide thermal stability is dependent upon the nature of the polymer backbone. Highly aromatic polymers are highly stable (> 500°C). Aliphatic character along the backbone usually leads to less stability (400-450°C). Long-term thermal aging results have shown that polyimide physical properties are retained after 20,000 hours at 185°C and 10,000 hours at 235°C.30

There are at least twelve different routes to the synthesis of polyimide. The most common is a two-step process involving (i) reaction
**Table I**

Some General Properties of Aromatic Polyimides$^{29}$

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Crystallinity</td>
<td>Usually somewhat crystalline</td>
</tr>
<tr>
<td>Solubility</td>
<td>Insoluble in organic solvents, soluble in H$_2$SO$_4$ or fuming HNO$_3$ with degradation</td>
</tr>
<tr>
<td>Film tensile strength, MPa at</td>
<td></td>
</tr>
<tr>
<td>$25^\circ$C</td>
<td>172</td>
</tr>
<tr>
<td>$300^\circ$C</td>
<td>69</td>
</tr>
<tr>
<td>$500^\circ$C</td>
<td>28</td>
</tr>
<tr>
<td>Film % elongation at</td>
<td></td>
</tr>
<tr>
<td>$25^\circ$C</td>
<td>70</td>
</tr>
<tr>
<td>$300^\circ$C</td>
<td>120</td>
</tr>
<tr>
<td>$500^\circ$C</td>
<td>60</td>
</tr>
<tr>
<td>Film tensile modulus, MPa at</td>
<td></td>
</tr>
<tr>
<td>$25^\circ$C</td>
<td>2800</td>
</tr>
<tr>
<td>$300^\circ$C</td>
<td>1400</td>
</tr>
<tr>
<td>$500^\circ$C</td>
<td>280</td>
</tr>
<tr>
<td>Glass transition temperature, $^\circ$C</td>
<td>280-385</td>
</tr>
<tr>
<td>Volume resistivity at 50% relative humidity, $\Omega \cdot \text{cm}$</td>
<td></td>
</tr>
<tr>
<td>$23^\circ$C</td>
<td>1017 - 5.1018</td>
</tr>
<tr>
<td>$200^\circ$C</td>
<td>1014 - 1015</td>
</tr>
<tr>
<td>Dielectric constant at 1000 Hz</td>
<td></td>
</tr>
<tr>
<td>$23^\circ$C</td>
<td>3.1 - 3.7</td>
</tr>
<tr>
<td>$200^\circ$C</td>
<td>2.8 - 3.2</td>
</tr>
<tr>
<td>Color</td>
<td>Colorless to deep red</td>
</tr>
<tr>
<td>Density, g/cm$^3$</td>
<td>1.41 - 1.43</td>
</tr>
<tr>
<td>Radiation resistance</td>
<td>Fair to ultraviolet exellent to high energy (Van de Graff and thermal neutrons)</td>
</tr>
<tr>
<td>Flammability</td>
<td>Self extinguishing</td>
</tr>
</tbody>
</table>
of a diamine and a dianhydride in an aprotic, polar solvent to form the polyamic acid, (ii) fabrication of the polyamic acid as a film or some other form and (iii) curing to \(>150^\circ\text{C}\) in order to allow cyclization of the amic acid to the imide. This procedure is employed in order to allow processing of the polyamic acid, which is soluble in the reaction solvent. After imidization, the polyimide is no longer soluble and is processable only by sintering (as a powder) at high temperatures and pressures.

Figure 4 illustrates the previously described synthesis procedure for a common diamine/dianhydride pair. First the diamine is dissolved in a polar, aprotic solvent (N,N-dimethylacetamide or N-methyl pyrrolidone are commonly employed) in a \(\text{N}_2\)-purged flask with magnetic or mechanical stirring. After the diamine is totally dissolved, the dianhydride is added in small enough portions so that no clumping of product and reactants occurs. Rather vigorous stirring is required. A slight exotherm is observed as the dianhydride dissolves. Polymerization to the polyamic acid should be complete in 1-2 hours. If the polyamic acid is not to be used immediately, it should be stored in a freezer (\(-15^\circ\text{C}\)) until use. A \(\text{N}_2\) atmosphere should be maintained throughout the reaction and product-storage to exclude water vapor which can hydrolyze the polyamic acid to lower molecular weight segments. A 1:1 stoichiometry of reactants is crucial in obtaining high molecular weight products. Exact weighing of the monomers and extreme purity (\(>99\%\)) of monomers are essential.31

The polyamic acid may be fabricated into a polyimide film by (i)
Figure 4. Polyimide Synthesis.
spreading with a doctor blade onto a dust-free glass plate, (ii) drying at 80°C for 20 minutes to remove solvent and (iii) thermal cure of this "B-staged" material for one hour each at 100°C, 200°C and 300°C to form the polyimide and to totally dry the film of the solvent. Previous work has shown the final 300°C curing step to be essential for complete imidization and solvent removal.32

Polyimide's properties have led to their extensive use in the aerospace, electronics, and consumer market. Polyimides are available as pre-cured films and fibers, curable enamels, adhesives, and resins for fabrication as composite materials. End-products include insulative coatings, cookware exteriors, electrically and thermally insulative films, moldings, laminates and integrated circuitry components.29,30

C. Modification of Polyimides by Metal Complex Incorporation

Modification of polyimides through the incorporation of metal complexes was undertaken in order to produce conductive materials possessing the elevated temperature properties and environmental stability of polyimides. Polyimide materials are insulative with surface resistivity $> 10^{16}$ ohm and volume resistivity $> 10^{18}$ ohm-cm. Conductive polyimide materials would have applications in the aerospace industry as structural materials and in the electronics industry in circuit board fabrication, for example.

Linear, film forming polyimide systems have been employed and the resulting metal-modified materials have generally been studied as films. Use of metal powders as fillers was found to be impractical since a large amount of metal powder must be used and this prohibits the
fabrication of quality films. Therefore, metal complexes soluble in the solvent of choice (almost always N,N-dimethylacetamide) for the polymer were used by (i) adding the metal complex as a solid or solution to the polyamic acid or (ii) adding monomers and polymerizing in situ in the solvent containing the pre-dissolved complex.

Method (i) was more frequently employed. Metal complex to polymer loading ratio was generally 1:4 moles/polymer repeat unit. The polyimide/metal complex solutions were stirred until well mixed (two-four hours), spread as films on glass plates, and then cured to 300°C in air, or occasionally under an inert atmosphere.

Metal complexes employed as additives to polyimide must satisfy the following criteria:

(i) the additive must be highly soluble in the polymerization solvent (1 millimole in 10 mL).

(ii) reaction with the polyamic acid must not occur so as to coagulate the polymer (making film fabrication impossible).

(iii) polymer thermal and mechanical properties should not be greatly compromised by incorporation of the metal complex. To date hundreds of metal complexes have been screened for use as polyimide additives. In the more successful instances, where conductive or semiconductivive materials have been produced, the additives have served as precursor complexes which underwent oxidation, reduction, or other reactions to produce conductive species. Few complexes that have been used to date have had intrinsic conductive properties.

Table II lists some properties of six metal complex-modified
### Table II
Effect of Incorporation of Various Metal Complexes upon Polyimide Film Properties

<table>
<thead>
<tr>
<th>Additive</th>
<th>Resistivity&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Change in Thermal Properties&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface (ohm)</td>
<td>Volume (ohm-cm)</td>
</tr>
<tr>
<td>Pd(S(CH₃)₂)₂Cl₂</td>
<td>&lt;10⁵</td>
<td>&gt;10¹⁶</td>
</tr>
<tr>
<td>Li₂PdCl₄</td>
<td>9x5x10⁵</td>
<td>--</td>
</tr>
<tr>
<td>LiCl</td>
<td>4x10⁴</td>
<td>3x10⁶</td>
</tr>
<tr>
<td>Cu(TFA)&lt;sub&gt;c, 17&lt;/sub&gt;</td>
<td>9x10¹⁰</td>
<td>3x10¹²</td>
</tr>
<tr>
<td>[(n-Bu)&lt;sub&gt;3&lt;/sub&gt;PcCu₁]₄</td>
<td>1x10¹⁴</td>
<td>--</td>
</tr>
<tr>
<td>Al(ACAC)&lt;sub&gt;d, 16&lt;/sub&gt;</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

<sup>a</sup> Resistivity of unmodified polyimide = 10¹⁶ ohm (surface), >10¹⁸ ohm-cm (volume).

<sup>b</sup> Relative to unmodified polyimide, (-) = decrease, (+) = increase.

<sup>c</sup> TFA = trifluoroacetylacetate anion

<sup>d</sup> ACAC = acetylacetonate anion
polyimide materials. The best studied example to date involves the use of complexes of palladium. The complex Pd(S(CH₃)₂)₂Cl₂ (dichlorobis(dimethylsulfide)palladium(II)) was added to two different polyimide systems (Benzophenonetetracarboxylic acid dianhydride/oxydianiline (BTDA/ODA) benzophenonetetra carboxylic acid dianhydride/diaminobenzophenone (BTDA/DABP)) which, upon air curing, produced surface conductive materials having resistivities of less than 10⁵ ohm. The air-side of the film (side facing up during curing) possessed a very silvery, shiny appearance. The glass-side was dark in appearance and totally devoid of any metallic luster. Only the air (silvery) side was conductive; the glass side resistivity was not diminished significantly from the unmodified polyimide. A nitrogen curing atmosphere produced a film with nonmetallic air-side and glass-side, both nonconductive. Volume resistivity was initially thought to have also been decreased but more recent measurements have proven that the volume resistivity of the Pd(S(CH₃)₂)₂Cl₂ modified polyimide is in the insulator range.

Study of these palladium-modified materials via x-ray photoelectron spectroscopy showed large concentrations of Pd(0) on the air-side of surface-conductive films. Palladium was found to be present exclusively in the zero-valent state. Auger electron spectroscopy/argon ion etching experiments revealed a large concentration of palladium at the surface of the metallic (conductive) side of these films. This deposit was found to be contained within the first 1000 angstroms of the film surface after which palladium concentration diminished drastically.

It was, therefore, concluded that the air-side surface conductivity
of the Pd(S(CH₃)₂)₂Cl₂-modified polyimide films was due to a deposit of Pd(0) on the film surface. Oxygen curing was proven to be essential to formation of the Pd(0) charge carriers and to attaining surface conductivity. Formation of the Pd(0) surface was evidently the result of migration of the Pd(II) starting complex to the film surface, followed by reduction to Pd(0). The role of dioxygen in the Pd(0) formation and the nature of the species responsible for the reduction were not defined.

Other palladium complexes have been examined with limited success. For example, Li₂PdCl₄ (lithium tetrachloropalladate (II)) has been used to make semiconductive surface (10⁵ ohm) and volume (10⁷ ohm-cm) air-cured polyimide films. These films were nonmetallic and contained a dispersion of palladium present as Pd(0) and Pd(II) throughout the film. Both film sides were semiconductive. Nitrogen curing increased surface (x 10²) and volume (x 10³) resistivity, but not as dramatically as in the Pd(S(CH₃)₂)₂Cl₂ case. Lithium was found to be present via XPS. The charge carrier was not identified in these films.¹³

Thermal properties of palladium-modified films were somewhat disappointing. Polymer decomposition temperature (PDT) of the conductive Pd(S(CH₃)₂)₂Cl₂-modified films was found to be lowered by over 200°C. PDT of Li₂PdCl₄-derived materials was lowered about 150°C. Apparent glass transition temperature (AGT) were usually raised. Surface-conductive materials apparently are possible to fabricate, but at the great expense of polymer thermal stability.¹³

The semiconductive nature of the Li₂PdCl₄ modified materials
spurred a study of lithium complex incorporation into polyimide films. Lithium chloride (LiCl), lithium iodide and lithium acetylaconate were found to produce flexible, good quality films. LiCl was selected as the primary additive of interest due to its unique effect upon film electrical properties. Resistivity of LiCl-modified BTDA/ODA was measured to be $10^6$ ohm-cm (volume) and $10^4$ ohm (surface). Analysis of semiconductive lithium-containing system via Fourier-transform infrared spectrometry (FTIR) indicated appreciable amounts of bound H$_2$O were present, relative to the neat polyimide. Upon vacuum drying and measurement in a desiccated atmosphere, volume and surface resistivities were found to be $>10^{16}$ ohm(-cm). Water was therefore proven to be essential to the conduction process. Also, essential to conduction was some type of LiCl-derived species because films modified with other lithium complexes were insulative even though containing large amounts of bound H$_2$O. Most lithium was seen to be converted to a "Li$_2$O-like" species (via XPS) in the LiCl film. Lithium concentration was roughly homogeneous throughout the film. The nature of interaction of the species participating in the electrical conduction achieved with LiCl-modified polyimide films has yet to be resolved.

Lithium complex addition lowered polyimide PDT, generally 50-100°C. AGT was seen to rise in most cases. The lithium study provided volume and surface-semiconductive materials (under ambient conditions) with not as great an impact upon thermal stability as witnessed with palladium additives.

The electrical properties of copper metal along with a report on
semiconductive polymer systems modified via copper incorporation prompted a study on the effect of copper complexes upon polyimide properties. Six Cu(II) coordination complexes and one Cu(I) complex, tetrakis-tri[(n-butyl)phosphine]iodocopper(I), [(n-Bu3P)CuI]4, were used. Of the Cu(II) modified materials, the effect of one additive, bis(trifluoroacetylacetonato)copper(II), [Cu(TFA)2], was fairly representative. All copper modified polyimide films, from either Cu(I) or Cu(II) complexes, were nonconductive (volume and surface). Lowest resistivities measured for any films in this study were 10^{12} ohm (surface) and 10^{14} ohm-cm (volume). As seen with previous metal-containing polyimide systems, PDT was rather severely affected by copper incorporation. PDT was lowered 150°-200°C for both Cu(I) and Cu(II) additives. AGT was seen to rise in all cases.

Perhaps the most remarkable aspect of this study was the appearance and properties of the Cu(TFA)2-containing material. The air side of this film had a very silvery, metallic surface. Surface resistivity measurement of this silvery side were disappointingly high (10^{12} ohm). XPS measurements revealed the silvery material to be a form of Cu(II). Absence of fluorine on the silvery side indicated loss of ligand had occurred. Identity of the silvery material was speculated to be an ordered form of CuO. Other Cu(II) additives also exhibited air-side surfaces different than the film bulk. Cu(acetylacetonate)2 produced a film with a purple surface. Air curing promoted the formation of these diverse film surfaces; nitrogen curing produced black, homogeneous films. Auger depth profiling revealed a large copper concentration
within the silvery surface of the Cu(TFA)$_2$ film. This copper concentration dropped dramatically after argon ion sputtering through the surface layer. Removal of the surface with acid also revealed a consequent drop in surface copper as monitored via XPS.

Cu(I)-modified materials were also heterogeneous. They were brown in appearance with a black, air-side deposit, likely triphenyl phosphine oxide. XPS indicated oxidation of the additive to Cu(II) had occurred on the air-side of the film. Glass-side measurements suggested the complex was still intact as Cu(I). Auger depth profiling indicated a homogeneous distribution of copper throughout the film.

Another study surveyed the effect of some metal complexes upon the lap-shear strength of a polyimide adhesive. Detrimental effects upon adhesive strength were seen for LiCl, NiCl$_2$·H$_2$O and Cr(ACAC)$_3$. Adhesive strength of the polyimide was increased nearly four-fold at 275°C by Al(ACAC)$_3$. This was accomplished as a result of the effect that Al(ACAC)$_3$ has upon the thermal properties of the polyimide. The AGT was raised from 251° to 271°C, allowing the material a wider temperature range of use as an adhesive.$^{16}$

This study also sampled a number of complexes of different elements and their influence on thermal properties of polyimide films. Thermal effects were widely diverse. Electrical measurements were made on Al(ACAC)$_3$ and NiCl$_2$ modified materials and both were found to be insulators. Isothermal weight loss experiments (65 hours at 316°C) indicated acceleration of thermal degradation resulting from metal ion incorporation. This effect varied from 2% increased weight loss
(Al(ACAC)$_3$) to 48% (Cr(ACAC)$_3$). XPS measurements showed aluminum to be present in the +3 state, and nickel in the +2 state, after incorporation into polyimide.
Chapter III

EXPERIMENTAL

Experimental aspects of this research will be described in this section. Materials and equipment used, method of polymer synthesis and modification, and analytical techniques employed will be presented.

A. Polyimide Systems

Two polyimide systems (pyromellitic dianhydride –4,4' oxydianiline (PMDA/ODA) and 3,3', 4,4'-benzophenone tetracarboxylic acid dianhydride –4,4'-oxydianiline (BTDA/ODA)) were chosen for modification by tin complex incorporation (Figure 5). Relative ease of preparation and fabrication as films, along with their high temperature stability made these materials good candidates for tin complex incorporation.

B. Tin Additives

In order to be useful as additives to polyimide, the tin complexes used in this study had to meet the criteria listed in Chapter II, Part C of this thesis. A number of tin complexes, both Sn(II) and Sn(IV), were screened. Table III lists the compounds that meet the previously listed criteria (some marginally) and which served as polymer additives for this study. Some physical properties of these complexes are also listed.

These additives were employed with either BTDA/ODA and/or PMDA/ODA. Films were prepared under air, N₂, or occasionally forming gas (5% H₂ in N₂).
Figure 5. Monomers used in this Study.
<table>
<thead>
<tr>
<th>Additive</th>
<th>B.P. (°C)</th>
<th>M.P. (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_3\text{SnC}≡\text{CSn}_3$</td>
<td>--</td>
<td>153</td>
<td>35</td>
</tr>
<tr>
<td>1,2 bis (triphenyltin)acetylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{(n-Bu)}_2\text{SnCl}_2$</td>
<td>143/12 torr</td>
<td>43</td>
<td>36</td>
</tr>
<tr>
<td>di-n-butyltin dichloride</td>
<td>91-94/0.1 torr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{(n-Bu)}_3\text{SnH}$</td>
<td>76-81</td>
<td>--</td>
<td>37</td>
</tr>
<tr>
<td>tri-n-butyltin hydride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{(CH}_3\text{)}_2\text{SnCl}_2$</td>
<td>185-190</td>
<td>107-108</td>
<td>38</td>
</tr>
<tr>
<td>dimethyltin dichloride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Phi\text{SnCl}_3$</td>
<td>128/15 torr</td>
<td>--</td>
<td>39</td>
</tr>
<tr>
<td>phenyltin trichloride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{(CH}_3\text{)}_4\text{Sn}$</td>
<td>76.6</td>
<td>--</td>
<td>40</td>
</tr>
<tr>
<td>tetramethyltin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Phi_3\text{SnOH}$</td>
<td>--</td>
<td>150d</td>
<td>41</td>
</tr>
<tr>
<td>triphenyltin hydroxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{SnCl}_2•2\text{H}_2\text{O}$</td>
<td>d*</td>
<td>d</td>
<td>42</td>
</tr>
<tr>
<td>$\Phi_3\text{Sn}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>triphenyltin benzimidazole</td>
<td></td>
<td>298d</td>
<td>43</td>
</tr>
</tbody>
</table>

*d = decomposes
C. Materials Received

Pyromellitic dianhydride (PMDA) was received from commercial sources and purified by sublimation at 215°C and less than 1 torr (melting point, 497°C). 3,3',4,4'-Benzophenone tetracarboxylic acid dianhydride (BTDA) was received from commercial sources in a polymer pure grade and vacuum dried at 100°C for 2 hours before use (melting point, 558°C). 4,4'-Oxydianiline (ODA) was obtained commercially and sublimated at 185°C at less than one torr pressure, melting point, 461-463°C (with decomposition). All tin compounds were obtained commercially and used as-received. Reagent grade N,N-dimethylacetamide, (DMAC) glass distilled and packed under nitrogen was obtained from Burdick and Jackson.

Polymer Synthesis and Modification

Polymer synthesis was performed in DMAC at 15-20% solids concentration. ODA (0.004 mole) was added to a N₂-purged flask with DMAC and stirred until dissolved. The appropriate dianhydride was then added (0.004 mole). Stirring was continued at room temperature for 4-6 hours. Doping of the polyamic acid was carried-out by addition of the tin as a DMAC solution (0.001 mole of complex in 1-2 mL DMAC). The tin-modified polyamic acid was stirred for 2-3 hours and then cast as a film.

E. Film Preparation

Polyamic acid-tin complex solutions were centrifuged at ~1700 RPM before film casting. Solutions were poured onto acid-cleaned, dust-free
soda-lime glass plates and spread with a doctor blade having a 12-22 mil blade gap in order to obtain a film of 1 mil final thickness. These films were then dried in static air at 60°C for 2 hours. Thermal curing at 100°, 200° and 300°C each for one hour was done to imidize the materials. Curing atmospheres used were forced air, N₂, and forming gas (5% H₂, 95% N₂ mixture). After cooling to room temperature, polyimide-metal complex films were removed from the glass plates by soaking in distilled water.

F. **Elemental Analysis**

Galbraith Laboratories, Inc., Knoxville, Tennessee, performed elemental analyses on tin-modified polyimide films. Single analyses only were performed.

G. **Thermal Analysis**

Thermomechanical (TMA) analyses were performed with an E. I. Dupont Model 990 Thermomechanical Analyzer on film samples in static air at a 5°C/min. temperature program. Thermogravimetric analyses (TGA) were obtained in static air at a 2.5°C/min. temperature program. All analyses were performed at NASA-Langley Research Center, Hampton, Virginia.

H. **Room Temperature Resistivity Measurements**

Surface and volume resistivities of tin-modified polyimide films were measured following the ASTM Standard Method of Test for Electrical Resistance of Insulating Materials (D257-66) using a Keithley voltage supply, electrometer, and electrode assembly. A sample geometry of 3"
diameter and 1 mil thickness was employed.

I. Elevated Temperature Resistivity Measurements

Resistivity measurements obtained at elevated temperature and under dynamic vacuum were obtained on a 3-electrode apparatus based on the Keithley design constructed by Eugene Khor and Charles C. Johnson, graduate students in the Department of Chemistry at VPI and SU. The system was automated using an HP-85 computer. The voltage source employed was a Keithley 230 programmable power supply. The current measuring device used was a Keithley 619 Electrometer. An Omega Engineering 400 A Digicator served as the digital thermometer for temperature readout, and a Keithley Model 75 scanner was employed as a relay box for experiment control. All equipment (except the BCD interface equipped 400A digicator) was equipped with an IEEE 488 interface to facilitate command, control and data collection on the IEEE 488 Standard Bus. Electrode assembly was constructed per ASTM D-257, D-1829 and C-657. Dimensions of the electrode are identical to the Keithley model 6105 Resistivity Adapter. Figure 6 shows the electrode assembly. Data were obtained by placing the sample (circular, 3" diameter by 1 mil thick) between the electrodes, evacuating the electrode chamber, and starting the computer-controlled experiment. Current applied to the cartridge heaters controlled the electrode temperature and allowed resistivity to be measured as a function of temperature. An electrification time of thirty seconds was used. Applied voltage ranged from ten to fifty volts. Resistivity-temperature data were plotted using the HP-85 plotter and the HP-85
Figure 6. Elevated Temperature Resistivity Electrode Apparatus.
graphics package.44

J. Photoresistivity Measurements

Photoresistivity experiments were conducted with an argon lamp having continuous spectral output equipped with a UV filter. A two point probe was used with the probes attached to the film surface with silver paint. A Keithley Model 177 Digital Multimeter was used to measure film resistance as a function of irradiation time.

K. X-Ray Photoelectron/Auger Ion Spectrometry Experiments

X-ray photoelectron spectra were obtained on either a DuPont 650 B spectrometer or Physical Electronics 550 instrument, both equipped with Mg anode ($K_\alpha = 1253.6$ eV) target. Samples were mounted using double-stick tape. Binding energies of all electrons were measured relative to the instrumental background carbon (1s1/2) photopeak assumed to have a value of 284.0 eV. Auger Electron Spectrometry/auger ion etching experiments were performed on the previously mentioned Physical Electronics instrument. Gold was vapor deposited on to each film surfaces prior to analysis in order to alleviate charging difficulties. Argon ion sputter rate was approximated to be 500 angstroms/minute.

L. Infrared Spectrometry

Infrared spectra of the tin-modified polyimide films were obtained with a Nicolet Model 6000 Fourier Transform Infrared Spectrometer using a liquid nitrogen-cooled detector with a 4000-400 cm$^{-1}$ range. All spectra were taken via the attenuated total reflectance (ATR) technique, using a Harrick ATR attachment with KRS-5 elements. A 75° angle was
employed in order to obtain a penetration depth (into the film surface) of approximately one micron. 500 scans were taken of each sample. The ATR unit was then adjusted so the sample was held more loosely between the KRS-5 elements. Background spectra were thus taken and used as a reference.
Chapter IV

RESULTS AND DISCUSSION

This chapter divides the results of this study into two parts. The first involves an initial survey of the properties of a number of tin-modified polyimide films. The second part presents an in-depth study of surface-semiconductive films produced via the use of two additives, SnCl₂·2H₂O and (n-Bu)₂SnCl₂.

I.A. General Properties of Tin-Modified Polyimide Films

Table IV presents a list of polyimide/dopant combinations with either tin(II) or tin(IV) additives which produced films of fair to good quality. All materials shown were air-cured. All films were somewhat flexible and tough enough to undergo electrical resistivity measurement. The overall appearance and physical properties of these materials varied greatly. In order to compare general physical properties of the films and also to describe their individual unique properties, a comparison of all data will be presented initially followed by a more specific discussion of each dopant/polymer pair individually.

Electrical resistivity measurements on the tin-modified materials are presented in Table IV, along with resistivity measurements on the undoped BTDA-ODA and PMDA-ODA systems. Volume resistivity was somewhat similar for all the Sn(IV) modified materials. Significant differences, however, were found in the surface resistivity measurement for the air-side of the film (side facing up during cure) opposed to that of the glass-side (side facing down during cure). The lowest
<table>
<thead>
<tr>
<th>Film No.</th>
<th>Monomers</th>
<th>Tin Additives</th>
<th>Resistivity $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Volume (ohm-cm)</td>
</tr>
<tr>
<td>1</td>
<td>BTDA/ODA</td>
<td>1,2-bis(triphenyltin)acetylene ($\Phi_3SnCl_2$)</td>
<td>8x10$^{16}$</td>
</tr>
<tr>
<td>2</td>
<td>BTDA/ODA</td>
<td>triphenyltinbenzimidazole ($\Phi_3Sn(C_7H_5N_2)$)</td>
<td>$&gt;$10$^{18}$</td>
</tr>
<tr>
<td>3</td>
<td>BTDA/ODA</td>
<td>di-n-butyltin dichloride (n-Bu)$_2$SnCl$_2$</td>
<td>1x10$^{15}$</td>
</tr>
<tr>
<td>3a</td>
<td></td>
<td></td>
<td>2x10$^{15}$</td>
</tr>
<tr>
<td>3b</td>
<td></td>
<td></td>
<td>5x10$^{15}$</td>
</tr>
<tr>
<td>4</td>
<td>BTDA/ODA</td>
<td>tri-n-butyltin hydride (n-Bu)$_3$SnH</td>
<td>$&gt;$10$^{18}$</td>
</tr>
<tr>
<td>5</td>
<td>BTDA/ODA</td>
<td>dimethyltin dichloride (CH$_3$)$_2$SnCl$_2$</td>
<td>5x10$^{15}$</td>
</tr>
<tr>
<td>6</td>
<td>BTDA/ODA</td>
<td>phenyltin trichloride ($\Phi$SnCl$_3$)</td>
<td>$&gt;$10$^{18}$</td>
</tr>
<tr>
<td>7</td>
<td>PMDA/ODA</td>
<td>di-n-butyltin dichloride (n-Bu)$_2$SnCl$_2$</td>
<td>1x10$^{16}$</td>
</tr>
<tr>
<td>8</td>
<td>PMDA/ODA</td>
<td>tetramethyltin (CH$_3$)$_4$Sn</td>
<td>2x10$^{16}$</td>
</tr>
<tr>
<td>9</td>
<td>PMDA/ODA</td>
<td>triphenyltin hydroxide ($\Phi_3SnOH$)</td>
<td>3x10$^{16}$</td>
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<tr>
<td>10</td>
<td>BTDA/ODA</td>
<td>SnCl$_2$·2H$_2$O</td>
<td>1x10$^{15}$</td>
</tr>
<tr>
<td>11</td>
<td>PMDA/ODA</td>
<td>SnCl$_2$·2H$_2$O</td>
<td>5x10$^{14}$</td>
</tr>
</tbody>
</table>

$^a$Post-drying of film, inert atmosphere measurement

$^b$200° cure (maximum temperature)

$^c$BTDA-ODA and PMDA-ODA (no additive) surface and volume resistivities equal approximately 10$^{17}$
surface resistivities measured were $1 \times 10^5$ ohm for film 3 and $8 \times 10^7$ ohm for film 7. These values are lower by a factor of approximately $10^6$ over that of the next most surface-conductive material doped with a different Sn(IV) complex. Both films have been doped with di-n-butyltin dichloride. Film 11 exhibited the lowest resistivity of the Sn(II) doped films. Again, lowest resistivity was realized for the surface/air-side measurement with a value about $10^{12}$ times lower than the undoped polymer.

Other general trends regarding the resistivity data should be mentioned. Volume resistivity was lowered to a minimum value of about $10^{14}$ ohm-cm regardless of the dopant. In no case was surface resistivity for the glass side of any film lowered below $10^{12}$ ohm via doping. The same dopant in different polymer systems produced materials with different resistivity values. For example, comparison of films 3/7 and 10/11 show appreciable differences particularly in surface resistivity values for the air-side of the films.

Elemental analyses (Table V) revealed that nearly total vaporization of dopant must have occurred during the curing process for films 6 and 8. Tin-containing species were still present in all other films analyzed.

Thermal measurements on the tin-modified films (Table V) revealed an increase in the softening temperature (AGT) of nearly all materials analyzed. Thermomechanical Analysis (TMA) of one BTDA/ODA materials indicated expansion of the film sample under the probe during heating (Figure 7). This thickening could be caused by decomposition
Figure 7. TMA Curve for BTDA/ODA-Triphenyltin Benzimidazole.
Table V
Thermal Data for Some Tin-Containing Polyimides

<table>
<thead>
<tr>
<th>Film No.</th>
<th>AGT (°C)</th>
<th>PDT (°C)</th>
<th>% Tin Found</th>
<th>Calc'd</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTDA/ODA</td>
<td>286</td>
<td>550</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PMDA/ODA</td>
<td>405</td>
<td>580</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>310</td>
<td>514</td>
<td>7.00</td>
<td>6.24</td>
</tr>
<tr>
<td>2</td>
<td>357</td>
<td>517</td>
<td>5.21</td>
<td>4.56</td>
</tr>
<tr>
<td>3</td>
<td>404</td>
<td>548</td>
<td>3.47</td>
<td>4.92</td>
</tr>
<tr>
<td>7</td>
<td>Decomp.</td>
<td>534</td>
<td>4.05</td>
<td>5.97</td>
</tr>
<tr>
<td>8</td>
<td>363</td>
<td>558</td>
<td>&lt;0.01</td>
<td>6.46</td>
</tr>
<tr>
<td>9</td>
<td>472</td>
<td>516</td>
<td>6.44</td>
<td>5.87</td>
</tr>
<tr>
<td>10</td>
<td>280</td>
<td>544</td>
<td>4.24</td>
<td>5.23</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>6.20</td>
<td>5.05</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>-</td>
<td>&lt;0.01</td>
<td>5.00</td>
</tr>
<tr>
<td>3c</td>
<td>-</td>
<td>-</td>
<td>5.92</td>
<td>4.92</td>
</tr>
</tbody>
</table>

a: Apparent Glass Transition Temperature (Thermomechanical Analysis)
b: Polymer Decomposition Temperature (Thermal Gravimetric Analysis)
c: Cured at 200°C, 3 hours
of the Sn additive during the TMA measurement. Decomposition
temperature of the triphenyltin benzimidazole complex is 298°C (Table
III). This is about the same temperature that expansion is observed via
the TMA experiment. Decomposition of the tin additive producing
off-gases could cause the observed increase in thickness. Figure 8
shows the DSC (differential scanning calorimetry) experimental trace for
this material. A transition attributable to Tg is seen at 300°C
represented by the dashed line. The experiment was run twice, the first
run (solid line) apparently released bound water and some stresses
incorporated into the film. The second run exhibited only the
transition seen around 300°C. No crystallinity effect is observed; a
slight weight loss after 300°C is witnessed by the sloping line. Figure
9 shows the TGA curve for this tin-modified polyimide. An initial
weight loss is seen at ~ 300°C, concurring with the DSC data.
Apparently decomposition of the tin complex is being monitored and is
responsible for the interesting thermal properties observed. Table VI
presents the effect of annealing above 300°C upon the dimensions and
density of the BTDA/ODA triphenyltin benzimidazole film. Area of the
film was seen to decrease upon annealing, and thickness seen to
increase. Density was seen to slightly increase. It would appear that
voltilization of the tin complex somehow allows better packing of the
polymer chains, and subsequently an increase in density. Most other
tin-modified materials exhibited more typical TMA behavior (Figure 10).
Thermal gravimetric analysis (TGA) generally revealed some decrease
in polymer stability after addition of the tin dopants. Film 9 had the
Figure 8. DSC Curve for 4,4'-Azoxybenzene/4,4'-Diaminobenzidine Benzimidazole.
Table VI

Effect of Annealing upon Area and Density of BTDA/ODA-Triphenyltin Benzimidazole

<table>
<thead>
<tr>
<th>Film Dimensions (mm)</th>
<th>Length</th>
<th>Width</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Heating</td>
<td>79.2</td>
<td>18.5</td>
<td>0.04</td>
</tr>
<tr>
<td>After Heating (325°C, 12 hrs.)</td>
<td>73.5</td>
<td>15.2</td>
<td>0.05</td>
</tr>
</tbody>
</table>

% Area Shrinkage = 24

Densitya (g/cc)

<table>
<thead>
<tr>
<th>Before Heating</th>
<th>1.453</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.456</td>
</tr>
<tr>
<td>After Heating</td>
<td>1.463</td>
</tr>
<tr>
<td>(325°C, 12 hrs.)</td>
<td>1.463</td>
</tr>
</tbody>
</table>

a done in duplicate
Figure 10. TMA Curve for BTDA/ODA-SnCl2-2H2O.
lowest decomposition temperature measured, 64° below that of the undoped polymer. All films tested had decomposition temperatures above 500°C indicating that the tin dopants overall had a minimal effect on the elevated temperature stability of BTDA-ODA and PMDA-ODA polyimide materials.

XPS data were obtained (Table VII) on both sides of selected films. Information regarding (1) the relative binding energies of Sn found on air and glass-sides of the same film, (2) the presence of chlorine on the surfaces of films doped with a chlorine-containing complex and (3) the relative amount of tin present on each film's surface was of interest. All materials that were measured show a slightly higher binding energy for tin present on the glass-side of the film relative to tin on the air-side. In no instance, was chlorine present on the surface of any side of any film doped with a chlorine containing complex. Relative amounts of tin present on the air and glass-sides of these materials varied greatly between the Sn(IV) additives (Films 1 and 2) and the Sn(II) additives (Films 10 and 11). Films 1 and 2 which have high surface resistivities, have about the same amount of tin on either side; while, films 10 and 11, which exhibit low surface resistivities on the air-side, have about a factor of 102 times more tin on the air-side than the glass-side of the film.

Tin binding energies are essentially identical regardless of the tin dopant and monomer concentration. Unlike numerous elements, XPS binding energies for tin are not highly definitive concerning oxidation state.46 Tin compounds in divalent and tetravalent states have been
Table VII
XPS Binding Energy Data for Some Tin-Containing Polyimides

<table>
<thead>
<tr>
<th>Film No.</th>
<th>Air-Side</th>
<th>Glass-Side</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>486.3</td>
<td>486.5</td>
</tr>
<tr>
<td>2</td>
<td>485.1</td>
<td>486.8</td>
</tr>
<tr>
<td>3</td>
<td>486.6</td>
<td>--</td>
</tr>
<tr>
<td>10</td>
<td>486.3</td>
<td>486.8</td>
</tr>
<tr>
<td>11</td>
<td>485.8</td>
<td>486.2</td>
</tr>
</tbody>
</table>
shown to have quite similar binding energies. Considering the aerobic imidization conditions, tin(IV) is anticipated on the surface of these films. The absence of chlorine from films doped with chlorine-containing complexes indicates that some mechanism for loss of chlorine must exist at some stage in the film preparation process.

B. Individual Film Properties

Film 1: BTDA/ODA-\(\Phi_3\text{SnC=CSn}\Phi_3\)

This material has a yellowish-brown color and is transparent. The film is somewhat brittle. It is homogeneous except for a number of small holes unevenly dispersed through the film which apparently were made by escaping gas during imidization. The nature of the size and quantity of the holes suggests that they may have been formed via degradation and/or volatilization of small particles of tin complex which may have precipitated from the polyamic acid solution at some stage during imidization. A likely mechanism can be envisioned. The tin-acetylene bond is readily hydrolyzed and may have reacted with the water of imidization (released from the polymer near \(180^\circ\text{C}\)) as follows:

\[
\Phi_3\text{Sn-C=CSn}\Phi_3 + 2\text{H}_2\text{O} \xrightarrow{\Delta} 2\Phi_3\text{SnOH} + 2\text{HC=CH(g)}
\]

\[
\Phi_3\text{SnOH} \rightarrow (\Phi_3\text{Sn-0})_x + \frac{x}{2}\text{H}_2\text{O}
\]

The aryltin oxide may have precipitated from solution and volatilized, thereby causing the film peculiarities mentioned earlier. Not all the tin has vaporized from the polymer because XPS showed appreciable tin on both sides of the film. This material had relatively poor polymer
properties and was of interest primarily for its unique, "pocked" surface.

**Film 2: BTDA/ODA-Φ3Sn(C7H5N2)**

The dopant utilized for the preparation of this material was the only tin-nitrogen compound studied. It produced a very clear yellow, homogeneous film with no surface anomalies. The material was tough, flexible and possessed a static charge (i.e., seemingly more so than the undoped polymer film). Elemental analysis verified that more tin was present in the film than theoretically predicted. The tin-nitrogen bond is known to be hydrolytically unstable and may likely have been cleaved at some point during the film preparation. The amine residue, therefore, may have volatilized accounting for the higher % Sn. The other product of hydrolysis may be the triphenyltin oxide postulated in the formation of film 1. Based on results obtained with film 2, the imperfections in film 1 would therefore have come from the liberation of acetylene which should be more readily evolved than benzimidazole during thermal imidization. Alternately, a different form of tin may have been produced in this film. XPS of this material showed about equal amounts of tin on each side of the film. Thermal properties of this material have already been discussed at length.

**Film 3: BTDA/ODA-(n-Bu)2SnCl2**

This material had the overall resistivity properties of all those studied. It also had the most unusual physical features. The material was dark-brown in color and opaque. Large raised areas in the
film gave it a "bumpy" appearance. It was very tough and appeared to be cross-linked. Small amounts of a blackish material were present in some areas.

Electrical properties of this film were studied in some depth. The film was dried under vacuum and resistivity was measured under H2O-free conditions to determine if H2O played a role in its electrical properties. Resulting volume and surface resistivity measurements were about the same (Table IV). The surface resistivity was also measured at elevated temperature (max. 160°C) under vacuum (0.1 torr) and found to vary little from the room temperature value. Resistivity versus temperature data are shown in Table VIII. This result is quite different from previous resistivity studies with lithium-doped polyimides.16 Resistivity in the lithium case increased markedly on cyclic heating and pumping in vacuo because moisture was being removed from the film. A similar film was cast and cured at 200°C rather than 300°C. This film was found to be a rather smooth, homogeneous material with much poorer electrical properties (Table IV). No raised surface (presumably due to gas generation) was found with the 200°C cured film. Evidently decomposition of the (n-Bu)2SnCl2 complex is necessary for the polymer to acquire its enhanced surface electrical properties. Butane or possibly butene may be evolved during thermal curing at 300°C, due to the instability of the Sn-C bond above 200°C.49 Chlorine is lost during imidization probably via evolution of HCl. The final metal-containing product may be a form of tin-oxide which may be dispersed primarily on the air-side of the film. A faint surface
Table VIII
Elevated Temperature Resistivity Measurements for Film 3

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Surface Resistivity Air-Side (ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>7.5x10^5</td>
</tr>
<tr>
<td>44</td>
<td>7.1x10^5</td>
</tr>
<tr>
<td>61</td>
<td>6.4x10^5</td>
</tr>
<tr>
<td>80</td>
<td>5.5x10^5</td>
</tr>
<tr>
<td>123</td>
<td>3.2x10^5</td>
</tr>
<tr>
<td>143</td>
<td>2.7x10^5</td>
</tr>
<tr>
<td>154</td>
<td>2.4x10^5</td>
</tr>
<tr>
<td>160</td>
<td>2.3x10^5</td>
</tr>
</tbody>
</table>
deposit in fact appears on the air-side of the film.

**Film 4: BTDA/ODA-(n-Bu)_3SnH**

This dopant produced a clear, homogeneous film with high resistivity. Raised areas on the film surface were probably due to \( \text{H}_2 \) evolution arising from reaction of the hydride with \( \text{H}_2\text{O} \). The percentage of tin found and calculated were practically identical.

**Film 5: BTDA/ODA-(CH_3)_2SnCl_2**

Use of \((\text{CH}_3)_2\text{SnCl}_2\) as a dopant produced a film somewhat similar in appearance to film 3. Raised areas were present which may be due to methane and/or HCl generation during cure. Volume resistivity values for both materials were the same. Glass-side surface resistivities were also comparable for films 3 and 5. Air-side values differed significantly with film 5 being much higher.

**Film 6: BTDA/ODA-\(\phi\text{SnCl}_3\)**

Elemental analysis revealed this additive totally vaporized during the cure process. Boiling point of \(\phi\text{SnCl}_3\) is 128°C, 15 torr.\(^{39}\) Evidently there was no interaction of additive with the polymer solution. Electrical resistivity values were comparable to those of the undoped BTDA-ODA.

**Film 7: PMDA/ODA-(n-Bu)_2SnCl_2**

In contrast to film 3, which employed the same dopant but in BTDA-ODA, this dopant/polymer combination produced a relatively homogeneous, dark brown film of high quality. Resistivity was not as
low as was the case with the BTDA-ODA material. For PMDA-ODA doped films the air-side surface resistivity of this film was lower than with any other Sn(IV) additives. Some black material was present in the film in small quantities, which may be a decomposition product of the additive. Overall, this is the highest quality Sn(IV) doped material prepared in this study with significantly lower resistivity values.

**Film 8: PMDA/ODA-(CH₃)₄Sn**

The dopant utilized for this material also totally vaporized apparently due to its low boiling point (76.6°C). Elemental analysis indicated tin was present at less than 0.01% concentration. Properties of the PMDA-ODA polyimide, nevertheless, have been somewhat modified. Softening and decomposition temperatures have been slightly reduced along with electrical resistivity.

**Film 9: PMDA/ODA-4₃SnOH**

This material was homogeneous and slightly darker in color than the undoped PMDA-ODA polymer. The film was more brittle than other tin-containing films. Evidently the mechanical properties of the polymer were degraded to some extent by this additive. Tg has increased but the polymer decomposes ~60°C lower than the undoped material. Degradation of the polymer could have occurred through reaction of the additive hydroxyl group with the carboxyl moiety of the polyamic acid thereby altering the extent of imidization as pictured below.
This process could then be followed by cleavage of the tin-carboxyl linkage either thermally or hydrolytically, resulting in a loss of the structural integrity of the polymer.

**Film 10: BTDA/ODA-SnCl₂·2H₂O**

This material is fairly smooth, tough and flexible. Coloration is dark yellow with darker brown splotches running through the film. This material offered a somewhat lower resistivity in comparison to most of the Sn(IV) additives. Lowest resistivity was determined for the air-side of the film. XPS data showed several orders of magnitude more tin on the air-side than the glass-side, suggesting migration of the tin during cure. No chlorine was detectable on either side of the film. Tin is likely to be present on the surface in some oxide form, as a result of hydrolysis and air oxidation as shown below.

\[
\begin{align*}
\text{SnCl}_2 + 2\text{H}_2\text{O} & \rightarrow \text{Sn(OH)}_2 + 2\text{HCl} \\
2\text{Sn(OH)}_2 + \text{O}_2 & \rightarrow 2\text{SnO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

Glass transition temperature for this polyimide has been uniquely modified. \( T_g \) has decreased relative to the polymer-alone unlike all other tin additives examined in this study. As in the \( \text{(n-Bu)}_2\text{SnCl}_2 \) cases, approximately 1% tin has been lost during imidization.
Film 11: PMDA/ODA-SnCl$_2$·2H$_2$O

This film was more homogeneous in appearance than the previous film and overall was several orders of magnitude lower in resistivity. XPS data showed a factor of 102 times more tin on the air side than the glass-side of the film, which probably is the reason for its much lower air-side surface resistivity. XPS also indicated the absence of chlorine on either side of the film.

Summary, Part I

A number of thermally stable tin containing polyimides with interesting properties have been prepared. These materials ranged in color from clear yellow to heterogeneous, dark brown in appearance. The thermal behavior of one film indicated a thickening effect may be induced by one tin additive, triphenyltin benzimidazole upon heating. All tin-modified polyimides exhibited a PDT greater than 500°C. Volume resistivities of all films were measured to be greater than 10$^{12}$ ohm-cm.

Two additives, (n-Bu)$_2$SnCl$_2$ and SnCl$_2$·2H$_2$O, were found to produce surface-semiconductive films. Resistivity of one surface-semiconductive film, (n-Bu)$_2$SnCl$_2$, was found to be independent of atmosphere and humidity by both elevated temperature measurements under dynamic vacuum and measurements taken in a desiccated, inert atmosphere glove bag following cyclic heating and pumping. XPS measurements confirmed relatively high concentrations of tin on the air-side as opposed to the glass-side of these semiconductive films. Lowered surface resistivities, into the semiconductor region, therefore appears to be correlated with large concentrations of tin, most likely in the form of
SnO$_2$. The surface-semiconductive properties of some of the materials produced in this study warranted further investigation in order to characterize more fully their electrical properties and chemical composition. Part II of this thesis which follows, addresses these points.

II. Surface Semiconductive Films Containing Tin Complexes

This section will attempt to describe the nature of the semiconductive species responsible for the lowered resistivity exhibited by certain of these tin-modified polyimide films. The effect of tin concentration and curing atmosphere upon film electrical properties will be discussed. Elevated temperature resistivity and photoconductivity data will also be described.

A. Thermal and Electrical Properties

Thermal data taken for the tin-modified polyimide films are shown in Table IX along with that of the corresponding polyimides containing no tin dopant. The apparent glass transition temperature (AGT) varies in an erratic manner with tin-complex incorporation. The effect of curing atmosphere is most striking. Air-cured films exhibit AGT's which are equal to or greater than the polyimide alone; whereas, PMDA/ODA doped films when cured in N$_2$ or forming gas demonstrate much lower (~100°C) AGT's unlike the one BTDA-ODA film cured in N$_2$. Polymer decomposition temperatures were seen to consistently decrease upon tin-complex incorporation. However, polymer decomposition temperature for all these materials was 500°C or greater. The thermal stability of
Table IX
Thermal Properties of Semiconductive Tin-Containing Polyimide Films

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Dopant</th>
<th>Cure Atmosphere</th>
<th>PDT (°C)</th>
<th>AGT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMDA-ODA</td>
<td>SnCl$_2$·2H$_2$O</td>
<td>air</td>
<td>546</td>
<td>450</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td>(n-Bu)$_2$SnCl$_2$</td>
<td>air</td>
<td>534</td>
<td>Decomp.</td>
</tr>
<tr>
<td>BTDA-ODA</td>
<td>SnCl$_2$·2H$_2$O</td>
<td>air</td>
<td>544</td>
<td>280</td>
</tr>
<tr>
<td>BTDA-ODA</td>
<td>(n-Bu)$_2$SnCl$_2$</td>
<td>air</td>
<td>548</td>
<td>404</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td>SnCl$_2$·2H$_2$O</td>
<td>N$_2$</td>
<td>520</td>
<td>314</td>
</tr>
<tr>
<td>BTDA-ODA</td>
<td>(n-Bu)$_2$SnCl$_2$</td>
<td>N$_2$</td>
<td>500</td>
<td>304</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td>(n-Bu)$_2$SnCl$_2$</td>
<td>N$_2$</td>
<td>510</td>
<td>327</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td>SnCl$_2$·2H$_2$O</td>
<td>Forming gas</td>
<td>510</td>
<td>327</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td>--</td>
<td>air</td>
<td>580</td>
<td>405</td>
</tr>
<tr>
<td>BTDA-ODA</td>
<td>--</td>
<td>air</td>
<td>550</td>
<td>286</td>
</tr>
</tbody>
</table>

$^a$Polymer Decomposition Temperature (Thermal Gravimetric Analysis)

$^b$Apparent Glass Transition Temperature (Thermomechanical Analysis)
these polyimides appears, therefore, not to be compromised by tin-complex incorporation.

Surface resistivity measurements for the tin-modified polyimide films are listed in Table X as a function of cure atmosphere, and in the case of one dopant/polyimide, as a function of degree of tin loading. Values for the unmodified polyimide are also shown. For all tin-modified films cured in air, a resistivity decrease into the semiconductor range is noted for the atmosphere-side (side of film exposed to atmosphere during curing). A less dramatic resistivity decrease was realized for the glass-side of these films. Films cured in N₂ exhibited similar resistivities regardless of the film side and each film was close in value to that of the unmodified material. A film cured in forming gas showed a lower atmosphere-side surface resistivity, but again not to the same degree as with the air-cured films.

Elemental analyses listed in Table X, indicate the presence of 1.5 to 3 times more tin in air-cured films as opposed to N₂ or forming gas-cured materials. It is also important to recognize that tin is apparently lost during the curing of all films except one (PMDA/ODA-SnCl₂·2H₂O, air cured). More tin is found than calculated for this material, indicating loss of polymer or loss of ligand (Cl or H₂O) by the metal during thermal imidization. X-ray photoelectron spectroscopy (XPS) measurements suggest the latter possibility, vide infra.

The effect on resistivity of increasing the metal complex
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Dopant</th>
<th>Cure Atmosphere</th>
<th>Surface Resistivity (Ω)</th>
<th>% Sn</th>
<th>% Sn Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Atmosphere Side Glass Side</td>
<td>Calc'd.</td>
<td>Found</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td>SnCl₂·2H₂O</td>
<td>Air</td>
<td>2×10⁶ 6×10¹²</td>
<td>6.36</td>
<td>6.62</td>
</tr>
<tr>
<td>BTDA-ODA</td>
<td>SnCl₂·2H₂O</td>
<td>Air</td>
<td>1×10⁸ 6×10¹²</td>
<td>5.22</td>
<td>4.88</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td>(n-Bu)₂SnCl₂</td>
<td>Air</td>
<td>8×10⁷ 5×10¹⁴</td>
<td>5.97</td>
<td>4.06</td>
</tr>
<tr>
<td>BTDA-ODA</td>
<td>(n-Bu)₂SnCl₂</td>
<td>Air</td>
<td>1×10⁵ 2×10¹³</td>
<td>4.92</td>
<td>3.47</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td>SnCl₂·2H₂O</td>
<td>N₂</td>
<td>1×10¹⁶ &gt;10¹⁸</td>
<td>6.36</td>
<td>2.08</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td>(n-Bu)₂SnCl₂</td>
<td>N₂</td>
<td>9×10¹³ 6×10¹³</td>
<td>5.95</td>
<td>1.64</td>
</tr>
<tr>
<td>BTDA-ODA</td>
<td>(n-Bu)₂SnCl₂</td>
<td>N₂</td>
<td>5×10¹⁵ 7×10¹⁴</td>
<td>4.94</td>
<td>1.02</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td>SnCl₂·2H₂O</td>
<td>Forming gas</td>
<td>6×10¹⁰ 3×10¹⁶</td>
<td>6.36</td>
<td>2.20</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td>SnCl₂·2H₂O</td>
<td>Air</td>
<td>7×10⁶ 4×10¹³</td>
<td>8.92</td>
<td>8.60</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td>SnCl₂·2H₂O</td>
<td>Air</td>
<td>3×10⁷ 7×10¹²</td>
<td>11.25</td>
<td></td>
</tr>
<tr>
<td>BTDA-ODA</td>
<td>--</td>
<td>Air</td>
<td>~10¹⁷ ~10¹⁷</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td>--</td>
<td>Air</td>
<td>&gt;10¹⁸ &gt;10¹⁸</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

\*a50% additional dopant used
\*b100% additional dopant used
concentration was evaluated for the PMDA-ODA/SnCl$_2$·2H$_2$O doped material. Films were cast and air-cured using 1:4, 1.5:4 and 2:4 complex/polymer millimolar ratios. All three of these films were of reasonably good quality. The lowest surface resistivity measured was for the film prepared employing a 1:4 mole ratio. The films prepared with higher metal/complex ratios exhibited higher resistivities, as shown in Table X. Apparently a lower resistivity limit of 10$^6$ is realized for this dopant/polymer pair, with the result that increased tin complex loading slightly increases rather than decreases resistivity.

B. Nature of Film Surfaces

Auger electron/argon ion etching spectra (AES) for tin-doped semiconductive polyimide films are shown in Figures 11-13. All films involve PMDA-ODA polyimide doped with either SnCl$_2$·2H$_2$O or with (n-Bu)$_2$SnCl$_2$ and cured in either air or nitrogen. The AES profiles, which are shown, are for the atmosphere-side of these films. The AES spectra reflect differences in depth-profile elemental concentrations which are apparently induced by curing in either air or nitrogen. Elements profiled include tin, chlorine, nitrogen, and carbon. In each Figure, atomic concentration is plotted as a function of sputter time, sputter rate being approximately 500 angstroms per minute. Baseline atomic concentration varies between 0-10%.

Air-cured PMDA/ODA-SnCl$_2$·2H$_2$O (Figure 11) exhibited a large concentration of surface tin-species (about 65 atomic percent) which sharply decreased upon further depth profiling. Very little chlorine was observed to be present. The same material when cured in nitrogen
Figure 11. Depth profile of PMDA/ODA-SnCl$_2$·2H$_2$O air-cured film monitored by Auger electron spectroscopy.
Figure 12. Depth profile of PMDA/ODA-SnCl₂·2H₂O nitrogen-cured film monitored by Auger electron spectroscopy.
Figure 13. Depth profile of PMDA/ODA-(n-Bu)$_2$SnCl$_2$ air-cured film monitored by Auger electron spectroscopy.
was found to charge greatly; therefore, a rather thick gold coating had to be applied. Sputtering through the gold coating required slightly over three minutes (Figure 12). A tin concentration of 28 atomic percent was seen at the surface of this N2-cured material, which tapered off quickly as sputtering continued into the bulk of the film. Chlorine was again only seen to be present in very low quantities. In comparison with the air-cured film, the nitrogen-cured film appeared to have much less surface tin species present.

Although the tin deposit was not as thick, the same trends are exhibited for PMDA/ODA-(n-Bu)2SnCl2 air and nitrogen-cured films as observed for the previous two SnCl2·2H2O films. A much greater amount of surface tin was present in the air-cured versus the nitrogen-cured material. Concentration of tin species in the air-cured film was observed to decrease abruptly as sputtering continued into the bulk of the material (Figure 13). Chlorine was undetectable in the air-cured film and was not analyzed in the nitrogen-cured film.

Comparison of these depth profiles provides information regarding the differences between the surfaces of the semiconductive (air-cured) films as opposed to the nonconductive (nitrogen-cured) films. It is apparent that the air-cured films have a deposit of a tin species concentrated within 1000-1500 angstroms of the film's surface. The nitrogen-cured films have a surface tin concentration also, but it is much lower in magnitude. These data indicate that the presence of a high tin surface concentration may be responsible for the lower surface resistivities shown by these air-cured films.
Tin binding energies were determined via x-ray photoelectron spectroscopy (XPS) for the four previously discussed materials. Tin (3D\textsubscript{5}/2, 3D\textsubscript{3}/2) binding energies for both sides of these materials along with one other tin-modified polyimide are shown in Table XI. Binding energies for all films were found to be essentially the same (within 1.0 eV) regardless of the method of cure, or the additive employed (Figure 14). The literature value for the binding energy of tin metal (3D\textsubscript{5}/2) is 484.5 eV.\textsuperscript{46} We have measured tin binding energies for tin in SnO\textsubscript{2} and found them to be 486.6 eV and 495.0 eV. Tin is indicated, therefore, to be in a rather oxidized form on the film surface, since, all binding energies appear closer in value to that of SnO\textsubscript{2} than to tin metal. A survey of the literature suggests that Sn(II) materials also exhibit binding energies in the same region\textsuperscript{46,47,48}, but the preferred oxidation state under air-cured conditions is most likely Sn(IV). For nitrogen-cured films, XPS measurements cannot reliably distinguish Sn(II) from Sn(IV). The higher resistivities observed for nitrogen-cured films may not only be due to a lower surface tin concentration but also may be due to a different less conducting tin species on the film surface.

XPS did furnish some useful, although somewhat quantitative information. Air-cured films were found to have much more tin on the atmosphere-side compared to the glass side, by approximately a factor of 100. Nitrogen-cured films also had more tin on the atmosphere side compared to the glass-side, but only by a factor of 10-30. Air-cured films were found to have more atmosphere-side tin than nitrogen-cured
Table XI
Binding Energies of Semiconductive Tin-Containing Polyimide Films

<table>
<thead>
<tr>
<th>Material</th>
<th>Cure</th>
<th>Side</th>
<th>Sn Photopack B.E.(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>3D5/2</td>
</tr>
<tr>
<td>PMDA-ODA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnCl₂·2H₂O</td>
<td>Air</td>
<td>Atmosphere Glass</td>
<td>485.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glass</td>
<td>486.2</td>
</tr>
<tr>
<td>SnCl₂·2H₂O</td>
<td>N₂</td>
<td>Atmosphere Glass</td>
<td>486.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glass</td>
<td>486.0</td>
</tr>
<tr>
<td>(n-Bu)₂SnCl₂</td>
<td>Air</td>
<td>Atmosphere Glass</td>
<td>485.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glass</td>
<td>485.6</td>
</tr>
<tr>
<td>(n-Bu)₂SnCl₂</td>
<td>N₂</td>
<td>Atmosphere Glass</td>
<td>486.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glass</td>
<td>486.4</td>
</tr>
<tr>
<td>BTDA-ODA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnCl₂·2H₂O</td>
<td>Air</td>
<td>Atmosphere Glass</td>
<td>486.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glass</td>
<td>486.8</td>
</tr>
</tbody>
</table>

Sn 3D5/2,3/2 binding energies in SnO₂ were measured to be 486.6 and 495.0 eV respectively. For tin metal, Sn 3D5/2 binding energy equal 484.5 eV (Reference 401).
Figure 14. X-ray photoelectron spectrum of Sn 3D photopeak region for the air-cured film derived from PMDA-ODA/SnCl$_2$·2H$_2$O, air-side. See Table III for corrected binding energies.
films as previously discovered via depth profiling with AES monitoring. Chlorine was not detectable via XPS regardless of cure environment or film side. One then is forced to conclude based upon AES and XPS data is not associated with tin on or near the film surface.

Further information regarding the identity of the surface tin deposit found on semiconductive tin-doped polyimide films was obtained via Fourier transform infrared-attenuated total reflectance (FTIR/ATR) analysis. Figures 15 and 16 show the FTIR-ATR spectra of a polyimide film and the same material modified with \((n\text{-Bu})_2\text{SnCl}_2\). While analyzing the FTIR-ATR spectra of these films, it was initially noted that in no case was there a dramatic shifts in the vibrational frequency of any polymer IR bands as a result of tin incorportion. Polymer carbonyl frequencies in particular were compared between tin-complex doped and undoped polyimide. Coordination of tin nuclei to polymer carbonyl moieties has been previously found to produce a shift in carbonyl stretching frequency of about 50 cm\(^{-1}\). IR evidence (Table XII) indicated no coordination of polymer carbonyl groups with the tin dopant for any films produced in this study, air- or N\(_2\)-cured.

Although IR band frequencies were not found to change significantly upon tin complex doping, a marked increase in IR absorption upon tin incorporation was observed in one spectral region. Figure 17 illustrates the 1400 cm\(^{-1}\) to 400 cm\(^{-1}\) region of the semiconductive surface (atmosphere-side) of the BTDA-ODA/(n-Bu)\(_2\)SnCl\(_2\) air-cured film compared with air-cured BTDA-ODA (no additive). A distinct broadening of the bands in the 800-500 cm\(^{-1}\) region of the spectrum of the
Figure 15. FTIR-ATR spectrum of BTDA/ODA air-cured film.
Figure 16. FTIR-ATR spectrum of BTDA/ODA (n-Bu)_2SnCl_2 air cured film.
<table>
<thead>
<tr>
<th>Polyimide</th>
<th>Additive</th>
<th>(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMDA/ODA</td>
<td>--</td>
<td>1776</td>
</tr>
<tr>
<td>PMDA/ODA</td>
<td>SnCl₂·2H₂O</td>
<td>1775</td>
</tr>
<tr>
<td>PMDA/ODA</td>
<td>(n-Bu)₂SnCl₂</td>
<td>1776</td>
</tr>
<tr>
<td>BTDA/ODA</td>
<td>--</td>
<td>1776</td>
</tr>
<tr>
<td>BTDA/ODA</td>
<td>SnCl₂·2H₂O</td>
<td>1777</td>
</tr>
<tr>
<td>BTDA/ODA</td>
<td>(n-Bu)₂SnCl₂</td>
<td>1775</td>
</tr>
</tbody>
</table>

Resolution of Spectrometer = 4 cm⁻¹
Figure 17. FTIR-ATR spectra of (n-Bu)_2SnCl_2-doped and undoped BTDA/ODA air-cured films.
tin-containing film was observed. A subtraction spectrum (polyimide film subtracted from tin-modified film) is shown in Figure 18. An absorption was discovered which is unique to the tin-doped film and no doubt accounts for the broadening effect. The FTIR spectrum of a sample of SnO₂, taken on the same instrument, is also shown in Figure 18. Based on this comparison it would appear that a concentration of SnO₂ is present at or near the surface of the (n-Bu)₂SnCl₂ modified BTDA-ODA film. Figure 19 provides the same comparison for the PMDA-ODA/SnCl₂·2H₂O air-cured film (semiconductive, atmosphere-side) versus air-cured PMDA-ODA. The presence of SnO₂ would again account for band broadening in the 800 cm⁻¹ to 500 cm⁻¹ region. Figure 20 is a spectrum taken of the PMDA-ODA/SnCl₂·2H₂O film, N₂-cured, atmosphere-side. Careful inspection revealed no broadening in the 800-500 cm⁻¹ region, relative to PMDA-ODA alone. Several rationalizations can be suggested to account for this observation. The surface concentration of Sn as SnO₂ may be so low that it is undetectable via FTIR-ATR and too dispersed to be conductive. Alternatively, the surface Sn may not be "SnO₂-like" and not IR active in the monitored region. In view of the fact that the film was cured in nitrogen, an oxidant source to convert Sn(II) to Sn(IV) is not readily apparent. A form of non-conductive Sn(II) oxide on the surface of the N₂-cured film seems more likely.

In summary, Auger, XPS and FTIR-ATR data indicate migration of tin to the atmosphere-side during curing, for both air and N₂-cured films. Incompatibility of the tin additive with the polymer system and
Figure 18. Subtraction FTIR-ATR spectrum of (n-Bu)_2SnCl_2-doped and undoped BTDA/ODA air-cured films compared with the spectrum of SnO_2.
Figure 19. FTIR-ATR spectra of SnCl₂·2H₂O-doped and undoped PMDA/ODA air-cured films.
Figure 20. FTIR-ATR spectrum of SnCl$_2$·2H$_2$O-doped PMDA-ODA nitrogen-cured film.
volatility of the tin additive are probably promoting this surface segregation effect. On only one film (BTDA-ODA/(n-Bu)2SnCl2) is a surface deposit evident by visual inspection; all others have comparatively homogeneous appearances. Surface-semiconductive films are found to have SnO2 surfaces extending several thousand angstroms into the bulk of the film. The SnO2 surface is apparently tightly bonded to the polymer since attempts to etch the deposit resulted in destruction of the film. The chemical state of the tin in nonconductive films (cured in N2) which have a much smaller amount of surface tin has not been conclusively identified.

C. Chemical Fate of Tin(II) and Tin(IV) Additives

Well established tin chemistry can be invoked to rationalize the formation of SnO2 and loss of chlorine during thermal imidization of these films in air. Reaction of the chlorine-containing tin additives during curing can be thought to occur as follows. For the Sn(II) additive, hydrolysis of the Sn-Cl bond to yield HCl and Sn(OH)2 followed by air oxidation of the Sn(II) to ultimately produce a form of SnO2 is expected.

\[
\begin{align*}
SnCl_2 + 2H_2O & \rightarrow Sn(OH)_2 + 2HCl \\
2Sn(OH)_2 + O_2 & \Delta \rightarrow 2SnO_2 + 2H_2O
\end{align*}
\]

For the Sn(IV) additive, hydrolysis is again anticipated initially thereby freeing HCl. Thermal cleavage of the Sn-C bond to yield n-butane or a higher alkane concurrent with some dehydration could then be envisioned to produce SnO2. The latter proposed Sn(IV) scheme would
be likely for both air and N₂-cured films. The nature of SnO₂ in both cases, however, may be different since air-cured and nitrogen-cured films have dissimilar surface electrical properties.

\[(n-\text{Bu})_2\text{SnCl}_2 + 2\text{H}_2\text{O} \rightarrow (n-\text{Bu})_2\text{Sn(OH)}_2 + 2\text{HCl} \]

\[(n-\text{Bu})_2\text{Sn(OH)}_2 \xrightarrow{\Delta} \text{SnO}_2 + 2n-\text{Bu-H}\]

A different mechanism must be considered for Sn(II) doped films cured under nitrogen. An initial hydrolysis followed by dehydration (300°C imidization) to give probably a polymeric form of tin(II) oxide appears at this time to be reasonable.

\[\text{SnCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Sn(OH)}_2 + 2\text{HCl} \]

\[\Delta \]

\[x\text{Sn(OH)}_2 \rightarrow (\text{Sn-O})_x + x\text{H}_2\text{O}\]

H₂O is generated at >150°C during imidization of the polymer. More tin was found to be retained by air-cured films than N₂-cured films via elemental analysis. This could be due to oxidation (in the case of Sn(II)) or alteration (in the case of Sn(IV)) of the tin complex in air to the more nonvolatile SnO₂ before evaporation of the tin additive could occur. N₂ curing apparently allows for considerably more volatilization of the complex from the film. It is highly likely for the Sn(IV) additive that polymeric tin species and alkyl side products other than those shown are generated during imidization, particularly under N₂-cure. As shown, the Sn(IV) compound could, in theory, react with H₂O at elevated temperature in the absence of O₂ to give SnO₂. The alkyl-tin, on the other hand, bond is unstable at >200°C49 and seems to
be cleaved in both air and N₂-cured films.

D. Resistivity Properties as a Function of Elevated Temperature and Irradiation

Figures 21 and 22 are plots of surface resistivity versus temperature for two semiconductive tin-containing polyimide films. Both experiments were conducted under dynamic vacuum and both the heating and cooling curves are shown. Resistivities of both films are seen to decrease upon heating. Semiconductive properties are still present after heating in vacuo, indicating ambient atmosphere has little effect upon resistivity. A hysteresis effect is observed upon cooling in both cases (i.e. lower resistivity values are exhibited by both films after thermal cycling).

SnO₂ has been studied extensively as an electrode material.⁵¹ SnO₂ is an n-type semiconductor, with a resistivity ranging from 10⁸ ohms into the conductor region, depending upon the amount and kind of impurities (dopants) present.⁵¹ The hysteresis seen in Figures 21 and 22 could be induced by diffusion of impurities from the polymer into the SnO₂ surface layer during heating. Support for this observation comes from the fact that annealing has been seen to affect the electrical properties of SnO₂ in other studies.⁵¹

The nature of these semiconductive films prompted a photoconductivity experiment. Since SnO₂ is an n-type semiconductor, irradiation with a UV source should cause an observable decrease in resistivity. Surface resistivity as a function of irradiation time is shown in Table XIII for (i) the semiconductive side of a film under full
Figure 21. Surface resistivity versus temperature for air-cured PMDA/ODA-SnCl$_2$·2H$_2$O.
Figure 22. Surface resistivity versus temperature for air-cured BTDA/ODA-(n-Bu)₂SnCl₂.
Table XIII

Resistivity of PMDA-ODA/SnCl$_2$·2H$_2$O as a Function of Irradiation

<table>
<thead>
<tr>
<th>Irradiation Time (min.)</th>
<th>ρ (x10^3Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>251 (247)$^a$ [236]$^b$</td>
</tr>
<tr>
<td>1.0</td>
<td>[238]</td>
</tr>
<tr>
<td>2.5</td>
<td>125 (174)</td>
</tr>
<tr>
<td>5.5</td>
<td>122 (162)</td>
</tr>
</tbody>
</table>

$^a$Numbers in parentheses are for UV irradiation only (IR filter)
$^b$Numbers in brackets are for irradiation of glass-side (nonconductive side) of film.
irradiation from an argon lamp and (ii) the same sample under irradiation through a filter transmitting UV but not IR radiation. Data show that the film is photoactive since resistivity decreases by about half upon irradiation. Filtering out the IR radiation showed that the decrease in resistivity was of an electronic, rather than a thermal nature. Irradiation of the reverse, nonconductive side of the same film failed to cause any lowering of resistivity. The polyimide itself was therefore seen to have no photoactivity. This also ruled out any thermal contributions.

Summary, Part II

Air-cured films fabricated from PMDA-ODA or BTDA-ODA polyimide and SnCl₂·2H₂O or (n-Bu)₂SnCl₂ were found to have atmosphere-side surface resistivities from 10⁵ to 10⁸ ohm. Most films are homogeneous and each exhibits good thermal stability. Characterization of air-cured film surfaces revealed a relatively thick layer of SnO₂ which is responsible for decreased resistivity values relative to the undoped polymer. Production of the SnO₂ surface layer is thought to be due to migration, and chemical reaction, of the tin additive during curing. N₂ curing produced nonconductive film surfaces with much lower concentrations of tin species. Air curing is presumed to allow, or to accelerate formation of SnO₂; while, N₂ curing allows more substantial volatilization of the added tin complex. Air-cured films exhibited lower surface resistivities upon heating (atmosphere-side). Irreversible migration of impurities from the polymer film to the SnO₂ layer lowered resistivity after annealing in vacuum. The
atmosphere-side of air-cured films was found to be photoactive, decreasing in resistivity twofold upon irradiation with a strong UV source.
Chapter V

FINAL SUMMARY AND CONCLUSIONS

A number of tin-modified polyimide films have been fabricated which have diverse properties. The electrical properties and thermal behavior of these materials have been characterized. The chemical nature of some films has been explored in order to elucidate the fate of the tin complexes after incorporation into the polyimides.

Appearance of these films ranged from clear yellow (indistinguishable from unmodified polyimide) to dark brown and heterogeneous. Most films were relatively homogeneous, flexible, and tough. In only a few instances were materials produced which were brittle and obviously inferior to the original polyimide.

All tin-modified polyimide films were found to have polymer decomposition temperatures (PDT) $> 500^\circ$C. The PDT was usually lowered by tin complex incorporation, in the worst case by 64$^\circ$C. All materials appear to be relatively thermally stable; tin incorporation does not appear to have severely affected the elevated temperature stability of polyimide. Apparent glass transition temperatures (AGT) were in most cases raised by tin complex incorporation. Expansion of the sample during the TMA experiment was observed for one material.

Electrical properties of tin-modified polyimide films were found to depend greatly upon the tin additive and cure atmosphere employed. Volume resistivities of all films were measured to be 1012 ohm-cm or greater. Films with semiconductive surfaces were prepared via the use of SnCl$_2$·2H$_2$O or (n-Bu)$_2$SnCl$_2$ as additives. Air-cured films produced
via these additives exhibited surface resistivities from 105 to 108 ohm. This represented an enhancement of 1011 to 108 over the surface resistivity of the polyimide alone. These air cured films were found to be photoactive; a decrease in resistivity by a factor of 1/2 was exhibited upon irradiation. N2-cured films were found to have nonconductive surfaces.

The fate of the tin additive was somewhat speculative for many of the nonconductive materials. Total volatilization apparently occurred in several cases (\(\PhiSnCl_3, (CH_3)\PhiSn\)). Partial volatilization of some species during the curing process led to heterogeneous features in one instance, (\(\Phi3SnC≡CSn\Phi3\)). Complexation with the polyamic acid (preventing complete imidization) led to brittle films in one case (\(\Phi3SnOH\)). Decomposition of triphenyltin benzimidazole appears to have caused drastic changes in the thermal behavior of the polyimide. Off-gas released during the decomposition of the complex at \(\approx300^\circ C\) may have induced a shrinkage effect, thereby, causing the film to thicken during the TMA measurement. Nonconductive films derived from additives other than \(SnCl_2\cdot2H_2O\) or \((n-Bu)_2SnCl_2\) appeared to have a relatively homogeneous distribution of tin species throughout the bulk, as suggested by XPS. The nonconductive nature of many of these films apparently was due to: (i) lack of surface segregation by additives during cure and (ii) failure of these complexes to be converted to a semiconductive or conductive species.

The fate of the tin additive was extensively studied for air-cured materials prepared from the complexes \(SnCl_2\cdot2H_2O\) or \((n-Bu)_2SnCl_2\). The
semiconductive and photoactive features of these films made them of particular interest. The air-cured films obtained via use of these complexes have been demonstrated via FTIR-ATR, AES and XPS to have large air-side concentrations of SnO₂. The presence of this SnO₂ concentration is a criterion for the semiconductivity of these films. The films' glass-sides are found to lack this SnO₂ deposit and are nonconductive. This tightly-bound, ~1500 angstrom thick layer is apparently the result of surface segregation of either the SnCl₂·2H₂O or (n-Bu)₂SnCl₂ additives followed by hydrolysis, dehydration, and oxidation (Sn(II)) or hydrolysis, dehydration, and thermal bond cleavage (Sn(IV)). Air-curing enhances oxidation (Sn(II)) and apparently accelerates alteration (Sn(IV)) to nonvolatile SnO₂. N₂ curing allows more volatilization of the tin complex. Surfaces of N₂-cured films derived from SnCl₂·2H₂O or (n-Bu)₂SnCl₂ have tin-rich atomosphere-sides, confirmed by XPS and AES. Surfaces of N₂-cured films were found to be nonconductive, however. The identity of the tin-rich surface deposits found on N₂-cured films was not elucidated.
References


24. R. V. Subramanian, B. K. Gang and Jamie Corredor in ref. 21, p. 181.


43. Reference 35, p. 764.

44. E. Khor, Ph.D Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, VA (in press).


VITA

Stephen A. Ezzell was born November 29, 1958 in Charlotte, North Carolina. He graduated from Parkwood High School, Monroe, N.C. in 1977. In September, 1977 he was enrolled at St. Andrews Presbyterian College, Laurinburg, North Carolina. The summers of his junior and senior years were spent in employment as a research technician at NASA-Langley Research Center, Hampton, Virginia.

In May of 1981 he graduated from St. Andrews with a Bachelor of Science in Chemistry. He entered Virginia Polytechnic Institute and State University in September of 1981 as a graduate student in Chemistry. He received his Master of Science in Chemistry in August of 1983.

Stephen A. Ezzell
Modification of Polyimide Films Via Tin Complex Incorporation

by

Stephen A. Ezzell

(ABSTRACT)

The modification of polyimide films by tin-complex incorporation has been studied with the aim of producing materials with the mechanical and thermal properties of polyimide with enhanced electrical properties. A variety of Sn(II) and Sn(IV) complexes have been incorporated into BTDA/ODA (3,3',4,4'-benzophenonetetracarboxylic acid dianhydride / 4,4'-oxydianiline) and PMDA/ODA (pyromellitic dianhydride/4,4'-oxydianiline) derived polyimides in a 1:4 (complex/polymer repeat unit) molar ratio.

Tin-complex incorporation was seen to have a variety of effects upon polyimide properties, depending upon the particular tin-complex employed. All films produced were thermally stable with decomposition temperatures > 500°C. Most films were homogeneous and flexible.

Use of the complexes SnCl₂·2H₂O and (n-Bu)₂SnCl₂ produced materials having semiconductive surfaces on the side facing up during thermal curing. Other cure atmospheres than air produced nonconductive films. Auger, X-ray photoelectron spectrometry, and attenuated total reflectance/Fourier transform infrared measurements indicated the semiconductive properties of some surfaces to be due to a tightly bound surface layer of SnO₂. Apparently during thermal curing the two
previously mentioned complexes undergo migration to the film surface, hydrolysis, and alteration or oxidation to the final semiconductive SnO₂. This SnO₂ surface layer became more conductive as the film was annealed in vacuum, and was seen to be photoactive.