SYNTHESIS OF POLYARYLENE ETHER SULFONE)-POLYIMIDE SEGMENTED COPOLYMERS

by

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Synthesis of Poly(Arylene Ether Sulfone)-Polyimide Segmented Copolymers

by

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(Abstract)

Poly(arylene ether sulfone) oligomers have been synthesized by nucleophilic aromatic substitution using potassium carbonate as base and N-methyl pyrrolidinone (NMP) as solvent. m-Aminophenol was used as an endcapper to control the molecular weight of the oligomers and to provide functional amine termination. These amine terminated oligomers can then be utilized in a variety of post reactions.

Poly(arylene ether sulfone)-Polyimide segmented copolymers were synthesized using a solution imidization procedure with NMP as the solvent and o-dichlorobenzene as the azeotroping agent. The polysulfone oligomers were reacted into the system via the diamine oligomer. The segmented copolymers demonstrated good solubility characteristics, high thermal stability, and high glass transition temperatures.

Previously, polyimides containing pyromellitic dianhydride (PMDA) did not remain soluble in the NMP solvent during the solution imidization, but rather precipitated out of solution when partially imidized. Incorporation of the amine terminated polysulfone oligomers into PMDA containing copolymers resulted in systems that remained soluble even after completion of imidization. The resulting copolymers were completely soluble in many of the high boiling solvents. The copolymers demonstrated high thermal stability and high glass transition temperatures.
Dedication

I dedicate this thesis to my parents and to Jefferson for their encouragement and support.
Acknowledgements

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Chapter 1 - Introduction

The development of high performance thermoplastics and thermosetting engineering plastics has been a major thrust in polymer chemistry for many years. The primary requirement is for the materials to maintain structural integrity at very high temperatures for extended periods of time. There are many applications for these high temperature polymers, such as electronic and microelectronic components, gaskets, sealants, tubing, binding systems in brake shoes, structural resins for advanced aircraft, space vehicles and missiles, nuclear reactor components, fire-resistant materials, automotive components, and coating on cookware\textsuperscript{17}.

There are both chemical and physical factors that can influence the heat resistance of a polymer. The chemical factors include primary bond strength, hydrogen bonding, resonance stabilization, molecular symmetry, rigid intrachain structure, cross-linking and branching. Some of the important physical factors are molecular weight and molecular weight distribution, crystallinity, molecular interactions and purity.

There are several polymer systems that meet the high temperature requirements, namely polyimides, polyquinoxalines, polyquinolines, and polybenzimidazoles. One of the most successful areas of investigation has been that of the aromatic polyimides.

Polyimides are cyclic-chain polymers that are superior to linear-chain polymers in thermal stability, heat resistance, and
physicomechanical properties. The initial work in this area was concentrated on synthesizing materials with high heat resistance, but the processibility of these materials was poor. In the late 1950's a two-stage synthesis was developed by the DuPont Company, this process was limited to producing thin films. More recently, the focus in this area has been to synthesize soluble, processable polyimides that maintain high strength and thermal stability. There have been many approaches to this goal, such as incorporation of flexible linkages or flexible oligomers, endcapping oligomers, molecular weight control, careful selection of monomers, and synthesis of various copolymers. A solution imidization technique has been developed to synthesize polyimides in a highly soluble form. Several of these approaches have been utilized in the research to be discussed in this thesis.
CHAPTER 2 - Literature Review

2.1 INTRODUCTION

Polyimides are classified as high performance polymers with high strength and high temperature resistance. They are also known as engineering polymers, defined as polymers that are used in place of metals and other materials of construction in many applications. The imide moiety is a nitrogen attached to two carbonyls, an aromatic imide is shown below:

\[
\begin{align*}
\text{O} & \\
\text{R} & \text{N} \\
\text{C} & \\
\text{O} & \\
\end{align*}
\]

A typical polyimide will contain a fairly high percentage of these imide linkages. The incorporation of ring structures such as this into organic polymer chains provides chain stiffening. Aromatic rings in particular are valuable for their thermal stability. The actual thermal and mechanical properties of a polyimide will depend upon the concentration of imide linkages and also on the structure and properties of the non-imide functional groups.
Polyimides have become increasingly more important, particularly in the aerospace and electrical/electronic industries. To specify a few examples, polyimides are used in aircraft engine parts, printed circuit boards, high speed-high load bearings, and insulation in electric motors, wire and cable. There are several commercial polyimides currently available: Kapton® by DuPont, Ultem® by General Electric, Upilex® by UBE Ind., and LARC-TPI by NASA and PMR-15 by several suppliers.

2.1.1 Synthesis of Polyimides

The first polyimide synthesized was reported in 1908 by Bogert and Renshaw¹. The reaction is, as shown below, the self-polymerization of 4-aminophthalic anhydride.

![Polymerization Reaction](image)

The first high molecular weight polyimide was not reported until 1955 by Edwards and Robinson². This reaction involved the melt polycondensation of an aliphatic diamine with a diacid/diester as shown in Scheme 1. This method was limited to polyimides
Scheme 1: Polyimides by Melt Polycondensation$^2$
synthesized from long chain aliphatic diamines that had melting points in a range low enough for molten conditions to be maintained. The wholly aromatic polyimides could not be synthesized by this method due to high transition temperatures and their inability to form salts with carboxylic acids.

The classical route to polyimide synthesis is a two step approach developed by DuPont Company in 1959\textsuperscript{3-6}. The first step consists of the synthesis of a poly(amic acid) precursor, and the second involves the cyclodehydration of the poly(amic acid) to form the polyimide, as shown in Scheme 2. The synthesis of the poly(amic acid) is most often achieved by reacting aromatic dianhydrides with diamines. The cyclodehydration is achieved by either thermal or chemical means, these methods and their effect on the resulting polymers will be discussed later in this chapter.

2.1.2 Poly(Amic Acids)

The poly(amic acid) or poly(amide acid) is a soluble polyimide precursor that can be synthesized at room temperature. The monomers are combined in a dipolar aprotic solvent or in some cases ether solvents have been utilized, several examples of both types of solvents are listed in Table 1. The monomers must be completely soluble in the reaction solvent in order to insure high molecular weight poly(amic acid). Also, the monomers must be extremely pure, moisture must be excluded from the reaction system, the monomers
Scheme 2: Classical Polyimide Synthesis$^{3-6}$
Table 1

Solvents for Poly(Aamic Acid) Synthesis

Conventional

- Dimethylacetamide
- N-methylpyrrolidone
- Dimethylformamide
- Dimethylsulfoxide
- N-methylcaprolactam

Ethers

- Dioxane
- Tetrahydropurran
- Diglyme
- Triglyme
must be reacted in a 1:1 stoichiometric ratio, and low reaction temperatures must be maintained. Conventional wisdom suggests that reaction temperatures should be in the range of -20°C to +70°C to prevent premature imidization, generally room temperature is utilized. The sequence of monomer addition may also affect molecular weight. In most cases, the solid dianhydride is added to a solution of diamine, which minimizes the possibility of the moisture sensitive dianhydride reacting with any residual moisture in the system and causing side reactions that could lower molecular weight.

The poly(amic acid) is a soluble, flexible polymer that is hydrolytically unstable. The poly(amic acid) once formed is stored in an inert atmosphere at low temperatures. Contact with moisture degrades the amic acid chains and results in lower molecular weight. The low temperatures are also required to prevent partial imidization which would release water as a by-product and cleave the remaining chains as above.

2.1.3 Imidization

Imidization involves the intramolecular evolution of water and is achieved by thermal or chemical means. Chemically a dehydrating agent, such as acetic, propionic, or valeric anhydrides, is used in combination with basic catalysts to cyclodehydrate the poly(amic acid)\textsuperscript{4.7}. Common catalysts are tertiary amines such as pyridine, trimethylamine, and triethylenediamine. The poly(amic acid) film is
immersed in a solution containing the dehydrating agent and the
catalyst, after several hours of immersion the imidization is complete
and the film is removed and dried. The reaction proceeds partially
through an isoimide intermediate which upon heating converts into
the imide. Incomplete conversion results in polyimides with inferior
physical properties.

Thermal imidization can be achieved by bulk or solution
imidization. Bulk imidization is achieved by putting a thin solution
cast poly(amic acid) film through a staged heating cycle such as the
one below:

2 Hours at 70°C
1 Hour at 100°C
1 Hour at 200°C
1 Hour at 300°C
Cool down to ambient temperature

Complete imidization is once again not achieved, possibly due to
chain immobility. The imidization can be followed and imide content
evaluated using IR techniques\textsuperscript{7-11}. There are four imide bands,
1780-1770 cm\(^{-1}\) (carbonyl), 1400-1340 cm\(^{-1}\) (axial vibration), 1140-
1100 cm\(^{-1}\) (transverse vibration), 760-720 cm\(^{-1}\) (out of plane
vibration)\textsuperscript{10}. The two most important ones being 1780-1770 cm\(^{-1}\)
and 740-710 cm\(^{-1}\). There is also an amic acid band that can be
monitored at 1540-1550 cm\(^{-1}\). There are several factors affecting
the rate of imidization, such as the casting solvent, the film thickness,
the imidization temperature, and the chemical structure of the
polyimide. The evolution of volatiles during the condensation prevents imidization of thick poly(amic acid) films or molded parts. The bulk imidization must be performed on a thin film or fiber and this is the final form of the product, which greatly limits its end use.

In 1981, Kumar used NMR to study the mechanism of polyimide formation\textsuperscript{12}. The formation of poly(amic acid) and the conversion to polyimide were followed by \textsuperscript{1}H-NMR. The addition of solid dianhydride to a solution of diamine was compared to the addition of solid diamine to a solution of dianhydride, a complex mechanism was suggested for both. It was determined that solid dianhydride when added to a solution of the diamine followed the typical condensation polymerization reaction with no detectable side reaction; whereas when solid diamine was added to a solution of dianhydride a polymeric complex formed along with the normal poly(amic acid). It was concluded that the route without polymeric complex formation was the preferred route to high molecular weight poly(amic acid).

A solution imidization technique was developed by Summers at VPI & SU\textsuperscript{13}. The method is a thermal imidization performed in solution using a cosolvent system at moderate reaction temperatures. The cosolvent system consists of N-methylpyrrolidinone (NMP), used to solvate the monomers, and cyclohexylpyrrolidinone (CHP), used as an azeotroping agent. At elevated temperatures the CHP becomes immiscible with water and helps to eliminate it from the system. The poly(amic acid) and the azeotroping agent are heated at 160-170°C for approximately 24 hours. The polymer solution is cooled
and precipitated into a rapidly stirring solution of methanol and water. The fibrous particles that result are dried and can then be easily put back into solution or melt processed.

It was shown by FT-IR that the disappearance of the amic acid moiety and the appearance of the imide link are occurring simultaneously, hence no significant side reactions are present.

A major advantage to using this technique is the formation of more soluble polymers than the conventional bulk imidization. Summers compared solution imidization to bulk imidization for many polyimide homo- and copolymers. It was determined that many historically insoluble polyimides, such as BTDA, 3,3'-DDS homopolyimide, were highly soluble in dipolar aprotic solvents as a result of the solution imidization technique. Intrinsic viscosity data was comparable for both methods of imidization, hence there was no significant loss of molecular weight as a result of solution imidization. $^1$H-NMR spectra showed no residual poly(amic acid) after solution imidization, also thermoxidative stability and upper use temperature were not lowered significantly as determined by the thermal data.

There was one polyimide that was not polymerizable by this solution imidization technique. The highly rigid structure of polyimide synthesized from pyromellitic dianhydride and 4,4'-oxydianiline precipitated from solution as partially imidized material presumably because of high chain rigidity.
2.2 PROPERTIES OF POLYIMIDES

The mechanical properties and thermal stability of aromatic polyimides are superior to most other polymers. The benzene and imide rings produce strong intermolecular bonds resulting in high dimensional stability at high temperatures. Polyimide films are transparent, but usually amber with glass transition temperatures greater than 200°C. The very high thermal and thermooxidative stability of these polymers results in excellent mechanical properties even at high temperatures. The choice of monomers will greatly determine the physical properties of the resulting polymer. Imide linkages will raise thermal transitions and improve thermal stability, as well as imparting inherently high modulus and high strength. A high percentage of these linkages will result in an excellent high temperature polymer.

A major drawback of this type of material is that inherent insolubility and intractability creates processing problems. A classical aromatic polyimide is soluble only in concentrated sulfuric acid and cold fuming nitric acid and cannot be melted under typical processing temperatures.

In order to address this problem flexible (or "soft"), tractable, or kinked segments have been incorporated into the polyimide backbone to improve solubility characteristics, and hence improve processability\textsuperscript{14,15}. The effect that this has on the physical properties is highly dependent on the concentration of these flexible
segments to the imide linkage. Some typical flexible linkages are ether, methylene, ketone, sulfide, sulfone, or meta-linkages. These linkages in general will lower thermal transitions and possibly thermal stability$^8,16,17$. Mechanical properties may also be lowered, but solubility is greatly improved and thermal processing may be possible. A balance between physical properties and processibility must be developed to obtain the most useful polymer system.

2.3 STRUCTURAL VARIATIONS OF POLYIMIDES

There are several variations on how these flexible segments can be incorporated in the polyimide system. Polyimides can be synthesized using monomers that contain the flexible linkages in either the diamine or dianhydride portion. In a survey of scientific and patent literature from the past 5-10 years, Takekoshi reported on some new monomers that improve processability while maintaining good thermal stability. The diamines reported contained heterocyclic rings, perfluoroalkylenes, cycloalkylene bridges, or bulky substituents; the dianhydrides contained sulfone, ether, or tetraphenylene$^{18}$. Copolyimides can be made by stoichiometrically combining more than one diamine with one dianhydride, or more than one dianhydride with one diamine. This would result in a random copolymer with two or more types of structural segments, one of which contains a flexible unit. The properties of these
copolymides are usually intermediate between the homopolymers' properties. For example, a rigid dianhydride could make up 80% of the total dianhydride content and a dianhydride with a flexible linkage would make up the remaining 20%. There are numerous variations of diamines and dianhydrides that could result in hundreds of different copolymers.

2.3.1 Copolyimides

Copolymers can be synthesized that contain two functional groups such as poly(amide imides)\(^{19-28}\), poly(ester imides)\(^{29-40}\), and poly(heterocyclic imides)\(^{32-34}\). Poly(amide imides) can be synthesized by reacting excess diamine with diacid dichloride or pyromellitic dianhydride to form either amine-capped polyamide or amine-capped poly(amic acid). The polyamide would then be reacted with pyromellitic dianhydride and the poly(amic acid) would be reacted with diacid dichloride, both would form a poly(amide imide). These polymers are used as adhesives, composite matrices, coatings, films, foams and moldings. The advantage of the amide linkage is a more soluble, processable polymer than the comparable polyimide, although thermal performance in substantially inferior and water sorption is much higher\(^{35,41}\).

Poly(ester imides) can be synthesized by reacting bis(ester anhydrides) with aromatic diamines to form the poly(amic acid) precursor, which upon imidization yields the poly(ester imide)\(^{28,29}\).
Once again the polymers are processable, but at the expense of thermal stability. The mechanical and electrical properties of the poly(ester imides) were good.

Poly(heterocyclic imides) can be synthesized by preparing either a dianhydride or a diamine with a heterocyclic structure\textsuperscript{31,41,42}. Processability of the polymers is improved while maintaining reasonable mechanical and thermal properties.

2.3.2 \textit{Segmented Polyimide Copolymers}

Flexible, or "soft", segment oligomers could be synthesized with either amine or anhydride functionality. These oligomers could then be substituted in as a portion of the dianhydride or diamine, resulting in a segmented copolymer. For example, amine terminated polydimethylsiloxane oligomers were incorporated into several polyimide systems as part of the diamine content\textsuperscript{13,42}. The molecular weight of the oligomers and the percent substituted into the system are two important parameters that can be controlled in these polymers.

The aromatic monomers and the siloxane oligomers were reacted in a cosolvent system of NMP/THF to form the poly(amic acid). The amic acid was imidized both by bulk and solution imidization. The effect of siloxane incorporation on copolymer properties was evaluated. Solubility was greatly improved without significant lowering of the glass transition temperature or loss of
thermoxidative stability. The mechanical properties were greatly affected by the siloxane incorporation; low to moderate amounts of siloxane incorporation resulted in behavior similar to the unmodified controls, whereas high amounts of siloxane incorporation resulted in behavior classified as thermoplastic elastomers. The polymer could be tailored to the type of behavior desired within the two mechanical extremes. Varying the molecular weight of the oligomers did not greatly affect the polymer properties described above.

A final approach to incorporating imide and flexible segments into one polymer is to synthesize a preimidized monomer with functional termination, and then reacting those monomers into a thermoplastic polymer system. Hydroxyl terminated preimidized monomers have been synthesized and reacted in as a portion of the phenol in a nucleophilic aromatic substitution reaction to synthesize a poly(imide ether sulfone)\textsuperscript{42}. Benzophenone tetracarboxylic dianhydride was reacted with p-aminophenol in CHP to form the amic acid species. The amic acid solution was heated severely to cyclize the amic acid linkage and release water. The preimidized monomer, BPI 1, structure shown below, precipitated out of the

![Chemical structure](attachment:image.png)

17
solution as a dark, brown precipitate. This monomer was then reacted with 4,4'-dichlorodiphenyl sulfone and biphennol in a nucleophilic aromatic substitution reaction. The high molecular weight poly(amide ether sulfone) copolymers that were synthesized by this method exhibited good mechanical properties, thermal stability and good solvent resistance.

It is a major challenge in this field to synthesize a polyimide with improved processibility, while maintaining solvent resistance and excellent thermal and mechanical properties. This thesis will combine many of the techniques discussed above to synthesize a polyimide that fits in this category.

2.4 SYNTHETIC VARIATIONS IN POLYIMIDE SYNTHESIS

2.4.1 Polyimides from Diisocyanates

There are a few other synthetic routes that result in polyimides. The reaction of diisocyanates with dianhydrides or the acid or ester derivatives of the anhydrides produces polyimides of the same final structure as the classical route. The reaction proceeds partially through a 7-membered ring intermediate as shown in Scheme 3. There are several synthetic requirements necessary to obtain high molecular weight polyimide. A tertiary amine catalyst must be present, solid diisocyanate is added to
Scheme 3: Synthesis of Polyimides from Diisocyanates
anhydride/acid solution, the reaction temperature must be between 100°C and 100°C, and small amounts of water must be present. The condensation byproduct carbon dioxide can serve a very useful purpose in the synthesis of polyimide foams. The carbon dioxide serves as a foaming gas, with the proper catalyst rigid foam products were synthesized directly without foaming agents.

2.4.2 Polyimides through Nitro-Displacement Polymerization

Synthesis of polyimides through nitro-displacement is another important synthetic route. High molecular weight is difficult to obtain by this route. It is dependent upon several variables, such as the location of the nitro groups, bisphenate reactivity, choice of solvent, and anhydrous conditions. Nitro displacement could be used in the synthesis of the commercial polyetherimide Ultem by General Electric as shown in Scheme 4. The difficulty in obtaining high molecular weight would rule out this method for the synthesis of the polymer, but it is very possible that the nitro displacement could be used to synthesize the dianhydride monomer which is then purified and reacted with the diamine as shown in Scheme 5. Ultem 1000® is a polyether imide with a glass transition temperature of 217°C, excellent thermal and melt stability. The polymer has a wide process window due to completely imidized structure and stable chain end-capping.
Scheme 4: Synthesis of Polyimides through Nitro-Displacement$^{49}$
Scheme 5: Synthesis of Ultem$^{13}$
2.4.3 *Polyimides from the Diels-Alder Reaction*

The Diels-Alder reaction can also be used in the synthesis of polyimides\(^{50}\). There are two different synthetic routes. The first one uses preimidized monomers that are polymerized by a Diels-Alder reaction as in Scheme 6. The second one uses Diels-Alder to form the dianhydride monomer which is then polymerized in the classical method as in Scheme 7.

2.5 *POLYIMIDE COPOLYMERS CONTAINING THE SULFONE LINKAGE*

Polyimide copolymers previously described provided systems with enhanced solubility and processability at the expense of thermal stability. There has been much research effort focused on developing a polyimide or copolyimide that can combine processability with high thermal and mechanical performance. A successful avenue of this research has been in the incorporation of the aromatic sulfone linkage. This linkage has several attractive characteristics: the kinked nature of the linkage breaks up chain regularity and its size provides rigidity and the high oxidation state imparts good thermal and oxidative stability. Combining this aromatic sulfone linkage with an aromatic ether linkage has resulted in polymers with excellent mechanical properties and thermal
Scheme 6: Synthesis of Polyimide by Diels-Alder Reaction\textsuperscript{28}
Scheme 7: Synthesis of Polyimide by Diels-Alder\textsuperscript{28}
stability. Much attention has centered on a diamine containing both of these groups, sulfone ether diamine (SED)$^4$, of the structure shown below.

\[
\begin{array}{c}
\text{H}_2\text{N} \quad \text{O} \quad \text{SO}_2 \quad \text{O} \quad \text{NH}_2
\end{array}
\]

In this monomer the highly polar sulfone group is insulated by the ether linkage from the amine functionality. This diamine, when reacted with BTDA and PMDA, resulted in polymers with excellent mechanical and thermal properties. The SED/BTDA polymer was somewhat tractable, but could not be handled by conventional thermoplastic processing conditions. The SED/PMDA polymer was intractable and insoluble, some crosslinking had occurred upon imidization. In related work on poly(amide imides) it was determined that introducing diphenyl sulfone units into the polymer backbone improved flexibility, melt processability and solubility in some solvents while maintaining high thermal stability and high glass transition temperatures.$^5$ This work also demonstrated that by incorporating oxyphenylene or diphenylisopropylidene segments the glass transition temperature was reduced and processing under conventional thermoplastic conditions was possible. Therefore by balancing these two types of units, it could be possible to design a polymer with the desired physical and thermal properties. A variation of the previous work was to react sulfone ether diamine
oligomers with maleic anhydride, which was then chemically imidized to bismaleimide\textsuperscript{52}. The arylimides were then addition polymerized to produce a crosslinked system, these systems possessed high glass transition temperatures, moderate to high modulus plateaus above the Tg, and thermal stability up to \textasciitilde370\textdegree{C}.

Burks and St. Clair at NASA-Langley Research Center developed a polyimide with the aromatic sulfone linkage in both the dianhydride and the diamine\textsuperscript{53}. The structure of the polymer is as shown below:

![Polyimide Structure](image)

The purpose of the research was to develop hot-melt processable polyimides. This polymer did not build high molecular weight up until the imidization step, and resulted in a linear polymer with a glass transition temperature of 205\textdegree{C}. The polyimide has been characterized to be a potential melt processable polymer with good thermal stability and chemical resistance.

A different synthetic approach was taken by Jensen and Hergenrother at NASA Langley by synthesizing amine terminated poly(arylene ethers) and anhydride terminated poly(amic acid) oligomers of controlled molecular weight\textsuperscript{54}. A solution of the poly(arylene ether) was added to the amic acid solution and cloudy,
viscous solutions were formed. These solutions were centrifuged and films were cast. The films were thermally imidized. Tough, creasible copolymer films were formed.

2.6 POLY(ARYLENE ETHERS)

The high molecular weight poly(arylene ethers) are a well known class of high performance thermoplastics, a general structure is shown below. The sulfone containing Udel and Victrex and the ketone containing PEEK poly(arylene ethers) have gained significant commercial importance due to their high thermal and hydrolytic stability, coupled with chemical resistance and excellent mechanical properties. They can be processed by extrusion or injection molding which makes them very attractive industrially. The thermal stability of groups such as -SO₂-, -CO-, and -O- combined with the flexibility and mobility of -C-O-C- linkage and the hydrolytic stability of the aryl ether bond are the contributing factors to the properties described above. The toughness characteristics of the poly(arylene ethers) have rendered them particularly attractive as thermoplastic modifiers for brittle thermosetting systems, such as the epoxies.

\[
\begin{array}{c}
\text{X} = \text{C(CH₃)₂, SO₂,} \\
\text{Y} = \text{SO₂, C=O,} \\
\end{array}
\]
2.6.1 Poly(Arylene Ether Sulfones)

Poly(Arylene Ether Sulfones) can be synthesized by polysulfonylation or polyetherification. The polysulfonylation method uses ether monomers in an electrophilic aromatic substitution\textsuperscript{56-58}. A Friedel-Craft catalyst is present. The polyetherification method is a nucleophilic aromatic substitution in a dipolar aprotic solvent. The monomers used already contain the sulfone linkage. The polyetherification method involves the condensation of bisphenates with activated dihalides\textsuperscript{59}. The phenoxide displaces the halide to form the ether bond. The e\textsuperscript{-} withdrawing nature of the sulfone group activates the dihalide, facilitating nucleophilic aromatic substitution. Bisphenol-A polysulfone (UDEL Polysulfone by Amoco) can be synthesized by this method.

The first established synthetic method for high molecular weight poly(arylene ether sulfone) was a two step procedure. A solution of bisphenol in dimethylsulfoxide (DMSO) was reacted with a stoichiometric amount of aqueous sodium hydroxide to form the bisphenoxide. The water formed was carefully azeotroped off with chlorobenzene. The second step involves the addition of a stiochiometric amount of 4,4\textsuperscript{'}-dichlorodiphenyl sulfone in chlorobenzene to the bisphenoxide solution to form the polymer. This method was used by Johnson in 1967\textsuperscript{60} to synthesize many high
molecular weight poly(arylene ether sulfones). There were problems associated with this method involving polymer hydrolysis and bisphenate insolubility. Exact stoichiometry of sodium hydroxide was necessary, it was demonstrated that 1% deviation resulted in drastically decreased reduced viscosity of the polymer solution\textsuperscript{42}. An alternate route was suggested that utilized anhydrous potassium carbonate as the base and N,N'-dimethylacetamide as the aprotic solvent\textsuperscript{61,62}. It was determined that a 10-20% excess of potassium carbonate did not reduce the intrinsic viscosity of the polymer solution, and no significant hydrolysis took place\textsuperscript{63}. FT-IR and NMR analysis demonstrated the polymers obtained by both methods are structurally identical.

2.6.2 Poly(Arylene Ether Sulfone) Oligomers

Poly(arylene ether sulfone) oligomers comprise an essential portion of the research to be presented and the synthesis of those oligomers will be discussed. Molecular weight and end group control are essential aspects in the synthesis of melt processable poly(arylene ether sulfone) oligomers. The one step K$_2$CO$_3$/DMAC method was used to synthesize these oligomers, an endcapper is added into the system to control molecular weight and endgroup functionality, as shown in Scheme 8. There are many different endgroup functionalities possible, they can be reactive or non-
Scheme 8: General Synthetic Scheme for Poly(Arylene Ethers)\textsuperscript{55}
reactive in post reactions. Non-reactive endgroups are commonly chloro, methoxy or methyl, the non-reactivity of these groups enhances polymer melt and lifetime stability. Typical reactive endgroups are hydroxyl, acetoxy, carboxy and amino. These oligomers generally undergo chemical post reactions to produce block or segmented copolymers. This is the type relevant to this thesis.

The endcappers used are monomers that contain a functionality on one end that is unreactive in the polymerization, and one end which reacts with only one of the other monomers. They are mathematically treated as monofunctional reagents. The Carothers equation is then used to calculate the stiochiometric amount of endcapper needed to obtain the desired molecular weight oligomer.

In 1989, Jurek reported on the synthesis and characterization of amino-terminated poly(arylene ether sulfone) oligomers. The monomers used were Bisphenol-A, dichlorodiphenyl sulfone and either m-aminophenol, p-aminophenol or a novel endcapping reagent, 2-p-aminophenyl-2-hydroxyphenylpropane (MBA). The MBA was synthesized by reacting Bisphenol-A with aniline hydrochloride. The number average molecular weights were determined by non-aqueous potentiometric titration of the endgroups. These molecular weights were consistent with the theoretical or calculated molecular weights. The glass transition temperatures as determined by DSC increased systematically as a function of molecular weight. The molecular weight distributions were all monomodal and close to 2.0. Difunctionality of the oligomers
was established by first comparing the intrinsic viscosities of the amine terminated oligomers with hydroxy terminated oligomers of comparable molecular weight. Secondly, the oligomers were reacted with a diacid chloride, in this case terephthaloyl chloride. An extreme increase in molecular weight as determined by either gel permeation chromatography or intrinsic viscosity indicates difunctionality. These amine terminated poly(arylene ether sulfone) oligomers can be used in several post-reactions as shown in Scheme 9.
Scheme 9: Post-Reactions of Amine Terminated Poly(Arylene Ether Sulfone) Oligomers
CHAPTER 3. Experimental Procedures

3.1 MATERIALS

3.1.1 Solvents

The purity of reaction solvents is an important parameter in the synthesis of high molecular weight polymers. In particular, drying agents, distillation, and minimal atmospheric exposure were all techniques used to insure the purity of the reaction solvent. The drying agent used was phosphorus pentoxide (P₂O₅) obtained from Fisher Scientific. The constant boiling middle fraction was collected. To avoid significant degradation of the solvent, distillation was carried out under reduced pressure generated by a mechanical vacuum pump or water aspiration. To minimize atmospheric exposure, syringe techniques were used when handling the dried solvents; the flasks were sealed with a rubber septum using nitrogen to pressurize, and they were stored in a dessicator.

N-methyl-2-pyrrolidinone (NMP)

Source: Fisher Scientific
Density (25°C): 1.026
Boiling Point: 202°C
Structure: (on next page)
Purified grade N-methyl-2-pyrrolidinone was stirred over phosphorus pentoxide for at least 12 hours. The dried solvent was distilled under reduced pressure and stored under nitrogen.

o-Dichlorobenzene

Source: Fisher Scientific
Density (25°C): 1.3048
Boiling Point: 180.5
Structure:

Purified grade o-Dichlorobenzene was stirred over phosphorus pentoxide for at least 12 hours. The dried solvent was distilled under reduced pressure and stored under nitrogen.

Toluene

Source: Fisher Scientific
Density (25°C): 0.8669
Boiling Point: 110.6°C
Structure: (on next page)
Purified grade Toluene was used as received.

3.1.2 Monomers

Purity of reaction monomers is a very important parameter in the synthesis of high molecular weight polymers. Recrystallization and sublimation are the techniques used to purify monomers to polymer grade materials.

Bisaniline P (Bis P)

Source: Air Products Corporation
Empirical Formula: $C_{24}H_{28}N_2$
Molecular Weight: 344.54 g/mol
Structure:

Bis P was received as a fine white powder of monomer grade purity. The monomer was dried in a vacuum oven at 80°C for at
least 12 hours prior to being used, the dried monomer was stored in a dessicator.

3,3',4,4'-Benzophenone Tetracarboxylic Dianhydride (BTDA)

Source: Allco Chemical Corporation
Empirical Formula: $C_{17}H_6O_7$
Molecular Weight: 322.23 g/mol
Structure:

\[
\text{Structure Image}
\]

BTDA was obtained as a white, crystalline powder of monomer grade purity. The monomer was dried in a vacuum oven at 80°C for at least 12 hours prior to use, the dried monomer was stored in a dessicator. Sublimation or recrystallization may be necessary for purification of lower grade BTDA.

Pyromellitic Dianhydride (PMDA)

Source: Allco Chemical Corporation
Empirical Formula: $C_{10}H_2O_6$
Molecular Weight: 218.12 g/mol
Structure: (on next page)
PMDA was obtained as a white crystalline powder of monomer grade purity. The monomer was dried in a vacuum oven at 80°C for at least 12 hours prior to use, the dried monomer was stored in a dessicator. Sublimation or recrystallization may be necessary for purification of a lower grade material.

3,3'-Diaminodiphenyl Sulfone (3,3'-DDS)

Source: Aldrich
Empirical Formula: \( \text{C}_{12}\text{H}_{12}\text{N}_{2}\text{O}_{2}\text{S} \)
Molecular Weight: 248.32 g/mol
Structure:

\[
\begin{array}{c}
\text{NH}_2 \\
\text{S} \\
\text{NH}_2
\end{array}
\]

3,3'-DDS was obtained as a fine white powder that required recrystallization to be monomer grade purity. Methanol, L., was poured into an erlenmeyer flask and purged with nitrogen for several hours to deoxygenate the solvent. The methanol was then heated to the boiling point and approximately 200mL were
removed and placed in a beaker on a hot plate. With nitrogen bubbling through, the DDS was slowly added and allowed to dissolve until the solution was saturated. Hot methanol was added to the saturated solution until the solution was once again clear. The erlenmeyer was removed from the heat, wrapped in aluminum foil, and allowed to cool very slowly to room temperature. The flask was then placed in an ice bath to further induce crystallization. Crystals formed upon cooling. The crystals were vacuum filtered and washed with deoxygenated methanol. After washing, the crystals were dried in a vacuum oven at 70°C for 12 hours, crushed with a mortar and pestle, dried again at 70°C for 12 hours, bottled and stored in a dessicator.

Phthalic Anhydride (PA)

Source: Aldrich
Empirical formula: C₈H₄O₃
Molecular Weight: 148.12
Structure:

Phththalic anhydride was obtained as a white powder that requires sublimation to obtain monomer grade purity. A vacuum
sublimator was used with dry ice and acetone being placed in the cold finger. The material readily sublimes onto the cold finger under vacuum conditions. The phthalic anhydride is scraped off of the cold finger, bottled, and stored in a dessicator until used.

Bisphenol-A [2,2-bis(4-hydroxyphenyl) propane] (Bis A)

Source: Dow Chemical
Empirical Formula: $\text{C}_{15}\text{H}_{16}\text{O}_2$
Molecular Weight: 228.27 g/mol
Structure:

\[
\text{HO} - \text{C} - \text{CH}_3 - \text{C} - \text{CH}_3 - \text{OH}
\]

Bis A was obtained as monomer grade material and was used directly. Recrystallization from toluene may be necessary if lower grade material is obtained.

4,4'-Dichlorodiphenyl Sulfone (4,4'-DCDPS)

Source: Amoco
Empirical Formula: $\text{C}_{12}\text{H}_8\text{Cl}_2\text{O}_2\text{S}$
Molecular Weight: 287.16 g/mol
Structure:
4,4'-DCDPS was obtained as a monomer grade material. Recrystallization from toluene may be required. A solution of 4,4'-DCDPS (approximately 500 g) and toluene (800 mL) was placed in an erlenmeyer flask, stirred, and heated to boiling. Activated charcoal (2 g) was added to the stirring solution and the solution was filtered through Celite in a buchner funnel. The clear filtrate was once again brought to a boil and then allowed to cool slowly overnight. White crystals were formed. They were filtered, washed with cold toluene, and dried in a vacuum oven at 80°C for at least 12 hours. The crystals were crushed and dried at 90°C for 12 hours.

m-Aminophenol

Source: Aldrich
Empirical Formula: C₆H₇ONH₂
Molecular Weight: 109.14 g/mol
Structure:
m-Aminophenol was obtained as white flakes that require sublimation to obtain monomer grade material. The m-aminophenol was placed in a vacuum sublimator that was placed in an oil bath at 120°C. The cold finger was filled with dry ice and acetone. The monomer formed a white powder on the cold finger. The powder was removed, placed in a bottle, and stored in a dessicator until used.
3.2 SYNTHESIS OF Oligomers AND COPOLYMERS

3.2.1 Poly(Arylene Ether Sulfone) Oligomers

A four neck flask was equipped with a mechanical stirrer, a Dean-stark trap and condenser, and a thermometer adapter and gas inlet. The calculated amounts of DCDPS, Bis A, and m-aminophenol were charged into the reaction flask with NMP to make a 15 weight percent solids concentration. Toluene was used as an azeotroping agent; 50 volume percent, based on NMP, was added along with a 40 percent molar excess of K₂CO₃. The reaction flask was heated to 155°C for 2 hours, the toluene was removed and the reaction temperature was raised to 170°C for at least 8 hours. The viscous, dark-green reaction mixture was cooled to 80°C and filtered to remove the inorganic salts. The solution was coagulated into rapidly stirring methanol/water (80/20), acidified with glacial acetic acid. After filtration and washing, the oligomer was stirred in hot water to remove any remaining salts, and then dried. The oligomer was reprecipitated from methylene chloride into methanol and dried in a vacuum oven at 100°C for 24 hours.
3.2.2 Polyimides

3.2.2.1 Homopolymers

*Synthesis of Poly(Amic Acid)*

A three neck flask equipped with a mechanical stirrer, a gas inlet, and a drying tube was thoroughly flame dried with a fast nitrogen flow. The Bis P monomer was charged into the flask and dissolved in NMP, the flask had to be heated up to approximately 80°C to completely solvate the monomer. The flask was cooled down to room temperature; the dianhydrides, BTDA and PA, were slowly added to the flask and rinsed in with NMP. A clear yellow solution resulted, this solution was stirred under nitrogen for at least 8 hours. The viscosity increased with time.

*Solution Imidization of the Poly(Amic Acid)*

A four neck flask was equipped with a mechanical stirrer, a thermometer adapter with a gas inlet, a Dean-stark trap and condenser, a drying tube, and an addition funnel. The apparatus was thoroughly flame dried under a fast nitrogen flow. The azeotroping agent, o-C₆H₄Cl₂ (20% of total solvent), was added to the flask and heated up to 160°C-165°C by immersing the flask into a hot oil bath. The poly(amic acid) was transferred into the addition funnel. Once the o-C₆H₄Cl₂ had reached the reaction temperature, the poly(amic acid) was slowly dropped into the reaction flask from
the addition funnel. The imidization was stirred rapidly at a reaction temperature of 165°C for 24 hours. The water produced by the imidization was condensed and dropped into the Dean-stark trap.

The flask was allowed to cool to room temperature after the reaction time. The polymer solution was transferred into a separatory funnel and dropped into a rapidly stirring solution of methanol/water (80/20). The polymer was vacuum filtered and dried in a vacuum oven. The homopolymer was a yellow fibrous powder.

3.2.2.2 Synthesis of Poly(Arylene Ether Sulfone)-Polyimide Segmented Copolymers

*Synthesis of Poly(Amic Acid)*

A three neck flask was equipped with a mechanical stirrer, a gas inlet, and a drying tube. The apparatus was flame dried. The poly(arylene ether sulfone) oligomers were placed into the reaction flask and dissolved in NMP. The Bis P monomer was added to the flask and rinsed in with NMP. The flask was heated to approximately 80°C to solvate the Bis P. Once the Bis P was completely in solution, the reaction flask was allowed to cool to room temperature. BTDA and PA were slowly added to the diamine solution and rinsed in with NMP. A clear yellow solution resulted,
this solution was stirred rapidly with a nitrogen flow for at least 8 hours. The viscosity of the solution increased over the 8 hours.

*Imidization of the Poly(Amic Acid)*

A four neck flask was equipped with a mechanical stirrer, a thermometer adapter with a gas inlet, a Dean-stark trap and condenser, a drying tube, and an addition funnel. The apparatus was thoroughly flame dried under a fast nitrogen flow. The azeotroping agent, o-C₆H₄Cl₂ (20% of total solvent), was added to the flask and heated to 160-165°C by immersing the flask into a hot oil bath. The poly(amic acid) was transferred into the addition funnel. Once the o-C₆H₄Cl₂ had reached the reaction temperature, the poly(amic acid) was slowly dropped into the reaction flask from the addition funnel. The addition funnel was replaced with a glass stopper once the poly(amic acid) was all added to the reaction flask. The imidization was stirred rapidly at a reaction temperature of 165°C for 24 hours. The water produced by the imidization was condensed and dropped into the Dean-stark trap.

The flask was allowed to cool to room temperature after the 24 hours of reaction time. The polymer solution was transferred into a separatory funnel and dropped into a rapidly stirring mixture of methanol/water (80/20). The polymer was vacuum filtered and dried in a vacuum oven. The polymer product was as a yellow fibrous powder.
3.2.2.3 Poly(Arylene Ether Sulfone)-Polyimide Segmented Copolymers containing PMDA

One step solution imidization

A synthetic procedure utilizing only one reaction set-up was used to synthesize these copolymers. A four necked flask was equipped with a mechanical stirrer, a thermometer adapter with a gas inlet, a drying tube and a glass stopper. The flask was flame dried with a fast nitrogen flow. The poly(arylene ether sulfone) oligomers were charged into the reaction flask and dissolved with NMP. The DDS was added to the oligomer solution, rinsed with NMP, and stirred until it was completely dissolved. PMDA was added slowly and rinsed with NMP. The remaining dianhydrides, BTDA and PA, were slowly added and rinsed. The final percent solids of the solution was generally 15-20 weight percent. The poly(amic acid) was stirred rapidly with a moderate nitrogen flow for at least 8 hours.

A reverse Dean-stark trap and condenser were added to the reaction flask. The arm of the trap was wrapped with heat tape and the trap was filled with o-C$_6$H$_4$Cl$_2$. Approximately 10 volume percent of o-C$_6$H$_4$Cl$_2$, based on NMP, was added to the poly(amic acid). The reaction flask was immediately immersed into a hot oil bath. A reaction temperature of 165°C was maintained for 24 hours. The reaction was cooled to room temperature and precipitated into a methanol/water mixture (80/20). The filtered
product was a brown, fibrous product. The polymer was thoroughly dried in a vacuum oven for 2 days.

_Bulk or Thermal Imidization_

The bulk or thermal imidization was carried out by taking the poly(amic acid) through a staged heating cycle. The poly(amic acid) was poured onto a clean glass plate and drawn into a smooth flat film using a drawing blade set at 40 mils. The glass plate was placed in a high temperature vacuum oven. The temperature must be raised slowly to prevent bubble formation. The oven temperature was held at 70°C, 100°C, 200°C and 300°C for at least 1 hour at each temperature. The plate was slowly cooled and then removed from the oven. The films generally peel easily off the glass after loosening the edges with a razor blade. Some films had to be placed in a warm water bath to release from the glass plate, these would then be dried in a vacuum oven at 80°C for several hours.

Films of the copolymers were prepared to ease in the handling of the polymer for characterization. The polymer powder, 1.25 g, was weighed into a sample vial and dissolved in 7.5 mL of NMP. These solutions were then poured onto a glass plate and put through the same heating cycle as in thermal imidization.
3.3 CHARACTERIZATION

3.3.1 Intrinsic Viscosities

Intrinsic viscosity was used to measure relative molecular weight. A Cannon-Ubbelohde viscometer was used. The samples were dissolved in NMP at 25°C at four different concentrations. The data was analyzed by a linear extrapolation to zero concentration.

3.3.2 Spectroscopic Analysis

Fourier Transform Infrared Spectroscopy

A Nicolet MX-1 FTIR spectrometer was used to obtain IR spectra of either poly(amic acids) or the polyimide copolymers. The poly(amic acid) solution was dried on a salt plate in a vacuum oven at 70°C for several hours. The polyimide copolymers were analyzed either as free standing films or as a thin film dried onto a salt plate as above. The FTIR bands at 1778cm⁻¹ and 725cm⁻¹ were indicative of the imide structure and the band at 1546cm⁻¹ was indicative of the amic acid.
Proton Nuclear Magnetic Resonance

A Bruker WP 270 NMR was used to obtain $^1$H NMR Spectra. The samples were prepared by dissolving the polymer in either deuterated chloroform or dimethylsulfoxide at 3-5 % concentration. The samples were run at room temperature.

3.3.3 Thermal Analysis

Differential Scanning Calorimetry

A Dupont DSC 912 was used to determine glass transition temperatures by differential scanning calorimetry. The temperature range was from 50°C to 350°C at a rate of 10°C/min. The sample was heated, quickly cooled, and then heated a second time. The reported Tg’s were taken from the second scan. The Tg was determined by taking the midpoint of the change in slope of the baseline.

Thermogravimetric Analysis

A Dupont TGA 951 was used to determine the relative thermal stability of the copolymers. The samples analyzed were either
solution cast films or compressed powder samples. The temperature range was from 50°C to 800°C at a rate of 10°C/min in a nitrogen atmosphere. The weight loss is monitored as a function of time.

3.3.4 Solubility Studies

The solubility of the polyimide copolymers in various solvents was investigated. The sample, 0.56 g, was weighed into a sample vial and 5mL of the solvent was added. The solution was stirred with a magnetic stir bar for at least 12 hours; the solubility of the system was determined by the appearance of the final solution.

3.3.5 Gel Permeation Chromotography

Gel Permeation Chromotography was used as a qualitative measure of the molecular weights and molecular weight distributions of the copolymers. The polyimide samples were run in NMP on a Waters 150 GPC fitted with three styragel (10³, 10⁴, 10⁵) columns and utilizing a refractive index detector. The flow rate was 1.0 mL per minute.

3.3.6 Potentiometric Titration

Potentiometric titration was used to titrate the amine endgroups of the poly(arylene ether sulfone) oligomers. The
titration determines the absolute number average molecular weight of the oligomers. The oligomers were dissolved in a 2:1 (v/v) ratio of chlorobenzene to glacial acetic acid and titrated potentiometrically with 0.02 N anhydrous HBr in glacial acetic acid. Three determinations were run and averaged to determine oligomer molecular weight.
CHAPTER 4 - Results and Discussion

4.1 INTRODUCTION- Synthesis of the Segmented Copolymers

The polyimide copolymers in this work were all synthesized by a recently developed solution imidization method\textsuperscript{13}. This method used a cosolvent system to imidize the poly(amic acids) in solution at moderate temperatures. The solvent system used in this work was NMP/C$_6$H$_4$Cl$_2$, the NMP was used to solvate the system and the C$_6$H$_4$Cl$_2$ was used as the azeotroping agent.

All of the typical reaction conditions were adhered to in synthesizing the poly(amic acids). The glassware was clean, dried, and flame dried. The solvents were dried and freshly distilled, and the monomers were dried and stored properly prior to use. Syringes were used to handle the solvents and nitrogen was purged through the reaction set-up to maintain a dry system.

Number average molecular weight ($M_n$) of all the polymers was controlled through the addition of a monofunctional reagent, phthalic anhydride. The phthalic anhydride was added in a stoichiometric amount calculated from the Carothers equation, the target molecular weight was 25,000 g/mol. In addition to controlling the molecular weight, the monofunctionality ensured non-functional endgroups on the polymer preventing further chain extension during melt processing.
The research presented in this thesis involves the synthesis of two different series of poly(arylene ether sulfone)-polyimide segmented copolymers. The first series of copolyimides was synthesized from the monomers shown in Table 2, this group of polymers will be referred to as PAES-PI-A. The Bis-aniline P and the amine terminated poly(arylene ether sulfone) are both flexible segments in the polymer backbone, solubility and processability should be enhanced due to their presence. The BTDA is a polar, rigid structure and should contribute good thermal properties to the polymer characteristics. As described in the experimental section, the two step solution imidization method was employed here. The poly(amic acid) was synthesized and added dropwise to the hot azeotroping agent. The synthetic scheme is shown in Scheme 10. The poly(arylene ether sulfone) oligomers were substituted into the system as a weight percent of the total diamine content. Therefore if a polymer is referred to as having 10% PSF (13100), 10 weight percent of the diamine is the polysulfone oligomers and 90 weight percent is the Bis P diamine. The number in the parentheses is the molecular weight of the polysulfone oligomers.

The second series of copolyimides was synthesized from the monomers shown in Table 3, this group of polymers will be referred to as PAES-PI-B. The two dianhydrides, BTDA and PMDA, are both rigid structures that contribute to excellent thermal and mechanical properties. The DDS monomer introduces a kink in the backbone to
Table 2: Monomer Structures for Poly(Arylene Ether Sulfone)-Polyimide Segmented Copolymers

Bis Aniline P (Bis P)

Amine Terminated Polysulfone

Benzophenone Tetracarboxylic Dianhydride (BTDA)

Phthalic Anhydride (PA)
Scheme 10: Synthesis of Poly(Arylene Ether Sulfone)-Polyimide Segmented Copolymers
Table 3: Monomer Structures for Poly(Arylene Ether Sulfone)-Polyimide Segmented Copolymers Containing PMDA

Disaminodiphenyl Sulfone (DDS)

Amine Terminated Polysulfone

Benzophenone Tetracarboxylic Dianhydride (BTDA)

Pyromellitic Dianhydride (PMDA)

Phthalic Anhydride (PA)
break up the regularity of the chain. The -SO₂- group maintains high thermal stability as discussed previously. The poly(arylene ether sulfone) oligomers should once again provide flexibility, enhancing solubility and processability. Solubility is very important in this system. In earlier work, systems containing the PMDA monomer were not soluble throughout the solution imidization¹³. It was anticipated that the polysulfone oligomers would enhance solubility enough to allow solution imidization of these PMDA containing polymers. A slight variation in the original synthetic method was used for these polymers. Once again a two step method was employed, but only one reaction set-up was necessary. The poly(amic acid) was synthesized, the azeotroping agent was added to it and the solution was rapidly heated up to the imidization temperature. The synthetic scheme is shown in Scheme 11. The resulting polymer has four different segments as shown in Figure 1. In this system there were two diamines, two dianhydrides and the monofunctional endcapper. Once again weight percentages were used to substitute in the second diamine and dianhydride. The weight percentage of the polysulfone oligomers is displayed in the same manner as in the first series. The dianhydrides are displayed similarly. The weight percent shown will be the percentage of PMDA in the dianhydrides, the remainder being the BTDA in the system.
Scheme 11: Synthetic Scheme for Poly(Arylene Ether Sulfone)-Polyimide Segmented Copolymers Containing PMDA
Figure 1: Poly(Arylene Ether Sulfone)-Polyimide Segmented Copolymer Structure
4.2 SYNTHESIS OF POLY(ARYLENE ETHER SULFONE) OLIGOMERS

The amine terminated poly(arylene ether sulfone) oligomers were synthesized by nucleophilic aromatic substitution as shown in Scheme 12. All of the monomers and the potassium carbonate were charged into the reaction vessel and rinsed in with NMP and toluene. The potassium carbonate reacts with the bisphenol A to form a bisphenate salt. The e⁻ withdrawing sulfone group activates the dihalide. The phenoxide then displaces the halide and forms the ether linkage, the proposed mechanism is shown in Figure 2. The reaction is initially run at 155°C for approximately 2 hours. The toluene was then azeotroped off and the reaction was run at 160-170°C for 12 hours. The oligomers were precipitated into a methanol/water (4/1) mixture, filtered, washed and reprecipitated.

Three different molecular weights were synthesized: 8900, 13100, 18600 g/mol. The molecular weight was controlled by using a calculated amount of the endcapper, m-aminophenol, a sample calculation is shown in Sample Calculation 1. The actual molecular weight was determined by potentiometric titration of the amine endgroup. The amine is titrated with HBr as described in the experimental section. The titration results along with all other characterization data are shown in Table 5.

Intrinsic viscosities were run in methylene chloride or tetrahydrofuran at 25°C. The intrinsic viscosity was determined for the oligomer, the oligomer was chain extended and the intrinsic
**Dichlorodiphenyl Sulfone**

**Bisphenol A**

**m-Aminophenol**

\[ \text{K}_2\text{CO}_3 \]
\[ \text{NMP/} \beta \text{CH}_3 (15\% \text{ SOLIDS}) \]
\[ 155^\circ C \text{ for 2 hours} \]
\[ 160-170^\circ C \text{ for 12 hours} \]

**Amine Terminated Polysulfone**

Scheme 12: Synthesis of Poly(Arylene Ether Sulfone) Oligomers
Figure 2: Mechanism of Arylene Ether Sulfone$^{55}$
Sample Calculation 1: Amount of Monofunctional Reagent Needed to Control Molecular Weight

To calculate the amount of monofunctional reagent several equations are used. An example of the calculation is below for a polymer with a repeat unit molecular weight of 442.55 g/mol. The target molecular weight is 10,000 g/mol. The degree of polymerization (DP) is the average number of repeating units, and Xn is the number average degree of polymerization.

\[ \text{DP} = \frac{\text{Target Mol. Wt.}}{\text{Mol. Wt. of Repeat Unit}} \]
\[ \text{DP} = \frac{10,000 \text{g/mol}}{442.55 \text{g/mol}} = 22.60 \]

For difunctional monomers of the A-A, B-B type:
\[ Xn = 2(\text{DP}) = 45.19 \]
\[ Xn = 1+r/1-r \] where \( r \) is the stoichiometric imbalance of monomers with one present in excess. Rearranging and solving for \( r \) leaves:
\[ r = \frac{Xn-1}{Xn+1} = \frac{45.19-1}{45.19+1} = 0.9567 \]

In a system where the addition of small amounts of monofunctional reagent are used to control molecular weight of an A-A, B-B system \( r = \frac{\text{N}_A}{\text{N}_B}+2\text{N}_B' \), where \( \text{N}_A \) and \( \text{N}_B \) are the numbers of A and B functional groups. \( \text{N}_A \) and \( \text{N}_B \) will be twice the number of A-A, B-B molecules. \( 2\text{N}_B' \) is the number of B molecules present, which is the monofunctional reagent. The 2 is required because 2 moles of the monofunctional reagent are needed to maintain the stoichiometric imbalance \( r \). Assume \( \text{N}_A = 1 \) and \( \text{N}_B = r \):
\[ 0.9567 = 1/(.9567 + 2\text{N}_B'), \] solve for \( 2\text{N}_B' \)
\[ 2\text{N}_B' = .0886 \text{ mol. of monofunctional reagent.} \]
**Table 5: Experimental data for Poly(Arylene Ether Sulfone) Oligomers**

<table>
<thead>
<tr>
<th></th>
<th>8900</th>
<th>13100</th>
<th>18600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight of Oligomer (g/mol)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titrated Molecular Weights (g/mol)</td>
<td>8846</td>
<td>13172</td>
<td>18498</td>
</tr>
<tr>
<td></td>
<td>8846</td>
<td>13110</td>
<td>18641</td>
</tr>
<tr>
<td></td>
<td>8907</td>
<td>13083</td>
<td>------</td>
</tr>
<tr>
<td>([n]) in CH(_2)Cl(_2) at 25(^\circ)C (dL/g)</td>
<td>0.251</td>
<td>0.263</td>
<td>0.319*</td>
</tr>
<tr>
<td>*sample run in THF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([n]) in CH(_2)Cl(_2) at 25(^\circ)C (dL/g)</td>
<td>0.655</td>
<td>0.500</td>
<td>------</td>
</tr>
<tr>
<td>After chain extension with terephthaloyl chloride</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

T\(_g\) by DSC (\(^\circ\)C)  
172 175 181
viscosity was run again under the same conditions. The doubling of the intrinsic viscosity indicates a high value of difunctionality of the oligomer.

4.3 SOLUBILITY

Solubility and processability are two important characteristics studied in this research. The effect of incorporating poly(arylene ether sulfone) oligomers into this system was a major focus. The effect of oligomer molecular weight on the system was also examined. The solubility was determined by placing a sample of the polymer in a solvent at a 5% solution and allowing it to stir for 12-24 hours.

The PAES-PI-A polymers demonstrated good solubility prior to incorporation of the polysulfone oligomers. The control polymer (100% Bis P diamine) was soluble in NMP, DMAc, CHCl₃, CH₂Cl₂; as expected all of the copolymers were also soluble in these solvents. The Bis P diamine imparts enough chain flexibility to result in solubility in these solvents. A dependence on the polysulfone oligomers for solubility was evident in THF and C₆H₄Cl₂. At low percentages of polysulfone oligomer incorporation the polymers were either marginally soluble or insoluble in these solvents. At 40-60 weight percent polysulfone oligomer incorporation the polymers displayed complete solubility as shown in Table 6. The solubiliities
Table 6: Solubility Study of PAES-PI-A

<table>
<thead>
<tr>
<th>Wt% PSF</th>
<th>(C_6H_4Cl_2)</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>MS</td>
<td>IS</td>
</tr>
<tr>
<td>10%(8900)</td>
<td>MS</td>
<td>IS</td>
</tr>
<tr>
<td>20%(8900)</td>
<td>MS</td>
<td>IS</td>
</tr>
<tr>
<td>40%(8900)</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>60%(8900)</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>10%(13100)</td>
<td>MS</td>
<td>MS</td>
</tr>
<tr>
<td>20%(13100)</td>
<td>MS</td>
<td>MS</td>
</tr>
<tr>
<td>40%(13100)</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>60%(13100)</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>40%(18600)</td>
<td>MS</td>
<td>IS</td>
</tr>
<tr>
<td>60%(18600)</td>
<td>S</td>
<td>IS</td>
</tr>
</tbody>
</table>

**KEY:**
- \(C_6H_4Cl_2\): Dichlorobenzene
- THF: Tetrahydrofuran
- IS: Insoluble
- MS: Marginally Soluble
- S: Soluble
are defined as soluble, marginally soluble, or insoluble. Soluble meaning that all of the polymer went into the solvent and a clear solution was formed, marginally soluble meaning that some of the polymer went into solution but the solution was either cloudy or had particles of polymer remaining, and insoluble meaning apparently none of the polymer went into the solvent.

The PAES-PI-B polymers showed very different solubility characteristics due to the different monomer selection. The objective was to synthesize polymers containing PMDA through solution imidization that were soluble in dipolar, aprotic solvents and melt processable. As mentioned previously, PMDA containing homo- and random copolymers generally precipitated during solution imidization. The incorporation of poly(arylene ether sulfone) oligomers was proposed to help solubilize this system. The first reaction contained 10 weight % polysulfone oligomers of molecular weight 13100 g/mol and 10 weight % PMDA. This reaction remained soluble, hence the diamine content was kept constant (10 weight % polysulfone oligomers) and the PMDA weight percentages were increased until precipitation occurred. The precipitation occurred at 10 weight % polysulfone and 40 weight % PMDA. The weight percent of PMDA was kept at 40 and the weight percent of polysulfone was raised to 20. This reaction remained soluble, but the 20 weight % polysulfone, 50 weight % PMDA reaction precipitated. At this point the two other molecular weights were examined. The 10 weight % polysulfone, 40 weight % PMDA reactions of both 8900 and 18600
g/mol were run, and remained soluble throughout the imidization. The 10 weight % polysulfone, 50 weight % reactions were run for both molecular weights and both precipitated.

The solubility of the polymers that remained soluble throughout the imidization were studied. The solubility of the copolymers was not adversely affected by incorporation of the polysulfone oligomers or the PMDA. The incorporation of PMDA did not induce insolubility, and the incorporation of polysulfone oligomers did not induce solubility in low boiling solvents. All of the polymers are soluble in NMP, DMAc, DMSO and DMF and insoluble in CH$_2$Cl$_2$, CHCl$_3$, THF and C$_6$H$_4$Cl$_2$.

4.4 MOLECULAR WEIGHT ANALYSIS

Intrinsic viscosity measurements and gel permeation chromatography were used to analyze molecular weight. The intrinsic viscosity measurements were used to determine relative molecular weight. Gel permeation chromatography was used to examine the molecular weight distribution.

Intrinsic viscosity measurements were made in NMP at 25°C. The viscosities for the PAES-PI-A polymers are shown in Table 7 and
Table 7: Intrinsic Viscosity Data for PEAS-PI-A

<table>
<thead>
<tr>
<th>Wt% PSF</th>
<th>PSF $M_n$</th>
<th>$[n]$ (dL/g)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-----</td>
<td>0.69</td>
</tr>
<tr>
<td>10</td>
<td>8900</td>
<td>0.53</td>
</tr>
<tr>
<td>20</td>
<td>8900</td>
<td>0.49</td>
</tr>
<tr>
<td>40</td>
<td>8900</td>
<td>0.48</td>
</tr>
<tr>
<td>60</td>
<td>8900</td>
<td>0.30</td>
</tr>
<tr>
<td>10</td>
<td>13100</td>
<td>0.31</td>
</tr>
<tr>
<td>20</td>
<td>13100</td>
<td>0.49</td>
</tr>
<tr>
<td>40</td>
<td>13100</td>
<td>0.42</td>
</tr>
<tr>
<td>60</td>
<td>13100</td>
<td>0.39</td>
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<tr>
<td>40</td>
<td>18600</td>
<td>0.47</td>
</tr>
<tr>
<td>60</td>
<td>18600</td>
<td>0.41</td>
</tr>
</tbody>
</table>

* Intrinsic Viscosities were run in NMP at 25°C
for the PAES-PI-B polymers in Table 8. All of the viscosities are in the range from 0.30 to 0.69 dL/g. These values are consistent and high, concluding that high molecular weight polymer has been formed. The PAES-PI-A polymers formed tough, creasible films and the PAES-PI-B polymers formed brittle films.

Gel permeation chromatography was performed in NMP (0.1% LiBr) using styrigel columns. A typical GPC trace is shown in Figure 3. The bell shape of the raw trace indicates a Gaussian distribution of polymer chains.

4.5 THERMAL ANALYSIS

Differential scanning calorimetry (DSC) was used as the method of analysis to determine the glass transition temperatures of the copolymers synthesized. Thermogravimetric analysis (TGA) was used to determine the thermal stability of the copolymers. Solution cast films from NMP were used as the samples for analysis. The films were dried using a staged heating cycle similar to that used for bulk thermal imidization, it is important that an upper temperature of 300°C is maintained for 1 hour. Any residual solvent in the polymer will lower glass transition temperatures and result in poor thermal stability and mechanical behavior.
Table 8: Intrinsic Viscosity Data for PAES-PI-B

<table>
<thead>
<tr>
<th>Wt% PSF</th>
<th>PSF Mn</th>
<th>Wt% PMDA</th>
<th>[n] (dL/g)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>13100</td>
<td>0</td>
<td>0.38</td>
</tr>
<tr>
<td>10</td>
<td>13100</td>
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<td>13100</td>
<td>30</td>
<td>0.43</td>
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<tr>
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<td>13100</td>
<td>0</td>
<td>0.38</td>
</tr>
<tr>
<td>20</td>
<td>13100</td>
<td>40</td>
<td>0.44</td>
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<td>10</td>
<td>8900</td>
<td>0</td>
<td>0.46</td>
</tr>
<tr>
<td>10</td>
<td>8900</td>
<td>40</td>
<td>0.47</td>
</tr>
<tr>
<td>10</td>
<td>18600</td>
<td>0</td>
<td>0.34</td>
</tr>
<tr>
<td>10</td>
<td>18600</td>
<td>40</td>
<td>0.42</td>
</tr>
</tbody>
</table>

*Samples were run in NMP at 25°C*
Figure 3: GPC Trace for Poly(Arylene Ether Sulfone-Polyimide Segmented Copolymer
The DSC scans were run at a rate of 10°C/min from 50°C to 350°C. The sample is heated once, cooled to room temperature, and then heated a second time at the same rate. The glass transition temperatures reported are all taken from the second heat. A representative DSC scan for the copolymers is shown in Figure 4.

The PAES-PI-A polymers showed an interesting trend in the glass transition temperatures (T_g) as shown in Table 9. The glass transition temperature of the control polymer (100% Bis P) was the highest of the series. As the weight percent incorporation of polysulfone oligomers increases the T_g decreases. A plot of 1/T_g vs. Weight Fraction Polysulfone is shown in Figure 5. There appeared to be no significant effect of the molecular weight of the oligomers on the T_g's for the molecular weight range shown. For example, at 60 weight % incorporation polysulfone oligomers the T_g's for the three molecular weights are 212, 212 and 209°C.

The PAES-PI-B polymers also showed some interesting glass transition temperature trends, as shown in Table 10. Four control polymers were synthesized, these polymers contained percentages of the polysulfone oligomers with 100% BTDA. They were made to compare to the PMDA containing polymers. The control polymers compositions were 10% (13100), 20% (13100), 10% (8900) and 10% (18600). All four of these polymers have T_g's around 260°C, once again molecular weight does not seem to affect the T_g. The T_g of a BTDA/3,3'-DDS homopolymer containing no polysulfone oligomers was reported to be 265°C^{13}. It seems that the incorporation of the
Figure 4: DSC trace for Poly(Arylene Ether Sulfone)-Polyimide Segmented Copolymer
Table 9: Glass Transition Temperatures for PAES-PI-A

<table>
<thead>
<tr>
<th>Wt% PSF</th>
<th>PSF $M_n$</th>
<th>$T_g(°C)$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>---</td>
<td>264</td>
</tr>
<tr>
<td>10</td>
<td>8900</td>
<td>255</td>
</tr>
<tr>
<td>20</td>
<td>8900</td>
<td>239</td>
</tr>
<tr>
<td>40</td>
<td>8900</td>
<td>229</td>
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<td>20</td>
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<td>13100</td>
<td>212</td>
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<tr>
<td>40</td>
<td>18600</td>
<td>216</td>
</tr>
<tr>
<td>60</td>
<td>18600</td>
<td>209</td>
</tr>
</tbody>
</table>

*By DSC
Figure 5: Plot of 1/Tg vs Weight Fraction Of Polysulfone (PAES-PI-A)
### Table 10: Glass Transition Temperatures for PAES-PI-B

<table>
<thead>
<tr>
<th>Wt% PSF</th>
<th>PSF Mn</th>
<th>Wt% PMDA</th>
<th>Tg(°C)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>---</td>
<td>0</td>
<td>265 **</td>
</tr>
<tr>
<td>10</td>
<td>13100</td>
<td>0</td>
<td>261</td>
</tr>
<tr>
<td>10</td>
<td>13100</td>
<td>10</td>
<td>253</td>
</tr>
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<td>0</td>
<td>260</td>
</tr>
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<td>20</td>
<td>13100</td>
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<tr>
<td>20</td>
<td>13100</td>
<td>50</td>
<td>PPT</td>
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<tr>
<td>10</td>
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<td>286</td>
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<tr>
<td>10</td>
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<td>PPT</td>
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<td>286</td>
</tr>
<tr>
<td>10</td>
<td>18600</td>
<td>50</td>
<td>PPT</td>
</tr>
</tbody>
</table>

*By DSC

**Ref. 12

PPT- Polymer precipitated during polymerization
polysulfone oligomers did not have a drastic effect on the thermal transition as it did in the PAES-PI-A polymers.

The incorporation of PMDA into the polymer system along with the polysulfone oligomers produced some interesting results. As the percent of PMDA incorporated increased the glass transition temperature also increased significantly. The increase of polysulfone incorporation from 10 to 20% (13100) for the 40% PMDA polymer resulted in a soluble system with a high Tg, 284°C. The polysulfone oligomer molecular weight does not affect the Tg, demonstrated by comparing the three copolymers containing 40 weight % PMDA.

This series of polymers is an important step in the synthesis of modified polyimides. They demonstrate that by incorporating poly(arylene ether sulfone) oligomers, PMDA containing polyimides can be solution imidized. The rigid PMDA structure imparts excellent high temperature thermal and mechanical properties. The solution imidization advantage is that fully imidized are polymers in a highly usable physical form and melt processability may be possible with these polymers.

High thermal stability of polyimides is one of the most important characteristics to maintain in synthesizing modified systems. The poly(arylene ether sulfone) oligomers also exhibit high thermal stability, hence the copolymers should remain stable up to high temperatures.
TGA determines at what temperature the polymer sample starts to degrade by monitoring weight loss as a function of temperature. The film sample was heated at a rate of 10°C/min from 50°C to 800°C. A representative TGA trace for the segmented copolymers is shown in Figure 6. The polymers in both series displayed very similar behavior to the one shown, thermal stability was maintained up to 500°C by this method of analysis. This is typical behavior for polyimides in general, therefore thermal stability is not sacrificed with the incorporation of polysulfone oligomers.

4.6 Spectroscopy

Fourier Transform Infrared Spectroscopy is a method used to determine whether or not imidization is complete. There are several bands associated with either the poly(amic acid) or the imide structure. These bands can be monitored for their appearance or disappearance in the spectra. Figures 7 and 8 are representative FT-IR spectra of a poly(amic acid) and a copolyimide from the PAES-PI-A series.

The poly(amic acid) spectra shows strong absorption around 3300 cm⁻¹, this is the amide and carboxylic acid bands. There is a saturated region in the 1750-1000 cm⁻¹ range due to hydrogen bonding that can occur between highly polar groups. At 1546 cm⁻¹
Figure 6: TGA Trace for Poly(Arylene Ether Sulfone)-Polyimide Segmented Copolymer
Figure 7: FT-IR Spectrum of Poly(Amic Acid)
Figure 8: FT-IR Spectrum of Solution Imidized Polyimide
there is an amic acid band, this band can be monitored for conversion to imide.

The solution imidized polyimide spectra shows the 3300 cm⁻¹ peak no longer evident, and the 1750-1000 cm⁻¹ region sharpened. Peaks at 1776 and 702 cm⁻¹ have appeared, these are the imide carbonyl stretch and the imide band respectively. Other bands that can be identified are the following: 3100 cm⁻¹- aromatic protons, 2960 cm⁻¹- aliphatic protons, 1725 cm⁻¹- BTDA carbonyl stretch, 1480 cm⁻¹ aromatic C-C stretch and 1503 cm⁻¹- aromatic C-C stretching. Both of these spectra display the expected poly(amic acid) absorptions.

¹H-NMR was used to examine the chemical composition of the copolymers synthesized. A representative NMR spectra from each series of polymers is shown in Figures 9 and 10. The PAES-PI-A polymer contains 10% (13100) polysulfone oligomers, the spectra was run in deuterated chloroform. The PAES-PI-B polymer contains 10% (13100) polysulfone oligomers and 10% PMDA, this spectra was run in deuterated DMSO. Both spectra are void of peaks above the 10 ppm region where residual carboxylic protons would appear within experimental limitations. This demonstrates that quantitative conversion of the amic acid took place. The expected aromatic and aliphatic proton peaks were also present.
Figure 9: $^1$H-NMR Spectra of PAES-PI-A
Figure 10: $^1$H-NMR Spectra of PAES-PI-B
Chapter 5 - Conclusions

There were two major objectives to this research: 1) to improve solubility and processability of a polyimide system by incorporating poly(arylene ether sulfone) oligomers into the polymer chain, and 2) to maintain solubility of a PMDA containing polyimide system throughout the solution imidization procedure.

The poly(arylene ether sulfone) oligomers were synthesized by a nucleophilic aromatic substitution reaction. The molecular weight was controlled by adding a calculated amount of amine endcapper. The actual number average molecular weight of the oligomers was determined by potentiometric titration of the amine endgroups. The intrinsic viscosities were also indicative of the molecular weights. These amine terminated oligomers were substituted into the polyimide system as a weight percentage of the diamine, being readily soluble in NMP the oligomers were easily incorporated into the synthetic procedure.

The PAES-PI-A segmented copolymers synthesized from BTDA, Bis P, polysulfone oligomers, and monofunctional endcapper, phthalic anhydride, formed transparent, flexible films soluble in both high and low boiling solvents. In some cases, solubility was dependent upon the percentage of polysulfone oligomers. The copolymers maintained high thermal stability and relatively high glass transition temperatures, there was a dependence of the transition temperature on the level of polysulfone incorporation. Spectroscopy, both FT-IR
and NMR, showed complete conversion of the poly(amic acid) to polyimide.

Synthesis of PMDA containing polyimides (PAES-PI-B polymers) by solution imidization required the incorporation of poly(arylene ether sulfone) oligomers into the system. The oligomers solubilized the system to prevent precipitation of partially imidized species. The solubility of the resulting polymers was not affected by PMDA or polysulfone incorporation up to 40 weight percent PMDA. Excellent thermal stability and glass transition temperatures up to 286°C were demonstrated by these polymers. And an increase in the transition temperature with increasing PMDA content is an extremely important feature of these segmented polymers. FT-IR and NMR spectra were consistent with complete conversion of the poly(amic acid) segment to polyimide.
CHAPTER 6 - References


Societe Rhodiaceta, Netherland Pat. #6,690,214, 1967.


H.D. Burks and T.L. St.Clair, NASA TM# 84621, 1983


VITA

Diana Lee Wilkens, daughter of Larry and Joyce Wilkens, was born on June 23, 1965 in Westfield, New York. She attended elementary through high school at Westfield Academy and Central School, graduating in 1983. During her senior year, she attended college full-time at State University of New York at Fredonia through an early admission program. She graduated from SUNY @ Fredonia in May of 1987 with a Bachelor of Science degree in Chemistry and a minor in Psychology. During the summer of 1987, she moved to Blacksburg, Virginia, and joined Dr. James E. McGrath's research group at Virginia Polytechnic Institute and State University. In the fall of that year she entered graduate school there working towards a Master's degree. Her research efforts have been concentrated on the synthesis of modified polyimides.

Diana has accepted a product development chemist position at GE Silicones in Waterford, New York.