Synthesis and Characterization of High Performance Polyimide Homopolymers and Copolymers

by

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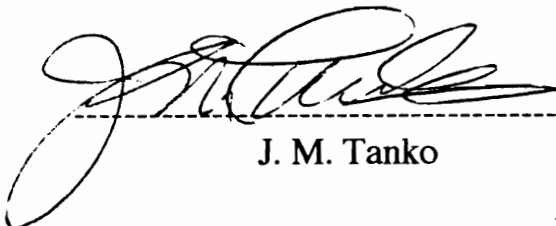
Doctor of Philosophy

in

Chemistry

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Synthesis and Characterization of High Performance Polyimide

Homopolymers and Copolymers

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(Abstract)

Polyimides are generally formed by combining a dianhydride and a diamine monomer in a polar aprotic solvent to form a poly(amic acid). The poly(amic acid) is then cyclodehydrated by either thermal or solution imidization at high temperatures to give the fully cyclized polyimides. This research focuses on the development of a low temperature solution polymerization route utilizing a transimidization method to make fully cyclized polyimide homopolymers and polyimide siloxane copolymers.

Polyimide oligomers endcapped with 2-aminopyrimidine were reacted with aminopropyl terminated poly(dimethyl siloxane) to give perfectly alternating segmented polyimide siloxane copolymers. The polymerization was conducted under very mild conditions. At reaction temperatures of only 100 - 110 °C in chlorobenzene, high molecular weight, fully imidized polyimide siloxane copolymers were obtained. The polyimide siloxane copolymers were cast into tough transparent films. Properties of the polyimide siloxane copolymers were found to be dependent on the molecular weight of the starting polyimide and poly(dimethyl siloxane) oligomers. The transimidization method was also applied to the synthesis of soluble, fully cyclized polyimide homopolymers at reaction temperatures as low as 60 °C. Utilizing the transimidization route, fully cyclized polyimides were made at lower temperatures than can be made by

conventional polyimide synthetic methods. The polymerization of the bis(N-pyrimidine phthalimide) derivative of 6F dianhydride and 4, 4' oxydianiline at ~65 °C in N-methyl pyrrolidone with acetic acid as a catalyst resulted in a high molecular weight, cyclized polyimide.

Fully cyclized, processable, fluorine containing polyimides were developed with very high glass transition temperatures and good thermal stability. The 1, 1-bis(4-aminophenyl)-1-phenyl-2, 2, 2-trifluoroethane (3F diamine) based polyimides were soluble and amorphous, probably as a result of the non-coplanar structure. DSC and dynamic mechanical analysis showed a glass transition temperature exceeding 420 °C for the PMDA-3F diamine based polyimide. These polyimides showed good thermooxidative stability at 600 °F in air after 500 hours.

This dissertation is dedicated
to Cheryl
who is my inspiration
and to my family for their unfaltering support.

Acknowledgments

Dr. Young Kim, Dr. Tom Moy, Mr. Gerry Meyer and Ms. Heather Brink for sharing their knowledge and expertise and for making the lab fun.

Ms. Cheryl Heisey, my wife, ~~who's~~ whose intellect, wisdom, work ethic and professionalism has been an example for me. I thank her for her constant love and support.

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CHAPTER 1 - INTRODUCTION

Since their development in the 1960's, polyimides have become an increasingly important class of materials finding a wide range of applications in the aerospace and microelectronics industry including composite matrix resins, moldings, adhesives, foams, coatings and interlayer dielectrics. Contributing to the success of the polyimides are their many desirable properties including good thermooxidative stability and excellent mechanical behavior (1-5). Several polyimides have been developed that are suitable as adhesives, coatings and matrix resins. However, further development of polyimides is required to meet increasing demands on high performance materials. For example, in advanced polymer composites, there is a well established need to produce polyimide resins that are processable and cost-effective, and can withstand temperatures of 600-700 °F (316-371 °C) for extended periods of time (6).

One approach to improve the properties of polyimides has been the introduction of fluorine containing monomers (7,8). The fluorine substituents can be incorporated as flexible bridging groups, bulky side groups or as substituents on aromatic rings. Fluorine containing polyimides have improved properties such as good thermal stability, better processability, and lower dielectric constants and water absorption.

A considerable effort has also been spent on synthesizing copolymers containing polysiloxane and polyimide segments (9,10). The incorporation of poly(dimethyl siloxanes) into polyimides has given copolymers with good processability, low water absorption, atomic oxygen resistance, low dielectric constants and excellent adhesion. The unique properties of the polyimide siloxane copolymers make them especially attractive for applications in microelectronics and as structural adhesives .

The most common approach to the synthesis of polyimides is the classical two step method (1). First, a dianhydride and a diamine are combined in a polar aprotic solvent to

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form the intermediate poly(amic acid). The poly(amic acid) is generally soluble but is hydrolytically unstable and has a relatively short shelf life. The second step is the cyclodehydration or imidization of the poly(amic acid) to the polyimide. Imidization can be carried out in several ways. One method, the bulk imidization method, involves casting films of the polyamic acid solutions and then heating the films in a stepwise process to effect imidization . The films must be heated to 300°C or higher to generate fully cyclized polyimides. Although the bulk imidization method is often used for insoluble polyimides, crosslinking can occur during thermal treatment which can limit the processability of the polyimides.

Soluble polyimides can be made by imidizing polyamic acids in solution at milder temperatures (11, 12). A cyclodehydrating agent is added to the polyamic acid solution and imidization is carried out at 150 to 180°C. The polyimide is then isolated in the fully imidized form and can be further processed. Synthesis of polyimides at ambient temperatures is carried out using chemical imidization methods (25, 26). The polyamic acid is cyclized by treating it with an aliphatic carboxylic acid dianhydrides and tertiary amines. However, due to isoimide formation, heat treatment of the polyimides is often necessary to achieve full cyclization.

The polyimide siloxane copolymers are also made through a poly(amic acid) precursor by combining a dianhydride and diamine monomer and an aminopropyl terminated polysiloxane (13). The polyamic acid is then cyclodehydrated by either thermal or solution imidization methods to give randomly segmented polyimide siloxane copolymers. A one step, solution polymerization process can also be used by combining the dianhydride and diamine monomer and an aminopropyl terminated polysiloxane in refluxing o-dichlorobenzene to form the randomly segmented polyimide siloxane copolymer (14).

One disadvantage of the classical two step polyimide synthesis is the poly(amic acid) intermediate. The poly(amic acid) is hydrolytically unstable and, thus, must be prepared under anhydrous conditions. Subsequently, the previously mentioned methods of imidization all require higher temperatures (> 150°C) or chemical agents to complete the cyclodehydration of the polyamic acids.

The first part of this research focuses on the synthesis and characterization of fully cyclized, soluble polyimides with very high glass transition temperatures to meet the demands for high performance applications. The 3F diamine containing a trifluorophenylethylidene bridging group was combined with several dianhydrides and diamines in an effort to form processable, thermally stable, high Tg polyimides. These polymers were made by solution imidization techniques, and the polymer molecular weights were controlled by adding a monofunctional, nonreactive endgroup. All of the 3F diamine containing polyimides were soluble and had Tg's which varied from 315 °C to 430 °C. Several of the 3F diamine containing polyimides were evaluated for their long term thermal stability.

The second part of the research describes the use of a transimidization method in the synthesis of polyimide homopolymers and multiblock copolymers. Model reactions were carried out to determine the conditions under which the transimidization reaction would proceed. It was discovered that soluble, aromatic polyimides could be made at low temperatures using the transimidization route. Subsequently, aminopropyl terminated poly(dimethyl siloxane) oligomers reacted quickly with functionalized polyimide oligomers using the transimidization technique. The polysiloxane and polyimide oligomers were combined in chlorobenzene to make perfectly alternating segmented polyimide siloxane copolymers. The transimidization reactions were optimized for the synthesis of polyimide homopolymers and polyimide siloxane copolymers.

Since the architecture of the perfectly alternating segmented polyimide siloxane copolymers is novel, the thermal and mechanical properties of these copolymers were explored. These properties were related to the size and composition of the polyimide and polysiloxane segments. Randomly segmented polyimide siloxane copolymers were also synthesized. The thermal and mechanical properties of the randomly segmented polyimide siloxane copolymers were compared to analogous perfectly alternating segmented copolymers.

In the Chapter 2 literature review, a discussion of common synthetic methods used to make polyimides and polyimide siloxane copolymers will be presented. In addition, structure-property relationships of polyimides, fluorine containing polyimides, and polyimide siloxane copolymers will be reviewed. Chapter 3 will outline various monomers and reagents used in this research along with the synthetic and analytical procedures. Chapter 4 presents and discusses the experimental results, followed by the conclusions.

CHAPTER 2 - LITERATURE REVIEW

2.1 INTRODUCTION

Over the past three decades, polyimides have become an increasingly important class of polymers. Their excellent thermal and mechanical properties make them well suited for many high performance applications such as composite matrix resins, moldings, adhesives, foams, coatings, electronic packaging and interlayer dielectrics. There are literally thousands of published articles concerning the synthesis and properties of polyimides. Several good review articles and books are available on polyimides (1-5).

This literature review is not comprehensive, but serves as a background to the experimental section that follows. The research in this dissertation and the literature review cover several topics in polyimide chemistry. The first section discusses common synthetic methods used to make polyimides. The next section deals with molecular weight control and the properties of several fluorinated polyimides. The final sections cover some aspects of block copolymers and the synthesis and structure-property relationships of polyimide siloxane copolymers.

2.2 SYNTHESIS OF POLYIMIDES

The most common and documented method of making polyimides is the classical two step synthesis depicted in Figure 2.2.1 (15-20). In the first step, a poly(amic acid) is made by adding a dianhydride to a diamine dissolved in a polar aprotic solvent. The poly(amic acid) can then be cyclodehydrated by either thermal or chemical means to form the polyimide.
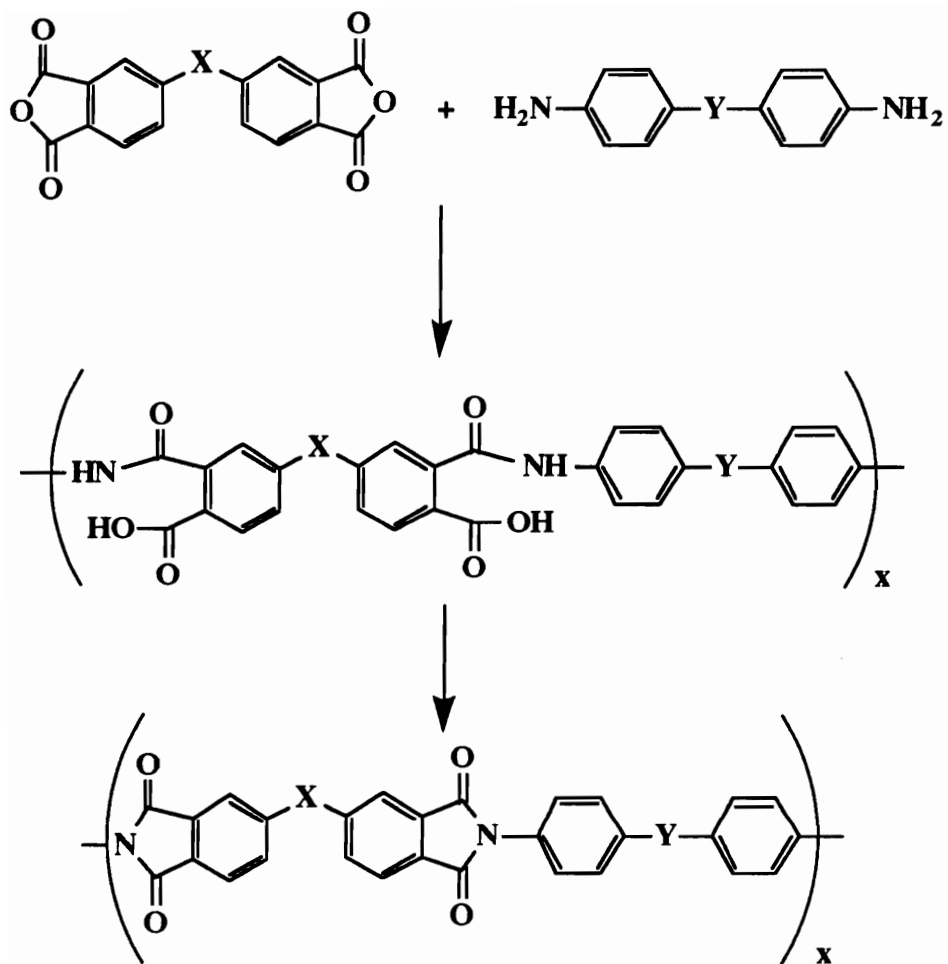
Figure 2.2.1 - Two Step Synthesis of Polyimides

2.2.1 Poly(amic acid) Synthesis

The synthesis of the poly(amic acid) is an equilibration reaction that proceeds by the mechanism shown in Figure 2.2.2 (21, 22). The reaction involves the nucleophilic substitution of one of the anhydride carbonyl carbons by an amine. One unique feature of this reaction is that the carboxyl group that is formed from the substitution reaction cannot be physically removed from the reaction mixture. However, the acid can be "chemically" removed to drive the reaction to the right (21, 22). Polar aprotic solvents such as N-methyl pyrrolidone (NMP) or dimethyl acetamide (DMAc) form strong hydrogen bonds with the protons of the carboxyl group. The solvation of the carboxyl groups limits the reverse reaction and drives the reaction to the right. High molecular weight poly(amic acid)s can then be made from a wide variety of dianhydrides and diamines. Relatively unreactive monomers can still combine to form high molecular weight polyimides in polar aprotic solvents but in a longer period of time.

The equilibration of the poly(amic acid) has a significant effect on the molecular weight and molecular weight distribution of the polymer. In the past, it was observed that the viscosity of the poly(amic acid) deteriorated over time. At first, it was thought that chain scission of the poly(amic acid) occurred through hydrolysis (16, 23). But, it was later found that the decrease in the molecular weight and viscosity was due to the equilibrium of the poly(amic acid) with the starting anhydride and amine.

It appears that upon adding a solid dianhydride to a diamine solution the weight average molecular weight, <Mw>, builds rapidly (1). Since the dianhydride was slow to dissolve, the stoichiometric reaction of the solid dianhydride and the diamine solution occurs at the interface (24). Large molecules were formed and, initially gave a large molecular weight distribution. Over time, the poly(amic acid) equilibrated and the <Mw> decreased to a most probable molecular weight distribution.

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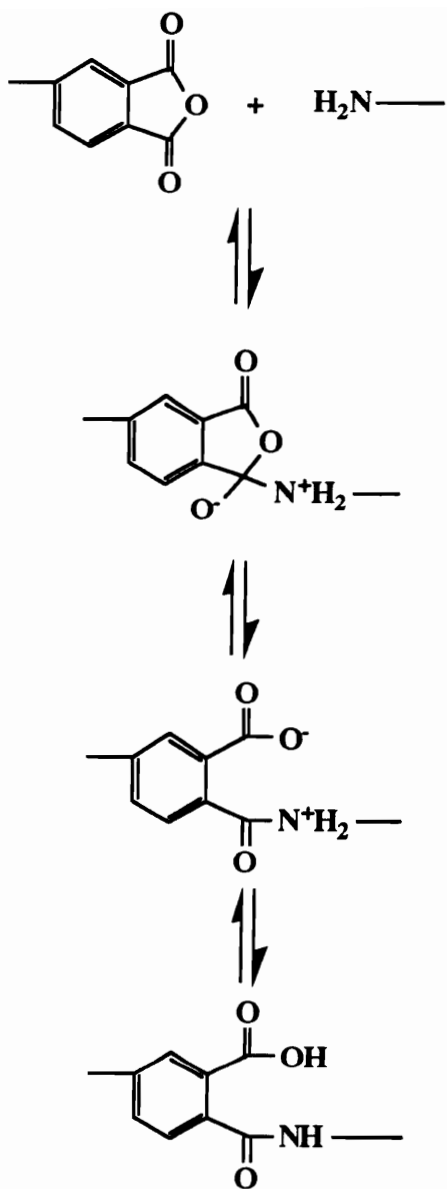
Figure 2.2.2 - Mechanism of Poly(amic acid) Formation (1)

This equilibration was dramatically demonstrated by Cotts and coworkers (25). Two poly(amic acid)s with different molecular weights were combined and observed by gel permeation chromatography (GPC). At first, the GPC traces showed two peaks, but over time, the peaks merged to give one peak with a gaussian or most probable molecular weight distribution.

The viscosity decrease was thought to occur by either hydrolysis (15, 16) or equilibration through transamidation (25, 26). Recently, it was shown that the equilibration occurs through the degradation of the poly(amic acid) to generate anhydride and amine end groups (27, 28). The poly(amic acid) cleaved and recombined in a statistical fashion so that a most probable molecular weight distribution was achieved.
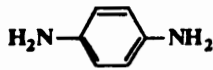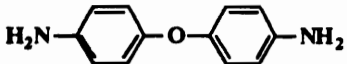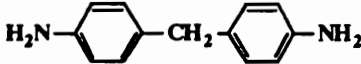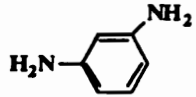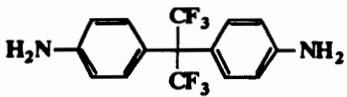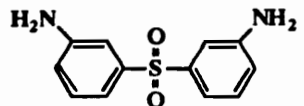
The equilibration of the poly(amic acid) with the starting anhydride and amine was consistent with other observations. For example, the poly(amic acid) formation is an exothermic reaction. Raising the reaction temperature decreased the polymer molecular weight (29). In addition, adding excess dianhydride or diamine monomers to a poly(amic acid) solution decreased the poly(amic acid) molecular weight (1). Finally, the molecular weight of the poly(amic acid) solution was lowered when the solution was diluted (1).

As was mentioned, poly(amic acid) formation involves the nucleophilic substitution of an anhydride carbonyl by an amine. The more electrophilic the anhydride is the quicker the reaction will proceed. A good estimate of an anhydrides electron acceptor properties is its electron affinity, Ea (1). The electronic affinity of several dianhydrides are given in Table 2.2.1. Higher Ea values suggest greater reactivity of the dianhydride. Ando and coworkers related the [15]N n.m.r chemical shift to the reactivity of aromatic diamines (30). Higher [15]N n.m.r. chemical shift values indicate lower reactivity. Table 2.2.2 lists the [15]N n.m.r. chemical shifts of several diamines. This order of chemical shifts can be regarded as the order of acylation reactivity. As expected,

Table 2.2.1 - Electron Affinity Values for Several Dianhydrides (1)

Dianhydride	Abbreviation	Ea(eV)
	PMDA	**1.90**
	DSDA	**1.57**
	BTDA	**1.55**
	BPDA	**1.38**
	ODPA	**1.30**

Table 2.2.2 - ^{15}N NMR Chemical Shifts of Several Diamines (30)

Diamine	Abbreviations	^{15}N Chemical Shift
H_2N—⟨ ⟩—NH_2	pPD	53.8
H_2N—⟨ ⟩—O—⟨ ⟩—NH_2	4, 4'-ODA	57.9
H_2N—⟨ ⟩—CH_2—⟨ ⟩—NH_2	MDA	59.4
H_2N—⟨ ⟩ with NH_2	mPD	60.8
H_2N—⟨ ⟩—C(CF_3)_2—⟨ ⟩—NH_2	6F diamine	64.0
H_2N—⟨ ⟩—SO_2—⟨ ⟩—NH_2	mDDS	65.7

diamines with electron withdrawing bridging groups are less reactive than those with electron donating bridging groups.

The synthesis of the poly(amic acid)s must be performed under anhydrous conditions. The presence of water in the poly(amic acid) solution has resulted in the hydrolysis of the anhydride and, thus, limits the molecular weight of the poly(amic acid). Therefore, the monomers and solvents should be carefully dried.

2.2.2 Bulk Imidization

The poly(amic acid) can be thermally imidized by either bulk imidization methods or solution imidization methods. Bulk imidization is the most common method of imidization and often used when making insoluble polyimides (31-39). The poly(amic acid) maybe in film, fiber or powder form. Bulk imidization is then carried out by heating the poly(amic acid) in stages. Complete cyclization and solvent removal is accomplished by heating the sample above the ultimate Tg of the polyimide. Insoluble and infusible polyimides cannot be processed once they are imidized. Side reactions can occur during bulk imidization which lead to crosslinking (33, 40, 41). These crosslinking reactions often yield insoluble polyimides which otherwise might be soluble.

2.2.3 Solution Imidization

Soluble polyimides can be completely cyclized by imidization of a poly(amic acid) in solution (11, 12, 42, 43). Since the poly(amic acid) has greater mobility in solution than in the solid state, imidization can be achieved at lower temperatures. To effect imidization, the poly(amic acid) solution is heated to 150 °C to 180°C. An azeotroping agent, such as o-dichlorobenzene (ODCB), xylene or cyclohexyl pyrrolidone (CHP), is added to remove the water that is generated during the reaction. Complete imidization can be achieved within 16 to 24 hours. If the polyimide is insoluble, it precipitates during the

reaction before imidization is complete. Otherwise, the system will remain homogeneous.

The solution imidization method does not expose the polymers to the high temperatures required in the bulk imidization method. Subsequently, there are few, if any, side reactions which occur during solution imidization that can cause crosslinking and insolubility. Solution imidized polyimides were more soluble than the analogous bulk imidized polyimides (13).

Kim and coworkers investigated the mechanism of solution imidization (44). Figure 2.2.3 shows the relation of % amic acid and intrinsic viscosity to reaction time. Initially, the viscosity of the polymer decreased until it reached a minimum. The viscosity then increased and leveled off near the end of the reaction. Kim was able to demonstrate that the poly(amic acid) chain cleaved to form anhydride (carboxyl) and amine endgroups. As the reaction proceeded, the endgroups could be recombined to form imides.

Kim and coworkers proposed the mechanism for imidization depicted in Figure 2.2.4 (44). The solution imidization was determined to proceed by auto acid catalyzed second order kinetics. The rate determining step was the nucleophilic substitution of the carboxyl carbon by the amide nitrogen. The water generated was removed from the system and complete cyclization was achieved.

Other solution imidization methods have involved the use of phenolic solvents. Polyimides have been formed in one step at 180 to 220 °C in such solvents as m-cresol (45-47).

2.2.4 Chemical Imidization

Polyimides can be prepared at ambient temperatures using chemical imidization methods (48-51). The poly(amic acid) is cyclized by treating it with an aliphatic carboxylic acid dianhydrides and tertiary amines. The mechanism of chemical
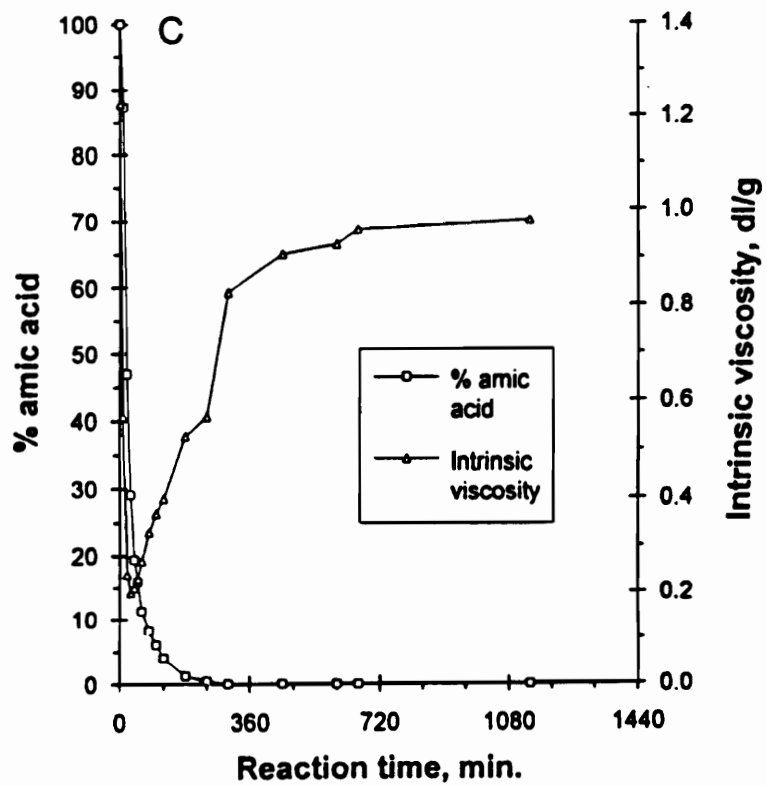
Figure 2.2.3 - Relation of % Amic Acid and Intrinsic Viscosity to Reaction Time in the Solution Imidization of a Poly(amic acid) (44)
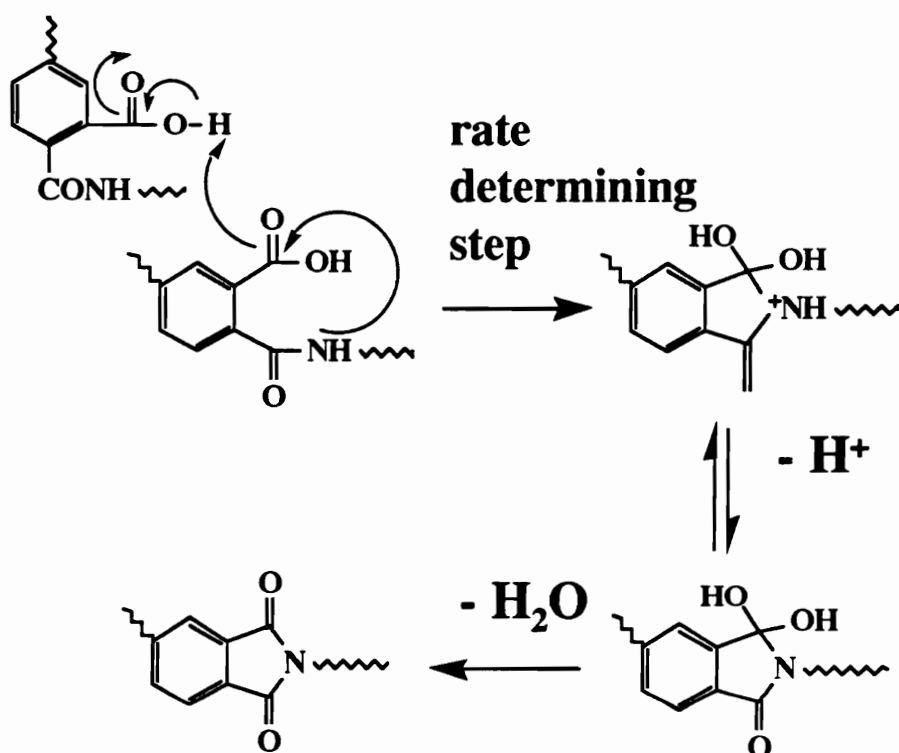
Figure 2.2.4 - Mechanism of Imidization in the
Solution Imidization of Poly(amic acids) (44)

imidization is shown in Figure 2.2.5 (1). The acid group on the polymer reacts with the acetic acid to form an acetate group. The acetate is an improved leaving group so cyclization takes place at low temperatures. However, due to isoimide formation, heat treatment of the polyimides is often necessary to achieve full cyclization.

2.2.5 Ester-acid Route to Polyimides

Another synthetic route to polyimides involves the combination of diester-diacid derivatives of aromatic tetracarboxylic dianhydrides and aromatic diamines in solution (52). The synthesis of polyimides by the ester-acid route is shown in Figure 2.2.6. The diester-diacid derivative is made by combining a dianhydride with an alcohol such as ethanol. The diester-diacid is then combined with a diamine in an NMP/ODCB mixture and heated to 180 °C. High molecular weight polyimide is achieved within 8 to 24 hours.

The ester-acid route has several advantages over the poly(amic acid) route using dianhydrides and diamines. As mentioned previously, the dianhydrides and the poly(amic acid)s are very susceptible to hydrolysis. The diester-diacid monomers are not sensitive to hydrolysis and, therefore, small amounts of moisture have little effect on the polymerization (52).

2.2.6 Transimidization Route

Spring and Woods first reported the transimidization reaction using a phthalimide and methyl amine (53). Later, Imai adapted the transimidization reaction to make high molecular weight polyimides (54). As depicted in Figure 2.2.7, reacting N,N' bis (ethoxycarbonyl) pyromellitimide and an aromatic diamine for 7 days at ambient temperatures gave a high molecular weight polyamide amide. It was necessary to heat the intermediate to 240 °C to obtain the cyclized polyimide.
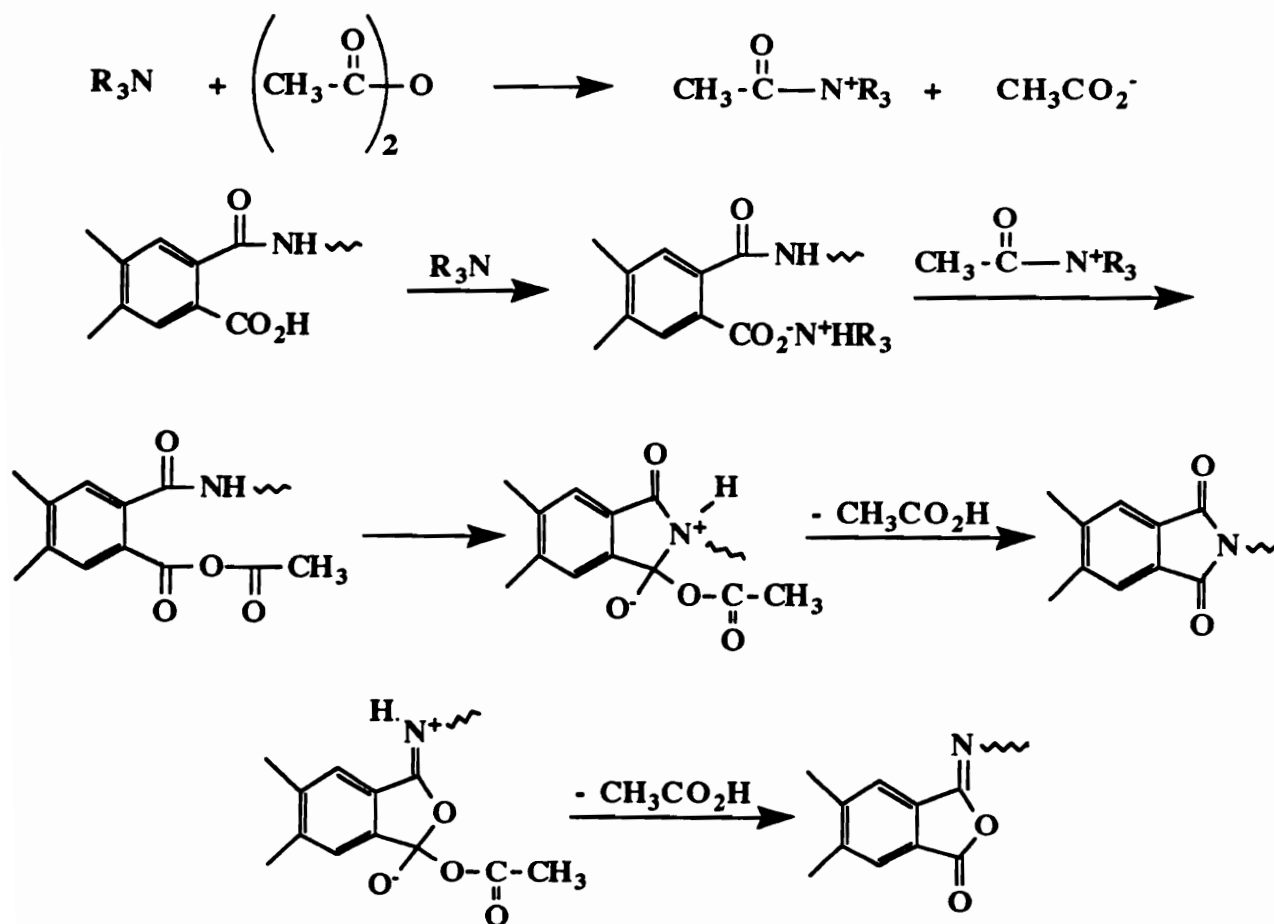
Figure 2.2.5 - Reaction Mechanism for the Chemical Imidization
of a Poly(amic acid) (1)
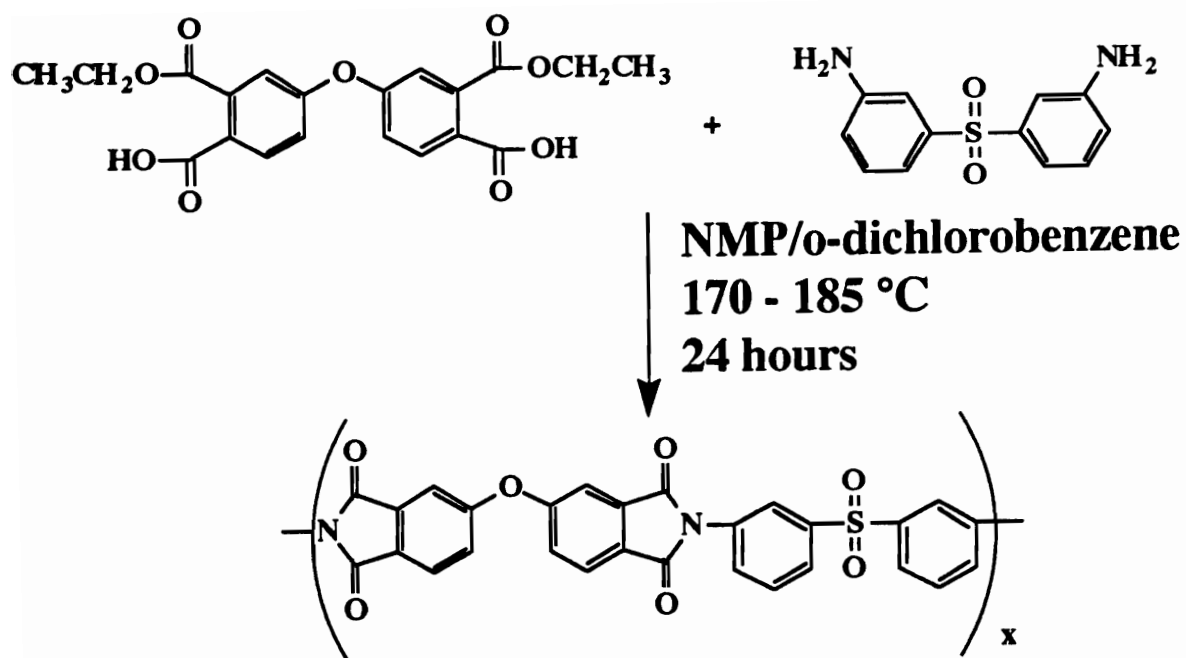
Figure 2.2.6 - Synthesis of Polyimides by the Ester-Acid Route (52)
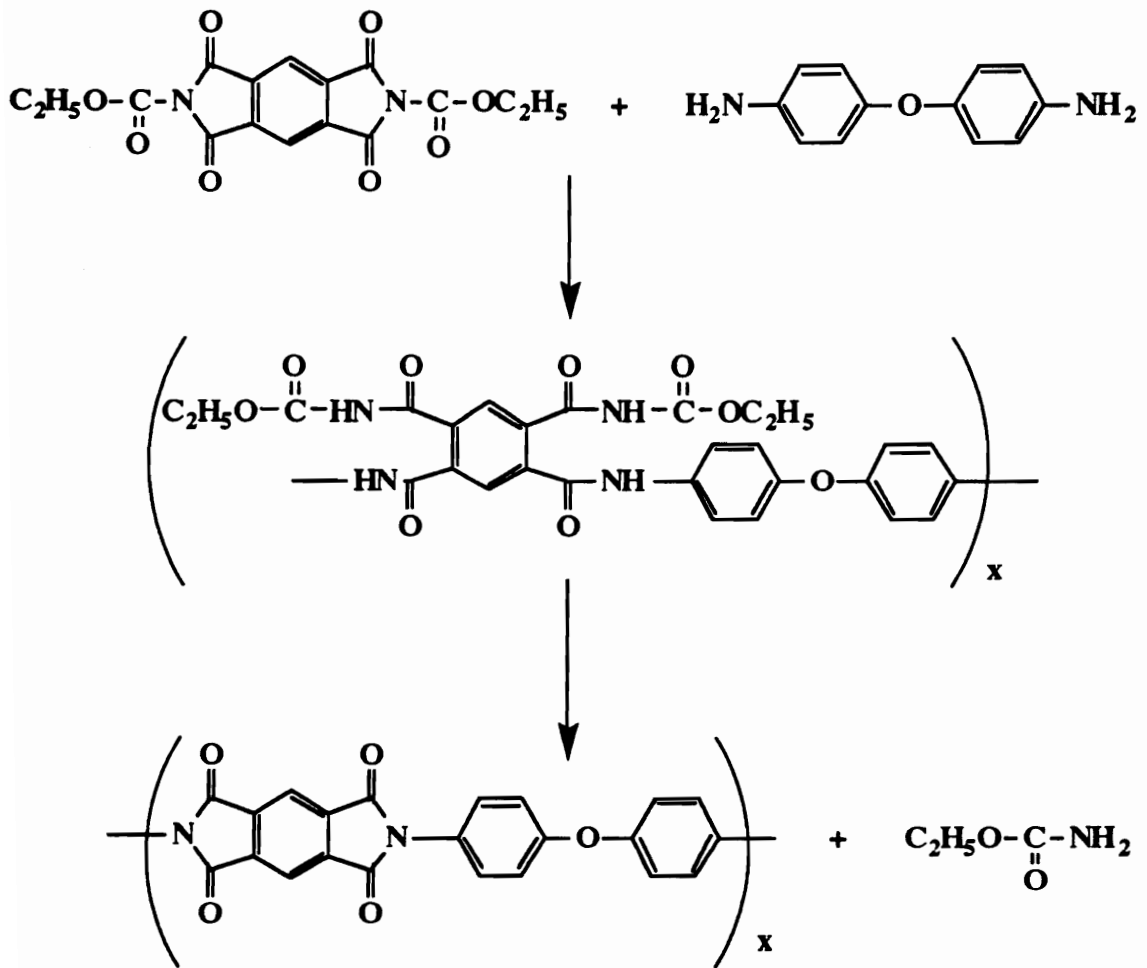
Figure 2.2.7 - The Synthesis of a Polyimide by the Transimidization Route (54)

Takekoshi and coworkers studied the transimidization reaction extensively (55, 56). Results of model studies between p-toluidine and several N-substituted phthalimides are listed in Table 2.2.3. The reactions were performed at high temperatures without any catalyst. Of the six N-substituted phthalimides studied, N-pyridine phthalimide was the most effective in reacting with p-toluidine. Subsequent model studies showed that metal compounds, such as zinc acetate, were effective in catalyzing the reaction of N-substituted phthalimides and aromatic amines.

For the imide-amine exchange reaction between a phthalimide and a diamine to proceed to high conversion, the diamine should be more nucleophilic or basic than the monoamine that is displaced. 2-aminopyridine with a pKa value of 27.7 (57) is less basic than most aromatic and aliphatic diamines and, as demonstrated, is readily displaced in the transimidization reaction.

Various N, N' - pyridine bisphthalimides were reacted with various diamines to make poly(ether imide)s (55, 56). In the first step, prepolymer or oligomer was formed in *o*-dichlorobenzene. The solvent was then removed and the reaction was completed in the melt at 230 °C to 290 °C. High molecular weight polymers were formed using transimidization chemistry.

2.3 MOLECULAR WEIGHT CONTROL OF POLYIMIDES

There is generally a dependence between the molecular weight, MW, and the physical properties of a polymer (58, 59). Figure 2.3.1 shows the relation between the number average molecular weight, <Mn>, and properties such as modulus, tensile strength and the glass transition temperature. The properties increase significantly with increasing molecular weight until the critical entanglement molecular weight of the polymer is obtained. Upon entanglement, a plateau is reached and increasing the

Table 2.2.3 - Model Reactions of the Reaction between p-Toluidine and N-Substituted Phthalimides (55)
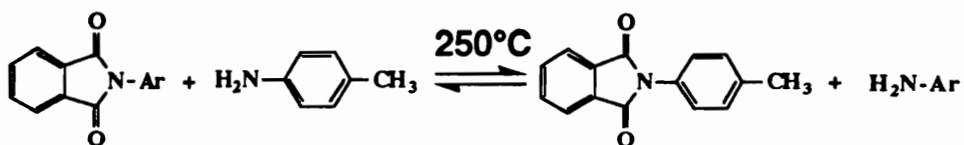
Ar	Conc. (mol/l)	k_1 (l·mol^{-1}·min^{-1})	K
(2-pyridyl)	3.0	27	2000
(2-nitrophenyl)	2.67	12.0×10^{-2}	1100
(3,5-dichlorophenyl)	2.5	1.2×10^{-2}	264
(2,3-dichlorophenyl)	2.5	1.3×10^{-2}	173
(2-chlorophenyl)	2.7	$0.44 + 10^{-2}$	46
(4-chlorophenyl)	2.7	0.34×10^{-2}	2.7
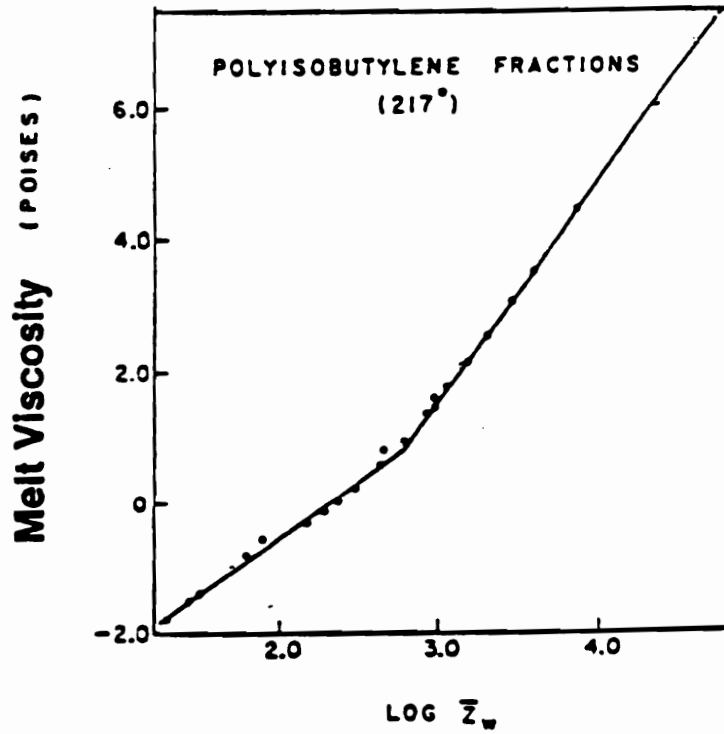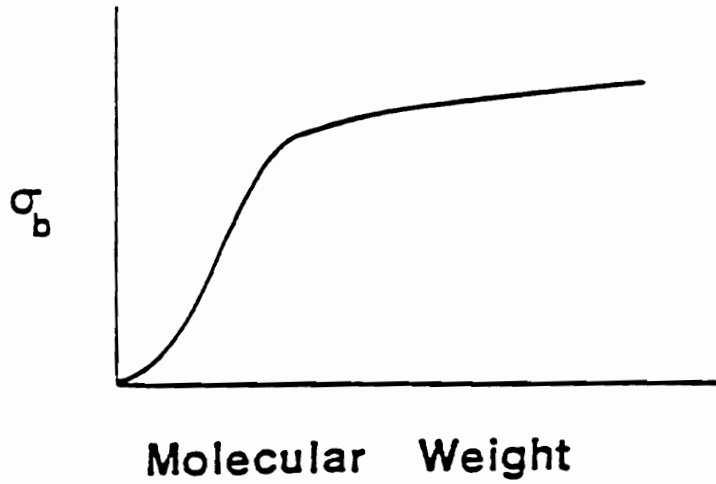
Figure 2.3.1 - Relation of Molecular Weight to Physical Properties
and Processability (58, 59)

molecular weight only has a small effect on polymer properties. The relationship between molecular weight and polymer properties can be estimated as:

Polymer Property = Polymer Property at infinite MW - K$<$Mn$>^{-1}$

where K is a constant.

Rheological properties, such as melt viscosity, increase with increasing weight average molecular weight. The relationship between melt viscosity and molecular weight is depicted in Figure 2.3.1. At low molecular weight, the melt viscosity is given by **n = K$<$Mw$>^{1.0}$**. The melt viscosity is given as **n = K'$<$Mw$>^{3.4}$** above the critical molecular weight or entanglement of the polymer.

Above the entanglement point, increasing the molecular weight only modestly increases the polymer physical properties, but tremendously increases the melt viscosity. Increasing the molecular weight not only increases the viscosity but decreases the solubility and processability in general. The molecular weight must be above the entanglement molecular weight to obtain good physical properties. However, the molecular weight can be controlled to preserve processability.

For many linear polyimides, the molecular weight required to attain good physical and mechanical properties is approximately 20 to 30 kg/mole (60). The molecular weight is generally controlled by offsetting the stoichiometry in an exact way as determined by the Carothers equation (61). The endgroups of the polymer consists of the reactive group, either an amine or anhydride, of the monomer used in excess. Reactive end groups, particularly amines, significantly decrease the thermal stability of the polyimides (62). The polymers can be endcapped with monofunctional endgroups to obtain controlled molecular weight polymers with nonreactive endgroups (12). Examples of monofunctional, nonreactive endgroups include phthalic anhydride and aniline. The nonreactive end groups also improve the processability of polyimides, since they do not react even at the higher temperatures experienced during melt processing. Amine

endgroups can react during melt processing causing the polymers to crosslink and the melt viscosity to increase.

Molecular weight control techniques have been used to make functional oligomers with reactive endgroups (63-66). Polyimide oligomers with maleimide, norbornene or ethynyl end groups have been reacted to form crosslinked polymers.

2.4 PROPERTIES OF FLUORINATED POLYIMIDES

In general, polyimides have excellent mechanical and thermal properties which make them very attractive in a variety of high performance applications as high temperature, composite matrix resins, moldings, adhesives, wire coatings and interlayer dielectrics . As the requirements for many applications, particularly in the microelectronics and aerospace industries, have become more sophisticated, there has been a need for improving the properties of conventional polyimides. Polyimides with high glass transition temperatures, good long term thermal stability, lower dielectric constants and water absorption, improved optical properties and better processability are necessary (6, 67, 68). For example, the most common polyimide is the PMDA-ODA (Kapton™) polyimide shown below in Figure 2.4.1. Kapton is a rigid polymer with a high Tg, and good thermal stability and mechanical properties, but is unsuitable for many applications due to its insolubility and infusibility. In addition, it has a high water absorption and high dielectric constant which limits its use in the microelectronics industry (69, 70).
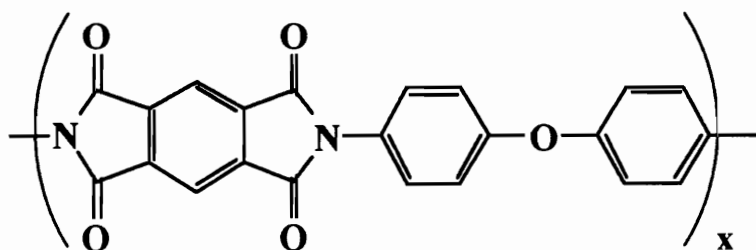
Figure 2.4.1 - PMDA-ODA or Kapton Polyimide
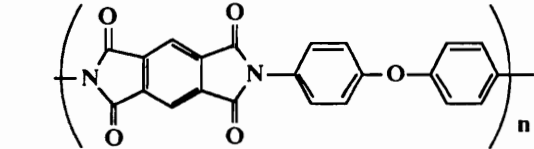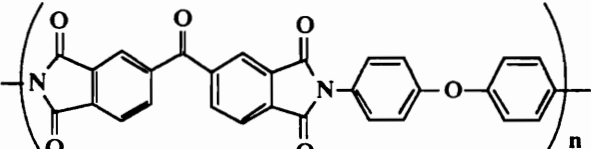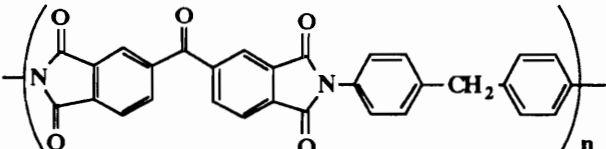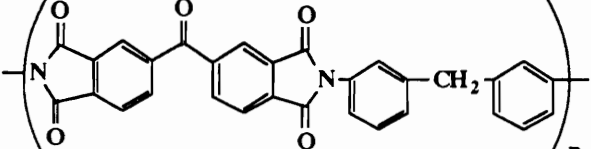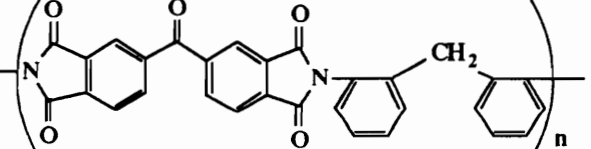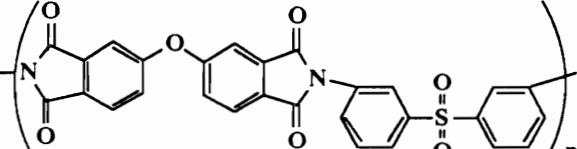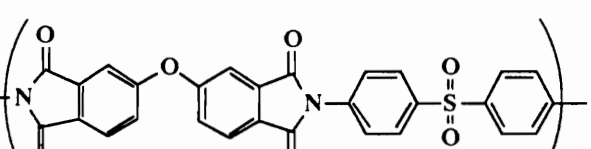
A major effort in the past few decades has been directed at improving the properties of polyimides. Processability of polyimides has been greatly enhanced by incorporating flexible spacers (69-73). Hexafluoroisopropylidene, isopropylidene, oxygen, carbonyl and sulfonyl bridging groups between rings increase opportunities for bond rotation which decreases Tg's and increases solubility. Also, incorporating non-symmetrical monomers with meta and ortho linkages cause structural disorder in the polymer chain which improves processability (4, 69). Table 2.4.1 lists numerous polyimides which shows the effect of polyimide structure on the Tg.

Flexible bridging groups, such as ether and carbonyl groups, have been incorporated in processable, semicrystalline polyimides. A recent example is the LARC-CPI polyimide developed by NASA-Langley (73). LARC-CPI has a melting point near 370 °C and a Tg of 220 °C. The semicrystalline nature of LARC-CPI has been extensively investigated by Muellereile and coworkers (74).

Gains in flexibility are sometimes offset by decreases in thermal stability. Figure 2.4.2 compares the relative thermal stability of a number of dianhydrides and diamines. While the dianhydride structure does not profoundly effect polyimide stability, the effect of the diamine structure is significant (75). In general, electron deficient diamines afford more oxidatively stable polyimides than electron rich diamines (69, 75).

Fluorine containing polyimides show improved processability, lower dielectric properties, and good optical properties while maintaining excellent thermal stability. Fluorine can be incorporated as bridging groups, as bulky side groups or as substituents on aromatic rings. Fluorine containing polyimides have found applications as composite matrix resins (76, 77), interlayer dielectrics used in microelectronics (78-82) and as gas separation membranes (83-85).

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Table 2.4.1 - Effect of Polyimide Structure on the Glass Transition Temperature (4, 73)

Polyimide	Tg (°C)
	399
	279
	290
	232
	285
	253
	310
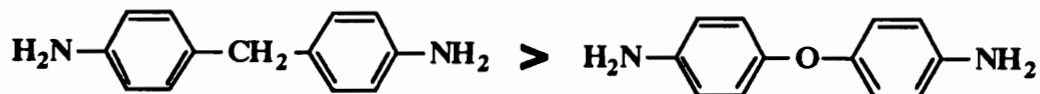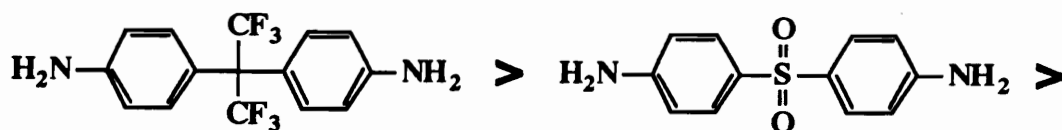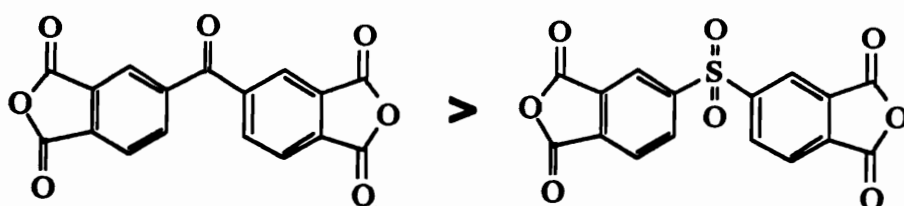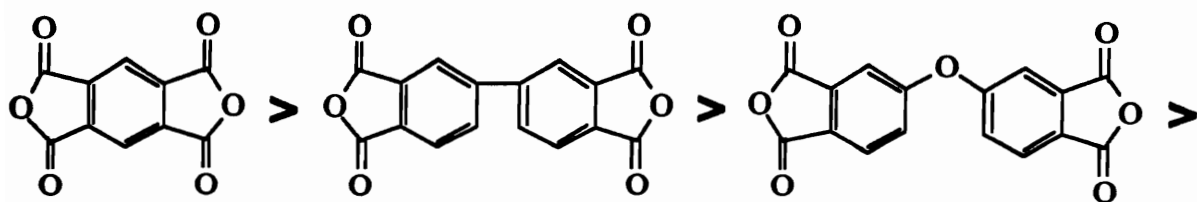
Figure 2.4.2 - Relative Thermal Stability of Dianhydrides and Diamines (75)

27

The most common fluorine containing polyimides are derived from monomers with the hexafluoroisopropylidene or 6F bridging group (7). One of the first polyimides incorporating the 6F group was patented by Rogers in 1967 (86). Later, commercial fluorine containing polyimides appeared in 1972 in the form of Du Pont's NR-150™ polyimides. NR-150B™ (Avimid N), Figure 2.4.3, is one of the most thermally stable commercial polyimides available with a maximum use temperature of 316 °C (76).
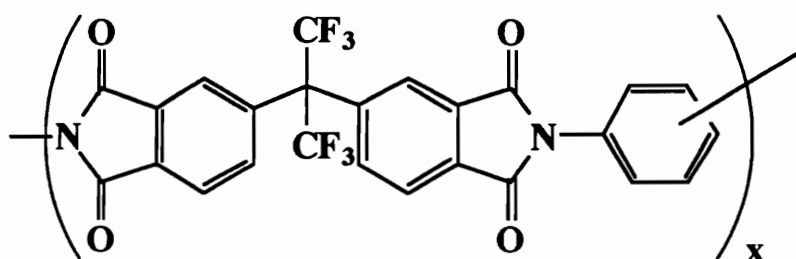
Figure 2.4.3 - NR-150B (Avimid N)

The glass transition temperatures of several polyimides made from 6F dianhydride are listed in Table 2.4.2. The Tg's range from 229 °C to 365 °C with the more rigid diamines giving higher Tg's (87). All of the polyimides are melt processable and many can be made by solution imidization methods since they remain soluble in the fully imidized form (12, 63).

The 6F group has also been successfully incorporated into the diamine portion of polyimides. 4, 4'-(hexafluoroisopropylidene) dianiline or p-6FDAM, Figure 2.4.4 has been reacted with several dianhydrides. Polyimides from p-6FDAM and PMDA have Tg's near 430 °C while the meta - 6FDAM gives a Tg near 290 °C (88). Polyimides from the m-6FDAM and 6F dianhydride form colorless films with a Tg of 260 °C (89).

28

Table 2.4.2 - Glass Transition Temperatures of 6F Dianhydride Containing Polyimides (87)

Polyimide	Tg (°C)
	229
	285
	283
	291
	348 ref. 46
	297
	336
	365
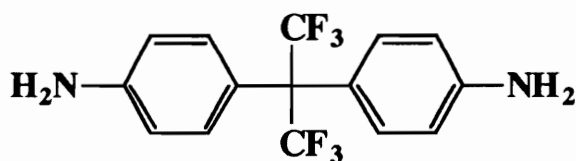
Figure 2.4.4 - p-6FDAM Monomer

2, 2-Bis[4-(4-Aminophenoxy)phenyl] hexafluoropropane (4-BDAF) is a commercially available diamine containing ether as well as the 6F bridging groups (90). Polyimides from 4-BDAF show good thermal stability, low dielectric constants and form colorless films (91, 92). Negi and coworkers compared the properties of 4-BDAF containing polyimides with analogous nonfluorinated polyimides made from 2, 2-Bis[4-(4-Aminophenoxy)] propane (93). The nonfluorinated polyimides generally displayed lower thermal stability and higher dielectric constants. Polyimides made from 4-BDAF and pyromellitic dianhydride (PMDA), depicted in Figure 2.4.5, were insoluble and exhibited Tg's near 300 °C (91). Recently, it was demonstrated that the lack of solubility in the PMDA-4-BDAF polyimide was due to its semicrystalline nature (94). PMDA-4-BDAF endcapped with phthalic anhydride exhibited a melting point near 470 °C which could be lowered by incorporating 6F dianhydride as a comonomer.
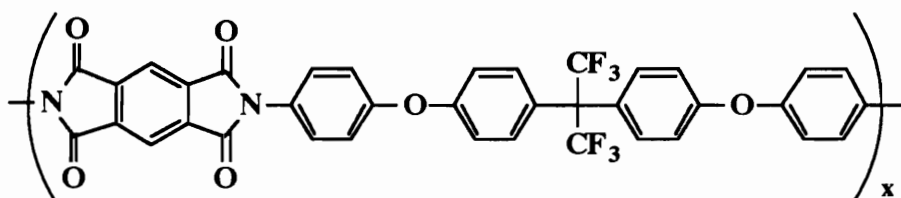
Figure 2.4.5 - PMDA-4-BDAF Polyimide

Alston and Gratz explored the use of trifluorophenylethylidene (3F) bridging groups (88). Polyimides with diamines containing the 3F group had properties that were similar

to polyimides made with 6F diamine. The 3F diamine monomer is depicted in Figure 2.4.6. PMDA-3F diamine polyimides exhibited Tg's near 430 °C (88). However, very little work has been done on determining the solubility or processability of controlled molecular weight 3F or 6F diamine containing polyimides.
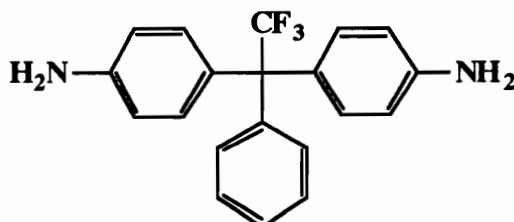
Figure 2.4.6 - 3F diamine Monomer

One major advantage of the 3F diamine is its relative ease of synthesis. The 3F diamine can be made from trifluoroacetophenone in refluxing aniline (95, 96).

Brink and coworkers made the 3F analogue of 4-BDAF named 3FEDAM (97). PMDA-3FEDAM polyimides were also semicrystalline with a Tg of 308 °C and a Tm of 476 °C.

Several interesting polyimides have been developed where the trifluoromethyl has been incorporated as a bulky side group. One example are the polyimides based on 2, 2'-bis(trifluoromethyl)-4, 4' -diaminobiphenyl (TFDB), Figure 2.4.7 (8, 98-100). The bulk imidized PMDA-TFDB was insoluble and had a Tg > 400°C. The 6FDA-TFDB polyimide was highly soluble in a variety of solvents including acetone and ethyl acetate.
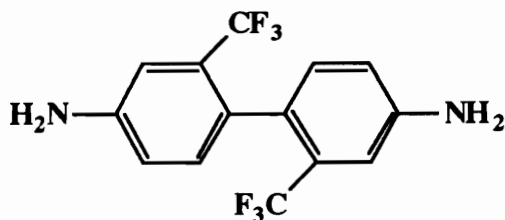
Figure 2.4.7 - TFDB Monomer

The 6FDA-TFDB polyimide had a Tg of 335 °C, a low dielectric constant of 2.8 and

formed optically transparent films. Polyimides from biphenyl dianhydride (BPDA) and

TFDB were semicrystalline and were spun into fibers with good thermal stability and a

tensile modulus as high as 130 GPa (101). Other polyimides with pendant

trifluoromethyl groups also showed good thermal stability, low dielectric constants and

water absorption (102-104). Polyimides with longer fluorinated alkyl and alkoxy side

chains are less thermally stable, but have low dielectric constants and water absorption

(105, 106).

Several polyimides have also been made with fluorine present as a substituent on an

aromatic ring (107-109). These polyimides exhibit good thermal stability. Fluorine

bonded to the aromatic ring is more effective in lowering the dielectric constant than

aliphatic fluorine groups (107). The perfluorinated polyimide, 10FEDA-4FMPD, shown

below in Figure 2.4.8 has a Tg of 309 °C and shows good optical clarity making it useful

in fiber optic applications (108).
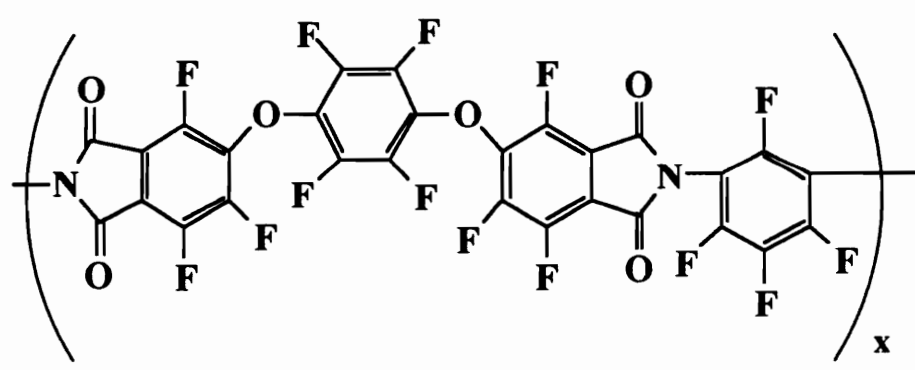
Figure 2.4.8 - 10FEDA-4FMPD Polyimide

2.5 POLYIMIDE SILOXANE COPOLYMERS

Polyimide homopolymers are the most widely used type of polyimide. However, a

variety of applications are being developed in which the properties of polyimide

homopolymers are not sufficient. As a result, the properties of the polyimides are being significantly altered and improved by combining them with chemically dissimilar polymers to form multiblock copolymers.

A large number of polyimide copolymers have been investigated. One of the most important copolyimides arises from the combination of a polyimide with a polysiloxane. Polyimide siloxanes have many unique properties which are used in a variety of applications including, toughening of thermosets (110-113), as encapsulents and interlevel dielectrics for integrated circuits (114-117), photosensitive poly(siloxane imides) (118-121), adhesives (122-124) and gas separation membranes (125-128). The synthesis and properties of polyimide siloxanes copolymers are discussed in this section.

2.5.1 Polysiloxanes

Polysiloxanes are interesting polymers with many peculiar and unique properties. They have been extensively studied and are of considerable commercial importance. In general, the polysiloxanes have many beneficial properties including good thermal and ultraviolet stability, highly flexible backbone, low surface energy, hydrophobicity, gas permeability, etc. (129-132) The most common polysiloxanes are the poly(dimethyl siloxane)s (PDMS).

The physical properties of polysiloxanes result from the unusual structural features of the siloxane polymer chains. The unique siloxane backbone is more flexible than almost any other polymer (133). The Si-O bond has a length of 1.64 Å. When compared to the C-C bond length (1.53 Å) of most hydrocarbon polymers, the Si-O bond is significantly longer. The larger bond length minimizes steric interferences or intramolecular congestion (133). In addition the oxygen skeletal atom contains no side groups to interfere with rotation. Finally, the Si-O-Si bond angle at 143 ° is much larger than the usual tetrahedral bond angle of hydrocarbons at 110 °(133). The combination of

these structural features results in a siloxane backbone where the barriers to rotation are very low. The result is polymer backbone of great flexibility. The glass transition temperature of poly(dimethyl siloxane) is near -123 °C (134).

The thermal stability of polysiloxanes is associated with the high bond dissociation energy of 110 kcal/mol (135) for the Si-O bond. This is much higher than the bond dissociation energies of the C-C bond (82.6 kcal/mole) and C-O bond (85.5 kcal/mole). The large bond energies of the Si-O bond may be attributed in part to the ionic character of the silicon-oxygen bond. The electronegativity difference between the two atoms is 1.7 and the ionic character has been estimated at 40 to 50 percent (136). However, the strong ionic character of the Si-O bond leaves siloxanes susceptible to cleavage by acids and bases.

α,ω-Functionally terminated siloxane oligomers have been made by anionic or cationic polymerization of cyclic siloxanes through an equilibration reaction.(135, 137) In this equilibration process, Si-O bonds are constantly being broken and reformed in the presence of a catalyst to form a mixture of cyclic and linear siloxanes. The procedure for the synthesis of aminopropyl terminated poly(dimethyl siloxane)s is depicted in Figure 2.5.1. An aminopropyl functional disiloxane is combined with a cyclic tetramer. A suitable catalyst, such as potassium or tetramethylammonium siloxanolate, can be prepared by combining potassium or tetramethylammonium hydroxide and a cyclic siloxane. At equilibrium, the reaction mixture consists mostly of linear polymer and 10 to 15 % of cyclic siloxanes. The cyclic siloxanes can be removed by distillation, leaving the linear functionalized polysiloxane oligomer. The molecular weight of the polysiloxane oligomers is controlled by the ratio of aminopropyl functional disiloxane to the cyclic tetramer. The molecular weight of the amine functionalized oligomers is generally determined by titration with an acid (137).

34
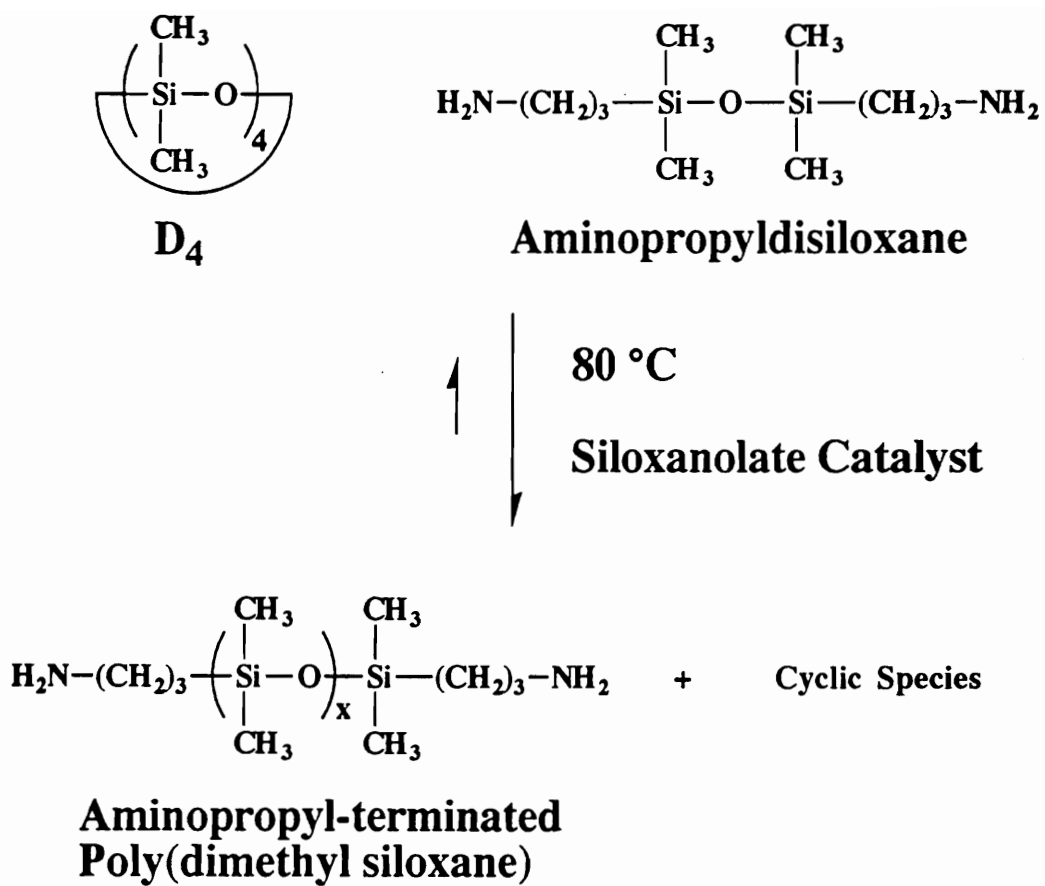
Figure 2.5.1 - Synthesis of Aminopropyl Terminated Poly(dimethyl siloxane)s (137)

2.5.2 Block Copolymers

Block copolymers are composed of two different polymer segments that are chemically bonded (138, 139). The sequential arrangement of block copolymers can vary from A-B diblock or A-B-A triblock copolymers, with two or three segments respectively, to (A-B)n multiblock copolymers containing many segments. Figure 2.5.2 lists the schematic representation of various block copolymer architecture. They also include graft and radial block copolymers. Copolymers made from polyimides, including polyimide siloxane copolymers, fit into the category of segmented or multiblock copolymers.

When two different polymers are combined, a heterogeneous mixture is formed if the free energy of mixing is positive. If incompatible polymers are physically blended then large phases of homopolymers are formed with low interfacial adhesion. This results in poor mechanical properties. For block copolymers, incompatibility of the various segments causes phase separation, but the segments are prevented from macroscopically separating by the chemical bonds between the segments. The two segments form microphases with strong interfacial adhesion. A critical molecular weight of the block copolymer segments is necessary to achieve microphase separation (138).

A variety of morphologies and properties can be achieved with microphase separated block copolymers. Figure 2.5.3 displays a generalized scheme for the solid state morphology of these copolymers as a function of block composition (139). Copolymers of "hard" and "soft" polymer segments have a variety of properties depending on their composition. Copolymers with small amounts of a "soft" segment will behave as toughened glassy polymers (140) while copolymers made predominantly of the soft segment will act as thermoplastic elastomers (141).

The thermal properties of block copolymers are similar to physical blends of the same polymer segments. Each phase of the copolymers displays unique thermal

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A-B Diblock Copolymer

A-B-A Triblock Copolymer

Multiblock Copolymer
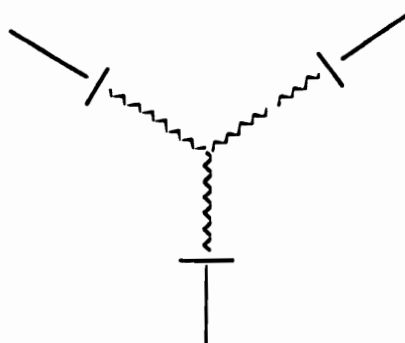
Radial Copolymer
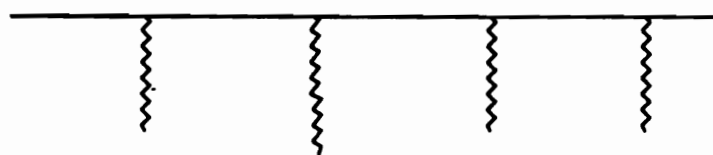
Graft Copolymer

Figure 2.5.2 - Various Block Copolymer Architectures (138)

A   A   A, B   B   B
Spheres   Cylinders   Lamellae   Cylinders   Spheres

Increasing A — content

Decreasing B — content
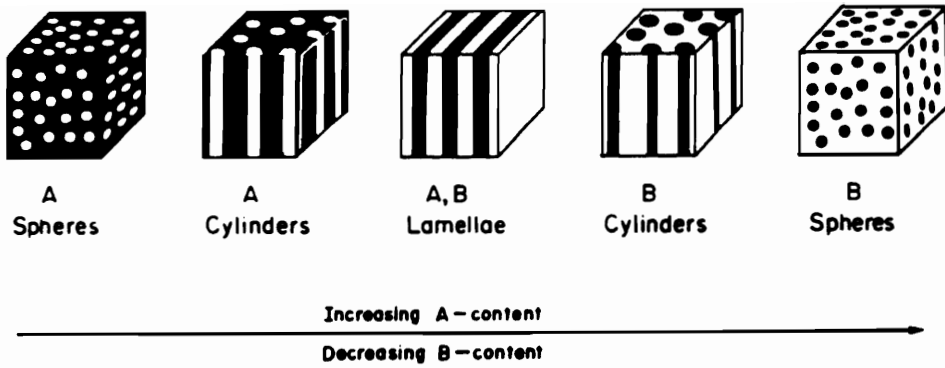
Figure 2.5.3 - Solid State Morphology as a Function of Block Composition (139)

transitions, such as a glass transition and/or a crystalline melting point, characteristic of each of the components. The thermal transition of one phase will be affected by the other in as much as they are able to intermix.

Almost all segmented or multiblock copolymers are synthesized by condensation or step growth polymerization methods. There are two types of multiblock copolymers. One type is referred to as a randomly segmented copolymer and the other is a perfectly alternating segmented copolymer. The two types of multiblock copolymers are depicted in Figure 2.5.4.

Randomly segmented copolymers are made by combining a functionally terminated oligomer with two monomers shown in Figure 2.5.4. Often the oligomer is flexible and forms the soft block while the two monomers combine to form the hard block (138). This method is commonly used in the synthesis of segmented copolymers, including the commercially important polyurethane copolymers and the polyimide siloxane copolymers (138).

Combining two functionalized oligomers with mutually reacting endgroups gives perfectly alternating copolymers, Figure 2.5.4. In these copolymers, both segments are well defined. Perfectly alternating segmented copolymers are less common than the randomly segmented copolymers. An example of a perfectly alternating segmented copolymer includes the polysulfone-poly(dimethyl siloxane) copolymers (142).

The perfectly alternating segmented copolymers have a higher structural regularity and more ordered morphology than the randomly segmented copolymers. The higher structural regularity results in better defined microphase separation (143). Thus, depending on the composition, well defined perfectly alternating segmented copolymers may afford higher Tg's and improved tensile strength and modulus relative to randomly segmented copolymers.

Synthesis of Randomly
Segmented Copolymers

$$Y-Y \quad + \quad X-X \quad + \quad Y\sim\sim\sim\sim\sim Y$$

$$\downarrow$$

$$-\left(Y-YX-X\right)_n Y-Y\left(X-XY\sim\sim\sim\sim Y\right)_m-$$

Synthesis of Perfectly
Alternating Segmented Copolymers

$$X\sim\sim\sim\sim\sim\sim X \quad + \quad Y\text{———}Y$$

$$\downarrow$$

$$\left(\sim\sim\sim\sim\sim\sim\sim\mid\text{————————}\right)_n$$
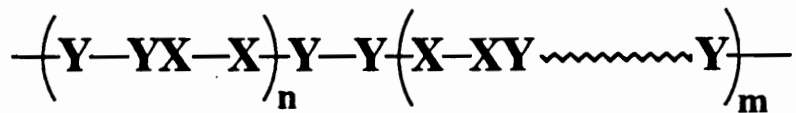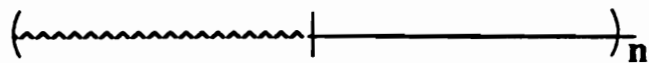
Figure 2.5.4 - Randomly and Perfectly Alternating Segmented Copolymers

There are several examples in the literature where the properties of the perfectly alternating segmented copolymers are compared to randomly segmented copolymers. For example, Kajiyama and coworkers investigated the difference between perfectly alternating and randomly segmented poly(dimethyl siloxane) - polyurea copolymers (144). The randomly segmented copolymers were made by combining an amine terminated poly(dimethyl siloxane) oligomer with a diamine and diisocyanate. To make the perfectly alternating segmented copolymers, the diamine and diisocyanate were first combined to form the polyurea segment which was then reacted with the polysiloxane oligomer. The thermal and mechanical properties of random and perfectly alternating segmented copolymers with analogous compositions were compared. The graph in Figure 2.5.5 shows the relation of the upper and lower Tg of the random and perfectly alternating segmented copolymers as a function of polysiloxane content. The perfectly alternating segmented copolymers had Tg's closer to the Tg's of the polyurea and polysiloxane homopolymers. This suggested that the perfectly alternating copolymers had a higher structural regularity and more distinct phase separation. The greater depression of the upper Tg and the larger increase of the lower Tg suggests that the randomly segmented copolymers had a poorly defined morphology and more interfacial mixing. In addition, the perfectly alternating poly(dimethyl siloxane) - polyurea copolymers had a higher tensile strength, tensile modulus and elongation than the randomly segmented copolymers of the same composition.

The differences in the perfectly alternating and randomly segmented architecture was also evident in poly(dimethyl siloxane) - polyamide copolymers (145) and poly(ether sulfone) - polyimide copolymers (146). In both cases, the randomly segmented copolymers exhibited a single phase morphology and only one Tg. The perfectly alternating segmented copolymers of the same composition displayed a two phase morphology as a result of the greater structural regularity. The perfectly alternating

41
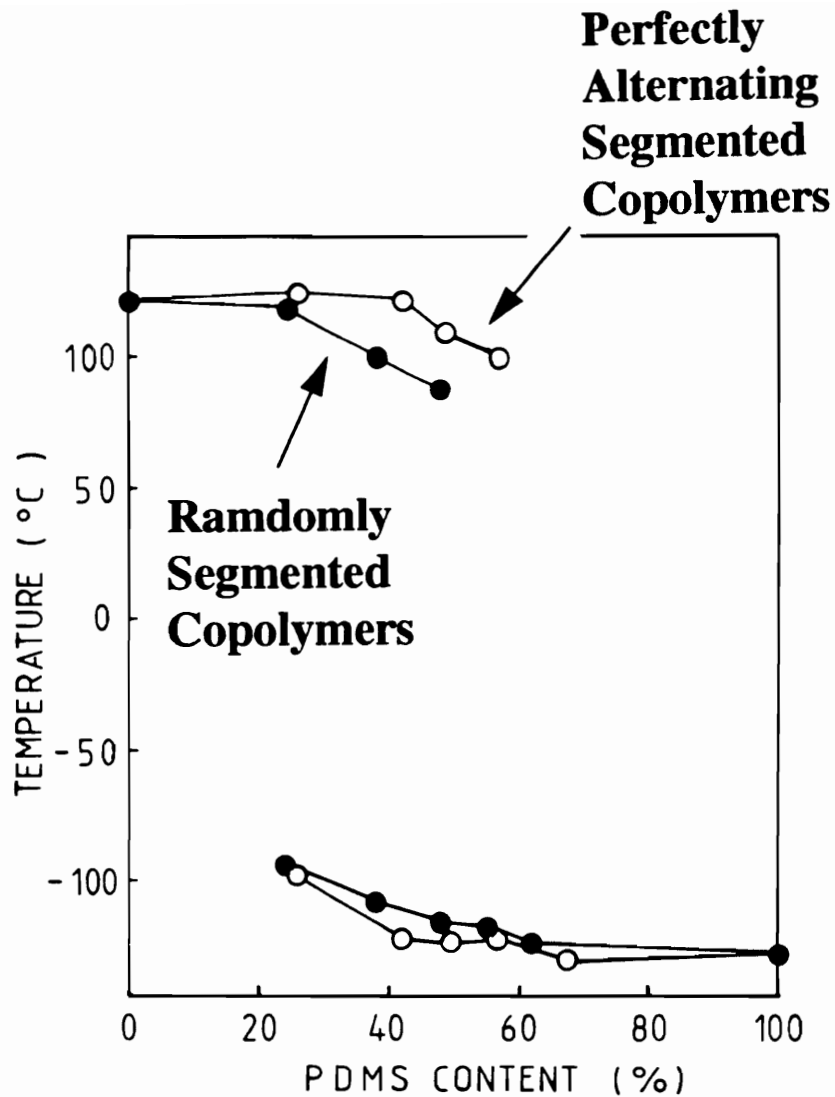
Figure 2. Glass transition temperatures of PDMS–polyurea multiblock copolymers: –O–, 3(II) series block copolymers; –●–, 3(I) series block copolymers.

Figure 2.5.5 - Random Versus Perfectly Alternating Segmented N-Phenylated Polyureas - Poly(dimethyl siloxane) Copolymers (144)

segmented copolymers also had better mechanical properties. Similar differences between randomly and perfectly alternating segmented copolymers has been observed in other systems (147-149).

2.5.3 Synthesis of Polyimide Siloxane Copolymers

Polyimide siloxane copolymers have usually been made by methods similar to the synthesis of polyimide copolymers (150-152). Generally, dianhydride and diamine monomers are combined with a polysiloxane oligomer to produce the randomly segmented structure. The general scheme for the synthesis of the randomly segmented polyimide siloxane copolymers is shown in Figure 2.5.6. The polymerizations are generally done in two steps. First, the poly(amic acid) is formed by the combination of a dianhydride and a diamine. The poly(amic acid) copolymer is then cyclodehydrated using classical imidization methods. Since polyimide siloxane copolymers are usually more soluble than their polyimide counterparts, a wider variety of polymerization solvents can be employed in their synthesis.

The aminopropyl terminated poly(dimethyl siloxane)s are often used when preparing polyimide siloxane copolymers. When making the poly(amic acid) copolymers, maintaining solubility of the starting monomers is crucial in obtaining high molecular weight polymers. One method to maintain solubility has involved the use of a cosolvent system (13, 153-156). The polysiloxanes are not soluble in the polar aprotic solvents often used in polyimide synthesis so, the poly(amic acid) copolymers are made in a cosolvent system such as an NMP/Tetrahydrofuran (THF) mixture. THF helps solvate the polysiloxane while NMP dissolves the aromatic monomers and prevents precipitation of the poly(amic acid). The solubility of the monomers can be improved by changing the order of monomer addition (13). The polysiloxane is added to an NMP/THF solution of the dianhydride. The dianhydride effectively endcaps the polysiloxane and improves
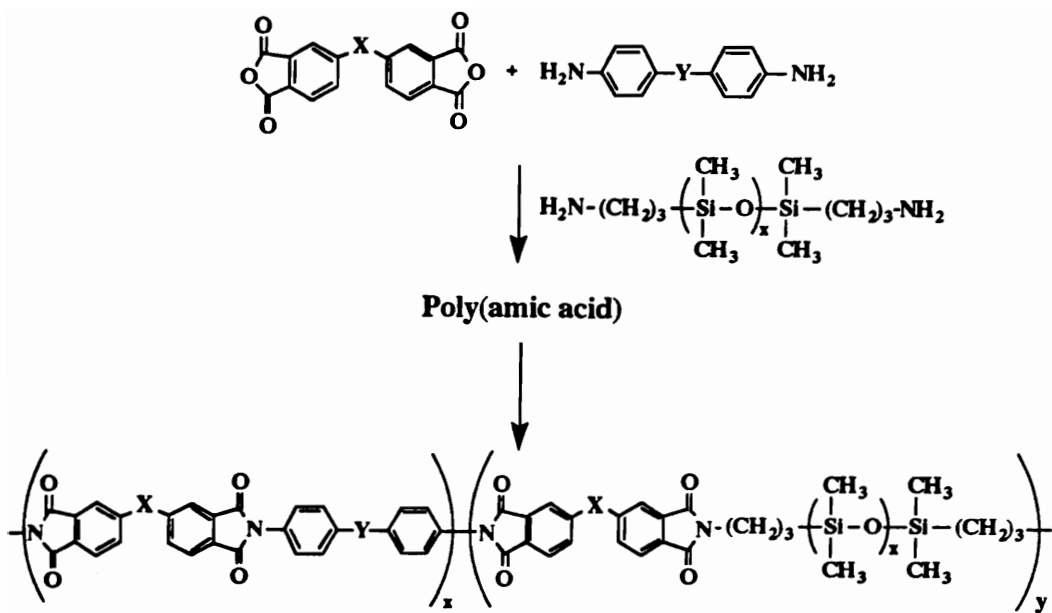
Figure 2.5.6 - Synthesis of Randomly Segmented Polyimide
Siloxane Copolymers (13)

its solubility in the polymerization solvent. Low molecular weight siloxane oligomers (< 0.9 kg/mole) and siloxane containing monomers can be polymerized in polar aprotic solvents without using any cosolvents (116, 157, 158).

The order of monomer addition is not only important in improving the solubility of the starting reactants but it also affects the architecture of the copolymer. The aminopropyl terminated poly(dimethyl siloxane) reacts much faster than most aromatic amines (151). Adding a dianhydride to a mixture of aromatic diamines and oligomers can lead to chain extension of the polysiloxane since the polysiloxane will react quickly with the dianhydride as it dissolves. Adding the oligomer to a dianhydride solution and then adding the diamine insures random incorporation of the polysiloxane into the copolymer. Rojstaczer varied the monomer addition to make "extended block" polyimide siloxane copolymers (159). This was done by mixing one block made from a dianhydride and a diamine terminated siloxane oligomer and another block made from a dianhydride and a diamine.

The poly(amic acid) copolymers are usually imidized by either solution imidization of bulk imidization techniques. Siloxane containing copolymers have also been made by the ester acid route (150) and by using chemical imidization methods (160). Tsutsumi and coworkers made siloxane containing polyimides from an aromatic dianhydride and a combination of 1,3-bis(3-aminopropyl) tetramethyl disiloxane and dodecamethylene diamine. These polyimides can be made by either melt or solution polycondensation methods (161).

Other siloxane oligomers have been used besides the aminopropyl terminated poly(dimethyl siloxane)s. Norbornene anhydride terminated poly(dimethyl siloxane)s have been used in the synthesis of polyimide siloxane copolymers (162, 163). These copolymers were made using a one pot solution imidization method. The anhydride capped oligomer was first capped with an excess of the diamine followed by the addition

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of the aromatic dianhydride. It was necessary to use a condensation catalyst, 2-hydroxypyridine, to insure incorporation of the siloxane oligomers.   Smith and coworkers made perfectly alternating polyimide siloxane copolymers from norbornene anhydride terminated polysiloxane oligomers and amine terminated polyimide oligomers (164). The perfectly alternating copolymers were made in refluxing ODCB using 2-hydroxypyridine as a catalyst. Phthalic anhydride terminated polysiloxanes have also been used (158, 165, 166). Imidizations with phthalic anhydride terminated polysiloxane were conducted in refluxing ODCB using dimethyl aminopyridine as a catalyst.

Aminophenyl terminated poly(dimethyl siloxane) have been made and employed in the synthesis of polyimide polysiloxane copolymers (167, 168). Perfectly alternating segmented polyimide siloxane copolymers were made by a transimidization route. The aminophenyl terminated poly(dimethyl siloxane) was reacted with N-pyridine phthalimide terminated polyimide in refluxing chlorobenzene using zinc acetate as a catalyst (168). Aminophenoxy terminated poly(dimethyl siloxane) oligomers have also been used to make polyimide siloxane copolymers (169).

Some problems have been reported in the synthesis of polyimide siloxane copolymers by the poly(amic acid) route. Cella and coworkers found cyclic siloxanes after polymerizing a dianhydride, diamine and aminopropyl terminated poly(dimethyl siloxane) (165). It was postulated that in the presence of the poly(amic acid) acid functional group, siloxane equilibration takes place and cyclic oligomers are formed. This can lead to decreases in the polysiloxane molecular weight. However, it was not stated whether a significant amount of cyclics were formed. The transimidization reaction was shown to produce no cyclics.

Instead of the segmented multiblock copolymers, Nagase and coworkers developed silicone grafted copolyimides. (125-127). The graft copolyimides were made through the classical poly(amic acid) route. An aromatic diamine and a dianhydride were combined

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with a diaminophenyl terminated dimethylsiloxane macromonomer. The silicone grafted poly(amic acid)s were thermally imidized. Connell also made a series of silicone grafted polyimides (170). However, the silicon-oxygen-carbon bonds in these silicone grafted polyimides may not show sufficient hydrolytic stability.

2.5.4 Properties of Polyimide Siloxane Copolymers

The introduction of siloxane groups into polyimides remarkably changes the polyimide properties. Incorporation of polysiloxanes affects the solubility, glass transition temperature, adhesive characteristics, dielectric constants, moisture absorption, gas permeability and oxygen plasma etch resistance.

2.5.4.1 <u>Solubility</u>: Improving the solubility of polyimides is important in obtaining processable polymers. In addition, polyimides which can be processed in lower boiling solvents can be easily dried.

Introduction of the flexible siloxane containing monomer or oligomer improves the solubility of polyimides (9, 10, 13, 153). Most rigid polyimides are insoluble in organic solvents. By incorporating siloxane containing monomers, polyimides show solubility in solvents such as DMAc, diglyme and chloroform (113). Adding siloxane oligomers improves the solubility of the polyimides in solvents such as tetrahydrofuran and diglyme. The solubility of polyimide siloxane copolymers containing siloxanes depends on the amount and size of the polysiloxane segments. When the block size of the polysiloxane is increased the weight % of that polysiloxane must be increased in order to see improvements in the polyimide solubility (10).

2.5.4.2 <u>Glass Transition Temperature</u>: Siloxane oligomers with only 1 to 5 repeat units have a single phase morphology and show only one glass transition temperature (10).

Such low molecular weight oligomers cannot form separate phases within the copolymer. The flexible -Si-O-Si- moiety of the siloxane monomers lowers the Tg of the polyimides significantly. Table 2.5.1 lists the Tg's of a variety of single phase siloxane containing polyimides. The first two entries show that increasing the number of siloxane units without causing phase separation decreases the Tg (158). Replacing 3, 3'-diaminobenzophenone with the siloxane dimer decreases the Tg by 186 °C (113).

Polyimide siloxane copolymers with higher molecular weight oligomers exhibit a two phase morphology (171, 172). The Tg of the polysiloxane phase occurs between -115 to -123 °C (10, 160). There is also an upper Tg which corresponds to the Tg of the polyimide phase. The Tg varies greatly and depends on the chemical composition of the polyimide block. The size of the polyimide block and polysiloxane block also has a significant influence on the Tg. As the length of the polyimide block decreases the upper Tg decreases (160, 173). Figure 2.5.7 shows the effect of the polyimide block length, L, on the upper Tg of a polyimide siloxane copolymer where the polysiloxane segment has a molecular weight of 874 g/mole.

Arnold and coworkers concluded that low molecular weight polysiloxanes could also mix with the polyimide phase (153). This phase mixing depressed the Tg. Chemical composition seemed to effect the phase mixing. The greater the polarity of the polyimide the less the upper Tg was depressed. The Tg's of several of these polyimide siloxane copolymers are listed in Table 2.5.2.

2.5.4.3 Thermal Stability: The thermal stability of aromatic polyimides is usually higher than that of the siloxanes. Therefore, incorporating siloxanes into polyimides can be expected to decrease the thermal stability of the polyimides (13). Thermal stability of the polyimides is often reported as 5 or 10 % weight loss values determined by dynamic thermogravimetric analysis. The thermal stability of the polyimide siloxane copolymers

Table 2.5.1 - Glass Transition Temperatures of Siloxane
Containing Polyimides (113, 158)

Polyimide	Tg (°C)
	232
	220
	277
	91
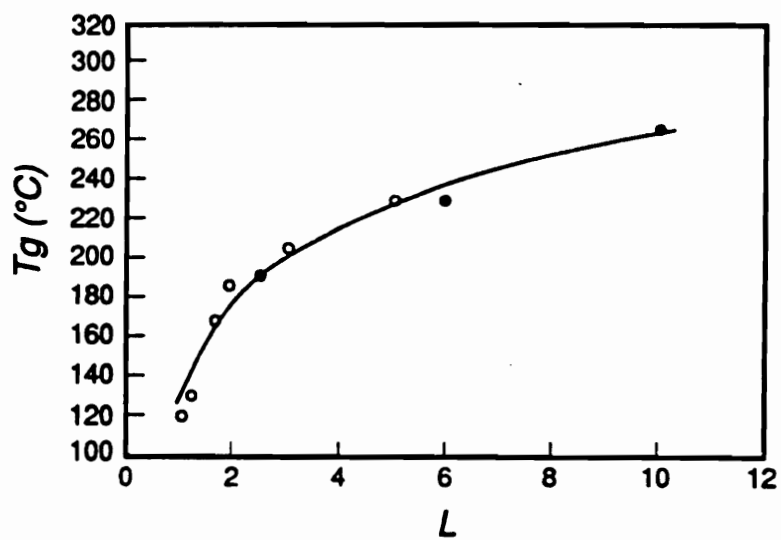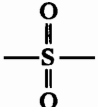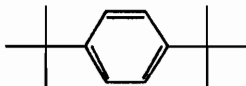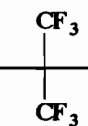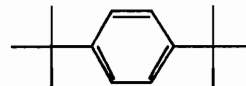
Figure 2.5.7 - Effect of Polyimide Block Length, L, on the Upper Tg of a Randomly Segmented Polyimide Siloxane Copolymers (173)

Table 2.5.2 - Glass Transition Temperatures of Randomly Segmented Polyimide Siloxane Copolymers (13)
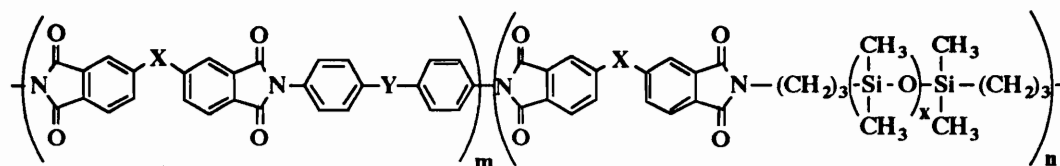
X	Y	Weight % PDMS	PDMS \<Mn\> kg/mole	Tg(°C)
—C— (C=O)	—S— (O=S=O)	0	0	265
		10	0.9	251
		10	2.1	260
		10	5.0	264
—C— (C=O)	—C(CH₃)₂—C₆H₄—C(CH₃)₂—	0	0	264
		10	0.8	241
		10	2.5	258
		20	2.5	245
		30	2.5	242
		50	2.5	202
—C(CF₃)₂—	—C(CH₃)₂—C₆H₄—C(CH₃)₂—	0	0	267
		10	0.8	232

decreases with increasing amounts of siloxane. However, polyimide siloxanes do show higher char yields at temperatures of 750 °C which may be related to retardation of cyclic generation and formation of organosilicates at high temperatures in air (13). The high char yield has been considered to enhance the flame resistance of these materials.

The effects of long term exposure of polyimide siloxane copolymers has also been reported (10, 175, 176). Figure 2.5.8 shows the weight loss of polyimide siloxane copolymers at various temperatures as a function of time under a nitrogen atmosphere. After an initial weight loss, the polyimide siloxane remained stable at the aging temperatures. However, the initial weight loss became higher as the aging temperature was increased. Mechanical properties began to degrade in some polyimide siloxane copolymers after aging at temperatures as low as 200 °C (10).

2.5.4.4 Morphology: Amorphous polyimide homopolymers and the afore mentioned single phase siloxane containing polyimides do not exhibit any significant morphological features. Polyimide siloxane copolymers containing oligomeric siloxane segments separate into two phases. These phase separated polyimide siloxane copolymers have distinct morphologies that are dependent on the block size, the amount of polysiloxane, and on the chemical composition of the polyimide phase (143, 160, 172, 176-179). Since the siloxane and polyimide segments are chemically bonded, the phase separation occurs on a very small scale. Films of polyimide siloxane are usually transparent. So, the phase separation must be investigated by such techniques as transmission electron microscopy (TEM).

In the polyimide siloxane copolymers, relatively low weight %'s of polysiloxane form a co-continuous phase. York observed that in a compression molded polyimide siloxane sample containing 15 weight % polysiloxane, the siloxane existed in a co-
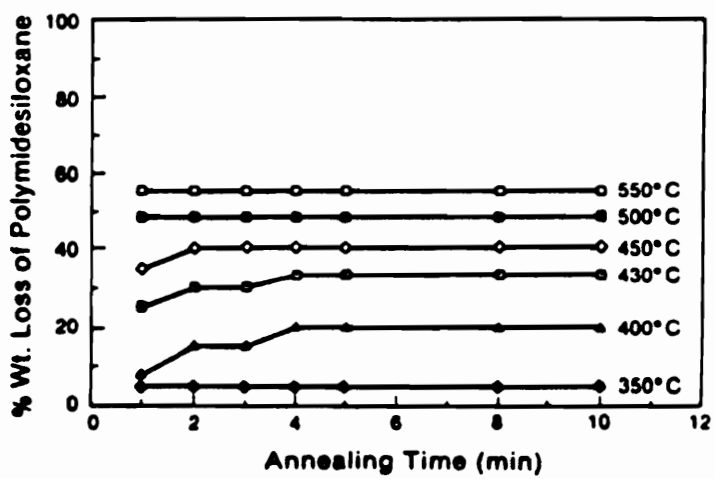
Figure 2.5.8 - Thermal Stability of Polyimide Siloxane Copolymers in Nitrogen (175)

continuous or rod-like morphology (143). However, in polyimide siloxane copolymers containing 15 weight % polysiloxane and a less polar polyimide, the siloxane formed spherical phases in a continuous polyimide matrix. Solution cast films of both polyimide siloxane containing 15 weight % polysiloxane copolymers exhibited a spherical texture.

Others have shown that solution cast films of polyimide siloxane copolymers containing at least 40 weight % siloxane, the siloxane exists in a continuous phase (176, 177). The morphological features of these copolymers often appeared mottled and were not distinct. Morphological structure depends on the processing condition including type of solvent, rate of solvent removal and temperature (171, 177, 178).

The morphological irregularities of the polyimide siloxane copolymers were accounted for in the three phase model proposed by Saraf and coworkers (171). They proposed that there are three phases in polyimide siloxane copolymers: a siloxane rich phase, a siloxane poor phase, and an intermediate phase. The content of the siloxane rich and siloxane poor phase were independent of the amount of polysiloxane in the copolymer. But, the siloxane content in the intermediate phase increased as the amount of siloxane in the copolymer increased.

The morphology of the copolymers has a significant effect on its physical properties. Copolymers where the siloxane segments makes up the continuous phase behave as thermoplastic elastomers. Subsequently, copolymers with a polyimide continuous phase have high stiffness and strength.

2.5.4.5 Mechanical Properties: As expected, incorporation of the flexible siloxane oligomers into a polyimide has tremendous impact on the mechanical properties. Polyimides are generally characterized as having a high tensile modulus and tensile strength (1). Table 2.5.3 lists the tensile properties and fracture toughness values of a series of polyimide siloxane copolymers (169). As already discussed, copolyimides

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Table 2.5.3 - Mechanical Properties of a Randomly Segmented Polyimide
Copolymers (169)

PDMS Content Weight %	Tensile Strength kpsi	Tensile Modulus kpsi	Fracture Toughness K_{1c} psi in. $^{1/2}$
0	9.9	270	1124
5	13.0	255	3197
10	13.0	243	3119
15	9.7	201	3284

containing small amounts of polysiloxane oligomers have morphologies in which the siloxane exists in spheres in a continuous polyimide matrix. The fracture toughness values in Table 2.5.3 show that the small amounts of polysiloxane serves to toughen the copolymer relative to the polyimide homopolymer. The small amount of polysiloxane also has little effect on the tensile modulus or strength of the polyimide.

As more polysiloxane is incorporated, the morphology changes until the siloxane becomes the continuous phase. The stress-strain behavior depicted in Figure 2.5.9 demonstrates the effect of morphology (13). Between 20 and 40 weight % siloxane, the modulus and tensile strength of the polyimide siloxane copolymers significantly decrease. In addition, the % elongation of the copolymer increases. These changes correspond to changes in the morphology of the copolymers. At 40 weight % siloxane, the siloxane becomes the continuous phase and the mechanical properties reflect the properties of the polysiloxane segment.

2.5.4.6 <u>Other Properties</u>: Some other advantageous properties of polyimide siloxane copolymers includes their low water adsorption (13), atomic oxygen resistance (13) and lower dielectric constants (116, 153). The lower water adsorption and atomic oxygen resistance appears to result from the surface segregation or surface enrichment of the copolymer by the siloxane segments. X-ray photoelectron spectroscopy studies of polyimide siloxane films demonstrated that the surface composition was predominantly siloxane, even when the bulk siloxane compositions were relatively low (13). In aggressive oxygen environments such as an oxygen plasma or in the presence of atomic oxygen, the surface siloxane segments form a protective ceramic like silicate. This barrier prevents further erosion of the bulk material.

The hydrophobic siloxane surface also reduces the amount of water absorbed by the copolymer (13). Many polyimides absorb as much as 2 to 3 weight percent water. However, polyimide siloxane copolymers containing 30 weight % PSX absorb less than 1 wt % water.
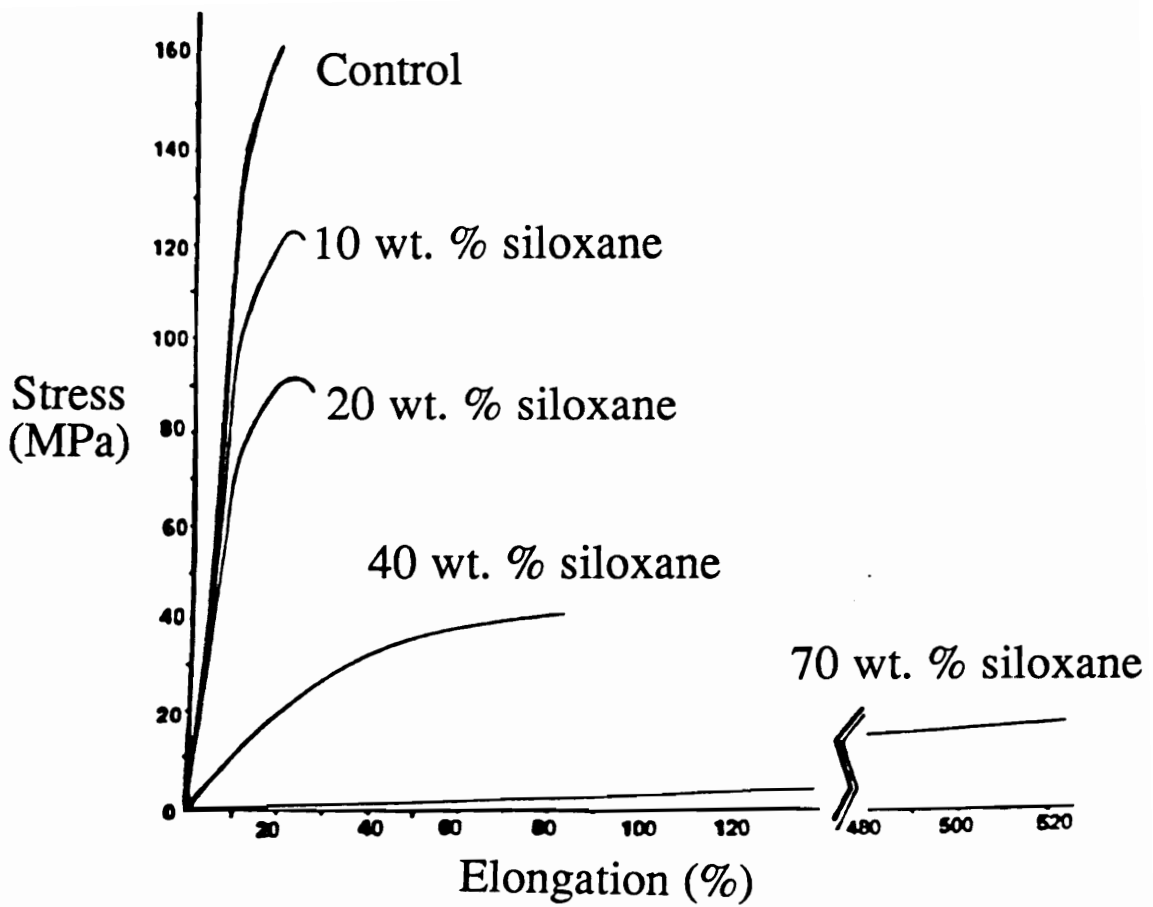
Figure 2.5.9 - Stress - Strain Behavior of Randomly Segmented
Polyimide Siloxane Copolymers (13)

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CHAPTER 3 - EXPERIMENTAL

3.1 PURIFICATION OF REAGENT AND SOLVENTS

Pure reagents, solvents and monomers are important in the synthesis of monomers, model compound studies and for obtaining high molecular weight polymers. Therefore, monomers and reagents were carefully purified and dried before use. Polymerization solvents were generally distilled from drying agents using the apparatus shown in Figure 3.1.1. This apparatus allows reduced pressure distillations and refluxing over drying agents prior to solvent collection. The distilled solvents were collected in round bottom flasks and sealed under a dry nitrogen atmosphere with a rubber septa. The solvent was transferred to reaction vessels using syringe techniques to minimize moisture exposure.

3.1.1 Solvent Purification

3.1.1.1 1-Methyl-2-Pyrrolidinone (NMP: Fisher) was dried over P_2O_5 for at least 8 hours and then distilled under reduced pressure (water aspirator). The distilled NMP was again dried over P_2O_5 and distilled under reduced pressure prior to use. (b.p. 205 °C/760 mm)
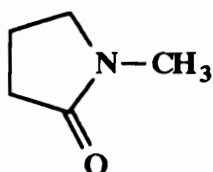
3.1.1.2 N-Cyclohexyl-2-Pyrrolidinone (CHP: Aldrich) was dried over P_2O_5 for at least 8 hours and then distilled under reduced pressure (water aspirator). (b.p. 290 °C/760 mm)
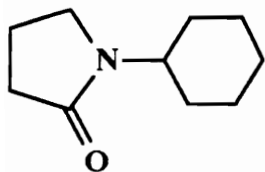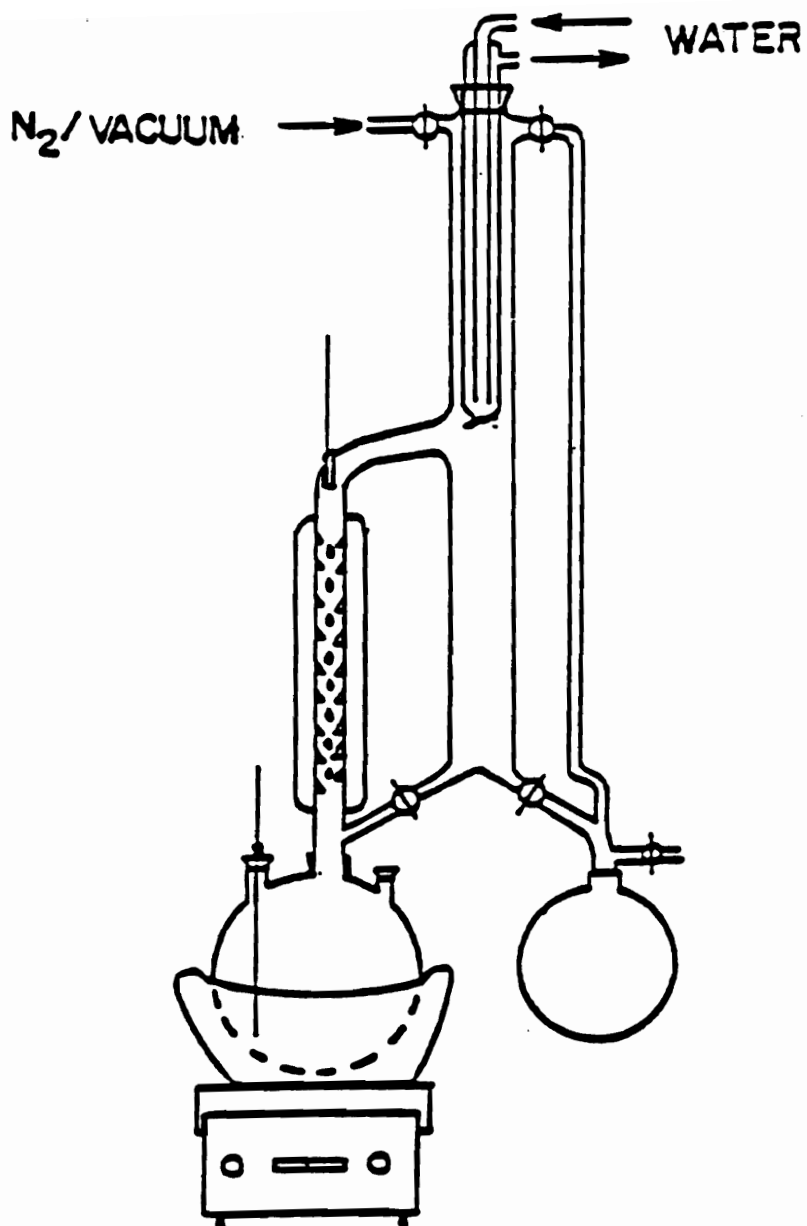
Figure 3.1.1 - Distillation Aparatus

60

3.1.1.3 _o_-Dichlorobenzene (ODCB: Fisher) was dried over P_2O_5 for at least 8 hours and then distilled under reduced pressure (water aspirator). (b.p. 180 °C/760 mm)
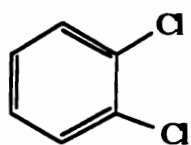
3.1.1.4 Chlorobenzene (CB: Fisher) was distilled under reduced pressure (water aspirator) and utilized with no further drying treatment. (b.p. 132 °C/760 mm)
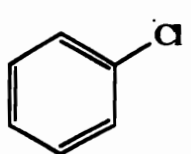
3.1.1.5 Tetrahydrofuran (THF: Fisher) was dried over sodium for at least 18 hours and distilled at atmospheric pressure under a nitrogen gas purge. (b.p. 76 °C/760 mm)
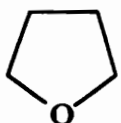
3.1.1.6 Deuterated Chloroform (CDCl3:Aldrich) was used as an n.m.r. solvent in model reactions. The CDCl3 was dried over molecular sieves for at least 24 hours. The CDCl3 was not distilled prior to use. (b.p. 61 °C/760 mm)
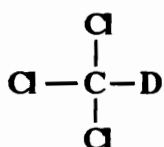
3.1.1.7 Deuterated Dimethyl Sulfoxide (DMSO-d6: Aldrich) was used as an n.m.r. solvent in model reactions. The DMSO-d6 was dried over molecular sieves for at least 24 hours. The DMSO-d6 was not distilled prior to use. (b.p. 55 °C/5 mm)
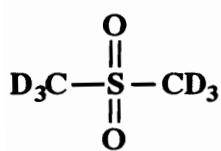
3.1.1.8 <u>Aniline (Aldrich)</u> was stirred over calcium hydride for 20 hours. The solvent
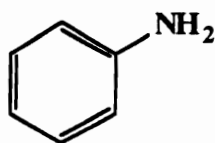
NH_2 was then distilled under reduced pressure (water aspirator). (b.p. 184 °C/760 mm)

3.1.1.9 <u>N,N'-dimethylpropyleneurea (DMPU: Aldrich)</u> was distilled under reduced
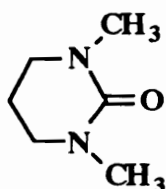
CH_3 pressure (water aspirator). (b.p. 146°C/44mm)

3.1.2 Monomers and Reagents

3.1.2.1 Pyromellitic dianhydride (PMDA)

Supplier:	Allco
Empirical Formula:	$C_{10}H_2O_6$
Molecular Weight, g/mole:	218.12
Melting Point (pure), °C:	286
Structure	
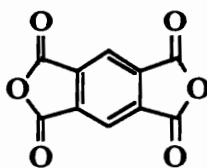
Purification: Polymer grade PMDA was used after drying at 180 °C for at least 6 hours to obtain high molecular weight polyimides.

3.1.2.2 3,4,3',4'-biphenyltetracarboxylic dianhydride (BPDA)

Supplier: Chriskev

Empirical Formula: $C_{16}H_6O_6$

Molecular Weight, g/mole: 294

Melting Point (pure), °C: 300

Structure
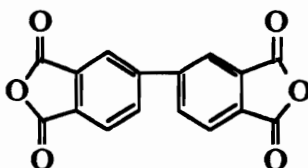
Purification: Polymer grade BPDA was used after drying at 180 °C for at least 6 hours to obtain high molecular weight polyimides.

3.1.2.3 4, 4' -oxydiphthalic anhydride or 5, 5'-oxybis-1,3-isobenzofurandiane (ODPA)

Supplier: Occidental Chemical Corporation

Empirical Formula: $C_{16}H_6O_7$

Molecular Weight, g/mole: 310.23

Melting Point (pure), °C: 228

Structure
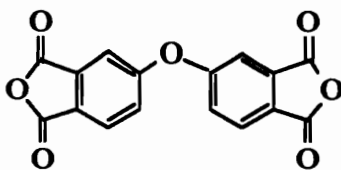
Purification: Polymer grade ODPA was used after drying at 180 °C for at least 6 hours to obtain high molecular weight polyimides.

3.1.2.4 5, 5'-[2, 2, 2-Trifluoro-1-(trifluoromethyl) ethylidene] bis-1, 3-isobenzofurandione (6FDA)

Supplier: Hoechst Celanese Corporation

Empirical Formula: $C_{19}H_6F_6O_6$

Molecular Weight, g/mole: 444

Melting Point (pure), °C: 247

Structure
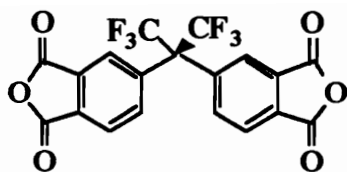
Purification: Polymer grade 6FDA was used after drying at 180 °C for at least 6 hours to obtain high molecular weight polyimides.

3.1.2.5 5, 5'-[phenyl-1-(trifluoromethyl) ethylidene] bis-1, 3-isobenzofurandione (3FDA)

Supplier:	Dr. William Alston, NASA Lewis
Empirical Formula:	$C_{19}H_6F_6O_6$
Molecular Weight, g/mole:	444
Melting Point (pure), °C:	247
Structure	
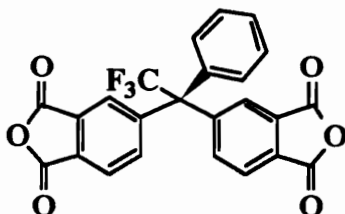
Purification: Polymer grade 3FDA was used after drying at 180 °C for at least 6 hours to obtain high molecular weight polyimides.

3.1.2.6 Phthalic Anhydride (PA)

Supplier:	Aldrich Chemical Company
Empirical Formula:	$C_8H_4O_3$
Molecular Weight, g/mole:	148.12
Melting Point (pure), °C:	134
Structure	
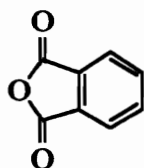
PA

Purification: PA was sublimed under vacuum at a temperature of ~ 125°C.

3.1.2.7 4-t-Butylphthalic Anhydride (t-butyl PA)

Supplier:	TCI
Empirical Formula:	$C_{12}H_{12}O_3$
Molecular Weight, g/mole:	204.23
Melting Point (pure), °C:	78
Structure	
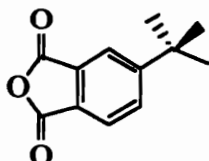
Purification: PA was sublimed under vacuum at a temperature of ~ 125°C.

3.1.2.8 4, 4'-[1, 4-phenylene-bis-(1-methyl ethylidene)] bisaniline (Bis P)

Supplier:	Air Products and Chemicals, Inc.
Empirical Formula:	$C_{24}H_{28}N_2$
Molecular Weight, g/mole:	344
Melting Point (pure), °C:	165
Structure	
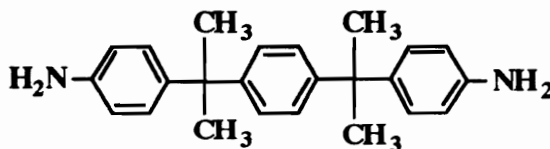
Purification: Bis P was dried overnight in a vacuum oven at ~110 °C before use.

3.1.2.9 4-Aminophenyl ether or 4, 4'-Oxydianiline (4, 4'-ODA)

Supplier: Aldrich Chemical Company
Empirical Formula: $C_{12}H_{12}N_2O$
Molecular Weight, g/mole: 200.24
Melting Point (pure), °C: 192
Structure

$$H_2N-\!\!\left\langle\bigcirc\right\rangle\!\!-O-\!\!\left\langle\bigcirc\right\rangle\!\!-NH_2$$
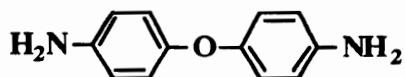
Purification: 4, 4' -ODA was sublimed under vacuum at ~170°C.

3.1.2.10 1, 4-Phenylenediamine (pPD)

Supplier: Aldrich Chemical Company
Empirical Formula: $C_6H_8N_2$
Molecular Weight, g/mole: 108.14
Melting Point (pure), °C: 145
Structure

$$H_2N-\!\!\left\langle\bigcirc\right\rangle\!\!-NH_2$$
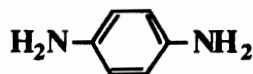
Purification: pPD was sublimed under vacuum at ~130°C. pPD oxidizes readily in air and must be used soon after sublimation.

3.1.2.11 1, 3-Phenylenediamine (mPD)

Supplier: Aldrich Chemical Company
Empirical Formula: $C_6H_8N_2$
Molecular Weight g/mole: 108.14
Melting Point (pure), °C: 66
Structure

$$H_2N-\!\!\left\langle\bigcirc\right\rangle\!\!\overset{NH_2}{}$$
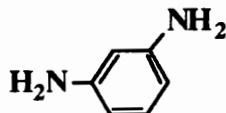
Purification: mPD was sublimed under vacuum at ~50°C. mPD oxidizes readily in air and must be used soon after sublimation.

3.1.2.12 3, 3'-Diaminodiphenyl Sulfone (mDDS)

Supplier: Aldrich Chemical Company

Empirical Formula: $C_{12}H_{12}N_2O_2S$

Molecular Weight, g/mole: 248.3

Melting Point (pure), °C: 173

Structure
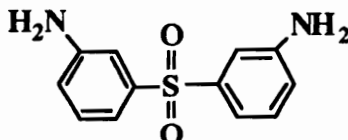
Purification: mDDS was received at 97 % purity and was recrystallized once from methanol. mDDS was then dried at ~110°C for 24 hours.

3.1.2.13 Bis(4-aminophenyl) phenyl phosphine oxide (DDPPO)

Supplier: Dr. Harvey Grubbs, Phillip Morris,

                                             Richmond VA

                                             (see reference 91)

Empirical Formula: $C_{12}H_{12}N_2O_2S$

Molecular Weight, g/mole: 248.3

Melting Point (pure), °C: –

Structure
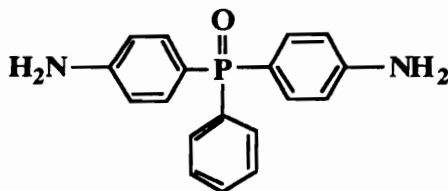
Purification: DDPPO was used as received.

3.1.2.14 2-Aminopyridine (2AP)

Supplier:	Aldrich Chemical Company
Empirical Formula:	$C_5H_6N_2$
Molecular Weight, g/mole:	94.12
Melting Point (pure), °C:	60
Structure	

$$H_2N-\text{(ring structure)}$$
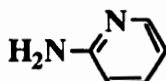
Purification: 2AP was recrystallized from a mixture of 75 % (by volume) chloroform and 25 % petroleum ether. 2AP was dried in a vacuum oven at 30 °C for at least 24 hours.

3.1.2.15 2-Aminopyrimidine (2APm)

Supplier:	Aldrich Chemical Company
Empirical Formula:	$C_4H_5N_3$
Molecular Weight:	95.11
Melting Point (pure), °C:	127
Structure	

$$H_2N-\text{(ring structure)}$$
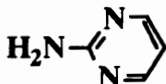
Purification: 2APm was sublimed under a vacuum at ~120 °C.

3.1.2.16 Hexylamine (HA)

Supplier:	Aldrich Chemical Company
Empirical Formula:	$C_6H_{15}N$
Molecular Weight:	101.19
Boiling Point (pure), °C:	131-132°C
Structure	

$$CH_3(CH_2)_5-NH_2$$
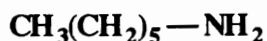
Purification: HA was dried over calcium hydride and distilled at atmospheric pressure under a nitrogen purge. HA was stored over molecular sieves.

3.1.2.17 m-Anisidine

Supplier:	Aldrich Chemical Company
Empirical Formula:	C_7H_9NO
Molecular Weight:	123.16
Boiling Point (pure), °C:	251 °C
Structure	
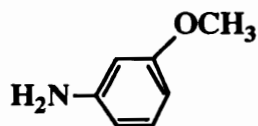
Purification: HA was dried over calcium hydride and distilled under reduced pressure generated by a vacuum pump. m-Anisidine was stored over molecular sieves.

3.1.2.18 2, 2, 2-Trifluoroacetophenone

Supplier:	Dr. Harvey Grubbs, Phillip Morris, Richmond VA (see reference 91)
Empirical Formula:	$C_8H_5F_3O$
Molecular Weight:	172.12
Boiling Point (pure), °C:	165-166 °C
Structure	
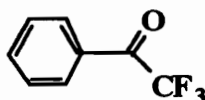
Purification: 2, 2, 2-Trifluoroacetophenone was distilled under reduced pressure generated by a vacuum pump.

3.1.2.19 <u>1, 1-bis(4-aminophenyl)-1-phenyl-2, 2, 2-trifluoroethane (3F diamine or 3FDAM)</u>: The synthesis of the 3F diamine is depicted in Figure 3.1.2. In a typical experiment, 75 g of 2, 2, 2-trifluoroacetophone (0.43 moles) and 300 ml of aniline were

Aniline Hydrochloride reflux, 24hours
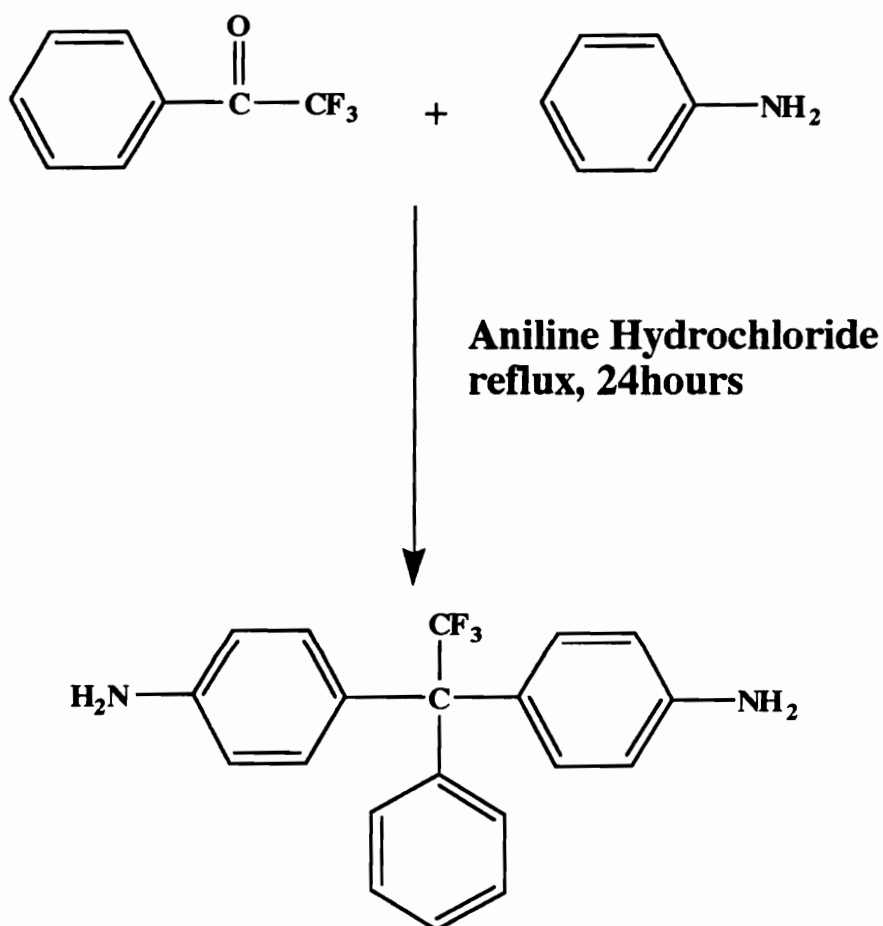
3.1.2 Synthesis of 1, 1-bis(4-aminophenyl)-1-phenyl-2, 2, 2-trifluoroethane
(3F diamine or 3FDAM)

placed in a three neck, 1-liter round bottom flask equipped with a magnetic stirrer, reflux condenser and thermometer. Aniline hydrochloride (75 g, 0.58 mole) was added with stirring; the reaction mixture forming a solid cake until heated to about 60 °C. The reaction mixture was refluxed at 160 °C for twenty-four hours. The reaction was cooled below 100 °C and 75 g (0.88 mole) of sodium carbonate slurried in 200 ml of water was added in small portions. The purple solution was steam distilled until the distillate was clear. The aqueous solution was cooled and the solid purple residue was collected by filtration. After washing with 200 ml of water, the crude material was dried in a vacuum oven at 110 °C for at least 18 hours.

The crude 3F diamine was purified as follows. 50 grams of the crude material was put into 100 ml of 95 % ethanol along with 100 ml of concentrated HCl (12 N) and 100 ml of H_2O. The deep purple solution was treated with activated charcoal and boiled for ~ 5 minutes. The charcoal was removed by filtration through Celite[TM]. The solution was treated with charcoal two more times. A 50 weight % solution of KOH in water was added to the purple solution until it became basic by pH paper. The solution was then extracted with 200 ml of toluene and then with 100 ml of toluene. The toluene fractions were combined and the toluene was removed under reduced pressure to leave a tan powder. Finally, the 3F diamine was recrystallized from 95 % ethanol. 3F diamine was added to the ethanol at a 1 to 9 ratio by weight. The mixture is heated until the 3F diamine is dissolved. The solution is cooled below 0 °C and the off-white crytals are collected by filtration. The recrystallized 3F diamine was dried at 110 °C in a vacuum oven. The overall yield is 50 - 70 %. The pure 3F diamine has a melting point of 218-220 °C. (The procedure for the synthesis and purification of 3F diamine is credited to Dr. Harvey Grubbs, Phillip Morris, Richmond VA. His work can be consulted for further details (91, 179).)

3.2 POLYMER SYNTHESIS

The high molecular weight polyimide homopolymers, randomly segmented polyimide siloxane copolymers and polyimide oligomers studied in this research were synthesized by first combining a diamine and a dianhydride to form the intermediate poly(amic acid). The poly(amic acid) was cyclodehydrated in solution in the presence of an azeotroping agent. Generally, an amine or anhydride monofunctional reagent was added to control molecular weight and endgroups.

All of the polyimides were made in a three neck, round bottom flask pictured in Figure 3.2.1. The size of the flask varied according to the amount of polymer being made. The flasks were fitted with a nitrogen gas inlet, an overhead stirrer and a reverse Dean Stark trap to which a condenser was attached. The apparatus was flamed dried prior to use with a Bunsen burner. A nitrogen purge was maintained through the flask while drying and during the polymerization. If ODCB was used during imidization then the reverse Dean Stark was filled with ODCB. If CHP was used then the reverse Dean Stark trap was left empty. Synthetic procedures will be outlined for the synthesis of high molecular weight polyimides, and polyimide oligomers terminated with 2-aminopyridine and 2-aminopyrimidine.

3.2.1 - Molecular Weight Control and Determination of Monomer Stoichiometry

Throughout this work, molecular weight control techniques were used to obtain well defined functionalized polyimide oligomers and processable polyimide homopolymers and copolymers. The principles of molecular weight and end group control in step growth polymers were first derived from by Carothers (181). The molecular weight of a step growth polymer is dependent on the extent of conversion of the reacting functional groups. Thus, the stoichiometric imbalance of the difunctional monomers or

monofunctional monomer must be carefully controlled to obtain desired molecular weights. This section describes the derivations for the equations used in designing polyimides of controlled molecular weight and end groups. Complete information on the Carothers equation can be found in basic polymer texts by Rudin (58) and Odian (61).

In the Carothers equation, the number average degree of polymerization, X_n, relates to the extent of reaction, p, and average functionality, f_{avg} of the polymer system.

$$(3\text{-}1) \quad X_n = \frac{2}{2 - pf_{avg}}$$

Xn is related to polymer molecular weight by

$$(3\text{-}2) \quad X_n = 2\frac{M_d}{M_{ru}}$$

where M_d is the desired molecular weight of the polymer and M_{ru} is the molecular weight of the repeat unit. The molecular weight of a polymer will be reduced if either the extent of conversion or the average functionality is decreased. The molecular weight may also be related to a stoichiometric imbalance, r, which is normally defined to be less than 1.

$$(3\text{-}3) \quad X_n = \frac{(1+r)}{(1-r)} \quad \text{or} \quad r = \frac{X_n - 1}{X_n + 1}$$

The number averaged molecular weight of a polymer may be controlled by offsetting the stoichiometry of two dissimilar mutually reactive difunctional monomers. The polymer will have the same end group functionality as that of the monomer used in excess. For a generic polymer made from a difunctional monomer AA with "A"

functional groups and an excess of difunctional monomer BB with "B" functional groups, r is defined as

$$(3\text{-}4) \qquad r = \frac{Na}{Nb}$$

where Na is the moles of "A" functional groups and Nb is the moles of "B" functional groups. The amount of AA and BB monomer used is then $\frac{1}{2}Na$ and $\frac{1}{2}Nb$, respectively.

The molecular weight can also be contolled by adding a monofunctional endgoup. The monofunctional endgroup, B, has the same functionality as monomer BB. In this case, the moles of "A" functional groups in the difunctional monomer, AA is given as Na and the moles of AA is $\frac{1}{2}Na$. The moles of "b" functional group in the difunctional monomer, BB, is given as Nb and the moles of BB is $\frac{1}{2}Nb$. The moles of "b" functionality in the monofunctional endgroup, B is given as Nb' which is also equal to the moles of B. The moles of monomers, both mono- and difunctional, containing "B" function groups is $\frac{1}{2}Nb + Nb'$. Thus, the stoichiometric imbalance is defined as

$$(3\text{-}5) \qquad r = \frac{\frac{1}{2}Na}{\frac{1}{2}Nb + Nb'}$$

Equation 3-5 simplifies to

$$(3\text{-}6) \qquad r = \frac{Na}{Nb + 2Nb'}$$

which can be found in Odian (55).

Equation 3-6 is used to determine the relative amount of monomers needed to obtain a desired molecular weight. Generally, N_a is assigned an arbitrary value and the values of N_b and N_b' must be calculated. To determine N_b and N_b', two equations must be solved. The first comes from equation 3-6 which rearranges to

$$(3\text{-}7) \quad N_b + 2N_b' = \frac{N_a}{r}$$

In order to obtain polymers that are only endcapped with the monofunctional end group, the moles of "B" functional groups must equal the moles "A" functional groups. This is expressed in a second equation as

$$(3\text{-}8) \quad N_b + N_b' = N_a$$

By solving equations 3-7 and 3-8 simultaneously, N_b and N_b' can be determined.

3.2.2 - Example of Monomer Stoichiometry Calculations

The variables used in determining the amount of monomers are listed below.

MWPMDA: **molecular weight of PMDA** = 218.12 g/mole

MW3FDAM: **molecular weight of 3FDAM** = 342.36 g/mole

MWPA: **molecular weight of PA** = 148.12 g/mole

X_n is determined in equation 3-2 where M_d is 30.0 kg/mole and M_{ru} is defined below

$$(3\text{-}9) \quad M_{ru} = MWPMDA + MW3FDAM - 36 = 218.12 + 342.36 - 36 = 524.48$$

Since two water molecules are evolved for every repeat unit that is formed, 36 is subtracted from the combined molecular weight of PMDA and 3FDAM. X_n is then calculated as

$$(3\text{-}10) \quad X_n = 2\frac{M_d}{M_{ru}} = 2\frac{30,000}{524.48} = 114.3990$$

The stoichiometric imbalance, r, is determined according to Equation 3-3

$$(3\text{-}11) \quad r = \frac{X_n - 1}{X_n + 1} = \frac{114.3990 - 1}{114.3990 + 1} = 0.98267$$

The moles of monomers to be used in the reaction are determined by solving equations 3-7 and 3-8 for N_b and N_b'. N_a is given a value of 0.1.

$$(3\text{-}12) \quad N_b + 2N_b' = \frac{N_a}{r} = \frac{0.1}{0.98267} = 0.10176$$

$$(3\text{-}13) \quad N_b + N_b' = N_a = 0.1$$

Equation 3-13 is subtracted from Equation 3-12 to give a value for N_b'

$$(3\text{-}14) \quad \begin{aligned} N_b + 2N_b' &= 0.10176 \\ -\,(N_b + N_b' &= 0.1\,) \\ N_b' &= 0.00176 \end{aligned}$$

Substituting N_b' into Equation 3-13 gives

$$(3\text{-}15) \quad N_b + 0.00176 = 0.1$$

$$N_b = 0.09824$$

The moles of PMDA used is $\frac{1}{2}N_b$. The moles of 3FDAM used is $\frac{1}{2}N_a$ and the moles of

PA is N_b'. The values moles and mass of the monomers are summarized below:

	MOLES	**GRAMS**
PMDA	$\frac{1}{2}N_b$ = 0.04912 mole	0.04912 mole x 218.12 g/mole = 10.7137 g
3FDAM	$\frac{1}{2}N_a$ = 0.50000 mole	0.50000 mole x 342.36 g/mole = 17.1180 g
PA	N_b' = 0.00176 mole	0.00176 mole x 148.12 = 0.2612

The amounts of monomers used can be scaled as desired.

3.2.3 - High molecular weight polyimides:

A typical high molecular weight polyimide homopolymer was made by the solution imidization of a poly(amic acid) which was formed from the combination of a dianhydride and a diamine. The molecular weight of the polyimide was controlled by offsetting the stoichiometry of the dianhydride and diamine. A monofunctional anhydride, phthalic anhydride was added to endcap the polyimide with a nonreactive endgroup.

The following is a representative high molecular weight polyimide homopolymer polymerization procedure. The polymer synthesized was a PMDA-3FDAM-PA polyimide with a target molecular weight of 20.0 kg/mole. The 3FDAM (11.4120 grams: 33.33 mmoles) was added via a glass powder funnel to a 250 ml, 3 neck round bottom flask as pictured in Figure 3.2.1. The 3FDAM was rinsed in with 35 ml of NMP and allowed to dissolve. PA (0.1845 gram: 1.25 mmoles) was added and then rinsed in with 10 ml of NMP. Finally, PMDA (7.1361 grams: 32.72 mmoles) was added and rinsed in with 25 ml of NMP to give a concentration of 20 weight % solids. The poly(amic acid)

solution turned yellow and gradually increased in viscosity. The solution was stirred for 1 hour under a nitrogen purge. To imidize the poly(amic acid), 18 ml of ODCB was added to the flask and the reaction was heated to 165-170 °C. The solution was stirred at 165-170 °C for 24 hours. After imidization, the solution was allowed to cool to room temperature. The polyimide was isolated by slowly adding the reaction solution through an addition funnel to 500 ml of methanol stirring in a high speed blender. The polyimide precipitated on contact with the methanol which dissolves the NMP and ODCB but is a nonsolvent for the polyimide. The polyimide was collected by filtration and air dried. The PMDA-3FDAM-PA is dried in a vacuum oven for at least 18 hours at 220-250 °C.

3.2.4 - Polyimide oligomers endcapped with 2-aminopyridine

This section describes the synthesis of an ODPA-Bis P-2AP polyimide oligomer with a target <Mn> of 4.0 kg/mole. The poly(amic acid) and subsequent polyimide preparation was performed in a four-neck flask equipped with a mechanical stirrer, nitrogen inlet and a condenser with drying tube. The ODPA (38.7788 grams: 125.00 mmoles) was dissolved in NMP with slight heating, then cooled to ambient temperature. 2-aminopyridine (3.8743 grams: 41.16 mmoles) was added to the reaction mixture and allowed to react with the ODPA while stirring for 15 to 20 minutes. Bis P (36.4984 grams: 106.1 mmoles) was then added as a powder. All of the monomers were added through a glass powder funnel and rinsed in with NMP to bring the final reaction solids content to 20 weight percent. The reaction was allowed to proceed for 20 hours. Imidization was carried out by first adding 60 ml of ODCB to the poly(amic acid) solution. A reverse Dean Stark trap with a condenser filled with ODCB replaced the drying tube on the flask. The reaction mixture was heated to 165°C by immersion in a hot silicone oil bath. The reaction was allowed to stir for a total of 24 hours to ensure complete imidization. The solution was cooled to ambient temperatures, and the
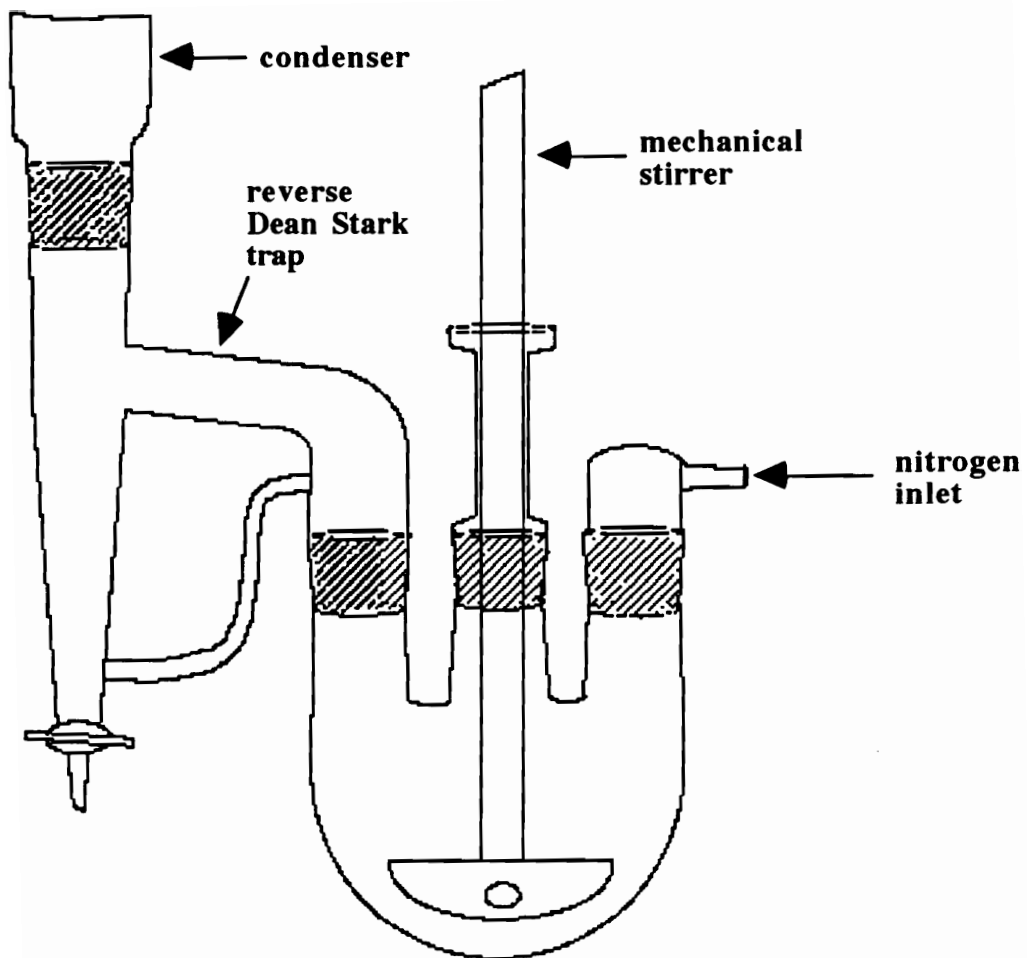
Figure 3.2.1 - Polyimide Reaction Apparatus

polyimide oligomer was precipitated in methanol in a high speed blender. Upon cooling, the ODPA-Bis P solutions became turbid. The polyimide oligomers were collected by filtration and dried in a vacuum oven for 18 hours at 200°C and for 1 hour at 300°C.

3.2.5 - N-(2-pyrimidyl)phthalimide terminated polyimide oligomers

Since the 2-aminopyrimidine is less reactive than the 2-aminopyridine, the order of monomer addition was changed in the synthesis of the N-(2-pyrimidyl)phthalimide terminated polyimide oligomers. The polyimide oligomers were made in the same manner as described for the synthesis of 6FDA-Bis P-2Apm below. The polyimides were synthesized through the formation of a poly(amic acid) precursor. The poly(amic acid) preparation was performed in a four-neck flask equipped with a stopper mechanical stirrer, nitrogen inlet and a reverse Dean Stark trap with a condenser. Bis P (13.6099 grams, 0.0396 mole) was dissolved in 50 ml of NMP. 6FDA (22.2000 grams, 0.05 mole) was then added as a powder and rinsed with 50 ml of NMP. To remove water generated during the imidization, 26 ml of CHP was added to bring the final solids content to 30 wt%. The poly(amic acid) solution stirred for 1 hour during which an increase in the solution viscosity was observed. To effect imidization of the poly(amic acid), the solution was heated in an oil bath to 175 °C. The solution was allowed to stir for 12 hours then a large excess of the 2-aminopyrimidine (6.0 grams, 0.06 mole) was added to the reaction flask. The solution was stirred for an additional 12 hours at 175 °C. The polymer solution was then cooled and the product was precipitated in methanal. The polyimide oligomer was filtered, washed with methanol and dried in a vacuum oven at ~ 230°C for 15 hours.

3.2.6 - Perfectly alternating polyimide siloxane copolymers

The copolymer synthesis was carried out in a three neck round bottom flask equipped with a mechanical stirrer, stopper and a condenser. For example, the 6FDA-Bis P-2APm polyimide oligomer (10.000 grams, 2.16 mmoles) was dissolved in chlorobenzene and heated to ~110°C. The aminopropyl terminated polydimethyl siloxane (2.3121 grams, 2.12 mmoles) was added slowly and rinsed with chlorobenzene to bring the final reaction solids content to 15 percent. The reaction was stirred at ~110°C for 3 to 5 hours. The solution was cooled to ambient temperatures and cast onto silynated glass plates. The films were put in a vacuum oven at room temperature for 18 to 20 hours. They were then heated under vacuum to 100 °C for 1 hour and 250 to 280 °C for 3 hours.

The high molecular weight ODPA-Bis P-2APm (<Mn> = 11.0 kg/mole) polyimide oligomer was less soluble in chlorobenzene. Accordingly, ODPA-Bis P-2APm-11K (15.00 grams, 1.37 mmoles) was dissolved in 60 ml of $CHCl_3$ and the solution was heated to 60°C. PSX was added slowly and rinsed with 10 ml of $CHCl_3$. The reaction was stirred for 2 hours and then 70 ml of chlorobenzene was added and then heated to 110°C while distilling off the $CHCl_3$. After 2 more hours, the reaction was cooled and films were made as described above. The ODPA-mDDS4.3-PSX1.09 copolymer was made in a 70:30 (by volume) chlorobenzene:NMP mixture to maintain homogeniety.

3.2.7 - Randomly Segmented Polyimide Siloxane Copolymers

The random segmented polyimide siloxane copolymers were prepared by a one step solution imidization method similar to that described by Wescott et. al. (14). The <Mn> was controlled for 40.0 kg/mole. For the synthesis of a ODPA-Bis P-21% PSX1.09, ODPA (7.6133 grams, 24.54 mmoles) was dissolved in 30 ml of ODCB with 3 ml of NMP in a 250 ml four neck round bottom flask equipped with a mechanical stirrer,

nitrogen inlet, stopper, and a reverse Dean Stark trap filled with ODCB and fitted with a condenser. The solution was heated to 165 °C, and PSX1.09 (4.0112 grams, 3.68 mmoles) was added slowly and the solution was allowed to stir for 30 minutes. Bisaniline P (7.3341grams, 21.32 mmoles) was added with 20 ml of ODCB. After another 45 minutes, phthalic anhydride (0.1361 gram, 0.92 mmole) was added with 10 ml of ODCB. The reaction was stirred at 165°C for 24 hours then the reaction was cooled and the product was precipited in methanol. Films were made by dissolving the polymer in chlorobenzene at a 15 wt % concentration, cast on silylated glass plates and heated in the same way as the perfectly alternating polyimide siloxane copolymers.

3.3 - MODEL STUDY

3.3.1 - Synthesis of N-(2-pyrimidyl)phthalimide

The synthesis of N-(2-pyrimidyl)phthalimide was performed in a 50 ml, one neck round bottom flask to which a reverse Dean Stark trap with condenser was attached. Phthalic anhydride (5.00 grams, 0.034 mole) and 2-aminopyrimidine (3.50 grams, 0.037 mole) was added to flask with 30 ml of ODCB. The mixture was heated to reflux and stirred for 24 hours. The reaction was cooled during which the product precipitated from solution. The product was filtered and washed with 20 ml of ODCB and then 150 ml of hexane. The product was then stirred in 100 ml of acetone, filtered and dried at 120 °C under vacuum for 20 hours. Yield 85 %. [1]H n.m.r. (400 MHz, DMSO-d6) 7.40-7.44 (t, 1H), 7.80-7.86 (m, 2H), 7.98-8.4 (m, 2H), 8.94 (d, 2H). Anal. Calcd: C, 64.00; H, 3.11; N, 18.67. Found: C, 64.12; H, 3.11; N, 18.71

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3.3.2 - Model Study - Reaction of hexylamine with N-(2-pyrimidyl)phthalimide

N-(2-pyrimidyl)phthalimide (0.4007 gram, 1.779 mmoles) was added with the deuterated solvent (4.4 ml of DMSO-d_6 or 3.5 ml of CDCl$_3$) to a 1 dram vial. Hexyl amine (0.235 ml, 1.779 mmoles) was syringed into the vial. After the solution became homogeneous, a portion was transferred to an n.m.r. tube and the reaction was then monitered by ^{1}H n.m.r. at the appropriate temperature.

3.3.3 - Model Study - Reaction of m-anisidine with N-(2-pyrimidyl)phthalimide

N-(2-pyrimidyl)phthalimide (0.5376 gram, 2.387 mmoles) was added to 7.5 ml of deuterated DMSO followed by the addition of 0.0052 gram of Zn(OAc)$_2$•2H$_2$O to a 50 ml, 1 neck round bottom flask. The solution was heated to 75°C and then m-anisidine (0.2940 gram, 2.387 mmoles) was added. Samples were taken at various times and examined by ^{1}H n.m.r.

3.4 POLYIMIDE SYNTHESIS THROUGH THE TRANSIMIDIZATION ROUTE

3.4.1 - Synthesis of N, N' -(2-pyrimidyl) bisphthalimides

The N, N'-(2-pyrimidyl)bisphthalimides were synthesized in the same reaction apparatus used in the synthesis of the polyimides. 6FDA (0.06 mole, 26.6 grams) and 2-aminopyrimidine (0.15 mole, 14.3 grams) was added to the reaction flask with 93 ml of ODCB. The reaction mixture was turbid until it was heated to reflux and then the solution cleared. After several hours at reflux temperatures, the product began to precipitate from solution. The reaction was stirred at reflux for 24 hours. The solution was then cooled and the product was collected by filtration. The product was rinsed with 50 ml of ODCB and then 100 ml of acetone. The product was then stirred in 200 ml of acetone, collected by filtration and dried in a vacuum oven at 125 °C for 20 hours. Yield

- 94 %. When PMDA and BPDA was used, the reaction mixture was refluxed for 48 hours and remained turbid the entire time. The N, N' pyrimidine bispthalimides that were made are listed below.

3.4.2.1 N, N'-(2-pyrimidyl)bisphthalimide Derivative of 6F dianhydride (6FDA-2APm)

Empirical Formula:	$C_{27}H_{12}F_6N_6O_4$
Elemental Analysis:	Calcd: C, 54.18; H, 2.00; N, 14.05
	Found: C, 54.28; H, 2.03; N, 14.11
Molecular Weight, g/mole:	598.22
Melting Point (pure), °C:	309 - 311
Structure	
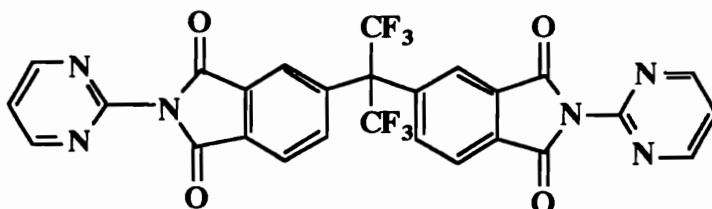
3.4.2.2 N, N'-(2-pyrimidyl)bisphthalimide Derivative of Oxydiphthalic Anhydride (ODPA-2APm)

Empirical Formula:	$C_{24}H_{12}N_6O_5$
Elemental Analysis	Calcd: C, 62.07; H, 2.59; N, 18.10
	Found: C, 61.96; H, 2.56; N, 18.03
Molecular Weight, g/mole:	464.45
Melting Point (pure), °C:	320 - 322
Structure	
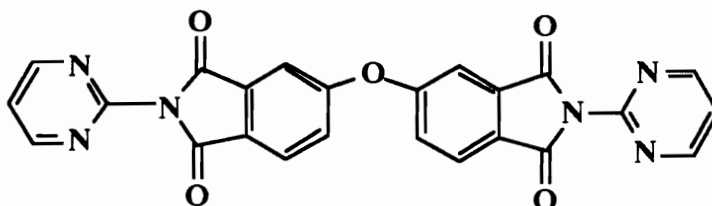
3.4.2.3 N, N'-(2-pyrimidyl)bisphthalimide Derivative of Pyromellitic Dianhydride (PMDA-2APm)

Empirical Formula: $C_{18}H_8N_6O_4$

Molecular Weight, g/mole: 372.34

Melting Point (pure), °C: > 400

Structure
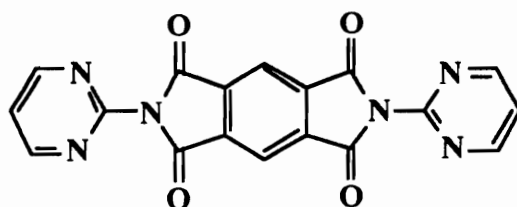
3.4.2.4 N, N'-(2-pyrimidyl)bisphthalimide Derivative of Biphenyl Dianhydride (BPDA-2APm)

Empirical Formula: $C_{24}H_{12}N_6O_4$

Molecular Weight: 448.42

Melting Point (pure), °C: > 400 °C

Structure
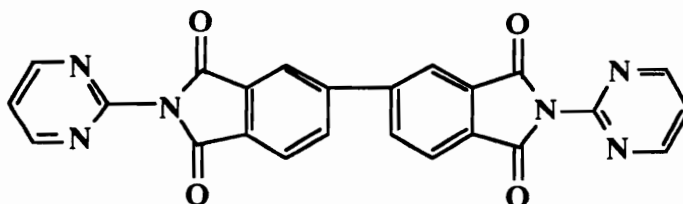
3.4.2 - Synthesis of the polyimide homopolymers through the transimidization route

Using the transimidization route, polyimides were made by combining the N,N'- (2-pyrimidyl)-bisphthalimides and an aromatic diamine. The reactions were carried out in a three neck flask equipped with a mechanical stirrer, stopper and condenser. The monomers were reacted in equimolar amounts. For example, 4,4'-ODA (1.0012 grams, 0.005 mole) was dissolved in NMP and heated to 65 to 70 °C. 1 ml of glacial acetic acid

was then added. 6FDA-2APm (2.9911 grams, 0.005 mole) was added and rinsed in with NMP to bring the final concentration to 20 weight % solids. The reaction was stirred for 24 hours. The polymer was isolated by pouring the solution into a high speed blender containing methanol. The polymer was isolated by filtration. The polymer was dried at 70 °C for 24 hours for spectroscopic characterization and dried at 200 °C for 24 hours for intrinsic viscosity determination.

3.5 - CHARACTERIZATION OF POLYMERS AND MONOMERS

3.5.1 - Intrinsic and Inherent Viscosities

Intrinsic viscosities were determined for all of the soluble polyimide homopolymers and polyimide siloxane copolymers to determine relative molecular weights. Cannon-Ubbelohde dilution viscosometers with various capillary sizes were used to collect data to determine intrinsic viscosities. The polyimide homopolymers were generally run in NMP at 25 °C and the polyimide siloxane copolymers were run in chloroform at 25 °C. The intrinsic viscosity values were obtained by using four different polymer concentrations and the results were linearly extrapolated to the zero concentration. Inherent viscosities were determined at a concentration of 0.5 g/dl.

3.5.2 - Nuclear Magnetic Resonance (n.m.r.) Spectroscopy

Proton nuclear magnetic resonance (^{1}H n.m.r.) was used to obtain chemical composition information of both polymers and monomers synthesized. All the n.m.r. analysis was done on a Varian Unity 400 MHz NMR. Polyimide homopolymer samples

were run in deuterated solvents, such as, deuterated DMSO and chloroform at concentrations of 1 to 10 % solids. 48 to 64 scans were usually taken of the polyimide homopolymers. The polyimide siloxane copolymers were analyzed by [1]H n.m.r. in CDCl3 dried over molecular sieves. The n.m.r. analysis of the polyimide siloxane copolymers had to be done in dry solvent to obtain reproducible integral values. [1]H n.m.r. was also used to follow the extent of reaction in the model studies of the transimidization reaction. The model studies could be followed in the Varian Unity 400 MHz NMR at the desired reaction temperatures.

Carbon 13 nuclear magnetic resonance ([13]C n.m.r.) was also run on the Varian Unity 400 MHz NMR. [13]C n.m.r. was done in deuterated chloroform.

[1]H n.m.r. was used to estimate the number average molecular weight, <Mn>, of polyimide homopolymers endcapped with t-butyl phthalic anhydride and of polyimide oligomers endcapped with 2-aminopyridine or 2-aminopyrimidine. The <Mn> was estimated from the following equations.

The <Mn> of a polymer can be determined from the equation

3-16 $\langle Mn \rangle = M_{ru} \cdot n + M_{end}$

where M_{ru} is the molecular weight of the repeat unit, **n** is the number of repeat units and M_{end} is the molecular weight of the endgroups. [1]H n.m.r. was used to determine **n**. The calculations assume that all of the end groups are derived from the monofunctional endcapper. The integral ratio of the resonance peak of endgroup protons was compared to the integral ratio of the resonance peak of protons in the repeat unit. **n** was determined as follows

$$3\text{-}17 \quad \frac{Pru * n}{Pend} = \frac{Iru}{Iend}$$

where $\mathbf{P_{ru}}$ is the number of protons examined in the repeat unit, $\mathbf{P_{end}}$ is the number of protons examined in the endgroup, $\mathbf{I_{ru}}$ is the integral value of the resonance peak of the protons in the repeat unit, and $\mathbf{I_{end}}$ is the integral value of the resonance peak of endgroup protons.

Below is a sample calculation for the <Mn> determination of a PMDA-3FDAM-t-butyl PA polyimide with a target molecular weight of 10,000 g/mole. The [1]H n.m.r. of the PMDA-3FDAM-t-butyl PA polyimide is depicted in Figure 3.5.1. The resonance peak of the t-butyl groups occurs at 1.4 ppm and is ratioed to the resonance peak at 8.4 ppm which results from the proton of the PMDA group. Various values are listed below.

$$\mathbf{M_{ru}} = 524.52 \text{ g/mole}$$

$$\mathbf{M_{end}} = 714.84 \text{ g/mole}$$

$$\mathbf{P_{ru}} = 2$$

$$\mathbf{P_{end}} = 18$$

$$\mathbf{I_{ru}} = 14.05$$

$$\mathbf{I_{end}} = 7.55$$

Using equation 3-17, n is determined as follows:

$$3\text{-}18 \quad \frac{2 * n}{18} = \frac{14.05}{7.55} \qquad n = 16.75$$

Then <Mn> can be determined from n.

88
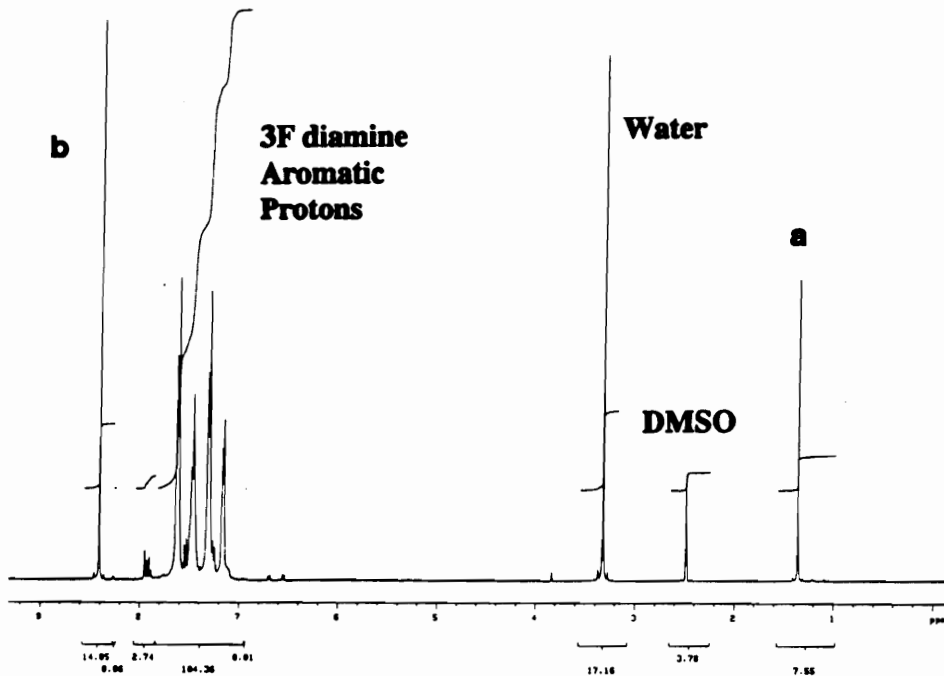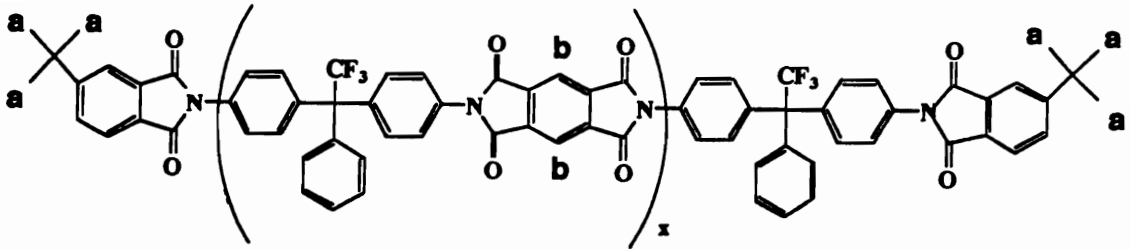
Figure 3.5.1 - ^{1}H n.m.r. Spectrum of a
10.0 kg/mole PMDA-3F diamine-t-butyl PA Polyimide

$$3\text{-}19 \quad <Mn> = 524.52 \text{ g/mole} * 16.75 + 714.84 \text{ g/mole} = 9500 \text{ g/mole}$$

3.5.3 - Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to obtain IR spectra of the final polymers and monomers using a Nicolet MX-1 spectrophotometer. Polymer samples were analyzed by casting thin films on salt plates and monomers were run as KBr pellets. FTIR was used to measure the extent of imidization of polymer samples by examining the spectral imide bands at 1778 cm^{-1}, 1728 cm^{-1} and 725 cm^{-1}.

3.5.4 - Differential Scanning Calorimetry (DSC)

DSC was used to determine the glass transition tempertures of the polyimide homopolymers and the upper glass transition temperatures of the polyimide siloxane copolymers. DSC was conducted on a Perkin Elmer Model DSC7. DSC scans were run under a nitrogen atmosphere at 10 °C per minute. All of the polyimides were scanned twice. The Tg values were obtained from a second heating cycle after rapid cooling from above the Tg of the polymer samples. The transition temperature was taken as the midpoint of the endotherm.

3.5.5 - Dynamic Mechanical Analysis (DMA)

The glass transition temperature of the polyimide siloxane copolymers and some of the polyimide homopolymers were measured by DMA. DMA was carried out on polymer films using a Seiko Model 200 DMS. The storage modulus, loss modulus and tan delta curves were obtained for all samples run. The DMA samples were monitored at a heating rate of 10 °C/min and a frequency of 1 Hz. The glass transition temperature was taken as the peak of the tan delta curves.

3.5.6 - Thermogravimetric Analysis (TGA)

Dynamic TGA was performed on a Perkin Elmer TGA7 in order to determine the relative thermal stabilities of polyimide homopolymers and polyimide siloxane copolymers. Thin films were placed in a platinum pan. The samples were heated at a rate of 10 °C per minute in an air atmosphere. Weight loss of the sample was measured as a function of time and temperature. The thermal stability of the polymers is generally reported as the temperature for the 5 weight % loss. Isothermal TGA could also be run on the Perkin Elmer TGA7 under an air atmosphere. The samples were held at a constant temperature and the weight loss was measured as a function of time

Isothermal TGA was also run on larger samples in a Blue M forced air oven. The sample films (5 -10 mils thick) were dried to a constant weight and heated in the Blue M oven to the test temperature. The samples were aged under an air atmosphere flowing over the samples at 25 cubic feet per hour. The films were periodically removed and weighed on an analytical balance. The weight of the sample was plotted as a function of time.

3.5.7 - Mechanical Testing

The samples used in the stress-strain analysis of the polyimide siloxane copolymers were taken from either solution cast or compression molded films. The solution cast films were made from chlorobenzene and dried in a vacuum oven at or near the Tg of the polymer. The compression molded samples were pressed at 70 - 100 °C above the Tg of the polymer under a pressure of 15,000 PSI for 20 minutes.

Instron model 1123 were used to determine the room temperature mechanical behavior of the polyimide siloxane copolymers. Dogbone shaped specimens were cut from films using a steel rule die (ASTM-638IV) against a polyethylene cutting board.

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The specimen gauge length was 10 mm and the width was 2.76 mm. Sample thicknesses were ~0.005 to 0.010 inch. The crosshead extension rate was 0.10 inch per minute. Reported results are an average of 3 to 5 samples.

3.5.8 - Gel Permeation Chromatography

GPC measurements were performed on a Waters 150-CALC/GPC with viscosity detector. <Mn> and <Mw>/<Mn> values for the polyimides were determined using universal calibration techniques (182).

CHAPTER 4 - RESULTS AND DISCUSSION

4.1 INTRODUCTION

The research in this section is presented in seven sections. The first section reports the synthesis of polyimide and investigates the effect of the poly(amic acid) equilibration time on the molecular weight distribution of the final polyimide. The second section includes the synthesis and characterization of soluble, fully cyclized polyimide homopolymers with very high glass transition temperatures. The third section discusses the synthesis and characterization of perfectly alternating segmented polyimide siloxane copolymers made from 2-aminopyridine terminated polyimide oligomers and aminopropyl terminated polydimethyl siloxanes. The last four sections explores the use of N-(2-pyrimidyl)phthalimides in the transimidization route. N-(2-pyrimidyl)phthalimides were used in a low temperature synthesis of polyimide homopolymers and perfectly alternating segmented polyimide siloxane copolymers. Also, physical properties of the perfectly alternating segmented polyimide siloxane copolymers were investigated and compared to analogous randomly segmented polyimide siloxane copolymers.

To promote a clear discussion of polyimides, an unmistakable identification of each polyimide system must be made. The nomenclature to describe the polyimide systems will consist of a complete listing of the monomers and oligomers employed in its synthesis, starting with the dianhydrides, then diamines, followed by the monofunctional reagents. For example, a polyimide made from pyromellitic dianhydride (PMDA), 3F diamine (3FDAM) and phthalic anhydride is designated as:

PMDA-3FDAM-PA

Polyimides consisting of one dianhydride and one diamine will be referred to as homopolymers. Polyimides consisting of multiple dianhydrides or multiple diamines

will be referred to as copolyimides. For the copolyimides, a corresponding molar percentage of the total dianhydride or diamine content will be indicated. Polyimide systems with monomers and oligomers or two different oligomers will referred to as copolymers. The perfectly alternating segmented polyimide siloxane copolymers will be designated by listing the polyimide oligomer first and its <Mn> followed by the polydimethyl siloxane (PSX) oligomer and its <Mn>. A perfectly alternating polyimide siloxane copolymer made from ODPA-Bis P-2AP4.0 and PSX1.07 is listed as:

ODPA-Bis P4.0-PSX1.07

Randomly segmented copolymers will be listed with the dianhydride first, then the diamine, followed by the weight % of the PSX oligomer, the <Mn> of PSX oligomer and the monofunctional endcapper. A copolymer made with ODPA, Bis P, PA and 20 weight % PSX1.07 is designated as:

ODPA-Bis P-20% PSX1.07

4.2   POLYIMIDES SYNTHESIS

Synthesis of polyimides by the solution imidization route was generally performed in two steps. First, the polyamic acid was formed from the combination of a diamine and a dianhydride in a polar aprotic solvent, after which, an azeotroping agent was added and the reaction was heated to 165 °C to complete the imidization. Before the poly(amic acid) was heated, it was stirred from 8 to 24 hours to allow for equilibration to a most probable molecular weight distribution (11). However, Kim, et. al. showed that there was a significant amount of chain cleavage and recombination during imidization (44). Assuming this was a random process, equilibration to a most probable molecular weight distribution should also occur

during imidization. Therefore, the molecular weight distribution of a polyimide was investigated with respect to the equilibration time of the poly(amic acid).

Figure 4.2.1 depicts the synthesis of a 6FDA-Bis P-t-butyl PA polyimide. The poly(amic acid) was formed by first dissolving Bis P in NMP. The solution was briefly heated in order to dissolve the Bis P. t-Butyl PA was added followed by 6FDA. The monomers were rinsed in with NMP to bring the final concentration to 20 weight % solids. The target molecular weight was 30.0 kg/mole. Two poly(amic acid) solutions were made. One poly(amic acid) solution stirred for only one hour before imidizing and will be referred to as the 1 hour poly(amic acid). Another poly(amic acid) solution was stirred for 24 hours and will be referred to as the 24 hour poly(amic acid). In both cases, solution imidization was carried out using o-dichlorobenzene as an azeotroping agent. The poly(amic acid)s were heated for 24 hours at 165 °C to form the fully cyclized polyimides.

The polyimides made from the 1 hour and 24 hour poly(amic acid) were investigated using GPC and ^{1}H n.m.r. GPC traces for the two polyimides are shown in Figure 4.2.2. Both polyimides made from the 1 hour and 24 hour poly(amic acid) had <Mn>'s of 31.0 kg/mole and molecular weight distributions of 1.9. The <Mn>'s determined by ^{1}H n.m.r., Figure 4.2.3, were in close agreement with the <Mn>'s determined by GPC. GPC values of other polyimides that were imidized immediately after poly(amic acid) formation also showed narrow molecular weight distributions. For example, a PMDA-3Fdiamine-PA polyimide that was imidized immediately after the poly(amic acid) was formed had a <Mn> of 23.0 kg/mole (the target <Mn> was 35.0 kg/mole) and a <Mw>/<Mn> of 2.0. Thus, no equilibration of the poly(amic acid) is necessary prior to solution imidization in order to achieve gaussian molecular weight distributions (<Mw>/<Mn> = 2).
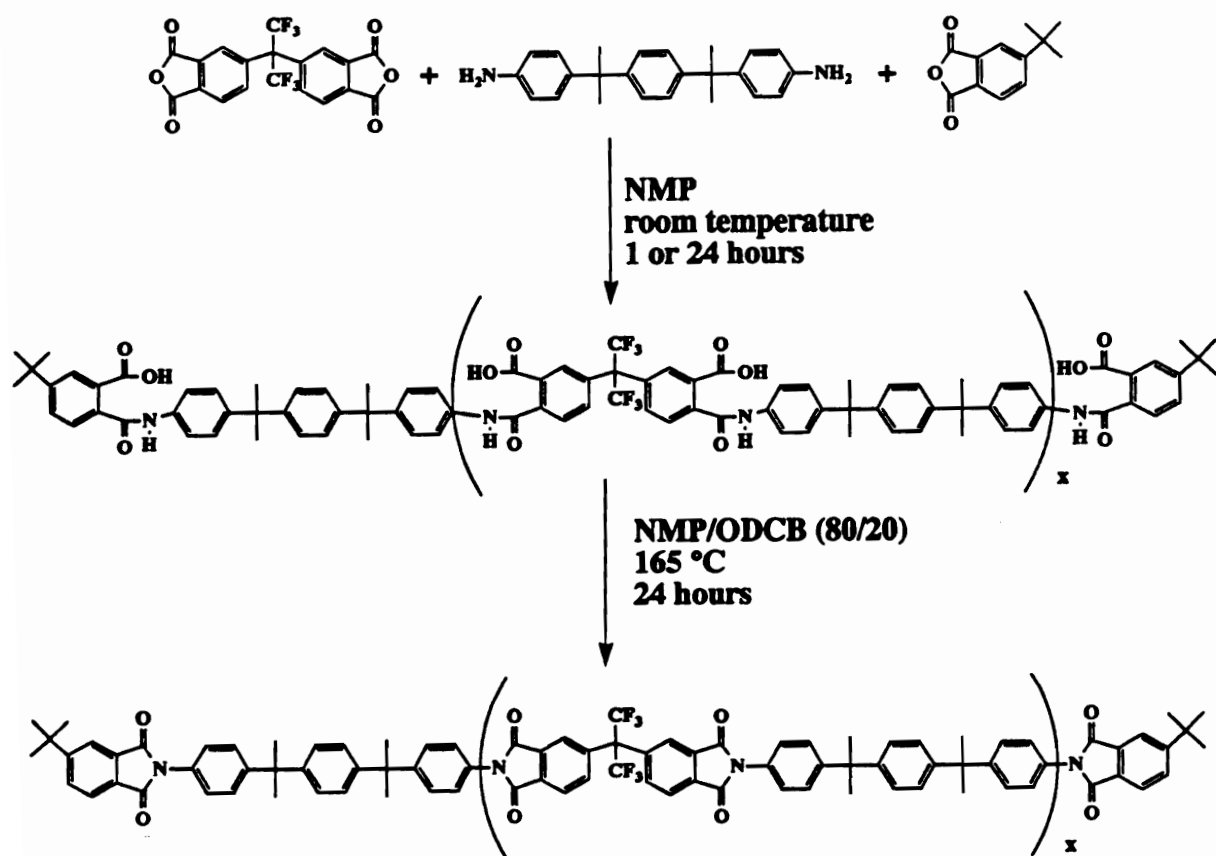
Figure 4.2.1 - Synthesis of 6FDA-Bis P-t-butyl PA Polyimides
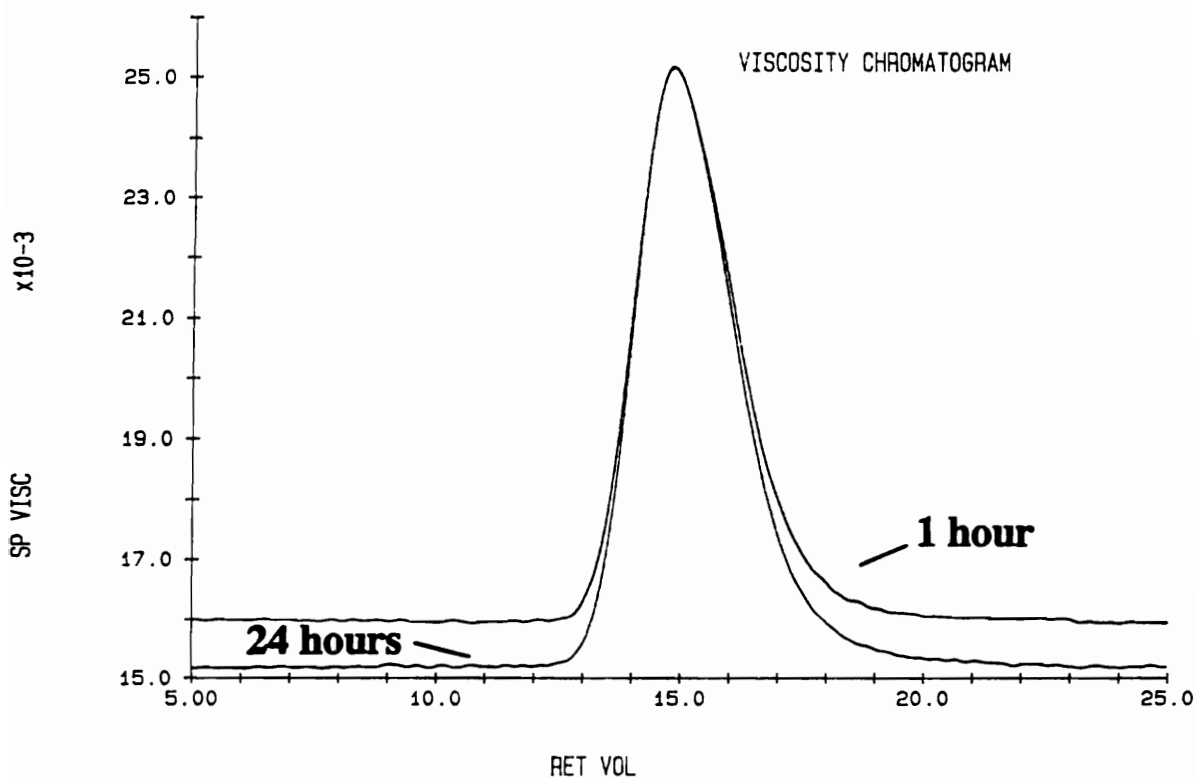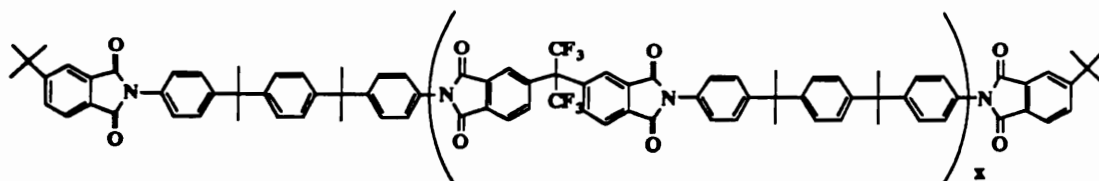
Figure 4.2.2 - GPC Traces of 6FDA-Bis P-t-butyl PA Polyimides

Figure 4.2.3 - ^{1}H n.m.r. Spectrum of a 6FDA-Bis P-t-butyl PA Polyimide
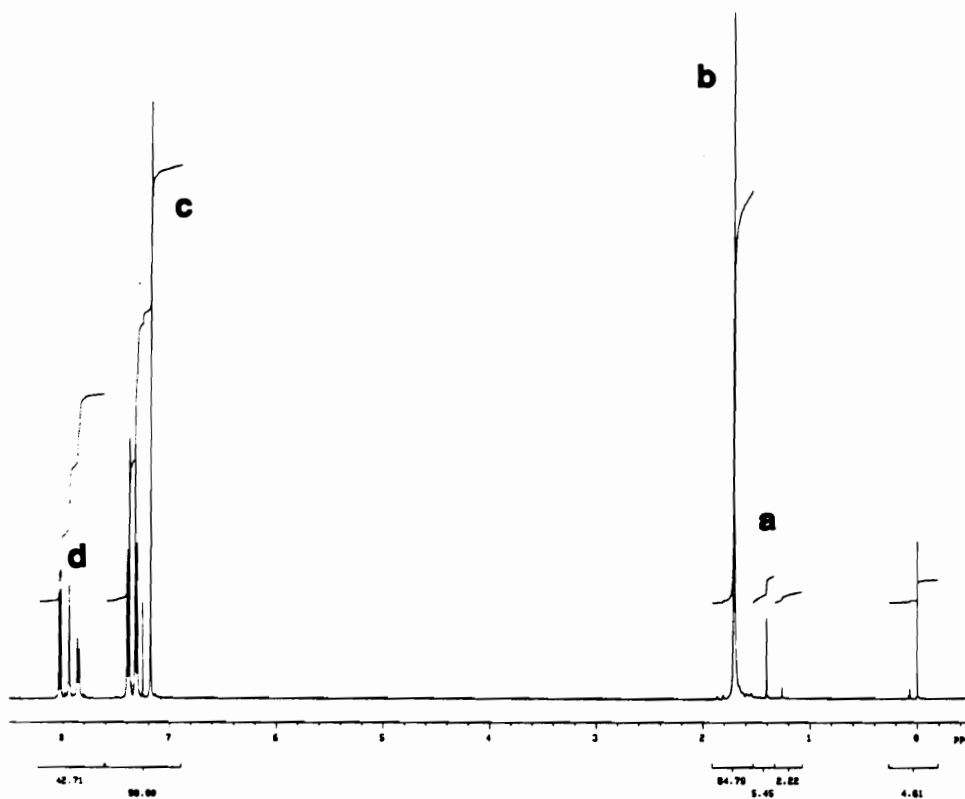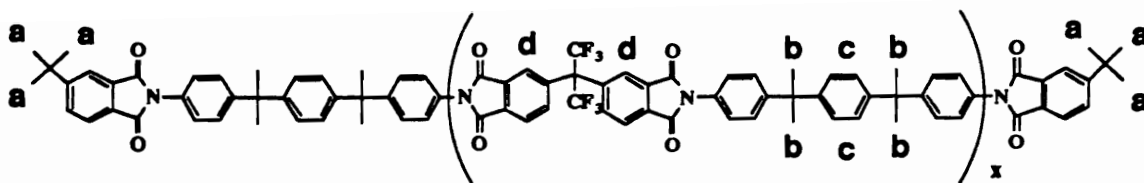
1 hour PAA
<Mn> by n.m.r. = 32.0 kg/mole

24 hour PAA
<Mn> by n.m.r. = 36.0 kg/mole

4.3   HIGH TG POLYIMIDES

4.3.1   Synthesis

The PMDA-3FDAM-PA polyimide synthesis depicted in Figure 4.3.1 is an example of the method used in making the high Tg polyimides. The poly(amic acid) intermediate was formed by dissolving the 3F diamine in a polar aprotic solvent, NMP. To insure complete incorporation, the monofunctional endcapper was added next and was rinsed in with additional NMP. Finally the dianhydride was added as a solid and rinsed in with NMP to bring the final concentration to 20 weight % solids. The solution was stirred at ambient temperature until it became homogeneous.   Ten to fifteen minutes after dissolution of the dianhydride, a notable increase in the viscosity of the poly(amic acid) solution was observed. The increase in viscosity indicated that the molecular weight of the poly(amic acid) was increasing. The color of the poly(amic acid) solution was generally yellow.

Cyclization of the poly(amic acid) was affected by heating the solution to temperatures of 150 °C to 180°C. On cyclization of the poly(amic acid) solution, water was generated which had to be removed in order to achieve complete cyclization. This was achieved by using an azeotroping agent in the reaction mixture. o-Dichlorobenzene (ODCB) was added to the poly(amic acid) solution as an azeotroping agent.   An 8:2 mixture of the NMP/ODCB was sufficient for the efficient removal of water which was formed upon the conversion of the amic acid to the imide. The poly(amic acid) solution was then heated to 170 °C and allowed to stir for 20 to 24 hours. During this time, water was seen collecting in the reverse Dean-Stark trap. The reaction mixture also turned very dark in color which was likely the result of degradation of the NMP.
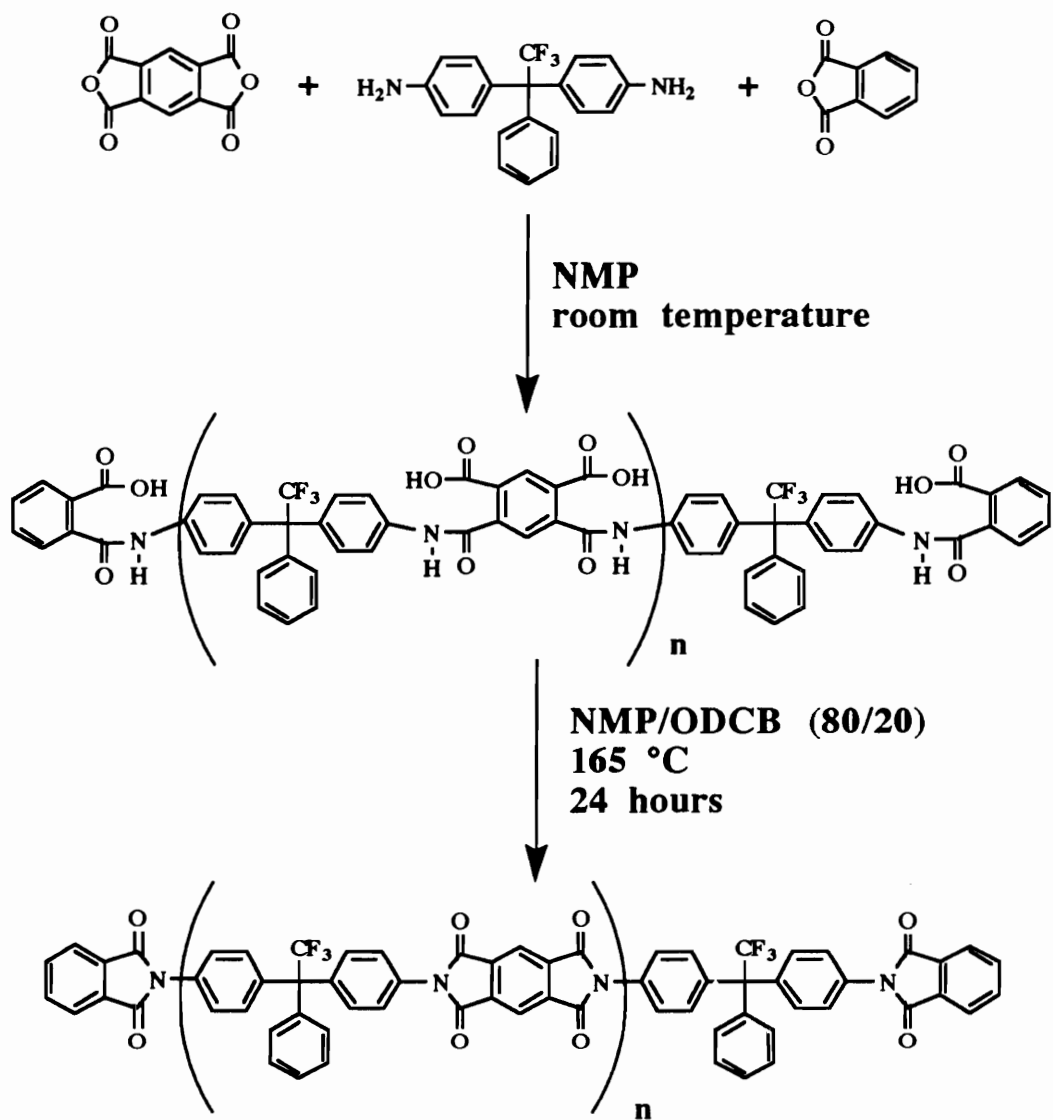
Figure 4.3.1 - Synthesis of a PMDA-3FDAM-PA Polyimide

At the end of the reaction, the solution was cooled. The polymer was isolated by pouring the reaction mixture into methanol which was rapidly stirred in a blender. Methanol was a nonsolvent for the polyimides but was miscible with NMP and ODCB, so the polyimide precipitated when the solution was added to the methanol. About 10 parts of methanol were used to one part of the polymer solution. Often, the polyimide solutions were very viscous and needed to be diluted with additional NMP before precipitating in methanol. The polyimide was collected by filtration and dried in a vacuum oven at 220 °C to 250 °C for 20 hours.

The polyimide homopolymers with the phosphorus containing monomer, DDPPO, were made by the same solution imidization method used with the 3F diamine containing polyimides. However, no attempt was made to control the molecular weight or the endgroups of the polyimides. Thus, equimolar amounts of the diamine and the dianhydride were used in the polymerization, and no endcapper was added.

The properties of the 3F diamine containing polyimides were modified through the incorporation of various comonomers. The order of monomer addition was very important in the synthesis of the poly(amic acid). For example, the PMDA/6FDA-3FDAM-PA poly(amic acid)s was made by adding the less reactive dianhydride, 6FDA, to the 3FDAM in NMP and allowing the solutions to stir for 10 to 15 minutes. Phthalic anhydride was then added followed by PMDA. This order of addition was followed to maximize the possibility that a statistical or random copolymer would be obtained.

For the BPDA-3FDAM copolymers the least reactive diamine, 3FDAM and the dianhydride, BPDA, were first combined. The comonomer, mPD or pPD, was then added followed by PA. The polymers were then solution imidized as described

above. Using this method, only 10 % of the pPD and 25 % of the mPD could be incorporated into the polyimide and still maintain solubility.

The order of monomer addition was changed in the synthesis of the BPDA-3FDAM-pPD polyimide copolymer in order to incorporate larger amounts of pPD. The BPDA and 3F diamine were first mixed together in NMP. The mixture was stirred for one hour. The azeotroping agent, ODCB was added, and the reaction was heated to 165°C for 24 hours to form an anhydride terminated polyimide. pPD was then added and finally PA was added . The solution was stirred for an additional 20 hours at 165°C. The polyimide copolymer was isolated as described above. By this method, the BPDA-3FDAM containing 25 mole % pPD was soluble in NMP. A BPDA-3FDAM containing 33 mole % pPD was also made by this method. After the pPD was added to the imidized solution of BPDA-3FDAM, the copolyimide precipitated within 8 to 10 hours. The solution was stirred for an additional 14 hours at 165 °C. At the end of the reaction the solution was very turbid and appeared to contain very fine particles. Since the copolyimide did not precipitate until late in the reaction, one might expect that the polyimide particles should have been highly imidized. Small polyimide particles suspended in NMP or preferably water may have applications in powder prepregging of composites (183). Relatively small amounts of crystallization may dramatically assist in the generation of these fine particles.

The FTIR spectrum of a PMDA-3Fdiamine-PA polyimide is shown in Figure 4.3.2. Complete imidization was confirmed by the appearance of characteristic imide related infrared absorption bands in the range 1770-1780 cm^{-1} (asymmetrical imide I), 1710-1735 cm^{-1} (symmetrical imide I) and disappearance of an amic acid band at 1535 cm^{-1}.
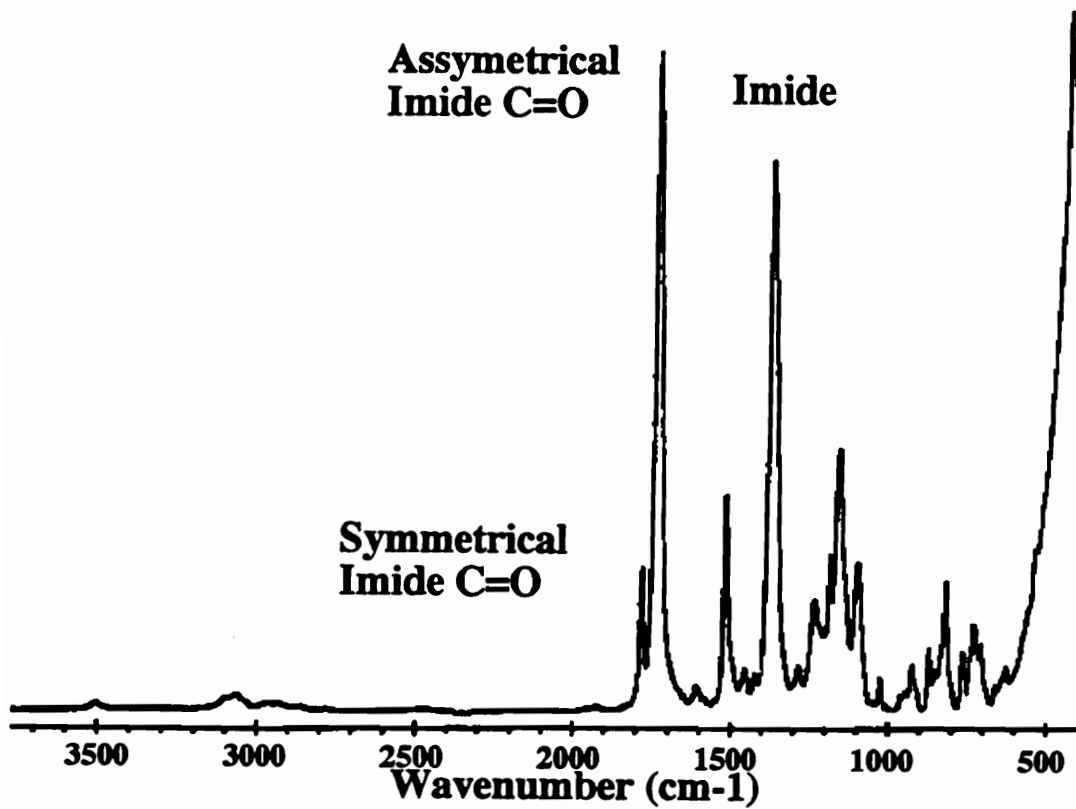
Figure 4.3.2 - FTIR spectrum of a PMDA-3Fdiamine-PA Polyimide

4.3.2 Molecular Weight

Intrinsic viscosities of the various polyimide homopolymers and copolymers are listed in Table 4.3.1 and Table 4.3.2. The intrinsic viscosities were all relatively high and indicated that high molecular weight was obtained for all of the polyimides. The solution imidization method was effective in obtaining fully cyclized, high molecular weight polyimides.

A series of PMDA-3FDAM polyimides was endcapped with t-butyl phthalic anhydride to demonstrate the effectiveness of molecular weight and endgroup control. With the t-butyl group at the end of the polymer chain, [1]H n.m.r. was used to estimate the number average molecular weight of the polyimide. [1]H n.m.r. was accurate in determining <Mn> only if quantitative endcapping was achieved. Figure 4.3.3 shows the [1]H n.m.r. spectrum of a PMDA-3FDAM-t-butyl PA with a target <Mn> of 20.0 kg/mole. The resonance observed at about 1.4 ppm was due to the t-butyl group which was ratioed to the aromatic proton resonance at 8.4 ppm to allow an estimate of the number average molecular weight. As can be seen in Table 4.3.3, the number average molecular weights determined by [1]H n.m.r. were in good agreement with the theoretical calculations. GPC traces of the 10.0 and 20.0 kg/mole PMDA-3FDAM-t-butyl PA polyimides are shown in Figure 4.3.4. The GPC traces were symmetrical in shape and the molecular weight distributions were approximately 2 for both polymers. The <Mn> values determined by GPC are listed in Table 4.3.3. For the 10.0 and 20.0 kg/mole polyimides, the <Mn> determined by GPC and the <Mn> determined by [1]H n.m.r. agreed considerably well which indicates that near quantitative endcapping was achieved. The intrinsic viscosities also correlated well with the determined molecular weights. The molecular weight and endgroups of the polyimides were effectively controlled utilizing the solution imidization method.

Table 4.3.1 - Solution and Thermal Characterization of High Performance Polyimide Homopolymers

Polyimide	Target <Mn> kg/mole	[η] NMP, 25°C dl/g	Tg at heating rate of 10 °C/min °C	5% wt loss by TGA in air °C
PMDA-3FDAM-PA	30.0	0.65	432 by DMA	561
BPDA-3FDAM-PA	30.0	0.53	349 by DSC	560
6FDA-3FDAM-PA	30.0	0.36	314 by DSC	527
3FDA-pPD-PA	30.0	0.49	359 by DSC	536
PMDA-DDPPO	not controlled	0.49	425 by DMA	550 20% char yield at 800°C
BPDA-DDPPO	not controlled	0.89	382 by DSC	542 20% char yield at 800°C

Table 4.3.2 - Solution and Thermal Characterization of 3F diamine Containing Copolyimides (Target <Mn> = 30.0 kg/mole)

Polyimide	$[\eta]$ NMP, 25°C dl/g	Tg at heating rate of 10°C/min °C	5% wt. loss by TGA in air °C
BPDA-3FDAM-PA	0.53	349 by DSC	560
BPDA-3FDAM(0.75)-mPD(0.25)-PA	0.57	346 by DSC	571
BPDA-3FDAM(0.9)-pPD(0.1)-PA	0.51	357 by DSC	562
BPDA-3FDAM(0.8)-pPD(0.2)-PA	0.67	359 by DSC	590
BPDA-3FDAM(0.75)-pPD(0.25)-PA	0.38 in DMPU	345 by DSC	548
BPDA-3FDAM(0.67)-pPD(0.33)-PA	insoluble	---	562
PMDA-3FDAM-PA	0.65	432 by DMA	561
PDMA(0.8)6FDA(0.2)-3FDAM-PA	0.50	392 by DSC	547
PMDA(0.7)6FDA(0.3)-3FDAM-PA	0.46	379 by DSC	562
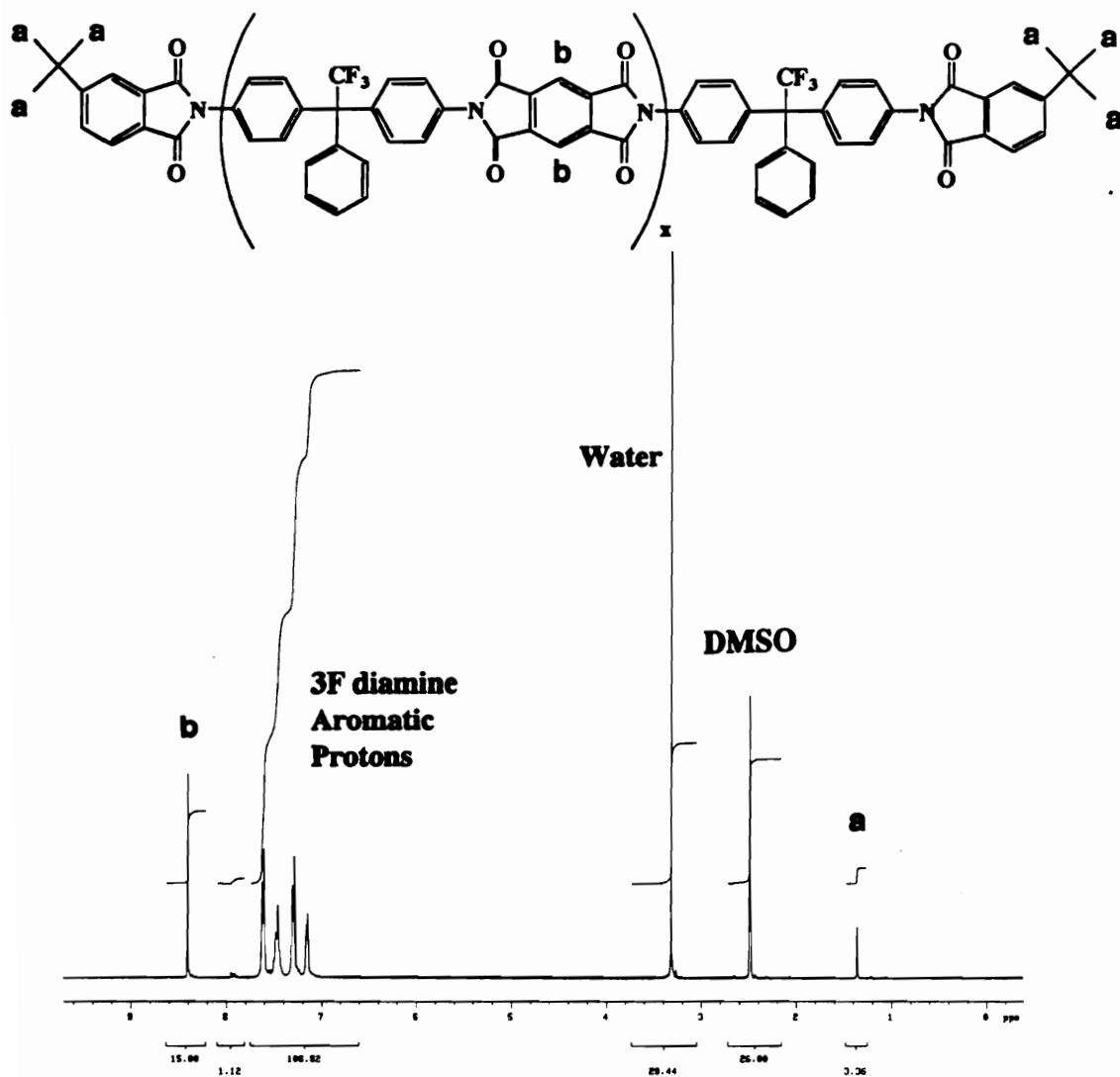
Figure 4.3.3 - ^{1}H n.m.r. Spectrum of a PMDA-3FDAM-t-butyl PA Polyimide

Table 4.3.3 - Molecular Weight and Intrinsic Viscosity Data of
PMDA-3FDAM-t-butyl PA Polyimides

<Mn> Target kg/mole	<Mn> by [1]H n.m.r. kg/mole	<Mn> by GPC kg/mole	<Mw> by GPC kg/mole	<Mw>/<Mn>	[η] 25 °C NMP g/mole
10.0	9.5	10.0	19.2	1.92	0.32
20.0	18.5	18.3	38.4	2.10	0.47
30.0	33.6	---	---	---	0.65
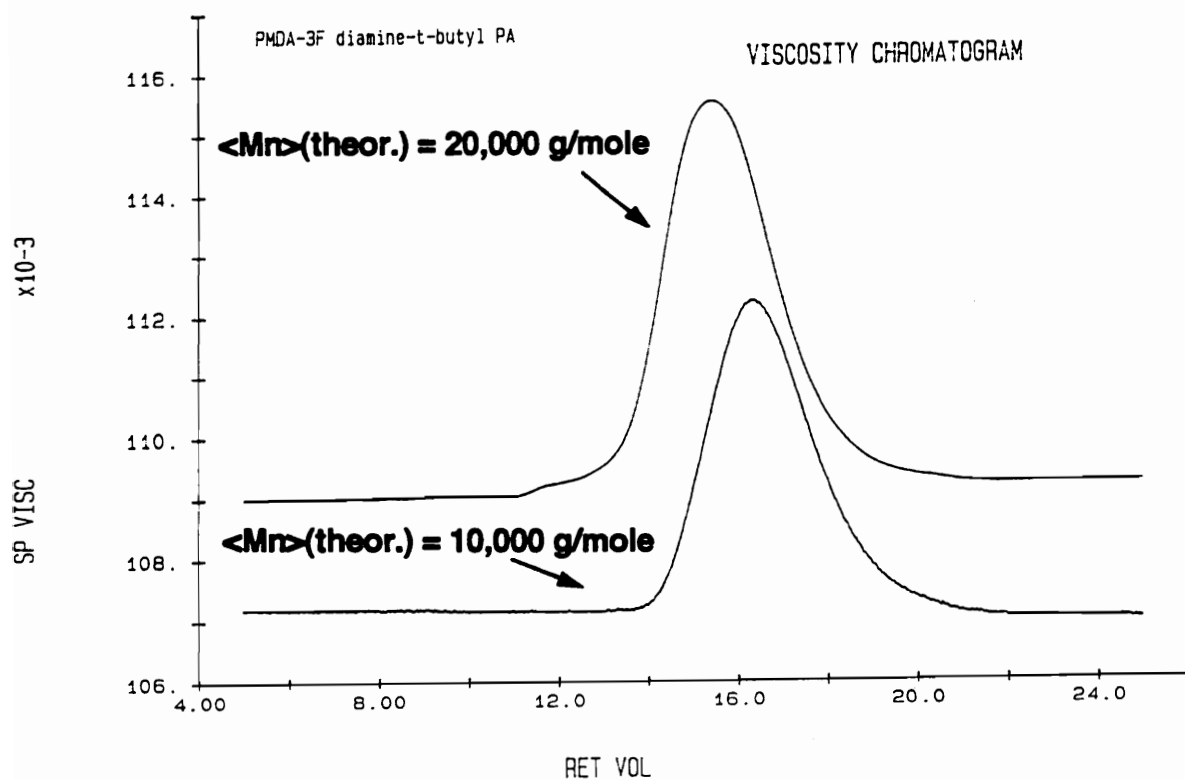
Figure 4.3.4 - GPC Traces for PMDA-3FDAM-t-butyl PA Polyimides

4.3.3 - Solubility of High Tg Polyimides

Table 4.3.4 indicates the solubility of some of the 3F diamine and phosphorus containing polyimide homopolymers. All of the polymers were soluble in the polar aprotic solvent, NMP. PMDA-3Fdiamine-PA showed poor solubility in the chlorinated solvent, CHCl3, and the ether solvent, THF. As the more flexible and less polar dianhydrides were used in place of PMDA the solubility of 3FDAM containing polyimides increased. The BPDA-3FDAM-PA and 6FDA-3FDAM polyimides were soluble in CHCl3 and THF. 3FDA-pPD-PA, which has the phenyl trifluoroethane moiety in the dianhydride portion of the polyimide, is an isomeric structure of PMDA-3FDAM-PA. However the 3FDA-pPD-PA polyimide showed greater solubility in CHCl3 and THF. The more polar, phosphorus containing polyimides, PMDA-DDPPO and BPDA-DDPPO, were only soluble in NMP. None of the 3F diamine containing or phosphorus containing polyimides were soluble in toluene.

Incorporation of the comonomers into the 3Fdiamine containing polyimides changed their solubility behavior as seen in Table 4.3.5. While the BPDA-3FDAM-PA was soluble in NMP, CHCl3 and THF, increasing amounts of pPD as a comonomer to the 3F diamine dramatically decreased the solubility. As more of the 3FDAM was replaced by pPD, the polyimide became more rigid, thus, decreasing the solubility. Incorporating just 25 % of the pPD rendered the polyimides insoluble in THF and CHCl3, and the polyimide with 33 % pPD was only marginally soluble in NMP. Subsequently, replacing PMDA in the PMDA-3FDAM-PA polyimides with the more flexible 6FDA improved the solubility of the polyimide. The 3FDAM containing polyimide with 20 and 30 % 6FDA were soluble in NMP, CHCl3 and THF.

Table 4.3.4 - Solubility of Polyimide Homopolymers at 10 Weight % Solids

Polyimide	Target <Mn> kg/mole	NMP	CHCl3	THF	Toluene
PMDA-3FDAM-PA	30.0	S	M	M	I
BPDA-3FDAM-PA	30.0	S	S	S	I
6FDA-3FDAM	not controlled	S	S	S	I
3FDA-pPD-PA	30.0	S	S	S	I
PMDA-DDPPO	not controlled	S	I	I	I
BPDA-DDPPO	not controlled	S	M	I	I

S - Soluble; M - Marginally Soluble; I - Insoluble

Table 4.3.5 - Solubility of 3F diamine Containing Copolyimides at
10 Weight % Solids (Target <Mn> = 30.0 kg/mole)

Polyimide	NMP	CHCl$_3$	THF
BPDA-3FDAM-PA	S	S	S
BPDA-3FDAM(.8)-pPD(.2)-PA	S	M	I
BPDA-3FDAM(.75)-pPD(.25)-PA	S	I	I
BPDA-3FDAM(.67)-pPD(.33)-PA	M	I	I
PMDA-3FDAM-PA	S	M	M
PDMA(0.8)6FDA(0.2)-3FDAM-PA	S	S	S
PMDA(0.7)6FDA(0.3)-3FDAM-PA	S	S	S

S - Soluble; M - Marginally Soluble; I - Insoluble

4.3.4 Thermal Properties of the High Tg Polyimides

The Tg's of the 3F diamine containing polyimides are listed in Table 4.3.1 and Table 4.3.2. The PMDA-3FDAM polyimides exhibited glass transition temperatures exceeding 420°C. The bulky phenyl trifluoroethane linkages which contributes to the solubility of the polyimide also effected the Tg. The phenyl trifluoroethane groups limits the rotation of the polymer chain, thus, producing a rather stiff macromolecule which results in a high Tg. The Tg was dramatically demonstrated in the dynamic mechanical analysis, Figure 4.3.5, of a 25.0 kg/mole PMDA-3FDAM-PA polyimide. The PMDA-3FDAM-PA polyimide showed a dynamic storage modulus of 4 GPa at 27°C which decreased with increasing temperature. A sharp decline in the storage modulus occurred at 430°C, corresponding to the glass transition temperature. The tan δ had a large relaxation with a maximum at 457°C resulting from the cooperative segmental motions which occurred at the Tg of the polyimide.

Replacing PMDA with the more flexible and less polar dianhydrides in the 3F diamine containing polyimides improved solubility but lowered the glass transition temperature. However, the Tg's of the more soluble polyimides were still relatively high. The BPDA-3F diamine polyimide had a Tg of 350°C, and the 6FDA-3F diamine polyimide had a Tg of 313°C. PMDA-DDPPO, which has an analogous structure to the PMDA-3Fdiamine polyimide, also had a Tg of ~ 425°C. Dynamic mechanical analysis of the PMDA-DDPPO, Figure 4.3.6, gave a storage modulus-temperature curve that looked similar to that of the PMDA-3FDAM-PA polyimide. The Tan δ - temperature curve had a large relaxation with a maximum at ~450 °C. Just as the BPDA-3FDAM-PA polyimide had a lower Tg than the PMDA-3FDAM-PA polyimide, BPDA-DDPPO had a Tg of 382 °C which was lower than the Tg of the PMDA-DDPPO polyimide.

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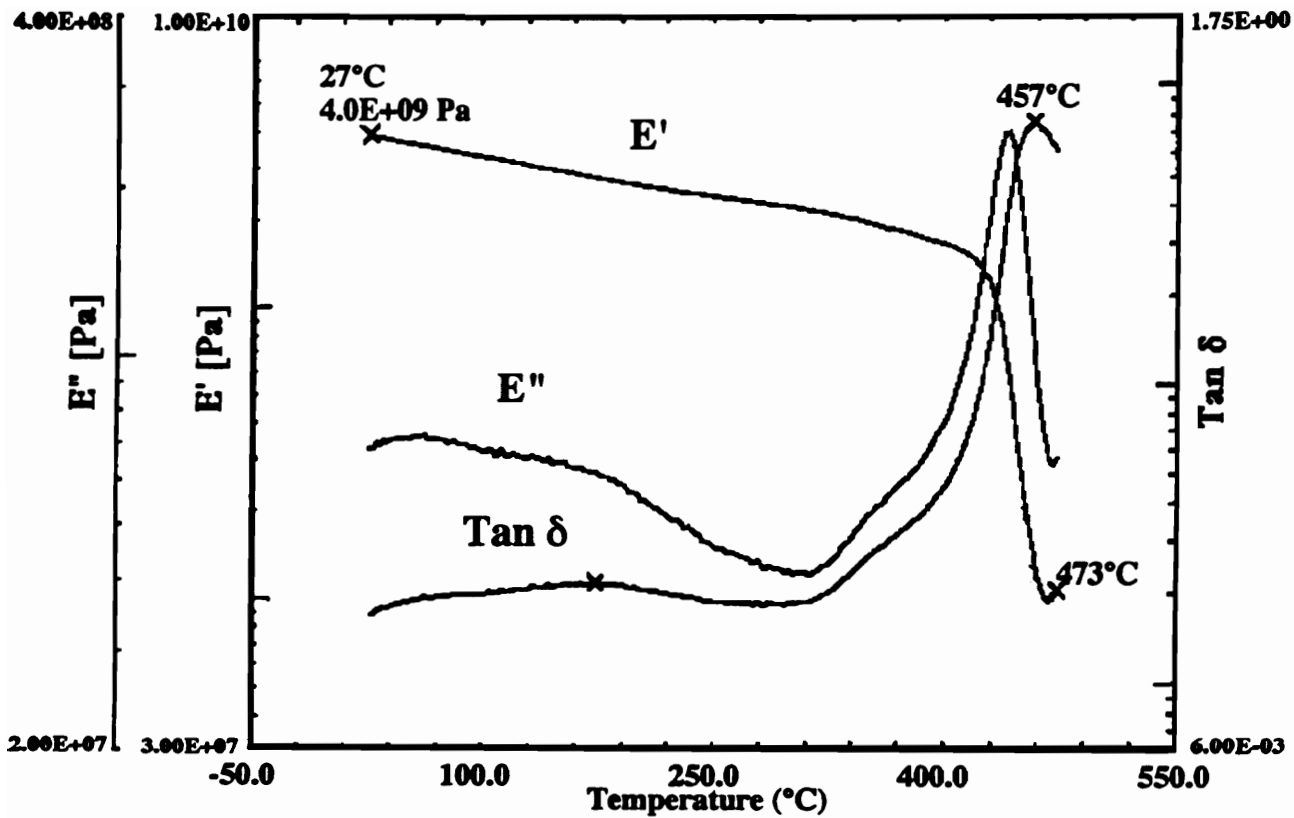
Figure 4.3.5 - Dynamic Mechanical Analysis of a 25.0 kg/mole
PMDA-3FDAM-PA Polyimide (Heating rate - 10 °C/min; Frequency - 1 Hz)

114
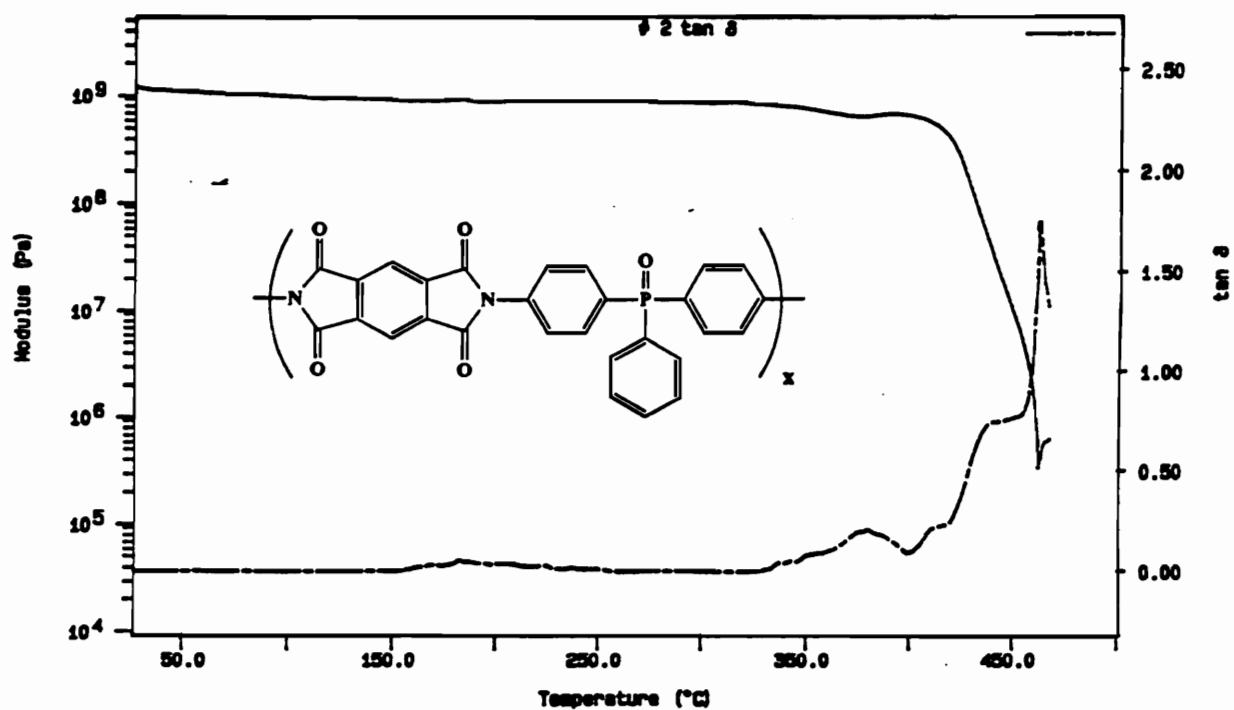
Figure 4.3.6 - Dynamic Mechanical Analysis of the PMDA-DDPPO Polyimide
(Heating rate - 10 °C/min; Frequency - 1 Hz)

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Copolymers incorporating 6FDA into the PMDA-3F diamine polyimide showed a reduced glass transition temperature. As seen in Table 4.3.2, the 3F diamine copolyimide containing 20 mole% 6FDA had a Tg of 392°C, and 30 mole% 6FDA gave a Tg of 379°C. The effect of incorporating 6FDA into the PMDA-3F diamine polyimide was demonstrated effectively in Figure 4.3.7 by comparing the storage modulus-temperature curves of the copolyimides to that of a 25.0 kg/mole PMDA-3F diamine-PA polyimide. The sharp decline in the storage modulus corresponding to the Tg of the PMDA-3Fdiamine-PA polyimide was about 25°C higher than that of the copolyimides.

Table 4.3.2 lists the Tg's of the BPDA-3FDAM/pPD or mPD-PA copolymers. Adding 25 mole % mPD had no effect on the Tg of the BPDA-3FDAM polyimide. Incorporation of pPD only raised the Tg by ~ 10 °C. The BPDA-3FDAM/pPD or mPD-PA copolyimides had good thermal stability. Dynamic thermogravimetric analysis measured 5 % weight losses of 550 °C to 590 °C in air for the copolyimides.

Dynamic thermogravimetric analysis (TGA) of the 3F diamine containing polyimide homopolymers given in Table 4.3.1 demonstrated thermal stability above 450°C in air with 5% weight loss values of 525°C to 560°C. A typical dynamic TGA thermogram of a PMDA-3FDAM polyimide is presented in Figure 4.3.8. Replacing PMDA with BPDA or 6FDA had little effect on the 5% weight loss values. The 5 % weight loss values of the copolymers listed in Table 4.3.2 were all similar to the homopolymers. The PMDA-DDPPO and BPDA-DDPPO also had high 5 % weight loss values of 550 °C and 540 °C, respectively. However, the dynamic TGA thermogram of the phosphorus containing polyimides was distinctly different than the thermograms of the 3F diamine containing polyimides. The dynamic TGA thermogram of a phosphorus containing polyimide in Figure 4.3.9 shows a high char yield at temperatures of 700°C and above. This behavior

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116
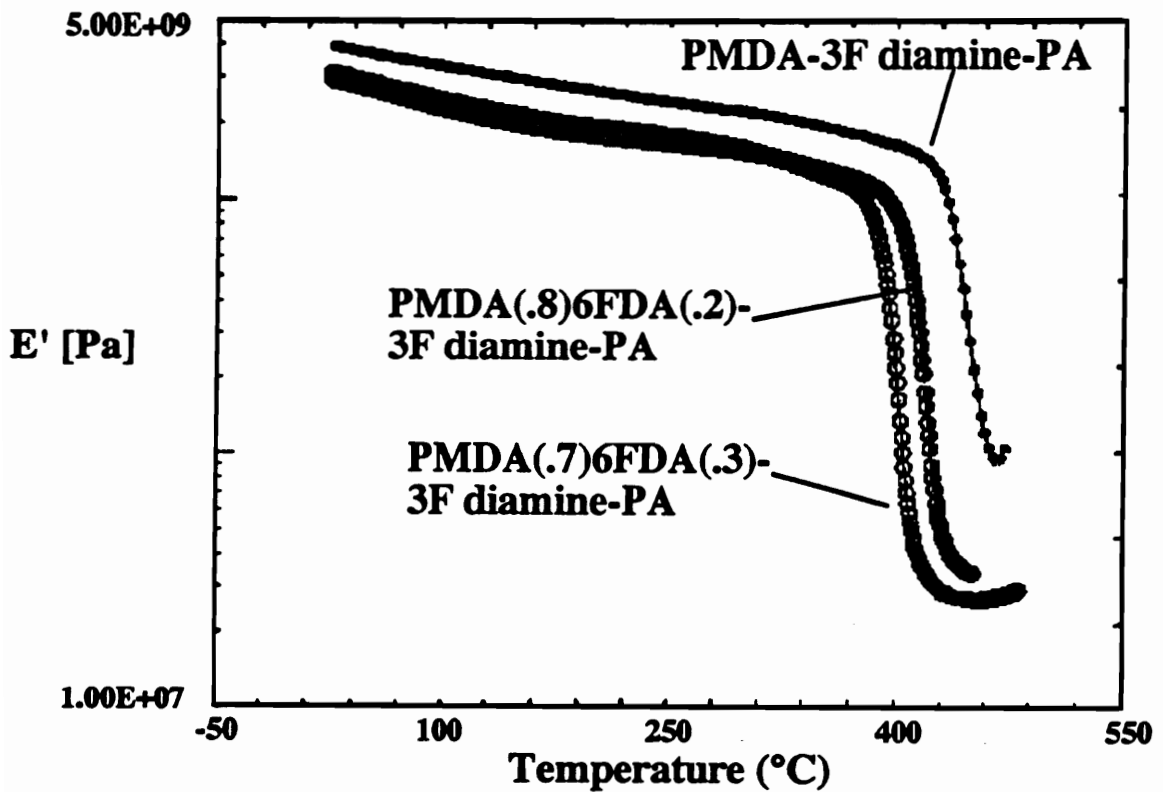
Figure 4.3.7 - Storage Modulus-Temperature Curves of
PMDA/6FDA-3FDAM-PA Polyimides (Heating rate - 10 °C/min; Frequency - 1 Hz)
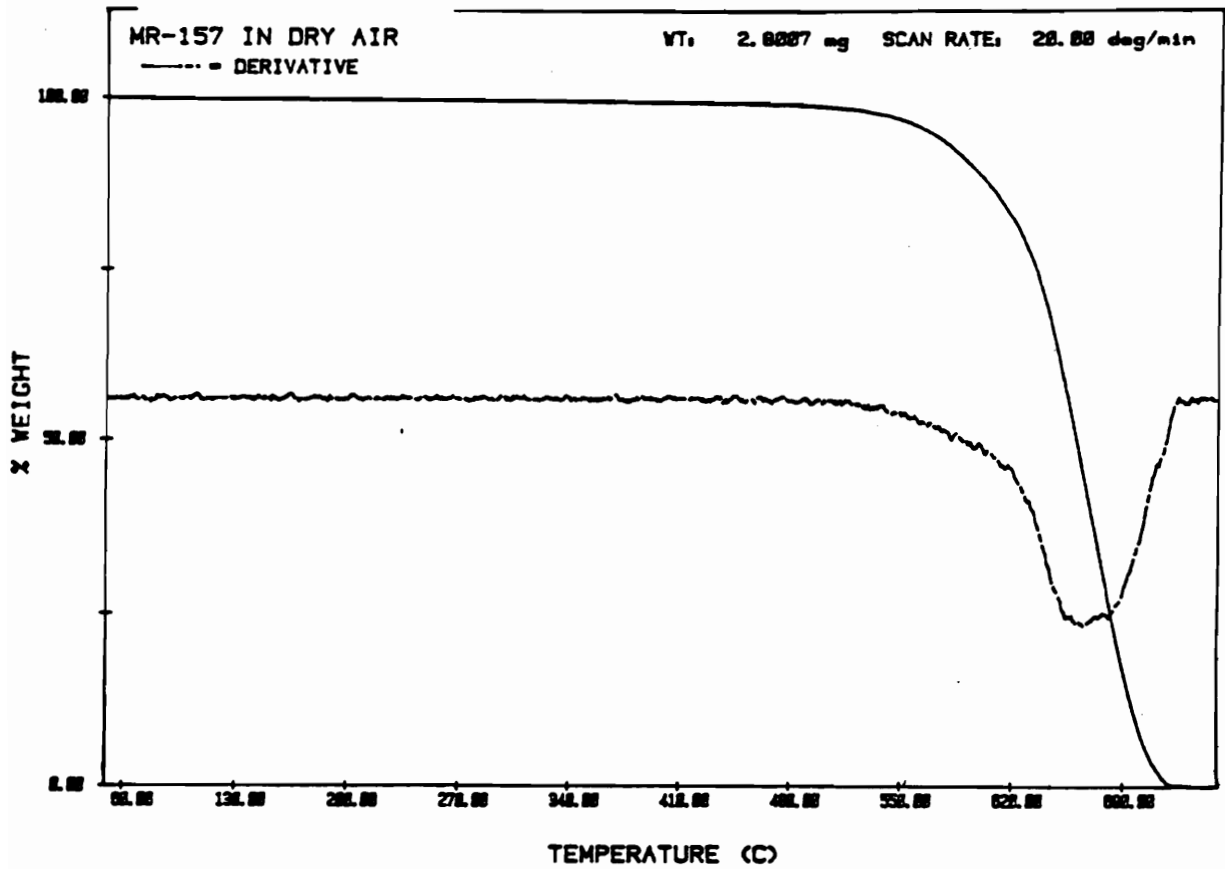
Figure 4.3.8 - Dynamic TGA Thermogram of a PMDA-3FDAM-PA Polyimide
(Air atmosphere; Heating rate - 10 °C/minute)
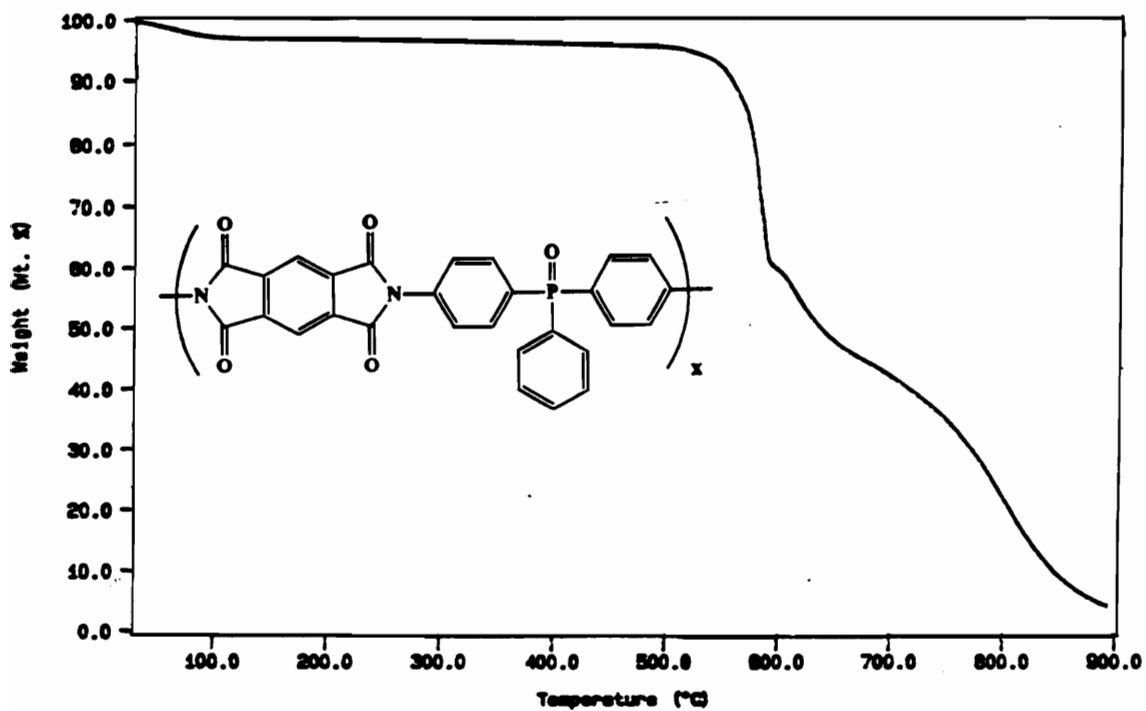
Figure 4.3.9 - Dynamic TGA Thermogram PMDA-DDPPO
(Air Atmosphere; Heating rate - 10 °C/minute)

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has been reported for other phosphorus containing polyimides and has significant importance in fire retardant applications (14, 184).

Since dynamic TGA is not a realistic measure of a materials long term stability, isothermal TGA was performed. An isothermal TGA of the 25.0 kg/mole PMDA-3F diamine polyimide, Figure 4.3.10, showed that relatively little weight loss occurred after 48 hours at 371°C (700°F) in air.

Extended isothermal aging of the polymers was done in a forced air oven under an air atmosphere. To investigate stability at higher temperatures, they were aged for 145 hours at 371 °C (700 °F) and for 500 hours at 316 °C (600 °F). Figure 4.3.11 and Figure 4.3.12 show plots of the weight % of the polymer sample versus time at 371 °C and 316 °C, respectively. At 371 °C, the PMDA-3FDAM-PA polyimide lost 35 % of its weight after 145 hours. The PMDA(0.8)/6FDA(0.2)-3FDAM-PA copolyimide was more stable losing only 19 weight %. However, neither polymer performed well at 371 °C. After 145 hours, both polymer turned black and became very brittle.

The 3F diamine containing polymers retained 95 to 99% of their weight for 500 hours at 316 °C. The PMDA/6FDA-3FDAM-PA copolyimides showed better thermal stability than either PDMA-3FDAM-PA or BPDA-3FDAM-PA. The copolyimides only lost 1 weight % after 500 hours while BPDA-3FDAM-PA and PMDA-3FDAM-PA each lost 6 weight %. After 500 hours, the films darkened a little and became slightly more brittle.

None of the 3F diamine containing, linear polyimides will hold up for extended periods of time at 371°C. However, use temperatures of 316 °C seems reasonable for these polymers.
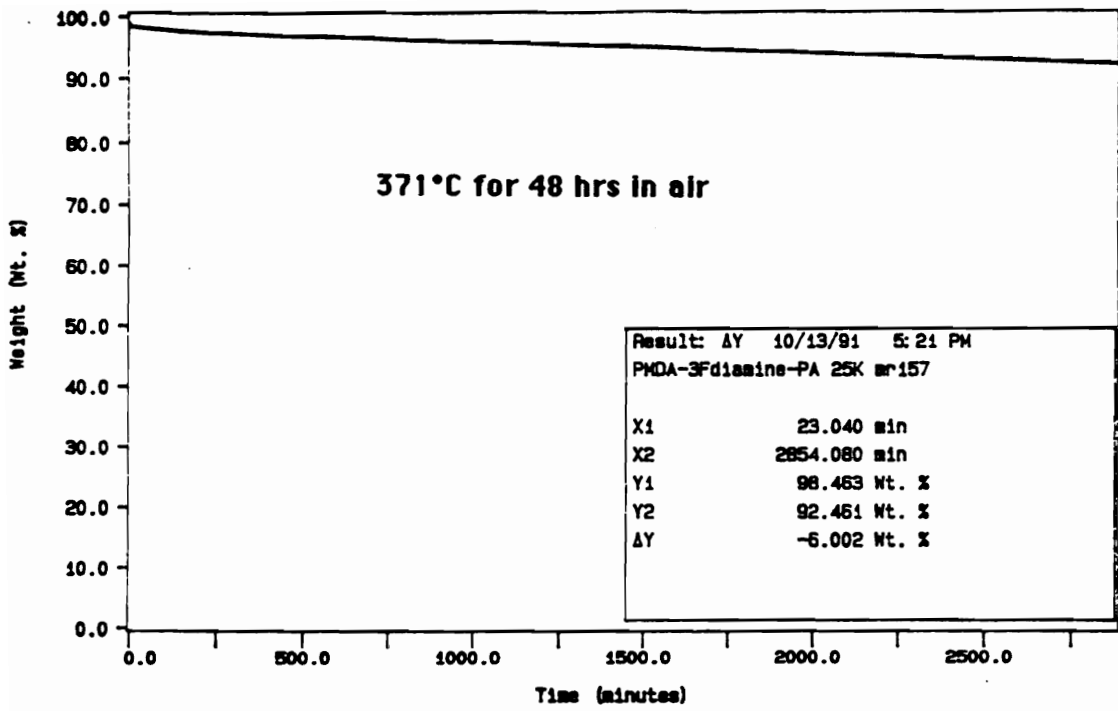
Figure 4.3.10 - Isothermal TGA Thermogram of PMDA-3FDAM-PA (Air atmosphere)

121
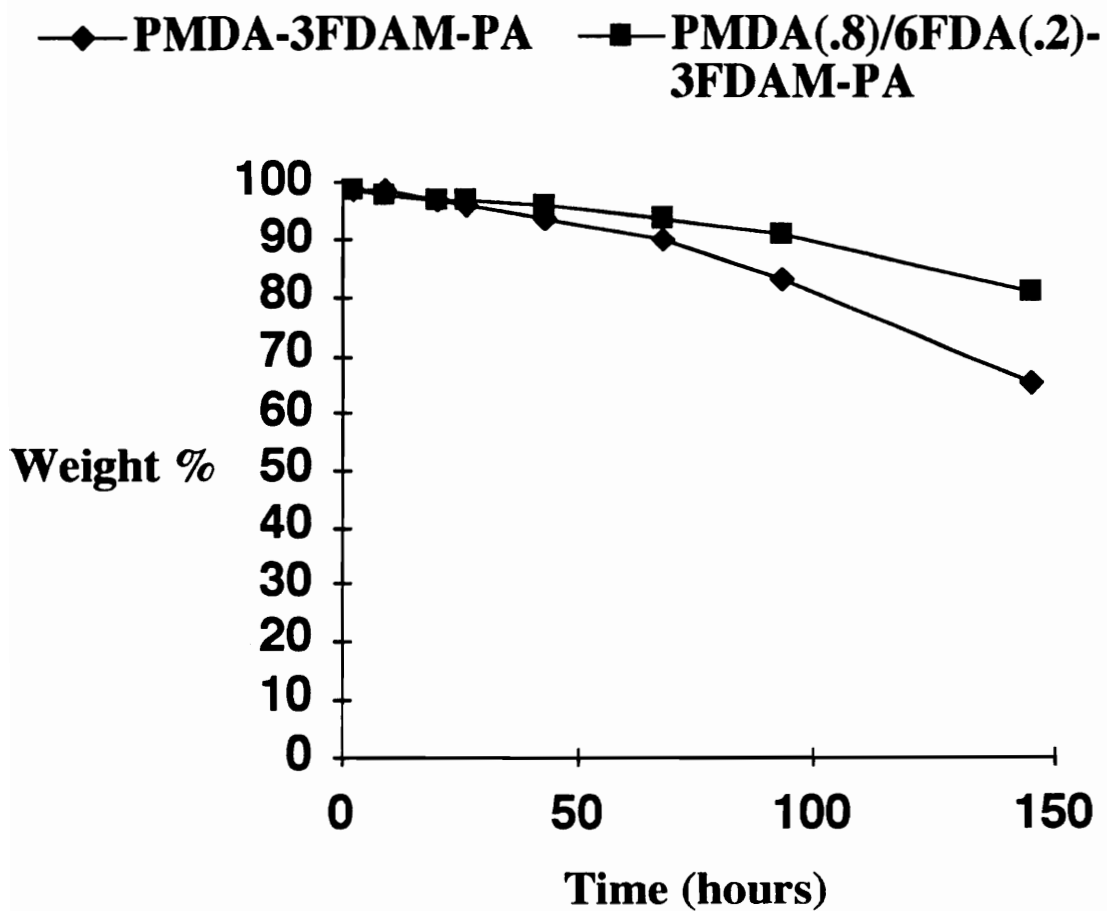
Figure 4.3.11 - Long Term Isothermal Aging at 371 °C in Air

PMDA(0.8)/6FDA(0.2)-3FDAM-PA
PMDA(0.7)/6FDA(0.3)-3FDAM-PA

PMDA-3FDAM-PA
BPDA-3FDAM-PA
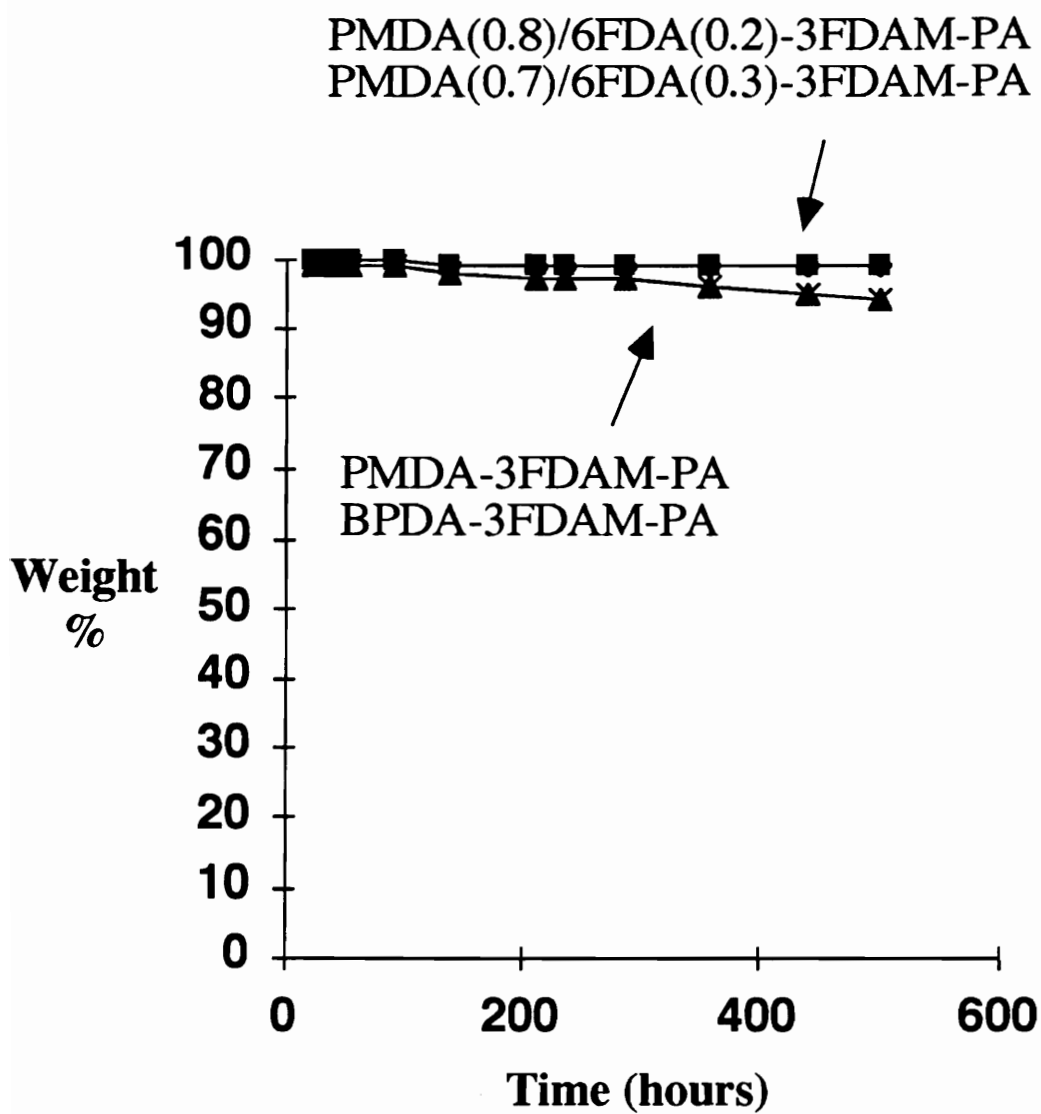
Figure 4.3.12 - Long Term Isothermal Aging at 316 °C in Air

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4.4 PERFECTLY ALTERNATING POLYIMIDE SILOXANE COPOLYMERS FROM N-PYRIDYL PHTHALIMIDE TERMINATED POLYIMIDE OLIGOMERS

4.4.1 Polyimide Oligomer Synthesis

The polyimide oligomers endcapped with the reactive pyridine phthalimide group were made by the solution imidization route described for the synthesis of the endcapped 3F diamine containing polyimides. The synthesis of an ODPA-Bis P-2AP polyimide is depicted in Figure 4.4.1. In this case, the monofunctional endcapper was 2-aminopyridine (2AP) and the order of monomer addition was reversed. The 2AP was added to the dianhydride dissolved in NMP. The solution was allowed to stir for 15 to 20 minutes. The diamine was added last as a powder and rinsed in with NMP to bring the final solids content to 15 to 20 wt. %. The imidization of the poly(amic acid) was carried out using ODCB as the azeotroping agent. The imidization was done at ~165 °C for 24 hours. One peculiar property of the ODPA-Bis P-2AP polyimide was its insolubility in NMP. The ODPA-Bis P-2AP polyimide remained soluble during the entire imidization procedure but on cooling, the polyimide oligomer precipitated from solution.

FTIR analysis of the ODPA-Bis P-2AP polyimide oligomer, seen in Figure 4.4.2, revealed it to be completely cyclized. The [1]H n.m.r. spectra of the ODPA-Bis P-2AP polyimide is pictured in Figure 4.4.3. The small peak at 8.7 ppm was associated with the aromatic proton adjacent to the nitrogen on the pyridine ring at the end of the polyimide chain. Number average molecular weights of the oligomers were evaluated by end group analysis using ^{1}H-NMR. The <Mn> was calculated from the integral ratio of the proton for 2AP, at 8.7 ppm, to the Bis P methyl protons at 1.7 ppm. <Mn>'s were also determined by GPC using an universal calibration method. Table 4.4.1 shows the comparison of the target <Mn>,the <Mn> determined by ^{1}H NMR and the <Mn> determined by GPC. The low intensity of the 2AP proton at 8.7 ppm limited the accuracy of
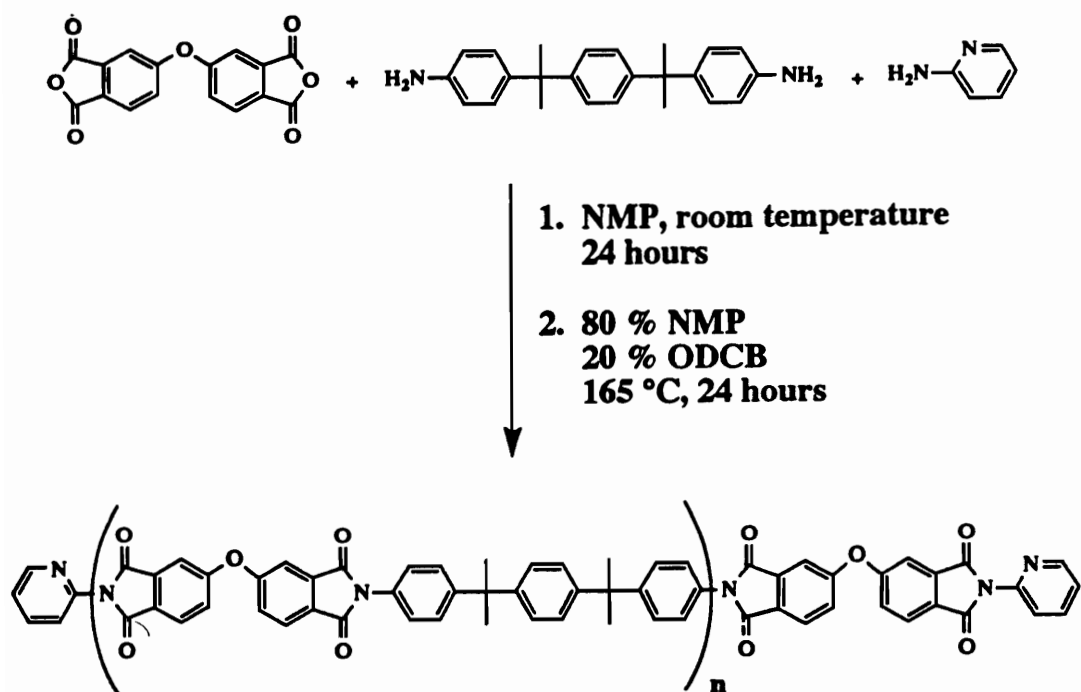
Figure 4.4.1 - Synthesis of ODPA-Bis P-2AP Polyimide Oligomers
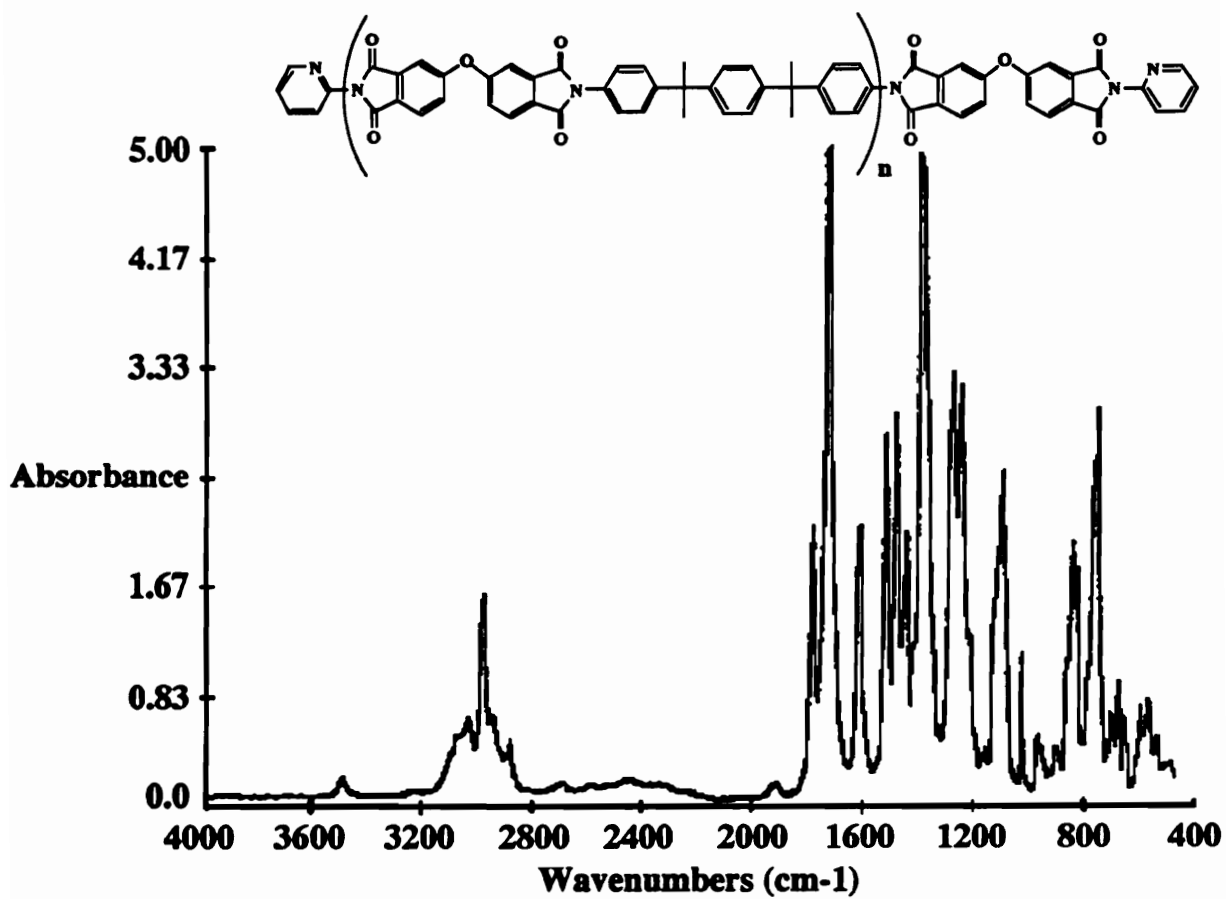
Figure 4.4.2 - FTIR Spectrum of an ODPA-Bis P-2AP Polyimide Oligomer

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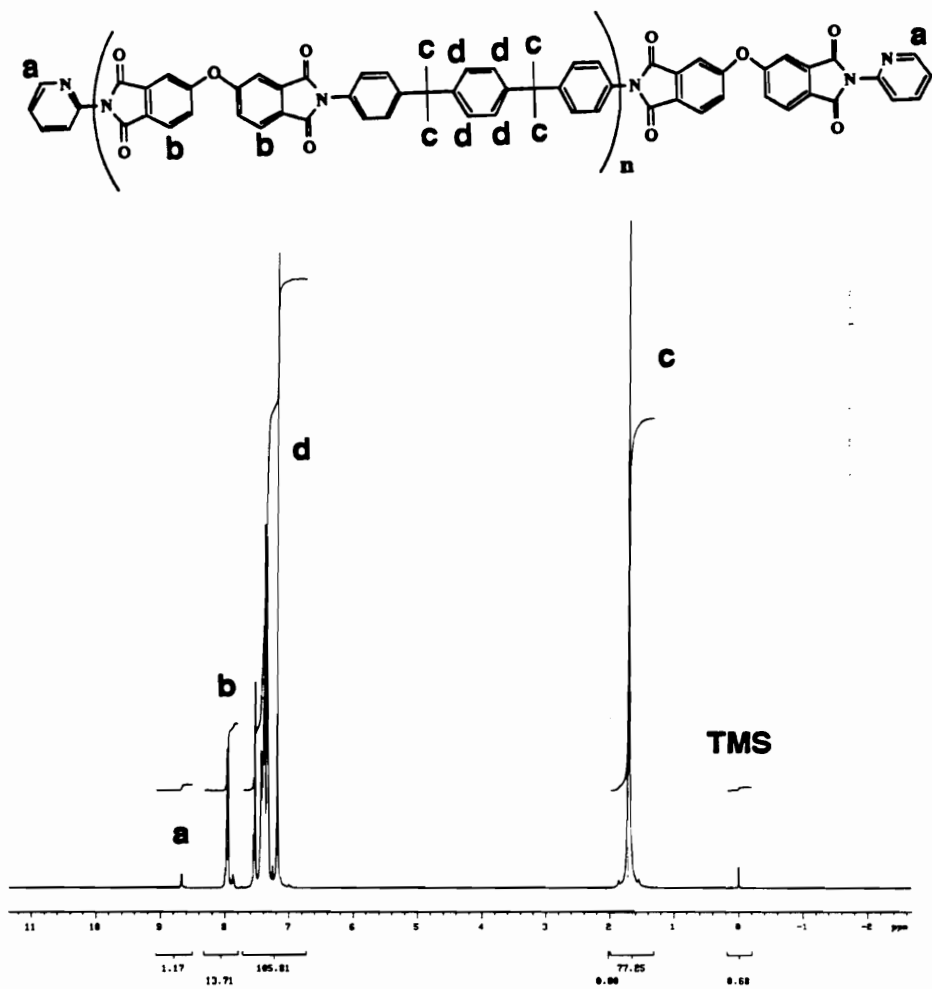
Figure 4.4.3 - ^{1}H n.m.r. Spectrum of an ODPA-Bis P-2AP Polyimide Oligomer

Table 4.4.1
Solution Characterization of ODPA-Bis P-2AP Polyimide Oligomers

$<Mn>$ Target kg/mole	$<Mn>$ by ^1H n.m.r. kg/mole	$<Mn>$ by GPC kg/mole	$<Mw>/<Mn>$	$[\eta]$, $CHCl_3$ dl/g
4.0	4.9	4.9	2.0	0.21
6.0	7.3	8.1	2.0	0.27
8.0	9.7	11.5	2.1	0.33

the integration, but nevertheless, the <Mn> determined by ^{1}H NMR was in reasonable agreement with the <Mn> determined by GPC. However, in all three polyimide oligomers, the <Mn> determined by GPC was higher than the target <Mn>. The molecular weight distributions of the ODPA-Bis P-2AP polyimide oligomers were all close to 2.0.

4.4.2 Synthesis of Perfectly Alternating Polyimide Siloxane Copolymers

The synthetic scheme for the perfectly alternating segmented polyimide siloxane copolymers is shown in Figure 4.4.4. The perfectly alternating segmented polyimide siloxane copolymers were made by first dissolving the polyimide oligomer in chlorobenzene and heating the solution to 110°C. Chlorobenzene was chosen as the polymerization solvent since it can dissolve both the ODPA-Bis P-2AP polyimide oligomers and the aminopropyl terminated poly(dimethyl siloxane) (PSX). Homogeneity of the reaction mixture was necessary since accessibility of the reacting endgroups is required for high conversions and high molecular weights. Chlorobenzene was also a low boiling solvent and easily removed from films of the copolymers.

Zn(OAc)•2H$_2$O was found to be an effective catalyst in the transimidization reaction involving aromatic amines and bis(pyridine phthalimides) (49). For the synthesis of the perfectly alternating segmented polyimide siloxane copolymers from the pyridine phthalimide terminated polyimide oligomers and the aminopropyl terminated poly(dimethyl siloxane)s, the zinc acetate catalyst was not necessary. This was not surprising considering the much higher reactivity of an aliphatic amine as compared to an aromatic amine. Table 4.4.2 lists the intrinsic viscosities of the copolymers as a function of reaction time. Without any catalyst, very high viscosities were reached within 10 minutes. In fact, the
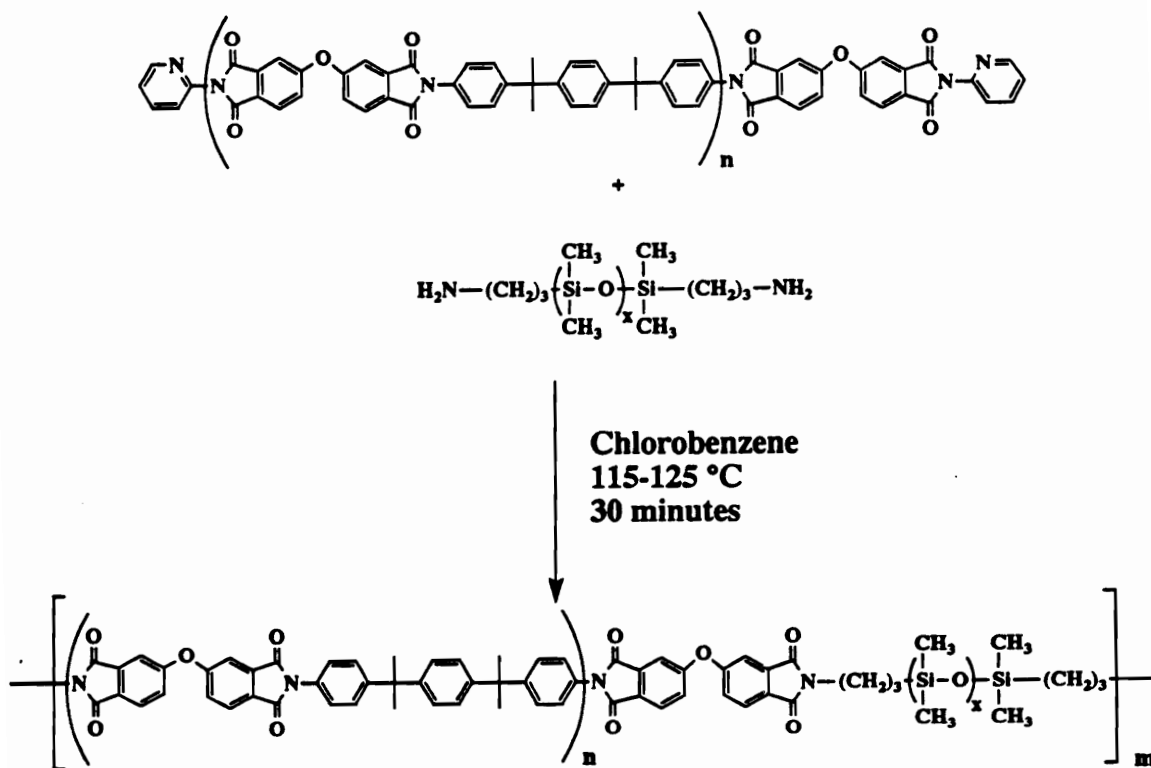
Figure 4.4.4 - Synthesis of Perfectly Alternating Polyimide Siloxane Copolymers

Table 4.4.2
Copolymerization Results of ODPA-Bis P-2AP
and PSX in Refluxing Chlorobenzene

Catalyst Zn(OAc)$_2 \cdot$2H$_2$O	Reaction Time minutes	[η], CHCl$_3$ dl/g
100 PPM	10	0.79
	20	0.80
	120	0.96
NONE	10	0.89
	20	0.81
	30	0.87

intrinsic viscosity did not increase with longer reaction times. High viscosities were also achieved using the zinc acetate catalyst, but it was clearly not necessary.

The ODPA-Bis P-PSX perfectly alternating segmented polyimide siloxane copolymers were made in chlorobenzene at 110 °C and stirred for 30 minutes before being cast as films on glass plates. Two series of polyimide siloxane copolymers were investigated. In the PI-PSX1.07 series, an aminopropyl terminated polydimethylsiloxane oligomer having a molecular weight of 1.07 kg/mole was reacted with three polyimide oligomers of ODPA-Bis P-2AP with theoretical molecular weights of 4.0, 6.0, and 8.0 kg/mole. In the PI-PSX2.67 series, an aminopropyl terminated polydimethylsiloxane oligomer with a molecular weight of 2.67 kg/mole was reacted with the same polyimide oligomers used in the PI-PSX1.07 series. In all cases, the molecular weight was controlled to 40.0 kg/mole by adding an excess of the ODPA-Bis P-2AP polyimide oligomer.

Intrinsic viscosity data of the PI-PSX1.07 and PI-PSX2.67 series is given in Table 4.4.3. For a relatively short reaction time of 30 minutes, high molecular weight was achieved as evidenced by the increase in intrinsic viscosities of the copolymers over intrinsic viscosities of the polyimide oligomers. Compared with the ODPA-Bis P-PA homopolymer, having a theoretical <Mn> of 40.0 kg/mole and an intrinsic viscosity of 0.54 dl/g, the polyimide-siloxane copolymers all showed higher intrinsic viscosities. The incompatibility of the polyimide and siloxane segments in the copolymer results in a more extended chain conformation as compared to the polyimide homopolymer of a similar molecular weight, thus, explaining the higher intrinsic viscosities observed for the copolymers.

The polyimide siloxane copolymers were fully cyclized as evidenced by the FTIR spectrum in Figure 4.4.5. Figure 4.4.6 shows a representative ^{1}H NMR of a polyimide siloxane copolymer with 31 wt% polysiloxane. The theoretical molecular weight of the polyimide oligomer was 4.0 kg/mole and the polysiloxane had a number average molecular

Table 4.4.3
Intrinsic Viscosity Values* of Polyimide Precursors and the Resulting Perfectly Alternating
Segmented Polyimide Siloxane Copolymers

[η] of PI** Oligomer (dl/g)	[η] of PI-PSX1.07 Copolymer (dl/g)	[η] of PI-PSX2.67 Copolymer (dl/g)
0.21	0.71	0.64
0.23	0.87	0.71
0.33	1.05	0.73

* Intrinsic viscosities were measured in chloroform
**The theoretical <Mn> of the PI oligomers are 4.0, 6.0 and 8.0 kg/mole respectively.
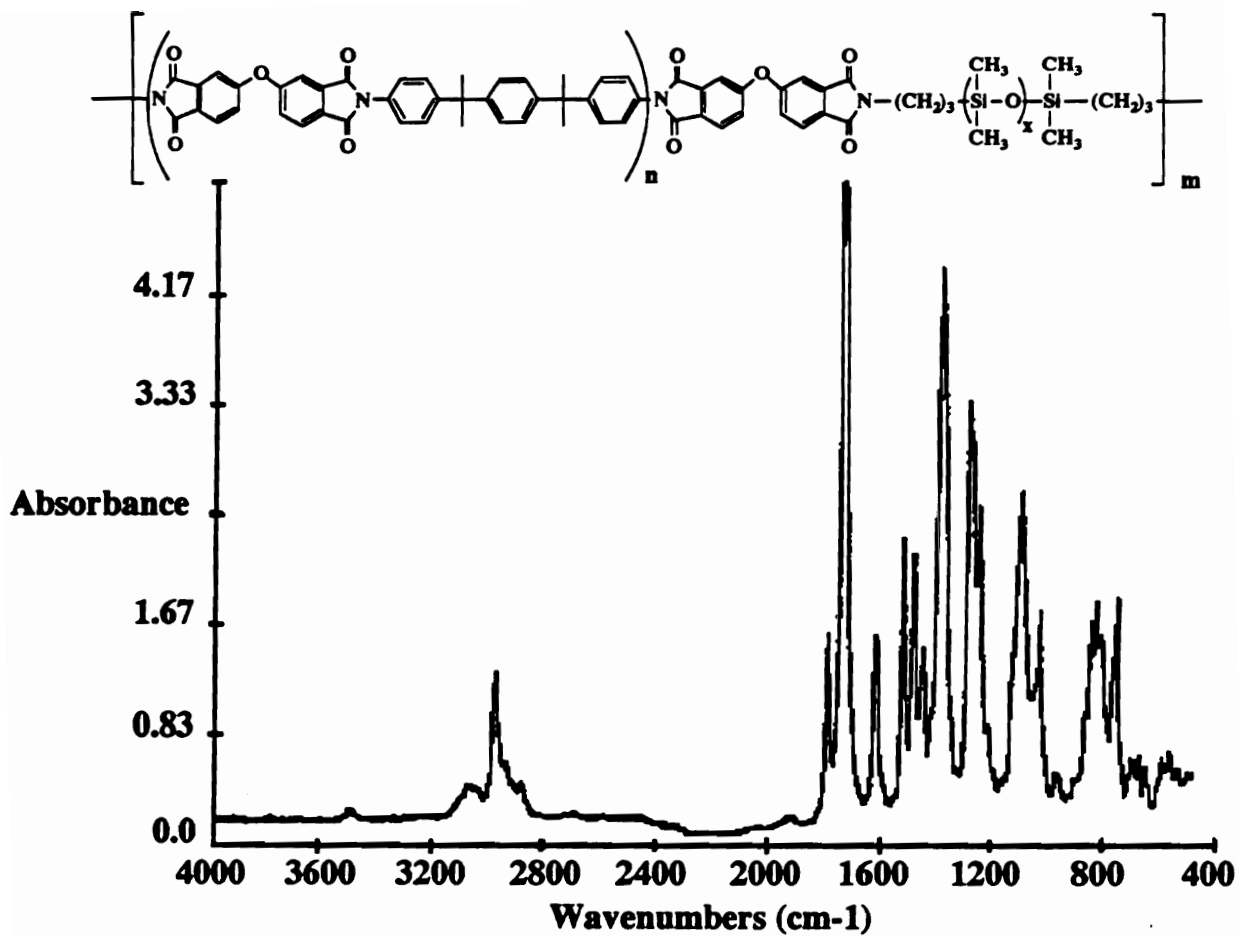
Figure 4.4.5 - FTIR Spectrum of a Perfectly Alternating Polyimide Siloxane Copolymer

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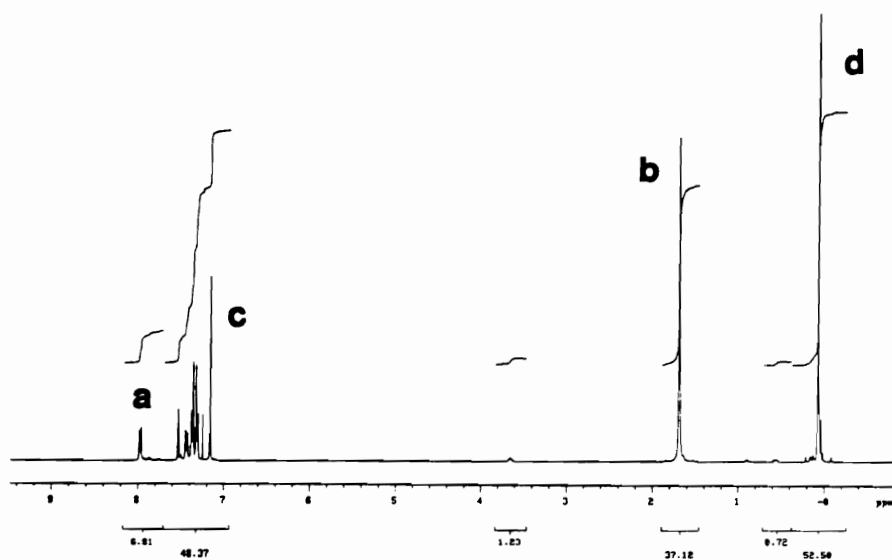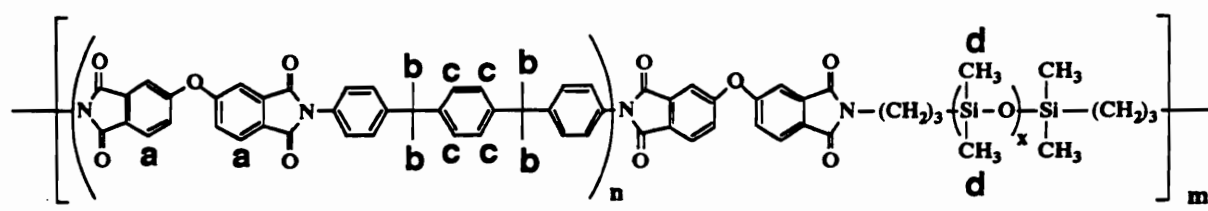
Figure 4.4.6 - ^{1}H n.m.r. Spectrum of a Perfectly Alternating Polyimide Siloxane Copolymer

weight of 2.67 kg/mole. The disappearance of the 2AP proton at 8.7 ppm indicated that the reaction went to nearly complete conversion.

4.4.3 Thermal Properties

DSC data of the two polyimide siloxane series and a high molecular weight ODPA-Bis P-PA homopolymer is presented in Table 4.4.4. All of the copolymers exhibited two Tg's, as determined by DMA, indicating phase separation in the copolymers. The DSC was used in determining the upper Tg. The Tg's of the polyimide oligomers ranged from 219°C to 240°C and the high molecular weight polyimide homopolymer showed a Tg of 267°C. The upper Tg's, which resulted from the polyimide phase of the polyimide-siloxane copolymers, were 201°C to 233°C for the PI-PSX1.07 series and 212 to 235°C for the PI-PSX2.67 copolymers. In both series, the Tg of the copolymers was less than the Tg of the corresponding polyimide oligomers indicating that there was some mixing between the polyimide and PSX phases. The depression of the Tg was even more pronounced when the lower molecular weight polyimide oligomer (4.0 kg/mole) was used. The lower molecular weight PSX oligomer used in the PI-PSX1.07 series resulted in a greater depression of the upper Tg's than the higher molecular weight PSX used in the PI-PSX2.67 series. The depression of the upper Tg was not dependent on the weight % PSX incorporated but depended on the size of the polyimide and PSX oligomers with the lower molecular weight oligomers giving lower upper Tg's and greater phase mixing.

Dynamic mechanical analysis at 1Hz from -150°C to 300°C displays trends which were analogous to those found in the DSC results. In Figure 4.4.7. the dynamic storage modulus for the three copolymers in the PI-PSX1.07 series had a value of ~4 GPa at -150°C and decreased as the temperature was raised. The decrease in the storage modulus was greatest for the copolymer with a 4.0 kg/mole polyimide and least for the 8.0 kg/mole polyimide copolymer. The sharp decrease in the storage modulus of the copolymers at the

Table 4.4.4 - Thermal Analysis of Polyimide Homopolymers and Perfectly Alternating Segmented Polyimide Siloxane Copolymers

Theoretical \<Mn\> of PI Oligomer kg/mole	Tg of PI oligomer °C	Target Weight % PSX	Upper Tg of PI-PSX °C	5% wt. loss by TGA in air °C
PI-PSX2.67 Series				
4.0	219	31	212	445
6.0	232	22	229	453
8.0	240	17	235	468
PI-PSX1.07 Series				
4.0	219	16	201	472
6.0	232	11	227	498
8.0	240	8	233	511
ODPA-Bis P-PA				
40.0	267	--	--	544
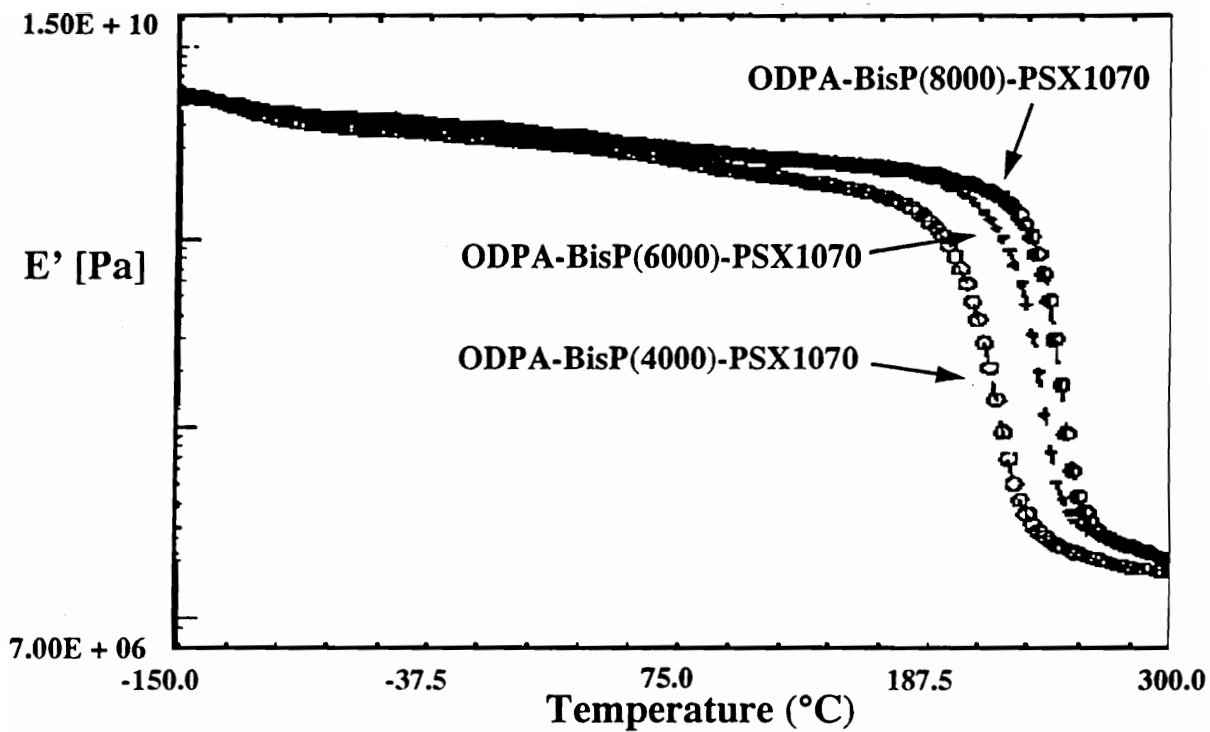
Figure 4.4.7 - Storage Modulus-Temperature Curves for the PSX1.07 Series of
Polyimide Siloxane Copolymers (Heating Rate - 10 °C/minute; Frequency - 1 Hz)

glass transition temperature also depended upon the oligomer molecular weight with the Tg increasing with increasing molecular weight of the polyimide oligomers.

The two phase nature of the perfectly alternating polyimide siloxane copolymers is dramatically seen in the pictures of the copolymers taken from transmission electron microscopy. The TEM photographs of two ODPA-Bis P-PSX copolymers in Figure 4.4.8 clearly showed two regions. The dark colored regions corresponded to the polysiloxane rich phase while the light regions were the polyimide rich phase. The resolution of the TEM was poor so it is difficult to draw any conclusions about the nature of the phase separation.

Also included in Table 4.4.4, is the 5% weight loss measured by TGA. The thermooxidative stability of the copolymers was less than the polyimide homopolymer due to the presence of the PSX oligomers. A dynamic TGA thermogram is shown in Figure 4.4.9. The 5% weight loss was dependent on the weight % PSX incorporated since the thermooxidative stability of the copolymers decreased as greater weights of the PSX were incorporated into the copolymer. An isothermal TGA thermogram of a polyimide siloxane copolymer containing 22 weight % siloxane is shown in Figure 4.4.10. After 22 hours at 250°C, ~20°C above Tg, the polyimide siloxane copolymer showed very little weight loss.
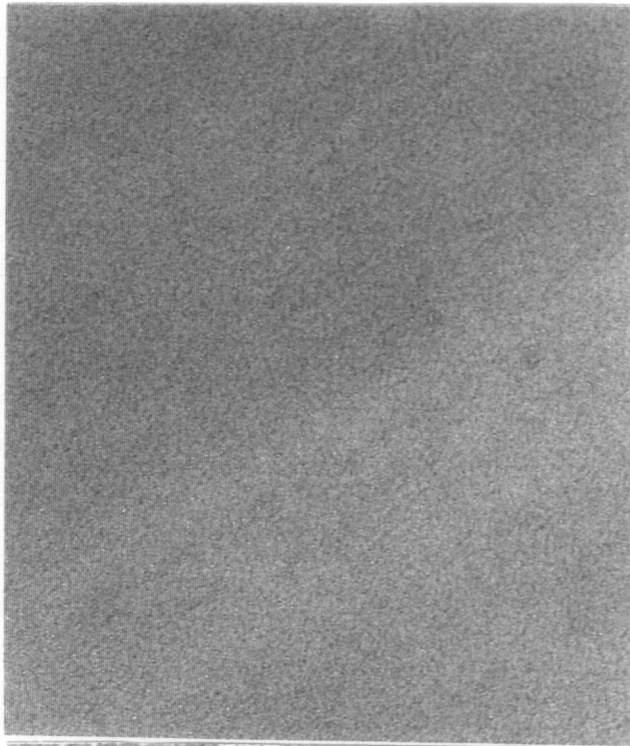
ODPA-Bis P4000-PSX1070

0.15 microns
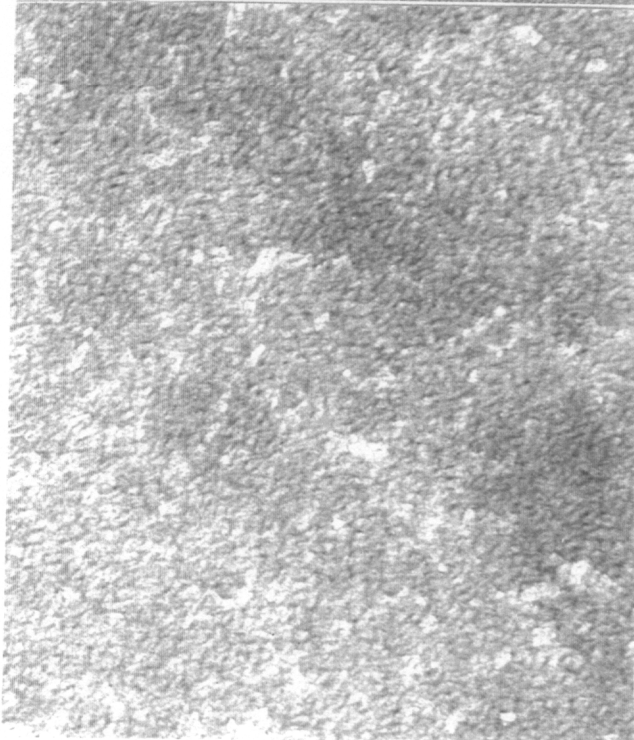
ODPA-Bis P4000-PSX2670

Figure 4.4.8 - TEM Photographs of Two ODPA-Bis P-PSX Copolymers
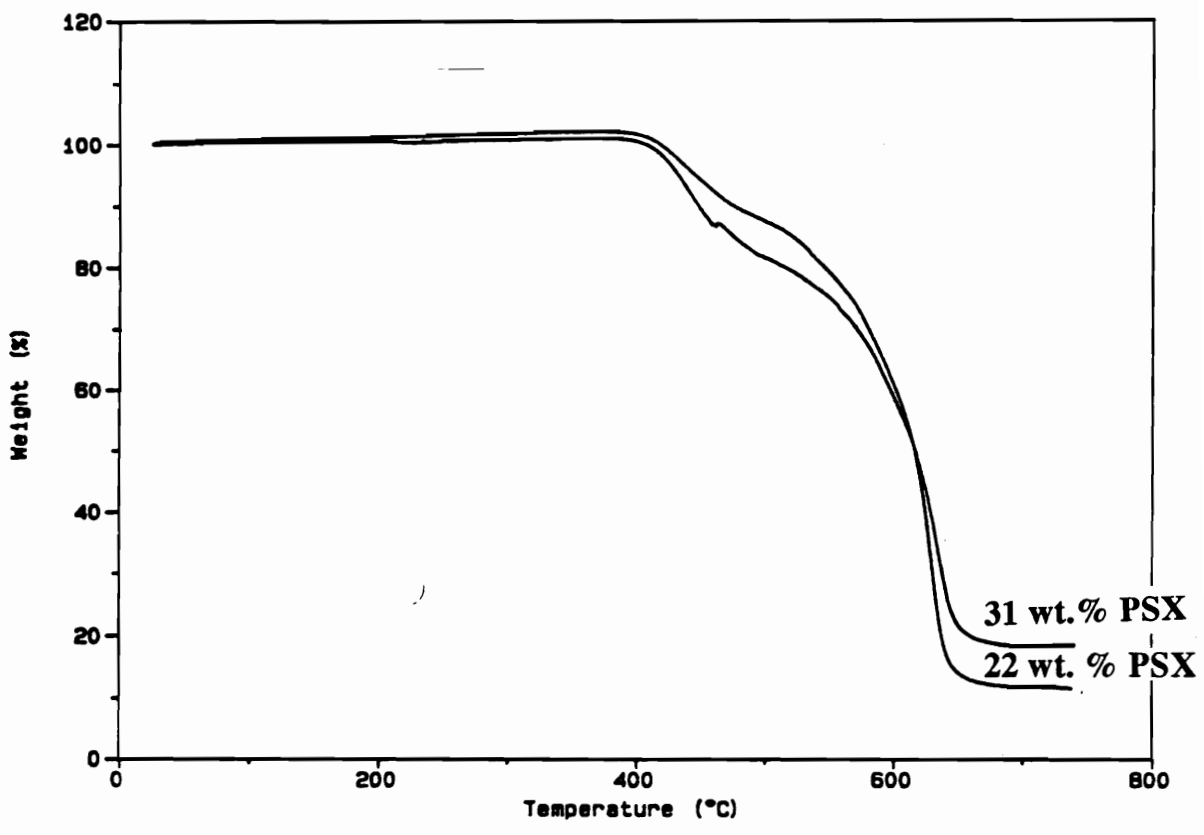
Figure 4.4.9 - Dynamic TGA Thermogram of ODPA-Bis P-PSX
Polyimide Siloxane Copolymers (Air atmosphere; Heating rate - 10 °C/minute)

141
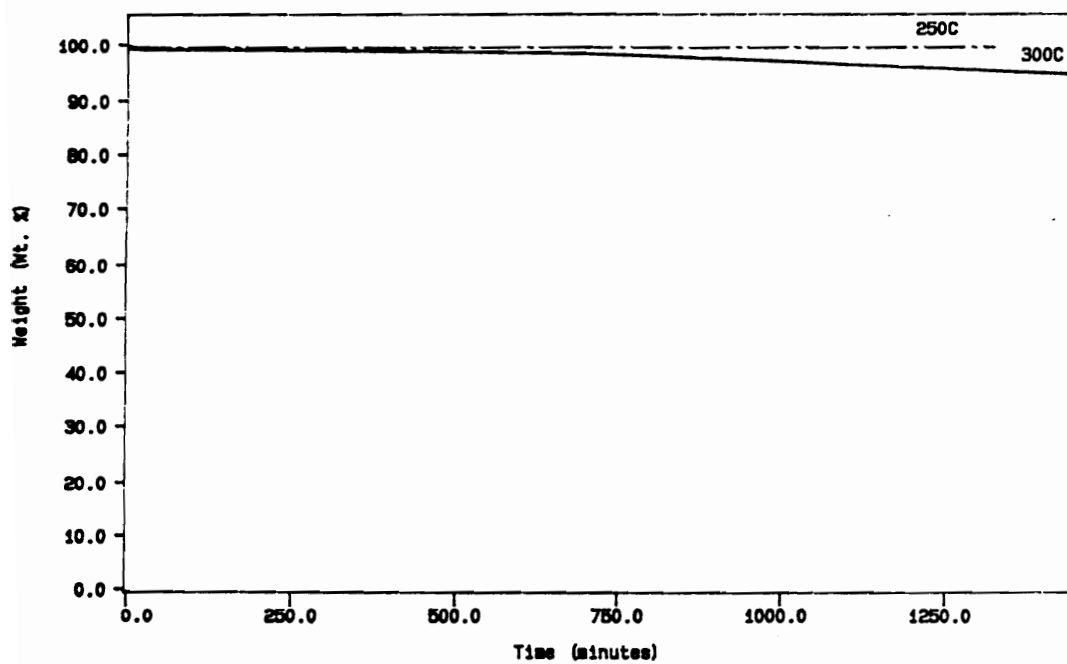
Figure 4.4.10 - Isothermal TGA Thermogram of a ODPA-Bis P-PSX
Polyimide Siloxane Copolymer (Air atmosphere)

4.5 MODEL STUDIES OF THE TRANSIMIDIZATION REACTION

In order to obtain high molecular weight polymers using the transimidization reaction or any step growth polymerization method, it is necessary to obtain high conversion of the starting reactants (61). Model studies of the transimidization reaction were performed to determine the degree of conversion that could be obtained from the reaction of an N-(2-pyrimidyl)phthalimide and an aromatic or aliphatic amine. The study also verified the presence of an amide-amide intermediate which formed in the transimidization reaction, and the conditions under which this intermediate cyclized to the desired imide.

4.5.1 Model Studies of N-(2-pyrimidyl)phthalimide and Hexylamine

Figure 4.5.1 displays the imide-amine interchange of N-(2-pyrimidyl)phthalimide, 1, and hexylamine, 2 which models the reaction of N-(2-pyrimidyl)phthalimide terminated polyimides and aminopropyl terminated poly(dimethyl siloxanes) to make the perfectly alternating segmented polyimide siloxane copolymers. Figure 4.5.2 and Figure 4.5.3 charts the progress of the reaction by plotting the mole percent of each chemical moiety as a function of time. The mole percent was determined by ^{1}H n.m.r.

At 25 °C in both chloroform and dimethyl sulfoxide (DMSO), Figure 4.5.2, 1 and 2 combined readily to form the intermediate amide-amide, 3. Figure 4.5.4 shows the ^{1}H n.m.r. of the reaction done in CHCl$_3$ at 25 °C after 180 minutes. The polar effect of the solvent became evident in the ring closure of 3 to give the N-hexyl phthalimide and 2-aminopyrimidine. Cyclization occurred much faster in the more polar solvent, DMSO, than in chloroform. Within 3 hours in DMSO, nearly all of reactants, 1 and 2, combined and over 85 % of the intermediate, 3, cyclized to form the N-hexyl phthalimide. After 3 hours in chloroform, only 10 % of the final product, 4, was present.

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1
N-(2-pyrimidyl)phthalimide

2
Hexylamine

$H_2N(CH_2)_5CH_3$

+

3
Amide-Amide
Intermediate

4
N-hexylphthalimide

+

5
2APm
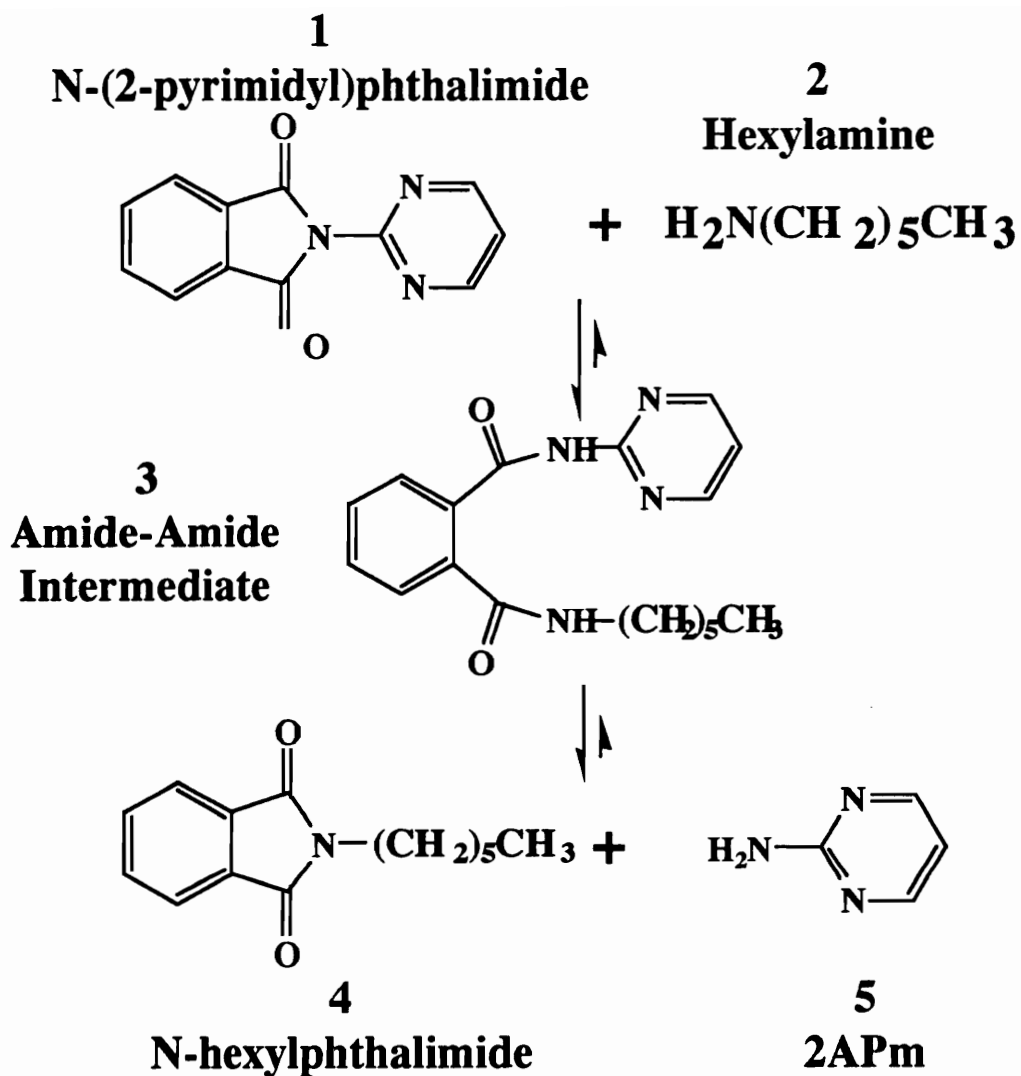
Figure 4.5.1 - Model Study Reaction of N-(2-pyrimidyl)phthalimide and Hexylamine

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DMSO at 25 °C

mole %

Time (hours)

CHCl₃ at 25 °C

mole %

Time (hours)
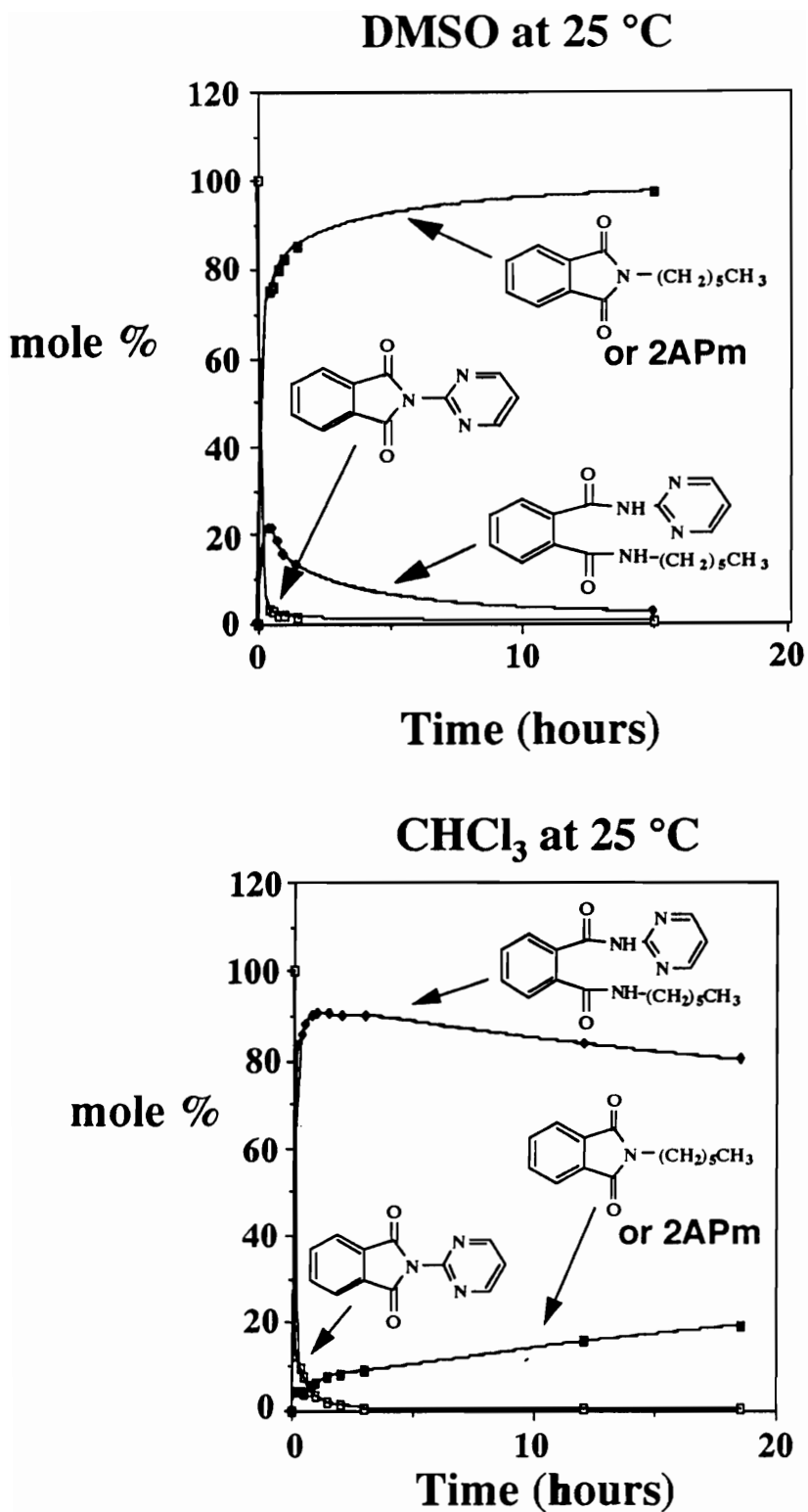
Figure 4.5.2 - Influence of Reaction Time and Solvent on
Model Transimidization Reactions at 25 °C

145
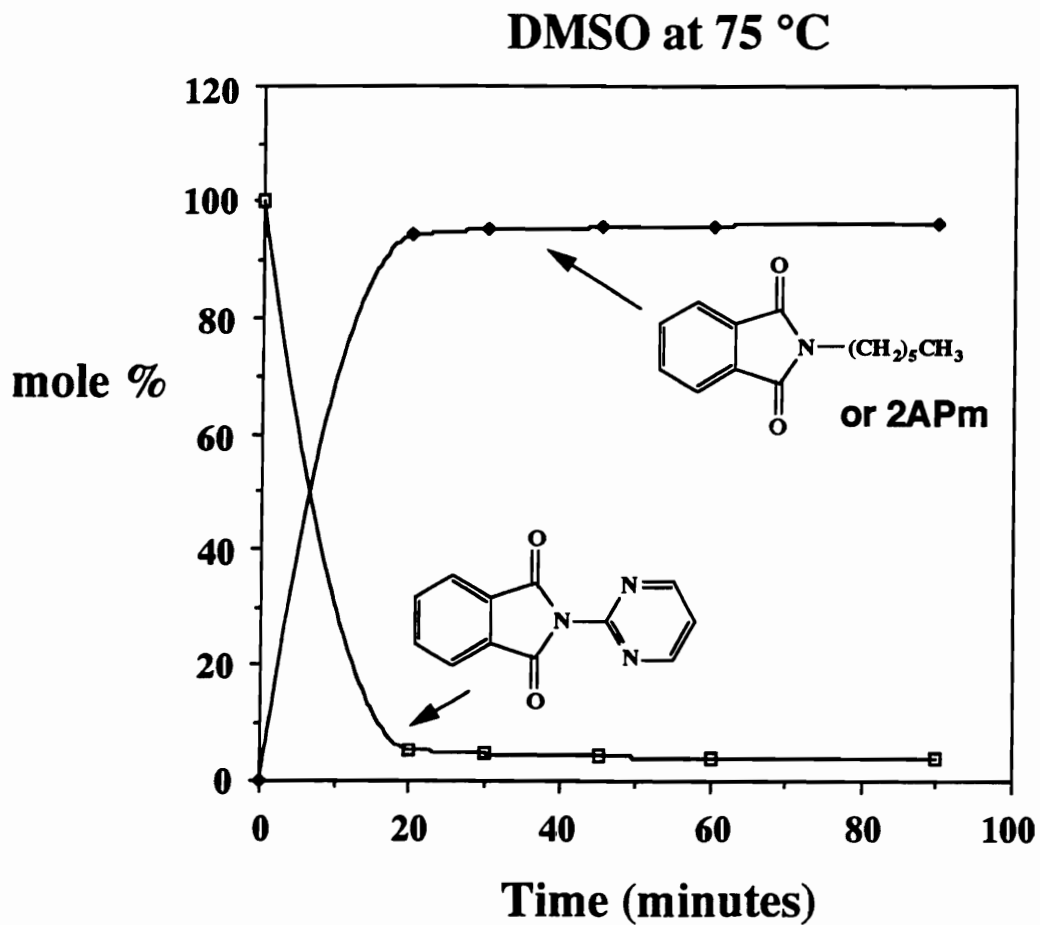
Figure 4.5.3 - Influence of Reaction Time in DMSO at 75 °C on the Transimidization
Reaction with an Aliphatic Amine
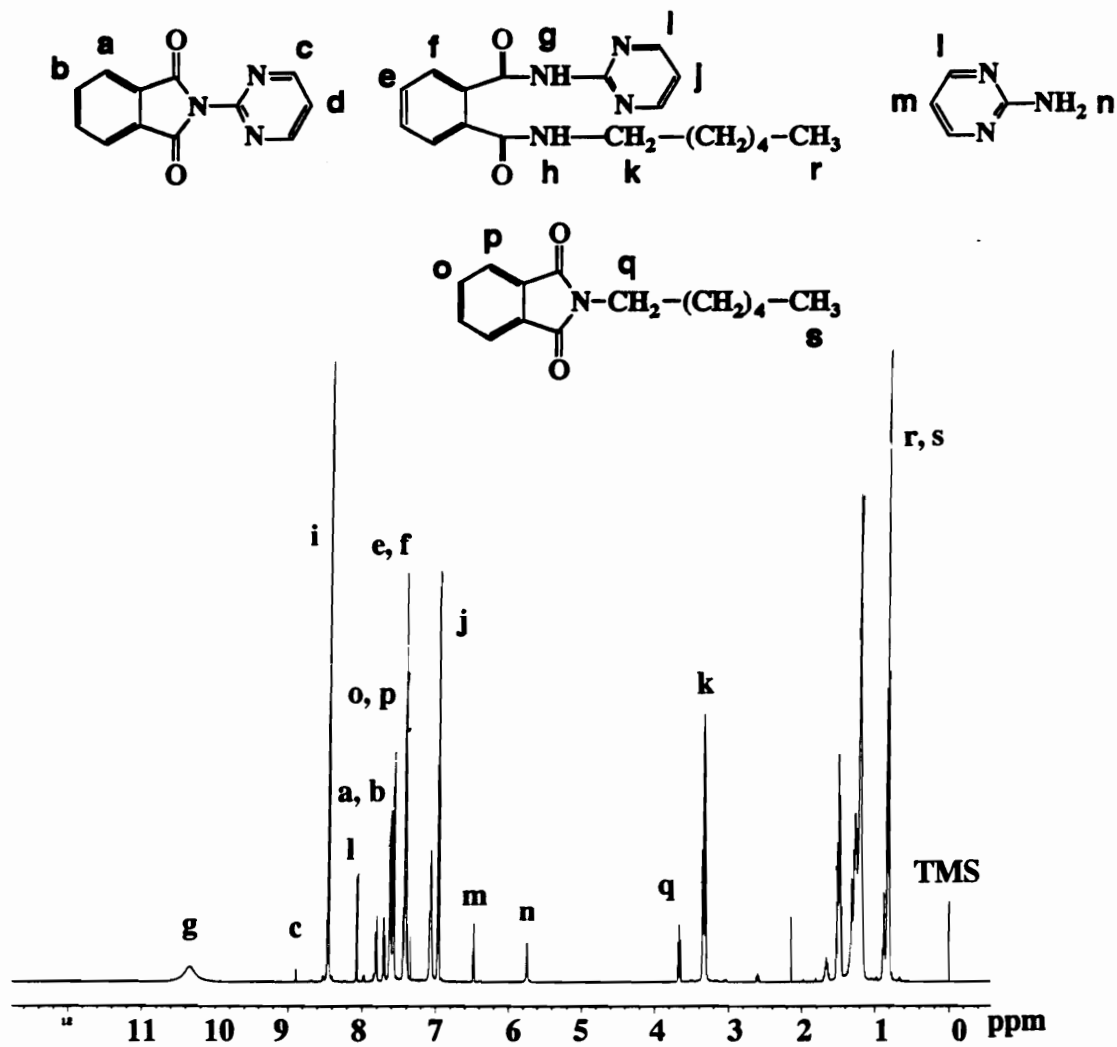
Figure 4.5.4 - ^{1}H n.m.r. Spectrum - N-(2-pyrimidyl)phthalimide and Hexylamine in CHCl$_3$ after 180 Minutes at 25 °C

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In DMSO at 75 °C, Figure 4.5.3, the reaction proceeded to very high conversions, >95 %, within 1 hour with almost all of the intermediate, 3, cyclizing to form the N-hexyl phthalimide. A representative ^{1}H n.m.r. taken at 20 minutes is shown in Figure 4.5.5. Note that the n.m.r. spectrum showed no indication of the intermediate, 3.

The model study of an N-(2-pyrimidyl)phthalimide and an aliphatic amine clearly demonstrated the utility of the transimidization reaction in the synthesis of perfectly alternating segmented polyimide siloxane copolymers. The reaction between an N-(2-pyrimidyl)phthalimide and an aliphatic amine occurred very quickly at low temperatures in mild solvents without the use of a catalyst.

4.5.2 Model Study of N-(2-pyrimidyl)phthalimide and an Aromatic Amine

In the presence of the zinc acetate catalyst, the reaction of N-(2-pyrimidyl)phthalimide and an aromatic amine, m-anisidine, was slow but high conversions were still possible. A schematic of the reaction was shown in Figure 4.5.6. As seen in Figure 4.5.7, the reaction proceeded to 98+ percent conversion within 24 hours at 75 °C. A ^{1}H n.m.r. taken at 24 hours is depicted in Figure 4.5.8. At this temperature, very little of the amide-amide intermediate was detected in the n.m.r. spectrum of any of the aliquots. After the N-(2-pyrimidyl)phthalimide and the m-anisidine combined, the intermediate quickly cyclized to form the final phthalimide.

Since high conversions were reached in the reaction of N-(2-pyrimidyl)phthalimide and an aromatic amine, the transimidization reaction could be applied to the synthesis of polyimide homopolymers. By reacting N, N'-(2-pyrimidyl)bisphthalimides with various aromatic diamines, high molecular weight, fully cyclized polyimides could achieved at low temperatures.

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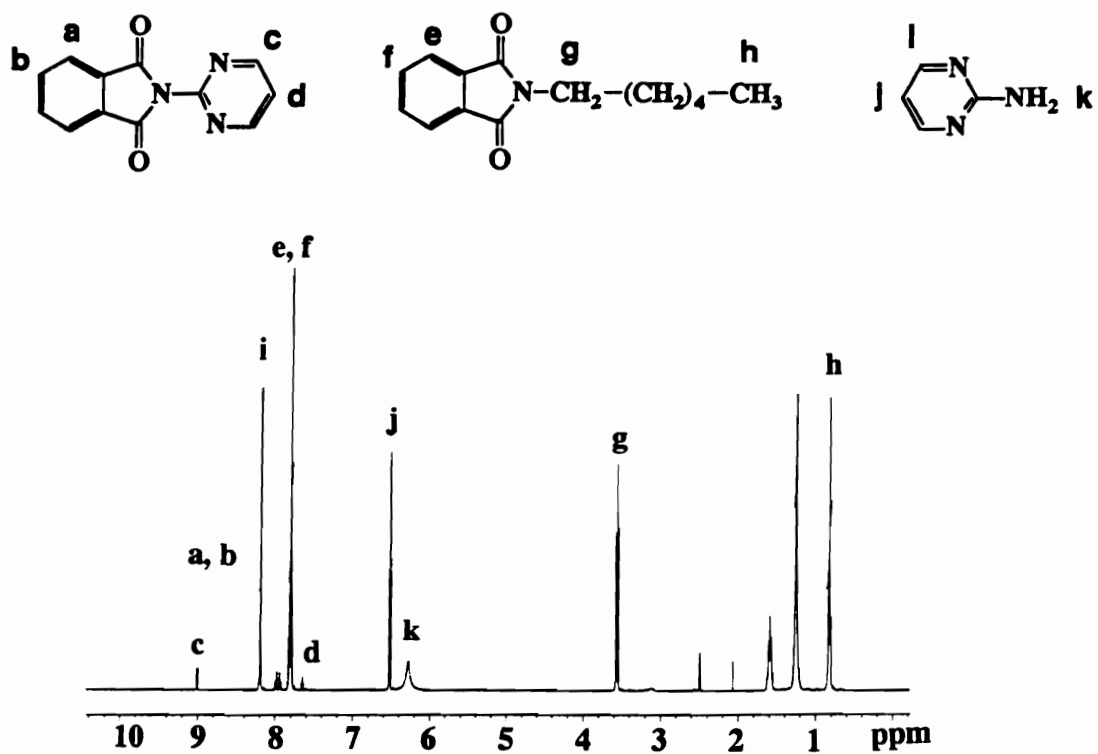
Figure 4.5.5 - ^{1}H n.m.r. Spectrum- N-(2-pyrimidyl)phthalimide and Hexylamine in DMSO after 20 Minutes at 75°C

149

PA-2APm

m-anisidine

Amide-Amide intermediate

PA-m-anisidine

2APm
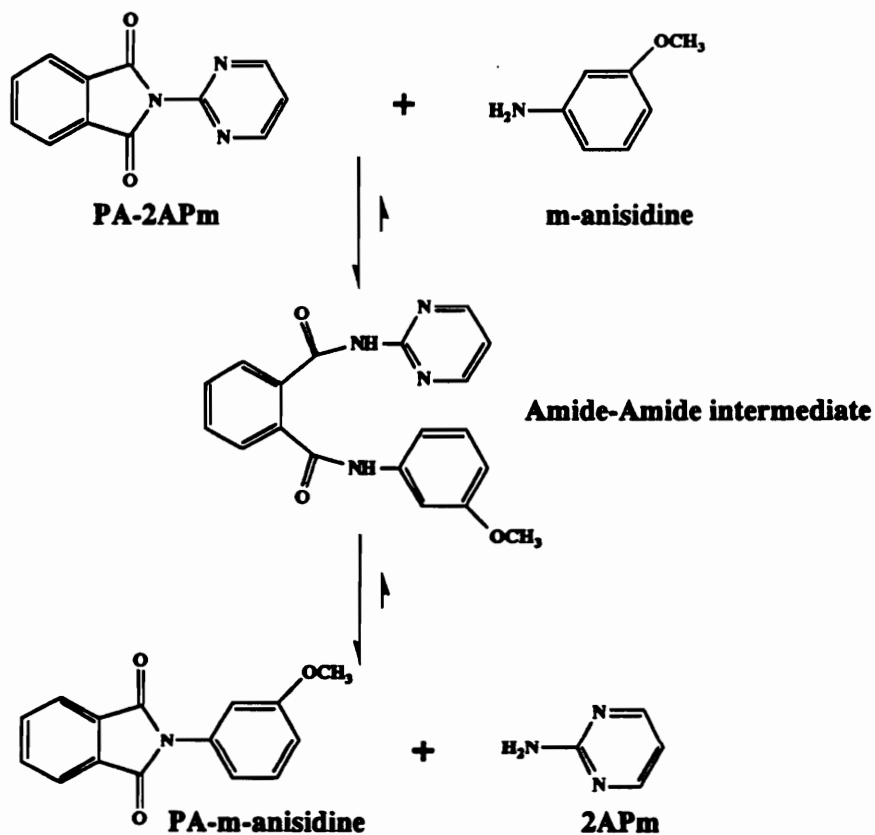
Figure 4.5.6 - Model Study of the Transimidization Reaction of N-(2-pyrimidyl)phthalimide and m-Anisidine
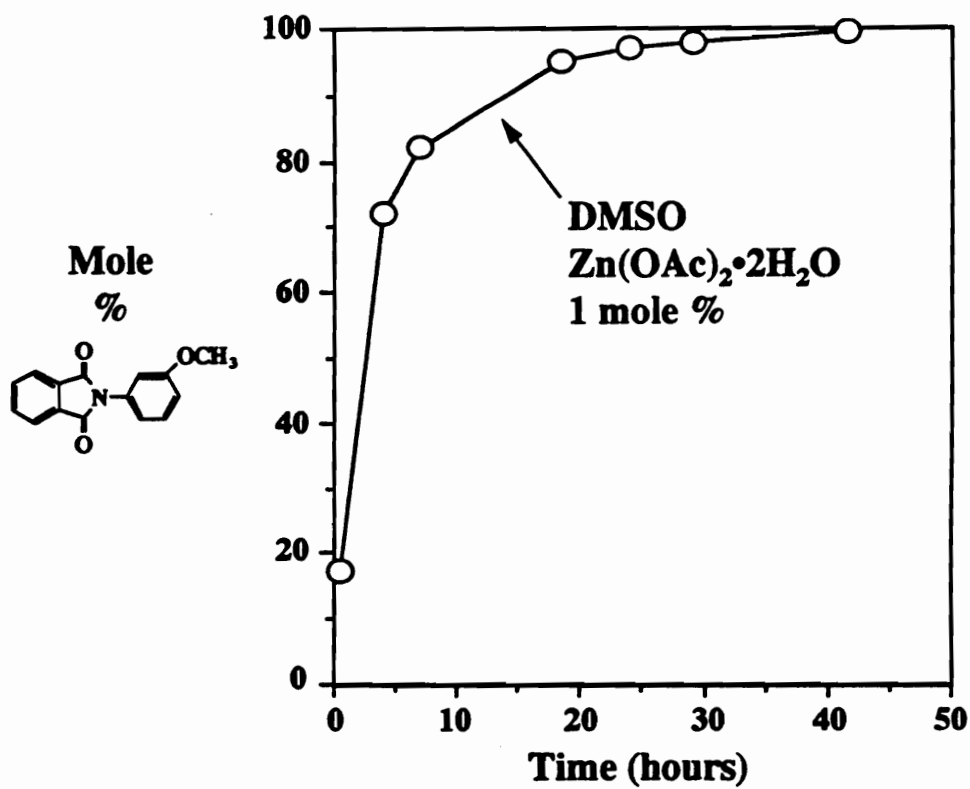
Figure 4.5.7 - Influence of Reaction Time on the Transimidization Reaction of N-(2-pyrimidyl)phthalimide and m-Anisidine in DMSO at 75 °C
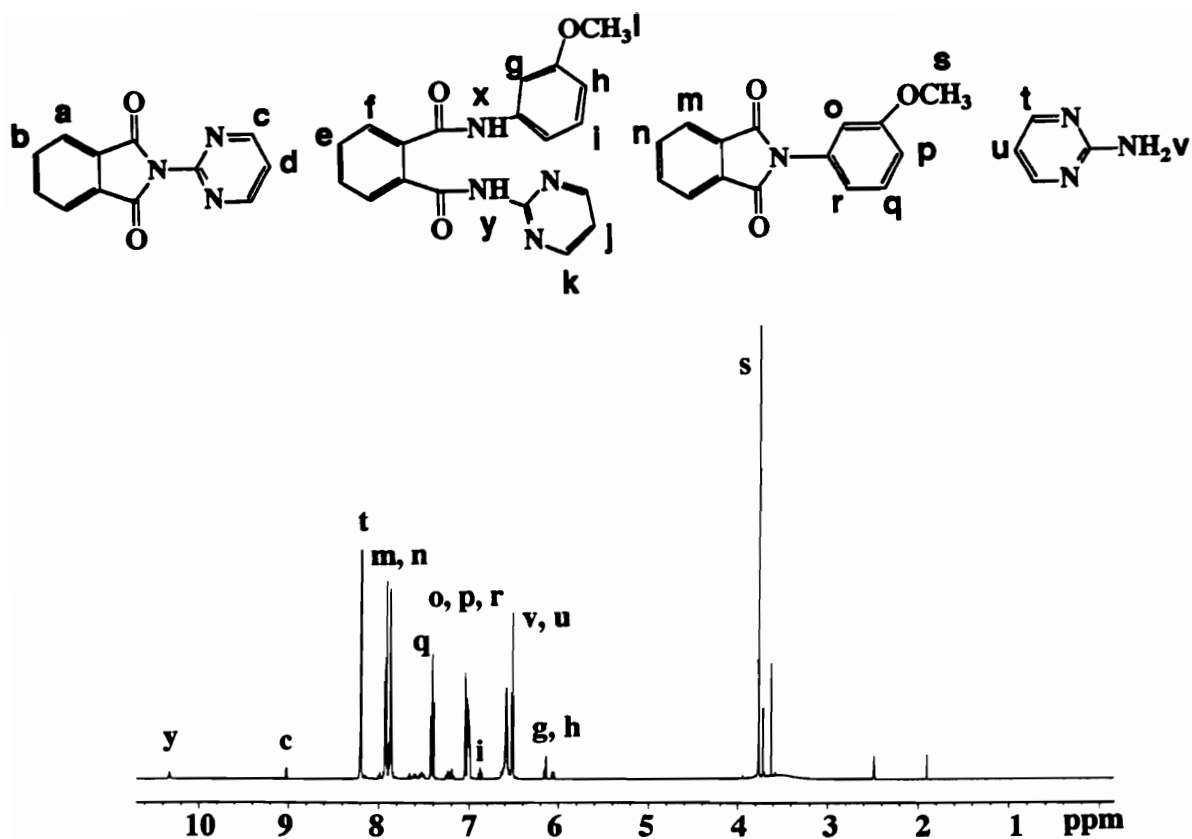
Figure 4.5.8 - ^{1}H n.m.r Spectrum - N-(2-pyrimidyl)phthalimide and m-Anisidine
in DMSO after 24 hours at 75 °C

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4.5.3 Proposed Mechanism of the Transimidization Reaction

Figure 4.5.9 depicts a proposed mechanism for the reaction of N-(2-pyrimidyl)phthalimide and an amine to form an amide-amide intermediate. The proposed mechanism is similar to the mechanism determined for the synthesis of poly(amic acid)s which is described in the literature review. The rate determining step occurs in the first step with the nucleophilic substitution at one of the imide carbonyl carbons. From the model studies, it is clear that high conversion was achieved for the reaction of N-(2-pyrimidyl)phthalimides with both aromatic and aliphatic amines under very mild conditions. The low basicity of 2-aminopyrimidine (pKa=25.3 in DMSO (57) and 3.45 in water (185)) relative to most aromatic and aliphatic amines signifies that the pyrimidine group is a strong electron withdrawing group. In the N-(2-pyrimidyl)phthalimide, the imide carbonyls are sufficiently electrophilic to allow substitution from most other amines. The hexylamine with a pKa of 10.64 (measured in water (185)) is more nucleophile than m-anisidine, pKa=4.20 (measured in water (185)). It is not surprising that the transimidization reaction occurs much faster with hexylamine than with m-anisidine.

Cyclization of the amide-amide intermediate, Figure 4.5.10, which forms during the transimidization reaction, occurred at much lower temperatures than the cyclization of a poly(amic acid). Kim, et. al. propose that the rate determining step in the cyclization of a poly(amic acid) during solution imidization was the nucleophilic attack of the amide nitrogen on the carbon of the carboxylic acid (44). The rate limiting step in the cyclization step of the transimidization reaction is probably the nucleophilic attack of the amide nitrogen on the carbon of the N-pyrimidyl amide. The pKa of 2-aminopyrimidine in DMSO is much lower than the pKa of water (pKa = 31.2 in DMSO (57)). Thus,
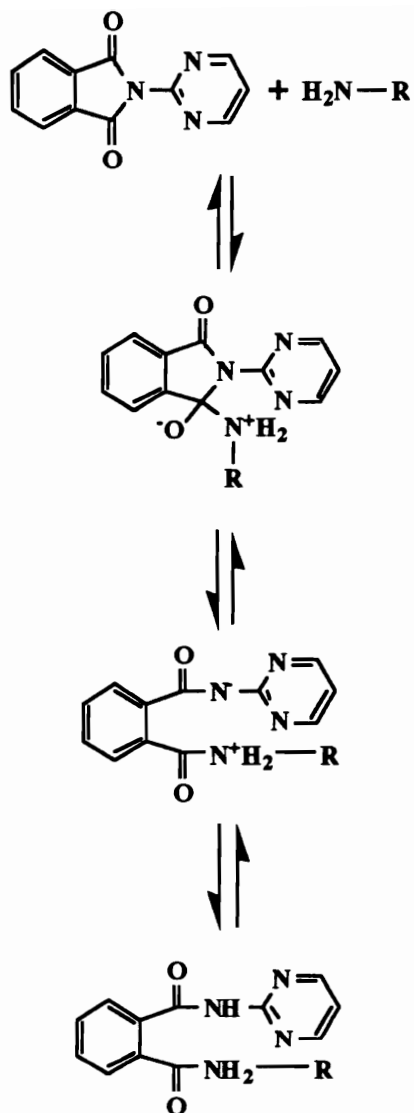
Figure 4.5.9 - Proposed Mechanism for the Combination of
N-(2-pyrimidyl)phthalimide with an Amine
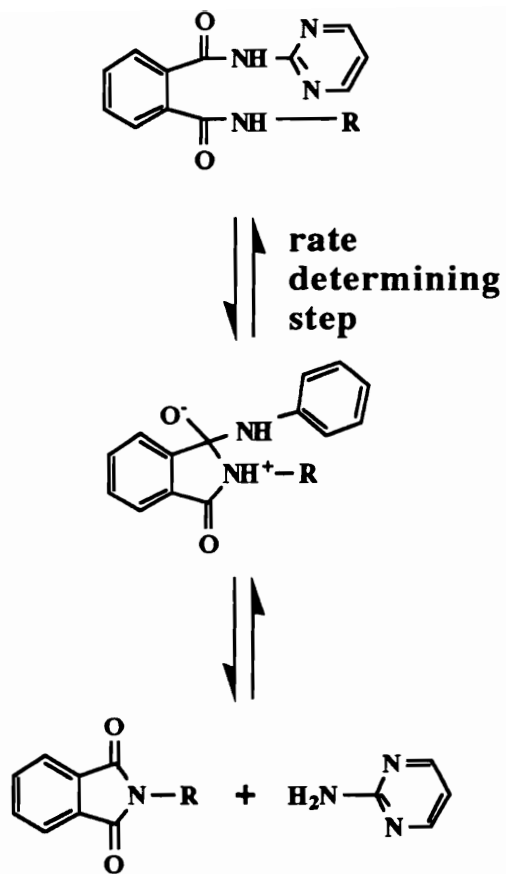
Figure 4.5.10 - Proposed Mechanism for the Ring Closure
in the Transimidization Reaction

aminopyrimidine should act as a stronger electron withdrawing group than a hydroxyl group. In the amide-amide intermediate, the carbonyl carbon of the N-pyrimidine amide is more electropositive than the carboxylic acid carbon of the poly(amic acid). The carbon of the N-pyrimidine amide is then more susceptible to nucleophilic attack than the carbon of the carboxylic acid in the poly(amic acid). The activation energy in the first step of the transimidization reaction would then be lower than the corresponding step in the cyclization of the poly(amic acid). Therefore, cyclization of the amide-amide intermediate in Figure 4.5.8 will occur at lower temperatures than the cyclization of the poly(amic acid).

In addition to the fact that 2-aminopyrimidine is a good leaving group, its low reactivity limits the reverse reaction of 2-aminopyrimidine with the phthalimide product. This is very important since 2-aminopyrimidine cannot be readily removed from the reaction mixture to drive the reaction to the "right". The equilibrium constant of the transimidization reaction of N-(2-pyrimidyl)phthalimide and other amines seems to be large enough that high conversion can be achieved without removing the 2-aminopyrimidine from the reaction mixture.

4.6 POLYIMIDE HOMOPOLYMERS MADE THROUGH THE TRANSIMIDIZATION ROUTE

As the model studies demonstrate, the transimidization route should be effective in making high molecular weight polymers at temperatures below 100°C since high conversions can be achieved. Thus, polyimide homopolymers can be made by combining a N, N'-(2-pyrimidyl)bisphthalimide and a diamine at low temperatures.

4.6.1 Synthesis of N, N' -(2-pyrimidyl)bisphthalimides

The N, N'-(2-pyrimidyl)bisphthalimide were made by combining a dianhydride with two equivalents of 2-aminopyrimidine as shown in Figure 4.6.1. The reactions were done in ODCB at 170 °C for 24 to 48 hours. The water generated was azeotroped off and collected in a reverse Dean Stark trap. As the N, N'-(2-pyrimidyl)bisphthalimide was formed, it precipitated from solution. At the end of the reaction, the product was easily isolated by filtration. The N, N'-(2-pyrimidyl)bisphthalimide was purified by simply washing it with acetone and drying it in a vacuum oven at 180°C for 24 hours.

One problem with using the N, N' - pyrimidine bisphthalimides was their lack of solubility. All of the N, N'-(2-pyrimidyl)bisphthalimides were insoluble in NMP, THF and CHCl3 at a concentration of 10 weight % solids. However, 6FDA-2APm quickly reacted into an NMP solution during polymerization, but the other N, N'- pyrimidine bisphthalimides did not. NMP was only suitable as a polymerization solvent when 6FDA-2APm was used. The N, N'-(2-pyrimidyl)bisphthalimides were more soluble in m-cresol. m-Cresol can be used as a polymerization solvent. m-Cresol is an environmentally dangerous solvent, but it is often used in the experimental synthesis of polyimides. The N, N'-(2-pyrimidyl)bisphthalimides were not very soluble in dimethyl propylene urea (DMPU), but PMDA-2APm reacted into a DMPU solution containing 3F diamine.

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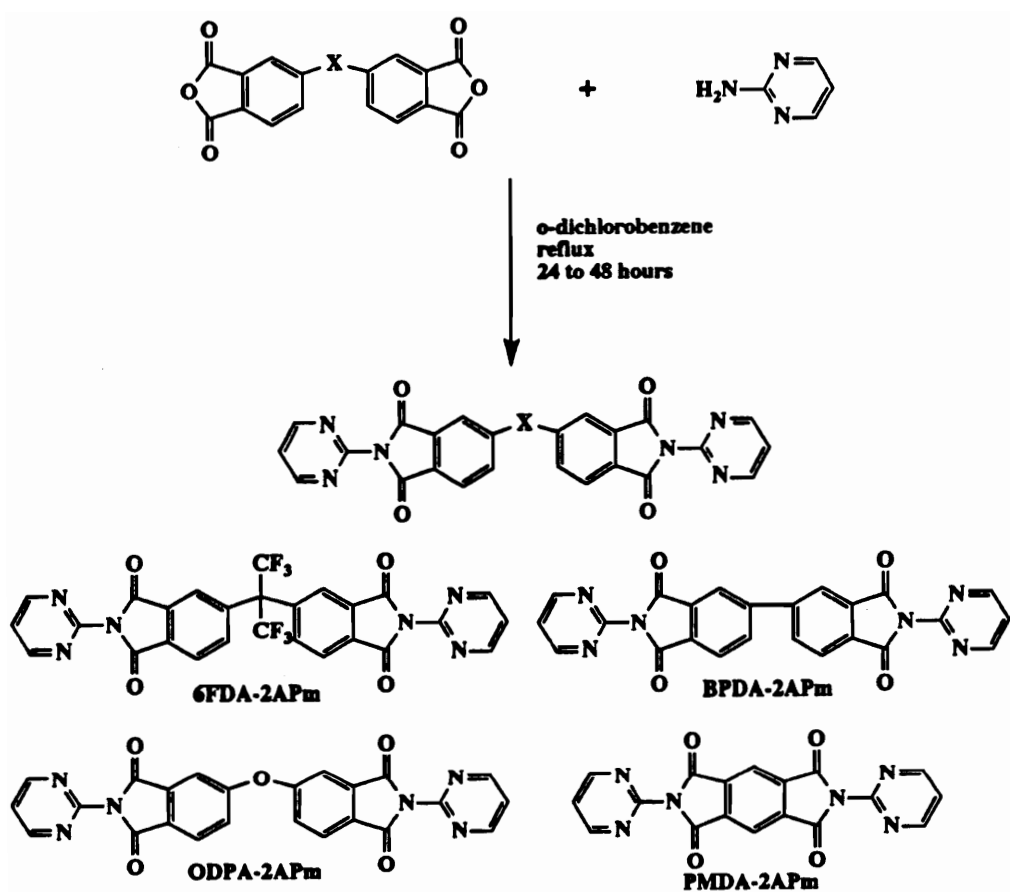
Figure 4.6.1 - Synthesis of N, N' -(2-pyrimidyl)bisphthalimides

4.6.2 Synthesis of Polyimide Homopolymers Through the Transimidization Route

The synthesis of polyimide homopolymers utilizing the transimidization route is seen in Figure 4.6.2. First the diamine was dissolved in the polymerization solvent followed by the addition of the catalyst. The solution was then heated to 75°C and the bisphthalimide was then added with enough solvent to bring the final concentration to ~20 wt. %. Even though the solvents were distilled prior to use, no precaution was taken to exclude water from the polymerization.

The polymerization of 6FDA-2APm and 4,4'-ODA was conducted under various conditions using both NMP and the phenolic solvent, m-cresol. The results are shown in Table 4.6.1. To obtain high molecular weight polyimides in a reasonable period of time, 24 hours or less, a catalyst of some type was clearly necessary when reacting N, N'-(2-pyrimidyl)bisphthalimides with aromatic amines. Mixing 6FDA-2APm with 4,4'-ODA in NMP without a catalyst gave a polyimide with a low inherent viscosity after 48 hours. However, adding just 10 mole% zinc acetate resulted in a polyimide with a higher inherent viscosity or molecular weight in just 24 hours. p-Toluenesulfonic acid worked very well as a catalyst giving polyimides with even higher inherent viscosities. Acetic acid also effectively catalyzed the transimidization reaction. Using just 10 mole % acetic acid relative to the pyrimidine, inherent viscosities as high as 1.06 dl/g were achieved within 24 hours. Increasing the concentration of the acetic acid appeared to speed up the reaction significantly. With a large amount of acetic acid, 500 mole %, the polyimide reached high viscosities within just 2.5 hours. Since acetic acid was inexpensive and easily removed from the resulting polyimides, it was the preferred catalyst in the polyimide synthesis using the transimidization route.

Spectroscopic investigations revealed that the resulting polymers from the transimidization reaction were fully cyclized polyimides. The ^{1}H n.m.r. in Figure 4.6.3,
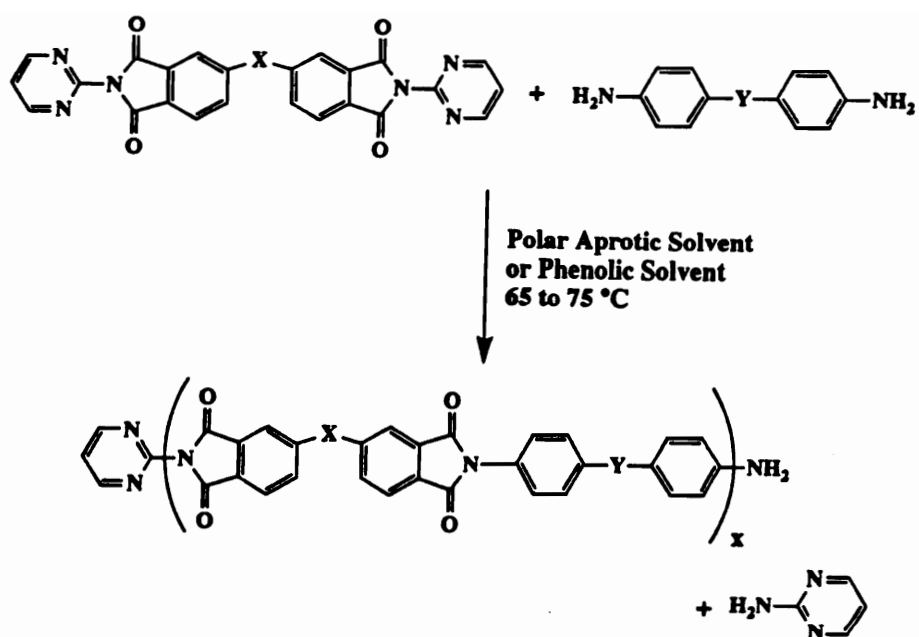
Figure 4.6.2 - Synthesis of Polyimide Homopolymers Using the Transimidization Route

Table 4.6.1 - Influence of Catalyst and Reaction Time on the Synthesis of
Polyimides from 6FDA-2APm + 4,4'-ODA

Reaction Conditions	Time hours	ηinh at 0.5 g/dl dl/g	\<Mn\> by GPC kg/mole	\<Mw\> by GPC kg/mole	\<Mw\>/\<Mn\>
NMP	48	0.42	---	---	---
NMP Zinc Acetate 10 mole %	24	0.54	17.0	37.0	2.2
NMP p-toluene sulfonic acid 10 mole %	24	1.22	---	---	---
NMP Acetic Acid 10 mole %	24	1.06	---	---	---
NMP Acetic Acid 100 mole %	24	1.25	57.0	136.0	2.4
NMP Acetic Acid 500 mole %	2.5	0.76	41.0	112.0	2.7
m-cresol	48	0.66	41.0	82.0	2.0
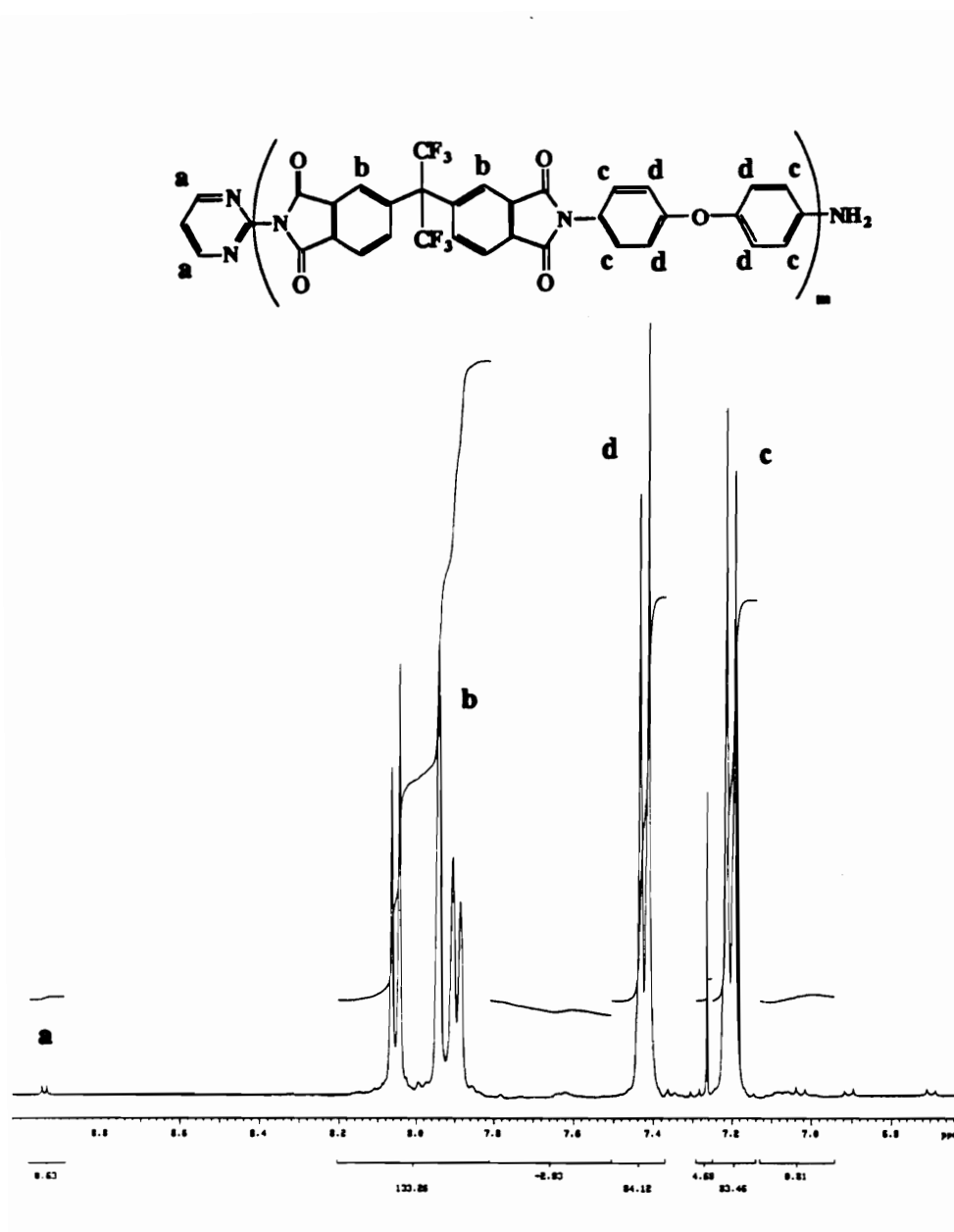
Figure 4.6.3 - ^{1}H n.m.r. of a 6FDA-4,4'-ODA Polyimide Made by the Transimidization Route

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showed only trace amounts of the pyrimidine phthalimide present with no evidence of any amide-amide intermediates. [13]C n.m.r., Figure 4.6.4, revealed only the two expected peaks at 166 ppm for the carbonyl carbons of the imide ring and no other peaks that would be associated with an amide carbonyl. Evidence for the fully cyclized polyimide was also seen in the FTIR spectrum in Figure 4.6.5. There were peaks present at 1784, 1729, 1377 and 723 cm^{-1} which were typically associated with polyimides.

Some of the polyimides made by the transimidization route were investigated by GPC. The <Mn> and <Mw> listed in Table 4.6.1 were determined by a universal calibration method and are absolute values.

The 6FDA-4,4' ODA polyimide made with 100 mole % acetic acid catalyst had a <Mn> of 57.0 kg/mole which represented a 98.9 % conversion of the starting functional groups. The GPC curve of this polyimide is depicted in Figure 4.6.6. The GPC trace was a nearly symmetrical bell curve with a slightly broad molecular weight distribution of 2.4 which was a little higher than the 2.0 MWD predicted for step growth polymers. The 6FDA-4,4'ODA polyimide made with a 500 mole % acetic acid catalyst had a <Mn> of 41.0 kg/mole and a broader molecular weight distribution of 2.7. The broad distribution indicated that the polymerization did not proceed in a statistical fashion generally expected for step growth polymers. This was probably due to the slow solvation of the N, N'-(2-pyrimidyl)bisphthalimide and its fast reaction with the diamine in the presence of the catalyst. High molecular weight polymer formed at the interface of the solid N, N'-(2-pyrimidyl)bisphthalimide and the diamine solution. This phenomena has been observed in the synthesis of poly(amic acid)s made from dianhydrides of poor solubility (1). In m-cresol where the N, N'-(2-pyrimidyl)bisphthalimide readily dissolves, a polyimide with a <Mn> of 41.0 kg/mole and a narrower molecular weight distribution of 2.0 was obtained.
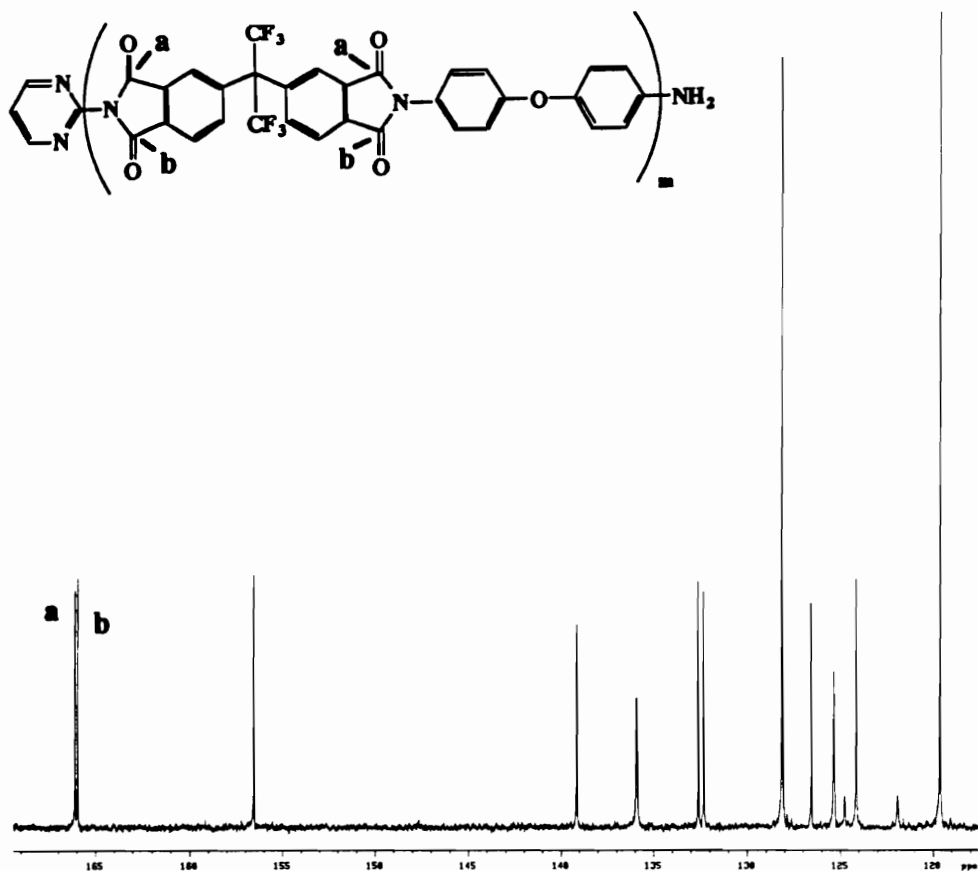
Figure 4.6.4 - ^{13}C n.m.r. of a 6FDA-4,4'-ODA Polyimide Made
by the Transimidization Route

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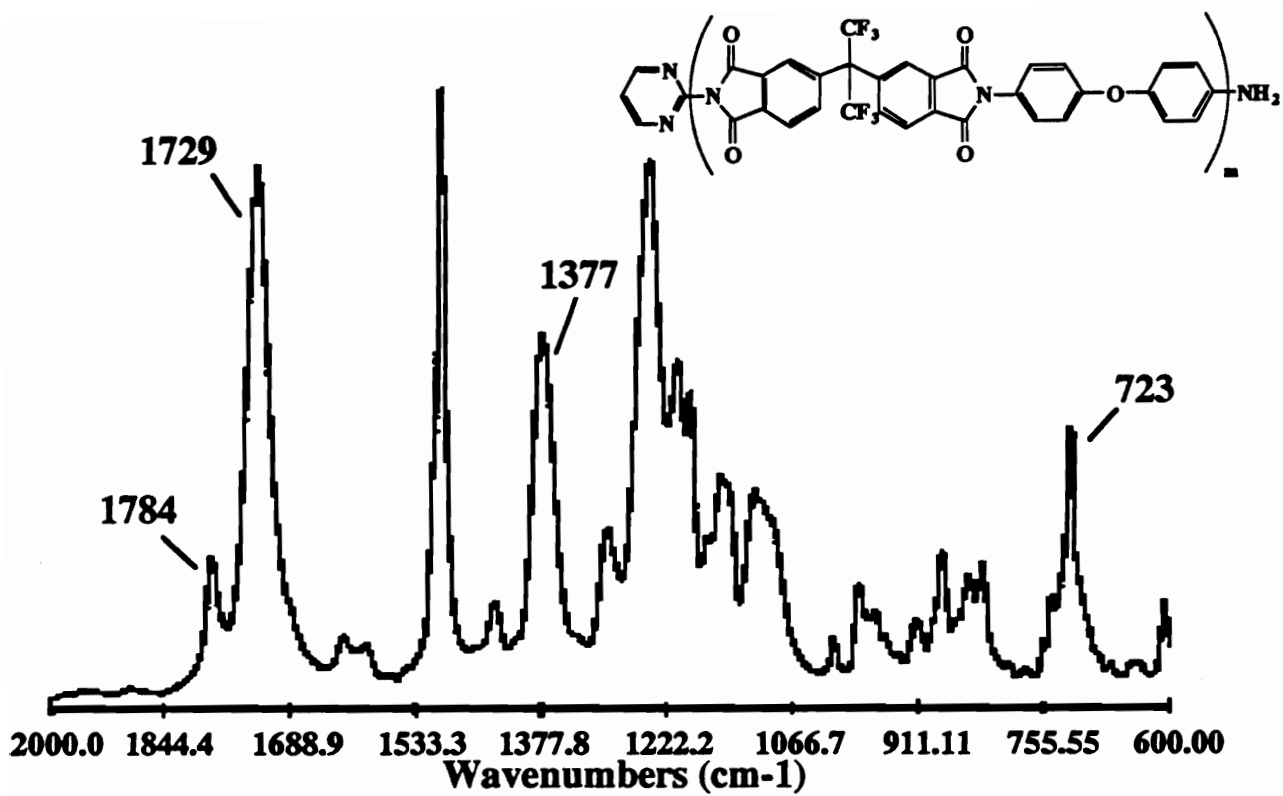
Figure 4.6.5 - FTIR Spectrum of a 6FDA-4,4'-ODA Polyimide Made
by the Transimidization Route
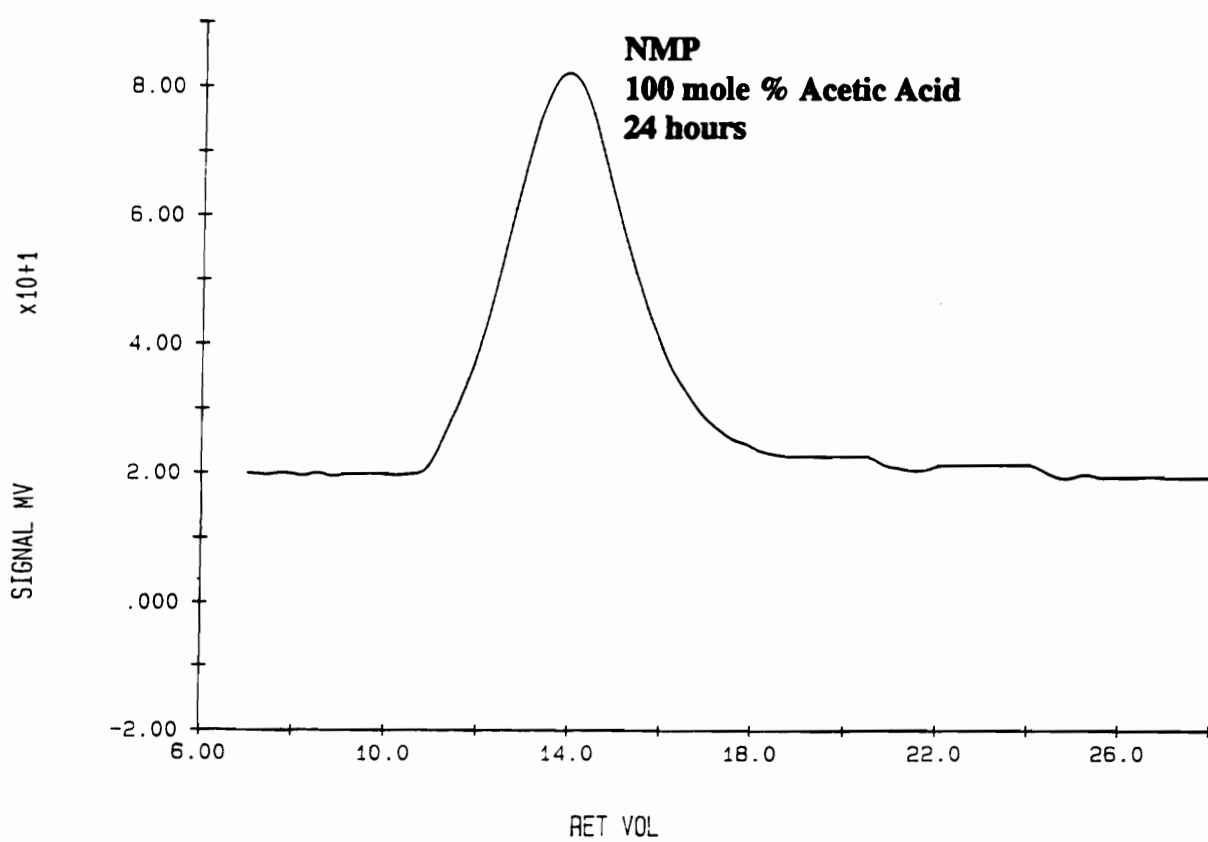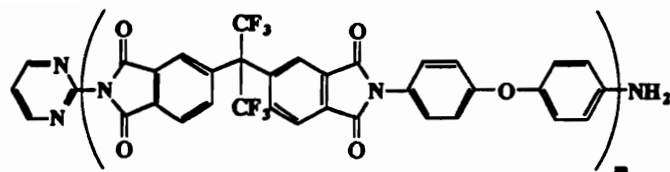
Figure 4.6.6 - GPC Trace of a 6FDA-4,4'-ODA Polyimide Made
by the Transimidization Route using 100 mole % Acetic Acid as a Catalyst

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For the 6FDA-4,4' ODA polyimide made in NMP with 10 mole % zinc acetate, a low <Mn> of 17.0 kg/mole was obtained. This molecular weight corresponds to a conversion of 93.1 % of the starting functional groups. The molecular weight distribution of this polymer was 2.2. The GPC trace of this polymer is depicted in Figure 4.6.7.

Table 4.6.2 lists several other polyimides made by the transimidization route. ODPA-2APm and Bis P were combined in m-cresol to form high molecular weight polyimides without using any catalyst. In 48 hours, an ODPA-Bis P polyimide was made with an intrinsic viscosity of 1.03 dl/g. A polyimide was made from PMDA-2APm in DMPU. PMDA-2APm was combined with 3F diamine in DMPU using acetic acid as a catalyst. The PMDA-2APm was relatively insoluble in DMPU, but it reacted into solution within 8 to 12 hours. BPDA-2APm did not react into solution when mixed with 3F diamine.

A comparison of two 6FDA-3FDAM polyimides are depicted in Figure 4.6.8. One of the 6FDA-3FDAM polyimides was synthesized by the solution imidization of a poly(amic acid) made from 6FDA and 3FDAM. The other 6FDA-3FDAM polyimide was made through the transimidization route, where 6FDA-2APm and 3FDAM were combined in NMP with an acetic acid catalyst. The <Mn> and <Mw> values were determined by GPC using a universal calibration technique. The 6FDA-3F diamine made through the transimidization route actually had a higher <Mn> than the same polyimide made through the solution imidization of the 6FDA-3FDAM poly(amic acid). Both polyimides had molecular weight distributions of 2.0. The FTIR spectra in Figure 4.6.9 show that both of the polyimides were fully cyclized.

It took about the same amount of time to make the 6FDA-3FDAM polyimides by the two methods. However, using the transimidization route, the fully cyclized 6FDA-3FDAM polyimide was made at a temperature 100°C lower than the temperature for the imidization of the 6FDA-3FDAM poly(amic acid). The transimidization route is a

credible alternative to the conventional two step poly(amic acid) synthesis of soluble polyimides.
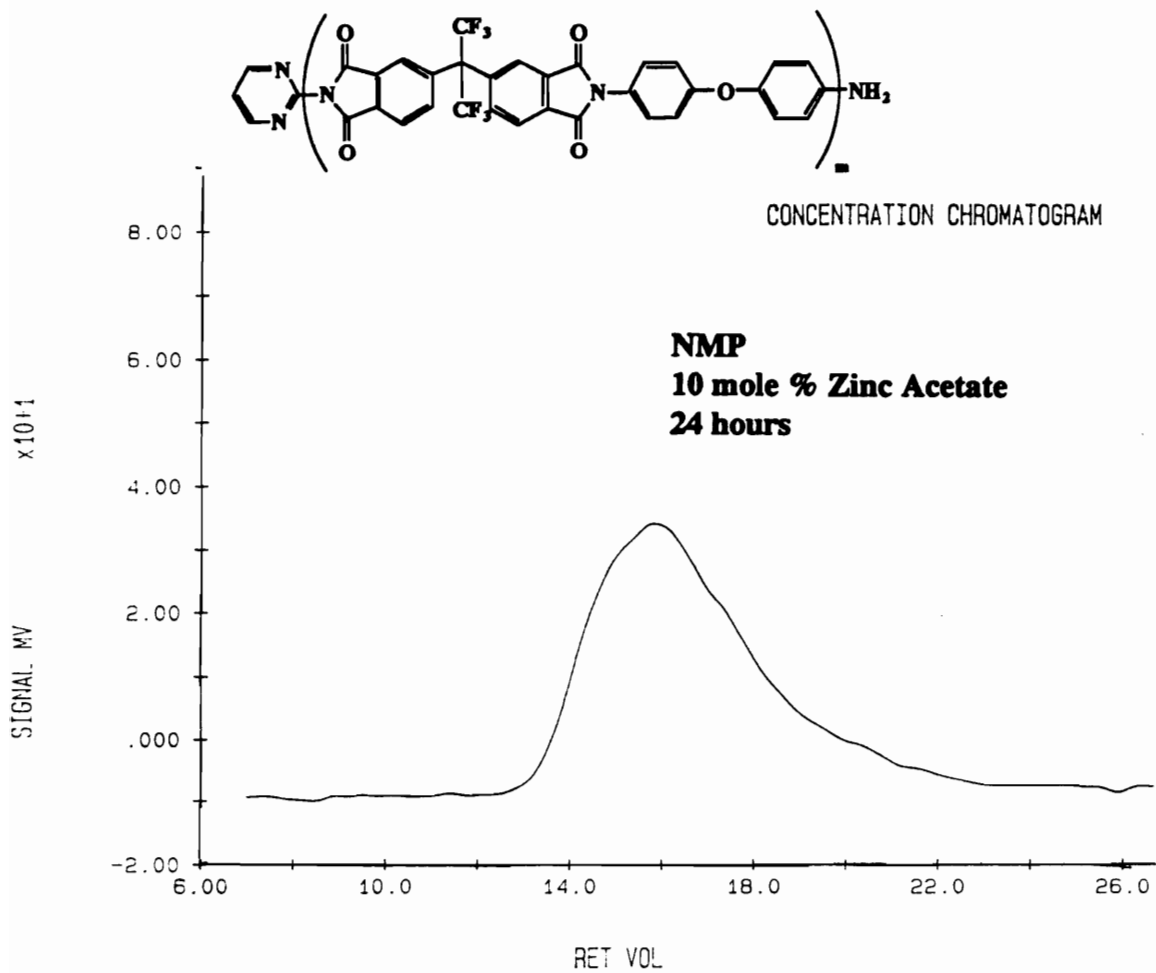
Figure 4.6.7 - GPC Trace of a 6FDA-4,4'-ODA Polyimide Made by the Transimidization Route using 10 mole % Zinc Acetate as a Catalyst

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Table 4.6.2 - Examples of Polyimides Successfully Synthesized via Transimidization

Polyimide	Solvent Reaction Temperature and Time	$[\eta]$ dl/g
ODPA-Bis P	m-cresol 75 °C, 48 hours	1.03 (CHCl$_3$)
PMDA-3FDAM	DMPU 75 °C, 48 hours Acetic Acid	0.41 (NMP)
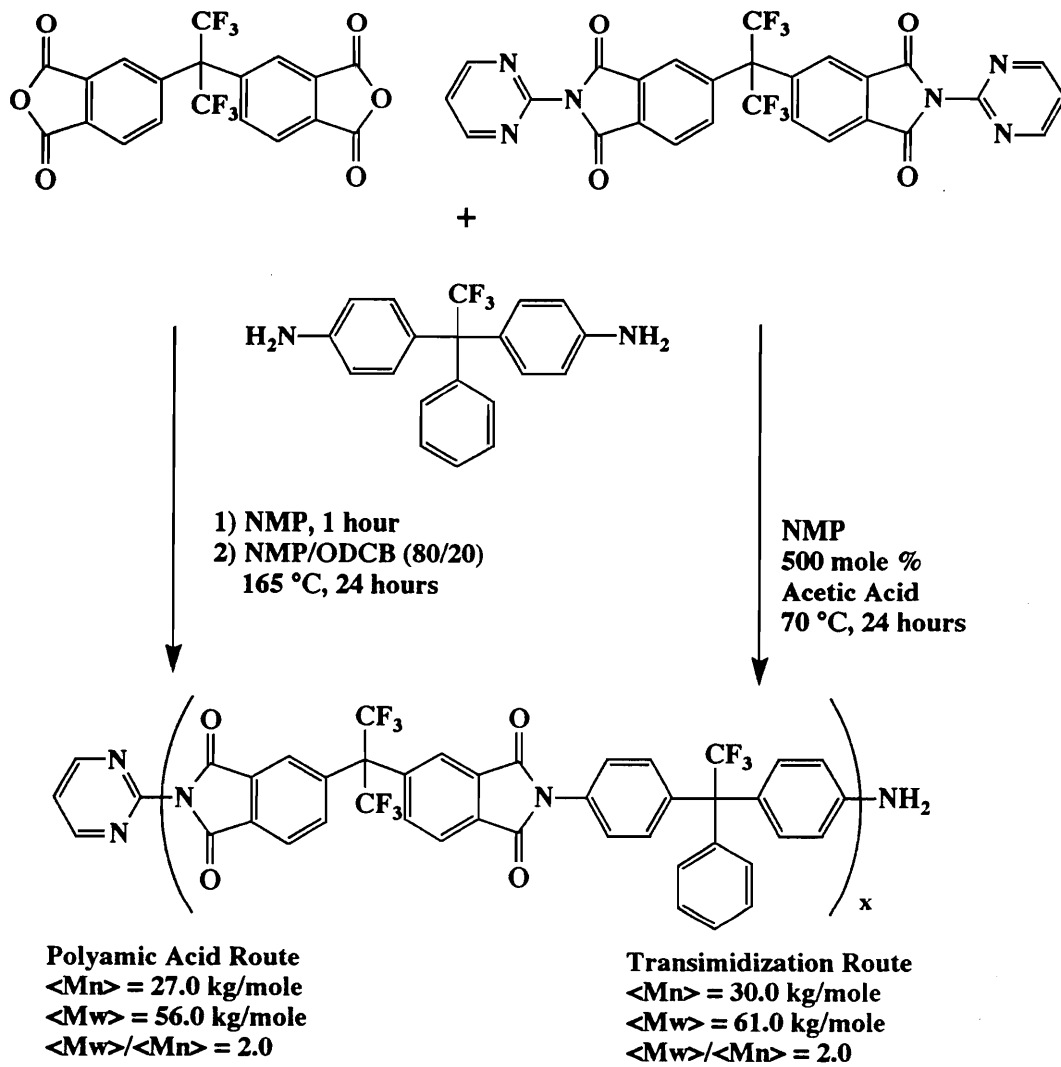
Figure 4.6.8 - A Comparison of 6FDA-3FDAM Polyimides Synthesized by the Transimidization Route and by the Polyamic acid Route

4.7 PERFECTLY ALTERNATING SEGMENTED POLYIMIDE SILOXANE COPOLYMERS MADE FROM N-(2-PYRIMIDYL)PHTHALIMIDE TERMINATED POLYIMIDES

4.7.1 Oligomer Synthesis

The precursor polyimide and poly(dimethyl siloxane) oligomers must first be synthesized to prepare perfectly alternating segmented polyimide siloxane copolymers. The aminopropyl terminated poly(dimethyl siloxane)s were made by the base catalyzed equilibration of cyclic siloxanes as previously reported (134). Aminopropyl terminated poly(dimethyl siloxane)s with <Mn>'s of 1.09, 2.55, 4.5 and 9.3 kg/mole, as determined by potentiometric titration, were used in the copolymer synthesis.

The synthesis of N-(2-pyrimidyl)phthalimide terminated polyimide oligomers was first tried with the solution imidization method used in the synthesis of N-pyridyl phthalimide terminated polyimide oligomers. In an attempt to make 6FDA-Bis P-2APm, 2-aminopyrimidine was added to 6FDA dissolved in NMP. After 15 to 20 minutes, bisaniline P was added. The poly(amic acid) stirred for 24 hours at room temperature before being solution imidized in an 80:20 mixture of NMP:ODCB for 24 hours at 165 °C. The target <Mn> of the 6FDA-Bis P-2APm polyimide was 6.0 kg/mole, but the <Mn> determined by [1]H n.m.r. was 12.0 kg/mole. The 2-aminopyrimidine was not successfully incorporated in the 6FDA-Bis P polyimide oligomer using this technique.

Several experiments were then carried out to determine the reactivity of 2-aminopyrimidine towards the 6F dianhydride. First, 6FDA and 2-aminopyrimidine were mixed in NMP at a 2 to 1 ratio, respectively, and the concentration investigated was 10 weight % solids. After stirring for 3.5 hours at room temperature, the [1]H n.m.r. spectra of the mixture indicated that no reaction had taken place between the 6FDA and 2-aminopyrimidine. After 48 hours, some of the 2-aminopyrimidine had reacted to form an amide acid but not quantitatively. A NMP solution of 6FDA and 2-aminopyrimidine at

the same composition as above was heated to 165 °C. As determined by ^{1}H n.m.r., it took 3 to 6 hours for the 2-aminopyrimidine to completely react with the 6FDA.

Another experiment was carried out where just 2-aminopyrimidine was heated in an 80:20 mixture of NMP:ODCB under a nitrogen purge. These are the same conditions used in the solution imidization method. The ODCB that collected in the reverse Dean Stark trap was investigated by ^{1}H n.m.r. Within 8 hours, 2-aminopyrimidine was observed in the ODCB obtained from the trap. Under the solution imidization conditions, 2-aminopyrimidine was removed from the reaction flask by ODCB.

The low reactivity of the 2-aminopyrimidine was preventing its quantitative incorporation into the 6FDA-Bis P poly(amic acid). It was also slow to react during the solution imidization step. When the poly(amic acid) was solution imidized, some of the 2-aminopyrimidine was removed from the reaction mixture by the refluxing ODCB. Removing the 2-aminopyrimidine from the reaction flask prevented quantitative incorporation into the 6FDA-Bis P polyimide.

The N-(2-pyrimidyl)phthalimide terminated polyimide oligomers were made by a slight modification of the one pot solution imidization route. The procedure used to make N-(2-pyrimidyl)phthalimide terminated polyimide oligomers is shown in Figure 4.7.1. A stoichiometric excess of the dianhydride was added to the diamine in NMP. The solution was stirred for only one hour before a dehydrating agent, o-dichlorobenzene was added, and the reaction was heated to 175°C. Imidization took place, and an anhydride terminated polyimide was formed. After stirring the solution for 12 hours, a large excess of the 2-aminopyrimidine was added to ensure quantitative endcapping. The reaction was stirred at 175°C for an additional 12 hours. The oligomer was then isolated by precipitating the reaction solution in methanol.
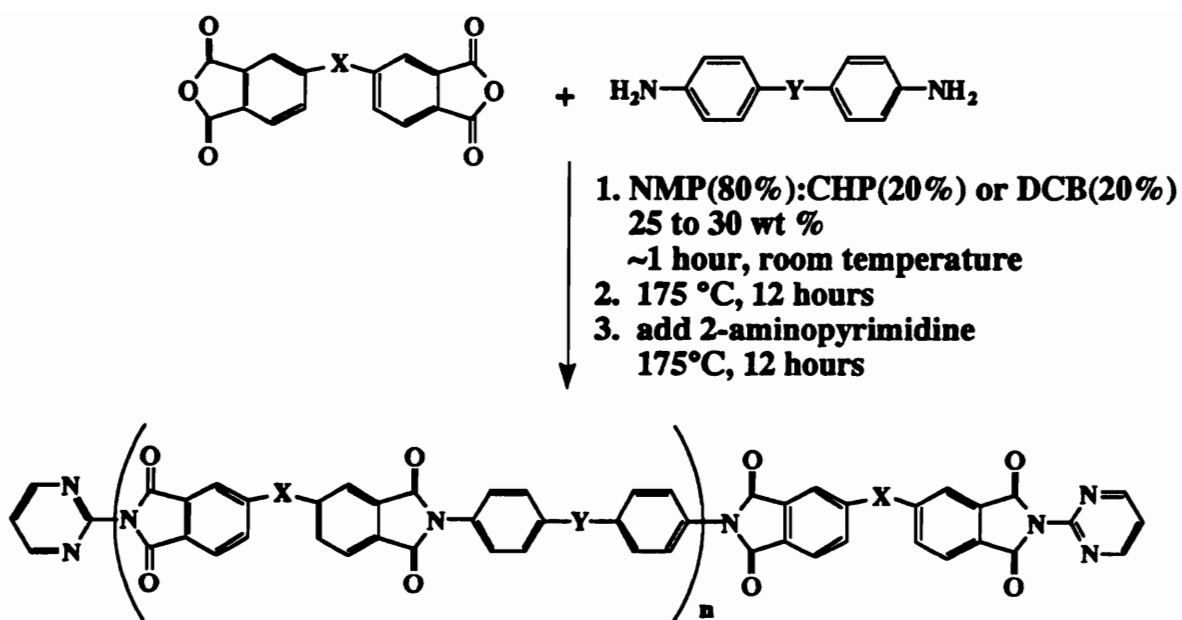
Figure 4.7.1 - Synthesis of N-(2-pyrimidyl)phthalimide
Terminated Polyimide Oligomers

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FTIR analysis, Figure 4.7.2, showed that the polyimide oligomers were fully

cyclized with characteristic imide peaks appearing at 1780 cm^{-1}, 1735 cm^{-1}, 1370 cm^{-1}

and 730 cm^{-1}. The ^{1}H n.m.r. spectrum of an 6FDA-Bis P-2APm polyimide is depicted

in Figure 4.7.3. ^{1}H n.m.r. was used to determine the number average molecular weight

of the polyimide oligomers by determining the ratio of integral values of the 2APm

endgroup proton peak at 8.9 ppm to that of other peaks associated with aromatic protons

in the polyimide backbone. Since the integral value of the endgroup proton peaks was so

small some inaccuracy was expected, but a reasonable estimate of the <Mn> was

achieved. The various polyimide oligomers used in the synthesis of the perfectly

alternating segmented polyimide siloxane copolymers are listed in Table 4.7.1.

4.7.2 Synthesis of the Perfectly Alternating Segmented Polyimide Siloxane Copolymers

Perfectly alternating segmented polyimide siloxane copolymers were made by

combining the N-(2-pyrimidyl)phthalimide terminated polyimide oligomers with

aminopropyl terminated poly(dimethyl siloxane) (PSX). The reaction conditions were

predominantly determined by the solubility of the starting oligomers. In order for the

polymerization to proceed to high conversion, the solution had to be homogeneous.

Therefore, a reaction solvent was used that dissolved both the polyimide and polysiloxane

oligomers. Chlorobenzene was often used as the polymerization solvent since it dissolves

most of the oligomers and was preferable for film casting. The high molecular weight

ODPA-Bis P-2APm polyimide oligomer, <Mn> = 11.0 kg/mole, was not very soluble in

chlorobenzene. It was first dissolved in chloroform before chlorobenzene was added to

maintain a homogeneous solution. The ODPA-mDDS-PSX polyimide siloxane

copolymer was made in a chlorobenzene:NMP solution to maintain homogeneity.

The synthesis of the perfectly alternating segmented polyimide siloxane copolymers

is shown in Figure 4.7.4. The polyimide oligomers were first dissolved in the
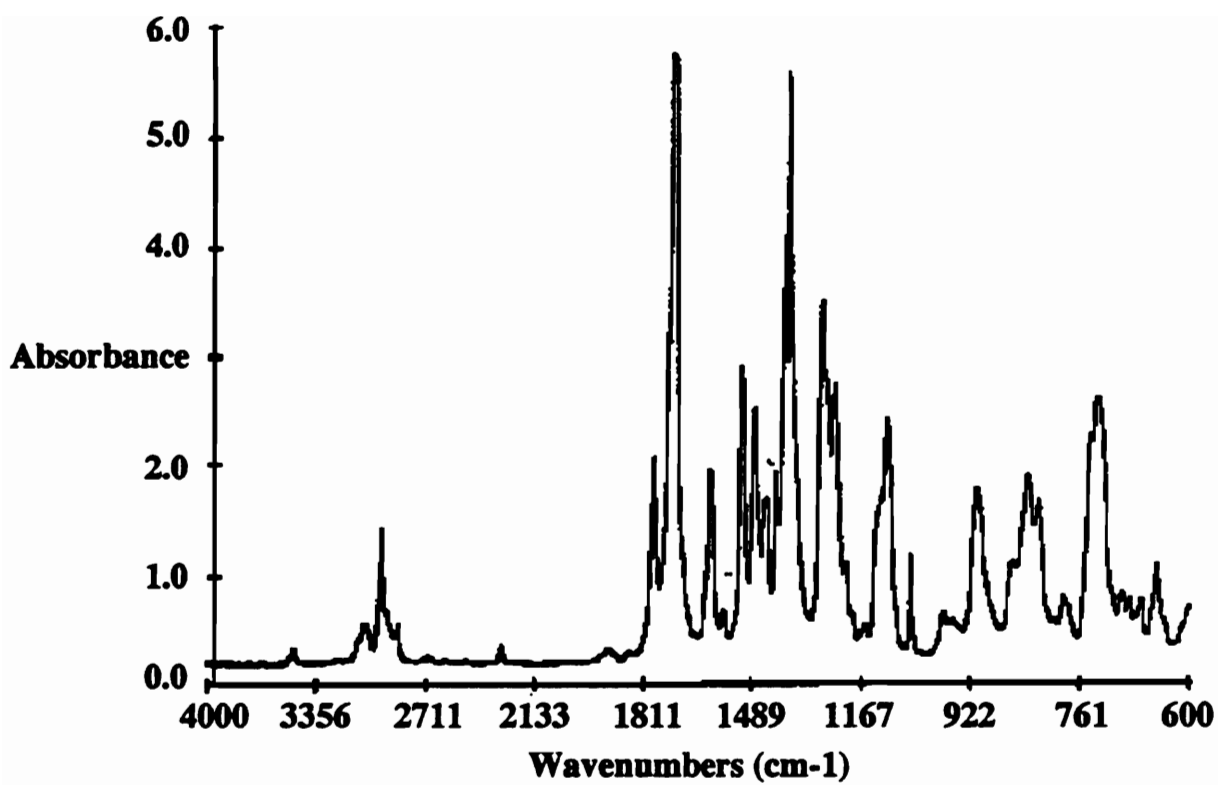
Figure 4.7.2 - FTIR Spectrum of an ODPA-Bis P-2APm Polyimide Oligomer

CF₃ → CF_3

CF_3

CF_3

CF_3

methyl
protons

Aromatic
Protons

2APm
Protons

TMS

6.31

89.73

103.57

87.87

1.18

9   8   7   6   5   4   3   2   1   ppm
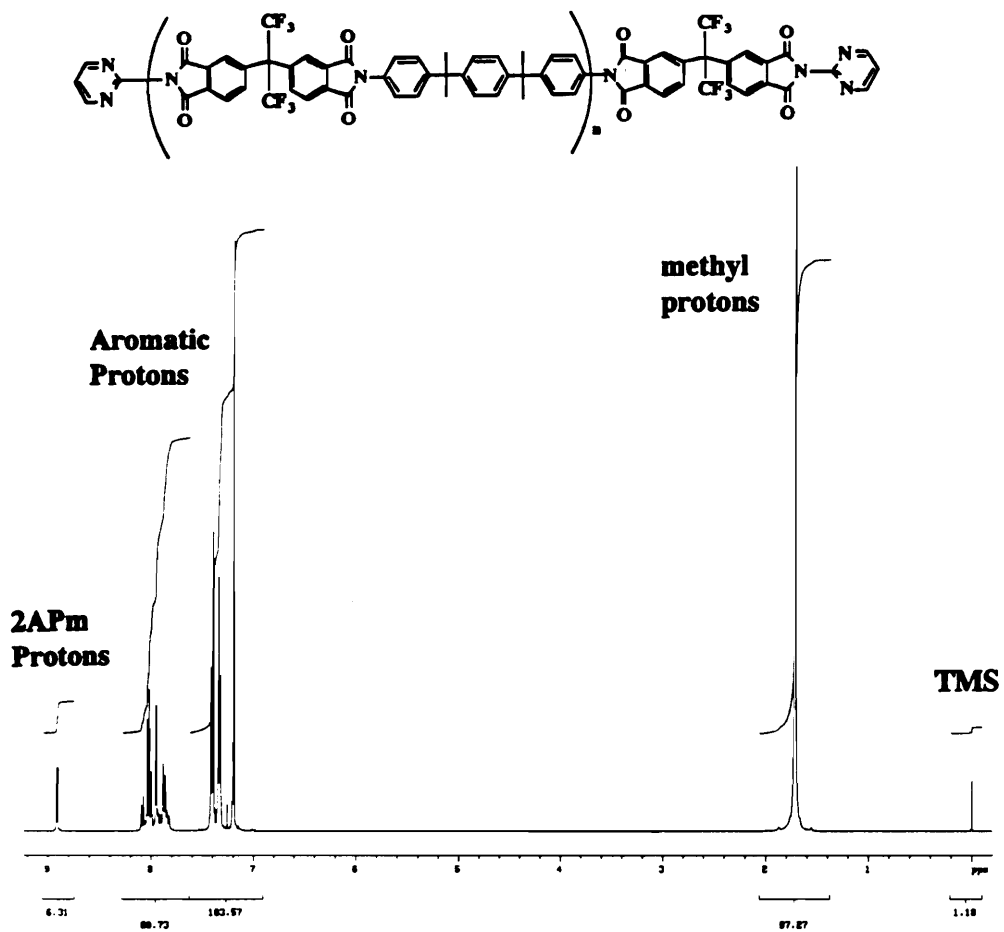
Figure 4.7.3 - ^{1}H n.m.r. Spectrum of an 6FDA-Bis P-2APm Polyimide Oligomer
with a <Mn> of 4.6 kg/mole

Table 4.7.1 - Characterization of Polyimide Oligomers

Polyimide	Target <Mn> kg/mole	<Mn> by ^{1}H n.m.r. kg/mole	$[\eta]$ CHCl$_3$, 25°C dl/g
ODPA-Bis P-2APm	4.0	4.1	0.14
ODPA-Bis P-2APm	8.0	11.0	0.34
6FDA-Bis P-2APm	4.0	4.6	0.13
ODPA-mDDS-2APm	4.0	4.3	0.15 in NMP
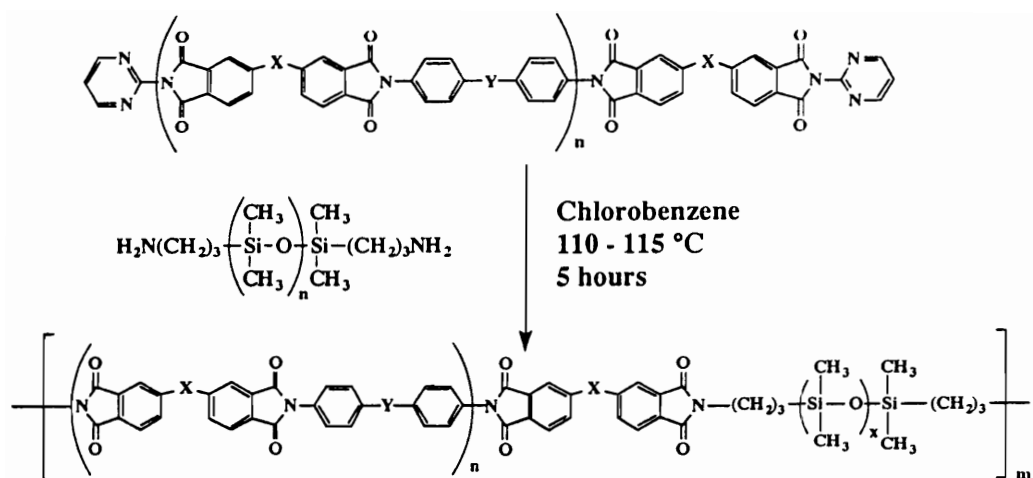
Figure 4.7.4 - Synthesis of Perfectly Alternating Segmented
Polyimide Siloxane Copolymers

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polymerization solvent as the reaction was heated to temperature. The poly(dimethyl siloxane) was then added slowly and the reaction was allowed to stir for 2 to 5 hours. The copolymer solution was then cooled and cast as a film on a glass plate. The films were dried at 220°C to 250°C to remove the solvent.

The aminopropyl endgroup of the poly(dimethyl siloxane) reacted selectively with the N-(2-pyrimidyl)phthalimide endgroup of the polyimide oligomers. After combining ODPA-Bis P-2APm and PSX in deuterated chloroform at 60 °C, the reaction mixture was examined directly by solution n.m.r. The [1]H n.m.r. of the reaction mixture in Figure 4.7.5 showed no evidence of imide-amine interchange taking place within the polyimide oligomer chain. Thus, the reaction of an N-(2-pyrimidyl)phthalimide terminated polyimide oligomer and an aminopropyl terminated poly(dimethyl siloxane) gave a perfectly alternating segmented polyimide siloxane copolymer with well defined polyimide and polysiloxane blocks.

Table 4.7.2 lists the intrinsic viscosities of the various perfectly alternating polyimide siloxane copolymers. All of the intrinsic viscosities were relatively high, indicating that high molecular weight was achieved in the copolymerization reaction.

[1]H n.m.r was used to determined the amount of PSX incorporated into the copolymer. The solution [1]H n.m.r. spectra of 6FDA-Bis P4.6-PSX1.09 is pictured in Figure 4.7.6. The polyimide siloxane copolymer was dissolved in $CDCl_3$ at concentrations of 5 g/dl. In order to obtain accurate n.m.r. measurements, the $CDCl_3$ was dried with molecular sieves prior to use. Incorporation of the poly(dimethyl siloxane) into the copolymer was nearly quantitative. Some of the polyimide siloxane copolymers were analyzed by solid state n.m.r. to determine the amount of siloxane incorporated in the polymer. The values determined by solid state n.m.r. agreed well the values determined by solution n.m.r.
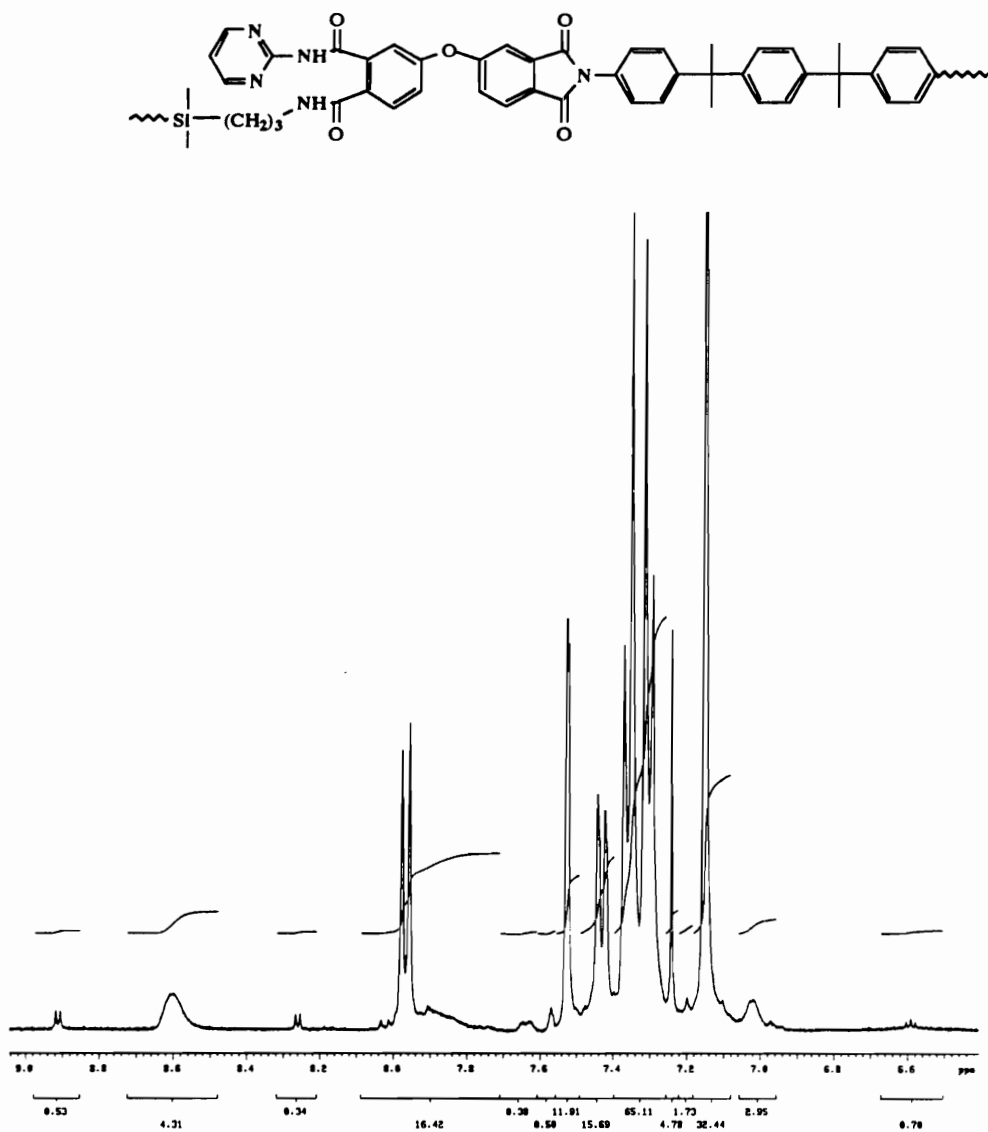
Figure 4.7.5 - ^{1}H n.m.r. of Polyimide Siloxane Reaction Mixture in CDCl$_3$ at 60 °C

Table 4.7.2 - Analysis of Perfectly Alternating Polyimide Siloxane Copolymers

Polyimide Oligomer <Mn> kg/mole	PSX <Mn> kg/mole	Target Weight % PSX	Weight % PSX by ^{1}H n.m.r. solution	Weight % PSX by Solid State n.m.r.	[η] CHCl$_3$ dl/g
ODPA-Bis P 4.1	1.09	21	20	22	0.62
ODPA-Bis P 4.1	2.55	37	35	---	1.08
ODPA-Bis P 4.1	4.5	52	48	40	0.41
ODPA-Bis P 11.0	1.09	9	9	---	1.07
ODPA-Bis P 11.0	2.55	18	17	---	1.03
ODPA-Bis P 11.0	4.5	28	26	27	1.16
6FDA-Bis P 4.6	1.09	19	17	---	0.56
6FDA-Bis P 4.6	2.55	35	32	---	0.60
6FDA-Bis P 4.6	9.3	65	58	---	0.53
ODPA-mDDS 4.3	1.09	20	–	---	0.95
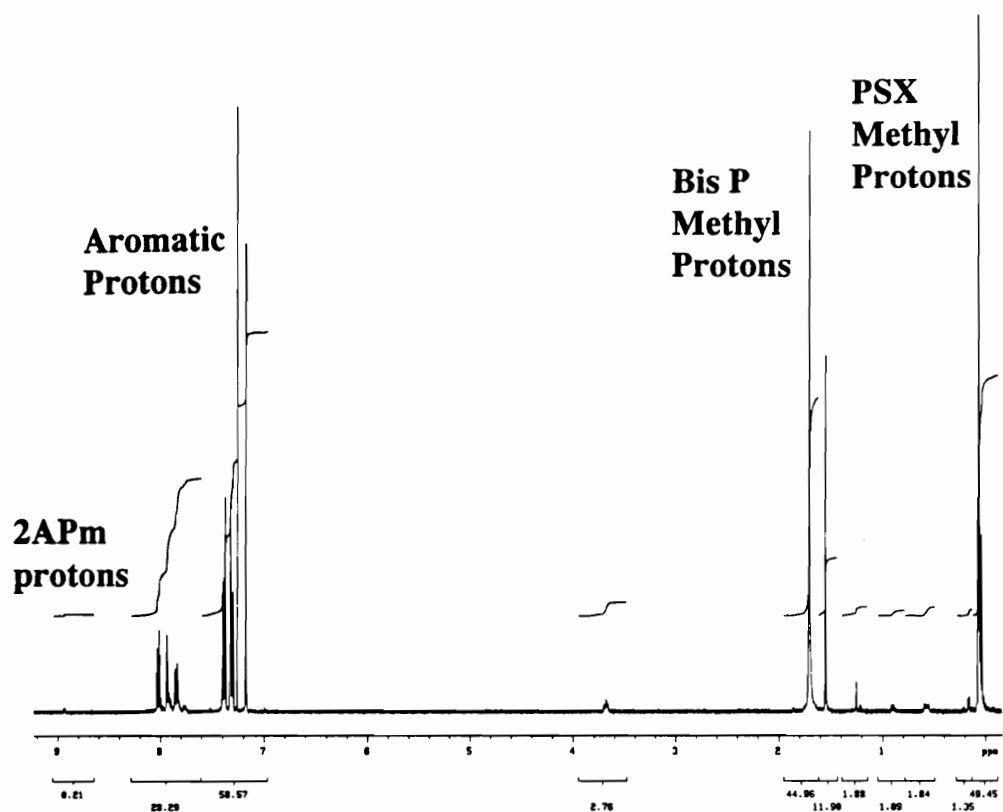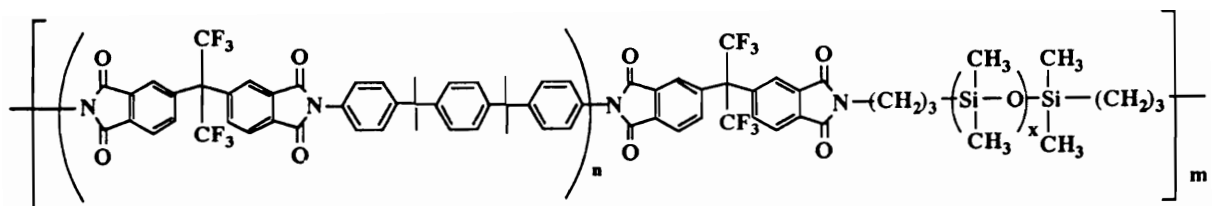
Figure 4.7.6 - ^{1}H n.m.r. Spectrum of an 6FDA-Bis P4.6-PSX1.09
Polyimide Siloxane Copolymer

All of the copolymers formed tough flexible films. Most of the films were clear and yellow in color. Some of the films, including the ODPA-Bis P-PA polyimide homopolymer film, were hazy. The haziness probably resulted from voids that form while the films are drying. As the film is drying, the concentration of the polymer in the solvent increased. Sometimes the polymers at these high concentrations phase separated from the solvent. The solvent was then removed to leave voids which caused the films to appear hazy. The haziness was not a result of unincorporated poly(dimethyl siloxane) since all of the copolymer reactions went to high conversions and were high molecular weight. Furthermore, all of the copolymers formed clear solutions in chlorobenzene and chloroform at 10 to 15 weight % solids.

4.7.3 Thermal Properties

Since a variety of perfectly alternating polyimide siloxane copolymers were made, the effect of oligomer size and chemical composition on the glass transition temperatures and thermal stability was determined. The polyimide siloxane copolymers were examined by DSC, DMA and TGA.

Incompatibility of the polyimide and polysiloxane segments resulted in the microphase separation of the copolymers. Dynamic mechanical analysis of the polyimide siloxane copolymers revealed two transitions corresponding to the lower glass transition of the poly(dimethyl siloxane) rich phase and an upper glass transition temperature for the polyimide rich phase. Table 4.7.3 shows the glass transition temperature values as determined by DSC and DMA for the ODPA-Bis P-PSX copolymers.

Figure 4.7.7 shows the storage-temperature curves and the tan δ-temperature curves determined by dynamic mechanical analysis of two perfectly alternating segmented polyimide siloxane copolymers. The copolymers had the same 4.1 kg/mole ODPA-Bis P polyimide segment, but each had a poly(dimethyl siloxane) segment of different

Table 4.7.3 - Glass Transition Temperatures of Perfectly Alternating Segmented Polyimide Siloxane Copolymers

Polyimide Oligomer <Mn> kg/mole	PSX <Mn> kg/mole	Weight % PSX by ^{1}H n.m.r.	Upper Tg by DSC °C	Upper Tg by DMA °C	Lower Tg by DMA °C
ODPA-Bis P-2APm 4.1	---	0	216	---	---
ODPA-Bis P 4.1	1.09	21	190	203	-123
ODPA-Bis P 4.1	2.55	37	203	212	-127
ODPA-Bis P 4.1	4.5	52	---	195	-122
ODPA-Bis P-2APm 11.0	---	0	241	---	---
ODPA-Bis P 11.0	1.09	9	233	248	-109
ODPA-Bis P 11.0	2.55	18	238	249	-131
ODPA-Bis P 11.0	4.5	28	242	253	-126
ODPA-Bis P-PA 40.0	---	---	267	---	---
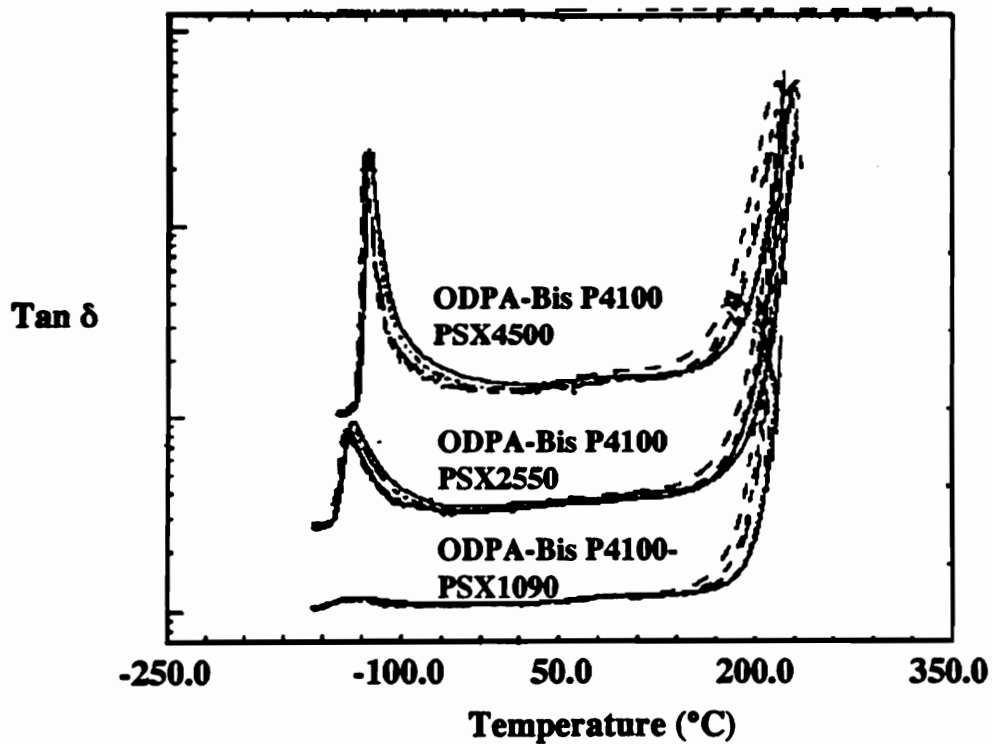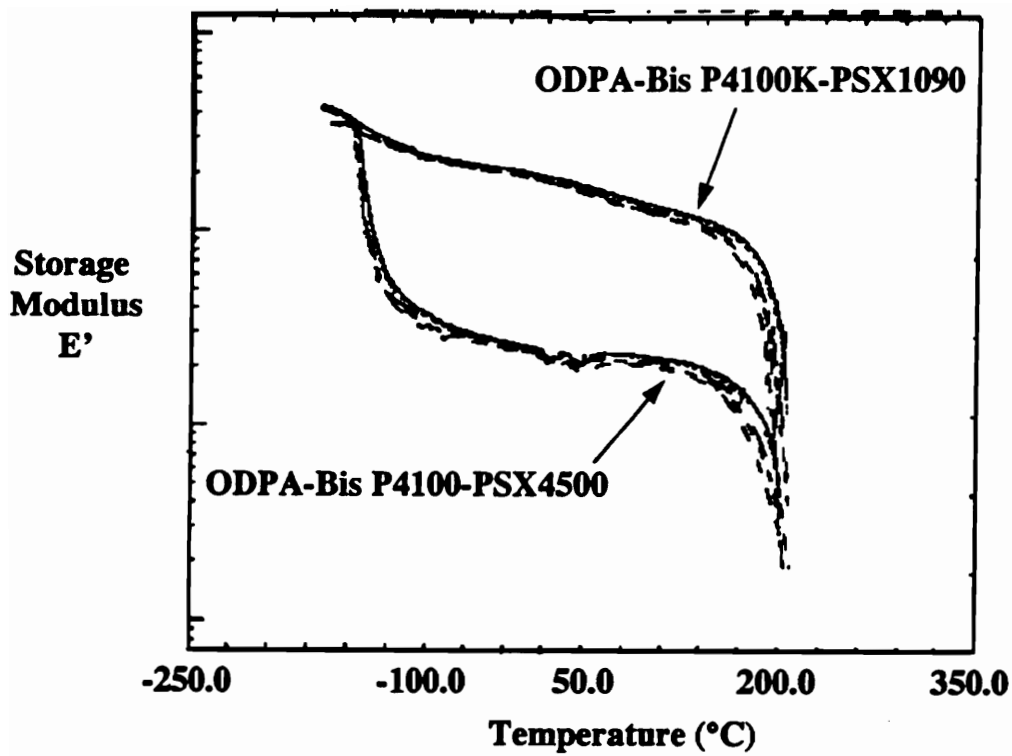
Figure 4.7.7 - DMA of ODPA-Bis P4.1-PSX Polyimide Siloxane Copolymers
(Heating rate - 10 °C/minute)

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molecular weight. The Tg's were signified by a change in the storage modulus or by peaks in the tan δ-temperature curves. The Tg of the PSX segments was ~-125°C and varied little with PSX molecular weight. However, the drop in the storage modulus at the Tg of the PSX segment increased with higher molecular weight PSX blocks. For the ODPA-Bis P4.1-PSX4.5 copolymer, the storage modulus decreased over an order of magnitude after passing through the Tg of the PSX phase. The magnitude of the tan δ peak also increased with increasing PSX block length. The change in the storage modulus and the presence of a tan δ peak at the higher temperatures was due to the Tg of the polyimide phase. The Tg of the polyimide phase occurred near 200 °C for both copolymers.

The storage modulus and tan δ-temperature curves depicted in Figure 4.7.8 were taken from the DMA traces of ODPA-Bis P11-PSX perfectly alternating segmented polyimide siloxane copolymers. The higher molecular weight of the polyimide segment gave copolymers with higher upper Tg's. In the ODPA-Bis P11-PSX copolymers, increasing the molecular weight of the PSX segment had little impact on the upper or lower Tg's. The magnitude of the storage modulus drop and Tan δ peak for the Tg of the polysiloxane segment increased with increasing PSX molecular weight as it did with the ODPA-Bis P4.1-PSX copolymers.

Figure 4.7.9 showed the storage modulus and Tan δ-temperature plots for an ODPA-Bis P11-PSX2.55 and an ODPA-Bis P4.1-PSX1.09 polyimide siloxane copolymer. These two copolymers had different polyimide and polysiloxane block sizes, but they both contained ~ 20 weight % siloxanes. The lower Tg's, as well as the magnitude of the storage modulus drops and the Tan δ peaks at the lower Tg, were similar for both copolymers. However, the upper Tg of the ODPA-Bis P4.1-PSX1.09 was much lower than the upper Tg of the ODPA-Bis P11PSX2.55 which has the higher molecular weight polyimide segment.

Storage Modulus E'

ODPA-Bis P11,000-PSX1090

ODPA-Bis P11,000-PSX2550

Temperature (°C)

Tan δ

ODPA-Bis P11,000-PSX2550

ODPA-Bis P11,000-PSX1090

Temperature (°C)
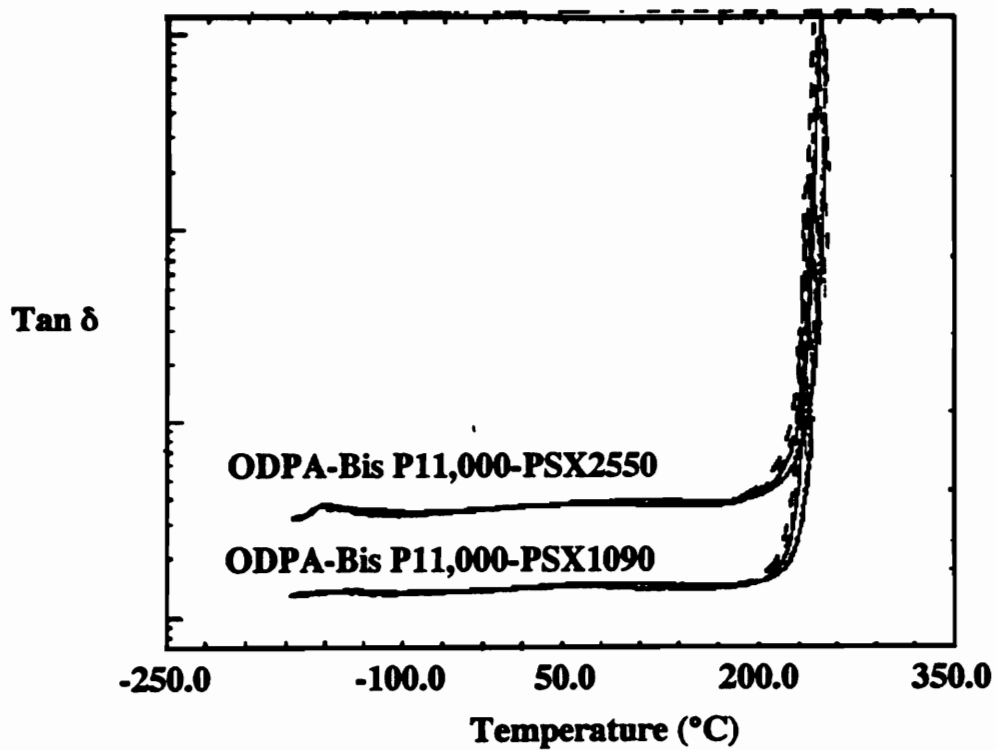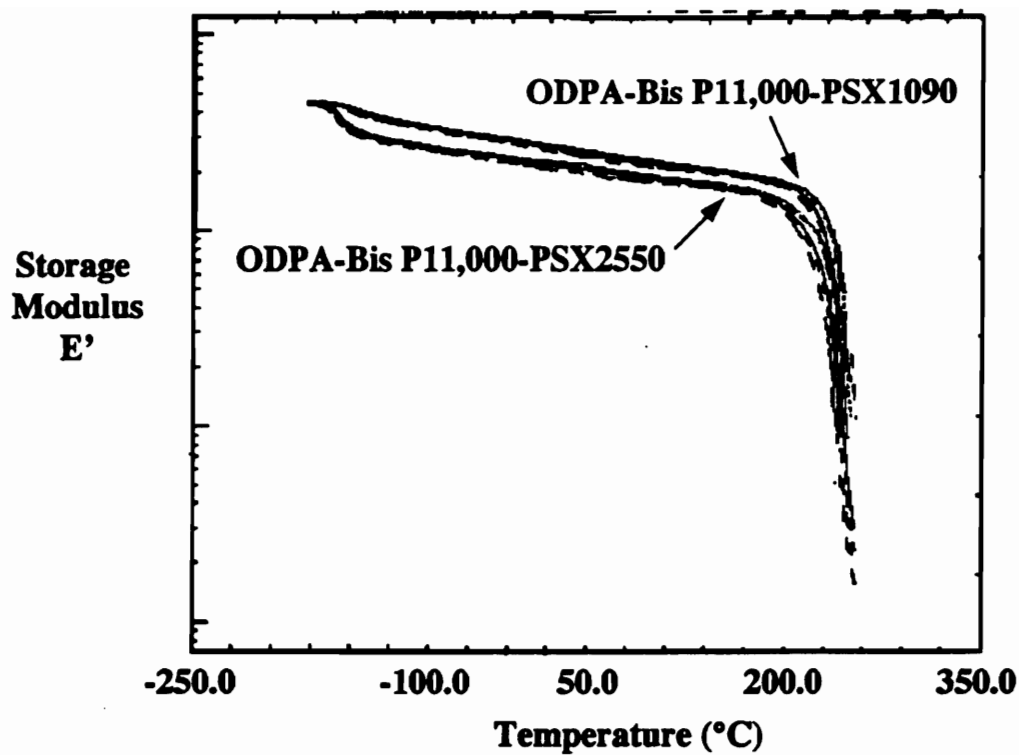
Figure 4.7.8 - DMA of ODPA-Bis P11.0-PSX Polyimide Siloxane Copolymers
(Heating rate - 10 °C/minute)

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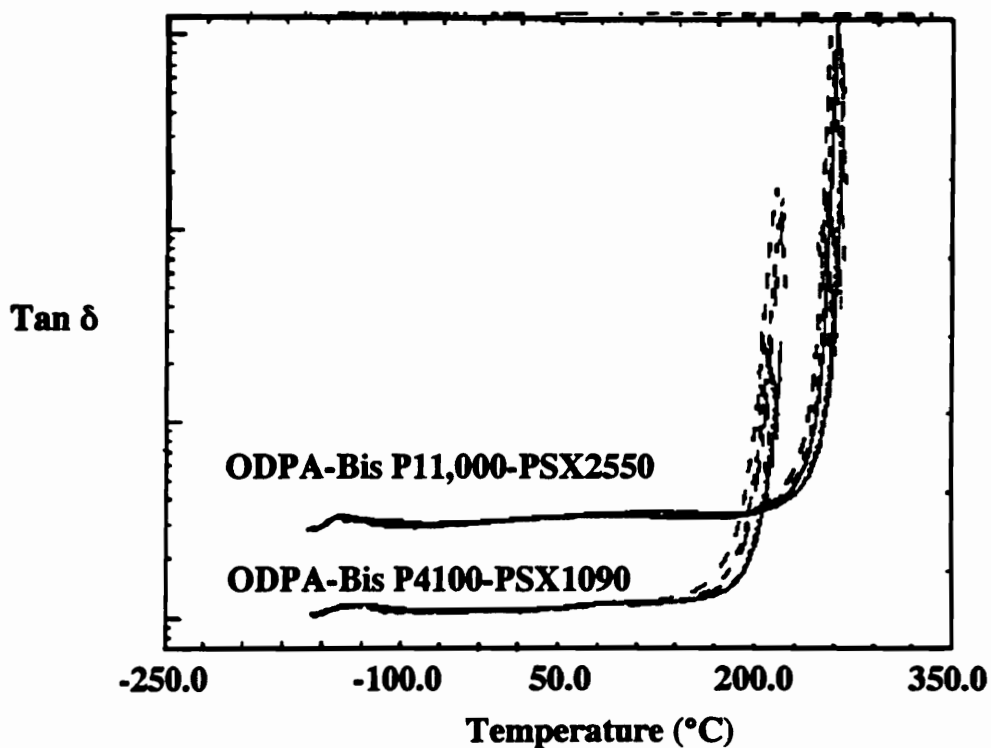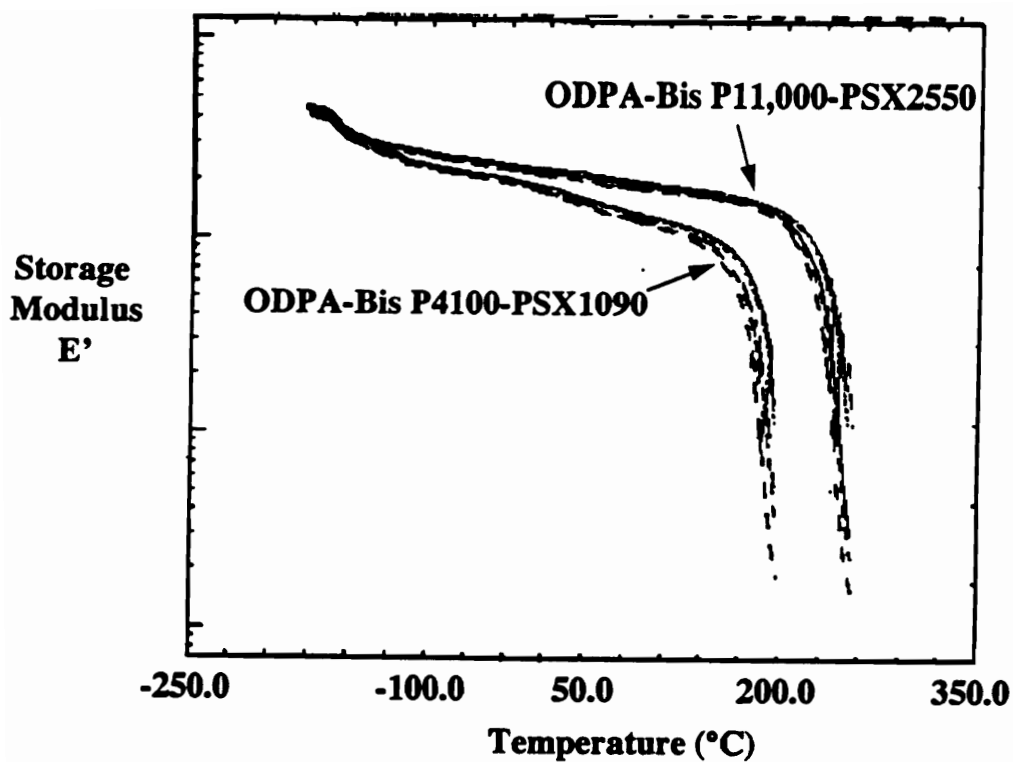
Figure 4.7.9 - DMA of ODPA-Bis P11.0-PSX2.55 and ODPA-Bis P4.1-PSX1.09
Polyimide Siloxane Copolymers (Heating rate - 10 °C/minute)

The DMA results show that the lower Tg of the PSX phase was not greatly effected by the block size of the oligomers. However, the storage modulus of the copolymers decreased after passing through the lower Tg, and the magnitude of the storage modulus drop increased with increasing amounts of PSX. The upper Tg was greatly affected by the size of the polyimide segment. The copolymers with the higher molecular weight polyimide segments had higher upper Tg's.

All of the ODPA-Bis P-PSX copolymers showed a small peak at 60 to 70 °C of the tan δ– temperature curves. This small peak was most likely due to secondary relaxations associated with the Bis P portion of the polyimide. The tan δ-temperature curves in Figure 4.7.10 are of three polyimide siloxane copolymers. Two of the copolymers, ODPA-Bis P4.1-PSX1.09 and 6FDA-Bis P4.6-PSX1.09, had Bis P in the polyimide segment and both showed small tan δ peaks at 60 to 70°C. In the ODPA-mDDS4.3-PSX1.09 polyimide siloxane copolymer, the polyimide segment contained mDDS and not Bis P. Consequently, the ODPA-mDDS4.3-PSX1.09 showed no peak in the tan δ curve at 60 to 70 °C. Other aromatic polymers reported in the literature which contain the isopropylidene link as in Bis P demonstrated secondary relaxations (186).

Investigation of the upper glass transition temperature by DSC gave results that were similar to what was observed by DMA. Figure 4.7.11 shows DSC curves for the ODPA-Bis P-2APm oligomer with a <Mn> of 4.1 kg/mole and subsequent perfectly alternating segmented polyimide siloxane copolymers made with that oligomer. The ODPA-Bis P-2APm 4.1 kg/mole oligomer showed a distinct Tg at 216 which was about 50 degrees lower than the Tg of the high molecular weight ODPA-Bis P-PA polyimide. The ODPA-Bis P4.1-PSX copolymers all had Tg's lower than the polyimide oligomer from which they were made. The Tg of the ODPA-Bis P4.1-PSX1.09 copolymer was 190 °C, and the Tg of the ODPA-Bis P4.1-PSX2.55 copolymer was 203 °C. It is well known that as the segment molecular weights of copolymers decrease, the mixing between phases becomes
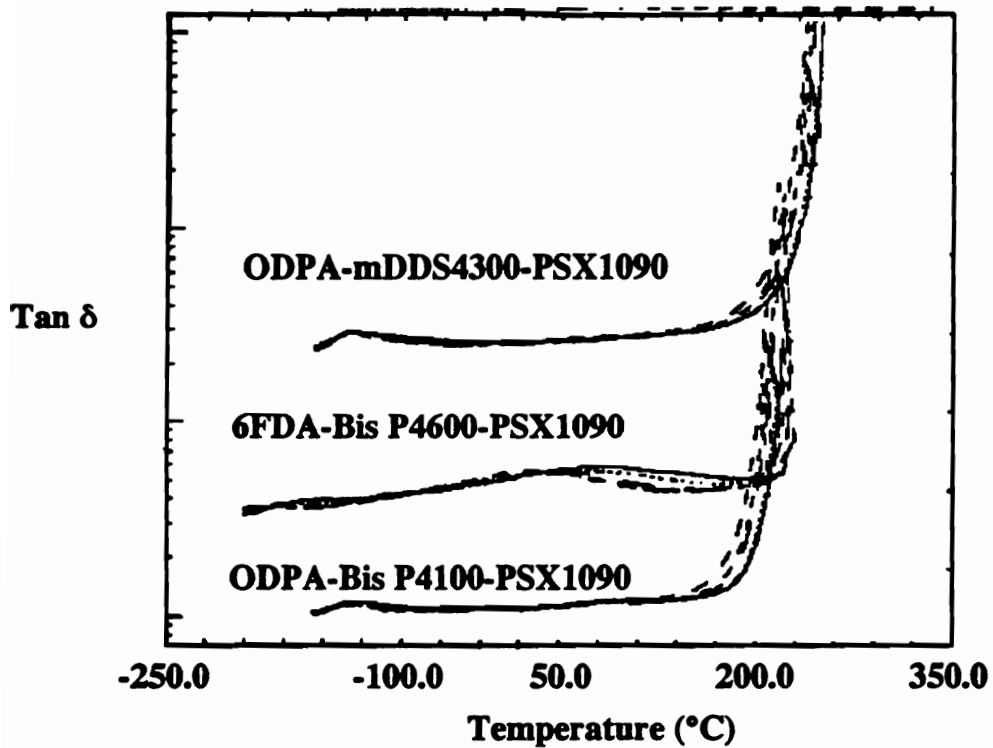
Figure 4.7.10 - Tan δ - Temperature Curves of Polyimide Siloxane Copolymers
(Heating rate - 10 °C/minute)
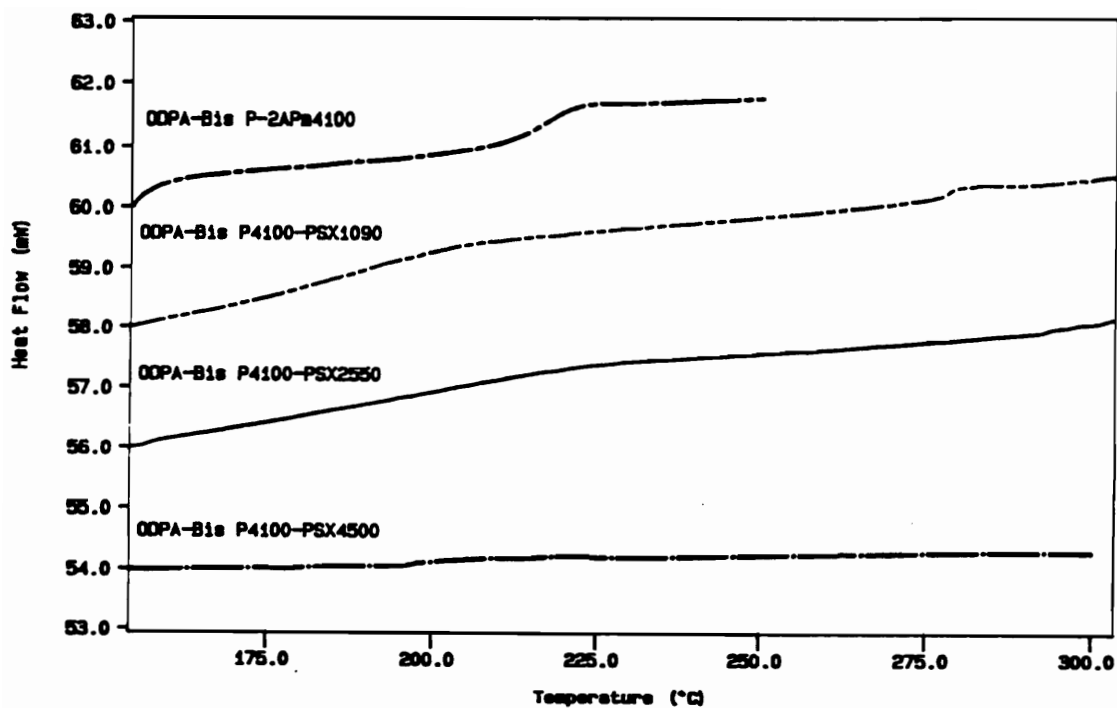
Figure 4.7.11 - DSC of an ODPA-Bis P-2APm Polyimide Oligomer and Subsequent
Polyimide Siloxane Copolymers (Heating rate - 10 °C/minute)

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greater (138). So, the depression of the Tg was probably due to mixing of the polysiloxane into the polyimide phase. The depression of the upper Tg or extent of phase mixing decreased as the molecular weight of the polysiloxane increased. Unfortunately, the Tg of the ODPA-Bis P4.1-PSX4.5 could not be clearly detected in the DSC scan.

The chemical composition of the polyimide phase had an effect on the mixing of the polysiloxane into the polyimide phase. The upper Tg's of the 6FDA-Bis P 4.6-PSX 1.09 and ODPA-Bis P 4.1-PSX 1.09 polyimide siloxane copolymers were much less relative to the Tg of the low molecular weight polyimide oligomers listed in Table 4.7.4. The ODPA-Bis P and 6FDA-Bis P are relatively less polar polyimides. Thus, a significant amount of mixing of the PSX into the polyimide phase occurred. The ODPA-mDDS 4.3-PSX 1.09 polyimide siloxane copolymer had a more polar polyimide component. Consequently, there was no significant difference in the Tg of the ODPA-mDDS-2APm polyimide oligomer and the upper Tg of the ODPA-mDDS4.3-PSX1.09 copolymer. The more polar ODPA-mDDS polyimide segment of the polyimide siloxane copolymer was less compatible with the poly(dimethyl siloxane) segment than the ODPA-Bis P or 6FDA-Bis P segment. The ODPA-mDDS4.3-PSX1.09 polyimide film was cast from NMP which could have also caused greater phase separation as demonstrated by York (143).

There was very little difference between the Tg of the polyimide oligomer and the upper Tg of the corresponding polyimide siloxane copolymers for the polyimide siloxane copolymers made with the high molecular weight polyimide oligomer ($<Mn> = 11.0$ kg/mole). The DSC scans of these polymers are shown in Figure 4.7.12. There was no significant mixing between the PSX phase and the higher molecular weight polyimide phase.

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Table 4.7.4 - Effect of Chemical Composition on the Upper Tg of Perfectly Alternating Segmented Polyimide Siloxane Copolymers

Polyimide Oligomer <Mn> kg/mole	PSX <Mn> kg/mole	Weight % PSX	Upper Tg* by DSC °C
ODPA-Bis P 4.1	---	---	216
ODPA-Bis P 4.1	1.09	21	190
6FDA-Bis P 4.6	---	---	233
6FDA-Bis P 4.6	1.09	19	205
ODPA-mDDS 4.3	---	---	228
ODPA-mDDS 4.3	1.09	20	225

*Measured at a heating rate of 10 °C/minute.
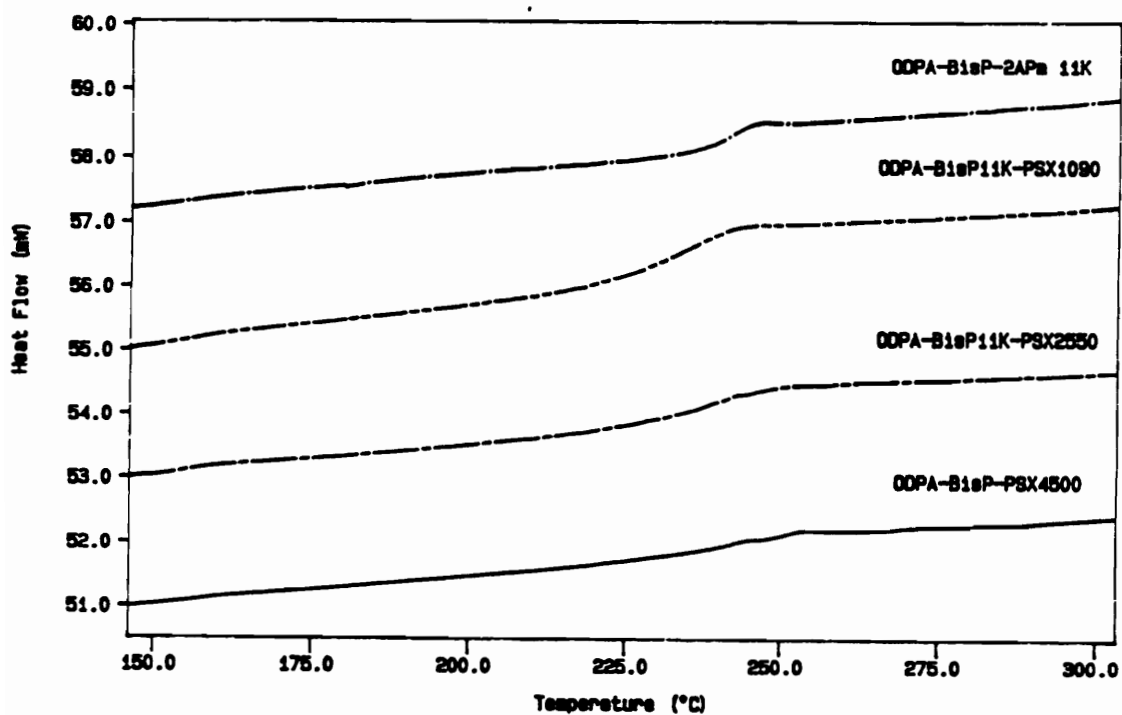
Figure 4.7.12 - DSC of an ODPA-Bis P-2APm Polyimide Oligomer and Subsequent
Polyimide Siloxane Copolymers (Heating rate - 10 °C/minute)

The thermooxidative stability of the copolymers is indicated by the values for 5% weight loss in Table 4.7.5 determined by thermogravimetric analysis. A typical thermogram is shown in Figure 4.7.13. Incorporating the poly(dimethyl siloxane) did decrease the thermooxidative stability of the copolymers relative to that of the corresponding polyimide homopolymer. The decrease in thermooxidative stability was dependent on the amount of poly(dimethyl siloxane) in the copolymer rather than the block lengths. Increasing the weight percent of polydimethylsiloxane in the copolymer decreased the 5% weight loss. The presence of poly(dimethyl siloxane) also resulted in substantial char yields at higher temperatures of 700 to 800 °C.

4.7.4 Mechanical Properties

The results of stress-strain analysis on the polyimide siloxane copolymers are listed in Table 4.7.6. The stress-strain values in Table 4.7.6a were determined from solution cast films dried at or near the Tg to insure that all of the solvent was removed. Incorporation of poly(dimethyl siloxane) reduced the tensile modulus and tensile strength of the copolymers relative to the high molecular weight polyimide homopolymers. The tensile modulus and strength decreased with increasing amounts of poly(dimethyl siloxane) in the copolymers. The different stress-strain values reflected the changing morphology of the copolymers as the amount of poly(dimethyl siloxane) increased. The ODPA-Bis P11.0-PSX1.09 copolymer with 9 weight % PSX had a high modulus and low strain at break. It probably had a morphology in which the PSX phase was dispersed in a continuous polyimide matrix. In contrast, the ODPA-Bis P4.1-PSX4.5 copolymer with 52 weight % PSX had a much lower modulus and a high strain at break. In this copolymer, the PSX existed as a continuous or co-continuos phase with the polyimide and, thus, behaved as a thermoplastic elastomer.

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Table 4.7.5 - Influence of Copolymer Composition on the Thermal Stability of
Perfectly Alternating Polyimide Siloxane Copolymers in Air

Polyimide Oligomer <Mn> kg/mole	PSX <Mn> kg/mole	Weight % PSX	5 % Weight loss by TGA °C	Char Yield 700 °C wt. %
ODPA-Bis P-PA 40,000	---	---	550	9
ODPA-Bis P 4.1	1.09	21	461	16
ODPA-Bis P 4.1	2.55	37	467	37
ODPA-Bis P 4.1	4.5	52	428	11
ODPA-Bis P 11.0	1.09	9	499	11
ODPA-Bis P 11.0	2.55	18	491	20
ODPA-Bis P 11.0	4.5	28	441	20
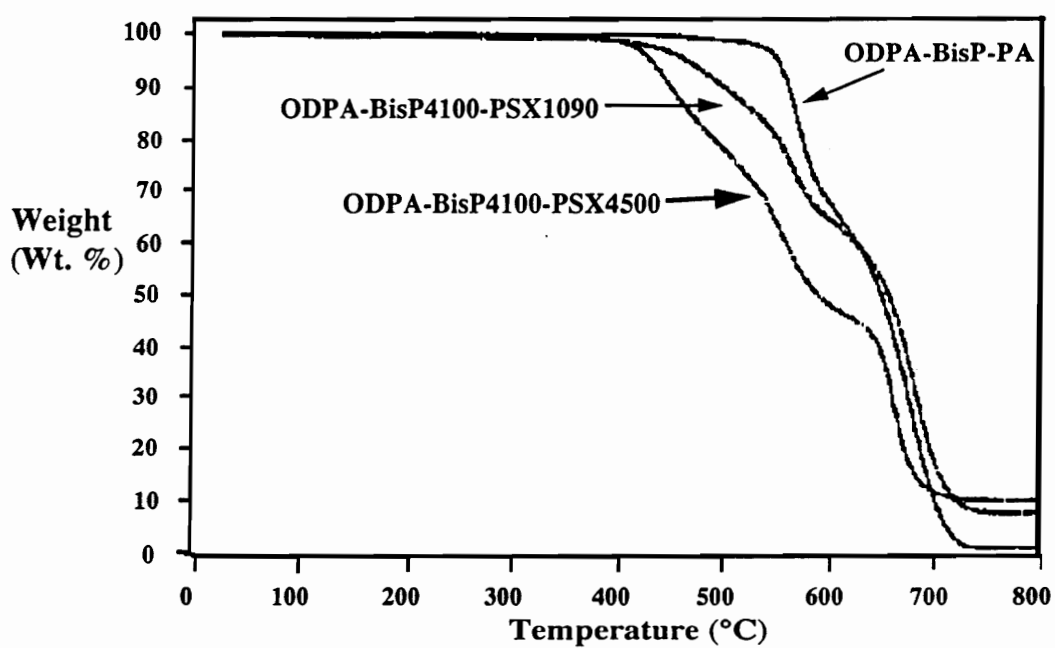
Figure 4.7.13 - Dynamic TGA Thermogram of ODPA-Bis P-PSX
Polyimide Siloxane Copolymers (Air atmosphere; Heating rate - 10 °C/minute)

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Table 4.7.6 - Mechanical Properties of the Perfectly Alternating
Segmented Polyimide Siloxane Copolymers

Table 4.7.6a - Stress-Strain Behavior of Solution Cast Films

Polyimide Oligomer <Mn> kg/mole	PSX <Mn> kg/mole	Wt. % PSX	Tensile Modulus ksi	% Strain at Break	Stress at Break ksi	Stress at Yield ksi
ODPA-Bis P-PA 40.0	---	---				
ODPA-Bis P 4.1	1.09	21	233 ± 11	20 ± 10	8.6 ± 0.4	9.1 ± 0.5
ODPA-Bis P 4.1	2.55	37	99 ± 4	25 ± 3	5.2 ± 0.1	5.0 ± 0.2
ODPA-Bis P 4.1	4.5	52	25 ± 2	41 ± 1	2.3 ± 0.04	----
ODPA-Bis P 11.0	1.09	9	299 ± 12	22 ± 7	12.3 ± 0.3	13.5 ± 0.4
ODPA-Bis P 11.0	2.55	18	218± 13	17 ± 8	9.3 ± 0.5	9.4 ± 0.5
ODPA-mDDS 4.3	1.09	20	239 ± 18	38 ± 4	10.5 ± 0.5	9.6 ± 0.5
6FDA-Bis P 4.6	1.09	19	233 ± 24	12 ± 4	8.0 ± 0.5	8.7 ± 0.4
6FDA- Bis P 4.6	2.55	37	117 ± 2	63 ± 13	5.0 ± 0.1	5.0 ± 0.1
6FDA- Bis P 4.6	9.3	66	0.5 ± 0.4	333 ± 16	0.9 ± 0.08	0.1

Table 4.7.6b - Solution Cast versus Compression Molded Films

Copolymer	Tensile Modulus Solution Cast From Chlorobenzene ksi	Tensile Modulus Compression Molded ksi
ODPA-Bis P4.1-PSX1.09	233 ± 11	222 ± 22
ODPA-Bis P4.1-PSX2.55	99 ± 4	71 ± 5
ODPA-Bis P4.1-PSX4.5	25 ± 2	5 ± 1
ODPA-Bis P11.0-PSX1.09	299 ± 12	303 ± 40
ODPA-Bis P11.0-PSX2.55	218± 13	150 ± 14

Three 6FDA-Bis P-PSX copolymers are compared in Figure 4.7.14. The effect of the amount of PSX and morphology on the tensile properties are dramatically demonstrated. A 6FDA-Bis P4.6-PSX1.09 with 19 weight % PSX had a tensile modulus of 233 ksi and a strain at break of 12 %. The 6FDA-Bis P4.6-PSX9.3 with 66 weight % PSX had a PSX continuous phase morphology. Consequently, this copolymer had a very low modulus of 0.5 ksi but a strain at break of 333 %.

The polymer segment lengths had little effect on the tensile properties. The ODPA-Bis P4.1-PSX1.09 and ODPA-Bis P11.0-PSX2.55 had similar amounts of PSX and also had similar tensile modulus and strength.

The chemical composition of the polyimide segment also had little effect on the tensile properties. The tensile modulus of ODPA-Bis P4.1-PSX1.09, 6FDA-Bis P4.6-PSX1.09 and ODPA-mDDS4.3-PSX1.09 are compared in Figure 4.7.15. They all had a tensile modulus near 235,000 psi and tensile strengths close to 9000 psi.

The effects of processing are demonstrated in the data listed in Table 4.7.6b. Tensile modulus of compression molded films were compared to the tensile modulus of solution cast films. In general, the solution cast films had greater tensile modulus values than analogous compression molded films. This was probably a result of greater orientation that often occurs in solution cast films.
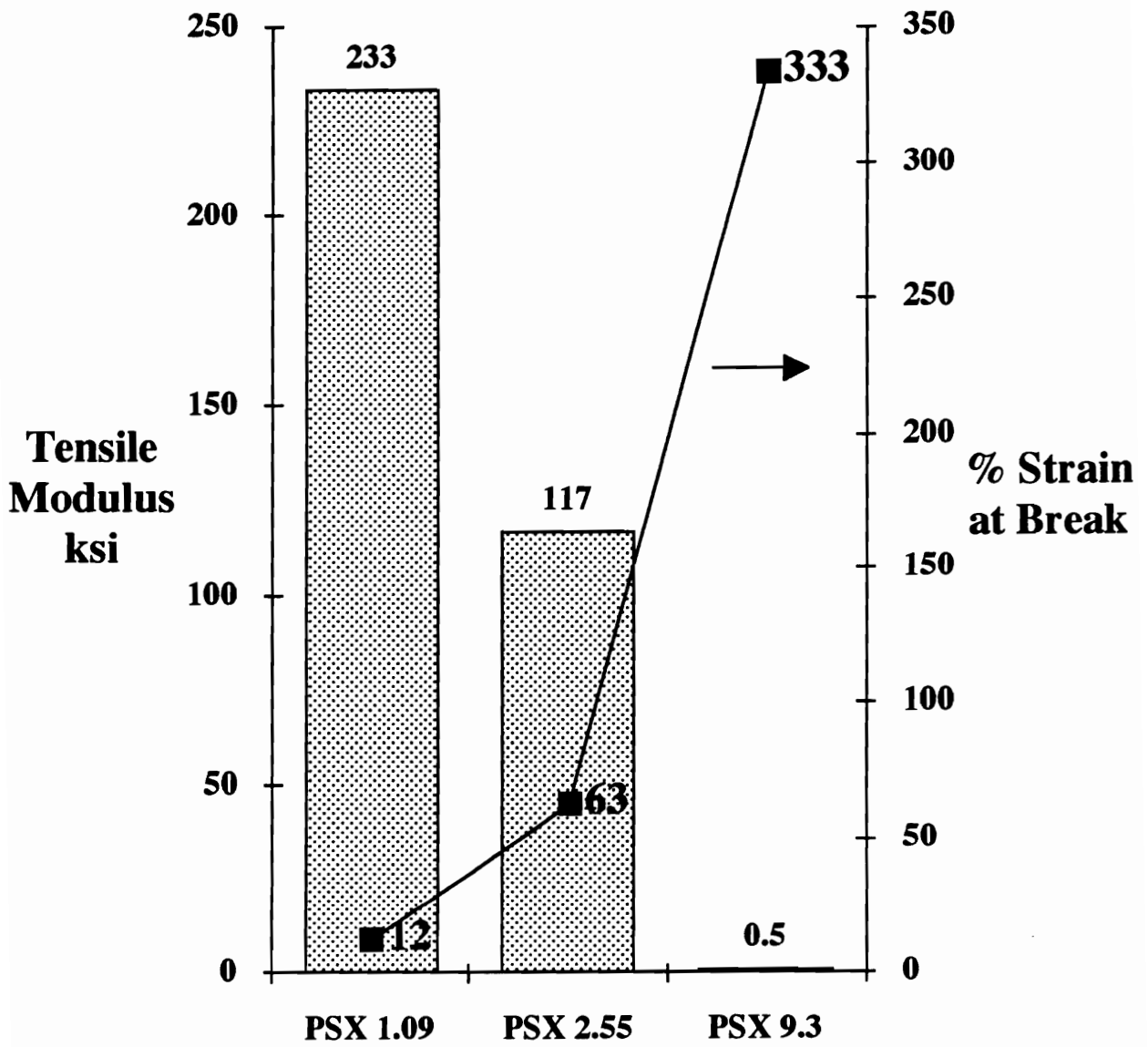
Figure 4.7.14 - Tensile Properties of 6FDA-Bis P-PSX Copolymers
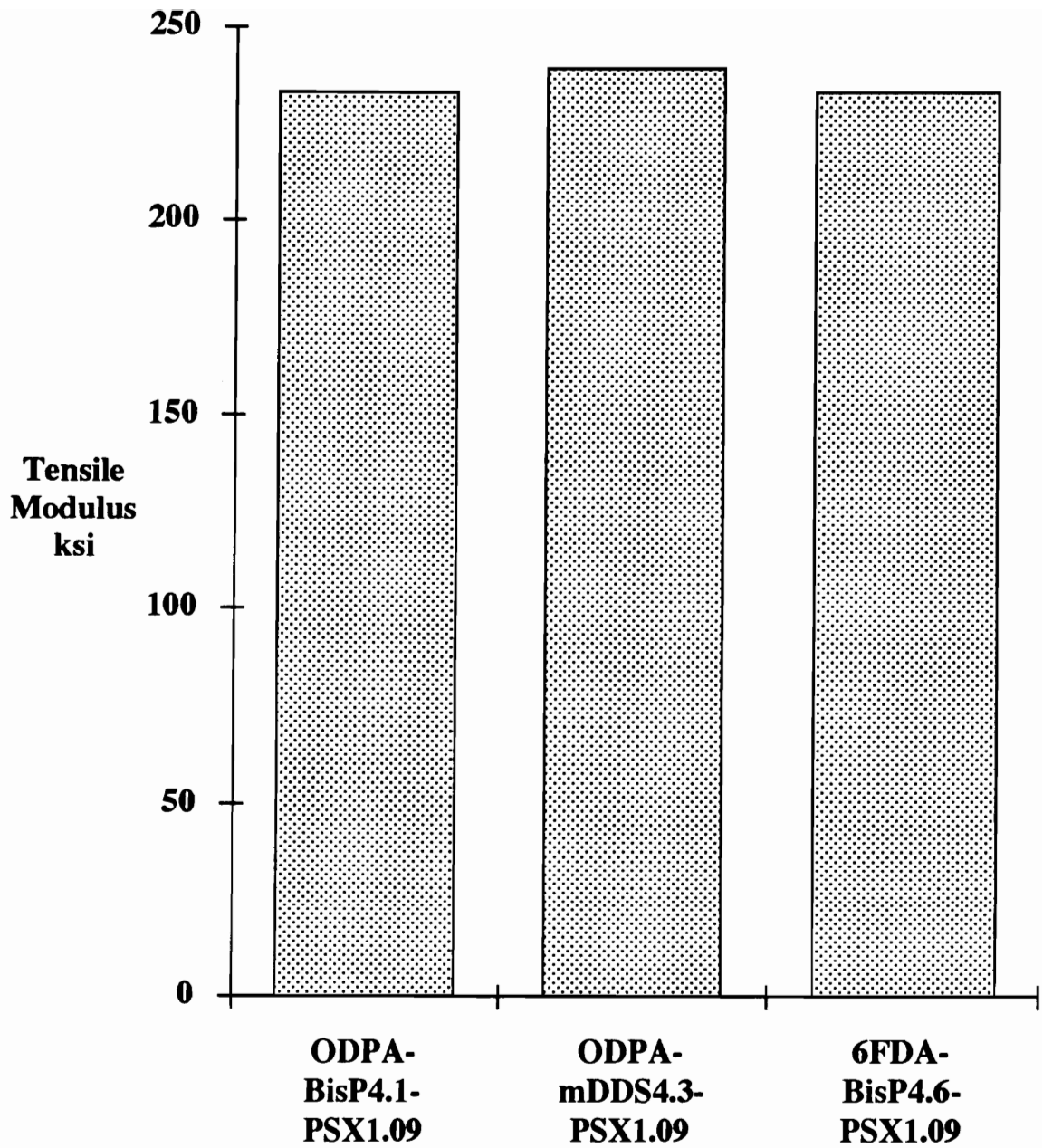
Figure 4.7.15 - Effect of Chemical Composition on Tensile Modulus

4.8 RANDOMLY SEGMENTED POLYIMIDE SILOXANE COPOLYMERS

4.8.1 Synthesis of the Randomly Segmented Polyimide Siloxane Copolymers

Randomly segmented polyimide siloxane copolymers were made from a one step solution imidization route similar to the method used by Wescott, et. al.(14). The randomly segmented polyimide siloxane copolymers do not have well defined polyimide segments since neither the molecular weight nor the molecular weight distribution of the polyimide segment is experimentally known. Thus, it was interesting to compare the thermal and mechanical properties of the randomly segmented polyimide siloxane copolymers to analagous perfectly alternating segmented polyimide siloxane copolymers.

The ODPA-Bis P-PSX randomly segmented polyimide siloxane copolymers were synthesized as shown in Figure 4.8.1. ODPA was dissolved in ODCB with a few milliliters of NMP by heating to 165°C. PSX was then added slowly over a fifteen minute period. The reaction was then allowed to stir for 30 minutes to give an anhydride capped PSX. This insured random incorporation of the PSX into the polyimide siloxane copolymer. Bis P was added and the solution was stirred for another 45 minutes before phthalic anhydride was added. The monomers were rinsed in with ODCB to give a final concentration of 20 weight % solids. The target molecular weight was 40.0 kg/mole. The reaction was stirred at 165 °C for 24 hours. In this time, water was observed collecting in the reverse Dean Stark trap. At the end, the reaction was cooled and then precipitated in methanol. The polymer was dried at 200 °C for 18 hours. Films of the randomly segmented copolymers were cast from chlorobenzene and dried at a final temperature of 220 to 250 °C.

Four ODPA-Bis P-PSX randomly segmented polyimide siloxane copolymers are listed in Table 4.8.1. The intrinsic viscosities of the randomly segmented copolymers were compared to intrinsic viscosities of corresponding perfectly alternating segmented
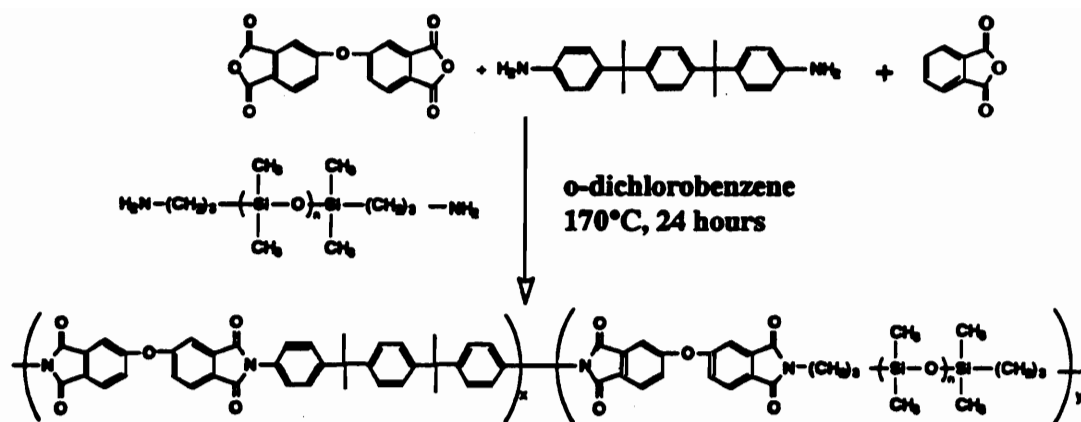
Figure 4.8.1 - Synthesis of Randomly Segmented Polyimide Siloxane Copolymers

Table 4.8.1 - Characterization of Randomly and Perfectly Alternating Segmented Polyimide Siloxane Copolymers

Polyimide Segment \<Mn>, kg/mole	PSX \<Mn> kg/mole	Target Weight % PSX	Weight % PSX by [1]H n.m.r.	$[\eta]$ CHCl$_3$ dl/g
ODPA-Bis P 4.1	1.09	21	20	0.62
ODPA-Bis P random	1.09	21	18	1.02
ODPA-Bis P 4.1	2.55	37	35	1.08
ODPA-Bis P random	2.55	39	33	0.92
ODPA-Bis P 11.0	1.09	9	9	1.07
ODPA-Bis P random	1.09	9	7	0.98
ODPA-Bis P 11.0	2.55	18	17	1.03
ODPA-Bis P random	2.55	19	17	0.98

polyimide siloxane copolymers. All of the copolymers had high viscosities ranging between 0.62 and 1.08 dl/g. Randomly and perfectly alternating segmented polyimide siloxane copolymer with the same weight % PSX had similar intrinsic viscosities and, thus, similar molecular weights. Other properties of the copolymers were compared without considering differences in molecular weight.

Incorporation of the polydimethyl siloxane into the randomly segmented polyimide siloxane copolymers and corresponding perfectly alternating polyimide siloxane copolymers were measured by [1]H n.m.r. The values are listed in Table 4.8.1. Incorporation of the PSX in the random copolymers was nearly quantitative.

4.8.2 Thermal Properties - Comparisons to the Perfectly Alternating Polyimide Siloxane Copolymers

The Tg's of the random and corresponding perfectly alternating polyimide siloxane copolymers are listed in Table 4.8.2. Tg's were determined by both DSC and tan δ peaks in the DMA scans. There was virtually no difference between the Tg's of the randomly segmented polyimide siloxane copolymers and corresponding perfectly alternating polyimide siloxane copolymers with the same weight % PSX. For example, the ODPA-Bis P-21%PSX1.09 randomly segmented polyimide siloxane copolymer had an upper Tg of 198 °C, and the corresponding perfectly alternating polyimide siloxane copolymer, ODPA-Bis P4.1-PSX1.09 had a Tg of 190°C by DSC. The similarities between the DSC scans of the two types of copolymers are seen in Figure 4.8.2 and 4.8.3. The DSC scans of the random and perfectly alternating copolymers with the same weight % PSX nearly matched.

The storage modulus-temperature curves and the tan δ-temperature curves determined by DMA are displayed in Figures 4.8.4 thru 4.8.5. The random and perfectly alternating copolymers with the same weight % PSX are shown in each figure. As can be

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Table 4.8.2 - Thermal Properties of Randomly and Perfectly Alternating
Polyimide Siloxane Copolymers

Polyimide Oligomer <Mn> kg/mole	PSX <Mn> kg/mole	Weight % PSX by ^{1}H n.m.r.	Upper Tg by DSC °C	Upper Tg by DMA °C	Lower Tg by DMA °C
ODPA-Bis P 4.1	1.09	21	190	203	-123
ODPA-Bis P random	1.09	21	198	207	-125
ODPA-Bis P 4.1	2.55	37	203	212	-127
ODPA-Bis P random	2.55	39	204	207	-127
ODPA-Bis P 11.0	1.09	9	233	248	-109
ODPA-Bis P random	1.09	9	234	247	-118
ODPA-Bis P 11.0	2.55	18	238	249	-131
ODPA-Bis P random	2.55	19	236	249	-128
ODPA-Bis P-PA 40,000	---	---	267	---	---
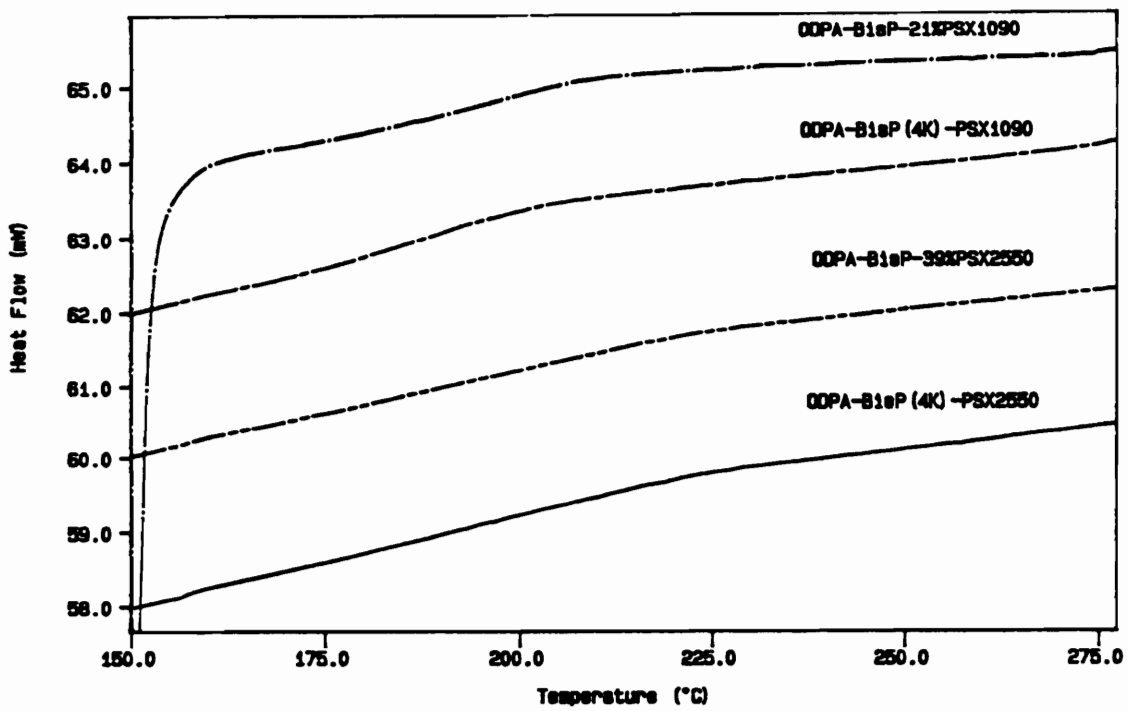
Figure 4.8.2 - DSC Curves of Randomly and Perfectly Alternating
Polyimide Siloxane Copolymers (Heating rate - 10 °C/minute)
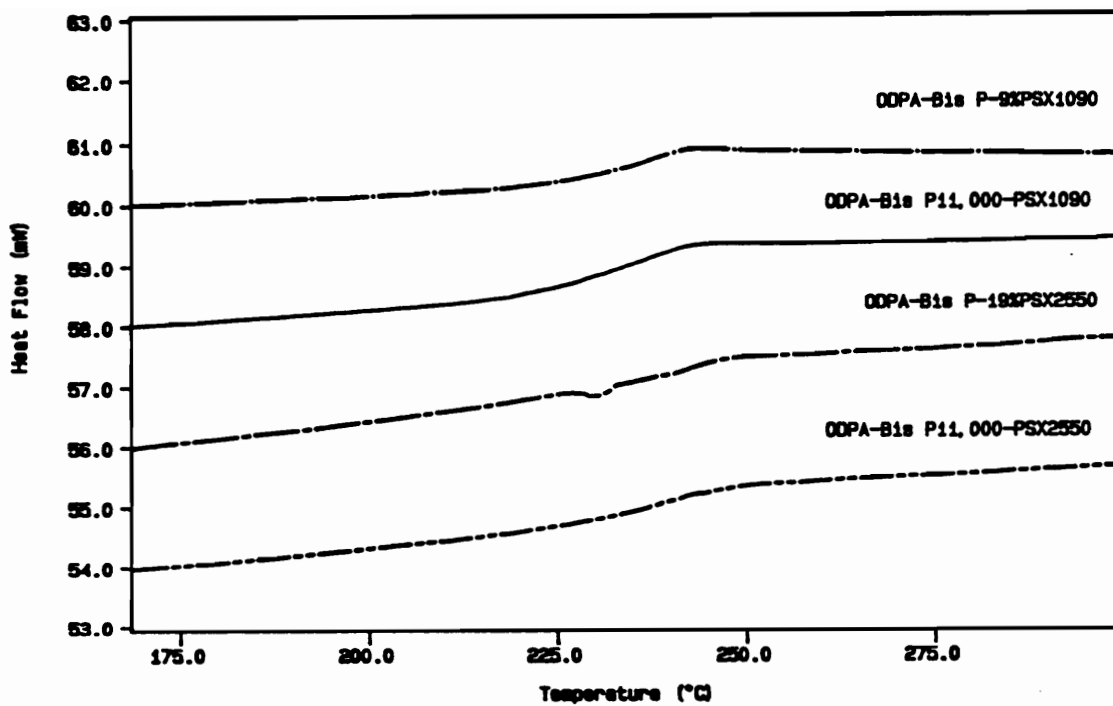
Figure 4.8.3 - DSC Curves of Randomly and Perfectly Alternating
Polyimide Siloxane Copolymers (Heating rate - 10 °C/minute)
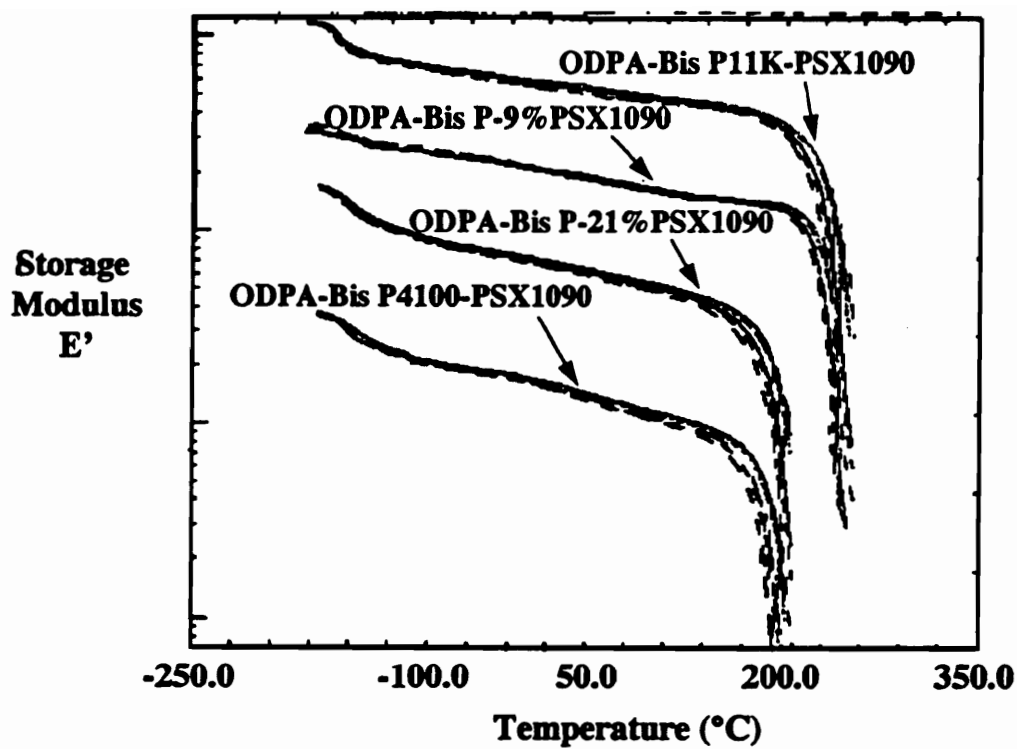
Figure 4.8.4 - DMA of Randomly and Perfectly Alternating
Polyimide Siloxane Copolymers (Heating rate - 10 °C/minute)
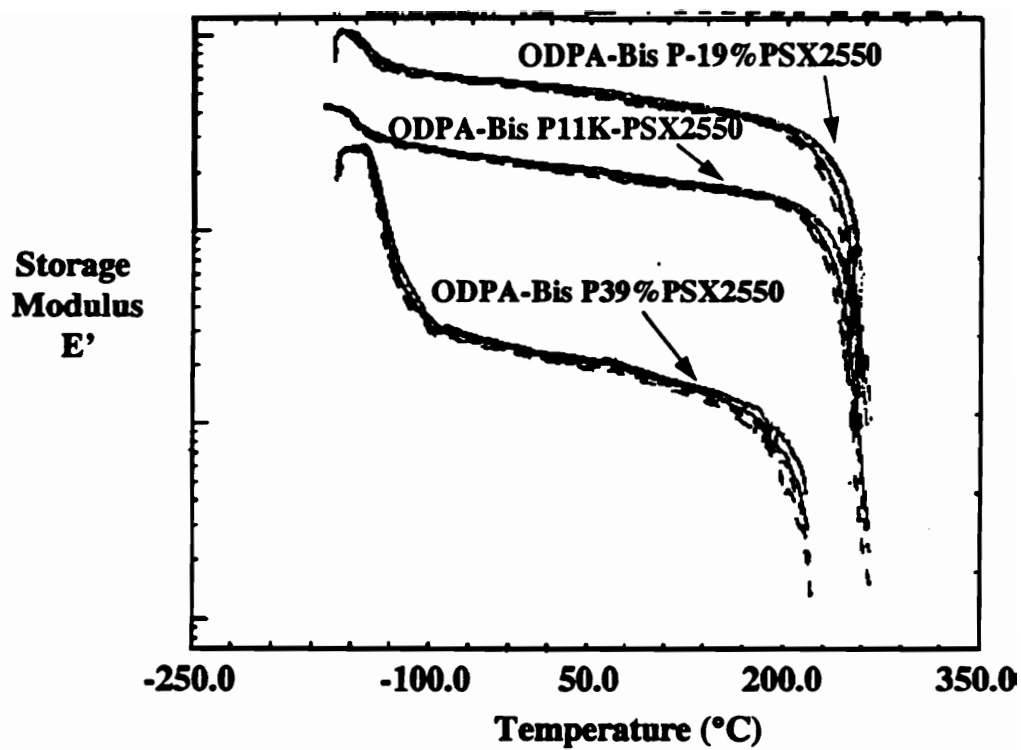
Figure 4.8.5 - DMA of Randomly and Perfectly Alternating
Polyimide Siloxane Copolymers (Heating rate - 10 °C/minute)

seen there was little difference in either the storage modulus or tan δ-temperature curves of corresponding polyimide siloxane copolymers.

The random and perfectly alternating polyimide siloxane copolymers showed no differences in the transition behavior as determined by DSC and DMA. The Tg of the polyimide segment in the copolymer was greatly dependent on the molecular weight of that segment. So, it was reasonable to conclude that the molecular weight of the polyimide segments was similar in the random and corresponding perfectly alternating segmented polyimide siloxane copolymers.

4.8.2 Mechanical Properties - Comparisons to the Perfectly Alternating Polyimide Siloxane Copolymers

The tensile properties of the random polyimide siloxane copolymers and corresponding perfectly alternating polyimide siloxane copolymers are listed in Table 4.7.3. Most of the tensile modulus and tensile strength values for the random polyimide siloxane copolymers were similar to the values of the corresponding perfectly alternating polyimide siloxane copolymers. The tensile modulus of the ODPA-Bis P39%PSX2.55 random copolymer was lower than the ODPA-Bis P4.1-PSX2.55 perfectly alternating copolymer.

Table 4.8.3 - Mechanical Properties of Randomly and Perfectly Alternating
Polyimide Siloxane Copolymers

Polyimide Oligomer \<Mn\> kg/mole	PSX \<Mn\> kg/mole	Weight % PSX	Tensile Modulus ksi	% Strain at Break	Stress at Break ksi	Stress at Yield ksi
ODPA-Bis P-PA 40.0	---	---				
ODPA-Bis P 4.1	1.09	21	233 ± 11	20 ± 10	8.6 ± 0.4	9.1 ± 0.5
ODPA-Bis P random	1.09	21	217 ± 7	19 ± 7	8.4± 0.4	8.7 ± 0.4
ODPA-Bis P 4.1	2.55	37	99 ± 4	25 ± 3	5.2 ± 0.1	5.0± 0.2
ODPA-Bis P random	2.55	39	48 ± 1	93 ± 30	4.6 ± 0.4	3.2 ± 0.2
ODPA-Bis P 11.0	1.09	9	299 ± 12	22 ± 7	12.3 ± 0.3	13.5 ± 0.4
ODPA-Bis P random	1.09	9	349 ± 44	15 ± 10	11.8 ± 0.6	12.4 ± 0.5
ODPA-Bis P 11.0	2.55	18	218 ± 13	17 ± 8	9.3 ± 0.5	9.4 ± 0.5
ODPA-Bis P random	2.55	19	218 ± 18	19 ± 2	8.9 ± 0.3	9.1± 0.3

Poly(amic acid)s were prepared from dianhydrides and diamines in polar aprotic solvents. Equilibration of the poly(amic acid)s was not necessary to produce polyimides with molecular weight distributions of 2. Immediately after the poly(amic acid)s were formed, they were cyclodehydrated in the presence of an azeotroping agent at 165 °C. Fully cyclized, soluble polyimides were formed within 24 hours. Using the solution imidization route, well defined polyimides of controlled molecular weight and end groups were made.

The one pot solution imidization route was used to synthesize amorphous fluorine and phosphorus containing polyimides that had very high glass transition temperatures. Polyimides prepared with 3F diamine were soluble in a variety of solvents and had temperatures ranging from 315 °C to 430 °C. Analogous phenyl phosphine oxide containing polyimides were also soluble and exhibited very high Tg's. The properties of the 3F diamine containing polyimides were modified through the incorporation of various comonomers.

Several of the 3F diamine polyimides and copolyimides were investigated for their long term thermal stabilities. At 371 °C, all of the 3F polyimides lost a significant amount of weight after 100 hours. However, the 3F diamine containing polyimides lost little weight at 316 °C after 500 hours. The 3F polyimides showed good long term thermal stability at the latter temperature.

A low temperature, solution polymerization method was developed for the synthesis of polyimide homopolymers and copolymers. Model studies showed that aliphatic and aromatic amines will combine with N-pyrimidine phthalimides through the transimidzation reaction. High conversions were quickly reached even at remarkably low temperatures. Utilizing the transimidization reaction, high molecular weight polyimide

homopolymer and polyimide siloxane copolymers were successfully made at low temperatures. Fully cyclized polyimide homopolymers were made from N, N'-pyrimidine bisphthalimides and aromatic amines at 75 °C. Subsequently, perfectly alternating polyimide siloxane copolymers were made in 2 hours from N-pyrimidine phthalimide terminated polyimide oligomers and aminopropyl terminated polydimethyl siloxanes.

The polyimide siloxane copolymers exhibited two Tg's due to the microphase separation of the polyimide and polysiloxane phases. The Tg of the polyimide phase was determined by the length of the polyimide block. However, phase mixing was evident from the DSC results in the polyimide siloxane copolymers with low molecular weight polyimide segments. The mechanical behavior was dependent on the amount of polysiloxane incorporated. Polyimide siloxane copolymers with 10 to 30 weight % polysiloxane had high tensile modulus and strength. Copolymers with 40 to 65 weight % polysiloxane had low tensile modulus and strength, but they had a high elongation and behaved as thermoplastic elastomers.

The properties of the perfectly alternating segmented polyimide siloxane copolymers were compared to analogous randomly segmented polyimide siloxane copolymers. Randomly and perfectly alternating segmented polyimide siloxane copolymers with same polymer composition had similar Tg's, and tensile modulus and strengths.

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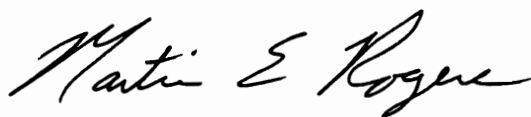
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Vita

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