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Synthesis of Next Generation Dielectric Materials through Rational Exploration of Chemical Space

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Abstract

The search for new dielectric materials has grown exponentially as more emphasis has been placed on the fabrication of new devices such as photovoltaics, transistors and capacitors. This dissertation focuses on the exploration of chemical space through rational design as a means of identifying such potential dielectric materials for capacitors, though these materials can be potentially used for any applications mentioned. Chapter 3. Dielectric materials that can operate at elevated temperatures are desired as space could be a limiting factor for the large capacitor banks that are envisioned. Polyimides are demonstrated to have thermal and dielectric stability up to 125-150 °C. It was found that as the conjugation length of the dianhydride monomer or the number of ether linkages in the diamine monomer was increased so was the dielectric constant. The polyimide based on the longest conjugated dianhydride and ether diamine achieved the highest reported dielectric constant, 7.8, but at a cost of low Tg. Copolymerization is undertaken to improve the thermal properties and further tested for breakdown strength. Chapter 4. The incorporation of silicon into a polymer theoretically increases the dielectric constant due to the increase of polarizability of silicon versus carbon. However, the synthesis of polysilanes is
problematic, as large amounts of salt impurities are formed. Attempts to wash out the impurity from the polymer proved futile as the polysilane films were still very conductive. The synthesis of polysilanes guided our other attempts to create new dielectric materials by enlightening us on the need for high purity of polymers. **Chapter 5.** A series of organotin polymers were synthesized and from this poly(organotin esters) were identified as the most promising candidate as a dielectric. Theoretically and experimentally it was found that the structure of the polymers were quite complex due to coordination of oxygen and tin. The dielectric constant of a series of aliphatic poly(dimethyltin esters) were evaluated and exhibited dielectric constants between 5.3-8.7. Further analysis of the role of aromaticity and chirality within the polymer backbone was also performed. Also blending a homopolymer that had protruding methyl groups aided in the reduction of crystal size, improving the quality of films. **Chapter 6.** Other metals are incorporated into the polymer backbone due to their lower electronegativity versus oxygen. It was shown that these polymers could have a dielectric constant ranging from 3.3 to approximately 8. The role of bound water on dielectric properties was also explored to start to build a fundamental understanding.
Synthesis of Next Generation Dielectric Materials through Rational Exploration of Chemical Space

Aaron F. Baldwin

B.S., University of Connecticut, 2007

A Dissertation
Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy at the University of Connecticut

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Aaron F. Baldwin

2014
Synthesis of Next Generation Dielectric Materials through Rational Exploration of Chemical Space

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I dedicate this dissertation to my parents, Harry and Rita Baldwin, for their love and support.

July 13, 2014
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Chapter 1. Introduction

1.1 Dielectric Theory

1.1.1. Polarization and Dielectric Constant

Upon application of an electric field \( E \) on a dielectric material the dipoles of molecules within the material are displaced from their equilibrium positions and orient with respect to the field, Figure 1.1. To understand this phenomenon, the link between the electric field, polarization/polarizability and dielectric constant must be established. First the electric displacement, \( D \), of the material is related to the applied field and polarization, \( P \), through the following equation;

\[
D = \varepsilon_0 E + P \quad (1.1)
\]

in which \( \varepsilon_0 \) is the vacuum permittivity constant \( (8.854 \times 10^{-12} \text{ Fm}^{-1}) \). However, the electric displacement is not affected by polarization of the material but only on external forces producing the external field, \( E_0 \). Therefore, the electric displacement relation can be rewritten as;

\[
D = \varepsilon_0 E_0 \quad (1.2)
\]

The effect of polarization is to actually reduce the electric field within the material since,

\[
E = E_0 - \frac{1}{\varepsilon_0} P \quad (1.3)
\]

Thus the electric displacement is more commonly written as,

\[
D = \varepsilon E = \varepsilon_0 \varepsilon_r E \quad (1.4)
\]
where the quantity $\varepsilon_r$ is the relative dielectric constant of the insulator and is given by,

$$\varepsilon_r = \varepsilon/\varepsilon_o$$  \hspace{1cm} (1.5)

The applied field induces an electric dipole moment, $m$, on each molecule with the magnitude being dependent upon the strength of the local field, $E_{loc}$, since the interactions of the applied field varies with the induced dipoles created within the dielectric material,

$$m = \alpha E_{loc}$$  \hspace{1cm} (1.6)

The constant $\alpha$ is termed the polarizability of the material and indicates how well the material will polarize when the external field is applied. The total polarization of the material is related with the following relation;

$$P = N\alpha E_{loc}$$  \hspace{1cm} (1.7)

in which $N$ represents the total number of molecules being affected by the local field. From the Lorentz relation,

$$E_{loc} = E + (1/3\varepsilon_o)P$$  \hspace{1cm} (1.8)

it can be seen that the local field is larger than the applied field. The combination of equations 1.7 and 1.8 gives,

$$P = (N\alpha/(1-(N\alpha/3\varepsilon_o)))E$$  \hspace{1cm} (1.9)

and solving for the relative dielectric constant taking into account the effect of the local field results in the Clausius-Mosotti relation,

$$\frac{(\varepsilon_r-1)}{(\varepsilon_r+2)} = N\alpha/3\varepsilon_o$$  \hspace{1cm} (1.10)

Rewriting equation 1.10 as,
(M/ρ)(ε_r-1)/(ε_r+2) = N_Aα/3ε_0 \quad (1.11)

illustrates that the polarizability of the material can be calculated from the measured quantities, M, ρ and ε_r. The left and right side of equation 1.11 represent the molar polarizability of the dielectric material and illustrates how the dielectric constant of the material is related to its polarizability.¹

![Figure 1.1. Illustrative representation of the polarization of a dielectric material when an electric field, E, is applied.](image)

The polarizability explained in the previous paragraph is better labelled as the total polarizability since it is actually the sum of three different components; 1) electronic, 2) atomic and 3) orientational. Electronic polarizability, Figure 1.2, is
characterized by the small displacement of the electrons within an atom versus the positively charged nucleus. This shift is small as a result of the fact that the intra-atomic field of an electron due to the nucleus is approximately two orders of magnitude larger than the applied electric field. At high frequencies the electronic polarization is the cause for the refraction of light, \( n \), and in terms of the dielectric constant follows,

\[
\varepsilon_r = n^2
\]  

Equation 1.12

The electronic polarizability with respect to frequency is written as,

\[
\alpha_e(\omega) = \left( \frac{e^2}{m} \right) \left( \frac{f_{10}}{\left( \omega_{10}^2 - \omega^2 \right)} \right)
\]  

where \( \omega_{10} = (E_1 - E_0)/\hbar \) and \( f_{10} \) is the oscillator strength.\(^1\) Equation 1.13 exhibits that the electronic part of the dielectric constant is inversely proportional and thus limited by \( (E_1 - E_0) \) which corresponds to the energy band gap, \( E_g \), of the material.

**Figure 1.2.** Electronic polarization represented by (a) the unpolarized atom and (b) the polarized atom as a result of an applied electric field.
Atomic polarization also called ionic polarization, **Figure 1.3**, occurs when the electric field causes a distortion in the arrangement of the atomic nuclei in the molecule or lattice. Compared to electronic polarization, the movement of heavy nuclei is much slower versus electrons and results in the contribution to the total polarization being about one tenth that of the electronic part. The ionic contribution can be increased if the bending modes cause large deviation from the normally symmetric arrangements of positive and negative centers since the force constants of bending modes are much lower than the stretching or twisting modes.¹

![Electric Field](image)

**Figure 1.3**. Atomic (ionic) polarization illustrated as the lengthening of the ionic bond of NaCl when an electric field is applied.

Orientational (dipolar) orientation exists in materials in which there is already a permanent dipole moment, **Figure 1.4**. In the absence of an electric field there is no net polarization due to the random orientation of the dipole in all directions. However, when a field is applied there is an alignment of the dipole towards the electric field resulting in a net polarization. The magnitude of the orientational polarization to the dielectric constant can be quite large, but it does
take some time to develop. That is, when the field is applied sufficient time is needed for dipole alignment. If the field is applied and quickly removed then the orientational polarization would not contribute and therefore at high frequencies is absent as the dipoles are more or less stationary as the field switches rapidly.\textsuperscript{1,2} When a sufficient amount of time is given for the dipoles to orient then the maximum or static dielectric constant, $\varepsilon_r(0)$, is obtained.

![Figure 1.4](image)

**Figure 1.4.** Upon application of an electric field, the nonpolar CO\textsubscript{2} (a) molecule will not exhibit orientational polarization whereas the polar water molecule (b) would.

### 1.1.2. Dielectric Loss

The dielectric constant is a complex function,

$$\varepsilon_r = \varepsilon_r' + i\varepsilon_r''$$

(1.14)

where $\varepsilon'$ and $\varepsilon''$ represent the real part or the ability of the dielectric constant to store energy and the imaginary part or the dielectric loss, respectively. The ratio of the two parts, $\varepsilon''/\varepsilon'$, is termed the dissipation factor, tanδ. The loss factor represents that the dipole experiences friction as the result of collisions with other molecules, which increases the temperature within the material. The frequency dependence of the real and complex part are describe with Debye’s equations,\textsuperscript{1}

$$\varepsilon_r'(\omega) = n^2 + (\varepsilon_r(0) - n^2)/(1 + \omega^2\tau^2)$$

(1.15)
and

\[ \varepsilon'_r(\omega) = (\omega \tau) \left( \varepsilon'_r(0) - n^2 \right) / \left( 1 + \omega^2 \tau^2 \right) \]  \hspace{1cm} (1.16)

When the frequency is much less than \(1/\tau\), the collision frequency, the real part remains constant and equal to \(\varepsilon'_r(0)\) and when \(\omega \geq 1/\tau\) then the real part decreases until it reaches a value of \(n^2\) which confirms the relationship shown in equation 1.12. As for \(\varepsilon''\), the maximum value is achieved when the frequency is equal to the collision frequency, \(\omega = 1/\tau\). The dielectric loss of the material also increases with increasing temperature, humidity, voltage and the frequency of the applied voltage. For polymers, as temperature is increased the forces between polymer chains is broken allowing for more susceptibility towards thermal motion. If there are polar groups within the material then they become freer to orient with the electric field. At very low temperature the segmental motion of the polar groups is frozen while at very high temperature the thermal motion is so strong that it disrupts orientation. In both cases the dielectric constant of the material will be reduced. There are three types of chain and segmental motion that the polymer could undergo as temperature is increased; \(\alpha\), \(\beta\) and \(\gamma\) relaxations. The first relaxation, \(\alpha\), occurs at the highest temperature and corresponds to Micro-Brownian motion of the whole chain, which is essentially the glass transition temperature, \(T_g\), of the polymer. At intermediate temperature \(\beta\) relaxation is observed and is attributed to the rotation of polar groups about the C-C bond. The last type of motion, \(\gamma\) relaxation, is observed at the lowest temperature versus the other types and is due to the oscillation motion of phenyl rings and limited C-H segmental chain motion.
1.1.3. Dielectric Breakdown

An insulator is characterized by its large band gap as a large band gap eliminates states that are available for an excited valence electron to migrate to higher energy states and thus has low conductivity. However, there is some voltage (breakdown voltage) at which there is enough energy to excite the valence electrons into these higher states. At this point, the dielectric material loses its insulating properties. Thus, the breakdown voltage is related to the dielectric strength, as physics defines the dielectric strength two ways; 1) the maximum electric field strength that the insulating material can withstand without breakdown and 2) for a given configuration of a dielectric material and electrodes, the minimum electric field that produces breakdown and the maximum electric stress that the dielectric material can withstand without breakdown. Simply breakdown is a kinetic process which is characterized as the point when an irreversible discontinuity in current is first observed.\(^4\)

The mechanism most used to describe dielectric breakdown is “treeing” and can be inclusive of all types of breakdown, i.e. intrinsic, avalanche, thermal and cavity breakdown.\(^4,5\) Treeing is defined as the partial electrical breakdown within the polymer, in which damage occurs at a point within the material and grows parallel with the electric field until it reaches the other electrode or both electrodes depending upon where the failure occurs.\(^6,7\) Intrinsic breakdown, purely electrical breakdown, is described as the point in which the energy gained from the system is larger than the loss of energy to the material and is a result of
electron collisions.\textsuperscript{2,4} Avalanche breakdown is the result of the production of free electrons within the material colliding with bound electrons causing ionization and higher conduction.\textsuperscript{4,8} Thermal breakdown occurs at the point in which the heat generated within the dielectric material supersedes heat removal. The last mechanism, cavity breakdown, occurs if there are voids or impurities within the material itself.\textsuperscript{4,9,10} These allow for localized states to arise in within the energy band gap. The breakdown potential can be increased by increasing the crystallinity of the material since a crystalline material has a lower conductivity compared to an amorphous material.\textsuperscript{11-13} In a recent work, a model for estimating the intrinsic breakdown strength, an upper bound of $E_{bd}$, was developed at the level of first-principle calculations, requiring a description of the electron-phonon interactions.\textsuperscript{14} Wang also developed a mathematical relationship between band gap and the intrinsic breakdown field.\textsuperscript{15}

1.2. Dielectric Applications

1.2.1. Capacitors

One of the most common applications for dielectric materials is capacitors. A parallel plate capacitor, Figure 1.5, consists of metallic conducting plates or foils that are separated by a thin layer, approximately 10 μm in most capacitors, of an insulating/dielectric material. The opposite plates are charged by a voltage source and the electrical charge produced is stored in the polarized insulating medium. Therefore, a capacitor allows the storage of electrical energy over a long charging time and then that same electrical charge is released as required.
over a short (submicroseconds to multimilliseconds) period under controlled conditions. The capacitance, the ability to store energy, is given by the following equation;

\[
C = \frac{Q}{V} = \varepsilon_\infty \varepsilon_r \left( \frac{A}{d} \right)
\] (1.17)

where, \(C\) is capacity (Farad), \(Q\) is charge (Coulomb), \(V\) is Voltage (Volt), \(\varepsilon\) is dielectric constant (Fm\(^{-1}\)), \(A\) is the area of the electrodes (m\(^2\)), and \(d\) is the distance between the plates (m). The amount of energy stored, \(W\), within a capacitor is,

\[
W = \frac{1}{2}QV = \frac{1}{2}CV^2
\] (1.18)

or in terms of energy density, \(U\), with respect to the electric field

\[
U = \frac{1}{2} \varepsilon_\infty \varepsilon_r \varepsilon_0 E^2 d^2
\] (1.19)

Both equations 1.18 and 1.19 are equivalent. Both capacitance and energy density are linearly related to the dielectric constant.\(^{16}\)

Numerous polymer films have been studied for their application as a dielectric film in high energy density capacitors. The first polymer film capacitors were originally studied as a replacement of Kraft paper, a paper or paperboard produced from chemical pulp using the Kraft process, impregnated with dielectric fluids which were thermally limited and very inefficient. In 1963, G.E. invented the MAGVAR® system which replaced most of the Kraft paper with a biaxially oriented polypropylene (BOPP) film. Polypropylene was used because in the early 1960’s, twenty-two different polymers were surveyed as to which one fit the following key requirements the best; 1) dissipation factor vs. frequency and temperature (thermal limitations), 2) dielectric strength (volume and cost), 3)
dielectric constant (capacitance per unit area), 4) cost of monomer, 5) processability, 6) dielectric oil compatibility, 7) machinability, and 8) dielectric wear out and monomer purity. The operating temperature range was set at 100-110 °C. This operating temperature eliminated polyethylene and polyvinylidene chloride as choices. The monomers used to produce the polysulfones and polyimides were too costly even though they had a higher dielectric constant. Polystyrene was used as a capacitor material but showed large variations in capacitance (>10 percent) over the operating temperature range. Polyethylene terephthalate and polycarbonate also cost more for the monomers and also possess critical property defects. Polyethylene terephthalate has a large dissipation increase in the operating temperature range (thermal runaway). Polycarbonate had good stability but a higher dissipation factor than polypropylene (0.25 vs. 0.1 percent). Therefore, polypropylene was the best choice to use as a dielectric insulator in capacitors. The biaxially oriented films showed an increase (about 2 fold) in dielectric strength versus unoriented films. The relation of improved dielectric strength versus orientation can be related to the improved mechanical properties of the oriented state.\textsuperscript{17} Recent advances in the production of high energy density biaxially oriented polypropylene (BOPP) have increased the energy density from 0.5 J/cm\textsuperscript{3} in the early 1990s to 5 J/cm\textsuperscript{3} at breakdown as of today. BOPP possesses a low dielectric constant of ca. 2.2 with the best achievable dielectric constant being 2.5. Besides exhibiting extremely low dissipation, BOPP also has an electronic polarizability breakdown of 720 V/μm for films that are ~10μm thick.\textsuperscript{18,19}
1.2.2. Photovoltaics

Increased research in photovoltaics, Figure 1.6, is garnering attention as the drive to develop “greener” energy alternatives to fossil fuels continues to rise. The basic principle of a photovoltaic device is the photovoltaic effect in which the absorption of light by a material causes the creation of voltage or electric current.\textsuperscript{20} Within the framework of inorganics this creation is from the promotion of electrons from the valence band to the conduction band to create and exciton. In contrast, the exciton formation in organic semiconductors arises from the same type of promotion of an electron but from the highest occupied molecular orbital (HOMO) to the lowest unoccupied orbital (LUMO). The role of dielectric constant in this application deals with the magnitude of Coulomb interaction between electron and electron hole that is formed upon exciton formation, or simply how facile recombination is.\textsuperscript{21} Ideally, the binding energy needs to be as
low as possible as this will allow for easier dissociation. The relationship between binding energy and dielectric constant is seen in the electrostatic force, $F_{es}$, equation;

$$F_{es} = \frac{e^2}{(4\pi\varepsilon_0\varepsilon_r R^2)}$$  \hspace{1cm} (1.20)

From equation 1.20 it is seen that the dielectric constant should be high to reduce the binding energy and lower the probability of recombination. If the dielectric constant of the material is equal to 10, then this would correspond to a binding force of 25 meV which has been deemed sufficient for the application.\textsuperscript{22}

**Figure 1.6.** Illustrative representation of a photovoltaic device in which the dielectric layer is represented by the p- and n-type doped layers.

1.2.3. Gate Dielectrics

Dielectric materials are used as an insulating layer in field effect transistor (FET) applications, **Figure 1.7**, and are termed the gate dielectric. The common gate dielectric used is silicon dioxide, $\text{SiO}_2$, since it meets certain requirements such as high electrical strength even for small layer thickness, smooth non-polar surface in order to increase the adsorption and growth of pentacene, low deposition temperature, low trap density at the interface and a dielectric constant,
3.9, that allows reduction of the operating voltage. However, SiO₂ is reaching its operating limits as devices become thinner since a decrease in thickness is needed to offset short channel effects but in turn increases the gate leakage current. Once the thickness of the SiO₂ layer goes below 1.4 nm then electron tunneling effects are seen which causes the high leakage currents.⁹³ Therefore, much research has been spent on identifying other materials, both inorganic and organic as a means to give the device flexibility, with higher dielectric constant as a higher εₐ leads to smaller area of the gate dielectric, reduced operating voltage and higher transconductance. The drain current, Iₜ, is also increased as a result of it being proportional to capacitance, which in turn is proportional to εₐ.

![Figure 1.7. An illustration of a Metal-Oxide-Semiconductor Field Effect Transistor (MOSFET) in which the gate dielectric layer is marked in green.](image)

**1.3. Increasing the Dielectric Constant of Polymers**

**1.3.1. Functionalization of Polyolefins and Polar Polymers**

As discussed in the previous section, there is a great demand for higher dielectric constant materials as the fabrication of greener more efficient devices continues to grow. This growth and the potential to harness enormous amounts
of energy has circumvented the cost of materials to achieve high dielectric constant polymers, which was one of the limiting factors in selecting BOPP over some higher dielectric constant polymers in the 1960s. Probably the simplest method to produce a material that exhibits the same breakdown strength of BOPP while increasing the dielectric constant and as a result the energy density is the functionalization of polypropylene to introduce side chain polar groups to increase the dipolar polarization. A number of synthetic procedures, Figure 1.8, for functionalizing polyolefins have been developed over the years.\(^{24}\) One such method consists of direct copolymerization of propylene with a functional monomer.\(^{25-32}\) However, problems can arise as a consequence from such things as catalyst poisoning or side reactions during polymerization. A second method involves reacting preformed polypropylene with a free radical initiator or radiation to cleave a C-H bond along the backbone.\(^{33,34}\) The radical created in the polymer backbone can then be further reacted with another species to introduce the functional group. However, the free radical can also cause intra-molecular \(\beta\) scission which reduces the molecular weight of the polypropylene chain and produces one chain containing an unsaturated end group and another chain with a radical end group. Some groups have used this depolymerization process to create a block copolymer by further reaction of the radical end group with maleic anhydride.\(^{35-37}\) The problem with this process is that chain composition and structure cannot be controlled due to the inert nature of the polyolefin and short reaction times.\(^{24}\) The third method involves the copolymerization of propylene with a “reactive” monomer that can be converted to different functional groups
through further synthesis. This process follows that the “reactive” monomer must have: 1) good stability with the metallocene catalyst, 2) high solubility in the reaction medium and 3) easy conversion of the “reactive” group to the desired functional side group. Chung, et. al. have championed this synthetic process with the goal of creating higher dielectric polypropylene through the incorporation of a small mole percent of “reactive” monomer. Figure 1.9 illustrates two synthetic methods developed by Chung to create polypropylene chains with hydroxyl and ammonium chloride/amine side groups. Chung was able to steadily increase the dielectric constant of polypropylene by incorporating the hydroxyl side group reaching a k value about two times that of normal polypropylene with 4.2 mole% of the hydroxyl monomer.

![Figure 1.8. Summary of the various synthetic methods used to produce functionalized polyolefins.](image)
Another common method to increase the dielectric constant of polymers is through incorporation of polar groups directly into the polymer backbone to increase the dipolar orientation. A number of polar polymers have been investigated for their dielectric properties and include functionalities as esters, carbonates, imides, ureas, sulfones, urethanes and amides.\textsuperscript{40-44} Some of these polar materials have been commercialized such as the polyimide Kapton® and biaxially oriented polyethylene terephthalate under the trade name Mylar by Dupont.\textsuperscript{45,46} \textbf{Figure 1.10} illustrates the repeat units of these polar polymers and the structures of Kapton and Mylar.
Two of the most common polar polymers being investigated now as dielectric materials are polythioureas and homo- and copolymers containing polyvinylidene fluoride (PVDF) as a result of the large dipole moments of the functional groups. Vasudaran et. al. first synthesized a thiourea-formaldehyde polymer but it proved to be challenging to process. Inagaki et. al. created polythioureas by reacting carbon disulfide with aliphatic diamines. The aliphatic diamines chosen in the Inagaki’s study contained an odd number of methylene (CH$_2$) units to obtain a polar polymer. The aliphatic polythioureas exhibited a larger dielectric constant than polyolefins, due to a dipole moment of 5.4 Debye, but also suffered from an increased dielectric loss. Zhang et. al. synthesized an aromatic polythiourea, Figure 1.11, through a microwave synthesis of thiourea with 4,4’-diphenylmethane diamine. The polymer exhibited a dielectric constant of approximately 4.5 which corresponded to a dipole moment of 4.89 Debye.
More importantly it was reported that this polymer did not suffer from large dielectric loss and exhibited a slightly higher breakdown field, \(800 \text{ MVm}^{-1}\), than BOPP and an energy density of \(> 12 \text{ Jcm}^{-3}\).

\[ \text{Figure 1.11. Synthetic route used by Zhang et. al. for the formation of aromatic polythiourea.}\]

Polyvinylidene fluoride, **Figure 1.12**, has garnered a lot of interest as a dielectric material since its discovery in 1971 as it exhibits a large dielectric constant, \(> 10\), and band gap, approximately 6 eV but again suffers from a large dielectric loss.\(^{50,51}\) To combat the dielectric loss, the copolymerization of PVDF with other fluorinated monomers, such as vinyl fluoride, trifluoroethylene (TFE), tetrafluoroethylene (TrFE) and hexafluoropropylene (HFP), have been attempted.\(^{52}\) Copolymerization of difluoroethylene with TFE and TrFE has proven to give more facile processing since the copolymer crystallized into a polar form without the normal stretching needed to form polar PVDF. Zhang et. al. have also copolymerized difluoroethylene with a mixed halide monomer, chlorotrifluoroethylene (CTFE), and which the co-PVDF-CTFE polymer exhibited and energy density of 25 Jcm\(^{-3}\).\(^{53}\) Li et. al. have also blended PVDF with polyamide 6 to improve the dielectric constant. An increase in dielectric constant versus PVDF was found at a blend of 20:80 (wt:wt) polyamide 6:PVDF.\(^{54}\) The increase in dielectric constant was credited to the increase in interfacial interactions between polymer chains. The reason for the increased loss found in polythioureas and PVDF is due to the ferroelectric nature of the materials.
Ferroelectricity is defined as at a certain magnitude of an electric field a
spontaneous polarization will arise that causes a switch to a more stable
direction. Upon removal of the electric field the polarization will not return to its
original direction and magnitude. Therefore, ferroelectricity is non-reversible and
will cause remnant polarization in the material which will not be released to the
environment which makes these materials undesirable for high energy storage
since the total stored energy cannot be recovered.

Figure 1.12. Chemical structure of polyvinylidene fluoride (PVDF) (top) and
some fluorinated monomers commonly used for copolymerization with
difluoroethylene.

1.3.2. Filled Polymers

Another common method to dramatically increase the dielectric constant
of polymer films is the incorporation of high dielectric constant inorganic
nanoparticles into the matrix, termed filled polymers. The nanoparticles most
used are variations of titanium oxide, and include barium strontium titanate ($\varepsilon = 500$),
barium titanate ($\varepsilon = 1250$-10000 depending upon temperature) or lead
zirconium titanate ($\varepsilon = 500$-6000). The cause of the large increase in dielectric
constant is due to the formation of large interfacial polarization regions between
nanoparticle and polymer, though with a much bigger magnitude than what was
reported for PVDF/polyamide-6 polymer blends described in the previous section. The resultant dielectric constant of the filled polymer is dependent on the degree of polarization and charge separation at the interface. The size of the nanoparticle also influences the dielectric constant, i.e. a decrease in the dielectric constant as the nanoparticle size is decreased, because the total surface area of the nanoparticle is reduced. A study of barium titanate has shown the decrease of dielectric constant from 5000 to hundreds when the size is reduced from 1 μm to 3nm. However, small nanoparticle size is needed in order to enhance the dielectric breakdown strength of the filled polymer by lowering the chance or avoiding all together avalanche breakdown. Hao related the reduced dielectric strength as being the result of aggregation and phase separation of the nanocomposite within the polymer matrix due to the high surface energy, driven by van der Waal’s forces, of the inorganic nanoparticle. These two factors lead to an increase in the defect density within the matrix. To alleviate the aggregation of nanoparticles chemical modification of the nanoparticle has been attempted to increase the interaction between polymer and nanoparticle. The nanoparticles used have hydroxylated surfaces and Jiang et. al. have used this to create a core double-shell, in which a layer of a hyperbranched aromatic polyamide is made around the particle with a second layer of polymethylmethacrylate on top, Figure 1.13. Improved dielectric properties have been reported using this technique. Guo et. al. have used carbon/silica hybrid nanoparticles with PVDF to increase the dielectric constant. They report dielectric constants of 303, 2226 and 246,000 with dissipation factors.
of 0.5, 2.0 and 22.0 for films made with 9, 9.5 and 10.0 weight percent carbon/silica nanoparticles, respectively. Therefore, it is seen in these studies that the use of nanoparticles has the benefit of largely increasing the dielectric constant of polymer films but are limited by aggregation of the nanoparticles and the resultant decrease in overall breakdown strength. Also, the increase in dielectric constant comes at the cost of needing large fractions of the nanoparticle incorporated into the matrix which hinders processability and increases the overall weight of the film due to the larger density of the inorganic particles.

![Figure 1.13](image)

**Figure 1.13.** Illustration of the core double-shell of barium titanate, aromatic polyamide and PMMA described by Jiang et. al.

1.4. Structure of Dissertation

The structure of this dissertation has one common theme, the exploration of the periodic table in search of high dielectric constant, low dielectric loss, high
band gap materials for use as insulating materials in high energy density capacitors, though these polymers could be optimized for any dielectric application. **Figure 1.14** summarizes the goal of this exploration; population of desired electric space, $k > 6$ and $E_g > 4.5$ eV, versus common polymers and inorganic oxides. Overall, the dissertation can be split into two parts; one dealing with the synthesis of traditional organic polyimides and the other describing the synthesis and characterization of various organometallic polymers.

**Figure 1.14**. Dielectric constant versus band gap of common polymers (A) and metal oxides (B). The blue shaded region represents the desired region for new dielectric materials to reside in.

**Chapter 2** details the experimental methods used in the synthesis of the dielectric materials as well as more in depth discussion of the instrumentation used to determine the dielectric properties of the polymers.

**Chapter 3** deals with the synthesis and characterization of organic polyimides. The chapter delves into the structure property relationships of polyimides in terms of dielectric constant with emphasis on the length and structure of the aliphatic diamine monomer and conjugation length of the dianhydride monomer. Processing techniques for some polyimides are also discussed.
Chapter 4 details the first attempt at synthesizing metal containing polymers, polysilanes, and their characterization. Problems with the synthesis and the lessons learned of proper methodology to create a dielectric material are discussed.

Chapter 5 deals with the synthesis of tin containing polymers. The chapter delves into computational and experimental studies that lead to the selection of the tin ester moiety as being the most beneficial to the dielectric constant. Also, a complete structure property relationship of tin esters is discussed that describes how aliphatic chain spacer, synthetic route, thermal processing, aromaticity and chirality affect the dielectric constant. In addition, a blending study of tin polymers is explained to improve film quality.

Chapter 6 details the synthesis of other metal containing polymers such as aluminum, cadmium, zinc and titanium and some mixed metal systems. The role of complex type and water on the dielectric constant is discussed.
1.5 References


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Chapter 2. Instrumentation and Materials

Summarized in this chapter is a discussion experimental instrumentation that is common to all polymer characterization described in the proceeding chapters. More detailed discussions are given to less commonly used instrumentation such as time-domain dielectric spectroscopy. The last section details instrumental setup of more well-known instrumentation, i.e. NMR, FTIR, that it is employed in this dissertation. The last section also lists the materials used to synthesize the polymers discussed in this dissertation. However, experimental procedures are described in the corresponding chapters.

2.1. Dielectric Measurements

2.1.1. Time-Domain Dielectric Spectroscopy (TDS)

Mopsik first published his invention of the time-domain dielectric spectrometer (TDS) in 1984, Figure 2.1.\textsuperscript{1} With the improvement of solid state electronics a spectrometer could be achieved with an accuracy of 0.1% and a minimum loss resolution in tan δ of $10^{-5}$ within a frequency range of $10^{-3}$ to $10^{4}$ Hz. If the loss resolution was reduced by an order of magnitude then the frequency range could be brought down to $10^{-4}$ Hz. Mopsik reported that continuous data could be collected over this range in a very short time frame, 300 s, with a computational time of approximately 12 minutes. Of course this computational time is much quicker with faster computers and is trivial now.
In order to measure the time-domain, a voltage source capable of switching from 0 to $E_0$ is placed across the sample in series with a charge amplifier. At time zero, the generator changes from 0 to $E_0$, which creates a charge, $Q(t)$, to flow through the sample. The time dependent capacitance is then described as:

$$C(t) = Q(t)/E_0$$  \hspace{2cm} (2.1)$$

Of course the capacitance is a complex function, $C^*$, and is shown by the equation:

$$C^*(\omega) = C'(\omega) - iC''(\omega) = \int_0^{\infty} C(t) e^{-i\omega t} \, dt$$  \hspace{2cm} (2.2)$$
A second generator and a reference capacitor are employed to electrically subtract out the initial response to the applied voltage. Therefore, the real and imaginary parts of the capacitance are expressed as:

\[ C'(\omega) = \int_0^\infty C(t) \cos(\omega t) dt + C(0) + C(ref) \]  

(2.3)

and

\[ C''(\omega) = \int_0^\infty C(t) \sin(\omega t) dt \]  

(2.4)

The minimum measurement time, \( t_1 \), and maximum measurement time, \( t_2 \), are defined as:

\[ \omega_{\text{max}} \sim \frac{1}{t_1} \quad \text{and} \quad \omega_{\text{min}} \sim \frac{1}{t_2} \]  

(2.5)

The integrals are evaluated at all times after the step voltage, 10 or 100 volts in the case of measurements described in this dissertation, is applied at time zero. Before the measurement is made, the instrument first checks that there is no short in the sample by applying a short voltage pulse with the detector held at reset and measuring voltage of the detector input. The sample is then measured at minimum gain and this initial data point is used to set the reference capacitor to a set point zero signal. The instrument also ensures that the excitation from the previous voltage step has decayed to the point where it will not interfere with the next measurement.

The time-domain dielectric spectrometer used to gather the data reported in this dissertation is an IMASS TDS, Figure 2.2. The sample, either drop casted onto McMaster Carr A666 stainless steel shim stocks with a diameter of 2" and a thickness of 0.1", pressed pellets or free standing films, is placed in a sample holder, Figure 2.3, developed by the EIRC at the University of Connecticut. The
sample is sandwiched in between two conductive silicon electrodes with an area of 0.78 cm$^2$ with a Teflon guard around the electrode. The TDS is attached with longer leads to allow for dielectric measurements to be done at various temperatures in an external oven.

**Figure 2.2.** IMASS time-domain dielectric spectrometer (bottom). The leads are extended to allow for the sample to be housed in an oven in order to determine the dielectric properties at various temperatures. (Image provided by JoAnne Ronzello)
2.1.2. Frequency Domain Dielectric Spectroscopy

As stated in the previous section, TDS allows for dielectric property measurements over a frequency range of $10^{-3}$-$10^4$ Hz. To compliment TDS, dielectric measurements are performed at higher frequencies, $20$-$10^6$ Hz, using an LCR (Inductance, Capacitance, Resistance) meter, Figure 2.4, in which an AC current is measured through the sample. The frequency domain measurements performed in this dissertation are done on an Agilent 4284A Precision LCR meter. The sample is placed in the same holder as used for the TDS measurements and the capacitance and dissipation are averaged for five measurements. The dielectric constant of the material is then calculated using equation 1.17. Again the leads are extended to allow for measurements to be done in an oven.

Figure 2.3. Sample holder for measuring dielectric properties developed by the EIRC at the University of Connecticut. The sample is sandwiched between the top and bottom electrode.
2.1.3. Setup for Measurements in vacuo

The role of free and bound water can affect the dielectric properties of a material and will be discussed in Chapter 6. In order to determine this affect an apparatus to measure the dielectric properties in vacuo was designed, Figure 2.5. Two holes are first drilled into a 9” x 9” x ½” piece of glass. Two high temperature wires are threaded through the holes and then the holes sealed with a Master Bond thermal adhesive that cures at room temperature for 18-24 hours. The glass is then placed in the door of a vacuum oven, and the leads attached to the sample holder. These leads are then attached to the TDS. The free and bound water can then be removed by setting the temperature in the vacuum oven to the appropriate level and the displaced water removed by applying vacuum and/or having a desiccant, such as drierite or phosphorus pentoxide, inside the chamber.
2.1.4. Refractive Index

As already discussed, at high frequencies the dielectric constant is equal to the square of the refractive index of the insulating material (equation 1.12), which corresponds to the electronic part of the dielectric constant, $\varepsilon_{\text{elec}}$. To measure $\varepsilon_{\text{elec}}$, ellipsometry, Figure 2.6, is used since it is highly sensitive to the change in polarization of the sample due to such properties as thickness, refractive index or dielectric function tensor, upon exposure to electromagnetic radiation. The radiation is emitted from a source and linearly polarized by a polarizer. The incident radiation may then be passed through a compensator before hitting the sample at an incident angle. Upon reflection from the sample the light may pass through another compensator and a second polarizer termed
the analyzer. After passage through the analyzer the light reaches the detector. The detector measures the complex reflectance ratio, \( \rho \), which relates to the amplitude ratio, \( \Psi \), and phase difference, \( \Delta \), through the following equation:\(^3\)

\[
\rho = \tan(\Psi) e^{i\Delta} \quad (2.6)
\]

The amplitude ratio and phase difference represent the optical constants and thickness parameters, but in order to determine these the data must be modelled which can become quite complicated.

![Figure 2.6. Block diagram of an ellipsometer.](image)

2.1.5. Dielectric Breakdown

As stated in the previous chapter the breakdown voltage/field is important for dielectric materials as it designates the operating voltage of the device and for the case of capacitors the maximum energy density. Breakdown strength measurements discussed in this dissertation were performed using a linear voltage ramp generated by a resistor capacitor (RC) circuit. Figure 2.7 illustrates the sample setup for breakdown measurements. First a strip of a film electrode to ground is placed down with the metallized surface facing up. On top of the
first electrode is placed the sample being tested and resting on top of that is a Kapton mask with a 2 cm$^2$ hole to ensure that breakdown occurs within the uncovered area. Lastly, a second film electrode to high voltage with metalized side facing down is placed over the area of exposed sample and mask. When the first breakdown event occurs, the power supply is shut off through an interlock input by a silicon controlled rectifier (SCR) circuit, which uses the breakdown-induced ground-rise voltage capacitively coupled to the gate of an SCR. The breakdown voltage of the sample is read from a peak-holding voltmeter. The sample thickness was determined using a thickness gauge (Model LE1000-2, MeasureItAll) as the average of several measurements near the breakdown site. The breakdown measurements are then analyzed through a Weibull distribution which determines the average breakdown of the material.

![Schematic of the sample setup for breakdown measurements.](image)

**Figure 2.7.** Schematic of the sample setup for breakdown measurements.

### 2.2. UV-vis
To determine the band gap of the insulating materials synthesized in this dissertation, UV-vis spectroscopy is performed. The absorption of UV-vis radiation results in the promotion of electrons from the ground state to the excited state. The electrons that are affected by this absorption are bonding, $\sigma$ or $\pi$, which are shared by more than one atom or non-bonding or unshared, $n$, electrons localized on atoms such as oxygen, sulfur, nitrogen or the halogens. Therefore, there are four types of transitions that can occur; 1) $\sigma \rightarrow \sigma^*$, 2) $n \rightarrow \sigma^*$, 3) $\pi \rightarrow \pi^*$ and 4) $n \rightarrow \pi^*$. Figure 2.8 illustrates the energy needed to achieve these transitions. The $\sigma \rightarrow \sigma^*$ transition requires the most amount of energy and mostly lies outside of the UV-vis region, $<185$ nm or the vacuum UV region. The $n \rightarrow \sigma^*$ region lies within the 150-250 nm region with most compounds exhibiting this transition $<200$ nm. This transition is dependent on the structure compound and the type of bond. The $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition are the two lowest energy transitions, occurring in the range of 200-700 nm and intuitively need an unsaturated functional group to occur.⁴
Figure 2.8. Energy diagram for electron transition when UV-vis radiation is absorbed.

To measure the band gap a solution of the dielectric materials is drop casted onto a quartz microscope slide. Quartz is used instead of the normal borosilicate glass because the absorption maximum of quartz occurs below 175 nm. The absorption spectra is collected using a Cary 5000 UV-vis spectrometer, Figure 2.9, over a wavelength range of 175-800 nm with a second quartz slide as a blank. The onset wavelength, $\lambda_{\text{onset}}$, of absorption is determined from the intersection point of the two extrapolated lines in the spectra. The band gap is then calculated using Planck’s relation;

$$E_g = \frac{hc}{\lambda}$$  \hspace{1cm} (2.7)

where $h$ is Planck’s constant, $c$ is the speed of light and $\lambda$ is the onset wavelength. To calculate the band gap in eV then the product of $h \times c$ is 1240 eVnm.
2.3. X-ray Diffraction

In order for diffraction to occur, the radiation wavelength must be on a similar order as the periodic features of the sample. Two types of x-rays are formed; 1) Bremsstrahlung or white x-rays generated by the deceleration of electrons or 2) characteristic x-rays. Characteristic x-rays are produced as a result of first an inner orbital electron be ejected by a higher energy electron and secondly a transition of an electron from an outer to inner orbital, Figure 2.10. This transition results in the generation of x-rays of specific energies and hence specific wavelengths. The generated x-rays then bombard the sample and a diffraction pattern is created from the constructive interference between parallel waves bouncing off of consecutive planes of atoms along a given sample orientation. Since the wavelength is determined from the source and the angle of
diffraction measured by the instrument, the d spacing of the material can be calculated using Bragg’s Law;

\[ n\lambda = 2d\sin\theta \]  \hspace{1cm} (2.8)

The d-spacing represents the spacing between planes and can be used as a fingerprint of the material.\(^5\) The x-ray diffraction (XRD) pattern of the materials synthesized in this dissertation is used as a structural characterization tool to compare to predicted patterns calculated by the Ramprasad group. The comparison of theoretical and experimental XRD patterns confirms what type of structural motifs the polymers take and discussed more in Chapter 5 and Chapter 6 where the structure of the organometallic polymers become quite complex. XRD is collected using a Bruker D2 Phaser with a Cu-K\(_\alpha\) (\(\lambda = 1.54184\ \text{Å}\)) radiation source.

![Image](image.png)

**Figure 2.10.** Illustration of the generation of characteristic x-rays used for XRD. The ejected electron is caused by collision with another high energy electron. The characteristic x-ray is then created by the transition of outer shell electrons to the inner shell at a certain energy and hence wavelength.

## 2.4. Hildebrand/Hansen Solubility Parameters
In simple terms, solubility corresponds to the adage that “like dissolves like”. In 1950 Hildebrand and Scott gave more substance to this by introducing the solubility parameter, $\delta_t$. The parameter is related to the square root of the cohesive energy density:

$$\delta_t = (ced)^{1/2} = \left(\frac{\Delta E}{V}\right)^{1/2}$$

where;

$$\Delta E = \Delta H - RT$$

However, Hildebrand’s definition did not satisfy the hydrogen bonding component of solubility. Therefore, Hansen built upon Hildebrand’s work and introduced his hydrogen bonding term;

$$(\delta_t)^2 = (\delta_D)^2 + (\delta_P)^2 + (\delta_H)^2$$

where, D corresponds to the nonpolar dispersion, P is the molecular, dipolar interactions and H represents the molecular, hydrogen bonding interactions. The components are determined by;

- $\delta_D$: corresponding states principles at 25°C,
- $\delta_P$: dipole moments or other parameters and
- $\delta_H$: what remains from equation 2.11

To determine whether a solute is soluble in a solvent two more terms must be defined. First the interaction radius, $R_a$, must be determined from the Hansen solubility parameters and is given by;

$$R_a^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2$$
\( R_a \) determines the distance between solubility parameters of the solute and solvent. The second term that must be defined is \( R_o \), or the radius of a Hansen solubility sphere. The ratio of \( R_a \) and \( R_o \) gives the RED number which is indicative of solubility;

\[
\text{RED} = \frac{R_a}{R_o} \quad (2.13)
\]

From equation 2.13 it is shown that if \( R_a \) is less than \( R_o \) then the solute is soluble in the solvent since the Hansen sphere will encompass the Hansen parameters of the solute and solvent.\(^6,7\)

2.5. Materials

2.5.1. Other Common Instrumentation

This section details the other characterization techniques utilized in this dissertation and any variation from the listed methods is described in the corresponding chapters. Fourier Transform Infrared (FTIR) spectra were recorded with a Nicolet Magna 560 FTIR (resolution 0.35 cm\(^{-1}\)). Solution \(^1\)H and \(^{27}\)Al NMR was performed on a Bruker DMX 500 high resolution digital NMR spectrometer. All chemical shifts were referenced to either acetic acid-\(d_4\) (\(\delta = 2.04\) ppm), dimethyl sulfoxide-\(d_6\) (\(\delta = 2.50\) ppm), deuterium oxide (\(\delta = 4.79\) ppm) or chloroform-\(d\) (\(\delta = 7.24\) ppm). Deuterated solvents were purchased from Cambridge Isotopes. For the solution \(^{27}\)Al NMR aluminum nitrate was used as the reference. Solid state \(^{27}\)Al NMR was performed on a Bruker Avance III 400 MHz solid-state NMR spectrometer. Differential Scanning Calorimetry (DSC) was done with a TA instruments DSC Q series with a heating rates between 10-
40 °C min\(^{-1}\). The samples were sealed in an aluminum pan with a second empty aluminum pan used as reference. Thermogravimetric Analysis (TGA) was performed using a TA instruments TGA Q500 at a heating rate of 10 °C min\(^{-1}\) under nitrogen atmosphere. For the determination of free and bound water in some of the organometallic polymers the sample is heated on the TGA to 115 °C and held isothermally for 60 minutes. A second heating cycle to 220 °C at a heating rate of 10 °C min\(^{-1}\) is done and held for another 60 minutes. A third heating cycle at 10 °C min\(^{-1}\) is done until thermal breakdown of the material. The first isothermal cycle determines the amount of free water in the sample while the second isothermal hold illustrates the amount of loosely bound and bound water. When films of polymers could not be casted onto shim stocks, pellets were pressed on a Carver pill press, Figure 2.11, in order to test the dielectric properties. Sample resistance was also measured using a Hewlett-Packard 4329A high resistance meter, Figure 2.12, in which a voltage from 10-1000 V can be charged through the sample.
Figure 2.11. Carver pill press used to press pellets in order to determine dielectric properties.

Figure 2.12. Hewlett-Packard 4329A high resistance meter.

2.5.2. Chapter 3 Materials
Pyromellitic dianhydride (PMDA), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), 4,4′-oxydiphthalic anhydride (ODPA), 1,4-diaminobutane (1,4-DAB), 1,6-diaminohexane (1,6-DAH), anhydrous dimethylformamide (DMF) and anhydrous N-methyl-2-pyrrolidone (NMP) were purchased from Aldrich Chemical Company. Ethylenediamine (EDA), 1,2-diaminopropane (1,2-DAP), 1,3-diaminopropane (1,3-DAP) was procured from Acros Organics. 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6-FDA) was procured from TCI America. Jeffamines EDR-104, D230 and HK511 were provided by Huntsman Corporation. Dianhydrides were recrystallized from acetic anhydride and dried in vacuo before use. Diamines were used as received.

Figure 2.13. Monomers used in the synthesis of the polyimides described in Chapter 3.

2.5.3. Chapter 4 Materials
Diphenyldichlorosilane, dimethyldichlorosilane, di-n-butyl dichlorosilane, di-n-octyldichlorosilane, phenylmethyldichlorosilane and bis(trimethylsiloxy)dichlorosilane were procured from Gelest, Inc. The silane monomers were purified by distillation before use. Sodium cubes in oil and bis(2-methoxyethyl)ether (diglyme) was purchased from Aldrich Chemical Company. Toluene HPLC grade was purchased from J.T. Baker Company.

Figure 2.14. Silicon containing monomers used in the synthesis of poly(silanes).

2.5.4. Chapter 5 Materials

Dimethyltin dichloride (DMT) and di-n-butyltin dichloride (DBT) were purchased from TCI America. All diacids, malonic (Mal), glutaric (Glu), adipic (Adi), pimelic (Pim), suberic (Sub), azelaic (Aze), sebacic (Seb), 1,10-decanedicarboxylic (Dec), terephthalic (Ter), isophthalic (Iso), L-tartaric (L-Tar), D-tartaric (D-Tar), 3,3-dimethyl glutaric (3,3-DMG), ethylenediamine (EDA), 1,2-diaminopropane (1,2-DAP), 1,3-diaminopropane (1,3-DAP), ethylene glycol (EG), 1,3-propanediol (1,3-PD), 1,2-dichloroethane (1,2-DCE), 1-butanol, and m-cresol were procured from Acros Organics. Succinic acid (Suc) was purchased as the disodium salt form and oxalic acid (Ox) was the dihydrate form from Acros.
Organics. 2,5-pyridinedicarboxylic acid (2,5-DPA), 2,6-pyridinedicarboxylic acid (2,6-DPA), DL-Tartaric acid (DL-Tar), 1,4-diaminobutane (1,4-DAB), 1,6-diaminohexane (1,6-DAH) and N,N-dimethylacetamide (DMAc) were purchased from the Aldrich Chemical Company. Jeffamines EDR-104, D230 and HK511 were provided by Huntsman Corporation. All monomers were used as received. 2,5-thiophenedicarboxylic acid (2,5-TDC) was purchased from Matrix Scientific. Sodium carbonate and tetrahydrofuran (HPLC grade) were purchased from J.T. Baker. Sodium hydroxide (NaOH), chlorobenzene and triethylamine (TEA) were purchased from Fisher Scientific. 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) was procured from Synquest Labs and chloroform was purchased from BrandNu. Deionized water was obtained using a Millipore purification system.

![Figure 2.15](image.png)

**Figure 2.15.** Monomers used in the synthesis of organotin polymers.
2.5.5. Chapter 6 Materials

Diethylaluminum chloride, calcium chloride, 1,2-dimethoxyethane (DME), 1,2-dichloroethane (1,2-DCE) and N,N-dimethylacetamide (DMAc) were purchased from the Aldrich Chemical Company. Diethoxytitanium dichloride was procured from Gelest, Inc. Copper(II) chloride, cadmium chloride and zinc chloride were purchased from Acros Organics. Acetonitrile (ACN), triethylamine (TEA) were purchased from Fisher Scientific. Tetrahydrofuran (HPLC grade) was purchased from J.T. Baker. Deionized water was obtained using a Millipore purification system.

Figure 2.16. Monomers used in the synthesis of various organometallic polymers.
2.6. References


Chapter 3. Polyimides

3.1. Introduction

Density functional theory (DFT) is a powerful tool in predicting the dielectric constant of a polymer. Based upon a quantum mechanical electronic structure method the determination of atomic level interactions can be done accurately and in which both the static (low frequency) and optical (electronic) dielectric constant for any given configuration of atoms are computed.\textsuperscript{1,2} Ramprasad et. al. have done extensive work using this methodology to create a screening tool for promising dielectric materials.\textsuperscript{3} In this work, a single all-trans polymer chain consisting of four repeating blocks, which were assigned as one of the following units: –CH2–, –NH–, –C(=O) –, –C(=S) –, –O–, –C6H4– (benzene ring) and –C4H2S– (thiophene ring), without inter-chain interactions being considered. By assembling these blocks into various combinations a set of different polymer types are formed which include polyimides, polyureas, polyurethanes, polyamides, etc. After removing the systems that have inversion and translational symmetry as well any unstable type structures, polyhydrazine for example, the new sub set results in 267 unique and synthetically reasonable structures. Many of these polymers have a predicted total dielectric constant > 4 and band gap > 3 and are considered the most desirable to pursue as promising dielectric materials.
In this study, based upon the DFT screening, polyimides are chosen to be explored as high dielectric constant and band gap polymers for two reasons. Due to the higher polarity and thus increased orientational polarization of polyimides versus polyolefins, they are attractive materials for dielectric applications. The thermal properties of polyimides make them even more desirable as they are thermally stable at temperatures exceeding 250 °C, about two times the operating temperature of most common polymer dielectrics. As a result of this stability, polyimides should be able to withstand the heat generation in these applications and will lead to lower emphasis on the need for cooling.\textsuperscript{4} Most common polymers used as dielectric materials exhibit severe decrease in dielectric strength beginning at approximately 70 °C.\textsuperscript{5}

Much of the research in polyimides is focused on creating materials that could be possible replacements for silicon dioxide in applications such as the insulating material in semiconductors, printed microelectronics, etc.\textsuperscript{6-10} Therefore, numerous studies of polyimides for electronic applications have ventured into methods to reduce the dielectric constant. The reduction of the dielectric constant has been controlled by lowering the total polarizability of the polymer through modification of the backbone through two methods. First, with the incorporation of bulky, space filling groups, such as aromatics, increases the free volume thus decreasing the dipolar and atomic polarizability. Secondly, the replacement of hydrogen with fluorine atoms causes a shrinkage in the total polarizability through the heightening of the hydrophobicity of the polymer.\textsuperscript{11-19}
Of course there is a third method which combines both aromatic and fluorine units in the polymer backbone.

In this study the focus is on the opposite end of polyimide chemical space in which an increase of the dielectric constant of the polymer is sought. This is achieved by the polymerization of a common aromatic dianhydride with various short-chain alkyl diamines or ether diamines. The polymerization using short-chain alkyl diamines is done to produce an overall reduction of the free volume as well as maintaining a high imide functional group density within the polymer backbone. The incorporation of the diamines with ether groups looks to determine the benefit of adding a second dipole in the polymer. In fact an ether containing polyimide, B8, achieved a very high dielectric constant, 7.8.

3.2. Results and Discussion

3.2.1. Synthesis and Characterization of Polyimides

Polyimides are synthesized through a condensation polymerization between a dianhydride and diamine. The only side product formed during condensation polymerizations are small molecules, water in the case of polyimidization, which makes this type of polymerization ideal for making dielectric materials since removal of impurities is more facile. The mechanism of imidization, Figure 3.1, is as follows. First the lone electron pair on the nitrogen of the amine attacks one of the carbonyl carbons of the anhydride functional group causing a ring opening of the anhydride and a hydrogen shift from the amine to the carboxylate to form the carboxylic acid. The second step of the mechanism occurs at higher temperatures, in which the lone pair of the nitrogen
attacks the carbonyl of the carboxylic acid functionality causing a ring closure to the imide functionality with the expulsion of water which is removed from the reaction. Polyimides can be either synthesized in a one-step or two-step reaction. The two-step reaction, the method employed the most, involves the generation of the poly(amic acid) precursor which is then either thermally or chemically modified to polyimide. The one-step method is used when the polyimide has high solubility in the reaction solvent. In this method the reaction between dianhydride and diamine is done at temperatures in which imidization will occur, 180-220 °C, and does not go through the isolation of the poly(amic acid) intermediate.

![Figure 3.1. Condensed mechanism for the formation of imide functionality.](image)

The polyimides described in this dissertation, Figure 3.2, are formed using the two-step method, in which the dianhydride is added to the diamine in a polar aprotic solvent, N,N-dimethylformamide, N,N-dimethylacetamide or N-methyl-2-pyrrolidone. For the polyimides synthesized here, we are limited to aromatic dianhydride monomers that are commercially available. However, to boost the overall polarizability of the polymer chain by increasing the amount of imide functionality per chain, short-chain aliphatic diamine monomers are employed. Longer-chain diaminoether monomers are also used to boost the total
polarizability of the polymer as a result of the secondary dipole from the ether segments. To confirm the formation of the imide functional group, IR spectroscopy, and in the case of soluble polyimides $^1$H NMR as well, was performed. Within IR, the presence of the imide functionality is marked by two absorptions at lower energies, Figure 3.3, versus the two peaks for the dianhydride, 1670-1740 versus 1775-1850 respectively.

Figure 3.2. Synthetic scheme for the formation of polyimides.
As mentioned previously, polyimides offer enhanced thermal stability versus polyolefins. The thermal properties of the polyimide homopolymers are listed in Table 3.1. With the exception of polyimides A3 and D8, the homopolymers exhibit degradation temperatures greater than 300 °C. A glass transition temperature is observed for all of the polyimides with the exception again of A3. The polyimides formed using aliphatic diamines exhibited higher glass transition, T_g, temperatures versus the diaminoethers, >150 °C versus 50-100 °C respectively. Polyimide B6, is synthesized using a diaminoether monomer, Jeffamine EDR-104, but has a higher T_g due to monomer being a fixed structure versus the oligomeric nature of the two other Jeffamines. A higher T_g versus operating temperature is desirable since the dielectric loss will increase dramatically as the temperature surpasses T_g due to the α-relaxation processes described in Chapter 1. Polyimides synthesized with the longer chain diaminoethers have slightly lower degradation temperatures due to the thermal susceptibility of the pendant methyl groups and ether linkages. Two polyimides,
and B5, were the only two polymers to exhibit a semi-crystalline nature, in which a melting transition, $T_m$, was observed at 271 and 234 °C, respectively.

**Table 3.1.** Thermal properties of polyimides that were also tested for dielectric properties.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>A3</th>
<th>A7</th>
<th>A8</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
<th>B5</th>
<th>B6</th>
<th>B7</th>
<th>B8</th>
<th>C7</th>
<th>C8</th>
<th>D7</th>
<th>D8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ (°C)</td>
<td>N/O</td>
<td>75</td>
<td>53</td>
<td>N/O</td>
<td>174</td>
<td>180</td>
<td>150</td>
<td>142</td>
<td>82</td>
<td>78</td>
<td>63</td>
<td>98</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>$T_m$ (°C)</td>
<td>N/O</td>
<td>N/O</td>
<td>N/O</td>
<td>N/O</td>
<td>271</td>
<td>N/O</td>
<td>234</td>
<td>N/O</td>
<td>N/O</td>
<td>N/O</td>
<td>N/O</td>
<td>N/O</td>
<td>N/O</td>
<td></td>
</tr>
<tr>
<td>$T_o$ (°C)</td>
<td>258</td>
<td>333</td>
<td>313</td>
<td>314</td>
<td>350</td>
<td>332</td>
<td>338</td>
<td>402</td>
<td>325</td>
<td>317</td>
<td>354</td>
<td>341</td>
<td>324</td>
<td>283</td>
</tr>
</tbody>
</table>

$T_g$: glass transition temperature measured at midpoint; $T_m$: melting transition temperature; $T_o$: onset of degradation temperature.

Incorporation of the longer chain diaminoether segments improved the solubility of the polymer. These polyimides were soluble at room temperature in various organic solvents such as THF, DMF, DMAc, DMSO, NMP and m-cresol which made solution casting feasible. Since polyimides (A7, A8, B7, B8, C7, C8, D7 and D8) were soluble in THF, 10 wt% solutions were casted onto a stainless steel shim stock and dried in vacuo at 40 °C for 10 hours, followed further annealing in vacuo at 150 °C for an addition 10 hours. Polyimides B2, B3, B4, B5 and B6 were only soluble in m-cresol due to the aliphatic segment more rigidity than the ether linkages. As a result of the low volatility and high boiling point of m-cresol, films were air dried for a day or two until the films were tacky and further dried in vacuo at 150 °C for 10 hours to drive off any residual solvent. In order to perform breakdown measurements larger films were needed. To accomplish this, large scale films were casted onto a glass plate and dried using the drying procedure explained prior. To remove the film, the glass plate was immersed in water and after peeling off the plate, the free standing film was dried.
again to remove water. As a result of polyimide A3 being insoluble in organic solvents, a pellet was pressed in order to measure the dielectric properties.

### 3.2.2. Dielectric Properties

Dielectric properties of polyimides based on the longer-chain Jeffamine monomers were tested first as a result of their increased solubility in the lower boiling point THF which made removal of solvent from the film easier \textit{in vacuo}. The dielectric properties of the polyimides based on Jeffamines 7 and 8 are displayed in **Figure 3.4**. The dielectric constant of each of the polyimides remains constant over the application frequency range of 1-1000 Hz. The polyimides based on Jeffamine 8 have a higher dielectric constant versus Jeffamine 7 due to the higher concentration of ether linkage. The polyimides do have the same trend in dielectric constant in relation to the dianhydride unit, 6FDA (D) \textless PMDA (A) \textless ODPA (C) \textless BTDA (B) which is attributed to the conjugation length of the dianhydride unit. The dielectric constant is boosted with longer conjugation length stemming from the increased mobility and delocalization of the \(\pi\) electron cloud. Therefore, the benzophenone unit allows for cross-conjugation of the benzene rings as opposed to the diphenyl ether unit in which the ether breaks the conjugation. Whereas, 6FDA contains two benzene rings compared to PMDA it is hindered by the two bulky trifluoromethyl groups which decrease the inter-chain electronic interactions reducing the molecular chain packing and total polarizability of the chain decreasing the dielectric constant as described previous. Polyimide B8 exhibits a dielectric
constant of 7.8 which based on literature searches is the highest dielectric constant polyimide achieved. The dissipation of all of the polyimides is on the order of $10^{-3}$ making them suitable for various applications. There is an absence of a trend in loss based on the dianhydride unit. However, at higher frequencies, >100 Hz for most of the polyimides with the exception of D7 which starts at approximately 75 Hz, a β-relaxation peak is apparent.

In order to reduce or eliminate the β-relaxation peak observed in the A7 and A8 polyimides, random compolymers were synthesized using Jeffamines 7 or 8 with 1,3-diaminopropane (3). The dielectric constant of the copolymers is higher compared to the homopolymers A7 and A8 due to the increased imide functional group density since 1,3-diaminopropane is a much shorter chain versus the Jeffamines, Figure 3.5. Polyimide A3 does not exhibit a β-relaxation

Figure 3.4. Dielectric constant and dissipation (A and B respectively) of polyimides based on Jeffamine 7 and dielectric constant and dissipation (C and D respectively) of polyimides based on Jeffamine 8.
peak and when copolymerized with Jeffamine 7 causes a slight reduction of the relaxation peak. The benefit of copolymerizing with 1,3-diaminopropane is more apparent in the copolymer with Jeffamine 8. The β-relaxation peak for homopolymer A8 has a maximum of 0.68% at 800 Hz whereas the copolymer has a maximum of 0.46% at 1000 Hz. In fact the β-relaxation peak of the copolymer saturates at a higher frequency and thus copolymerization is an option to bring the relaxation peak out of the operating frequency range.

**Figure 3.5.** Dielectric constant (A) and loss (B) of homopolymers and copolymers based on PMDA (A), 1,3-diaminopropane (3) and Jeffamines 7 and 8.

Since extended conjugation is beneficial to the dielectric properties of polymers, a series of polyimides based on BTDA (B) were also synthesized with both aliphatic diamine and diaminoether monomers, **Figure 3.6.** Of the aliphatic diamines, 1,2-diaminopropane (2) is expected to give the highest dielectric constant since the polymer B2 would have the highest imide functional group density. However, the dielectric constant overlays almost perfectly with polyimide B3 which uses 1,3-diaminopropane (3). Though the imide density in B2 is higher than B3, the 1,2-diaminopropane unit introduces a methyl side group which increases the free volume of the polymer decreasing the polarizability. As the number of methylene units between the pendant amine...
groups increases to four and six, **B4** and **B5** respectively, the dielectric constant decreases as expected. Using Jeffamine **6**, the dielectric constant is boosted to the same approximate level as polyimides **B2** and **B3**. Though there are 5 units between the amine groups in Jeffamine **6**, four methylene and one oxygen units, the dielectric constant increases because of the second dipole generated by the ether linkage. As the number of ether linkages is increased so is the dielectric constant; reaching a maximum of 7.8 as described before. The dielectric properties of the BTDA polyimides are given in **Table 3.2**.

![Figure 3.6](image)

**Figure 3.6.** Dielectric constant (A) and dissipation (B) of BTDA (B) based polyimides.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
<th>B5</th>
<th>B6</th>
<th>B7</th>
<th>B8</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\varepsilon_{\text{real}}^a)</td>
<td>4.03</td>
<td>4.03</td>
<td>3.78</td>
<td>3.62</td>
<td>3.97</td>
<td>4.54</td>
<td>7.85</td>
</tr>
<tr>
<td>Dissipation(^a) [%]</td>
<td>0.17</td>
<td>0.22</td>
<td>0.52</td>
<td>0.62</td>
<td>0.61</td>
<td>0.31</td>
<td>0.40</td>
</tr>
</tbody>
</table>

\(^a\)Average value over 1-1000 Hz

As described previously, polyimides offer greater thermal stability compared to polyolefins. The temperature dependence of the dielectric properties of two polyimides, one containing an aliphatic chain (B5) and one containing ether linkages (B7), are illustrated in Figure 3.7. Polyimide B5 exhibits a small decrease in dielectric constant as the measurement temperature is raised to 100 °C most likely due to the loss of residual water/solvent from the sample. As the temperature rises the dielectric constant increases as a result of enhanced dipole mobility. As for the dissipation exhibited by B5, the trend is an increase of loss with temperature, in which the loss is greatest at 150 °C corresponding to the T_g of the polymer. Still the dissipation suffered by B5 remains below 10% even at 150 °C. Polyimide B7 has the same trends in dielectric constant and loss as B5. However, at 100 °C the dielectric constant and loss increase dramatically since the measurement temperature is above the \(T_g\) of the polyimide (82 °C). In fact at 100 °C the \(\alpha\)-relaxation peak due to increased Brownian motion is seen at approximately 8 Hz.
Figure 3.7. Temperature dependence of the dielectric properties of polyimide B5 (A and B) and polyimide B7 (C and D). The appearance of α-relaxation can be seen in polyimide B7 as measurement temperature is increased above $T_g$.

3.2.3. Dielectric Breakdown Measurements

Breakdown of a dielectric material occurs when, at a certain voltage, electrons are promoted from the valence band to the conduction band causing an “avalanche of charge”. Therefore a large band gap, devoid of any defects, could be indicative of high breakdown strength. The band gaps of some of the polyimides are listed in Table 3.3. The band gaps of the polyimides are collectively lower than polyolefins due to the presence of π electrons which are promoted to the $\pi^*$ level much easier than the promotion of the σ electrons in a polyolefin to the $\sigma^*$ level. Thus, the polyimides, which have a yellow to brown hue, have band gaps that lie within the visible range. The band gaps of the polyimides range from 3.4-4.0 eV. Wang proposed a quantitative relationship between breakdown and intrinsic breakdown ($E_B$),\textsuperscript{22}
Polyimide $\text{B8}$, which has the highest dielectric constant, would have a theoretical intrinsic breakdown field of $895 \text{ MVm}^{-1}$. Of course this relationship has not been fully evaluated for polymers and is a generalization. Similarly, the theoretical intrinsic breakdown field of $\text{B5}$ would be $850 \text{ MVm}^{-1}$.

### Table 3.3. Band gaps of some of the synthesized polyimides.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>A7</th>
<th>A8</th>
<th>B3</th>
<th>B5</th>
<th>B7</th>
<th>B8</th>
<th>C7</th>
<th>C8</th>
<th>D7</th>
<th>D8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g [\text{eV}]$</td>
<td>3.79</td>
<td>3.42</td>
<td>3.48</td>
<td>3.39</td>
<td>3.50</td>
<td>3.48</td>
<td>3.62</td>
<td>3.58</td>
<td>3.98</td>
<td>3.93</td>
</tr>
</tbody>
</table>

To determine the breakdown strength, measurements of $\text{B5}$ and $\text{B8}$ were conducted using $\frac{1}{4}''$ diameter ball bearing electrodes in silicone oil. The measurements are then evaluated using the Weibull distribution, based on the weak-link theory, which is most commonly employed for characterizing breakdown data.$^{23}$ The Weibull distribution function, $F(x)$, is given as:

\[
\begin{cases} 
    F(x)=1-\exp \left[-\left(\frac{x-c}{\eta}\right)^\beta\right] & \text{for } x\geq c \\
    F(x)=0 & \text{for } x<c 
\end{cases}
\]  

(3.2)

where, $x$ is the electric field; $\eta$ is the scale parameter, defined as the Weibull characteristic breakdown field (here the breakdown field at 63.2% probability); $\beta$ is the shape parameter, which is a measure of data dispersion; and $c$ is the threshold field below in which breakdown will not occur. The 2-parameter Weibull distribution is obtained when $c = 0$. 

\[
E_B = 1.36 \times 10^3 \left(\frac{E_g}{4.0}\right)^3 
\]  

(3.1)
Measurements were conducted on B5 and B8 based on film forming qualities and dielectric constants (Figure 3.8). The Weibull characteristic breakdown fields of B5 and B8 are determined to be 812 MVm\(^{-1}\) and 676 MVm\(^{-1}\), respectively. Using these breakdown field measurements then the potential energy density of B5 and B8 are 9.98 Jcm\(^{-3}\) and 15.77 Jcm\(^{-3}\), respectively. Both the Anderson-Darling (AD) test parameter (critical value = 0.745 for 25 data points) for the fitting of B5 is better than B8 and the measured breakdown strength of B5 is closer to the calculated intrinsic breakdown strength compared to B8. These two observations suggest that the film quality of B8 needs to be improved by exploring different processing conditions, such as casting solvent and conditions. However, the measured breakdown field could indicate a possible extrinsic breakdown value, which is affected by conditions encompassing chemical impurities, cavities, uniformity in morphology and microstructure, surface roughness, etc. and are not characteristic to the material itself.

Figure 3.8. Weibull distribution of the breakdown field of polyimides B5 (left) and B8 (right) done at room temperature in silicone oil with ball bearing electrodes.
3.2.4. Comparison to Theoretical Calculations

To confirm the experimental structure-property relationship several polyimide structures were calculated by the Ramprasad group using density functional theory (DFT). DFT calculations were performed using the Vienna ab initio simulation package (VASP). The Perdew, Burke, and Ernzerhof functional (PBE), projector-augmented wave (PAW) frozen-core potentials and a cutoff energy of 400 eV for the plane wave expansion of the wavefunctions were used. The PBE optimized geometry was then used to determine the dielectric constant tensor using density functional perturbation theory (DFPT). In this study, only an isolated infinite chain of the polyimide was considered. The true dielectric permittivity of the polymer chain alone was then extracted by combining the DFPT computation of the supercell, containing a significant amount of vacuum, with effective medium theory, using a recently developed method. Given that the polyimides based on Jeffamines are not fixed structures, calculation times would be excessive for these polymers. Therefore, only similar but more regular structures, Figure 3.9, were investigated. Polyimides V and VI have the highest band gaps due to the lesser extent of conjugation within the polymer chain and match the experimental results. However, the calculated values of band gap are much lower than the experimental values, because of a well-known deficiency of the DFT approach. DFT underestimates the band gap as a result of the local or semi-local approximations due to the self-interaction error, the lack of long-range correlation.
effect and the poor description of the electron-hole interaction in the excited states.

As for the dielectric constant, the addition of an ether linkage in between the imide functional groups leads to a higher dielectric constant, which correlates with the experimental results. The total dielectric constant of polyimide III is higher than that of I and V, indicating that the benzophenone structure should give a higher dielectric constant, which applies for polyimides II, IV and VI as well, again correlating well with the experimental data. However, the accuracy of the calculated values to the experimental values, although the calculated trends fit the experimental data, exhibit some difference minor difference between dielectric constants and a much contrast in band gap. This is a result of limitations within the calculations in which only single chains were evaluated, without specification of polymer inter-chain interactions.
Figure 3.9. DFT calculations for some polyimide structures.

3.3. Conclusions

High dielectric constant, low dielectric polymers were achieved in which, based on literature searches, the highest dielectric constant, 7.8, of any polyimide was realized. The benefit to dielectric constant by the incorporation of multiple ether linkages and the benzophenone unit by increasing dipole density and conjugation length, respectively, was demonstrated both experimentally and through DFT computations. The experimental structure-property relationship trends were accurately predicted by DFT though the precision of these computations were skewed due to limitations of DFT. The polyimides based on aliphatic diamine units were able to be tested to higher temperatures versus the
Jeffamine based polyimides due to the higher $T_g$, but suffered from lower
dielectric constants. This fault can be alleviated by copolymerizing an aliphatic
diamine with a Jeffamine to produce a polymer with a $T_g$ above the operating
temperature, though the dielectric constant may not reach the 7.8 level. The
polyimides exhibited high breakdown potential on the small scale and thus a
higher energy density compared to BOPP. However, larger scale films and
improved film quality are needed in order to achieve the same quality as
capacitor grade BOPP film. In summary, polyimides offer a good alternative to
BOPP as a result of their higher dielectric constant and with DFT calculations a
rational design of a dielectric material is accomplished.

3.4. Experimental

3.4.1. General Synthetic Procedure for Homopolymerization

A three neck flask equipped with a Teflon™ coated magnetic stir bar was fitted
with a reflux condenser, a glass stopper and a glass apparatus for trapping
evolved water. The entire apparatus is flame dried under vacuum to remove
moisture and placed under an inert atmosphere. To the flask was added the
appropriate amount of diamine, 0.02 mL of isopropylamine (IPAm) and NMP.
The solution was stirred for 30 minutes at room temperature to disperse the
amine equally in solution. To the solution was added the appropriate amount of
dianhydride and this mixture was stirred at 50-100 °C for 2 hours. Once all of the
solids were dissolved the temperature was increased to 180 °C and the solution
was stirred for 10 hours. The polyimide was precipitated out of solution by the
addition of methanol. The solvent was filtered off and the polymer dried at 75 °C in vacuo. Deviations from this procedure are noted in the description of the polyimide.

**Polyimide A2:** To a dry 100 ml 3-neck flask 2.7136 g (12 mmol) of PMDA and 40 ml dry DMAc were added under nitrogen with stirring. After stirring for 30 min, 0.8700 g (12 mmol) of 1,2-diaminopropane was added. The reaction was carried out at room temperature for 6 h, followed by imidization at 170-180 °C for 6 h. The precipitate was then filtered and washed.

IR (KBr): ν = 3390, 2929, 1774, 1717, 1663, 1540, 1457, 1385, 1355 cm⁻¹. TGA (10°C min⁻¹): N₂ (onset): 245 °C.

**Polyimide A3:** The preparation is similar to that of A2, with 2.6347 g (12 mmol) of PMDA and 0.8800 g (12 mmol) of 1,3-diaminopropane.

IR (KBr): ν = 1774, 1717, 1664, 1395, 1363 cm⁻¹. TGA (10°C min⁻¹): N₂ (onset): 258 °C.

**Polyimide A6:** The preparation is similar to that of A2, with 4.0206 g (18 mmol) of PMDA, 0.0021 g (0.03 mmol) of isopropylamine, 1.934 g (19 mmol) of Jeffamine EDR104 and 50 mL of NMP.

IR (KBr): ν = 3460, 2477, 1772, 1717, 1684, 1394, 1369 cm⁻¹. TGA (10°C min⁻¹): N₂ (onset): 298 °C.
**Polyimide A7:** To a dry 100 ml 3-neck flask 2.140 g (10 mmol) of Jeffamine D230, 0.012 g (0.2 mmol) of isopropylamine, and 20 ml dry NMP were added under nitrogen with stirring. After stirring for 30 min, 2.180 g (10 mmol) of PMDA was added. The reaction was carried out at room temperature for 6 h, followed by imidization at 170-180 °C for 6 h. After cooling to room temperature, the mixture was poured into 150 ml of methanol, filtered and washed with methanol several times, and dried in vacuo. Light yellow solid was obtained in 85 % yield (3.362 g).

\(^1\)H NMR (500MHz, DMSO-\(d_6\), δ): 1.34 (m, 11H), 3.58 (m, 7H), 4.39 (m, 3H), 8.11 (s, 2H). IR (KBr): \(v = 2976, 2878, 1771, 1716, 1460, 1380, 1355, 1265, 1105, 1040, 731 \text{ cm}^{-1}\). DSC (10 °C min\(^{-1}\)): \(T_g = 75 ^\circ\text{C}\). TGA (10 °C min\(^{-1}\)): \(N_2\) (onset): 333 °C. GPC: \(M_n = 30167 \text{ g mol}^{-1}\), \(M_w = 61567 \text{ g mol}^{-1}\), PDI = 2.04.

**Polyimide A8:** The preparation is similar to that of A7, with 2.180 g (10 mmol) of PMDA, 2.316 g (10 mmol) of Jeffamine HK511. Light yellow solid was obtained in 82 % yield (3.381 g).

\(^1\)H NMR (500MHz, DMSO-\(d_6\), δ): 1.33 (m, 7H), 3.54 (m, 12H), 4.41 (m, 2H), 8.12 (s, 2H). IR (KBr): \(v = 2973, 2870, 1721, 1717, 1458, 1387, 1354, 1264, 1103, 1038, 730 \text{ cm}^{-1}\). DSC (10 °C min\(^{-1}\)): \(T_g = 53 ^\circ\text{C}\). TGA (10 °C min\(^{-1}\)): \(N_2\) (onset): 313 °C. GPC: \(M_n = 39776 \text{ g mol}^{-1}\), \(M_w = 84430 \text{ g mol}^{-1}\), PDI = 2.12.

**Polyimide B1:** To a dry 100 ml 3-neck flask 1.7980 g (30 mmol) of ethylene diamine, and 50 ml dry DMAc were added under nitrogen with stirring. After well
stirred for 30 min, 9.6541 g (30 mmol) of BTDA and 0.0458 g (0.3 mmol) of phthalic anhydride were added. The reaction was carried out at room temperature for 6 h, followed by imidization at 170-180 °C for 6 h. The precipitate was filtered and washed.

IR (KBr): v = 3481, 1773, 1717, 1653, 1636, 1623, 1395, 1250, 1066 cm⁻¹. TGA (10°C min⁻¹): N₂ (onset): 321 °C.

**Polyimide B2:** The preparation is similar to that of **B1**, with 1.7780 g (24 mmol) of 1,2-diaminopropane and 7.8964 g (25 mmol) of BTDA.

IR (KBr): v = 3470, 1777, 1716, 1659, 1385, 1287, 1250, 1104, 1079, 1057, 728, 712 cm⁻¹. TGA (10°C min⁻¹): N₂ (onset): 314 °C.

**Polyimide B3:** To a dry 100 ml 3-neck flask 0.741 g (10 mmol) of 1,3-diaminopropane, 0.012 g (0.2 mmol) of isopropylamine, and 20 ml dry NMP were added under nitrogen with stirring. After well stirred for 30 min, 3.221 g (10 mmol) of BTDA was added. The reaction was carried out at room temperature for 6 h, followed by imidization at 170-180 °C for 6 h. After cooling to room temperature, the mixture was poured into 150 ml of methanol, filtered and washed with methanol several times, and dried *in vacuo*. Light yellow solid was obtained in 89 % yield (3.206 g).

IR (KBr): v = 2972, 2876, 1773, 1716, 1659, 1455, 1425, 1243, 1098, 1044, 725 cm⁻¹. DSC (10 °C min⁻¹): T_g = 174 °C, T_m = 271 °C. TGA (10 °C min⁻¹): N₂ (onset): 350 °C.
**Polyimide B4:** The preparation is similar to that of B1, with 1.7540 g (20 mmol) of 1,4-diaminobutane and 6.4848 g (20 mmol) of BTDA in 115 mL of NMP. IR (KBr): v = 3470, 2942, 1773, 1712, 1620, 1441, 1394, 1387, 1340, 1295, 1248, 1181, 1157, 1098, 1037, 987, 932, 861, 726, 700, 622, 546 cm\(^{-1}\). DSC (10 \(^0\)C min\(^{-1}\)): \(T_g = 180 \, ^{\circ}\)C. TGA (10 \(^0\)C min\(^{-1}\)): \(N_2\) (onset): 332 \(^{\circ}\)C.

**Polyimide B5:** The preparation is similar to that of B3, with 0.741 g (10 mmol) of 1,6-diaminohexane and 3.221 g (10 mmol) of BTDA. Light yellow solid was obtained in 91 % yield (3.278g). IR (KBr): v = 2975, 2873, 1769, 1713, 1664, 1456, 1425, 1243, 1097, 1041, 724 cm\(^{-1}\). \(T_g = 150 \, ^{\circ}\)C, \(T_m = 234 \, ^{\circ}\)C. TGA (10 \(^0\)C min\(^{-1}\)): \(N_2\) (onset): 338 \(^{\circ}\)C.

**Polyimide B6:** The preparation is similar to that of B1, with 1.9340 g (19 mmol) of Jeffamine EDR104 and 6.0050 g (19 mmol) of BTDA. IR (KBr): v = 3471, 2871, 1776, 1714, 1669, 1436, 1391, 1295, 1247, 1097, 1030, 726 cm\(^{-1}\). \(T_g = 142 \, ^{\circ}\)C. TGA (10 \(^0\)C min\(^{-1}\)): \(N_2\) (onset): 402 \(^{\circ}\)C.

**Polyimide B7:** The preparation is similar to that of A7, with 3.221 g (10 mmol) of BTDA, 2.140 g (10 mmol) of Jeffamine D230. Orange solid was obtained in 94 % yield (4.714 g). \(^1\)H NMR (500MHz, DMSO-\(d_6\), \(\delta\)): 1.31 (m, 11H), 3.43 (m, 7H), 4.39 (m, 3H), 8.12 (broad, 1H), 7.98 (broad, 2H). IR (KBr): v = 2974, 2873, 1774, 1712, 1665, 1456,
1427, 1368, 1247, 1097, 1040, 728 cm\(^{-1}\). DSC (10 °C min\(^{-1}\)): \(T_g = 82\) °C. TGA (10 °C min\(^{-1}\)): \(N_2\) (onset): 325 °C. GPC: \(M_n = 41321\) g mol\(^{-1}\), \(M_w = 88631\) g mol\(^{-1}\), PDI = 2.14.

**Polyimide B8:** The preparation is similar to that of A7, with 3.221 g (10 mmol) of BTDA, 2.316 g (10 mmol) of Jeffamine HK511. Dark orange solid was obtained in 92 % yield (4.763 g).

\(^1\)H NMR (500MHz, DMSO-\(d_6\), ppm): 1.32 (m, 7H), 3.53 (m, 12H), 4.41 (m, 2H), 8.12 (broad, 1H), 7.98 (broad, 2H). IR (KBr): \(v = 2972, 2866, 1773, 1716, 1662, 1456, 1428, 1367, 1246, 1092, 1039, 728\) cm\(^{-1}\). DSC (10 °C min\(^{-1}\)): \(T_g = 78\) °C. TGA (10 °C min\(^{-1}\)): \(N_2\) (onset): 317 °C. GPC: \(M_n = 46982\) g mol\(^{-1}\), \(M_w = 80809\) g mol\(^{-1}\), PDI = 1.72.

**Polyimide C7:** The preparation is similar to that of A7, with 3.107 g (10 mmol) of ODPA, 2.140 g (10 mmol) of Jeffamine D230. Orange solid was obtained in 89 % yield of (4.341 g).

\(^1\)H NMR (500MHz, DMSO-\(d_6\), δ): 0.84, 1.28 (m, 11H), 3.50 (m, 7H), 4.35 (m, 3H), 7.96 (broad, 1H), 7.46 (broad, 2H). IR (KBr): \(v = 2975, 2873, 1773, 1716, 1474, 1437, 1363, 1263, 1230, 1091, 1038, 748\) cm\(^{-1}\). DSC (10 °C min\(^{-1}\)): \(T_g = 72\) °C. TGA (10 °C min\(^{-1}\)): \(N_2\) (onset): 354 °C. GPC: \(M_n = 39472\) g mol\(^{-1}\), \(M_w = 72810\) g mol\(^{-1}\), PDI = 1.84.
**Polyimide C8:** The preparation is similar to that of A7, with 3.107 g (10 mmol) of ODPA, 2.316 g (10 mmol) of Jeffamine HK511. Yellow solid was obtained in 87 % yield (4.405 g).

$^1$H NMR (500MHz, DMSO-$d_6$, δ): 1.30 (m, 7H), 3.52 (m, 12H), 4.37 (m, 2H), 7.96 (broad, 1H), 7.46 (broad, 2H). IR (KBr): ν = 2972, 2868, 1773, 1708, 1475, 1444, 1366, 1263, 1230, 1093, 1038, 748 cm$^{-1}$. DSC (10 °C min$^{-1}$): $T_g = 63$ °C. TGA (10 °C min$^{-1}$): N$_2$ (onset): 341 °C. GPC: $M_n = 40398$ g mol$^{-1}$, $M_w = 74551$ g mol$^{-1}$, PDI = 1.85.

**Polyimide D7:** The preparation is similar to that of A7, with 4.446 g (10 mmol) of 6-FDA, 2.140 g (10 mmol) of Jeffamine D230. Yellow solid was obtained in 93 % yield (5.781 g).

$^1$H NMR (500MHz, DMSO-$d_6$, δ): 1.27 (m, 11H), 3.49 (m, 7H), 4.38 (m, 3H), 7.96 (broad, 1H), 7.80 (broad, 1H), 7.62 (broad, 1H). IR (KBr): ν = 2977, 2880, 1780, 1716, 1439, 1378, 1354, 1256, 1210, 1104, 1043, 748, 721 cm$^{-1}$. DSC (10 °C min$^{-1}$): $T_g = 98$ °C. TGA (10 °C min$^{-1}$): N$_2$ (onset): 324 °C. GPC: $M_n = 50296$ g mol$^{-1}$, $M_w = 85653$ g mol$^{-1}$, PDI = 1.70.

**Polyimide D8:** The preparation is similar to that of A7, with 4.446 g (10 mmol) of 6-FDA, 2.316 g (10 mmol) of Jeffamine HK511. Yellow solid was obtained in 90 % yield (5.752 g).

$^1$H NMR (500MHz, DMSO-$d_6$, δ): 1.30 (m, 7H), 3.51 (m, 12H), 4.35 (m, 2H), 7.98 (broad, 1H), 7.80 (broad, 1H), 7.63 (broad, 1H). IR (KBr): ν = 2975, 2875, 1779,
1716, 1439, 1378, 1355, 1256, 1211, 1105, 1044, 748, 722 cm$^{-1}$. DSC (10 °C min$^{-1}$): $T_g = 81$ °C. TGA (10 °C min$^{-1}$): $N_2$ (onset): 283 °C. GPC: $M_n = 53662$ g mol$^{-1}$, $M_w = 112443$ g mol$^{-1}$, PDI = 2.09.

3.4.2. General Synthetic Procedure for Copolymerization

A three neck flask equipped with a Teflon™ coated magnetic stir bar was fitted with a reflux condenser, a glass stopper, a glass apparatus to trap evolved water and a rubber septum stopper. The apparatus was then flame dried under vacuum to remove moisture and placed under an inert atmosphere. To the flask was added the appropriate amount of the two diamines, 0.04 mL of IPAm and DMF. The solution was stirred for 30 minutes at room temperature to disperse the diamines equally in DMF. The appropriate amount of PMDA was added to an Erlenmeyer flask and stored under inert atmosphere. To the flask was added 75 mL of DMF. The flask is heated slightly until all of the PMDA is dissolved. The amine solution is heated to 50 °C and the PMDA/DMF solution is then canulated into the three neck flask. After the addition of PMDA/DMF solution is complete the temperature is raised to 150 °C and the solution is stirred until the polyamic acid is dissolved. After complete dissolution of the polyamic acid the temperature is raised to 180 °C and the solution is refluxed for 12-24 hours to form the polyimide.

*Polyimide A (20:80) 2:7:* To a flame dried round bottom flask was added 0.2267 g (3.1mmol) 1,2-diaminopropane, 3.4128 g (14.8 mmol) Jeffamine D230,
0.0278 g (0.5 mmol) of isopropylamine and 100 mL of DMF. The solution was stirred at room temperature for 30 minutes and then a solution of 4.0015 g (18 mmol) of PMDA in DMF was added. The solution is heated to 180 °C for 12-18 hours to complete imidization. The solid is filtered and washed.

$^1$H NMR (500MHz, DMSO-$d_6$, δ): 0.93 (m, 10H), 1.28 (m, 12H), 3.56 (m, 10H), 4.43 (m, 4H), 8.15 (m, 4H). FTIR (cm$^{-1}$): 2867, 1770, 1716, 1355, 1105, 1036, 728. DSC results: $T_g$ = 58°C. TGA (10°C min$^{-1}$): N$_2$ (onset): 350°C.

**Polyimide A (50:50) 2:7:** The procedure is similar to A (20:80) 2:7 with 0.7112 g (9.5 mmol) of 1,2-diaminopropylane, 2.1804 g (9.4 mmol) of Jeffamine D230 and 4.1007 g (19 mmol) of PMDA.

IR (KBr): $v$ = 2935, 1771, 1721, 1457, 1388, 1357, 1157, 1100, 1053, 728 cm$^{-1}$. DSC results: $T_g$ = 57°C. TGA (10°C min$^{-1}$): N2 (onset): 337 °C.

**Polyimide A (50:50) 2:8:** The procedure is similar to A (20:80) 2:7 with 0.5334 g (7.2 mmol) of 1,2-diaminopropylane, 1.4865 g (6.8 mmol) of Jeffamine HK511 and 3.0442 g (14 mmol) of PMDA.

IR (KBr): $v$ = 1771, 1717, 1653, 1457, 1388, 1354, 1100, 1049, 727 cm$^{-1}$. DSC results: $T_g$ = 88°C. TGA (10°C min$^{-1}$): N$_2$ (onset): 326 °C.

**Polyimide A (20:80) 3:7:** The procedure is similar to A (20:80) 2:7 with 0.2664 g (3.6 mmol) of 1,3-diaminopropylane, 3.4128 g (14.8 mmol) of Jeffamine D230 and 4.1861 g (19 mmol) of PMDA.
\(^1\)H NMR (500MHz, DMSO-\(d_6\), \(\delta\)): 1.01 (m, 10H), 1.28 (m, 8H), 3.64 (m, 10H), 4.43 (m, 3H), 8.14 (m, 4H). FTIR (cm\(^{-1}\)): 2975, 2936, 2873, 1771, 1717, 1458, 1358, 1266, 1157, 1110, 1067, 1040, 916, 828, 731. DSC results: \(T_g = 54^\circ\)C. TGA (10\(^\circ\)C min\(^{-1}\)): \(N_2\) (onset): 349\(^\circ\)C.

**Polyimide A (20:80) 3:8:** The procedure is similar to A (20:80) 2:7 with 0.2664 g (3.6 mmol) of 1,3-diaminopropane, 2.5766 g (11.7 mmol) of Jeffamine HK511 and 3.1564 g (14.5 mmol) of PMDA.

\(^1\)H NMR (500MHz, DMSO-\(d_6\), \(\delta\)): 1.08 (m, 16H), 4.18 (m, 10H), 8.17 (m, 4H). FTIR (cm\(^{-1}\)): 2975, 2936, 2873, 1771, 1717, 1458, 1358, 1266, 1157, 1110, 1067, 1040, 916, 828, 731. DSC results: \(T_g = 54^\circ\)C; \(T_m\) = not observed. TGA (10\(^\circ\)C min\(^{-1}\)): \(N_2\) (onset): 349\(^\circ\)C.
3.5. References


Chapter 4. Polysilanes

4.1. Introduction

The synthesis of polymers with silicon-silicon bonds were first reported in the 1920s by Kipping.\(^1\) In the initial paper, Kipping used a Wurtz reaction to couple diphenyldichlorosilane with sodium metal in boiling xylene, while in a later publication he lists the degree of polymerization as being between six and eight units, though this material was not definitively characterized.\(^2-4\) It was not until 1949 that the first polysilane was distinctly defined when Burkhard characterized poly(dimethylsilane) as a purely intractable material that was insoluble in organic solvents which did not soften or melt before thermal degradation at temperatures above 250 °C.\(^5\) As a result of these properties, research in polysilanes waned; with interest not increasing until West reported the synthesis of soluble polysilanes. Amusingly, these materials were found by accident, when researchers were attempting to form cyclic polysilanes from mixtures of dimethyldichloro- and phenylmethyldichlorosilane.\(^6,7\) With the advent of soluble polymers expanded effort has been put into developing silane monomers that could either be formed into polymers via Wurtz coupling or through other synthetic means such as catalytic dehydro-polymerization of hydrosilanes, ring opening polymerizations or polymerization through masked disilenes.\(^8-20\)

Polysilanes, even insoluble materials, synthesized through any number of methods, have been used for numerous methods. One of the first uses of
polysilanes was as precursors to silicon carbide. This was accomplished by first performing a thermolysis step to produce a polycarbosilane in which a methylene group is inserted between silicon-silicon bond and a silicon-hydrogen bond is formed. This polymeric material is melt-spun into fibers which are oxidized on the surface in the presence of oxygen and further thermolysis at 1300 °C in a nitrogen atmosphere to produce β-SiC. Polysilanes have found much use in the semiconductor field as photoresists and with doping exhibit improved conductivity. Seki et. al. have used polysilanes to fabricate organic light emitting diodes and UV emitting devices. Kwak et. al. have used polysilanes with fluoroalkyl groups to create ultrasensitive chemosensors that can be used to detect nitro aromatic compounds.

Ramprasad et. al. have used density functional theory to compute dielectric properties of polyethylene chains incorporated with silicon. Silicon is used as a means to place a larger more polarizable atom in the backbone while maintaining the local chemical environment compared to carbon. Therefore, a dielectric film based on silicon would offer increased polarization leading to both an enhanced electronic and ionic part of the dielectric constant. In constructing a polymer of purely silicon doped polyethylene, it was shown theoretically that both the electronic and ionic part of the dielectric constant was enhanced. The electronic part of the dielectric constant was improved due to the increase of σ-conjugation within the backbone stemming from the resonance integral of adjacent Si sp³ orbitals pointing toward each other. The σ conjugation of course will be greatest in systems in which there are Si-Si bonds and the least in
systems with C-C bonds, with systems of Si-C being intermediate. As for the enhancement of the ionic part of the dielectric constant, which is controlled by the IR active phonon modes, a theoretical IR spectrum of polysilane showed an increased amount of absorptions compared to the weak C-H stretching, 15 to 5 respectively, exhibited by polyethylene.\textsuperscript{29} In another study, Ramprasad \textit{et. al.}, showed increased improvement in the ionic part of the dielectric constant of polysilanes by replacing hydrogen with more electronegative atoms such as chlorine and fluorine.\textsuperscript{27,32} This aimed to increase the total amount of dipoles per volume as a result of the larger difference in electronegativity of Si-halogen versus C-halogen.

4.2. Results and Discussion

4.2.1. Synthesis and Characterization of Polysilanes

The polysilanes described in this study are synthesized through the Wurtz coupling reaction, Figure 4.1(A). The Wurtz reaction is a very exothermic reaction in which a dihalosilane monomer is dehalogenated in the presence of an alkali metal, usually lithium, sodium, potassium or a Na/K alloy, at the reflux temperature of the reaction solvent. Sodium is favored over the other metals as it has been reported that the lower reactivity of lithium favors cyclic silane formation and though potassium and Na/K alloy create linear polysilanes, they also induce polymer degradation through end-biting and back-biting reactions causing an increase in cyclic silanes.\textsuperscript{32} As a consequence of the reaction
conditions, only a few functional groups such as alkyl, aryl, silyl, fluoroalkyl or fluorocenyl, can withstand the reaction conditions.\textsuperscript{32}

Polymerization occurs at the surface of the metal.\textsuperscript{32} The mechanism for the propagation of a polysilane is illustrated in Figure 4.1(A). First the halogenated chain extracts an electron from the metal to form an anion/cation pair which degrades to the radical silyl chain end and alkali metal halide. The radical chain end then extracts another electron from a second metal atom forming an anionic chain end with the metal cation as the counter-ion. Finally, the anionic chain end couples with another monomer unit to propagate the chain and forming a second metal halide molecule.

In this study, the silane monomers are limited to symmetric dialkyl or diaryldichlorosilanes with the exception of phenylmethyldichlorosilane, Figure 4.1(B). The syntheses are carried out by dispersing two equivalents of finally divided sodium metal in aprotic solvents such as toluene, octane, dodecane or 1-Methoxy-2-(2-methoxyethoxy)ethane (diglyme), and refluxing at temperatures above the melting point of sodium metal. The silane monomer is then added to the refluxing mixture at a slow enough rate as to not cause the reaction to proceed unchecked, which is indicated by the presence of a cloud of smoke if silane is added too fast. As the reaction proceeds the color turns to a dark purplish hue which correlates to the polymer/metal halide agglomeration. After polymerization, the reaction is terminated with methanol to remove the chloride end groups and any excess sodium metal.
Figure 4.1. Wurtz coupling mechanism (A) illustrating propagation of a polysilane polymer chain and reaction scheme (B) of synthesized polysilanes.

The synthesized polysilanes are very crystalline materials with only the poly(di-\(n\)-octylsilane) being a viscous solid in low yield. Therefore, these materials do not exhibit any glass transition temperature or a melting temperature before thermal degradation. The solubility of the polysilanes is also affected by the crystallinity. Only poly(di-\(n\)-butylsilane) and poly(phenylmethylsilane) are soluble in slightly polar or non-polar solvents such as tetrahydrofuran and toluene due to the longer alkyl chain and disruption of chain packing, respectively. Copolymerizations of poly(diphenyl- or poly(dimethylsilane) with either the di-\(n\)-butyl or phenylmethyl silane unit did not improve the solubility. The lack of processing diversity led to only the soluble polysilanes to be spin cast into films.
using stainless steel shim stocks as the substrate. Ten to twelve layer thick films were made by spinning at 600 rpm to produce uniformly thick films without any holes, Figure 4.2.

![Figure 4.2. Stainless steel shim stock without (A) and with (B) film of polydi-n-butylsilane.](image)

**4.2.2. Dielectric Measurements and Purification**

The film of poly(di-n-butylsilane) when tested in the time-domain short circuited while the film of poly(phenylmethylsilane) was too conductive. The resistance of the film was measured at 1000 and 400 ohms using a DC ohm meter and HP impedance analyzer respectively. Assuming a resistance of 500 ohms and a film thickness of 10 microns the corresponding conductivity would be $1 \times 10^{-4}$ Scm$^{-1}$, much too conductive for the application. The increased conductivity of polysilanes can be attributed to the formation of salt as a byproduct that precipitates from the reaction along with the polymer. The polysilane was originally purified by washing the precipitate with a copious amount of water to remove as much salt as possible.
To determine the amount of salt, **Table 4.1**, inductively-coupled plasma mass spectrometry (ICP-MS) was performed. ICP-MS is a quantitative measurement as it compares the analyte signal, in this case sodium, with a calibration curve made using standard samples at different concentrations. The amount of measured sodium is then assumed to be equal to amount of sodium chloride within the sample. Both of the soluble polysilanes have a large amount of salt, 2 and 88 ppt for poly(di-n-butylsilane) and poly(phenylmethylsilane), respectively. To further purify the polymers Soxhlet extraction was performed. Soxhlet allows for the polymer to be washed continuously with fresh warm solvent. Approximately, 150 Soxhlet cycles were done using an ethanol/water mixture. Ethanol was used to allow the polymer chain to uncoil somewhat allowing for any trapped salt to be removed with water. Again ICP-MS was performed on the Soxhleted samples to determine how much salt remained. Though, the extraction removed much of the salt, the amount remaining was still too great to reduce the conductivity of the film.

**Table 4.1.** Amount of salt in pre- and post-Soxhlet samples of poly(di-n-butylsilane) and poly(phenylmethylsilane) determined from ICP-MS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polydi-n-butylsilane Pre</td>
<td>2267</td>
</tr>
<tr>
<td>Polydi-n-butylsilane Post</td>
<td>131</td>
</tr>
<tr>
<td>Polyphenylmethylsilane Pre</td>
<td>88162</td>
</tr>
<tr>
<td>Polyphenylmethylsilane Post</td>
<td>2664</td>
</tr>
</tbody>
</table>

The increased conductivity of the polymer film can also be attributed to any water present in the sample. The water can give mobility to the sodium and
chlorine ions along the polymer chain, thus giving a means for electrons to flow through the film. Thus a dried polymer film sample was produced by drying the spin-coated polymer film in a vacuum oven, overnight at 115 °C, and setting up the measurement apparatus in a dessicator under inert atmosphere that itself is stored in a glove bag. The leads are sealed attached to the polymer film and are then just hooked into the measuring device. Again, this drier polymer sample produced about the same resistance as the previously tested films proving that water does not play a significant role in the conductivity of the polymer.

4.3. Conclusions

Though the polysilanes proved to be too conductive for the measurement of dielectric properties, the method of their synthesis guided efforts for the other polymers described in this dissertation. Since the major byproduct in the synthesis of polysilanes is sodium chloride, the level of that impurity, less than a ppm, within the polymer matrix is set. Also, the importance of limiting an impurity formation is established and that future polymers made through condensation reactions should only produce only small molecules that can be removed from the reaction or in the case of any salt type impurities either do not co-precipitate with the polymer or are soluble in the precipitation solvent. A third observation made from the polysilane synthesis is that a fully conjugated chain, even σ-conjugation, is not desirable as that also increases conductivity and that if metal-metal bonds are needed to improve the dielectric properties, a break in the conjugation length is still needed. However, this type of polymer material will
require further functionalization and more complex monomer synthesis and polymerization.

### 4.4. Experimental

There are numerous procedures for synthesizing polysilanes through Wurtz coupling. The following is a general synthetic procedure while any changes in procedure, i.e. solvents, with references are listed with each individual polymer.

In general, a three-neck round bottomed flask equipped with addition funnel, reflux condenser, stir bar, and rubber septa is flame dried to remove water and refilled with nitrogen. The appropriate amount of solvent is then added to the reaction vessel by syringe or cannula after the glassware has cooled. Next, the appropriate amount of sodium is weighed and cut into fine pieces using a razor blade. The sodium pieces are washed with solvent to remove mineral oil and dumped into the reaction vessel by removing the rubber septa under increased nitrogen flow. The heterogeneous mixture is then heated to reflux and stirred. To the stirring mixture is slowly added the appropriate amount of silane monomer. After polymerization, the reaction is cooled, the product filtered and washed first with a copious amount of alcohol to remove excess sodium. Next, the polymer is washed with hexane, water, and hexane again and dried *in vacuo* at 115 °C overnight.
**poly(dimethylsilane) (PDMS):** 2.5 mL (2.34 g, 18.2 mmol) of dimethyldichlorosilane is reacted with 1.15 g (55.0 mmol) of finely dispersed sodium metal in 20 mL of octane.33

IR (KBr): $v = 3430, 2949, 2892, 1397, 1245, 834, 739, 691 634 \text{ cm}^{-1}$.

**poly(di-n-octylsilane) (PDOS):** 9 mL (8.46 g, 26.0 mmol) of di-n-octyldichlorosilane is reacted with 1.28 g (55.7 mmol) of finely dispersed sodium metal in a mixture of 35 mL of toluene and 14 mL of diglyme.34

IR (KBr): $v = 3430, 2924, 2844, 1467, 1410, 1375, 1258, 1160, 1100, 1024, 907, 869, 799, 720, 660 \text{ cm}^{-1}$.

**poly(phenylmethylsilane) (PPMS):** 5.9 mL (6.94 g, 36.3 mmol) of phenylmethyldichlorosilane is reacted with 1.61 g (70.0 mmol) of finely dispersed sodium metal in 20 mL of dodecane.35

IR (KBr): $v = 3129, 3069, 3050, 3006, 2955, 2889, 2791, 1958, 1882, 1815, 1771, 1641, 1591, 1486, 1429, 1252, 1100, 1068, 1021, 774, 698, 666, 619, 524, 457 \text{ cm}^{-1}$. 
4.5. References


Chapter 5. Organotin Polymers

5.1. Introduction

5.1.1. Tin Containing Polymers

Tin containing polymers are most commonly used as biocides, insecticides, fungicides, and anti-fouling agents. The tin atom is either incorporated into the polymer backbone or attached as a pendant group. In the 1950s and 1960s, Luitjen, Noltes and van der Kerk did extensive research in polymerization of dialkyltin dihydrides with olefinic double or triple bonds. The polymerization between a tin hydride monomer and diene required a functional group between the alkenes in order to proceed, while the reaction between a tin hydride and alkyne was exothermic enough to proceed spontaneously. Stiegman et. al. have reported a high refractive index thermoset material based on benzenedithiol and tetravinyltin. Some non-traditional polymers containing tin have also been reported. Albisetti and Lorenzotti created coordination polymers containing tin and using bis(1,2,4-triazol-1-yl)methane as the coordinating ligand. Butcher reported coordination polymers using pyridine dicarboxylic acids and bis(tributyltin) oxide that could be controlled to form one- and two-dimensional polymers depending upon the dicarboxylic acid used. Tin has also been used as a codopant to improve electron transfer in iron doped polymers.
5.1.2. Organotin Polymer Selection

Ramprasad et al. have done extensive calculations on polyethylene chains doped with varying degrees of other group IV atoms. It was shown that a polymer with a repeat unit of \(-\text{CH}_2\text{-SnF}_2\text{-SnF}_2\text{-SnF}_2\) would produce a total dielectric constant of 47 most likely due to the large dipole created between tin and fluorine.\textsuperscript{16-18} The simplest way to produce polymers of this type, i.e. doped polyethylene, without the formation of any salt impurities is through acyclic diene metathesis (ADMET) in which polymerization is done through an \(\alpha,\omega\)-diene in the presence of a tungsten based, Schrock or Grubbs’ Catalyst. The only byproduct formed during ADMET polymerization is ethane, but the resulting polymer is unsaturated and therefore needs to be hydrogenated to produce the desired polyethylene like polymer. The ADMET polymerization mechanism is illustrated in Figure 5.1(A). The Wagener group, who first successfully used ADMET to synthesize polyolefines from 1,5-hexadiene and 1,9-decadiene in 1991, have also used tin containing monomers for this polymerization technique, Figure 5.1(B).\textsuperscript{19} Their results concluded that a minimum of two methylene units were needed in between the double bond and tin atom in order to produce a linear polymer. However, a large portion of cyclic oligomeric species were also formed and it was therefore recommended to have a spacer of three methylene units to produce a high molecular weight linear polymer. Polymerization of 6,6-di-\textit{n}-butyl-6-stanna-1,10-undecadiene yielded a high molecular weight polymer but was a viscous oil, which was also the same result as polymerization of a mixture of 6,6-di-\textit{n}-butyl-6-stanna-1,10-undecadiene, 6,6,7,7-tetra-\textit{n}-butyl-6,7-distanna-1,11-
dodecadiene and \(6,6,7,7,8,8\)-hexa-\(n\)-butyl, \(6,7,8\)-tristanna-1,12-tridecadiene.\textsuperscript{20-22}

Therefore, the polymers produced from a tin monomer unit containing one, two and three tin atoms would have a tin functionality of 11, 20, and 27 \%, respectively. Again, since these polymers are unsaturated and would not produce the desired SnF\(_2\) functional group, polymer modification would need to be done by first cleaving the \(n\)-butyl group with a halide such as bromine and then a halogen exchange reaction with a fluoride source such as potassium fluoride. Some limitations that could arise are that the bromine could in fact cleave the polymer chain and with the conversion of the \(n\)-butyl group to fluorine the state of the polymer may not change from an oil to solid, though coordination of fluorine with multiple tin atoms may favor this change in state. Of course, these hypotheses have yet to be tested and are merely conjecture.

![Figure 5.1](image)

**Figure 5.1.** ADMET polymerization mechanism (A) and tin containing \(\alpha,\omega\)-dienes used in ADMET synthesis by the Wagener group.

The need to employ a reaction to cleave the alkyl chains attached to the tin could be avoided by polymerizing a tin monomer in which two halide atoms are already bonded. Based on commercial availability, this would be the
dichlorotin species. However, the dichloride would then make the tin monomer more acidic and the effect of this on the catalyst was studied using NMR. Grubbs’ 2nd generation, Figure 5.2(A), was chosen due to it being more stable versus tungsten and Schrock catalysts and it is assumed that any degradation of Grubb’s catalyst would also occur in the others. The NMR of the Grubbs’ catalyst, Figure 5.2(B), shows the carbene peak at 19.2 ppm. Upon addition of a drop of stannic chloride, the Grubbs’ catalyst solution turns from a bright red to a brown color and particulate matter is seen. Retaking the NMR of the solution, Figure 5.2(C), shows that the carbene signal is no longer present. Still stannic chloride is a much stronger Lewis acid than a dichlorotin monomer would be. Therefore, divinyl dichlorotin was added to a new Grubbs’ catalyst solution to probe the effect of the monomer with polymerization not expected due to absence of methylene units between the alkene and tin atom. Again, the solution turned brown and the carbene peak disappeared in the NMR, Figure 5.2(D), in the presence of the tin monomer. With these NMR results it is concluded that this type of monomer would play a role in the increase in the rate of degradation, most likely in the form of oxidation, of the metal catalyst making this synthetic route unfeasible.
As a consequence of the difficulty to synthesize tin doped polyethylene polymers other types of tin polymers were explored. Zilkha et al. reported the synthesis poly(organotin esters) through an interfacial polymerization technique between a dialkyldichlorotin and diacid in the mid-1960s. Carraher continued work on this polymerization technique but also expanded it to other types of difunctional monomers such as diols, diamines, etherdiamines, etc., to form organotin ether, amine and etheramine polymers, respectively. Some polymers of each of these types were synthesized, but only the poly(organotin esters) and poly(organotin ethers) proved to be sufficiently soluble to form films for dielectric testing. From the preliminary time-domain dielectric spectroscopy
results and theoretical calculations from the Ramprasad group it was decided that poly(organotin esters) would be pursued.

Figure 5.3. Structures of various tin-heteroatom containing polymers.

5.2. Results and Discussion

5.2.1. Aliphatic Poly(dimethyltin esters): Interfacial Polymerization

As described in the previous section, the synthesis of poly(dimethyltin esters) follows the interfacial polymerization technique described by Zilkha and Carraher with some modification, Figure 5.4. The polymerizations done by Zilkha involved either the diethyl or di-\textit{n}-butyldichlorotin dissolved in a nonpolar solvent such as petroleum ether.\textsuperscript{23} However, using these tin monomers would increase the free volume of the polymer and would then result in a decrease in the dipolar and atomic polarization. Carraher did use dimethyl dichlorotin dissolved in benzene with adipic acid as the other monomer, but only oligomeric species, 4 to 10 repeat units according to viscometry measurements run using dimethylsulfoxide as the solvent, were formed.\textsuperscript{25} When, the polymerization was attempted with the same reaction conditions it was found that the
dimethyldichlorotin did not exhibit the same solubility. Therefore, the organic phase was changed to tetrahydrofuran (THF) owing to the increased solubility of the tin monomer. The organic and aqueous phases are still immiscible since the aqueous phase is a salt solution of the diacid. During the reaction, the organic phase is added to a rapidly stirred solution of the aqueous phase containing the deprotonated diacid and polymerization occurs at the interface of the micelles formed. Higher molecular weight polymer is formed as a result of the increased solubility of tin monomer in the organic phase and it is believed that the polarity of THF is large enough to also solubilize the deprotonated acid chain end as polymer is being formed. The salt impurity formed during the interfacial polymerization is formed in the presence of water which keeps the salt from precipitating during reaction unlike in the polysilane synthesis where salt and polymer both precipitate.

![Figure 5.4](image)

**Figure 5.4.** Interfacial polymerization of dimethyldichlorotin with aliphatic acids of varying methylene linker segment.

### 5.2.2. Aliphatic Poly(dimethyltin esters): Structural Characterization

The structure of the poly(dimethyltin esters) is rather complex in the fact that tin has the ability to form four, five, six and even seven coordinate species. Peruzzo *et. al.* hypothesized that tin esters could form both an intra- and inter-chain octahedral coordination structure, herein labelled the α and β motifs,
respectively. These two motifs are illustrated in Figure 5.5. The Ramprasad group has used density functional theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP) to predict the structure of these polymers and determine theoretically if these coordination complexes exist. To begin the structural prediction, the polymer was built by first manually combining two methyl (CH$_3$) groups and two carboxylate (C(=O)O) groups to a central tin atom. Then the constructed dimethyltin dicarboxylate groups were connected with a chain of $n$ methylene (CH$_2$) groups. The lowest energy structures were then calculated using the minima-hopping method.

![Figure 5.5. Hypothesized intra- (right) and inter-chain (left) octahedral coordination complexes of organotin esters.](image)

From the arrangement of the four Sn-O bonds the predicted structures can be categorized into three different motifs; the α and β motif described before and a γ-motif, Figure 5.6(A). In the α-motif all four Sn-O bonds forming from the two carboxylate groups within the same repeat unit in which two Sn-O bonds are longer (> 2.5 Å) rather weak bonds and two are shorter (≈ 2.1 Å) stronger bonds.
The polymer is then characterized as a linear one-dimensional chain held together with long-range dispersion forces. In the β-motif, two of the Sn-O bonds are formed from the two carboxylate groups in the repeat unit while the other two are from the carboxylate groups of other chains. Therefore, the β-motif is characterized as a polymer with two-dimensional layers. The β-motif was also found to be the most stable structure of many of the polymers depending upon the number of methylene units. The γ-motif is a combination of characteristics of both α and β-motifs. That is three of the Sn-O bonds come from the two carboxylate groups in the repeat unit and the fourth bond is formed from a carboxylate group from another chain.

**Figure 5.6.** (A) Lowest-energy structures of α (intra-chain), β (inter-chain) and γ (hybrid) motifs predicted for p(DMTSub) and (B) four (out of numerous) of the possible folding geometries of the chains of methylene groups acting as organic linkers in p(DMTSub). In the figure, tin atoms (gray spheres) are six-fold coordinated by four oxygen atoms (red spheres) from ester groups and two carbon atoms (dark-brown) from two methyl groups. Hydrogen atoms are shown as pink spheres.

For each aliphatic poly(dimethyltin ester), numerous low-energy structures of the same motif were predicted, in which the only difference was the folding geometry of the methylene chains (see **Figure 5.6**(B) for an illustration). The predicted energy for the most-stable structures of each motif indicates that these motifs are slightly different by a few meV per atom, **Figure 5.7**. This is more
clearly seen by further examining the four most-stable predicted structures, labelled S1, S2, S3 and S4, of p(DMTGlu), Figure 5.8. These four structures represent each of the motifs, in which S3 and S4 are in the α-motif, S1 the β-motif and S2 is the γ-motif. Each motif is close in energy only varying by less than 200 meV. Table 5.1 illustrates how well the predicted bond lengths of S3 and S4 compare to the experimental results reported by Xiao et al. An “energy spectrum” is obtained for each motif due the sheer number of folding geometries of the methylene chains which increases rapidly as linker length is expanded. As a result of the heavy overlap of these spectra, it is hypothesized that all of these motifs coexist under ambient conditions.

![Figure 5.7](image_url)

**Figure 5.7.** DFT energy, EDFT, of the most-stable structures of α, β and γ predicted for the aliphatic poly(dimethyltin esters). The energy of the most-stable structures is set to zero.
Figure 5.8. Geometries and energies of S1, S2, S3, and S4, the structures predicted for the Sn-based polymer with repeat unit -COO-Sn(CH\(_3\)_2)-OOC-(CH\(_2\)_3). Tin, carbon, oxygen, and hydrogen atoms are represented by dark blue-gray, burgundy, red, and pink spheres, respectively. The energy of these structures is given with respect to that of S4, the most stable predicted structure.

Table 5.1. Sn-O and Sn-C bond lengths (in Å) of S3 and S4 given in a comparison with those of Complex 4 and Complex 5 reported in Ref. [20].

<table>
<thead>
<tr>
<th>Bond</th>
<th>S3</th>
<th>Complex 5</th>
<th>S4</th>
<th>Complex 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-O1</td>
<td>2.174</td>
<td>2.113</td>
<td>2.114</td>
<td>2.140</td>
</tr>
<tr>
<td>Sn-O2</td>
<td>2.517</td>
<td>2.511</td>
<td>2.432</td>
<td>2.552</td>
</tr>
<tr>
<td>Sn-O3</td>
<td>2.171</td>
<td>2.113</td>
<td>3.098</td>
<td>&gt;3</td>
</tr>
<tr>
<td>Sn-O4</td>
<td>2.553</td>
<td>2.511</td>
<td>2.105</td>
<td>2.136</td>
</tr>
<tr>
<td>Sn-C1</td>
<td>2.127</td>
<td>2.109</td>
<td>2.125</td>
<td>2.119</td>
</tr>
<tr>
<td>Sn-C2</td>
<td>2.126</td>
<td>2.109</td>
<td>2.132</td>
<td>2.130</td>
</tr>
</tbody>
</table>

An examination of the IR spectrum confirms that each of these motifs is present within the experimental samples due to the intra- and inter-chain carbonyl absorptions being distinct. The formation of the tin carboxylate bond is characterized by five absorptions: a combination skeletal C-CO-O- coupled with Sn-O stretching and both asymmetric and symmetric bridging and non-bridging carbonyl stretches. The skeletal stretching is observed in each of the
poly(dimethyltin esters) as indicated by an IR absorption peak in the 610-656 cm\(^{-1}\) range. The octahedral complex is characterized within IR with the asymmetric and symmetric bridging and non-bridging carbonyl stretches. As noted before, Peruzzo, et al. hypothesized that both inter- and intra-chain complexes were present in the sample. Carraher determined that the asymmetric non-bridging and bridging carbonyl absorption occurred at 1635-1660 cm\(^{-1}\) and 1550-1580 cm\(^{-1}\), respectively, while the symmetric bridging and non-bridging carbonyl absorption arose at 1410-1430 cm\(^{-1}\) and 1350-1370 cm\(^{-1}\), respectively. The region which corresponds to the complex formation in the aliphatic poly(dimethyltin esters) is depicted in Figure 5.9 (see Section 5.4.1 for individual IR spectra of the poly(dimethyltin esters). As illustrated in Figure 5.9 the absorptions for all four coordination carbonyl groups is present but vary in intensity due to the fact that all three motifs are present in varying degrees. For a majority of the aliphatic poly(dimethyltin esters) the intensity of the symmetric bridging and non-bridging carbonyl absorption peaks is relatively equal. The exceptions to this observation occur with p(DMTOx) and p(DMTSuc). P(DMTOx) is the only polymer that seems to favor one structure over the others. The two carbonyl absorptions observed in the IR correspond to the non-bridging carbonyl stretch which would result in the polymer favoring only the \(\alpha\)-motif. As for p(DMTSuc), it exhibits a much stronger peak for the non-bridging than the bridging carbonyl. However, the \(\alpha\) motif (intra-chain) of p(DMTSuc) does not form computationally which would correspond to non-bridging stretches having reduced intensity, but this is not observed. Therefore, the p(DMTSuc) is
assumed to favor a hybrid type structure that is more highly intra-chain coordinated versus inter-chain coordinated.

**Figure 5.9** IR region which corresponds to the coordination carbonyl absorptions for aliphatic poly(dimethyltin esters) with an even (top) and odd (bottom) number of methylene linker units.

The structural complexity of these polymers was confirmed using x-ray diffraction (XRD). The Ramprasad group performed calculations on each of the
structural motifs to generate predicted XRD patterns. A comparison of the experimental XRD patterns to the theoretical ones illustrate that the polymer structures are a conglomeration of the α, β and γ-motifs in some unknown ratio (see Section 5.4.1 for the XRD overlays). The four stable structures of p(DMTGlu), mentioned previously, also exhibit distinct XRD patterns and when compared to the experimental data are present in the polymer sample, Figure 5.10. The ratio of each of these structures is inherent to how the polymer precipitates from the reaction. The XRD of p(DMTGlu) after reprecipitation from m-cresol showed the loss of two peaks at 2θ values of 11.50 and 15.52, Figure 5.10(B). This suggested that the crystal structure was reorienting to a structure which favored a 2θ value of 15, corresponding to the predicted S4 structure. The S4 structure is the only motif of the four predicted ones that had a major peak at a 2θ value of 15 and two other major peaks below 15. This reorientation was also expected due to the S4 structure also being theoretically the most stable.

Figure 5.10. Theoretical (left) XRD patterns for the four predicted structures of p(DMTGlu). Overlay of the XRD patterns (right) of polymer powder of p(DMTGlu), black line, and after precipitating p(DMTGlu) from m-cresol, red line.
5.2.3. Aliphatic Poly(dimethyltin esters): Molecular Weight Determination by NMR

Polymer molecular weight was determined using NMR. The NMR of p(DMTSub) is shown in Figure 5.11 for two reasons, see Section 5.4.1 for the NMRs or the other aliphatic poly(dimethyltin esters). First it proves that the triplets labelled at $\delta = 2.55$ and 2.82 ppm are in fact chain ends and not $^{13}$C satellite peaks. This is concluded from the fact that the main peak at $\delta = 2.69$ is a singlet and if the other peaks were $^{13}$C satellite peaks then the splitting pattern would be the same. Also, the triplet at $\delta = 2.82$ ppm does not integrate to 0.55 % of the main body signal which would be the case if there were hydrogen atoms attached to a $^{13}$C atom as the isotopic abundance of $^{13}$C is 1.1 %. Secondly, it illustrates that the chain signals are resolved from the main body protons. To calculate the molecular weight first the integral per proton is first determined by dividing the integration of the chain ends, the signal at $\delta = 2.82$ ppm only since the other signal would be severely overestimated due to the peak tailing of the main signal, by the number of protons represented, four in this case since both chain ends are the same as a result of using a molar excess of the diacid. Next the number of repeat units is calculated by dividing the integration of the main signal at $\delta = 2.69$ ppm by the number of protons represented, again four, and dividing that result by the integral per proton determined before. With the number of repeat units now known, the molecular weight of the repeat unit is multiplied by this number and the formal weight of the chain end (the molecular weight of the diacid) is added to give the total molecular weight. Since the
molecular weight calculated through the NMR integrations is found from the ratio of the main body protons and chain end protons, this corresponds to the number average molecular weight, $M_n$. Using the Carother’s equation in which the diacid is in molar excess;

$$X_n = \frac{1+r}{1+r-2rp}$$

(5.1)

As $p \rightarrow 1$ equation 5 simplifies to;

$$X_n = \frac{1+r}{1-r}$$

(5.2)

For $p$(DMTSub) this would give a maximum $M_n$ of 37,688.95 g mol$^{-1}$. The $M_n$ calculated will be skewed somewhat again due to the peak tailing of the main body protons. However, it does suggest that the polymers synthesized in this dissertation are of a higher molecular weight than the oligomeric polymers reported by Carraher.
Figure 5.11. NMR spectra of p(DMTSub). The main body protons are represented by the singlet at $\delta = 2.69$ ppm. Chain ends are marked with the blue and red squares.

Zilkha reported that the organotin ester polymers they synthesized degraded in acetic acid but were stable in dilute acid conditions.\textsuperscript{23} Since the molecular weights of the polymers described in this dissertation were calculated from NMR in acetic acid-$d_4$ a study was performed on p(DMTGlu) to observe whether the chain end integrations varied with time. If the polymer were degrading in acetic acid then the chain end integrations would increase over time as a result of diacid functionality being supplanted by the acetic acid. If there was complete degradation of the polymer chain, then the chain ends would be absent as the diacid would be reformed in solution. The time study results are shown in Figure 5.12. From Figure 5.12 it is shown that the chain end
integration does not change drastically over a week, 0.162 to 0.152. Even after three weeks and the addition of a drop of concentrated hydrochloric acid, Figure 5.12(F), did not affect the integration, 0.162 to 0.156. The slight change in the values is just a result of normal variation in manual integration.

![Figure 5.12](image)

**Figure 5.12.** NMR time study for p(DMTGlu) at t = 0 (A), t = 10 minutes (B), t = 90 minutes (C), t = 24 hours (D), t = 1 week (E) and t = 3 weeks with the addition of one drop of concentrated hydrochloric acid (F).

### 5.2.4. Aliphatic Poly(dimethyltin esters): Thermal Properties

The aliphatic poly(dimethyltin esters) do not exhibit a glass transition temperature, $T_g$, down to -70 °C and because of this these polymers will not exhibit $\alpha$ relaxation. These polymers are stable to temperatures below 300 °C but do not show a melting transition below the degradation point. Therefore, the operating temperature of these polymers for various applications could be rather wide. Only p(DMTOx) shows a loss in mass before degradation which is due to the presence of water in the sample as a result of oxalic acid being able to take a hydrated form. The thermal data for the polymers is tabulated in Table 5.2.
Table 5.2. Degradation temperature ($T_d$), number average degree of polymerization ($X_n$) and number average molecular weight ($M_n$) of aliphatic poly(dimethyltin esters).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>#CH$_2$ units</th>
<th>$T_d$ (°C)</th>
<th>$X_n$</th>
<th>$M_n$ (gmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p(DMTOx)</td>
<td>0</td>
<td>265</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>p(DMTMal)</td>
<td>1</td>
<td>215</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>p(DMTSuc)</td>
<td>2</td>
<td>238</td>
<td>246</td>
<td>65,111.96</td>
</tr>
<tr>
<td>p(DMTGlu)</td>
<td>3</td>
<td>265</td>
<td>247</td>
<td>68,991.38</td>
</tr>
<tr>
<td>p(DMTAdi)</td>
<td>4</td>
<td>251</td>
<td>240</td>
<td>70,301.83</td>
</tr>
<tr>
<td>p(DMTPim)</td>
<td>5</td>
<td>260</td>
<td>230</td>
<td>70,718.79</td>
</tr>
<tr>
<td>p(DMTSub)</td>
<td>6</td>
<td>242</td>
<td>235</td>
<td>75,494.20</td>
</tr>
<tr>
<td>p(DMTAze)</td>
<td>7</td>
<td>248</td>
<td>239</td>
<td>79,945.36</td>
</tr>
<tr>
<td>p(DMTSeb)</td>
<td>8</td>
<td>240</td>
<td>252</td>
<td>88,003.51</td>
</tr>
<tr>
<td>p(DMTDec)</td>
<td>10</td>
<td>225</td>
<td>249</td>
<td>93,909.80</td>
</tr>
</tbody>
</table>

5.2.5. Aliphatic Poly(dimethyltin esters): Dielectric Measurements

Theoretical calculations done on each of the three motifs of the aliphatic poly(dimethyltin esters) showed a trend of decreasing static dielectric constant, herein referred to as $\varepsilon_{\text{total}}$, as the number of methylene units increased. Calculations were done up to eleven methylene groups with $\varepsilon_{\text{total}}$ as high as 4.0, approximately 50% higher than PE and the same order as SiO$_2$. Since $\varepsilon_{\text{total}}$, a second-rank tensor quantity, is comprised of an electronic dielectric constant tensor, $\varepsilon_{\text{el}}$, and an ionic dielectric constant tensor, $\varepsilon_{\text{ion}}$, both contributions were individually calculated. It was found that $\varepsilon_{\text{el}}$ was not dependent upon either the motif or the number of methylene units. Therefore, $\varepsilon_{\text{ion}}$ is more motif dependent and this can be illustrated in the case of p(DMTPim) which exhibits $\varepsilon_{\text{ion}}$ values of 1.74 and 3.44 for motifs $\alpha$ and $\beta$, respectively. The vibration modes that most contribute to $\varepsilon_{\text{ion}}$ were then determined, Figure 5.13. In the $\alpha$-motif all four Sn-O bonds are highly polarized and are in bending vibration modes whereas in the $\beta$-motif two of these bonds are in stretching vibration modes. As a result of the
two-dimensional nature of the β-motif the Sn-O orientations are “more isotropic” than the α-motif which give rise to this stretching vibration. The stretching vibration thus leads to larger changes in the Sn-O bond length and therefore increased polarizability of the β-motif.

Figure 5.13. The vibration mode that has the most significant contribution to $\varepsilon_{\text{ion}}$ of the most stable structures of motifs α and β of p(DMTPim). Atom types are indicated in color the same was as in Figure 2 within the manuscript. Between motif α and β, arrows describing the amplitude and direction of atomic displacements, are scaled using the same unit.

In order to test all of the polymers versus the theoretical values generated by the Ramprasad group, pellets of the aliphatic poly(dimethyltin esters) were pressed since some of the polymers were insoluble. The percent functionality in the backbone represented by these polymers ranges from 33 %, p(DMTDec), to 100 % p(DMTOx). The dielectric constant was averaged, $\varepsilon_{\text{avg}}$, from 1-1000 Hz to encompass the values usually reported in literature (60, 100, or 1000 Hz). From Figure 5.14A) it can be seen that the trend in the dielectric constant of the aliphatic poly(dimethyltin esters) follows the odd/even property rule found commonly in polymers. When comparing $\varepsilon_{\text{avg}}$ to the theoretical calculations the
experimental values fall within 44 % of the averaged value of the three motifs. With the exception of p(DMTSub), all of the the experimental dielectric constants correspond better to the α-motif. Comparing these values shows that a strong correlation between theoretical and experimental is met with the all of the polymers falling within 29 % of the predicted value and the best relation being 0.6 % for p(DMTPim). Experimentally, as the number of methylene units is increased from 0 to 3 the expected decrease in the dielectric constant is observed. However, a spike in dielectric constant occurs at six methylene units and then $\varepsilon_{\text{avg}}$ again decreases with increasing number of methylene units. The DFT calculation accurately predicted this trend for all of the motifs, though for the α and β motifs this spike occurs at five methylene groups while the γ-motif exhibits a spike at six methylene units. Since it was already shown through IR and XRD that these polymers have both intra- and inter-chain coordination then the second maximum at six methylene units is expected. As stated before the theoretical calculations showed that the minimum dielectric constant achieved was 4.0 for the polymer with a chain of eleven CH$_2$ units. Experimentally, though the polymer with eleven units was not synthesized, the minimum dielectric constant achieved was 5.3 for both p(DMTSeb) and p(DMTDec), 1.3 times higher than the predicted minimum value. The difference in the theoretical and experimental values can be attributed to both the DFT calculations being performed on systems on fully crystalline materials at 0 K and the values being the static dielectric constant with no frequency term.
The expected trend in dissipation should be a decrease as the number of methylene units is increased. This is expected since a decrease in the dipolar density within in the backbone would reduce the volume of dipoles trying to align with the applied field. However, these polymers do not follow this trend and a majority of them exhibit losses on the order of $10^{-2}$ which is of the same magnitude as PE and PP, Figure 5.14(E and F). All of the polymers show the same trend in loss as the frequency is increased. Of the aliphatic polymers only two, p(DMTOx) and p(DMTSuc), suffer from large loss due to DC conductivity at low frequency. This large dissipation for p(DMTOx) can be simply explained by the presence of residual water in the polymer even after aggressive drying of the pellet in vacuo. Comparing these polymers to commercially available insulating polymers used in high energy density capacitors, p(DMTSeb) polymer that exhibits a dissipation factor on the same order ($\approx 10^{-4}$).
5.2.6. Aliphatic Poly(dimethyltin esters): Band Gap Measurements

The Ramprasad group calculated the band gap, $E_g$, of the aliphatic poly(dimethyltin esters) using both the Perdew-Burke-Ernzerhof (PBE) exchange-correlation (XC) functional and Heyd-Scuseria-Ernzerhof (HSE06) XC hybrid functional since PBE usually underestimates this value.$^{35-37}$ For example...
PBE estimates the $E_g$, of highly crystalline PE as 6.8 eV while HSE06 calculates this value as 8.4 eV which is much closer to the experimental value of 8.8 eV.\textsuperscript{38}

The densities of states were also calculated and it was noted that the band gap was not dependent upon the motif. As shown in Figure 5.15, the band gap is limited to a maximum value of 6.0 as a result of the states related to the dimethylnitricarboxylate groups dominating the valence band maximum and the conduction band minimum.

Figure 5.15. Electron density of states calculated for the predicted most stable structures of the aliphatic poly(dimethylnit esters), shown by solid dark-green curves. Contribution from tin and its six coordinated (two carbon and four oxygen) atoms are shown by orange curves. Fermi energies are set to zero.
To determine the band gap of the polymers, films were casted from m-
cresol solutions, with the exception of p(DMTMal) and p(DMTSub) which were
casted from 3:1 (v:v) HFIP:CHCl3 and 2:1 (v:v) m-cresol:1,2-DCE respectively,
onto quartz glass slides. The $E_g$ was calculated using Planck's relation after
determining the onset wavelength of absorption ($\lambda_{onset}$). The polymers exhibit a
shoulder peak adjacent to the edge of the onset and this is presumed to be due
to localized electronic states lying above the valence band or below the
conduction band. This has been reported in other polymers, such as PE or PP,
measured using the same technique. The aliphatic poly(dimethyltin esters)
exhibited band gaps ranging from 4.7-6.7 eV, Figure 5.16. In comparison to the
theoretical band gaps of the three different motifs calculated using both PBE and
HSE06 functionals, the experimental values were within 25 % and were between
the PBE and HSE06 results. The only outlier in this comparison was p(DMTSub)
which had a stronger correlation to the HSE06 value. From the fact that
dielectric constant and band gap grow inversely of each other with respect to the
number of methylene groups, it can be surmised that a linker segment between
five and eight methylene units would give optimal properties for both dielectric
constant and band gap. Wang developed a mathematical relationship between
the band gap of an insulator and the intrinsic breakdown field, $E_{BI}$,
\[
E_{BI} = 1.36 \times 10^7 \left( \frac{E_g}{4.0} \right) \text{ (V/cm)} \tag{5.3}
\]
Based on the relationship between band gap and intrinsic breakdown, $E_{BI}$,
developed by Wang, the $E_{BI}$ of the poly(dimethyltin esters) would range from 1.6-
2.3$\times 10^7$ Vcm$^{-1}$. In perspective using the band gap of polypropylene (PP), 7.0 eV,
then the theoretical intrinsic breakdown field would be $2.38 \times 10^7 \text{ V cm}^{-1}$ or 2,380 Vμm$^{-1}$, where experimentally PP has a breakdown of 700 Vμm$^{-1}$. Going a step farther and calculating the maximum energy density these polymers would fall between 63-152 Jcm$^{-3}$ whereas the theoretical energy density of PP would be 55 Jcm$^{-3}$. Of course highly processed PP has an energy density at approximately 10 % of the theoretical value and these theoretical values are listed as a means of illustrating that aliphatic poly(dimethyltin esters) could meet or surpass the dielectric properties of PP.

![Figure 5.16](image)

**Figure 5.16.** Overlay of the theoretical and experimental band gaps (A) of the aliphatic poly(dimethyltin esters). UV-vis spectra of p(DMTGlu) (B), p(DMTPim) (C), p(DMTAze) (D), p(DMTSeb) (E) and p(DMTDec) (F).
The large band gap of p(DMTSub) puts in at nearly the same level as the values measured for LDPE and PP by Arai. It was also the only polymer that did not show any shoulder peak before the onset of absorption. Since the band gap was so large multiple films were measured to verify the band gap. The three films measured all had onset wavelengths between 185-189 nm resulting in an $E_g$ of 6.6-6.7 eV, Figure 5.17. It is expected that onset is due to the $n\rightarrow\pi^*$ or $\pi\rightarrow\pi^*$ discussed in Chapter 2, but this is slightly below the common minimum wavelength of these transitions, 200 nm. These transitions could be different for these polymers due to the carboxylate $\pi$-bond being delocalized and the electron lone pairs being shared with the tin atom to form the coordination complex. Therefore, the transition exhibited in p(DMTSub) falls in the range of a $n\rightarrow\sigma^*$ which occurs commonly below 200 nm, but is not high enough in energy to classify this transition as $\sigma\rightarrow\sigma^*, < 185$ nm.

Figure 5.17. Overlay of the UV-vis spectra of three different films of p(DMTSub).
With the dielectric properties and band gaps of the aliphatic poly(dimethyltin esters) a comparison to other insulating polymers and some oxides is discussed. The theoretical and experimental values for both dielectric properties and band gaps are shown in Tables 5.3 and 5.4, respectively. Figure 5.18 shows the dielectric constant versus band gap of the aliphatic polu(dimethyltin esters) in comparison to some common dielectric materials.

Table 5.3. Comparison of the theoretical and experimental dielectric properties.

<table>
<thead>
<tr>
<th>#CH₂ units</th>
<th>ε&lt;sub&gt;Total&lt;/sub&gt; [α]</th>
<th>ε&lt;sub&gt;Total&lt;/sub&gt; [β]</th>
<th>ε&lt;sub&gt;Total&lt;/sub&gt; [γ]</th>
<th>ε&lt;sup&gt;α)&lt;/sup&gt;</th>
<th>tanδ&lt;sup&gt;α)&lt;/sup&gt; [%]</th>
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<tr>
<td>0</td>
<td>7.22</td>
<td>5.18</td>
<td>6.70</td>
<td>66.12</td>
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<td>5.85</td>
<td>1.00</td>
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<td>4.86</td>
<td>6.20</td>
<td>43.59</td>
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<td>4.45</td>
<td>5.77</td>
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<td>5</td>
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<td>4.07</td>
<td>6.34</td>
<td>1.13</td>
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<td>6.64</td>
<td>1.75</td>
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<td>4.18</td>
<td>3.98</td>
<td>6.21</td>
<td>2.28</td>
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<tr>
<td>8</td>
<td>3.51</td>
<td>3.85</td>
<td>5.28</td>
<td>0.04</td>
<td></td>
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<tr>
<td>10</td>
<td>-</td>
<td>-</td>
<td>5.35</td>
<td>0.35</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a)</sup> Average value over 1-1000 Hz

Table 5.4. Comparison of the theoretical and experimental band gap values.

<table>
<thead>
<tr>
<th>#CH₂ units</th>
<th>E&lt;sub&gt;g&lt;/sub&gt; α (PBE) [eV]</th>
<th>E&lt;sub&gt;g&lt;/sub&gt; β (PBE) [eV]</th>
<th>E&lt;sub&gt;g&lt;/sub&gt; γ (PBE) [eV]</th>
<th>E&lt;sub&gt;g&lt;/sub&gt; α (HSE06) [eV]</th>
<th>E&lt;sub&gt;g&lt;/sub&gt; β (HSE06) [eV]</th>
<th>E&lt;sub&gt;g&lt;/sub&gt; γ (HSE06) [eV]</th>
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<tr>
<td>0</td>
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<td>2.964</td>
<td>3.306</td>
<td>5.049</td>
<td>4.631</td>
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<td>4.393</td>
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<td>4.323</td>
<td>6.310</td>
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<td>4.443</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.439</td>
</tr>
</tbody>
</table>

<sup>a)</sup>Determined by UV-vis; <sup>b)</sup>3:1 (v:v) hexafluoroisopropanol:chloroform solution; <sup>c)</sup>m-Cresol solution; <sup>d)</sup>2:1 (v:v) m-cresol:1,2-dichloroethane
5.2.7. Aliphatic Poly(dimethyltin esters): Effect of Solvent on Synthesis and Dielectric Properties

The use of THF as the organic phase in the interfacial polymerization of the poly(dimethyltin esters) was previously discussed. Higher polarity solvents were therefore investigated since high molecular weight polymers were obtained by using THF which itself is only slightly polar compared to solvents such as m-cresol, DMF, DMAc, DMSO and NMP. Table 5.5 tabulates the synthesis data of poly(dimethyltin glutarate) in various solvent systems. Increasing the monomer concentration in both the aqueous and THF phase results in an increase of the \( M_n \) of the polymer, ca. 66,000 to 71,000 gmol\(^{-1} \), but at a reduced yield, 73.9 to 51.1\%. Changing the organic phase to other polar solvents, such as DMAc, NMP and m-cresol, also resulted in an increase in molecular weight. Poly(dimethyltin glutarate) synthesized with NMP as the organic solvent gave the highest yield and molecular weight of the four solvent systems tested. The synthesis of poly(dimethyltin glutarate) was also carried out in all organic solvent to reduce the chance of base hydrolysis of the tin carboxylate in the presence of
water. The base was switched to triethylamine due to the insolubility of sodium hydroxide in the solvents. The molecular weight of the p(DMTGlu) was lower when comparing the all organic reaction with the interfacial polymerization using the same polar solvent. In comparison to the water/THF system the all DMAc reaction had lower molecular weight while the NMP system gave higher molecular weight. In all of the systems tested the molecular weight was fairly consistant, ca. 60,100 to 76,000 g mol⁻¹, which illustrates the versatility of this polymerization.

Table 5.5. Comparison of different synthetic reactions used in the formation of p(DMTGlu).

<table>
<thead>
<tr>
<th>Solvent System</th>
<th>Glutaric Acid [M]</th>
<th>Me₂SnCl₂ [M]</th>
<th>Yield [%]</th>
<th>Mₙ [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water/THF</td>
<td>0.78</td>
<td>0.68</td>
<td>73.9</td>
<td>66,139.23</td>
</tr>
<tr>
<td>Water/THF</td>
<td>1.10</td>
<td>1.09</td>
<td>66.9</td>
<td>68,991.38</td>
</tr>
<tr>
<td>Water/THF</td>
<td>1.50</td>
<td>1.48</td>
<td>51.1</td>
<td>71,184.35</td>
</tr>
<tr>
<td>Water/DMAc</td>
<td>0.77</td>
<td>0.67</td>
<td>66.8</td>
<td>63,513.94</td>
</tr>
<tr>
<td>Water/NMP</td>
<td>0.77</td>
<td>0.74</td>
<td>75.1</td>
<td>76,017.83</td>
</tr>
<tr>
<td>Water/m-Cresol</td>
<td>0.77</td>
<td>0.68</td>
<td>58.2</td>
<td>73,041.92</td>
</tr>
<tr>
<td>DMAc</td>
<td>0.78</td>
<td>1.02</td>
<td>62.2</td>
<td>60,106.31</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>0.78</td>
<td>1.03</td>
<td>58.2</td>
<td>66,532.12</td>
</tr>
</tbody>
</table>

Pellets were pressed of p(DMTGlu) synthesized using THF and DMAc to determine whether the solvent used for the organic phase had an effect on the dielectric properties of the polymer. Testing the polymer over a frequency range of 2.5 kHz to 1 MHz proved that the dielectric properties are not affected by organic phase, Figure 5.19. There was a slight increase in dielectric constant from 5.27 to 5.36 and dissipation from 0.23 % to 0.29 % for the THF and DMAc systems respectively. The difference in properties could be due to the minor
difference in molecular weight or some residual solvent in the polymer powder. This verifies that dielectric properties have saturated and that the polymerization can be carried out in a number of ways.

Zilkha also reported that the poly(organotin esters) that they synthesized also degraded in boiling m-cresol. However, the syntheses done m-cresol showed equivalent IR spectra. The dielectric spectra of a pellet of p(DMTGlu) and two m-cresol films are shown in Figure 5.20. The dielectric constant of the pellet is lower than the two films but the dissipation is better. These two trends can be attributed to the remnant m-cresol. In Figure 5.20 it was shown that the polymer reorients itself in a manner in which the orientation of the structure favors the predicted most-stable motif after reprecipitation of the polymer from m-cresol. This reorientation would mean that the polymer is favoring structures that have higher dielectric constants versus the pellet as a result of a higher ratio of lower k structures. The increased dissipation is a consequence of the high boiling point of m-cresol, 202 °C, which makes it tougher to fully remove from the
film. As the temperature of the dielectric measurements is increased both the pellet and film follow the same trend, increase in both dielectric constant and loss. At 100 °C the film and pellet have approximately the same dielectric constant and loss which indicates that the material is stable in m-cresol and that the solvent does not cause degradation.

Figure 5.20. Overlay of the dielectric constants (top) of a pellet and two films cast from m-cresol of p(DMTGlu). Temperature effect on the dielectric properties of a pellet (bottom left) and film (bottom right) of p(DMTGlu).
It has been reported that the dielectric properties of DNA films casted from either 1-butanol and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) resulted in different dielectric constants and losses.\textsuperscript{41} This difference was attributed to the fact that the alignment of the DNA chains was parallel with the electrodes when casting with 1-butanol and perpendicular in the HFIP cast film. It is expected that the dielectric properties of a film will be improved if the chains are already pre-aligned with the field. With that knowledge different casting solvents were used to make films of p(DMTGlu). Figure 5.21 illustrates the dielectric results for films casted from 3:1 (v:v) m-cresol:1-butanol and 2:1 (v:v) m-cresol:1,2-dichloroethane. The film casted from the m-cresol/1-butanol solution exhibits a very low dielectric constant, < 2.3, which indicates that the ionic portion of the dielectric constant has been suppressed, since it matches the theoretical and experimental value for the electronic part of the dielectric constant. This could be due to the dipoles being parallel to the field reducing the dipolar orientation to almost 0 and the atomic polarization being disrupted by the donation of the lone electron pairs on the hydroxyl group to tin atom effectively destroying the octahedral complex that is deemed to enhance the dielectric constant. If 1-butanol is now coordinated this would also increase the free volume as a result of the long carbon chain leading to a decrease in the dipolar density per unit volume. The film cast from a solution of m-cresol/1,2-dichloroethane also resulted in a lower dielectric constant but not as drastic a drop as the m-cresol/1-butanol film. The trend in the data follows what was observed for both the pellet
and m-cresol films of p(DMTGlu). Again the difference between the two could be due chain alignment or the ratio of different structures within the two films.

**Figure 5.21.** Dielectric properties of p(DMTGlu) cast from 3:1 (v:v) m-cresol/1-butanol (left) and 2:1 (v:v) m-cresol:1,2-dichloroethane.

From both of the dielectric constant traces of the m-cresol and 2:1 (v:v) m-cresol:1,2-dichloroethane it is seen that there is a large increase in the dielectric constant when the measurement temperature is raised from 100 °C to 125 °C. Within the thermogram generated from the DSC, the polymer exhibits some kind of transition around 127 °C that is not related to a glass transition or a melting transition, **Figure 5.22(A).** First the film of p(DMTGlu) cast from m-cresol/1,2-dichloroethane was heated to 125 °C, which is within the temperature range of transition seen in the DSC, and then the dielectric measurements were taken as the sample was cooled to 50 and 25 °C. The dielectric constant measured at 125 °C was >4 but the measurements done on the sample after cooling to 50 and
25 °C showed that the dielectric constant returned to the original measurements, approximately 3.5, **Figure 5.22(C)**. Therefore, the polymer in film form does not show improvement in the dielectric constant just through annealing the polymer at higher temperatures. Reorientation of the polymer structure in the film could not have been achieved during the simple cooling in the oven in which the dielectric measurements were taken. Therefore, the powder of p(DMTGlu) was annealed at 140 °C for 5 hours and quenched rapidly in an ice bath. The XRD of the two samples showed changes in peaks and peak intensities, **Figure 5.22(B)**. Pellets were pressed of both the quenched and unquenched polymer powder and frequency domain measurements taken. There was a slight improvement in the dielectric constant of the annealed sample, approximately 4.9 to 5.2, but this is an insignificant change to warrant the conclusion that annealing of the polymer material is a must, **Figure 5.22(D)**.
Figure 5.22. DSC trace (A) of p(DMTGlu) showing a thermal transition at 127 °C. Overlay of the XRD patterns (B) of the original p(DMTGlu) powder, black line, thermally annealed polymer powder, red line, and the m-cresol film, blue line. Dielectric properties of the annealed film of p(DMTGlu) (C) and powder (D).

5.2.8. Aliphatic Poly(dimethyltin esters): Effect of Blending on Film Quality and Dielectric Properties

Film quality is important in measuring reliable dielectric data. The aliphatic poly(dimethyltin esters) suffer from being opaque, brittle films that easily peel off of the shim stocks that they are cast on after removal of the silicon electrode. To alleviate this a homopolymer was synthesized using 3,3-dimethylglutaric acid as the diacid monomer. The two methyl groups will cause chain disruption, breaking reducing the size of the large crystal regions seen in the films of the aliphatic poly(dimethyltin esters). Figure 5.23 illustrates the films of p(DMT 3,3-DMG) and the 20:80 (w:w) blends of p(DMTGlu) and p(DMT) with p(DMT 3,3-
DMG). The homopolymer of p(DMT 3,3-DMG) looks like a clear glass with the yellowish tint being due to the remnant m-cresol and the blends exhibit this same appearance up to about 50/50 mixtures. Therefore, 3,3-dimethylglutarate is sufficient in reducing the large crystal regions. The drawback of adding another monomer that contains side chains is the increase in free volume. However, dielectric testing, Figure 5.23, illustrates that this is not a concern. The blends of p(DMTGlu):p(DMT 3,3-DMG) and p(DMTSub):p(DMT 3,3-DMG) exhibit dielectric constants in the range of 5.0-7.5 and 5.0-7.0 respectively. The trend in dielectric constant is expected to follow one of two trends. The first trend being that the dielectric constant would follow a linear relationship where the dielectric constant of the blends would be between the two homopolymers and the magnitude would be increase as the blends became more like p(DMT 3,3-DMG) since that polymer had a higher dielectric constant than the pellets of p(DMTGlu) and p(DMTSub). The second trend would be some sort of parabolic function in which at some blend concentration a maximum would be achieved in which the blends on either side would show a decrease in the dielectric constant. However, these trends are not met and there is in fact no trend in the dielectric data for the blends. This indicates that better processing conditions are needed to create films with a more uniform thickness or a means of controlling the drying rate, as different solvent evaporation rates also affect the clarity of the films.
5.2.9. Effect of Aromaticity

The effect of aromaticity on the dielectric constant of organotin esters was studied by synthesizing aromatic poly(dimethyltin esters) in which the aromatic ring is in the α position to the carboxylate group. The five aromatic monomers used in the study are either electron withdrawing (pyridine ring), “neutral” (benzene ring) or donating (thiophene ring) in nature. Synthetically, these polymers are insoluble even in acetic acid so molecular weight could not be determined. From the IR and XRD spectra the polymers exhibit both the inter- and intra-chain coordination complexes. Thermally, these polymers exhibit higher degradation temperatures, > 300 °C with the lowest polymer degrading at 303 °C, versus the aliphatic polymers.

The aromatic diacid monomers chosen have secondary dipoles, that is in the case of benzene ring systems the carboxylate groups are either para-, no
dipole, or meta-positioned, second dipole moment, to each other. The pyridine and thiophene ring systems also add a third dipole due to the heteroatom. Theoretically the dielectric constant of these polymers increases through the following trend; “neutral” < withdrawing < donating. However, the calculations do not follow the trend that the meta-positioning of the carboxylate groups would lead to a higher dielectric constant. Within the benzene ring system the meta-positioning shows a lower dielectric constant while the pyridine rings show the opposite.

Compared to the theoretical calculations the experimental dielectric results show that two para-positioned carboxylate polymers, p(DMTTer) and p(DMT 2,5-DPA), have the lowest dielectric constants and the other three polymers with the carboxylates in the meta-positioning, p(DMTIso), p(DMT 2,6-DPA) and p(DMT 2,5-TDC), have the highest dielectric constants, Figure 5.24. Comparing the polymers in terms of their electronic contribution, the electron withdrawing pyridine ring gives rise to a slightly higher dielectric constant than the benzene derivative, though this change is very small and cannot be described as significant. The thiophene containing polymer lies in between the benzene and pyridine ring system polymers. All of these polymers exhibit a dissipation on the order of \(10^{-2}\), with all of them being below three percent. The polymer, p(DMTIso), exhibits the lowest dissipation, on the order of \(10^{-3}\), up to measurement temperatures of 150 °C. Though this study does not correlate well to the theoretical calculations, it does show the benefit of having an aromatic ring in the α position on the dielectric constant up to high temperatures.
Figure 5.24. The structures of the aromatic diacids used (center) with the theoretical dielectric constants listed below. Overlay of the dielectric properties of the aromatic poly(dimethyltin esters) (left) and the temperature dependence of the dielectric properties of p(DMTIso).

5.2.10. Effect of Chirality

Like the blending study, the addition of a chiral monomer into the polymer chain could give enough chain disruption to reduce the size of the crystals. In this study tartaric acid is used because it is well characterized and commercially available in three chiral forms, D, L and the racemic DL. The other effect that could be introduced through the addition of tartaric acid is a disruption in the coordination complex. The electron pairs on the hydroxyl groups could also coordinate to the tin atom, in competition with the lone pairs on the carbonyls, forming stable five and six membered rings. The hydroxyl groups will also form hydrogen bonding complexes between chains as well as within chains. The homopolymers based on D- or L-tartaric acid took longer to precipitate from the reaction solution versus the DL-tartaric acid. This is explained by examining the XRD pattern, which shows that the D- and L-tartaric acid based polymers are
more amorphous than the crystalline DL-tartaric acid based polymer. The XRD patterns of the 50/50 copolymers of glutaric acid and the three different tartaric acid monomers exhibit some differences. The 50/50 glutaric acid/DL-tartaric acid has fewer peaks than the D- and L-tartaric acid polymers meaning that there is more symmetry in that particular polymer, which could be due tighter chain packing in the polymer, **Figure 5.25**.

The dielectric constant of p(DMT D-Tar) is expected to be higher than p(DMTGlu) due to the higher density of functionality in p(DMT D-Tar) which is what is observed experimentally, 6.2 versus 5.8, **Figure 5.25**. However, the copolymers glutaric acid and tartaric acid would be assumed to fall in between the two homopolymers which is not observed experimentally. All three copolymers exhibit lower dielectric constants than p(DMTGlu). The lower dielectric constant of the copolymers could be the result of having lower functional group density versus p(DMT D-Tar) and the secondary dipole from the hydroxyl groups may be not aligning quick enough with the dielectric field, since these measurements are done on pellets, causing the dielectric constant to be lower than p(DMTGlu). The crystallinity of the copolymers could also affect the dipole alignment as a more amorphous character would give the dipoles more freedom of movement. The dissipation is also higher with the addition of tartaric acid which can also be explained with how fast the dipoles align.
5.3. Conclusions

The addition of tin into the backbone of a polymer is a beneficial to enhancing the dielectric constant through the increase in the ionic contribution stemming from the large difference in electronegativity between tin and oxygen. It was shown experimentally and theoretically that the octahedral coordination found in poly(dimethyltin esters) was the reason for the increased dielectric constant versus other tin type polymers due to the delocalization of the electron density over a greater area which affects the atomic polarization. The dielectric constants for the aliphatic poly(dimethyltin esters) ranged from 5.3-8.7 with most of the polymers exhibiting dissipation on the order of $10^{-2}$ and band gaps $> 4.6$. 

Figure 5.25. Dielectric properties of p(DMTGlu), p(DMT D-Tar) and the copolymers based on glutaric and tartaric acids (left). Overlay of the XRD patterns of the homopolymers based on tartaric acid and copolymers based on glutaric and tartaric acids.
Dielectric constants can be tailored depending upon how the polymer was processed and film quality could be improved by blending with another homopolymer to cause disruption in chain packing. It was shown that including an aromatic group in the α position to the carboxylate groups improved dielectric performance at elevated temperatures, while the addition of a chiral monomer had no affect other than introducing some amorphous quality to the polymer. The theoretical calculations showed strong correlation with the experimental values. To better improve these materials other diacids should be tried to increase molecular weight and film forming properties. This could be achieved by synthesizing tin dicarboxylate monomers that are end functionalized to further polymerize with other monomers or vice versa.

5.4. Experimental

5.4.1. Synthesis of Poly(organotin esters)

A molar excess of the diacid was added to a round-bottomed flask and dissolved in 20 mL of water. To the diacid solution was added 2.1 equivalents, with respect to the diacid, of sodium hydroxide. To the rapidly stirred aqueous solution was added 20 mL of a dimethyltin dichloride solution in tetrahydrofuran. The precipitate is filtered and washed with 50-100 mL portions of tetrahydrofuran and water and dried in vacuo at 115 °C for 20 hours to remove any residual solvent.
Poly(dimethyltin oxalate) (p(DMTOx)): To a round bottom flask was added 2.130 g (16.9 mmol) oxalic acid dihydrate, 1.4823 g (37.1 mmol) NaOH, and 80 mL of water and stirred rapidly. To an Erlenmeyer flask was added 3.6558 g (16.6 mmol) of Me₂SnCl₂ and 25 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 2.9604 g (75.1 %) of polymer.

IR (KBr): ν = 3403 (vs; OH), 2929 (w; CH), 1699 (vs; C=O), 1625 (vs; νas(C=O)), 1351 (s), 1311 (s), 798 (vs), 656 (w), 585 (w), 481 cm⁻¹ (w); TGA (10 °C min⁻¹): \(N_2\) (onset): 265 °C.

Poly(dimethyltin malonate) (p(DMTMal)): To a round bottom flask was added 2.2893 g (22.0 mmol) malonic acid, 1.8598 g (46.5 mmol) NaOH, and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.7789 g (21.8
mmol) of Me₂SnCl₂ and 20 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 2.4178 g (44.3 %) of polymer. IR (KBr): ν = 3442 (vs; OH), 2922 (w; CH), 1639 (vs; νₐₛ(C=O)), 1591 (vs), 1375 (m), 1334 (m), 1252 (s), 1196 (w), 792 (m), 707 (m), 614 (m), 584 (m), 551 (m), 519 cm⁻¹ (w); TGA (10 °C min⁻¹): N₂ (onset): 216 °C.

**Poly(dimethyltin succinate) (p(DMTSuc))**: To a round bottom flask was added 3.5673 g (22.0 mmol) succinic acid disodium salt and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.7756 g (21.7 mmol) of Me₂SnCl₂ and 20 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly
added to the aqueous phase. The precipitate is filtered and purified as described above to yield 3.8887 g (71.3 %) of polymer.

$^1$H NMR (500 MHz, acetic acid-$d_4$, δ): 2.69 (s, 4H; CH$_2$), 0.97 (s, 6H; CH$_3$); IR (KBr): ν = 3446 (vs; OH), 3009 (w), 2923 (w; CH), 1639 (vs; ν$_{as}$(C=O)), 1563 (vs), 1378 (vs), 1303 (m), 1275 (m), 1214 (s), 1197 (m), 794 (s), 698 (m), 662 (s), 637 (s), 582 (m), 507 cm$^{-1}$ (s); TGA (10 °C min$^{-1}$): N$_2$ (onset): 238 °C; $M_n$($^1$H NMR): 65,111.96 g mol$^{-1}$. 

![Graphs and images related to the experimental results and analysis.](image-url)
Poly(dimethyltin glutarate) (p(DMTGlu)): To a round bottom flask was added 2.9070 g (22.0 mmol) glutaric acid, 1.8874 g (47.2 mmol) NaOH, and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.7763 g (21.7 mmol) of Me₂SnCl₂ and 20 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 4.0570 g (66.9 %) of polymer.

¹H NMR (500 MHz, acetic acid-d₄, δ): 2.46 (t, J = 7.5 Hz, 4H; CH₂), 1.93 (quintet, J = 7 Hz, 2H; CH₂), 0.98 (s, 6H; CH₃); IR (KBr): ν = 3442 (vs; OH), 3002 (w), 2955 (m), 2919 (m; CH), 1673 (s), 1656 (s), 1632 (vs; ν₉(C=O)), 1564 (vs), 1423 (s), 1378 (s), 1351 (s), 1294 (s), 1245 (s), 1220 (m), 1192 (s), 1152 (w), 1070 (w), 792 (s), 646 (s), 582 (s), 527 (s), 503 cm⁻¹ (s); TGA (10 °C min⁻¹): N₂ (onset): 265 °C; Mₙ(¹H NMR): 68,991.38 g mol⁻¹.
Comparison of theoretical and experimental XRD shown within context of dissertation
**Poly(dimethyltin adipate) (p(DMTAdi))**: To a round bottom flask was added 3.2152 g (22.0 mmol) adipic acid, 1.8400 g (46.0 mmol) NaOH, and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.7660 g (21.7 mmol) of $\text{Me}_2\text{SnCl}_2$ and 20 ml of THF. After dissolution of the $\text{Me}_2\text{SnCl}_2$ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 4.6100 g (72.6 %) of polymer.

$^1$H NMR (500 MHz, acetic acid-$d_4$, δ): 2.40 (t, $J = 6.5$ Hz, 4H; CH$_2$), 1.68 (quintet, $J = 3.5$ Hz, 4H; CH$_2$), 0.97 (s, 6H; CH$_3$); IR (KBr): ν = 3446 (vs; OH), 3004 (m), 2959 (m), 2917 (m; CH), 2865 (m), 1780 (m), 1630 (vs; ν$_{as}$(C=O)), 1567 (vs), 1456 (s), 1456 (s), 1420 (s), 1382 (vs), 1312 (m), 1292 (s), 1278 (s), 1223 (w), 1196 (m), 1143 (m), 992 (w), 922 (w), 790 (s), 642 (s), 581 (m), 501 cm$^{-1}$ (s); TGA (10 °C min$^{-1}$): N$_2$ (onset): 251 °C; $M_n$(1H NMR): 70,301.83 g mol$^{-1}$. 

![Graphs and images related to the poly(dimethyltin adipate) (p(DMTAdi)) synthesis process.](image-url)
**Poly(dimethyldimethyltin pimelate) (p(DMTPim))**: To a round bottom flask was added 3.5246 g (22.0 mmol) pimelic acid, 1.8852 g (47.1 mmol) NaOH, and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.7886 g (21.8 mmol) of Me₂SnCl₂ and 20 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 3.9390 g (71.2 %) of polymer.

¹H NMR (500 MHz, acetic acid-\(d_4\), δ): 2.38 (t, \(J = 7.5\) Hz, 4H; CH₂), 1.65 (quintet, \(J = 7.5\) Hz, 4H; CH₂), 1.40 (quintet, \(J = 7.5\) Hz, 2H; CH₂), 0.97 (s, 6H; CH₃); IR (KBr): ν = 3447 (vs; OH), 2921 (m; CH), 2859 (w), 1661 (s), 1634 (vs; νₐs(C=O)), 1567 (vs), 1414 (s), 1378 (s), 1291 (m), 1252 (m), 1228 (m), 1195 (m), 1088 (w),
790 (s), 644 (s), 614 (s), 578 (m), 503 cm\(^{-1}\) (m); TGA (10 °C min\(^{-1}\)): N\(_2\) (onset): 260 °C; \(M_n\) (\(^1\)H NMR): 70,718.79 g mol\(^{-1}\).
**Poly(dimethyltin suberate) (p(DMTSub)):** To a round bottom flask was added 3.8348 g (22.0 mmol) suberic acid, 1.8496 g (46.2 mmol) NaOH, and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.7755 g (21.7 mmol) of Me₂SnCl₂ and 20 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 4.6767 g (67.0 %) of polymer.

¹H NMR (500 MHz, acetic acid- d₄, δ): 2.37 (t, J = 7 Hz, 4H; CH₂), 1.64 (quintet, J = 7 Hz, 4H; CH₂), 1.37 (quintet, J = 3.5 Hz, 4H; CH₂), 0.98 (s, 6H; CH₃); IR (KBr): ν = 3442 (vs; OH), 2922 (m; CH), 2854 (m), 1625 (vs; ν as(C=O)), 1562 (vs), 1423 (s), 1381 (s), 1341 (m), 1316 (w), 1253 (m), 1234 (w), 1194 (m), 783 (s), 635 (s), 578 (m), 524 (m), 502 cm⁻¹ (s); TGA (10 °C min⁻¹): N₂ (onset): 242 ºC; Mₙ(¹H NMR): 75,494.20 g mol⁻¹.
**Poly(dimethyltin azelate) (p(DMTAze))**: To a round bottom flask was added 4.1454 g (22.0 mmol) azelaic acid, 1.8366 g (45.9 mmol) NaOH, and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.7740 g (21.7 mmol) of Me₂SnCl₂ and 20 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 3.8174 g (52.4 %) of polymer.

¹H NMR (500 MHz, acetic acid-d₄, δ): 2.37 (t, J = 7.5 Hz, 4H; CH₂), 1.63 (quintet, J = 7 Hz, 4H; CH₂), 1.36 (m, 6H; CH₂), 0.98 (s, 6H; CH₃); IR (KBr): ν = 3447 (vs; OH), 3005 (w), 2922 (m; CH), 2853 (m), 1654 (vs; ν as(C=O)), 1560 (vs), 1419 (s), 1308 (w), 1262 (m), 1245 (w), 1229 (w), 1194 (m), 1100 (w), 790 (s), 712 (w), 610 (s), 581 (m), 520 (w), 503 (w), 475 cm⁻¹ (s); TGA (10 °C min⁻¹): N₂ (onset): 248 °C; Mₙ(¹H NMR): 79,945.36 g mol⁻¹.
Poly(dimethyltin sebacate) (p(DMTSeb)): To a round bottom flask was added 4.4579 g (22.0 mmol) sebacic acid, 1.8865 g (47.2 mmol) NaOH, and 40 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.7728 g (21.8 mmol) of Me\(_2\)SnCl\(_2\) and 20 ml of THF. After dissolution of the Me\(_2\)SnCl\(_2\) the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 4.9809 g (65.7 %) of polymer.

\(^1\)H NMR (500 MHz, acetic acid-\(d_4\), \(\delta\)): 2.36 (t, \(J = 7.5\) Hz, 4H; CH\(_2\)), 1.63 (quintet, \(J = 7\) Hz, 4H; CH\(_2\)), 1.34 (m, 8H; CH\(_2\)), 0.98 (s, 6H; CH\(_3\)); IR (KBr): \(v = 3439\) (vs; OH), 2922 (s; CH), 2853 (m), 1641 (vs; \(\nu_{as}(C=O)\)), 1563 (vs), 1423 (s), 1383 (s), 1339 (w), 1304 (w), 1250 (m), 1233 (w), 1194 (m), 785 (s), 633 (s), 583 (m), 526 (w), 504 cm\(^{-1}\) (s); TGA (10 °C min\(^{-1}\)): N\(_2\) (onset): 240 °C; \(M_n\)(\(^1\)H NMR): 88,003.51 g mol\(^{-1}\).
Poly(dimethylin dodecanediate) (p(DMTDec)): To a round bottom flask was added 5.0678 g (21.8 mmol) 1,12-dodecanedioic acid, 1.9507 g (48.8 mmol) NaOH, and 60 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.7710 g (21.7 mmol) of Me₂SnCl₂ and 60 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 5.8006 g (61.9 %) of polymer.

¹H NMR (500 MHz, acetic acid-d₄, δ): 2.36 (t, J = 7.5 Hz, 4H; CH₂), 1.63 (quintet, J = 7 Hz, 4H; CH₂), 1.34 (m, 12H; CH₂), 0.98 (s, 6H; CH₃); IR (KBr): ν = 2923 (vs; CH), 2852 (vs), 1700 (m), 1642 (vs; νas(C=O)), 1564 (vs), 1416 (s), 1338 (m), 1284 (m), 1240 (m), 1194 (s), 1109 (w), 1058 (w), 910 (w), 794 (s), 634 (vs), 582 (m), 526 (w), 506 cm⁻¹ (s); TGA (10 °C min⁻¹): N₂ (onset): 225 °C; Mₙ(¹H NMR): 93,909.80 g mol⁻¹.
**Poly(dimethyltin 3,3-dimethylglutarate) (p(DMT 3,3-DMG))**: To a round bottom flask was added 2.4747 g (15.5 mmol) 3,3-dimethylglutaric acid, 1.4224 g (35.6 mmol) NaOH, and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 3.3694 g (15.3 mmol) of Me$_2$SnCl$_2$ and 18 ml of THF. After dissolution of the Me$_2$SnCl$_2$ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 1.8733 g (39.8 %) of polymer.

$^1$H NMR (500 MHz, acetic acid-$d_4$, δ): 2.50 (s, 4H; CH$_2$), 1.16 (s, 6H; CH$_3$), 0.98 (s, 6H; CH$_3$); IR (KBr): ν = 3440 (s; OH), 2960 (vs; CH), 2929 (vs; CH), 1672 (m), 1635 (s; v$_{as}$(C=O)), 1618 (s), 1560 (vs), 1471 (m), 1408 (m), 1365 (s), 1258 (m), 1179 (m), 1111 (w), 793 (s), 637 (m), 573 (w), 525 (w), 500 cm$^{-1}$ (m); TGA (10 °C min$^{-1}$): N$_2$ (onset): 257 °C; $M_n$(1H NMR): 56,838.89 g mol$^{-1}$.

**Poly(dimethyltin poly(ethylene glycol) bis(carboxylate-250) (p(DMT pEGBC-250))**: To a round bottom flask was added 55.2225 g (220.9 mmol) poly(ethylene glycol) bis(carboxymethyl) ether-250, 18.5873 g (464.7 mmol) NaOH, and 340 mL of water and stirred rapidly. To an Erlenmeyer flask was added 48.0355 g (218.7 mmol) of Me$_2$SnCl$_2$ and 325 ml of THF. After dissolution of the Me$_2$SnCl$_2$ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 39.5835 g (45.6 %) of polymer.

IR (KBr): ν = 3502 (s; OH), 3007 (w; CH), 2908 (s; CH), 1660 (s; v$_{as}$(C=O)), 1469 (m), 1421 (m), 1374 (vs), 1354 (vs), 1327 (vs), 1246 (s), 1179 (m), 1125 (vs),
1106 (vs), 1059 (m), 966 (s), 933 (m), 909 (s), 791 (s), 714 (s), 624 (vs), 592 (vs), 523 (w), 473 cm\(^{-1}\) (w); TGA (10 °C min\(^{-1}\)): N\(_2\) (onset): 231 °C.

**Poly(dimethyltin terephthalate) (p(DMTTer))**: To a round bottom flask was added 3.6636 g (22.1 mmol) terephthalic acid, 1.8731 g (46.8 mmol) NaOH, and 40 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.7723 g (21.7 mmol) of Me\(_2\)SnCl\(_2\) and 20 ml of THF. After dissolution of the Me\(_2\)SnCl\(_2\) the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 5.0230 g (73.9 %) of polymer.

IR (KBr): ν = 3442 (m; OH), 2927 (w; CH), 1637 (vs; ν\(_{as}(C=O)\)), 1572 (vs), 1507 (s), 1407 (vs), 1380 (s), 1365 (vs), 1196 (w), 1142 (m), 1104 (w), 1017 (m), 883 (m), 857 (m), 796 (s), 743 (vs), 642 (s), 586 (w), 557 (s), 502 cm\(^{-1}\) (s); TGA (10 °C min\(^{-1}\)): N\(_2\) (onset): 311 °C.
Poly(dimethyltin isophthalate) (p(DMTIso)): To a round bottom flask was added 3.6587 g (22.0 mmol) isophthalic acid, 1.8466 g (46.2 mmol) NaOH, and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.7713 g (21.7 mmol) of Me₂SnCl₂ and 20 mL of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 5.8355 g (85.9 %) of polymer.

IR (KBr): ν = 3440 (m; OH), 3066 (w; Ar CH), 1609 (vs; νas(C=O)), 1560 (vs), 1478 (w), 1372 (vs), 1315 (s), 1275 (w), 1157 (m), 1103 (w), 1077 (w), 947 (w), 858 (m), 802 (m), 736 (vs), 667 (w), 630 (m), 590 (m), 569 (m), 503 (w), 463 (m), 446 cm⁻¹ (s); TGA (10 °C min⁻¹): N₂ (onset): 331 °C.
**Poly(dimethylin 2,5-pyridinedicarboxylate) (p(DMT 2,5-DPA))**: To a round bottom flask was added 3.6758 g (22.0 mmol) 2,5-pyridinedicarboxylic acid, 1.8562 g (46.4 mmol) NaOH, and 30 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.7802 g (21.8 mmol) of Me₂SnCl₂ and 20 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 5.1131 g (74.9 %) of polymer.

IR (KBr): ν = 3421 (s; OH), 2921 (w; CH), 1691 (s), 1614 (vs; ν₁as(C=O)), 1483 (m), 1395 (vs), 1332 (vs), 1275 (w), 1265 (s), 1166 (m), 1146 (m), 1040 (s), 845
Poly(dimethyltin 2,6-pyridinedicarboxylate) (p(DMT 2,6-DPA)): To a round bottom flask was added 3.7877 g (22.7 mmol) 2,6-pyridinedicarboxylic acid, 1.9675 g (49.2 mmol) NaOH, and 30 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.9212 g (22.4 mmol) of Me₂SnCl₂ and 20 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 6.3576 g (90.4 %) of polymer.
IR (KBr): ν = 3435 (m; OH), 3062 (m; Ar CH), 3017 (m; Ar CH), 2925 (w; CH), 1672 (vs), 1614 (vs; v_{as}(C=O)), 1587 (vs), 1570 (vs), 1475 (w), 1430 (s), 1396 (s), 1344 (s), 1275 (s), 1179 (s), 1071 (s), 1029 (s), 811 (s), 768 (s), 740 (vs), 690 (m), 673 (m), 567 (m), 429 cm\(^{-1}\) (m); TGA (10 °C min\(^{-1}\)): N\(_2\) (onset): 303 °C.

**Poly(dimethyltin 2,5-thiophenedicarboxylate) (p(DMT 2,5-TDC)):** To a round bottom flask was added 3.7921 g (22.0 mmol) 2,5-thiophenedicarboxylic acid, 1.8492 g (46.2 mmol) NaOH, and 40 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.8361 g (22.0 mmol) of Me\(_2\)SnCl\(_2\) and 20 ml of THF. After dissolution of the Me\(_2\)SnCl\(_2\) the organic phase is rapidly added to the
aqueous phase. The precipitate is filtered and purified as described above to yield 4.6797 g (66.7 %) of polymer.

IR (KBr): v = 3434 (m; OH), 3090 (w; Ar CH), 3005 (w; Ar CH), 2920 (m; CH), 1618 (s; v\textsubscript{as}(C=O)), 1569 (vs), 1529 (vs), 1471 (m), 1395 (vs), 1348 (vs), 1301 (vs), 1200 (w), 1109 (w), 1026 (w), 845 (w), 792 (s), 771 (s), 679 (w), 648 (s), 580 (m), 495 (s), 472 cm\textsuperscript{-1} (s); TGA (10 °C min\textsuperscript{-1}): N\textsubscript{2} (onset): 324 °C.

**Poly(dimethyltin L-tartrate) (p(DMT L-Tar))**: To a round bottom flask was added 3.3085 g (22.0 mmol) L-tartaric acid, 4.4830 g (44.3 mmol) triethylamine, and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.8221 g (21.9 mmol) of Me\textsubscript{2}SnCl\textsubscript{2} and 20 ml of THF. After dissolution of the
Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 2.7202 g (41.7%) of polymer.

IR (KBr): ν = 3423 (s; OH), 3008 (w; CH), 2923 (m; CH), 2827 (w), 1651 (s), 1616 (s; νas(C=O)), 1577 (s), 1505 (m), 1365 (s), 1341 (s), 1301 (vs), 1291 (m), 1250 (w), 1203 (m), 1107 (s), 1084 (m), 1066 (s), 947 (s), 813 (s), 745 (m), 661 (m), 576 (m), 557 (s), 523 (m), 452 (w), 418 cm⁻¹ (w); TGA (10 °C min⁻¹): N₂ (onset): 243 °C.

**Poly(dimethyltin D-tartrate) (p(DMT D-Tar))**: To a round bottom flask was added 3.3178 g (22.1 mmol) D-tartaric acid, 4.4789 g (44.3 mmol) triethylamine,
and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.8088 g (21.9 mmol) of Me₂SnCl₂ and 20 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 2.3893 g (36.8 %) of polymer.

IR (KBr): ν = 3420 (s; OH), 3008 (w; CH), 2923 (m; CH), 2827 (w), 1650 (s), 1616 (s; νas(C=O)), 1576 (s), 1506 (m), 1365 (s), 1341 (s), 1291 (s), 1250 (m), 1203 (m), 1107 (s), 1084 (m), 1066 (s), 947 (s), 812 (s), 746 (s), 661 (m), 576 (m), 557 (s), 454 (w), 420 cm⁻¹ (w); TGA (10 °C min⁻¹): N₂ (onset): 231 °C.
**Poly(dimethyltin DL-tartrate) (p(DMT DL-Tar))**: To a round bottom flask was added 3.3091 g (22.0 mmol) DL-tartaric acid, 4.4841 g (44.3 mmol) triethylamine, and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.8358 g (22.0 mmol) of Me₂SnCl₂ and 20 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 3.6828 g (56.4 %) of polymer.

IR (KBr): ν = 3442 (s; OH), 3008 (w; CH), 2923 (m; CH), 2831 (m), 1655 (vs), 1615 (s; νas(C=O)), 1575 (s), 1506 (s), 1365 (s), 1345 (s), 1291 (s), 1203 (w), 1109 (s), 1061 (s), 946 (s), 813 (s), 760 (s), 665 (m), 575 (m), 559 (s), 454 (w), 419 cm⁻¹ (w); TGA (10 °C min⁻¹): N₂ (onset): 251 °C.
**Poly(dimethyltin 50/50 L-tartrate/glutarate) (p(DMT 50/50 L-Tar/Glu))**: To a round bottom flask was added 1.6516 g (11.0 mmol) L-tartaric acid, 1.4539 g (11.0 mmol) glutaric acid, 4.4800 g (44.3 mmol) triethylamine, and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.8348 g (22.0 mmol) of Me₂SnCl₂ and 20 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 4.7563 g (75.1 %) of polymer.

IR (KBr): \( \nu = 3440 \text{ (s; OH)}, 3011 \text{ (w; CH)}, 2977 \text{ (w; CH)}, 2926 \text{ (m; CH)}, 2853 \text{ (w)}, 1696 \text{ (s)}, 1643 \text{ (s; \nu_{as}(C=O))}, 1584 \text{ (s)}, 1533 \text{ (s)}, 1459 \text{ (s)}, 1387 \text{ (s)}, 1328 \text{ (s)}, 1286 \text{ (m)}, 1257 \text{ (m)}, 1204 \text{ (s)}, 1109 \text{ (s)}, 1067 \text{ (s)}, 945 \text{ (s)}, 818 \text{ (s)}, 741 \text{ (s)}, 694 \text{ (w)}, 649 \text{ (m)}, 574 \text{ (m)}, 559 \text{ (s)}, 525 \text{ (m)}, 420 \text{ cm}^{-1} \text{ (w)}; \) TGA (10 °C min⁻¹): N₂ (onset): 230 °C.
**Poly(dimethyltin 50/50 D-tartrate/glutarate)** (**p(DMT 50/50 D-Tar/Glu)**): To a round bottom flask was added 1.6788 g (11.2 mmol) D-tartaric acid, 1.4594 g (11.0 mmol) glutaric acid, 4.5283 g (44.8 mmol) triethylamine, and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.8056 g (219 mmol) of Me₂SnCl₂ and 20 ml of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 1.9180 g (30.5 %) of polymer.

IR (**KBr**): $\nu = 3434$ (s; OH), 2927 (m; CH), 2855 (w), 1697 (s), 1652 (vs; $\nu_{as}$(C=O)), 1533 (vs), 1418 (m), 1386 (m), 1340 (w), 1318 (m), 1296 (w), 1256 (w), 1200 (s), 1109 (s), 1067 (s), 961 (w), 945 (s), 819 (s), 746 (m), 694 (w), 651
(m), 574 (m), 560 (s), 525 (m), 423 cm\(^{-1}\) (w); TGA (10 °C min\(^{-1}\)): \(N_2\) (onset): 231 °C.

**Poly(dimethyltin 50/50 DL-tartrate/glutarate) (p(DMT 50/50 DL-Tar/Glu))**: To a round bottom flask was added 1.6533 g (11.0 mmol) DL-tartaric acid, 1.4546 g (11.0 mmol) glutaric acid, 4.4742 g (44.2 mmol) triethylamine, and 20 mL of water and stirred rapidly. To an Erlenmeyer flask was added 4.8383 g (22.0 mmol) of \(\text{Me}_2\text{SnCl}_2\) and 20 ml of THF. After dissolution of the \(\text{Me}_2\text{SnCl}_2\) the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 5.1282 g (80.9 %) of polymer.
IR (KBr): ν = 3432 (s; OH), 3011 (w), 2967 (w), 2924 (m; CH), 2847 (w), 1647 (vs; ν₁(C=O)), 1587 (vs), 1457 (s), 1330 (s), 1287 (m), 1273 (m), 1258 (m), 1204 (s), 1123 (s), 1067 (s), 945 (s), 798 (s), 735 (s), 645 (m), 573 (m), 554 (s), 524 (m), 423 cm⁻¹ (w); TGA (10 °C min⁻¹): N₂ (onset): 258 °C.

5.4.2. Synthesis of Poly(organotin ethers)

*Poly(dimethyltin 1,3-propanedioxide) (p(DMT 1,3-PD)): To a round bottom flask was added 1.0866 g (14.3 mmol) 1,3-propanediol, 0.4730 g (11.8 mmol) NaOH, and 5.027 mL of water and stirred rapidly. To an Erlenmeyer flask was added 2.8501 g (13.0 mmol) of Me₂SnCl₂ and 4.435 mL of THF. After dissolution of the Me₂SnCl₂ the organic phase is rapidly added to the aqueous phase. The*
precipitate is filtered and purified as described above to yield 1.7043 g (58.9 %) of polymer.

IR (KBr): $\nu = 3434$ (m; OH), 3007 (w), 2918 (m; CH), 1193 (m), 782 (s), 704 (m), 570 (s), 551 (vs), 519 (m), 464 cm$^{-1}$ (s); TGA (10 °C min$^{-1}$): N$_2$ (onset): 225 °C.

5.4.3. Synthesis of Poly(organotin amines)

Poly(dimethyltin ethylenediamine) (p(DMT EDA)): To a round bottom flask was added 0.5170 g (8.6 mmol) ethylenediamine, 1.8820 g (18.6 mmol) triethylamine, 6.321 mL of acetonitrile and 1.873 mL of water and stirred rapidly. To an Erlenmeyer flask was added 1.9144 g (8.7 mmol) of Me$_2$SnCl$_2$ and 4.435 ml of THF. After dissolution of the Me$_2$SnCl$_2$ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 0.6560 g (36.9 %) of polymer.

IR (KBr): $\nu = 3437$ (m; NH), 2963 (s), 2920 (s; CH), 1197 (m), 1179 (m), 758 (s), 579 (s), 549 (s), 518 (w), 437 cm$^{-1}$ (vs); TGA (10 °C min$^{-1}$): N$_2$ (onset): 170 °C.

Poly(dimethyltin 1,2-diaminopropane) (p(DMT 1,2-DAP)): To a round bottom flask was added 0.5528 g (7.5 mmol) 1,2-diaminopropane, 1.5362 g (15.2 mmol) triethylamine, 6.605 mL of acetonitrile and 1.839 mL of water and stirred rapidly. To an Erlenmeyer flask was added 1.6095 g (7.3 mmol) of Me$_2$SnCl$_2$ and 4.435 ml of THF. After dissolution of the Me$_2$SnCl$_2$ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 0.4072 g (25.2 %) of polymer.
IR (KBr): \( \nu = 3205 \text{ (m; NH)}, 3119 \text{ (w)}, 2989 \text{ (m)}, 2920 \text{ (m; CH)}, 1197 \text{ (m)}, 1179 \text{ (m)}, 1082 \text{ (m)}, 758 \text{ (s)}, 575 \text{ (s)}, 550 \text{ (s)}, 518 \text{ (m)}, 443 \text{ cm}^{-1} \text{ (vs)}; \) TGA (10 °C min \(^{-1}\)): \( \text{N}_2 \text{ (onset): 176 °C.} \)

**Poly(dimethyltin 1,3-diaminopropane) (p(DMT 1,3-DAP))**: To a round bottom flask was added 0.5147 g (6.9 mmol) 1,3-diaminopropane, 1.4332 g (14.2 mmol) triethylamine and 6.184 mL of acetonitrile and stirred rapidly. To an Erlenmeyer flask was added 1.5035 g (6.8 mmol) of \( \text{Me}_2\text{SnCl}_2 \) and 7.096 ml of THF. After dissolution of the \( \text{Me}_2\text{SnCl}_2 \) the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 1.0768 g (71.2 %) of polymer.

IR (KBr): \( \nu = 3428 \text{ (m; NH)}, 3060 \text{ (s)}, 2983 \text{ (s; CH)}, 2036 \text{ (m)}, 1595 \text{ (m)}, 1480 \text{ (s)}, 1407 \text{ (w)}, 1337 \text{ (w)}, 1219 \text{ (m)}, 1190 \text{ (s)}, 1102 \text{ (s)}, 1038 \text{ (m)}, 960 \text{ (s)}, 936 \text{ (s)}, 762 \text{ (s)}, 578 \text{ (s)}, 550 \text{ (s)}, 517 \text{ (w)}, 438 \text{ cm}^{-1} \text{ (vs)}; \) TGA (10 °C min \(^{-1}\)): \( \text{N}_2 \text{ (onset): 151 °C.} \)

**Poly(dimethyltin 1,4-diaminobutane) (p(DMT 1,4-DAB))**: To a round bottom flask was added 0.4938 g (5.6 mmol) 1,4-diaminobutane, 1.1348 g (11.2 mmol) triethylamine, 6.259 mL of acetonitrile and 1.811 mL of water and stirred rapidly. To an Erlenmeyer flask was added 1.2481 g (5.7 mmol) of \( \text{Me}_2\text{SnCl}_2 \) and 4.435 ml of THF. After dissolution of the \( \text{Me}_2\text{SnCl}_2 \) the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 1.0105 g (76.8 %) of polymer.
IR (KBr): $\nu = 2982$ (s; CH), 2029 (m), 1614 (m), 1596 (m), 1472 (s), 1448 (s), 1403 (w), 1345 (w), 1285 (s), 1196 (m), 1179 (m), 1112 (s), 1025 (m), 922 (s), 874 (m), 765 (s), 579 (s), 549 (s), 499 (w), 438 cm$^{-1}$ (vs); TGA ($10^\circ$C min$^{-1}$): N$_2$ (onset): 158 $^\circ$C.

**Poly(dimethyltin 1,6-diaminohexane) (p(DMT 1,6-DAH))**: To a round bottom flask was added 0.4823 g (4.2 mmol) 1,6-diaminohexane, 0.8583 g (8.5 mmol) triethylamine, 6.535 mL of acetonitrile and 2.014 mL of water and stirred rapidly. To an Erlenmeyer flask was added 0.9233 g (4.2 mmol) of Me$_2$SnCl$_2$ and 4.435 ml of THF. After dissolution of the Me$_2$SnCl$_2$ the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 0.6121 g (56.1 %) of polymer.

IR (KBr): $\nu = 3438$ (m; NH), 2983 (s; CH), 2924 (s), 2031 (w), 1610 (w), 1564 (m), 1508 (m), 1482 (m), 1400 (w), 1246 (w), 1197 (s), 1179 (m), 1137 (s), 1037 (w), 947 (m), 934 (m), 758 (s), 579 (s), 550 (s), 518 (w), 440 cm$^{-1}$ (vs); TGA ($10^\circ$C min$^{-1}$): N$_2$ (onset): 152 $^\circ$C.

5.4.4. Synthesis of Poly(organotin etheramines)

**Poly(dimethyltin Jeffamine EDR-104) (p(DMT EDR-104))**: To a round bottom flask was added 0.5620 g (5.4 mmol) EDR-104, 0.8283 g (8.2 mmol) triethylamine, 6.259 mL of acetonitrile and 1.886 mL of water and stirred rapidly. To an Erlenmeyer flask was added 1.1810 g (5.4 mmol) of Me$_2$SnCl$_2$ and 4.435 ml of THF. After dissolution of the Me$_2$SnCl$_2$ the organic phase is rapidly added
to the aqueous phase. The precipitate is filtered and purified as described above to yield 0.7922 g (58.5 %) of polymer.

IR (KBr): \( \nu = 3439 \text{ (m; NH)}, 2989 \text{ (m; CH)}, 2921 \text{ (m)}, 1653 \text{ (w)}, 1197 \text{ (m)}, 1179 \text{ (m)}, 758 \text{ (s)}, 575 \text{ (s)}, 549 \text{ (s)}, 518 \text{ (w)}, 493 \text{ cm}^{-1} \text{ (vs)}; \) TGA (10 °C min\(^{-1}\)): \( N_2 \text{ (onset): 226 °C.} \)

**Poly(dimethyltin Jeffamine D230) (p(DMT D230))**: To a round bottom flask was added 0.4874 g (2.1 mmol) D230, 0.4335 g (4.3 mmol) triethylamine, 6.223 mL of acetonitrile and 1.825 mL of water and stirred rapidly. To an Erlenmeyer flask was added 0.4454 g (2.0 mmol) of \( \text{Me}_2\text{SnCl}_2 \) and 4.435 ml of THF. After dissolution of the \( \text{Me}_2\text{SnCl}_2 \) the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 0.0608 g (8.0 %) of polymer.

IR (KBr): \( \nu = 3439 \text{ (s; NH)}, 2922 \text{ (m; CH)}, 1653 \text{ (w)}, 1197 \text{ (w)}, 1179 \text{ (w)}, 758 \text{ (s)}, 570 \text{ (s)}, 550 \text{ (s)}, 518 \text{ (w)}, 435 \text{ cm}^{-1} \text{ (vs)}; \) TGA (10 °C min\(^{-1}\)): \( N_2 \text{ (onset): 190 °C.} \)

**Poly(dimethyltin Jeffamine HK511) (p(DMT HK511))**: To a round bottom flask was added 0.4631 g (2.1 mmol) HK511, 0.4043 g (4.0 mmol) triethylamine, 3.098 mL of acetonitrile and 0.976 mL of water and stirred rapidly. To an Erlenmeyer flask was added 0.4366 g (2.0 mmol) of \( \text{Me}_2\text{SnCl}_2 \) and 2.252 ml of THF. After dissolution of the \( \text{Me}_2\text{SnCl}_2 \) the organic phase is rapidly added to the aqueous phase. The precipitate is filtered and purified as described above to yield 0.2489 g (34.1 %) of polymer.
IR (KBr): ν = 3440 (s; NH), 2989 (w), 2921 (m; CH), 1653 (w), 1197 (w), 1179 (w), 1106 (w), 757 (s), 582 (s), 549 (s), 518 (w), 436 cm$^{-1}$ (vs); TGA (10 °C min$^{-1}$): N$_2$ (onset): 160 °C.
5.5. References


Chapter 6. Alkaline Earth, Transition and Aluminum Metal Polymers

6.1. Introduction

One of the major roles of metals is as catalysts/initiators for the polymerization of various monomers. Ziegler and Natta independently discovered that using group I-III metal mediated polymerization could lead to certain stereochemistry, and these type of initiators have become a standard for the polymerization of alkenes in which tacticity is vital.\textsuperscript{1} Based from their work, numerous new types of metal initiators were developed. The polypropylene derivatives synthesized by Chung et. al. and described in Chapter 1 were made using either a Ziegler-Natta or metallocene catalyst.\textsuperscript{2-4} Metal-mediated polymerizations of numerous polar and nonpolar monomers have been reported and include functional groups such as acrylates and isocyanides.\textsuperscript{5,6} The ring opening polymerization of N-carboxy-\(\alpha\)-amino acid anhydrides has been reported to be successful using various transition metal catalysts, while asanedi et. al. have used a metal containing initiator to photo-generate radicals for the polymerization of vinylidene fluoride.\textsuperscript{7-9}

The incorporation of transition metals into polymers is well documented, with these polymers being formed through a coordination complex formed between metal and ligands such as imidazole dicarboxylates, tetrazole-1-acetate, bis(triazolyl)methane, modified amberlite or modified cyclopentadienyl rings,
etc.\textsuperscript{10-15} Papadimitrakopoulos \textit{et. al.} have created light emitting diodes with use of either terbium polyurea or zinc bisquinoline coordination polymers.\textsuperscript{16,17} Podeshvo \textit{et. al.} synthesized coordination polymers using copper, palladium and nickel to create a redox active material that could be further used for catalytic or electrocatalytic applications.\textsuperscript{18} Lambeth \textit{et. al.} have used a coordination polymer with copper and meBIP ligand to improve the mechanical strength of acrylate materials.\textsuperscript{19,20} Dong \textit{et. al.} created a mixed metal coordination polymer by first synthesizing a copper containing ligand as a precursor then forming a second coordination complex with silver.

One setback of using coordination polymers for dielectric applications is the bulky ligands that are needed increase the total free volume of the polymer thereby reducing the total polarizability. From Table 6.1, it is shown that there is a benefit in dielectric constant by fully coordinating the metal atom to the maximum number of electronegative oxygen atoms. Therefore, polymers that have both covalent and coordination bonds, like those described for the tin polymers (Chapter 5), are more ideal rather than some other metal containing polymers that have metal-carbon linkages in the polymer backbone.\textsuperscript{15} There are numerous references for forming small molecule metal carboxylates through a variety of synthetic procedures using metals such as aluminum, copper, titanium, zinc, lead and cadmium.\textsuperscript{22-27} However, there are few papers dealing with the formation of metal-carboxylate polymers. Wood \textit{et. al.} synthesized a polymer with 1,2,3,4,5,6-benzene hexacarboxylate hexanion with a paramagnetic transition metal to create magnetic nests that were separated from each other by
the aromatic rings and alkali metal ions that were also incorporated.\textsuperscript{28} However, this type of polymer would be heavily crosslinked making processing more challenging. Carraher \textit{et. al.} has reported the polymerization of linear hafnium, titanium and zirconium polymers through an interfacial technique, though these polymers contain cyclopentadienyl groups.\textsuperscript{29,30}

**Table 6.1.** Band gaps and dielectric constants of some common metal oxides.

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>Band Gap [eV]</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO\textsubscript{2}</td>
<td>3.57</td>
<td>9.86</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>3.2-3.35</td>
<td>86-173</td>
</tr>
<tr>
<td>CdO</td>
<td>2.16</td>
<td>-</td>
</tr>
<tr>
<td>V\textsubscript{2}O\textsubscript{5}</td>
<td>2.3-2.4</td>
<td>-</td>
</tr>
<tr>
<td>HfO\textsubscript{2}</td>
<td>6</td>
<td>25</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>9</td>
<td>3.9</td>
</tr>
<tr>
<td>ZrO</td>
<td>5-7</td>
<td>10-25</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.3-3.4</td>
<td>8.5</td>
</tr>
<tr>
<td>BeO</td>
<td>10.63</td>
<td>6.7</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>7-9.5</td>
<td>9.34-11.54</td>
</tr>
</tbody>
</table>

6.2. Results and Discussion

6.2.1. Synthesis and Characterization of Alkaline Earth, Transition and Aluminum Metal Polymers

The synthesis of the alkaline earth and transition metal ester polymers follows a similar reaction procedure to the tin ester polymers, \textbf{Figure 6.1}. The changes made to the procedure were as follows. Due to the metal monomers being the chloride salts, they had to be dissolved in the aqueous phase with the exception of the diethoxydichlorotitanium which exhibits better solubility in acetonitrile versus tetrahydrofuran. As a result of the aqueous phase containing
the metal monomer, the organic phase contained the diacid monomer and thus 1,2-dichloroethane was chosen because of better solubilization of the deprotonated diacid species. Triethylamine was substituted for sodium hydroxide as the base also as a consequence of solubility. Again, the only exception to this reaction scheme, was that the diacid was also solubilized and deprotonated in acetonitrile for the titanium ester formation. The synthesis of the metal esters was also attempted in a fully aqueous system with sodium hydroxide as the base, but the formation of metal hydroxides became much more apparent rather than polymerization.

Figure 6.1. Synthetic scheme for the formation of both transition and alkaline earth metals through the utilization of the interfacial technique.
Of the organometallic polymers described in this dissertation, the aluminum ester polymers are synthesized in a different manner, **Figure 6.2.** The deprotonation of the diacid is not required to form the aluminum carboxylate group as a result of the labile aluminum-carbon bonds, which has been reported for the syntheses of small aluminum carboxylate molecules.\(^\text{23}\) The evidence of this is seen with the evolution of ethane gas during polymerization. The solubility of the aluminum polymers is improved when a longer ether segment is present in the diacid monomer. In fact, using pEGBC-600 as the diacid monomer, the resulting aluminum polymer is soluble in water. However, the reaction solvent had to be changed from N,N-dimethylacetamide to lower boiling 1,2-dichloroethane or dimethoxyethane when polymerizing with pEGBC-600 due to thermal instability of p(ClAl pEGBC-600). A \(^1\)H NMR spectrum of p(ClAl pEGBC-600) synthesized in DMAc showed a large portion of DMAc remaining in the material and attempts to expel the residual solvent by heating at temperatures above 50 °C *in vacuo* caused the polymer to brown. The colored impurity could be removed by dissolving the polymer in water and precipitating with methanol, though the recovery yield is low.

**Figure 6.2.** Synthetic scheme for the formation of aluminum ester polymers.
6.2.2. Characterization of Alkaline Earth, Transition and Aluminum Metal Polymers

Like the tin polymers described in Chapter 5, the metal polymers form coordination complexes with the carbonyl oxygen atoms of the carboxylate groups. The formation of the metal-oxygen bond is seen with the lower energy asymmetric and symmetric stretching absorptions of the carbonyl groups compared with the carbonyl groups of carboxylic acids, Figure 6.3. The metal-oxygen bond is also present at much lower energies, approximately 450-550 cm\(^{-1}\), but is harder to distinguish as the peak intensities vary depending upon the metal. The difference between the asymmetric and symmetric stretching absorptions allow for the type of ligand binding mode to be determined, Table 6.2. The carbonyl oxygen and form three different types of ligand species, Figure 6.3(H); 1) monodentate type in which the carbonyl oxygen does not coordinate and there is only one metal-oxygen bond, 2) bidentate type in which both oxygen atoms bind to the metal center, the same binding seen in the tin polymers in which one metal-oxygen bond is a shorter, stronger covalent bond and the second a longer, weaker coordination bond and 3) a chelation type binding where both oxygen atoms of the carboxylate groups are bound to one metal atom. Based on the IR spectra of the metal polymers, each take a bidentate type ligand structure, since the difference between asymmetric and symmetric stretching absorptions are lower than what is exhibited for an ionic compound. Again the coordination of metal and carbonyl groups can occur.
between polymer chains with the exception being the copper based polymer which only exhibits two distinct peaks indicating that the coordination may only be of the intra-chain type. The reasoning behind this could be due to copper being a hydrated form, as seen by the bright blue color of the polymer, in which the water acts as a shield against coordination of two chains. Each polymer exhibits a broad peak in the IR spectra above 3000 cm$^{-1}$ indicating the presence of water. Of the metallic polymers, aluminum and titanium based systems show the greatest amount of water based on the intensity and broadness of the $–$OH absorption.

Figure 6.3. IR spectra of poly(cadmium sebacate) (A), poly(zinc sebacate) (B), poly(50/50 zinc/cadmium sebacate) (C), poly(copper sebacate) (D), poly(calcium sebacate) (E), poly(diethoxytitanium pEBGC-250) (F), poly(chloroaluminum sebacate) (G), and ligand binding type.
Table 6.2. Determination of ligating mode using the difference in asymmetric and symmetric stretching absorptions of carboxylate groups attached to metal center.

<table>
<thead>
<tr>
<th>Metal</th>
<th>( \nu_{\text{as}} ) (COO) [cm(^{-1})]</th>
<th>( \nu_{\text{s}} ) (COO) [cm(^{-1})]</th>
<th>( \Delta \nu = \nu_{\text{as}} - \nu_{\text{s}} ) [cm(^{-1})]</th>
<th>Binding Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(^{\text{a}})</td>
<td>1541</td>
<td>1427</td>
<td>114</td>
<td>Bidentate</td>
</tr>
<tr>
<td>Zn(^{\text{a}})</td>
<td>1535</td>
<td>1399</td>
<td>136</td>
<td>Bidentate</td>
</tr>
<tr>
<td>Zn/Cd(^{\text{a}})</td>
<td>1535</td>
<td>1399</td>
<td>136</td>
<td>Bidentate</td>
</tr>
<tr>
<td>Cu(^{\text{a}})</td>
<td>1590</td>
<td>1430</td>
<td>160</td>
<td>Bidentate</td>
</tr>
<tr>
<td>Ca(^{\text{a}})</td>
<td>1578</td>
<td>1435</td>
<td>143</td>
<td>Bidentate</td>
</tr>
<tr>
<td>Ti(^{\text{b}})</td>
<td>1575</td>
<td>1417</td>
<td>158</td>
<td>Bidentate</td>
</tr>
<tr>
<td>Al(^{\text{a}})</td>
<td>1605</td>
<td>1473</td>
<td>132</td>
<td>Bidentate</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\) Synthesized with sebacic acid; \(^{\text{b}}\) synthesized with pEGBC-250

Thermogravimetric analysis (TGA), Figure 6.4(A-G), confirms the presence of water in the organometallic polymers. From the thermograms, it is seen that two distinct weight losses occur for the polymers, each attributed to the removal of water from the system. It has been reported that water will form a layered shell around a metal nanoparticle within a polymer matrix. The first layer is water that is bound to the metal center and a second layer of loosely bound water held closer to the nanoparticle through van der Waals interactions.\(^{31}\) The third layer is formed by free water in the nanoparticle/polymer matrix.\(^{31}\) This trend seems to hold true for the organometallic polymers in which the free water is removed upon heating the polymer to 115 °C and holding for 60 minutes, while the loosely bound and bound water is removed at 220 °C. Each organometallic polymer has differing amounts of water with the aluminum and titanium systems exhibiting the highest quantity which corroborates what was seen in the IR spectra. The organometallic polymers all exhibit thermal degradation at temperatures > 250 °C, while poly(chloroaluminum pEGBC-600) is the only polymer to exhibit a glass transition temperature, -25 °C.
Figure 6.4. Thermogravimetric analysis (TGA) of poly(cadmium sebacate) (A), poly(zinc sebacate) (B), poly(50/50 zinc/cadmium sebacate) (C), poly(copper sebacate) (D), poly(calcium sebacate) (E), poly(diethoxytitanium pEBGC-250) (F) and poly(chloroaluminum sebacate). Differential scanning calorimetry (DSC) thermogram of poly(chloroaluminum pEGBC-600).
6.2.3. Dielectric Properties of Aluminum Polymers

The solubility of the aluminum polyesters that incorporate the ether dicarboxylates allow for them to be solution casted. A film of p(ClAl pEGBC-250) cast from a 50/50 (v/v) water/acetonitrile solution cracks upon drying and thus a multi-layer film is made in order to do dielectric measurements. On the other hand p(ClAl pEGBC-600) was solution cast from water onto a Teflon sheet to form a flexible free standing film that became more brittle as it was dried. The dielectric properties of the two polymers are shown in Figure 6.5. Though these polymers exhibit high dielectric constants, > 6, they also display both high a dissipation factor, > 10 % for most polymer films tested, as well as conductivities on the order of $10^6 \text{ pSm}^{-1}$. The high dielectric constant, high dielectric dissipation and conductivity is all attributed to the sheer amount of water in the sample, 4.9:1 and 3.4:1 (mol:mol) of water:aluminum for p(ClAl pEGBC-250) and p(ClAl pEGBC-600), respectively, though the 4.9:1 result is expected to be slightly higher due to the remaining DMAc in the sample which is observed in the $^1\text{H}$ NMR. The coordination of water to aluminum forms an octahedral complex, but versus the other metallic polymers the aluminum octahedral complex contains a negative charge on the aluminum due to the fact that aluminum has only three valence electrons, but in this case four bonds are formed with the aluminum. Therefore, the electrostatic charge created is adding to the total ionic polarizability of the polymer but also allowing for the increase in charge movement between chains due to the amount of free water in the polymer, approximately 9.7 and 3.0 % for p(ClAl pEGBC-250) and p(ClAl pEGBC-600),
respectively. Attempts were made to improve the dielectric properties through extensive drying. In the case of p(ClAl pEGBC-250), upon drying the sample at 115 °C for 3 days there was some improvement in the dissipation, though still much greater than 10 %. The dielectric constant and conductivity of the sample was decreased as a result of water and residual solvent being driven off which was expected. Comparing the dielectric results of p(ClAl pEGBC-250) to p(ClAl pEGBC-600), p(ClAl pEGBC-600) was expected to have a higher dielectric constant due to the increase in the number of ether linkages in EGBC-600 versus EGBC-250. Again the dissipation and conductivity of p(ClAl pEGBC-600) were quite large. Unfortunately, attempts to dry the sample while it was still in the sample proved to be futile because of the low \( T_g \), -25 °C, of the polymer. The sample is under pressure in the holder and upon heating the polymer flows away from under the electrode leaving only a very thin layer between the bottom and top electrode resulting in an increase in conductivity to the point where measurement in the time-domain was impossible. On account of these results the influence of free and bound water on the dielectric properties cannot be determined at this point, though the removal of free seems to improve dissipation and conductivity.
6.2.4. Dielectric Properties of Alkaline Earth and Transition Metal Polymers

Pellets of the titanium, cadmium and copper containing polymers were pressed and dielectric properties evaluated in the frequency domain, Figure 6.6. The trend in dielectric constant follows the expected trend, in which the lower the electronegativity value of the metal the higher the dielectric constant, Ti > Cd > Cu, due to the increased difference in electronegativity versus oxygen, Ti < Cd < Cu according to the Pauling scale. The much larger dielectric constant value of titanium may stem from the type of complex forming in which all three materials are in an octahedral geometry with the difference being the fact that titanium is covalently bound to four oxygen atoms and coordinated with two more whereas cadmium and copper only have two covalent bond with oxygen and the other bonds are coordination type. Therefore, titanium should have a larger
orientational polarization versus the others. Also, the diacid used in the synthesis of the titanium polymer is different than the cadmium and copper diacid. The titanium polymer has ether linkages in the backbone which increase the dipole density within the polymer. The increase in the dissipation of the titanium polymer may be attributed to the heightened facility of titanium to bind water which may increase the conductivity due to the water shell allowing the transfer of charge carriers.

![Graph](image)

**Figure 6.6.** Frequency domain measurements of poly(diethoxytitanium pEBGC-250) (black), poly(cadmium sebacate) (red) and poly(copper sebacate) (blue).

As a consequence of the increased dielectric dissipation in the titanium polymer, only the copper and cadmium polymers were tested in the time-domain, **Figure 6.7.** Poly(copper sebacate) shows a very consistent dielectric constant, with only a slight increase as the temperature is increased from room temperature to 150 °C, averaging 3.3 and 3.5, respectively. As for poly(cadmium
sebacate) the increase in dielectric constant is from 3.5 to 4.2 at room temperature and 125 °C, respectively. Again, the difference in the dielectric constant between the two polymers is attributed to the increased dipole moment of the cadmium-oxygen bond versus the copper-oxygen bond and the increased ionic nature of the water-cadmium and carboxylate-cadmium coordination bonds both being a result of the lower electronegativity of cadmium compared to copper. However, the trend in dielectric properties versus temperature is different for each polymer. The dielectric constant first increased for poly(copper sebacate) as the temperature was incrementally increased to 50 °C, followed by a decrease at both 75 and 100 °C, then increased as the temperature was raised to 150 °C. However, the dielectric constant increased as the temperature was raised for poly(cadmium sebacate). The difference in trends could be attributed to how strong the water is coordinated to the metal center as explained previously. Both polymers contain about the same mole ratio of water versus metal, 0.7:1 and 0.5:1 for the cadmium and copper polymer, respectively. The copper polymer is expected to lose water more easily and the increase in dielectric constant at 50 °C is from the increase of the copper-carboxylate dipole in addition to the water dipole. The decrease in dielectric constant is then from the loss of water in the polymer. At higher temperatures the dielectric constant increases as a result of the higher mobility of the copper-carboxylate dipole. Therefore, the free water in the polymer may not be as significant as the second layer of water and how tightly it is held by van der Waals forces to the metal since the cadmium only shows enhancement of the dielectric constant as
temperature increases. The trend in dissipation for both polymers follows that of their respective dielectric constants. The dissipation factor for poly(copper sebacate) remains on the order of $10^{-2}$ for all temperatures while the dissipation factor of poly(cadmium sebacate) increases to $10^{-1}$ orders of magnitude at 125 °C.

**Figure 6.7.** Temperature dependence of the dielectric constant (A and B) and dielectric loss (C and D) of poly(cadmium sebacate) and poly(copper sebacate).

From the time-domain spectra of poly(cadmium sebacate) at different measurement temperatures, the role of bound water on dielectric properties were further evaluated to begin to build some fundamental understanding, **Figure 6.8**. The pellet was first held at 125 °C overnight and measured again at 125 and 25 °C. The dielectric constant and dissipation remained the same for both measurements at 125 °C, purple solid and dashed line in **Figure 6.8**. However, when measuring the pellet a second time at 25 °C (black dashed line in **Figure**
6.8), there was a slight increase in the ε’ and a decrease in ε” which improves the
dissipation factor of the polymer as well as a decrease in conductivity. Again the
improvement can be attributed to the loss of water from the second layer, which
aids in charge carrier movement as described before. Gaudette, has reported
that in “wet” polyimides the dielectric constant increases due to the adsorbed
water but that the dipole moment of water was decreased due hindered dipole
mobility due to hydrogen bonding between water and amide group. This seems
to be what is observed for the cadmium polymer, in which the second layer not
only has van der Waals interactions with the metal center but is also hydrogen
bonding with the bound water which could be leading to a decrease in the dipole
moment. When this second layer of water is driven off, the total dipole moment
of the polymer increases leading to a higher dielectric constant. The heating
cycle was repeated at 150 °C and again when measuring the pellet at 25 °C,
black dash dot line in Figure 6.8, there was another increase in ε’ but the
dissipation factor remained constant signifying a slight increase in ε” as well. To
fully conclude what is occurring with the dielectric properties as water is driven
off, further heating studies are needed at temperatures in which the bound water
is completely driven off which would also change the geometry of the metal
centers from octahedral to tetrahedral.
Figure 6.8. Effect of water on the dielectric properties of poly(cadmium sebacate).

6.3. Conclusions

Various metal containing polymers were synthesized using a variation of the interfacial polymerization described by Zilkha and Carraher, with the exception of aluminum polymers which were synthesized in a manner similar to aluminum containing small molecules. Each polymer was found to form an
octahedral complexes, similar to the organotin polymers, with the four oxygen atoms of two carboxylate groups and water or in the case of the aluminum materials a chloride atom as well. The aluminium, copper, cadmium and titanium polymers exhibited dielectric constants > 3 and up to approximately eight for the titanium polymer, but, in the case of titanium and aluminum, depending upon the amount of water in the polymer, large dissipation and/or conductivity. As a result of the large dissipation of titanium and aluminum polymers, the copper and cadmium materials were further investigated in the time domain, though the other polymers should not be excluded from further study as they display the largest dielectric constants and their synthesis and processing needs to be further optimized. With the temperature dependent dielectric properties observed for poly(cadmium sebacate) the some clarity of the influence of water on those properties has taken shape, in which the dielectric properties show some slight improvement as water is removed from the material. However, the polymers described here are in their infancy and need to be further evaluated for things as molecular weight, reproducibility of the observations described previously for the cadmium polymer and how these properties align with theoretical results. Fortunately, the data presented here allows for a better understanding and may give guidance to theoreticians to improve dielectric properties by employing different linkages to the metal dicarboxylate group.

6.4. Experimental

6.4.1. Synthetic Procedure for Aluminum Polymers
The general polymerization technique for the formation of aluminum polyesters is as follows. First, a round-bottomed flask is equipped with a stir bar, reflux condenser, addition funnel and rubber septa. The apparatus is flame dried to remove atmospheric water and filled with nitrogen. Upon cooling, an ice bath is placed under the flask and the appropriate amount of diethylchloroaluminum is added. The appropriate amount of diacid is weighed and diluted with 15 mL of dimethoxyethane, N,N-dimethylformamide or N,N-dimethylacetamide and transferred to the addition funnel. The diacid solution is then added drop wise to the aluminum monomer solution at a rate as not to cause the exothermic reaction to proceed to quickly. Upon complete addition of the diacid solution the ice bath is removed and the solution allowed to warm to room temperature, some more solvent may be added to dissolve some of the precipitate, and the reaction proceeds until the evolution of ethane gas ceases. The product is filtered and washed with tetrahydrofuran and acetone and dried in vacuo at 50 °C overnight.

**poly(chloroaluminum glutarate) (p(CIAl Glu)):** 10 mL (25 wt% in toluene, 18.4 mmol) of diethylchloroaluminum is reacted with 2.4381 g of glutaric acid (18.5 mmol) dissolved in dimethoxyethane. Polymer yield is 3.1500 g.

IR (KBr): ν = 3420, 2979, 1589, 1472, 1356, 1327, 1301, 1164, 1065, 1019, 883, 810, 667 cm⁻¹. TGA (10 °C min⁻¹): N₂ (onset): 292 °C
**poly(chloroaluminum sebacate) (p(ClAl Seb))**

10 mL (25 wt% in toluene, 18.4 mmol) of diethylchloroaluminum is reacted with 3.7264 g of sebacic acid (18.4 mmol) dissolved in N,N-dimethylformamide. Polymer yield is 2.2068 g.

IR (KBr): \( \nu = 3438, 2929, 2855, 1653, 1473, 1373, 1325, 1254, 1107, 1064, 652, 519 \text{ cm}^{-1} \). TGA (10 °C min\(^{-1}\)): \( \text{N}_2 \) (onset): 277 °C

**poly(chloroaluminum poly(ethyleneglycol)bis(carboxymethyl) ether-250)**

10 mL (25 wt% in toluene, 18.4 mmol) of diethylchloroaluminum is reacted with 4.6365 g of pEGBC-250 (18.5 mmol) dissolved in N,N-dimethylacetamide. Polymer yield is 5.8291 g.

IR (KBr): \( \nu = 3421, 2933, 1616, 1476, 1423, 1338, 1295, 1261, 1141, 1109, 1022, 946, 856, 732, 637, 549 \text{ cm}^{-1} \). TGA (10 °C min\(^{-1}\)): \( \text{N}_2 \) (onset): 268 °C

**poly(chloroaluminum poly(ethyleneglycol)bis(carboxymethyl) ether-600)**

10 mL (25 wt% in toluene, 18.4 mmol) of diethylchloroaluminum is reacted with 11.0434 g of pEGBC-600 (18.4 mmol) dissolved in dimethoxyethane. Polymer yield is 8.6716 g.

IR (KBr): \( \nu = 3371, 2873, 1746, 1583, 1471, 1423, 1348, 1298, 1250, 1108, 951, 848, 731, 582 \text{ cm}^{-1} \). DSC (10 °C min\(^{-1}\)): \( T_g = -25 \text{ °C} \). TGA (10 °C min\(^{-1}\)): \( \text{N}_2 \) (onset): 288 °C

**poly(chloroaluminum glutarate:poly(ethyleneglycol)bis(carboxymethyl) ether-600) (p(ClAl 20:80**

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**pEGBC-600**: 10 mL (25 wt% in toluene, 18.4 mmol) of diethylchloroaluminum is reacted with 1.9577 g of glutaric acid (14.8 mmol) and 2.5923 g (4.3 mmol) of pEGBC-600 dissolved in dimethoxyethane. Polymer yield is 4.6491 g.

IR (KBr): \( \nu = 3429, 2875, 1617, 1474, 1348, 1335, 1301, 1253, 1109, 949, 854, 731, 634, 504 \text{ cm}^{-1} \). DSC (10 °C min\(^{-1}\)): \( T_g = -27 ^{\circ} \text{C} \). TGA (10 °C min\(^{-1}\)):

\( \text{N}_2 \) (onset): 290 °C

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**poly(chloroaluminum) 50:50 glutarate:poly(ethyleneglycol)bis(carboxymethyl) ether-600)** (p(ClAI 50:50 pEGBC-600): 10 mL (25 wt% in toluene, 18.4 mmol) of diethylchloroaluminum is reacted with 1.2138 g of glutaric acid (9.2 mmol) and 5.5125 g (9.2 mmol) of pEGBC-600 dissolved in dimethoxyethane. Polymer yield is 9.1011 g.

IR (KBr): \( \nu = 3433, 2874, 1652, 1474, 1426, 1349, 1337, 1301, 1253, 1146, 1113, 949, 855, 732, 636 \text{ cm}^{-1} \). DSC (10 °C min\(^{-1}\)):

\( T_g = -28 ^{\circ} \text{C} \). TGA (10 °C min\(^{-1}\)):

\( \text{N}_2 \) (onset): 298 °C

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**poly(chloroaluminum) 80:20 glutarate:poly(ethyleneglycol)bis(carboxymethyl) ether-600** (p(ClAI 80:20 pEGBC-600): 10 mL (25 wt% in toluene, 18.4 mmol) of diethylchloroaluminum is reacted with 0.4962 g of glutaric acid (3.8 mmol) and 8.9848 g (15.0 mmol) of pEGBC-600 dissolved in dimethoxyethane. Polymer yield is 6.5109 g.

IR (KBr): \( \nu = 3431, 2916, 1601, 1472, 1430, 1349, 1334, 1301, 1253, 1108, 951, 849, 639, 508 \text{ cm}^{-1} \). TGA (10 °C min\(^{-1}\)):

\( \text{N}_2 \) (onset): 291 °C
poly(chloroaluminum 50:50 poly(ethyleneglycol)bis(carboxymethyl) ether-250:3,3-dimethylglutarate) (p(ClAl 50:50 pEGBC-250:3,3-DMG): 10 mL (25 wt% in toluene, 18.4 mmol) of diethylchloroaluminum is reacted with 1.4732 g of 3,3-dimethylglutaric acid (9.2 mmol) and 2.3095 g (9.2 mmol) of pEGBC-250 dissolved in N,N-dimethylacetamide. Polymer yield is 5.1579 g.
IR (KBr): \( \nu = 3417, 2957, 1616, 1474, 1420, 1334, 1264, 1121, 1026, 977, 897, 855, 735, 628, 510 \text{ cm}^{-1} \). TGA (10 °C min\(^{-1}\)): \( \text{N}_2 \) (onset): 271 °C

poly(chloroaluminum 60:40 poly(ethyleneglycol)bis(carboxymethyl) ether-250:3,3-dimethylglutarate) (p(ClAl 60:40 pEGBC-250:3,3-DMG): 10 mL (25 wt% in toluene, 18.4 mmol) of diethylchloroaluminum is reacted with 1.1805 g of 3,3-dimethylglutaric acid (7.4 mmol) and 2.7777 g (11.1 mmol) of pEGBC-250 dissolved in N,N-dimethylacetamide. Polymer yield is 4.6212 g.
IR (KBr): \( \nu = 3483, 2949, 1670, 1616, 1475, 1420, 1334, 1265, 1151, 1122, 1029, 976, 897, 857, 737, 667, 624, 490 \text{ cm}^{-1} \). TGA (10 °C min\(^{-1}\)): \( \text{N}_2 \) (onset): 272 °C

poly(chloroaluminum 75:25 poly(ethyleneglycol)bis(carboxymethyl) ether-250:3,3-dimethylglutarate) (p(ClAl 75:25 pEGBC-250:3,3-DMG): 10 mL (25 wt% in toluene, 18.4 mmol) of diethylchloroaluminum is reacted with 0.7436 g of 3,3-dimethylglutaric acid (4.6 mmol) and 3.4531 g (13.8 mmol) of pEGBC-250 dissolved in N,N-dimethylacetamide. Polymer yield is 4.5430 g.
IR (KBr): v = 3415, 2953, 1675, 1624, 1474, 1420, 1334, 1266, 1151, 1120, 1029, 974, 946, 857, 735, 667, 627, 599, 486 cm$^{-1}$. TGA (10 °C min$^{-1}$): N$_2$ (onset): 277 °C

**poly(chloroaluminum 80:20 poly(ethyleneglycol)bis(carboxymethyl) ether-250:3,3-dimethylglutarate) (p(CIAI 80:20 pEGBC-250:3,3-DMG):** 10 mL (25 wt% in toluene, 18.4 mmol) of diethylchloroaluminum is reacted with 0.5911 g of 3,3-dimethylglutaric acid (3.7 mmol) and 3.6948 g (14.8 mmol) of pEGBC-250 dissolved in N,N-dimethylacetamide. Polymer yield is 4.4348 g.

IR (KBr): v = 3422, 2949, 1635, 1474, 1420, 1334, 1266, 1119, 1028, 974, 857, 737, 668, 630, 598, 486, 481 cm$^{-1}$. TGA (10 °C min$^{-1}$): N$_2$ (onset): 268 °C

**poly(chloroaluminum 90:10 poly(ethyleneglycol)bis(carboxymethyl) ether-250:3,3-dimethylglutarate) (p(CIAI 90:10 pEGBC-250:3,3-DMG):** 10 mL (25 wt% in toluene, 18.4 mmol) of diethylchloroaluminum is reacted with 0.2907 g of 3,3-dimethylglutaric acid (1.8 mmol) and 4.1060 g (16.4 mmol) of pEGBC-250 dissolved in N,N-dimethylacetamide. Polymer yield is 4.2629 g.

IR (KBr): v = 3421, 2935, 1616, 1475, 1423, 1339, 1295, 1261, 1141, 1108, 1022, 966, 947, 867, 732, 638, 543, 484, 455 cm$^{-1}$. TGA (10 °C min$^{-1}$): N$_2$ (onset): 278 °C

**poly(chloroaluminum 95:5 poly(ethyleneglycol)bis(carboxymethyl) ether-250:3,3-dimethylglutarate) (p(CIAI 95:5 pEGBC-250:3,3-DMG):** 10 mL (25
wt% in toluene, 18.4 mmol) of diethylchloroaluminum is reacted with 0.1455 g of 3,3-dimethylglutaric acid (0.9 mmol) and 4.3601 g (17.4 mmol) of pEGBC-250 dissolved in N,N-dimethylacetamide. Polymer yield is 4.7827 g. 

IR (KBr): $\nu = 3428, 2946, 1624, 1473, 1420, 1334, 1265, 1150, 1118, 1027, 967, 856, 733, 630, 600, 509 \text{ cm}^{-1}$. TGA (10 °C min$^{-1}$): N$_2$ (onset): 269 °C

6.4.2. Synthetic Procedure for Transition Metal Polymers

The general procedure for the formation of metal containing polymers is as follows. First in a round-bottom flask the appropriate amount of metal containing monomer is dissolved in 20 mL of water. In an Erlenmeyer flask the appropriate amount of diacid is dissolved in 20 mL of 1,2-dichloroethane. To this solution is added the appropriate amount of triethylamine to deprotonate the diacid. The diacid solution is then added to the rapidly stirred aqueous phase. The precipitate is then filtered, washed with tetrahydrofuran, water and acetone and dried $\text{in vacuo}$ at 115 °C overnight. Changes to this procedure are noted in the individual polymer sections.

**poly(cadmium sebacate) (p(Cd Seb)):** 4.9850 g (21.8 mmol) of cadmium chloride is dissolved in water and reacted with 4.4530 g (22.0 mmol) of sebacic acid deprotonated with 4.4711 g (44.2 mmol) of triethylamine to yield 6.1152 g of polymer.
IR (KBr): ν = 3419, 2940, 2853, 1541, 1473, 1453, 1394, 1366, 1324, 1288, 1259, 1191, 1123, 1066, 1050, 1001, 928, 859, 766, 756, 736, 710, 601, 549 cm⁻¹. TGA (10 °C min⁻¹): N₂ (onset): 287 °C

**poly(copper sebacate) (p(Cu Seb)):** 2.9407 g (21.9 mmol) of copper(II) chloride is dissolved in water and reacted with 4.4715 g (22.1 mmol) of sebacic acid deprotonated with 4.4979 g (44.5 mmol) of triethylamine to yield 5.0186 g of polymer.

IR (KBr): ν = 3447, 2926, 2849, 1590, 1328, 1256, 884, 771, 724, 686, 626, 488, 451, 417 cm⁻¹. TGA (10 °C min⁻¹): N₂ (onset): 255 °C

**poly(zinc sebacate) (p(Zn Seb)):** 2.9419 g (21.6 mmol) of zinc chloride is dissolved in water and reacted with 4.4504 g (22.0 mmol) of sebacic acid deprotonated with 4.4872 g (44.3 mmol) of triethylamine to yield 5.5164 g of polymer.

IR (KBr): ν = 3442, 2925, 2865, 2849, 1590, 1535, 1456, 1410, 1397, 1342, 1271, 1199, 1126, 1067, 1048, 1008, 950, 853, 744, 722, 580, 562, 455 cm⁻¹. TGA (10 °C min⁻¹): N₂ (onset): 317 °C

**poly(50:50 cadmium:zinc sebacate) (p(50:50 Zn:Cd Seb)):** 2.5353 g (11.1 mmol) of cadmium chloride and 1.4430 g (10.6 mmol) of zinc chloride are dissolved in water and reacted with 4.4694 g (22.1 mmol) of sebacic acid
deprotonated with 4.4897 g (44.4 mmol) of triethylamine to yield 5.5602 g of polymer.

IR (KBr): $\nu = 3445, 2940, 2925, 2914, 2850, 1535, 1455, 1410, 1399, 1337, 1305, 1199, 1106, 1067, 1048, 949, 858, 741, 722, 693, 581, 559, 452 \text{ cm}^{-1}$. TGA (10 °C min$^{-1}$): N$_2$ (onset): 283 °C

*poly(calcium sebacate) (p(Ca Seb))*: 2.3820 g (21.5 mmol) of calcium chloride is dissolved in water and reacted with 4.4681 g (22.1 mmol) of sebacic acid deprotonated with 4.4681 g (44.2 mmol) of triethylamine to yield 4.7087 g of polymer.

IR (KBr): $\nu = 3435, 2960, 2929, 2850, 1578, 1469, 1454, 1435, 1410, 1329, 1289, 1264, 1240, 1194, 1120, 1038, 1008, 939, 858, 765, 735, 721, 659, 498, 445 \text{ cm}^{-1}$. TGA (10 °C min$^{-1}$): N$_2$ (onset): 433 °C

*poly(diethoxytitanium poly(ethyleneglycol)bis(carboxymethyl) ether-250) (p((EtO)$_2$Ti pEGBC-250))*: To a round-bottomed flask is added 4.1955 g (16.8 mmol) of pEGBC-250 and 20 mL of acetonitrile. To the solution is added 3.4789 g (34.4 mmol) of triethylamine. In an Erlenmeyer flask, 3.6057 g (17.3 mmol) of diethoxydichlorotitanium is dissolved in 20 mL of acetonitrile. To the rapidly stirred diacid solution is added the titanium solution. The precipitate is then filtered, washed with methanol, water and acetone and dried *in vacuo* at 115 °C overnight to yield 2.6001 g of polymer.
IR (KBr): $v = 3397, 2925, 1575, 1455, 1417, 1330, 1118, 848, 709, 594 \text{ cm}^{-1}$.

TGA (10 °C min$^{-1}$): N$_2$ (onset): 253 °C
6.5. References


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