

NOVEL HIGH PERFORMANCE THERMOSETTING POLYIMIDES

by

Gerald W. Meyer

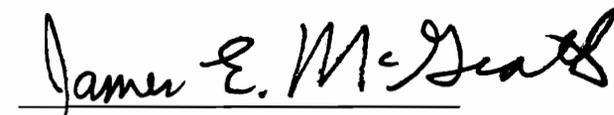
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(ABSTRACT)

Soluble imide thermosetting (reactive) oligomers of controlled molecular weights were synthesized utilizing 3-phenylethynylaniline, 4-phenylethynylphthalic anhydride or phenylmaleic anhydride as the reactive endcapping agents. The phenylethynyl endcapping agents were synthesized by a palladium-catalyzed coupling reaction in yields greater than 80 % after purification. The polyimide oligomers were synthesized via solution imidization techniques, using the ester-acid derivatives of various dianhydrides and various aromatic diamines. A "one pot" procedure utilizing NMP as the solvent and *o*-dichlorobenzene as the azeotroping agent reproducibly exhibit fully imidized soluble polyimides with $\langle M_w \rangle / \langle M_n \rangle$ values of ~ 2.0 determined by gel permeation chromatography (Universal Calibration). Successful molecular weight control was achieved using the reactive endgroups with imide oligomers synthesized with $\langle M_n \rangle$ values of 2,000 to 15,000 g/mole. The phenylethynyl and phenylmaleic endgroups permitted sufficient flow and low melt viscosities (< 10 PaS) *prior to* curing of the reactive endgroups at temperatures of 350°C or higher. Matrix composite and structural adhesives were also synthesized by the incorporation of triarylphosphine oxide moieties into the polyimide backbone, which generated char yields as high as 80% in air by TGA analysis.

Thermally cured samples displayed excellent solvent resistance with gel contents of 95 % or higher in most cases. Glass transition temperatures comparable to high molecular

weight linear analogs were also obtained upon thermal curing of the imide oligomers. Several systems exhibited excellent thermal stability at temperatures up to 700 °F (371°C) aged in air determined by dynamic and isothermal thermal gravimetric analysis. Graphite fiber composite specimens prepared from these reactive imide systems by conventional and small scale "powder prepregging" techniques displayed moduli values equal to or greater than specimens prepared from commercial materials.

Model studies were also conducted utilizing imide compounds analyzed by several spectroscopic techniques. These results indicate that crosslinking (possibly including cyclotrimerization) and chain-extension/branching both occur during the thermal curing of phenylethynyl groups. Phenylmaleic model imide studies indicate that Michael addition mechanisms at relatively high solution imidization temperatures may be a significant factor in limiting successful molecular weight control in phenylmaleic anhydride endcapped imide oligomers. However, two-stage reaction/curing permitted well defined networks to be generated.

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CHAPTER 1 - INTRODUCTION

Aromatic polyimides represent the state of the art for high performance materials since their development more than 30 years ago. Their success is most widely noted in the areas of aerospace and the microelectronics industries as both thermoplastics and thermosets. Polyimides are known for their many desirable properties which include excellent thermo-oxidative stability and mechanical behavior.¹⁻⁵ Applications of polyimides include adhesives, coatings, matrix resins, films, interlayer dielectric constants in computer chips and as wire insulation. Yet, further development of new polyimide systems and modifications of existing systems is an ongoing task to further enhance their desirable properties and applications. For example, in the proposed High Speed Civil Transport (HSCT) aircraft which will be designed for flights speeds of Mach 2.0-2.4, there is a need for polyimides resins that are processable and cost-effective and able to withstand temperatures of 177°C for 72,000 hours.⁶ In addition, these resins should exhibit high strength and excellent adhesion to metals, and be resistant to stresses, moisture, fuels, and solvents.

One approach to improve the properties (processability and solvent resistance) of polyimides has been the introduction of crosslinkable groups on the polyimide chain.^{7,8} The crosslinkable groups may be incorporated as endgroups or as pendant groups on the backbone of the polymer chain. Crosslinked or thermosetting polyimides have improved properties such as solvent resistance, good stress crack behavior and high moduli.

The first successful synthesis of a polyimide was reported in 1908,⁹ but it was not until the mid 1950's that high molecular weight polymers were prepared.¹⁰ This preparation involved the melt polymerization of aromatic diester-diacid monomer and aliphatic amines. However, these polyimides were not considered "high performance" materials since the aliphatic segments in the polymer backbone decreased thermal stability.

This led to the development of wholly aromatic polyimides with higher glass transition temperatures and better thermo-oxidative stability.

The desirable properties of polyimides were not initially realized because the aromatic and heteroaromatic units that makes the polymer thermally stable also made it of limited solubility and moldability and hence difficult to process. However, to overcome this intractable nature, stable flexibilizing groups such as carbonyl, oxygen, sulfone, and hexafluoroisopropylidene were incorporated between aromatic rings to improve solubility and moldability. In addition, pendant groups such as phenyl rings and *meta* catenation within the polyimide backbone were introduced which further improved the processability with only minor effects upon the thermal stability. This work, coupled with molecular weight control and endcapping opened the way for many soluble, readily processable, high temperature polyimides.

The most utilized method of preparing polyimides is the classical "two-step" method.¹ In this procedure, a dianhydride and a diamine are combined in a polar aprotic solvent to form a soluble intermediate poly(amic acid). The poly(amic acid) is somewhat hydrolytically unstable and has a relatively short shelf life. The next step involves the cyclodehydration or imidization of the poly(amic acid) to the polyimide with a loss of water. The imidization process made be carried out by bulk imidization, which involves heating the poly(amic acid) in a stepwise fashion to effect imidization and, indeed bulk or thermal imidization is often used for insoluble polyimides, including those with a semi-crystalline morphology.

Soluble amorphous polyimides can be made by imidizing polyamic acids in solution at milder temperatures.^{11,12} For example, the polyamic acid solution can be cyclodehydrated by adding an azeotroping agent to remove the liberated water at temperatures of 150°C to 180°C. The polyimide can be isolated in its fully imidized form

and can further processed. Ambient temperature polyimide synthesis can also be conducted by using chemical imidization techniques.^{13,14} In this method, the polyamic acid is cyclodehydrated by treating it with an aliphatic carboxylic dianhydride and tertiary amines. However, this method also usually produces isoimide (iminolactone) and heat treatment of polyimide is often necessary to achieve fully cyclized imide.

The research in this dissertation has focused on the synthesis and characterization of soluble, high glass transition, controlled molecular weight, reactive thermosetting imide oligomers. Specific objectives that were set forth to investigate in this research were as follows:

1. The synthesis of monofunctional reactive endcapping agents for use with high glass transition temperature polyimide oligomers. A number of different reactive endgroups were used to cap the imide oligomers. These endgroups included 3-phenylethynylaniline, novel 4-phenylethynylphthalic anhydride, and phenylmaleic anhydride which had previously never be used as a monofunctional endcapping agent.
2. The synthesis and characterization of polyimide oligomers functionalized with these phenylethynyl or phenylmaleic groups to increase processability over conventional systems.
3. Incorporation of phosphorus into the reactive imide oligomers to increase char yields and mechanical performance. A number of soluble reactive imide oligomers were successfully prepared utilizing a variety of monomer combinations including phenylphosphine oxide-containing monomers.
4. The synthesis and characterization of imide-siloxane copolymers with reactive endgroups for use as high performance gas separation membranes.
5. To examine the thermo-oxidative stability, mechanical properties, solvent resistance and rheological (flow) behavior of these reactive imide oligomers before and after crosslinking of the reactive endgroups.

6. Investigation of model phenylethynyl and phenylmaleic imide compounds using various spectroscopic techniques to gain insight into their curing and reactivity behavior.

The literature review in Chapter 2 contains discussions of common synthetic methods used to prepare polyimides, polyimide properties, phosphorus-containing polyimides, and commonly used reactive endgroups employed in thermosetting polyimides. Chapter 3 outlines the various monomers and reagents employed in this research along with the synthetic and analytical experimental methods. Chapter 4 presents a discussion of the experimental results, followed by conclusions (Chapter 5) and references (Chapter 6).

CHAPTER 2 - LITERATURE REVIEW

2.1 INTRODUCTION

Since the first commercialization of the Kapton polyimides by DuPont over three decades ago, a large number of new polyimides with unique properties have been introduced for various applications. Polyimides' excellent thermal and mechanical properties make them the choice for many high performance applications. Polyimide chains contain a phthalimide heterocyclic structure in the polymer backbone as shown in Figure 2.1.1. Many books and reviews on polyimides are available.¹⁻⁵

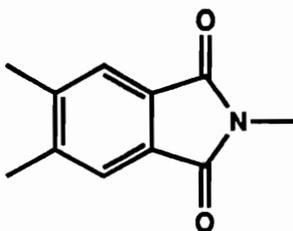


Figure 2.1.1 Imide Heterocycle

The literature dealing with polyimides is too extensive to be exhaustively reviewed here, but an overview of the more recent developments will serve as a background to the experimental section that follows. The first section will discuss common synthetic methods used to prepare polyimides. The next two sections deal with polyimide properties and phosphorous-containing polyimides, respectively. The final section covers different thermosetting polyimide systems.

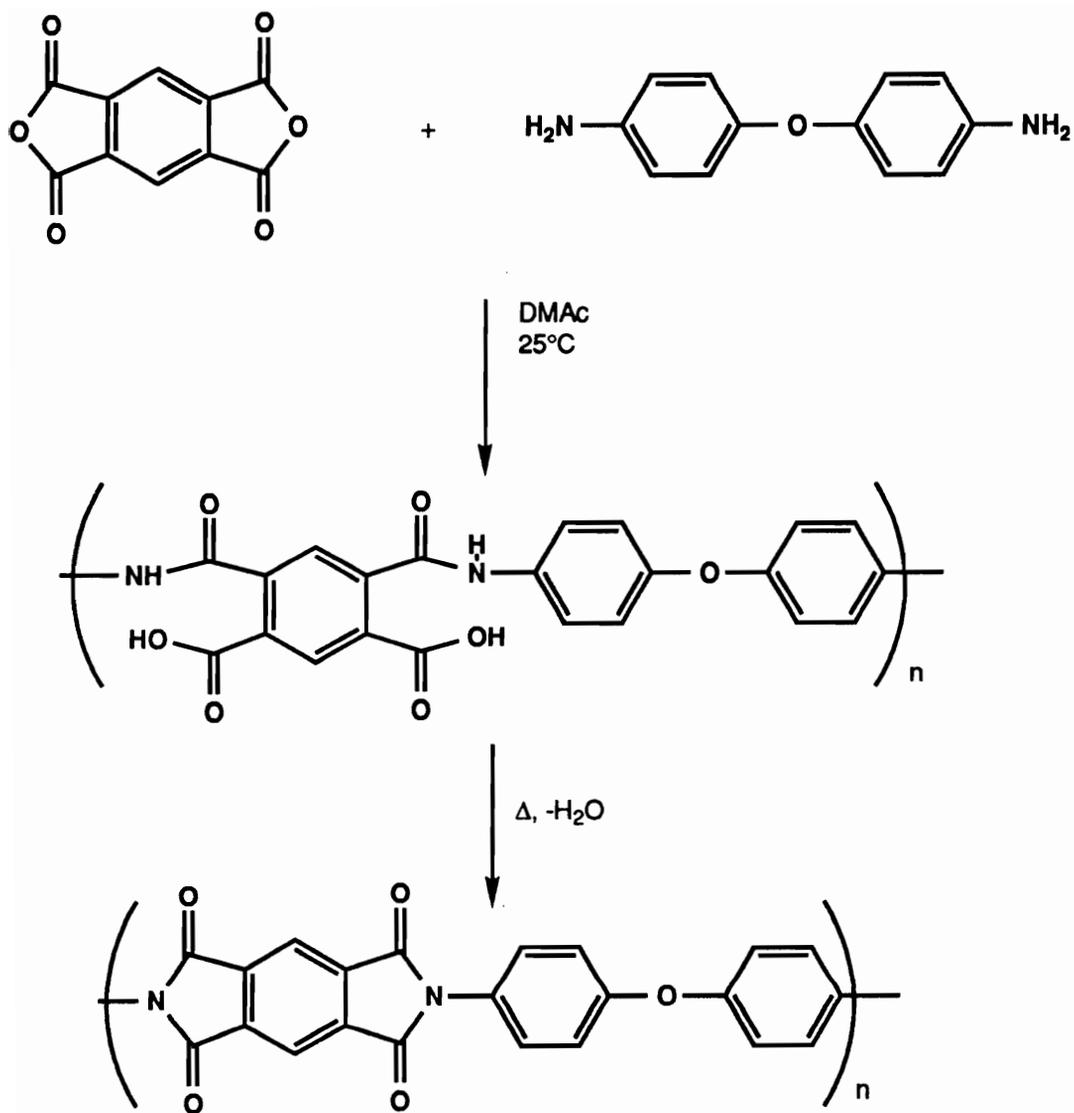
2.2 SYNTHESIS OF POLYIMIDES

Condensation polyimides were discovered by Bogart and Renshaw in 1908⁹; however, it was not until 1955 that Edwards and Robinson^{10,15} made polyimides practically using dianhydride or dianhydride derivatives and diamines. These were not true

"high performance" materials, but it was realized that fully aromatic polyimides were potential candidates for high temperature applications. The successful synthesis of polyimides overcame the insolubility and infusibility of early aromatic polyimides by the development of the most common and documented method of making polyimides, the classical two-step synthesis.¹⁶⁻²⁶

2.2.1 Two-Step or "Classical" Route

In the first stage, a poly(amic acid) is prepared by introducing a dianhydride with a diamine dissolved in a polar aprotic solvent. The poly(amic acid) may then be cyclodehydrated by either thermal or chemical processes to form the polyimide. The synthesis of the poly(amic acid) and the resulting polyimide is shown in Scheme 2.2.1.1. The formation of the poly(amic acid) is an equilibration reaction where the forward reaction is thought to start at least in some cases with the formation of a charge transfer complex between the dianhydride and the diamine and is shown in Figure 2.2.1.2.^{21,27,28} Propagation occurs immediately thereafter by nucleophilic substitution at one of the anhydride's carbonyl carbon atoms. The amine therefore, attacks the sp^2 carbon and displaces the adjacent carboxylate moiety. Hence the condensation by-product, the carboxyl group, is chemically attached to the product, and cannot be removed to drive the reaction to completion. However, the carboxyl group can be removed chemically to further the reaction. Polar aprotic solvents such as N-methyl pyrrolidone (NMP) or dimethyl acetamide (DMAc) can form strongly hydrogen-bonded complexes with the free carboxyl groups (Figure 2.2.1.3),²⁹ causing a decrease in the reverse reaction which drives the reaction towards polymer. Therefore, high molecular weight poly(amic acids) can be obtained from many combinations of dianhydrides and diamines. Unreactive monomers



Scheme 2.2.1.1 Conventional or "Two-Step" Polyimide Synthesis Route³

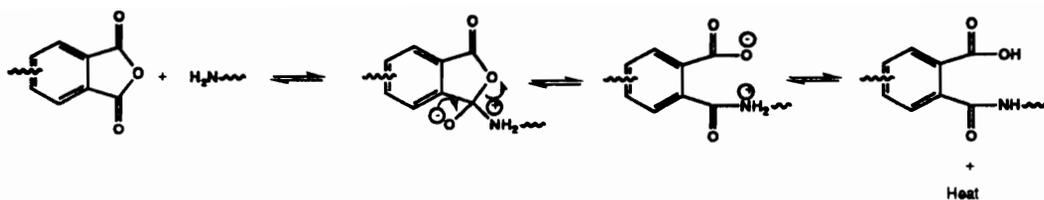


Figure 2.2.1.2 Charge Transfer Complex Between Diamine and Dianhydride ^{21,27,28}

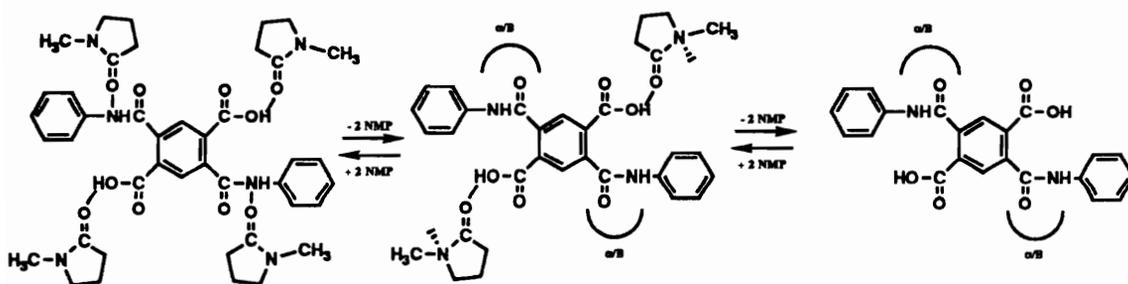


Figure 2.2.1.3 Complexation/Decomplexation Process of NMP with Free Carboxyl Groups ²⁹

can still be used to obtain high molecular weight polyimides in polar aprotic solvent with longer reaction times.

The choice of reaction solvent may also have a profound effect on the formation of high molecular weight poly(amic acid), especially if unreactive diamines are used. The rate of polymerization generally increases as the solvent becomes more polar and more basic.^{30,31} The rate was found to proceed in the order of THF < acetonitrile < DMAc < *m*-cresol.³² Ether solvents promote the formation of high molecular weight poly(amic acid) where complexation or hydrogen bonding of the ether oxygens with amino protons, is thought to increase nucleophilicity of the diamine.³³

As was mentioned earlier, the propagation of the poly(amic acid) proceeds via a nucleophilic substitution reaction at the carbonyl carbons of the anhydride. Therefore, the more electrophilic the dianhydride, the more susceptible it is to nucleophilic attack. A measure of an anhydride's electron acceptor properties is its electron affinity (Ea). Higher Ea values suggest greater reactivity of the dianhydride.⁵ The electron affinity values for many common dianhydrides are given in Table 2.2.1.1.

The reactivity of the diamine towards poly(amic acid) formation has been correlated through ¹⁵N, ¹H, and ¹³C NMR shifts. In particular, Ando et. al. have found that higher ¹⁵N NMR chemical shifts indicate lower reactivity of the diamine in solution.³⁴ Table 2.2.1.2 lists the ¹⁵N NMR chemical shifts for several common diamines. In addition, diamines with electron withdrawing bridging groups tend to be more reactive than those with electron donating groups.

Another factor affecting molecular weight buildup in poly(amic acids) is the monomer concentration of the reaction. Dilute poly(amic acid) solutions are generally less stable and have shorter shelf lives than more concentrated ones.^{35,36} Nevertheless, Cotts and Volksen have shown that total solids contents of less than 10 weight percent, good

Table 2.2.1.1 Electron Affinity Values for Several Dianhydrides⁵

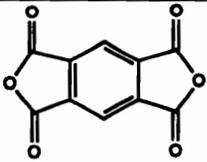
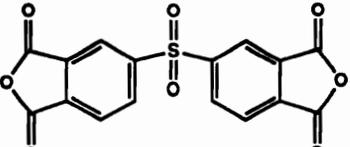
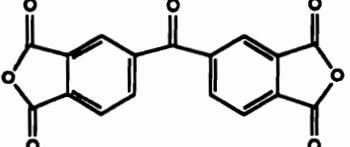
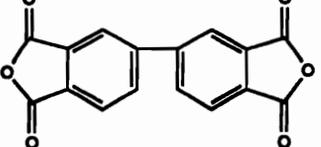
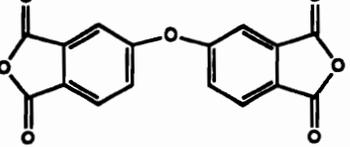
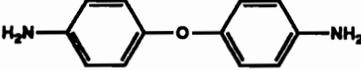
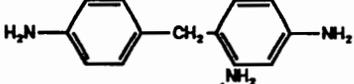
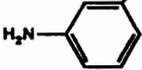
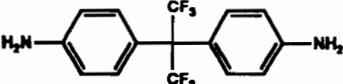
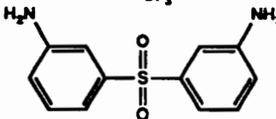
Dianhydride	Abbreviation	Ea (eV)
	PMDA	1.90
	DSDA	1.57
	BTDA	1.55
	BPDA	1.38
	ODPA	1.30

Table 2.2.1.2 ^{15}N NMR Chemical Shifts of Several Diamines³⁴

Diamine	Abbreviation	^{15}N Chemical Shift
	<i>p</i> -PDA	53.8
	4,4'-ODA	57.9
	MDA	59.4
	<i>m</i> -PDA	60.8
	6F Diamine	64.0
	<i>m</i> -DDS	65.7

agreement was found between calculated and actual molecular weights. However, for monomer concentrations of 20 percent, calculated and actual molecular weights agreed only when the dianhydride was introduced in solution; adding solid dianhydride to diamine solution greatly increased molecular weights.³⁷

As alluded to previously, the form of the dianhydride can have a significant effect on molecular weight. Studies utilizing light scattering on a series of PMDA-ODA poly(amic acid) solutions of controlled molecular weight indicated that addition of a dianhydride solution produced molecular weights in good agreement with the calculated values.³⁷ In contrast, when solid dianhydride was added, extremely high molecular weights were obtained, which were found to slowly equilibrate to the calculated values.

The reaction temperature is another factor influencing the extent of conversion. The initial stage of the reaction is usually conducted below 50°C to prevent cyclization to the imide. Premature imidization should be prevented for two reasons: first, the imidization process releases water, which can rapidly hydrolyze poly(amic acid),²¹ which reduces molecular weight. Second, in cases where the fully cyclized polyimide is insoluble, premature imidization in the initial stages of polymerization results in precipitation of low molecular weight oligomers.³⁸

As stated earlier, poly(amic acid) solutions are especially susceptible to hydrolysis if left standing for long time periods. The viscosities of PMDA poly(amic acids) rapidly decrease when stored as solutions. Other more hydrophobic systems are slower. However, studies have shown decrease in viscosity is also attributed to reversibility of the propagation reaction and the fact that the polymers were produced by interfacial polymerizations.⁵ The rate constants for the reverse reactions are quite small; however, the reactions can have a dramatic effect on the $\langle M_w \rangle$ of the polymer. This phenomenon is shown in Figure 2.2.1.4 where at 31°C, the $\langle M_w \rangle$ decreases with time. This process can be slowed in the solutions are stored below 10°C.

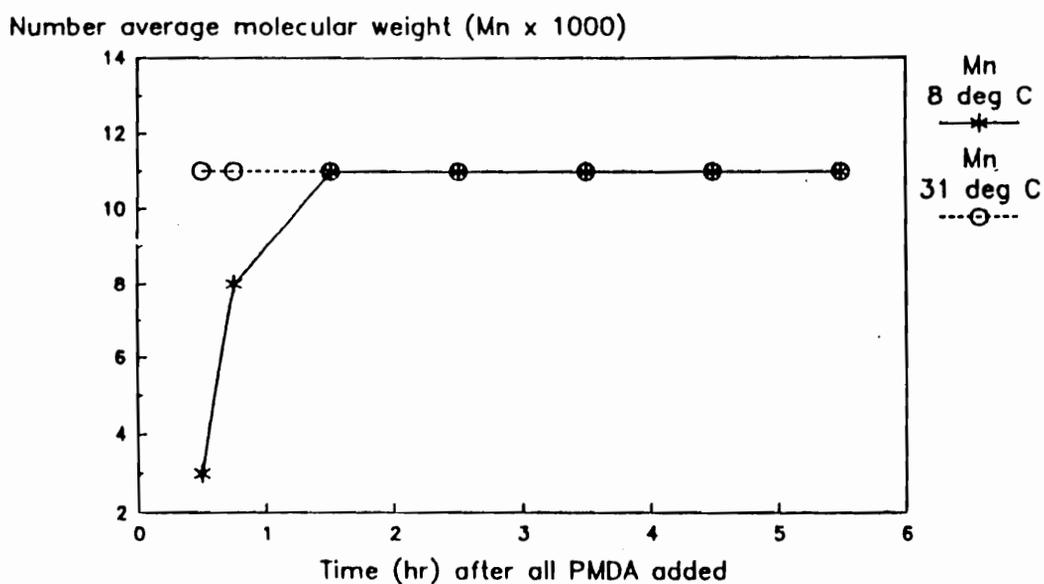
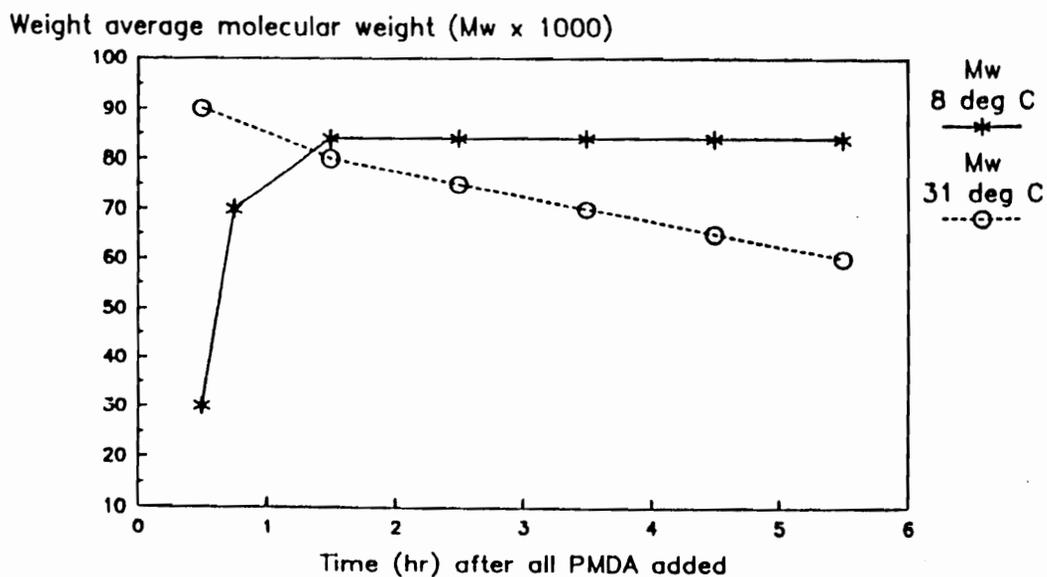


Figure 2.2.1.4 Molecular Weight of Poly[(4,4'-oxydiphenylene)pyromellitic acid] as a Function of Time at 8 and 31°C⁵

The synthesis of poly(amic acids) must be performed under anhydrous conditions. Carboxylic acid groups resulting from the hydrolysis of the dianhydride will fail to react with the diamine at low or even moderate temperatures. As a result, carefully dried solvents, glassware, and monomers are essential.

2.2.2 Bulk Imidization (Cyclodehydration)

The most common method of converting the poly(amic acid) to the polyimide is by bulk imidization and is often used for insoluble polyimides.³⁹⁻⁴¹ A film is usually cast of the poly(amic acid) and is heated in stages in order to remove the casting solvent, induce cyclization and remove the liberated water by the imidization process. A commonly used heating cycle may proceed by the following: 1 hour at 70°C; 1 hour at 100°C; 1 hour at 200°C; 1 hour at 300°C; followed by a slow cool to room temperature. Complete cyclization is usually accomplished by heating the polyimide above the ultimate T_g of the polyimide. However, ^{15}N solid state NMR studies have suggested that as much as 6 - 9 % of the final product may not be fully imidized for the PMDA/ODA system.⁴²

Investigations have found that the majority of imidization of PMDA/ODA poly(amic acids) occur in the range of 150 - 250°C as determined by DSC and TGA experiments.⁴³ This is illustrated in Figure 2.2.2.1. Kreuz et. al. have also found that the rate of imidization is initially rapid in the temperature range of 160 - 188°C but decreases over time and stops before complete conversion is obtained as determined by monitoring the imide by IR.⁴⁴

Side reactions can also occur during bulk imidization which can lead to some form of crosslinking.³⁹ Model imide compounds were monitored by Raman spectroscopy while heated under a typical imidization schedule. This study revealed that Raman bands formed at 1656 cm^{-1} indicating that imine bonds ($\text{C}=\text{N}$) formed during the imidization process.⁴⁵ The study suggests that this imine formation is responsible for crosslinking

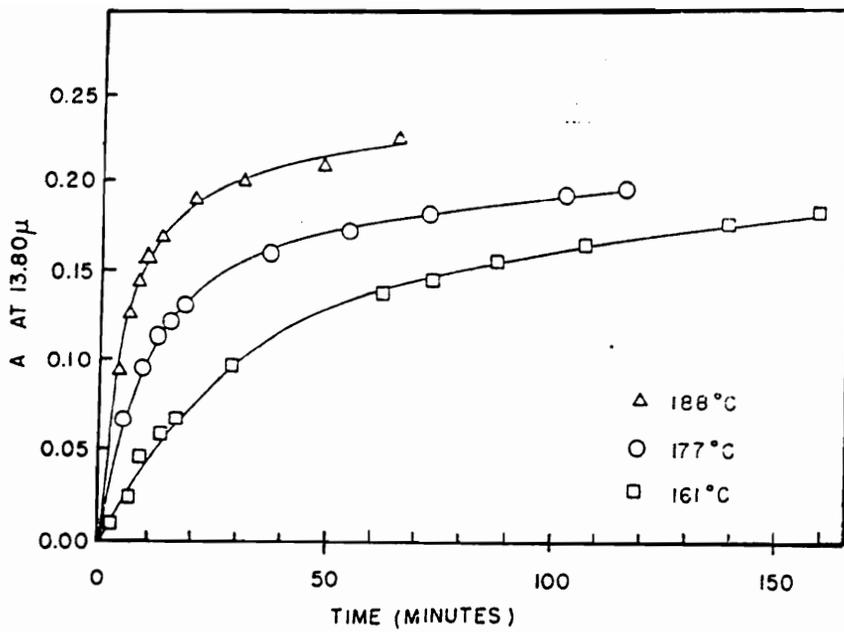


Figure 2.2.2.1 Conversion Rates of PMDA/ODA Poly(amic acid) at Various Temperatures

in the bulk polymer. These crosslinking reactions often result in polyimides which are insoluble that might otherwise be soluble.

2.2.3 Solution Imidization

With the development of structural modifications of polyimides to overcome the insolubility of the early aromatic systems, solution polymerization of high molecular weight, high T_g , fully cyclized polyimides was made possible. Solution imidization techniques represent as a major development in polyimide technology. As a result, "one pot" syntheses are possible, cyclodehydration can be effected at lower temperatures since the poly(amic acid) has much greater mobility in solution than in the solid state. This means that degradation and side reactions may be avoided, and polyimides may be stored in solution for long periods of time, whereas hydrolytically unstable poly(amic acids) can not.

Workers tried unsuccessfully as early as 1970 to synthesize polyimides via solution thermal imidization of poly(amic acids).⁴⁶ The reactions were run in N-methylpyrrolidone at 200°C, but did not result in high molecular weight polyimides perhaps because no attempts were made to remove the water of imidization which resulted in hydrolysis and consequently molecular weight reduction. However, advancements have shown that soluble polyimides can now be completely cyclized by imidization of a poly(amic acid) in solution.^{11,12,47} The imidization process is affected by heating the poly(amic acid) solution to 150°C to 180°C in the presence of an azeotroping agent such as *o*-dichlorobenzene (*o*-DCB), xylene or cyclohexyl pyrrolidone (CHP) which added to remove the water that is liberated during the reaction. CHP does not form an azeotrope with water; the immiscibility of CHP and water is the basis of water removal at high temperatures. Complete imidization can be achieved within 16 to 24 hours. Insoluble polyimides will precipitate during reaction before imidization is complete and can actually be used beneficially to form submicron polyimide particles for composite fabrication.^{48,49}

The mechanism of thermal solution imidization has not been thoroughly investigated as the bulk thermal imidization process; and hence there was little information about the processes occurring in solution. However, recently, Kim and coworkers have studied the solution imidization process.⁵⁰ The study revealed that during the initial stages of the imidization process a decrease in intrinsic viscosity was observed, followed by an increase during the latter stages of imidization. These observations were confirmed by ¹H NMR studies, which initially showed an increase in amine concentration during the early stages of imidization, and then gradually disappeared with time. The results of the intrinsic viscosity and percent amic acid correlation with reaction time are shown in Figure 2.2.3.1.

Kim et. al. were clearly able to show that the poly(amic acid) chain cleaved to form *o*-dicarboxylic acids and amine endgroups as water liberated from the reaction caused initial hydrolysis of the partially imidized poly(amic acid). As the reaction proceeded, the endgroups recombined or the chains "healed" to form polyimides resulting in an increase in molecular weight. This same phenomena is thought to occur in bulk thermal imidization.

Kim et. al. proposed a mechanism for imidization as depicted in Figure 2.2.3.2. The cyclodehydration was determined to be an acid-catalyzed second order process⁵⁰ which may possibly permit lower reaction temperatures and shorter reaction times. The rate-determining step was found to be the nucleophilic substitution of the carboxyl carbon by the amide nitrogen. The water generated was removed from the solution to give complete cyclization as judged by FTIR and non-aqueous titration of the residual amide acid.

Kim has also demonstrated the occurrence of crosslinking in ketone-containing polyimides with amine endgroups where the amine endgroups attack in-chain ketone carbonyl moieties to form imine-linked, insoluble polyimide networks.⁵¹ This imine bond formation is similar to those reported by Saini in bulk thermal imidization.⁴⁵ The polyimide "crosslinks" could be readily hydrolyzed, however, upon addition of a trace

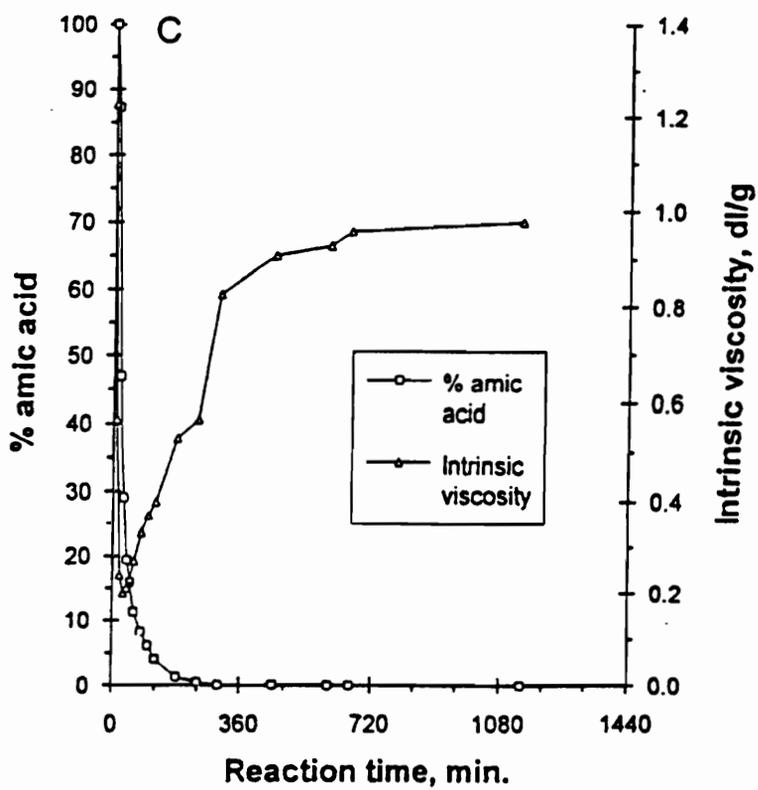


Figure 2.2.3.1 Relation of Percent Amic Acid and Intrinsic Viscosity to Reaction Time in the Solution Imidization of a Poly(amic acid) at 180°C⁵⁰

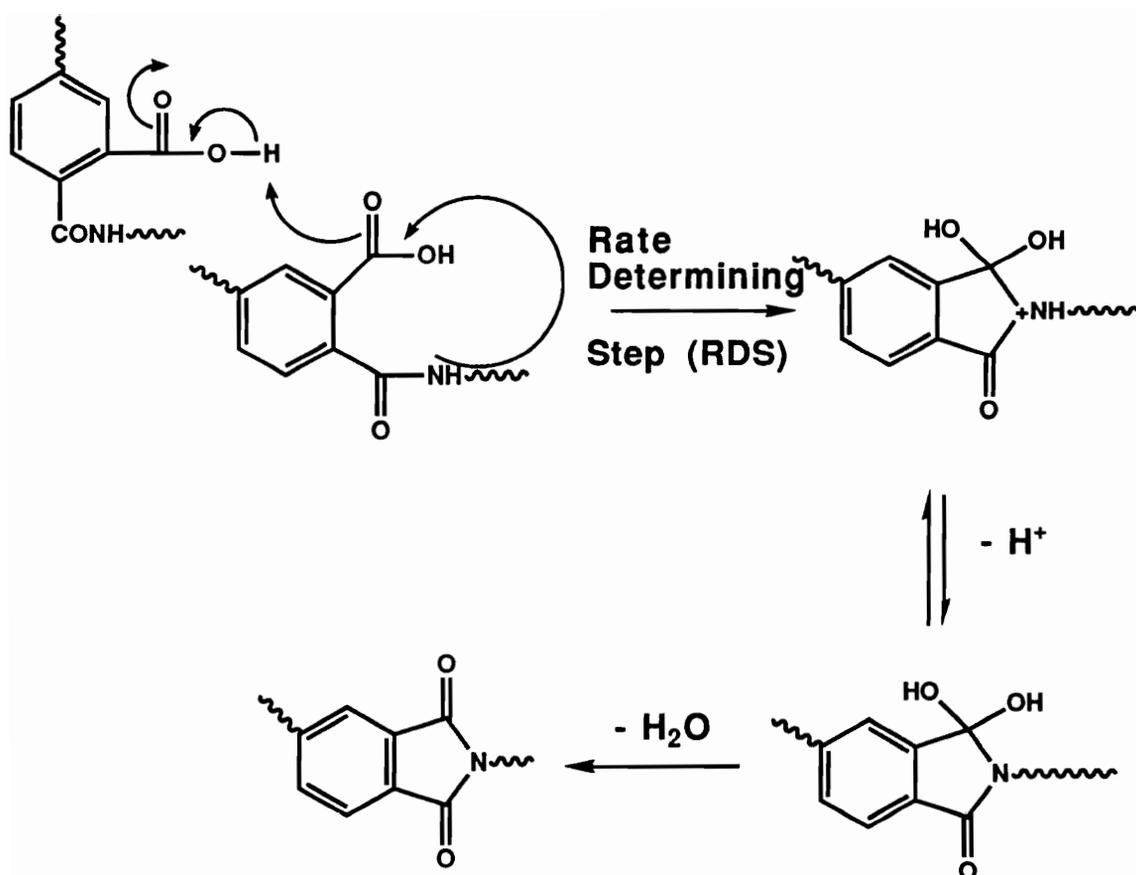


Figure 2.2.3.2 Mechanism of Acid Catalyzed Imidization in the Solution Imidization of Poly(amide acids)⁵⁰

amount of aqueous hydrochloric acid.

Phenolic solvents which are also, of course, acidic may be used in other solution thermal imidization methods to affect imidization.⁵² Polyimides have been formed in solvents such as the cresols at 180 to 220°C in a one-step process.^{46,53}

2.2.4 Chemical Imidization

Cyclodehydration on poly(amic acids) may also be performed at room temperature by chemical imidization methods.⁵⁴⁻⁵⁶ Various combinations of chemical agents may be used, but usually the poly(amic acid) is treated with aliphatic carboxylic acid dianhydrides (dehydrating agents) and tertiary amines (basic catalysts). Some of the basic catalysts which have been employed are pyridine, triethylamine, and isoquinoline. Dehydrating agents may include acetic anhydride, propionic anhydride, and n-butyric anhydride. The mechanism of chemical conversion is shown in Figure 2.2.4.1. The acid group on the polymer reacts with the acetic acid to form an acetate group. The acetate is an improved leaving groups so cyclization takes place at lower temperatures. Subsequent N-acylation yields the imide heterocycle, while O-acylation yields the iminolactone or isoimide heterocycle. The efficiency of the reaction varies according to the specific combination of chemical agents used. Heat treatment of the polyimides is often necessary to achieve 100 percent imide due to isoimide formation.

Chemical imidization utilizing anhydrides and triethylamine have reportedly afforded the imide moiety exclusively. However, a mixture of imide and isoimide is formed if pyridine is used in place of triethylamine.⁵⁷ Poly(amic acids) chemically imidized with trifluoroacetic anhydride or dicyclohexyl carbodiimide reportedly afford isoimide exclusively.^{58,59}

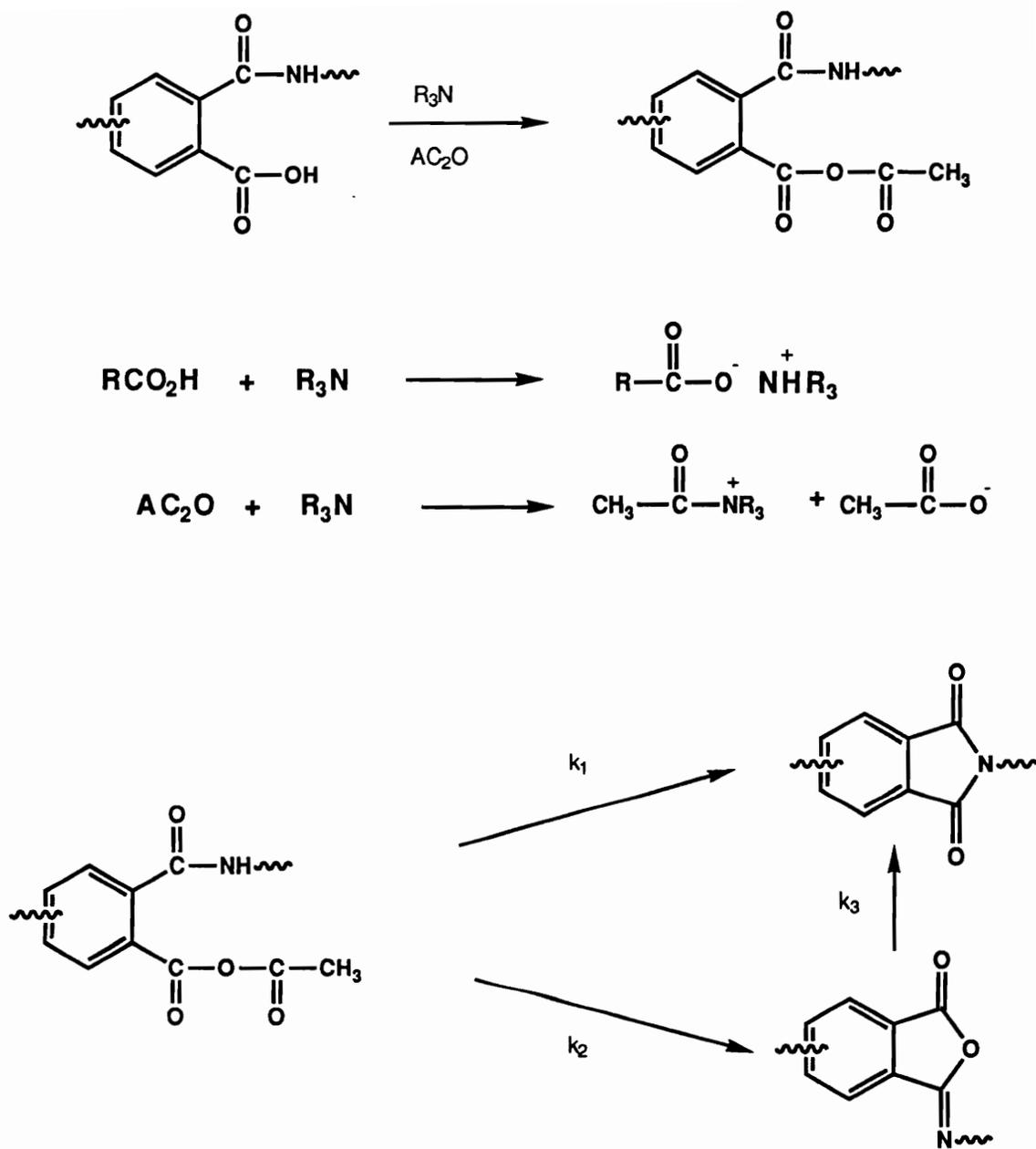


Figure 2.2.4.1 Mechanism of Chemical Conversion of Poly(amic acid) to Polyimide, with the Formation of Isoimide ⁵⁴⁻⁵⁶

Open chain amic acid and isoimide along the backbone of the resultant polymer represent unstable linkages which depress thermal and mechanical properties and is considered a disadvantage of chemical imidization. Nevertheless, polyimides formed by chemical conversion have found commercial application, most notably the acetylene terminated Thermid resins currently marketed by National Starch.⁶⁰ Their success is probably due to the improved processability (lower T_g's and increased solubility) associated with the presence of the amic acid and isoimide moieties.

2.2.5 Ester-Acid Route

Polyimides may also be synthesized from dianhydride derivatives, e.g. tetracarboxylic acids or bis(ortho-ester-acids). The first successful attempt utilizing diester-diacid dianhydride derivatives were reacted with aliphatic diamines in a bulk polymerization.¹⁰ In this type of polymerization, initially a salt is formed, as in aliphatic polyamide or nylon synthesis; subsequent heating causes amidation and water evolution during the intermediate stages followed by cyclization to polyimide at high temperatures. However, attempts to polymerize polyimides based on aromatic diamines failed to give high molecular weight by this route. Nevertheless, low molecular weight aromatic imide oligomers used in composite systems have utilized this process in what is termed "PMR" for *polymerization of monomeric reactants*.^{61,62}

This PMR approach offers several advantages over the conventional "two-step" route. The ester-acid form of the monomers are not moisture-sensitive and is very tolerant of water in solvents and reactors. In addition, ester-acids are more soluble in organic solvents and possibly less toxic than anhydrides. Furthermore, preparation of stable monomer solutions with good shelf lives are possible.

Moy recently investigated the factors necessary for the consistent synthesis of soluble polyimides by the ester-acid method.^{63,64} The synthesis of polyimides by the

ester-acid route is shown in Figure 2.2.5.1. The diester-diacid derivatives are conveniently prepared by dissolving pure dianhydride in refluxing alcohol. The addition of an amine catalyst (which acts as an acid acceptor), e.g. triethylamine, greatly enhances the rate of formation of the diester-diacid product. Moy studied the synthesis of N-phenyl phthalimide from monoethyl phthalate or diethyl phthalate and aniline. Diethyl phthalate and aniline failed to form amide-ester or imide either in solution or neat. Similarly, phenyl benzoate and aniline failed to form benzanilide under the conditions examined. Only monoethyl phthalate and aniline produced N-phenyl phthalimide in 70% yield in refluxing toluene. The model reactions are shown in Scheme 2.2.5.1. These results indicated that at moderate temperatures the solution reaction of aromatic ester-acids and aromatic amines is preceded by conversion of the ester-acid to anhydride, and that blocking anhydride formation will prevent amide and imide formation. From these studies, suitable polymerization conditions were found to produce high molecular weight as well as controlled molecular weight polyimides by using diester-diacid derivatives with aromatic diamines in N-methyl pyrrolidone/*o*-dichlorobenzene solvent mixtures. Reaction conditions included solids contents of 15 to 20 percent (wt/vol), temperatures of 170°C to 180°C, and reaction times of 24 hours or less; flaming of glassware was unnecessary.^{63,64}

2.2.6 Transimidization Route

Transimidization was first used by Spring and Woods using phthalimide and methyl amine.⁶⁵ High molecular weight polyimides were later synthesized by Imai using transimidization techniques.⁶⁶ However, Takekoshi and coworkers were the first to extensively use and refine the synthesis of polyimides via transimidization reactions.^{67,68} Based on model reactions with *p*-toluidine, N-pyridine phthalimide was the most reactive. Furthermore, compounds such as zinc acetate were effective in catalyzing the reaction of N-substituted phthalimides and aromatic amines.

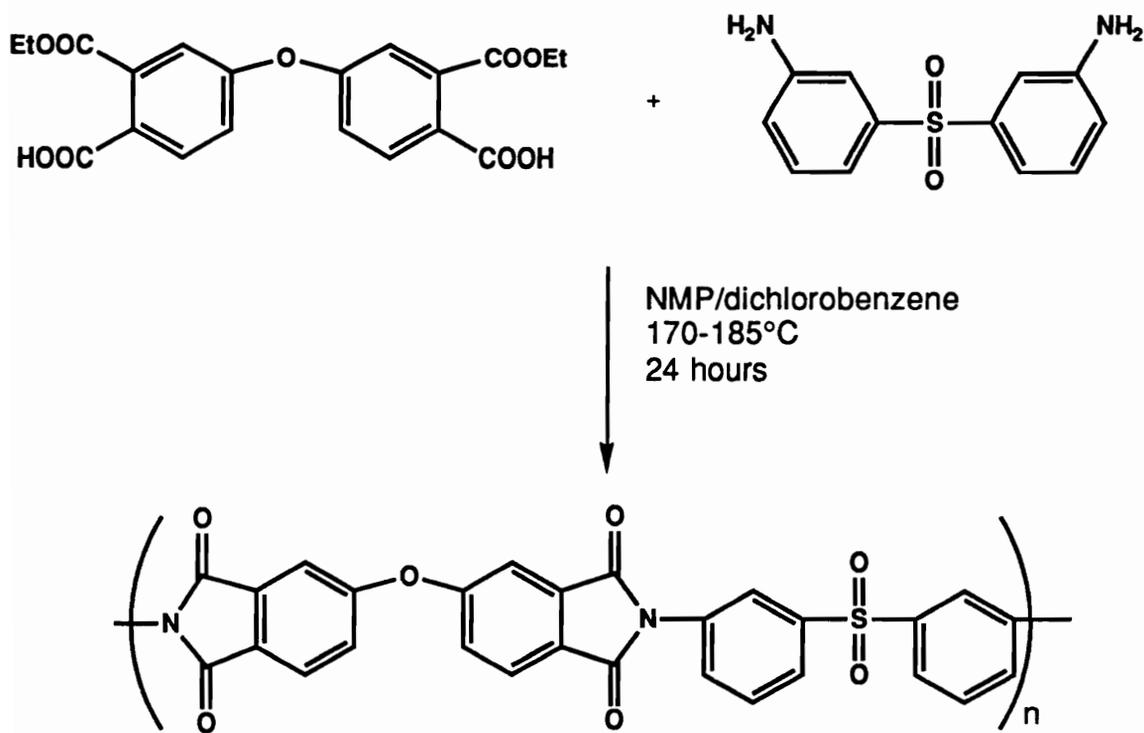
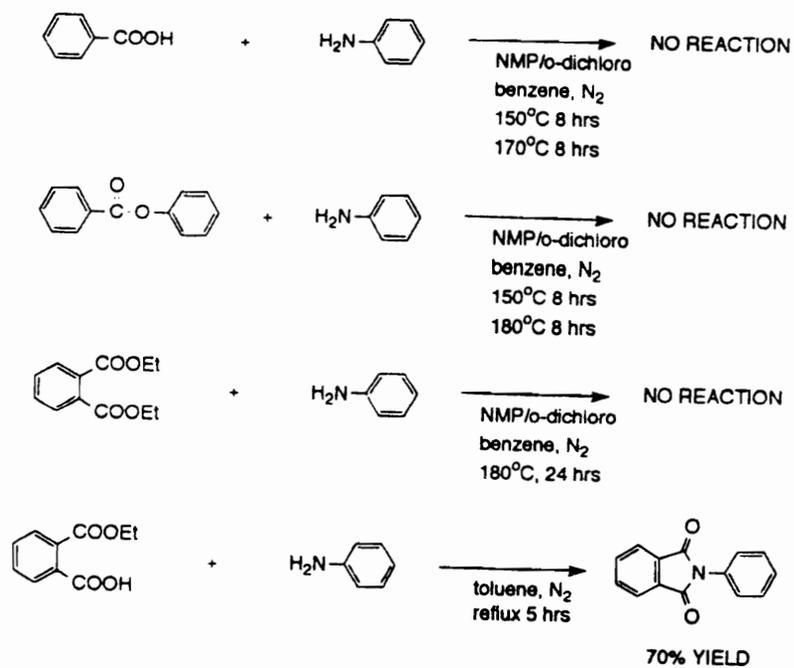


Figure 2.2.5.1 Polyimide Synthesis by the Ester-Acid Route ^{63,64}



Scheme 2.2.5.1 Model Investigations of the Ester-Acid Route ^{63,64}

High conversion between the imide-amine exchange with a phthalimide and a diamine; the diamine should be more basic or nucleophilic than the monoamine that is displaced. The most widely used monoamine used is 2-aminopyridine having a pKa value of 27.7⁶⁹ which is less basic than most aromatic and aliphatic diamines and is readily displaced in the transimidization process.

Rogers has utilized the transimidization reaction to synthesize high molecular weight perfectly alternating polyimide-polydimethyl siloxane copolymers.^{70,71} Imide oligomers endcapped with less toxic 2-aminopyrimidine were reacted with aminopropyl terminated (dimethyl siloxane) oligomers. High molecular weight, fully imidized perfectly alternating segmented imide siloxane copolymers were obtained within 2 hours at temperatures of 60-110°C. The synthesis of these perfectly alternating copolyimides is shown in Scheme 2.2.6.1.

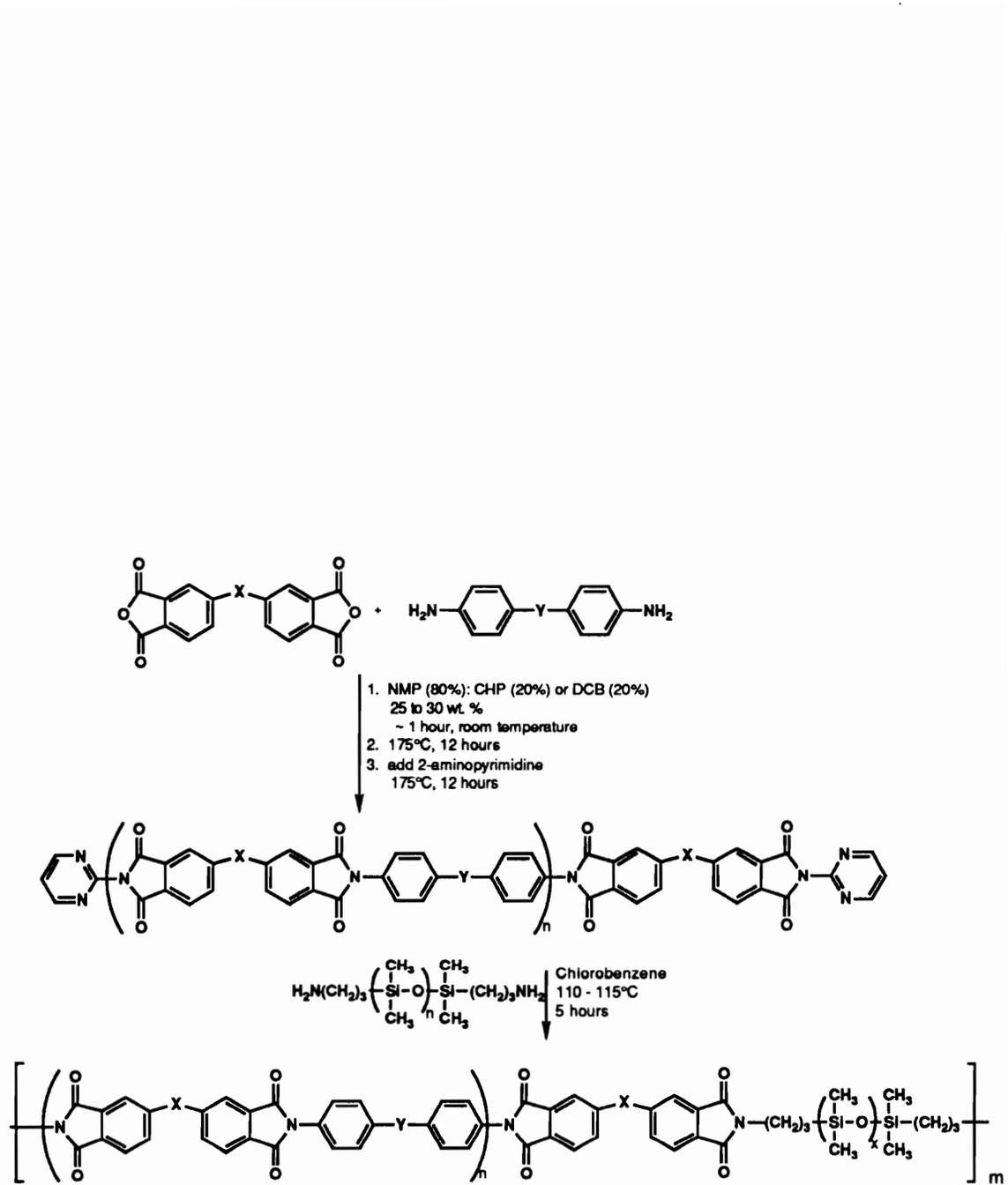
2.2.7 Additional Routes to Polyimides

2.2.7.1 "One-Step" Synthetic Route

Soluble polyimides made be prepared directly without going through the poly(amic acid) precursor formed by the conventional "two-step" route. Harris and coworkers have synthesized high molecular weight polyimides in refluxing *m*-cresol without azeotroping agents via a "one-step" route. No poly(amic acid) formation was needed to produce high molecular weight polyimides from aromatic diamines and dianhydrides.^{72,73}

2.2.7.2 Vapor Deposition Polymerization

Polyimides have been reportedly prepared without the use of solvents from aromatic diamines and dianhydrides. This process eliminates residual solvent or solvent decomposition products. Vapor deposition polymerization involves coevaporating



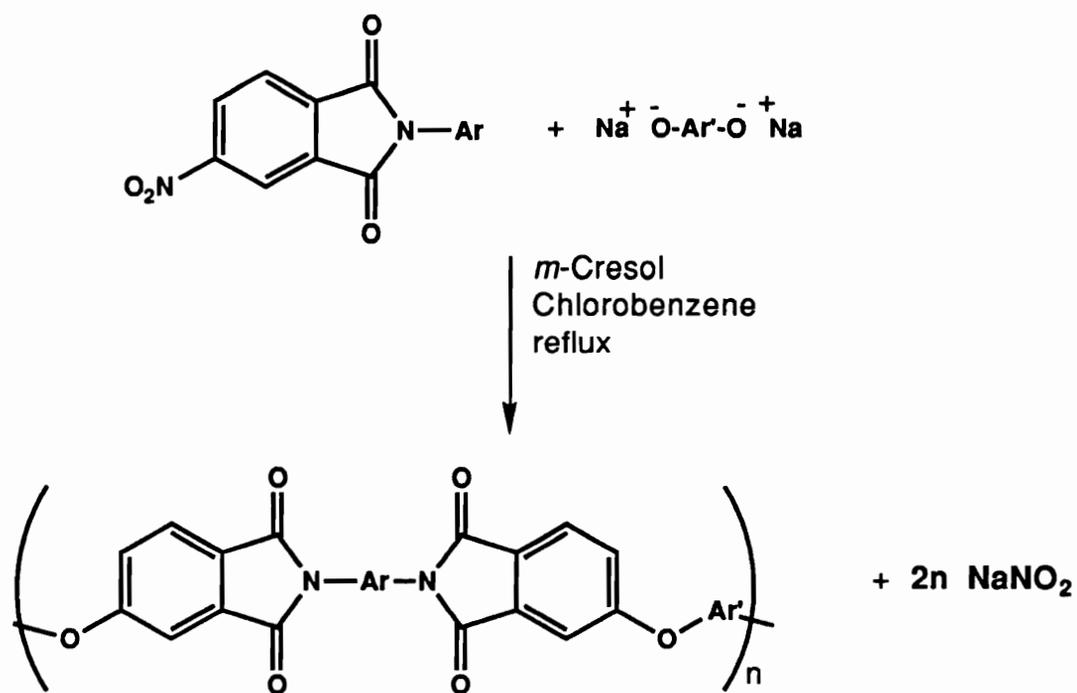
Scheme 2.2.6.1 Synthesis of Perfectly Alternating Segmented Imide Siloxane Copolymers
70,71

monomers under vacuum conditions at 200°C and then being deposited on the desired substrate. Unreacted monomers make up approximately 30-50% of the deposited films with poly(amic acid) oligomers comprising the remaining material. Further imidization and polymerization is only achieved by further heating the films and molecular weights are generally low.^{45,74} Much more effort appears to be needed before this can be considered a viable method.

2.2.7.3 Nucleophilic Aromatic Substitution

Nucleophilic aromatic substitution is a common method for the preparation of soluble, high molecular weight poly(arylene ether-ketone)s and poly(arylene ether-sulfone)s.⁷⁵⁻⁷⁹ An activated dihalide monomer, bisphenol, and potassium carbonate to generate the phenolate, the active nucleophile are used in these syntheses. Solvents such as N-methyl pyrrolidone or N,N-dimethylacetamide with toluene as the azeotroping agent cosolvent are employed. Poly(ether-imide)s can be prepared by a similar process using dinitro substituted bisimide monomers and pre-formed bisphenolates.^{52,80} A typical synthetic scheme is depicted in Scheme 2.2.7.3.1. Water removal is critical in these reactions in order to drive the reaction equilibrium to the right and prevent nitro as well as imide group hydrolysis. General Electric is believed to produce the commercially important Ultem dianhydride monomer by an indirect method utilizing nitro group displacement.⁸¹

Poly(ether-imide)s can alternatively be synthesized from preformed ether-linked monomers. Some common commercial examples are shown in Figure 2.2.7.3.1. Many researchers have also explored novel ether as well as carbonyl-containing monomers for polyimide synthesis. For example Davies and coworkers have synthesized new diether dianhydrides from common bisphenols and halophthalic anhydrides by two different aromatic nucleophilic substitution routes.⁸² In the first route, known as the Schwartz



Scheme 2.2.7.3.1 Poly(ether imide) Synthesis Via the Nucleophilic Aromatic Substitution Route ⁵²

Route,⁸³ aryl diether dianhydrides were prepared from bisphenols reacted with chloro- or fluorophthalic anhydride using a polar aprotic solvent at 185°C in the presence of a strong base. The formed dianhydride was then reacted with a diamine to form polyimide. This reaction sequence is shown in Scheme 2.2.7.3.2. Alternatively, a dihalo bisimide was formed and then reacted under nucleophilic aromatic substitution conditions to form polyimide as shown in Scheme 2.2.7.3.3. Hergenrother et. al. have also prepared a number of novel carbonyl-containing high molecular weight poly(ether-imide)s with moderately high T_g values by synthesizing novel ether-dianhydrides under nucleophilic aromatic substitution conditions.^{84,85} Some properties of these ether-containing polyimides are shown in Table 2.2.7.3.1.

2.2.7.4 Diels-Alder Polymerization

The Diels-Alder reaction has been used for the preparation of polyimides.⁸⁶⁻⁸⁸ Polyimides can be formed where the imide moiety is preformed in the monomers and polymerization occurs via the Diels-Alder reaction followed by an aromatization step. Low molecular weight polymers with incomplete aromatization are obtained by this method. Alternatively, a phenylated nucleus with anhydride terminated groups is initially formed which subsequently reacts with diamines to afford polyimides. This method provides enhanced solubility and higher molecular weights and complete aromatization is obtained since the aromatization step takes place prior to polymerization.

2.2.7.5 Syntheses Utilizing Diamine Derivatives-Diamine Dihydrochlorides

Diamine dihydrochlorides have been used in the synthesis of polybenzothiazoles⁸⁹ and polybenzoxazoles^{90,91} in polyphosphoric acid; which upon heating the

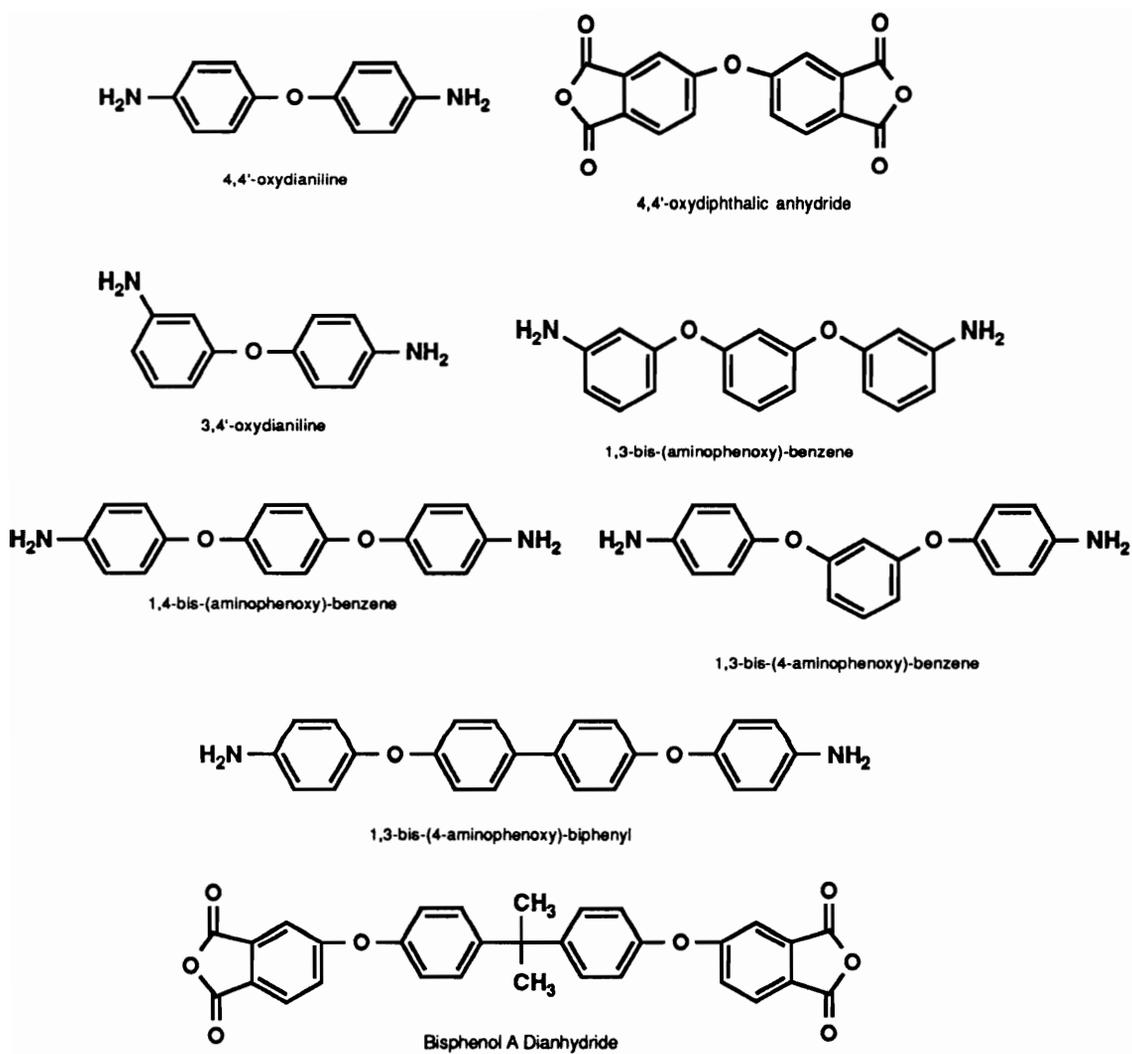
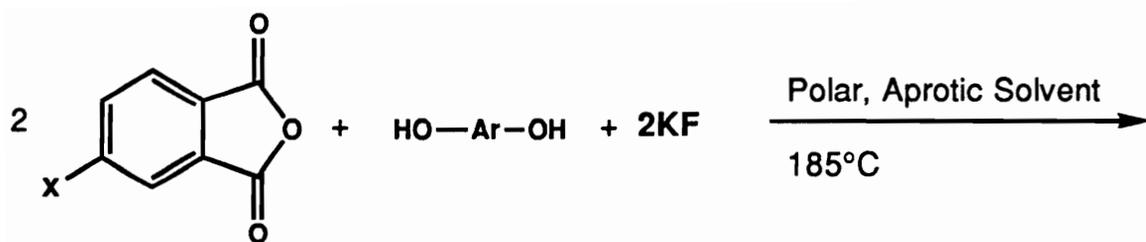
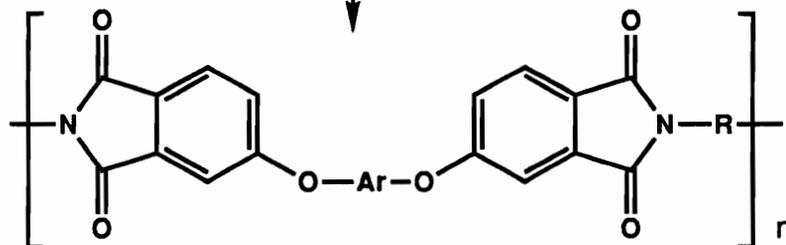
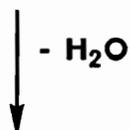
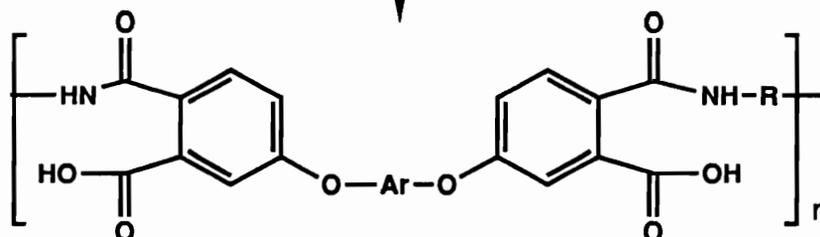
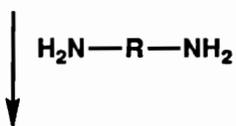
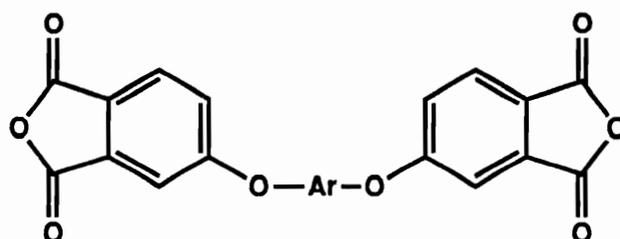


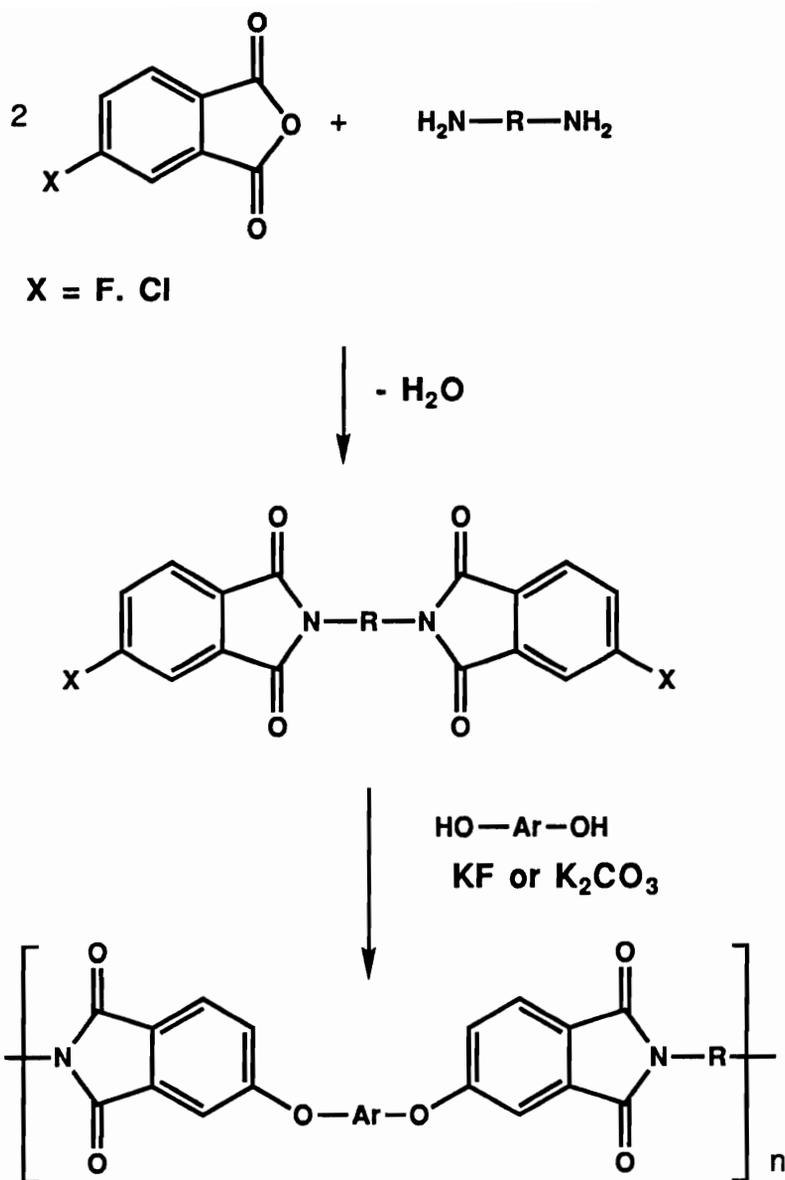
Figure 2.2.7.3.1 Commercially Available Monomers Containing Ether Connecting Groups



X = F, Cl

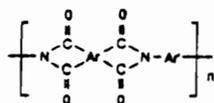


Scheme 2.2.7.3.2 Schwartz Route for Synthesizing Poly(ether imide)s⁸³



Scheme 2.2.7.3.3 Reverse Schwartz Route for Synthesizing Poly(ether imide)s⁸²

Table 2.2.7.3.1 Properties of Polyimides Containing Carbonyl and Ether Connecting Groups ⁸⁵



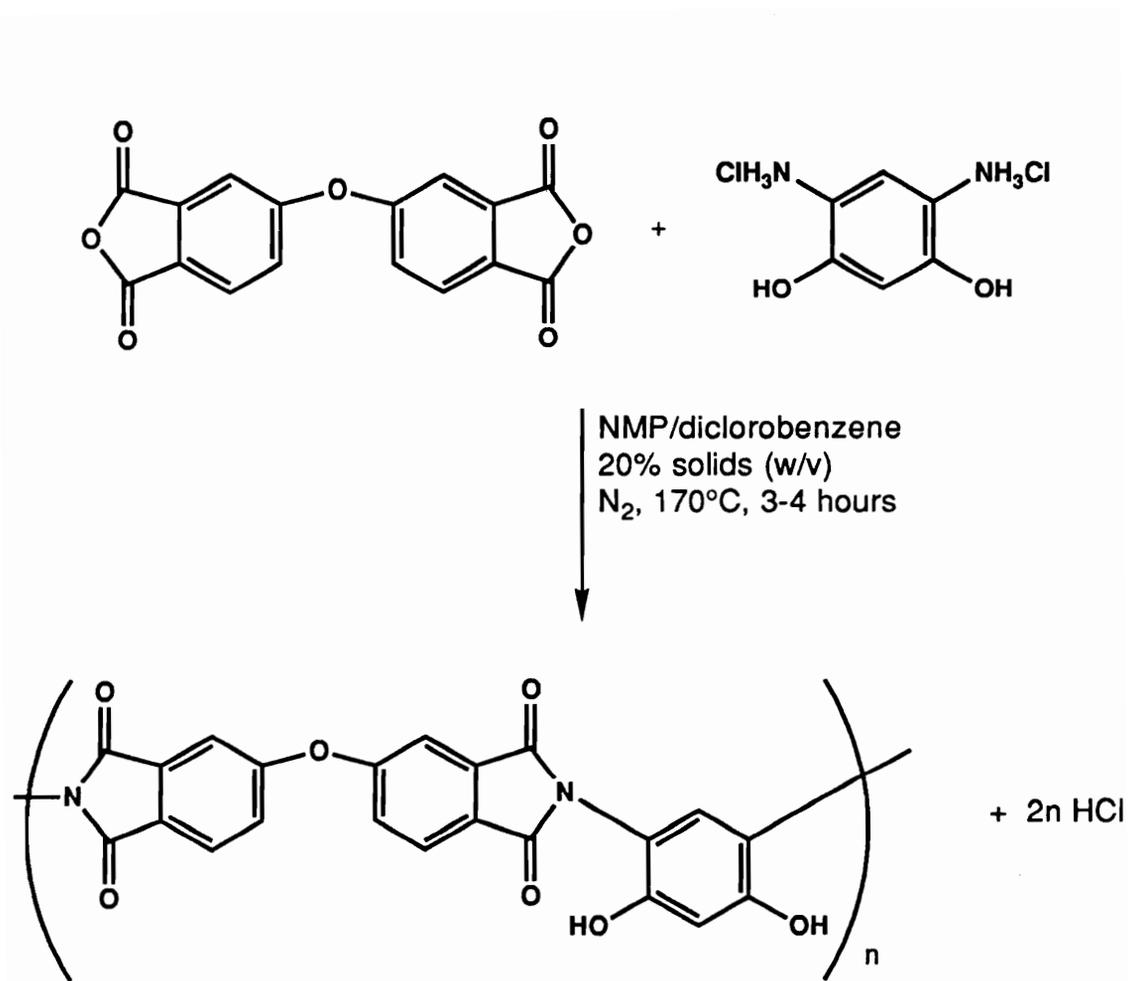
Polyimide designation	Ar	Ar	Polyimide acid η_{inh} (dL/g)	Polyimide	
				T_g (°C)	T_m (°C)
BTDA/1,3-B3ABB			0.67	207	ND*
BTDA/1,3-BABB			0.81	222	350
BTDA-2,6-BABN			0.42	246	424
BTDA/1,3-B3APBB			0.55	164	ND
BTDA/1,4-B4APBB			0.85	222	ND
BTDA/BAPO			0.64	258	ND
BPDA/1,3-BABB			1.25	222	ND
BPDA/1,4-BABB			0.41	245	414
SDA/1,3-BABB			1.10	208	ND
6FDA/1,3-BABB			1.40	236	ND
9,9-FDA/1,3-BABB			0.84	235	ND
9,9-FDA/1,4-BABB			1.28	253	ND

*ND-not detected.

dihydrochloride salt dissociates yielding hydrogen chloride gas and diamine which then reacts with an aromatic dicarboxylic acid to form polymer. Until recently, there have been no reports of dihydrochlorides being used in polyimide synthesis. Moy⁹² found that high T_g polyimides containing pendant phenolic hydroxyl groups could be synthesized in high molecular weight via a one-step solution polymerization of the dihydrochloride salt of 4,6-diaminoresorcinol with various dianhydrides. Polymerizations proceeded via initial dissociation of diaminoresorcinol dihydrochloride to hydrogen chloride gas and diaminoresorcinol, followed by rapid dissolution of diaminoresorcinol and polymerization with the dianhydride monomer to afford fully cyclized polyimides. The synthesis of polyimides utilizing dihydrochlorides is shown in Scheme 2.2.7.5.1. Amine hydrochlorides are generally easier to purify than their analogous free amines and have longer shelf lives and greater stability than their free bases.

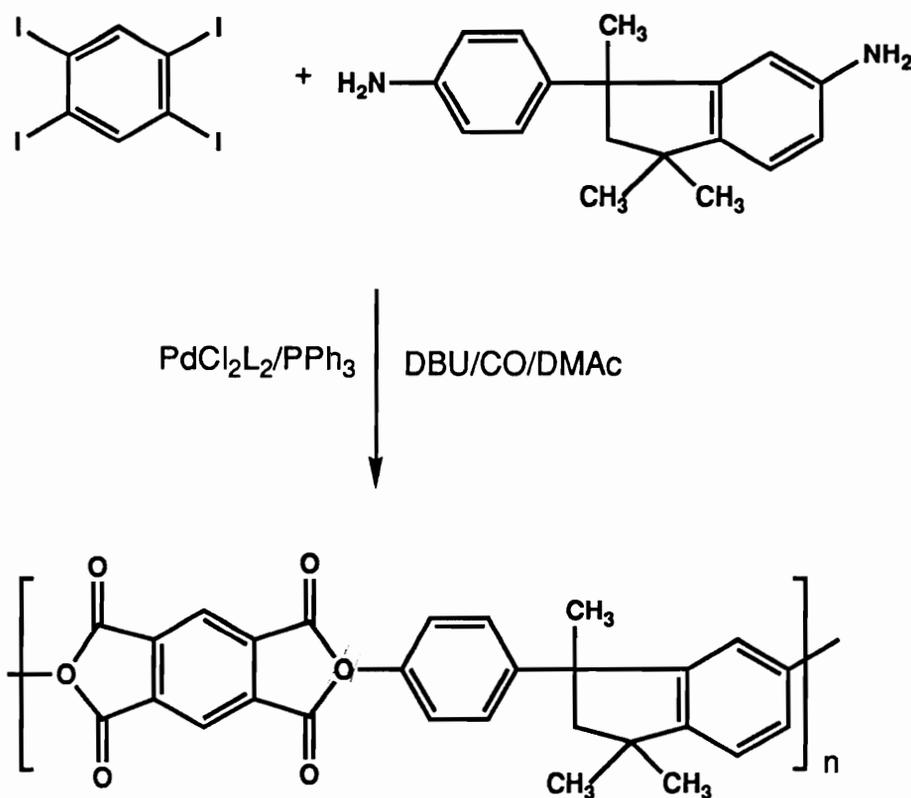
2.2.2.8 Palladium-Catalyzed Polymerizations

A method of preparing polyimides, polyamides, and poly(amide imide)s by a palladium-catalyzed coupling reaction of diaryl halide monomers was very recently reported.⁹³⁻⁹⁶ Schmitz and coworkers reported the synthesis of soluble, rigid-rod polyimides via palladium-catalyzed polycondensation of 2,5-didodecylbenzene-1,4-diboronic acid and 3,6-diphenyl-*N,N'*-bis(4-bromo-2,5-didodecylphenylene) pyromellitic diimide. High molecular weight polyimides were obtained to good yields.⁹⁶ More recently, Perry and Turner have synthesized polyimides and poly(amide imides) by a palladium-mediated carbonylation and condensation of diido imide monomers and aromatic diamines.⁹³⁻⁹⁵ For example, tetraido benzene was reacted with aromatic diamines under CO pressures of approximately 95 psi and in the presence of a palladium catalyst [bis(triphenylphosphine) palladium (II) chloride] at 115°C as shown in Scheme 2.2.2.8.1.



Scheme 2.2.7.5.1 Poly(hydroxy imide) Synthesis using the Dihydrochloride Salt of 4,6-Diaminoresorcinol ⁹²

High molecular weight polyamides and poly(amide imides) could be prepared; however, polyimides were lower in molecular weight due to unoptimized reaction conditions. This route has the advantage of making fully imidized polymers without using hydrolytically sensitive monomers.



Scheme 2.2.2.8.1 Palladium-Catalyzed Route to Polyimides⁹³⁻⁹⁵

2.3 POLYIMIDE PROPERTIES

2.3.1 Molecular Weight Control

In addition to modifying the structure of polyimides to increase their solubility and processability, controlling the molecular weight is another possibility. Three areas that are worth considering are: limiting the molecular weight of linear, thermoplastic polyimides,^{97,98} low molecular weight addition (thermosetting) imide oligomers with reactive endgroups, which may be subsequently reacted to yield a 3-dimensional network structure,⁹⁹ and blending high molecular weight polymer with low molecular weight oligomer terminated with reactive endgroups, producing semi-interpenetrating polymer networks.

The second approach is the focus of this research and will be discussed in greater detail in a following section of this literature review.

There is a general dependence between the molecular weight, MW, and the physical properties of a polymer.^{100,101} The relationship between the *number* average molecular weight on polymer properties such as modulus, tensile strength, density and the glass transition temperature is shown in Figure 2.3.1.1. A minimum molecular weight, near the onset of entanglements, is required in order to attain good physical and mechanical properties for linear polymers. For many commercial step growth thermoplastic polymers, this minimum molecular weight is approximately 15,000 to 30,000 grams per mole. Upon reaching this molecular weight, a plateau is reached and increasing the molecular weight only has a small effect on polymer properties. This relationship has been approximated by:

$$\text{Polymer Property} = \text{Polymer Property at infinite MW} - K \langle M_n \rangle^{-1}$$

where K is a constant. Decreasing the concentration of endgroups is also considered important.

Many rheological properties such as melt viscosity, increase with increasing *weight*

average molecular weight. Therefore, controlling molecular weight is critical in promoting processability. The relationship between melt viscosity and molecular weight is illustrated in Figure 2.3.1.1. The molecular weight dependence of the melt viscosity exhibits two distinct regions, depending on whether the chains are less than or greater than the entanglement molecular weight. Below the entanglement molecular weight, the melt viscosity is given by $\eta = K \langle M_w \rangle^{1.0}$ and the polymer exhibits inferior physical properties. The melt viscosity is given by $\eta = K' \langle M_w \rangle^{3.4}$ above the critical molecular weight or entanglement molecular weight. Above the entanglement molecular weight, increasing the molecular weight only modestly increases the polymer properties; however, the melt viscosity increases tremendously. This results in decreased processability in general.

The use of reactive endgroups on polyimides chains, especially amine, decreases the thermal stability of polyimides tremendously, as can be seen from the curves in Figure 2.3.1.2. Polyimide chains endcapped with excess dianhydride (A) or excess diamine (B), are much less thermally stable as compared to an equimolar stoichiometry (C).¹⁰² Amine endgroups may potentially react under certain conditions, such as a subsequent process step, which destabilizes melt flow.¹⁰²

Molecular weight control can be achieved by the incorporation of a monofunctional reagent, such as phthalic anhydride or aniline, to obtain nonreactive phthalimide endgroups.¹² The molecular weight is generally controlled by offsetting the stoichiometry in an exact way as determined by the Carothers equation.¹⁰³ Alternatively, imide oligomers may be endcapped with reactive endgroups which may be subsequently reacted to form a network structure. An overview of thermosetting polyimides will be presented in a following section.

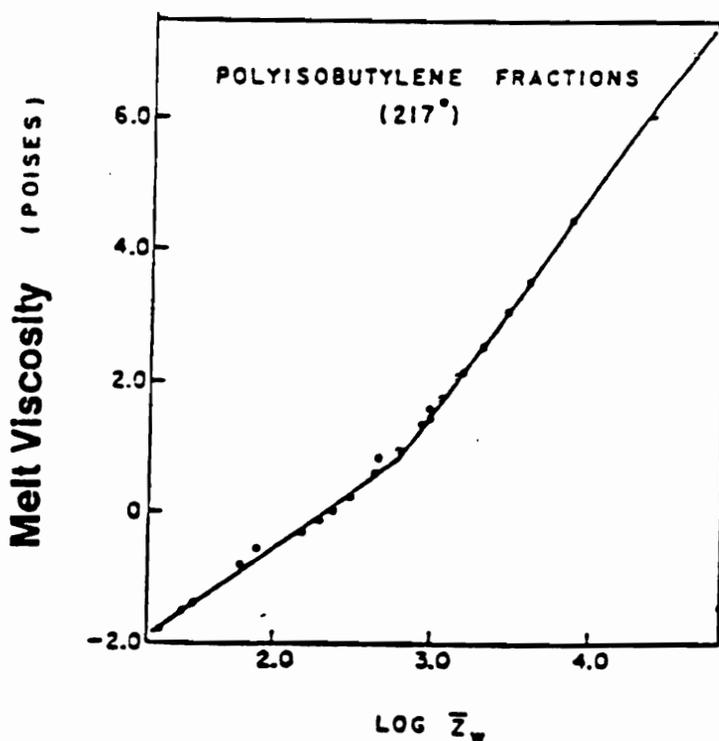
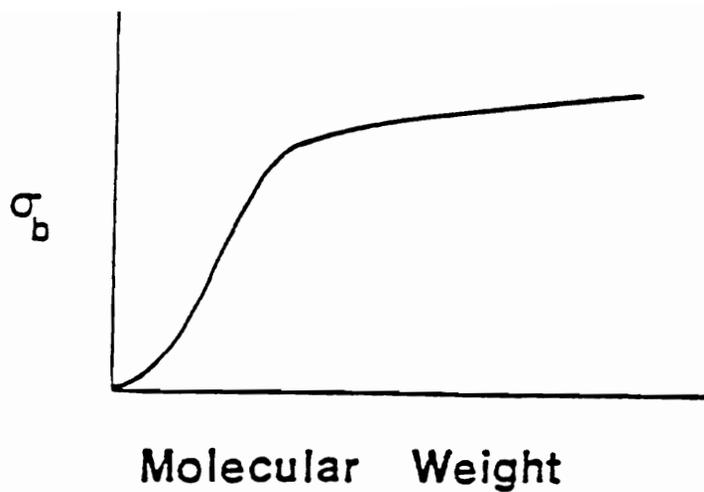


Figure 2.3.1.1 Influence of Molecular Weight: Influence of Number Average Molecular Weight on Tensile Stress (upper) and the Influence of Weight Average Molecular Weight on Melt Flow and Processability (lower) ^{100,101}

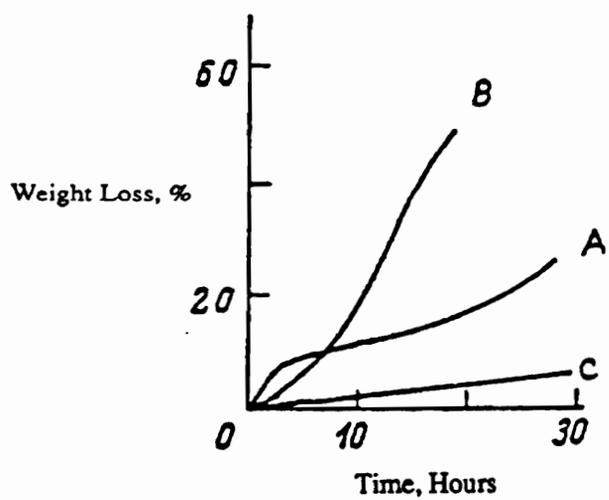


Figure 2.3.1.2 Influence of Endgroups on Thermal Stability At 400°C: (A) Anhydride, (B) Amine, (C) Equimolar Stoichiometries Used ¹⁰²

2.3.2 Insolubility/Infusibility

One of the most common explanations for the insolubility and infusibility of many polyimides is crosslinking or network formation.^{45,104,105} The crosslinks are formed by intermolecular imide formation or form intermolecular imine formation arising from the condensation of endgroups with imide carbonyl groups. Linear polyimides are also known to undergo crosslinking reactions; however, these systems contain moieties or connecting groups that can easily form free radicals at high temperatures or upon exposure to radiation.¹⁰⁶⁻¹⁰⁸ Methyl and methylene groups have readily shown the tendency to form crosslinks during thermal imidization. However, the existence of soluble polyimides seriously challenges the crosslinking theory as a general explanation of polyimide insolubility.

Extreme chain rigidity or orientation has also been used to explain the insolubility of many polyimides. For example, Kapton (structure shown in Figure 2.3.2.1) is soluble in sulfuric acid, but insoluble in common organic solvents. If the polyimide can be solubilized, then it is argued that it cannot be crosslinked. In fact, a comparison of molecular weights of fully cyclized Kapton dissolved in concentrated sulfuric acid with soluble poly(amic acid)s indicate practically no change in molecular weights or dimensions occurred during the cyclization process.^{109,110} This seems to suggest that polymer chain rigidity is responsible for insolubility.

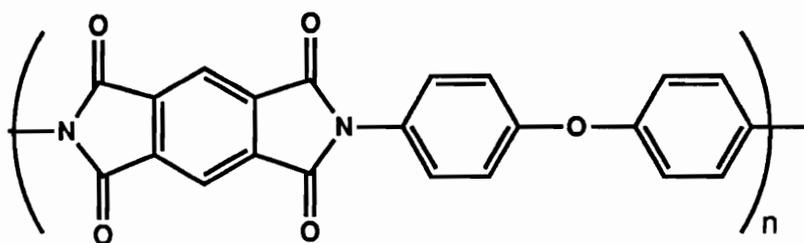


Figure 2.3.2.1 Repeat Unit of Kapton

Polyimide insolubility is also thought to arise from the formation of charge transfer complexes.^{111,112} High and low regions of electron density may exist in some polymer backbone due to resonance and inductive effects. When these regions align in adjacent polyimide chains, charge transfer complexes develop giving rise to insolubility and the characteristic yellow color of many insoluble polyimides.

A number of strategies have been employed successfully to improve the solubility and processability of polyimides. For example one strategy involved the incorporation of flexible segments to reduce chain rigidity. These segments include ether, sulfone, perfluoro, carbonyl, alkyl and phenylphosphine oxide moieties. These structures provide a kink or bend to lower rigidity in the polymer chain. Several monomers utilizing these flexible linkages are illustrated in Figure 2.3.2.2. Gains in flexibility are sometimes offset by decreases in thermal stability. Combinations of these connecting groups readily afford soluble polyimides with T_g 's in excess of 250°C; however, incorporation of these flexible groups does not always impart solubility. For example, LARC-CPI contains both ether and carbonyl connecting groups,¹¹³ and yet it is still semicrystalline in nature. The repeat units of some semicrystalline polyimides with flexible connecting groups are shown in Figure 2.3.2.3.

Fluorine containing polyimides generally exhibit improved processability without sacrifice in thermal stability. The most common fluorine containing polyimides are derived from monomers with the hexafluoroisopropylidene or 6F group.¹¹⁴ However, there are numerous soluble fluorine containing polyimides based on a wide variety of fluorine based monomers.¹¹⁵⁻¹¹⁸ The polyimides derived from the 3F diamine containing a pendant phenyl group has proven to provide very soluble polyimides with T_g 's in excess of 400°C.¹¹⁹ Repeat units of some soluble fluorine based polymers are illustrated in Figure 2.3.2.4.

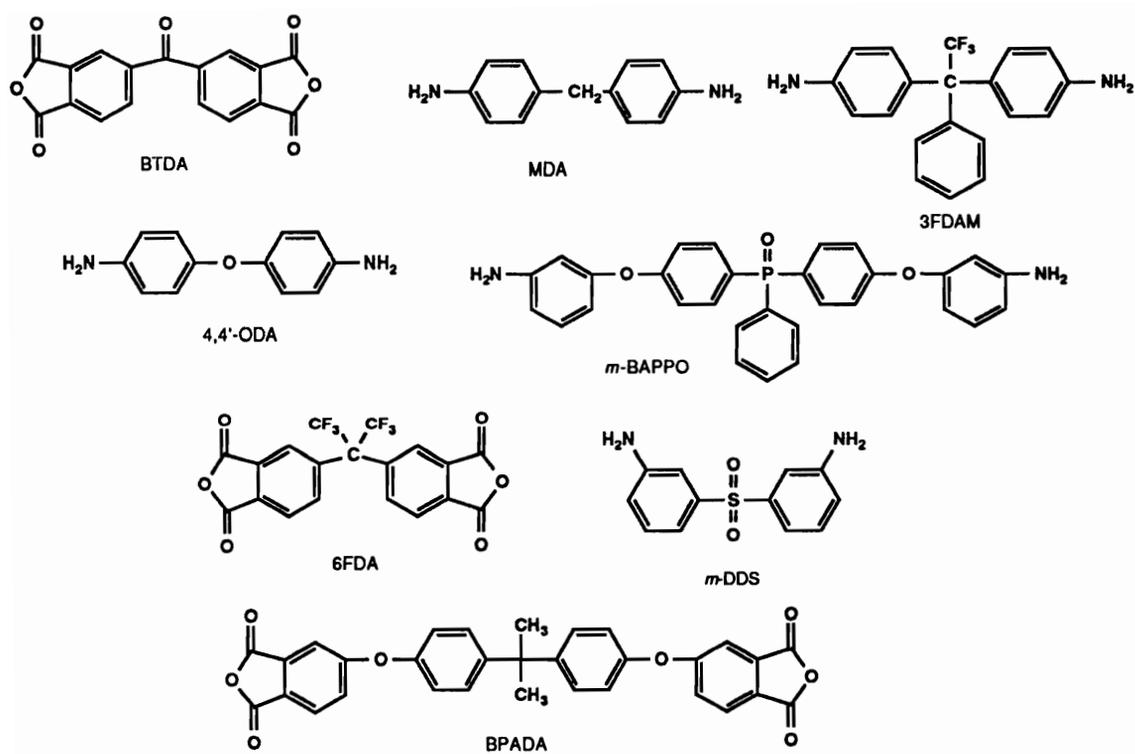
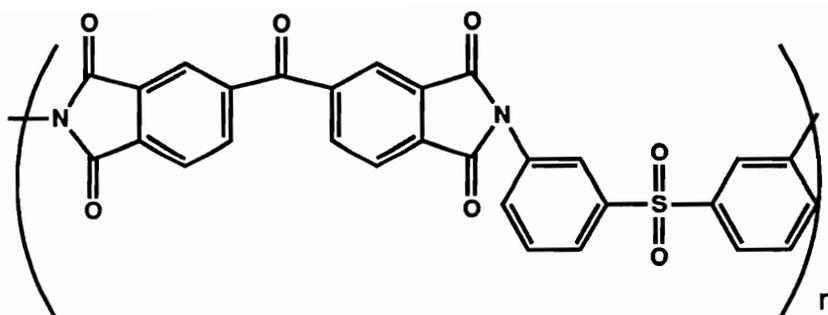
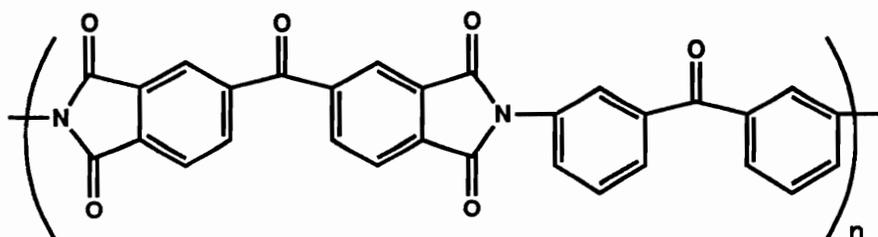


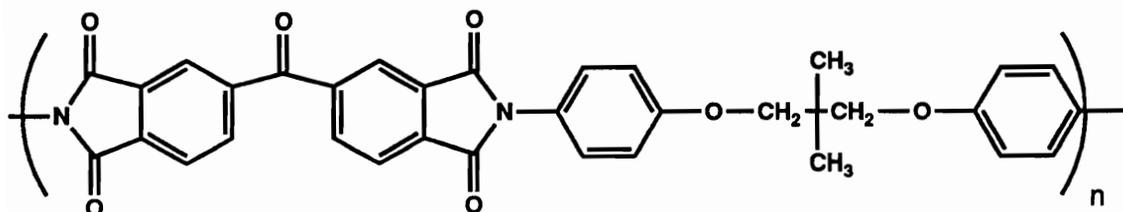
Figure 2.3.2.2 Monomers Containing Flexible Connecting Groups



BTDA/3,3'-DDS Tg = 265°C



LARC-TPI Tg = 260°C



BTDA/1,3-bis(4-aminophenoxy)-2,2-dimethylpropane Tg = 230°C

Figure 2.3.2.3 Semicrystalline Polyimides Containing Flexible Connecting Groups

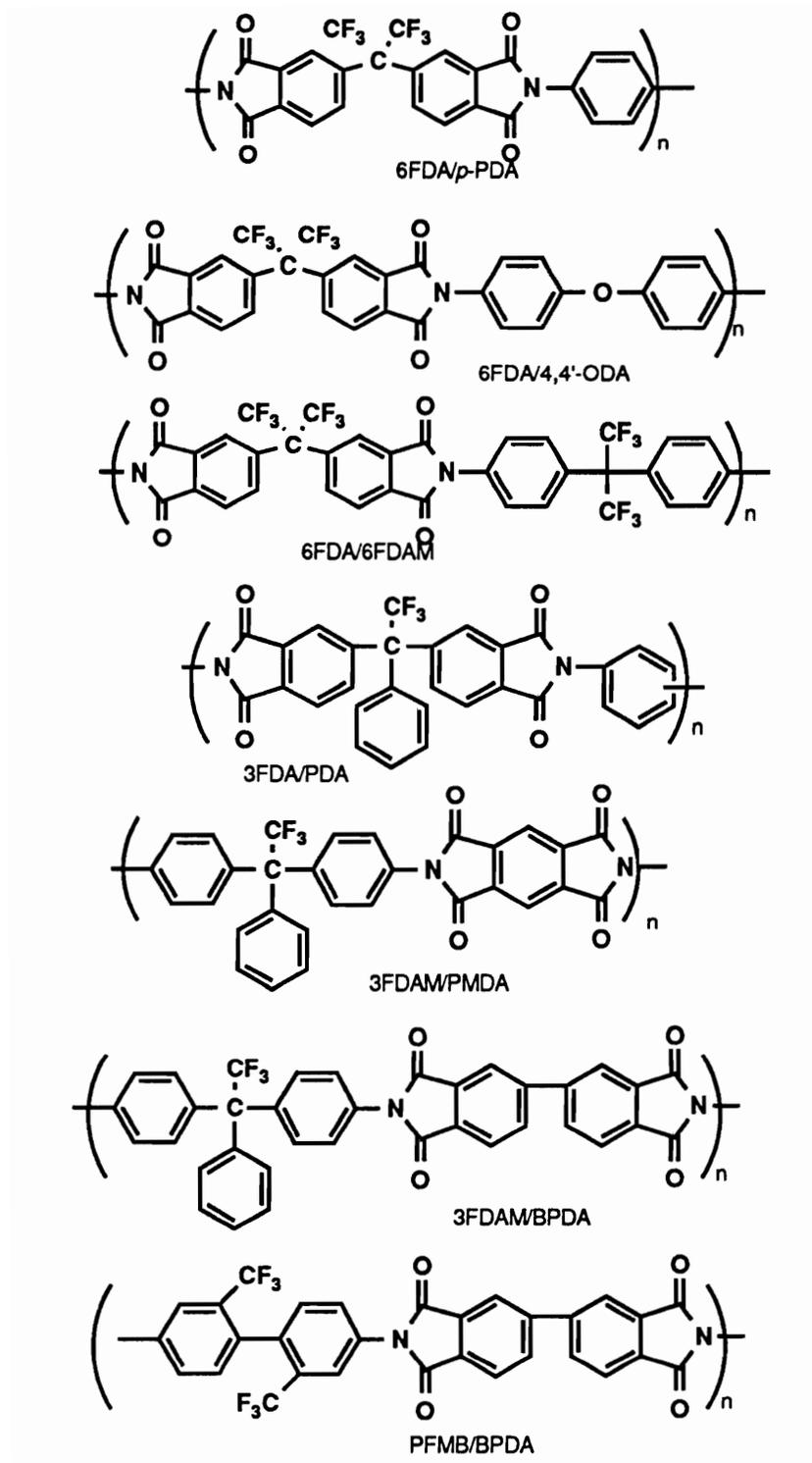


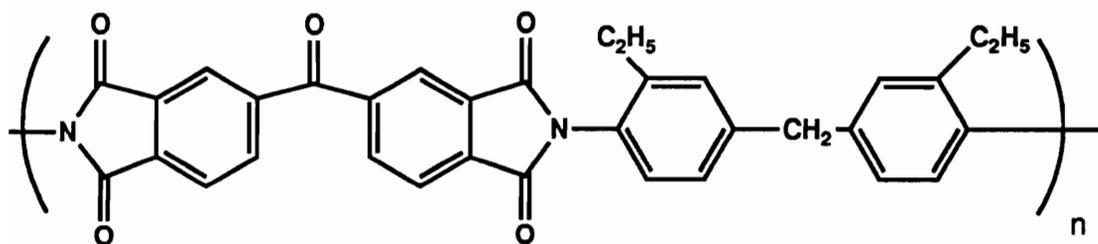
Figure 2.3.2.4 Fluorine Based Soluble Polyimides ^{48,115,116,118}

As illustrated in the previous section, monomers containing pendant groups tend to greatly increase the solubility of polyimides. Methyl substitution has been demonstrated to be effective in the synthesis of soluble polyimides. BTDA has been polymerized with methyl-substituted diamines to give soluble polyimides.¹²⁰ Repeat units are shown in Figure 2.3.2.5. Pendant phenyl groups placed along the backbone of polyimide chains usually enhances polymer solubility. For example, 4,4'-diaminotriphenylamine imparts solubility to polyimide systems.^{121,122} A diphenyl thiophene based diamine has also been successfully polymerized with various dianhydrides to produce high T_g , soluble polyimides.¹²³

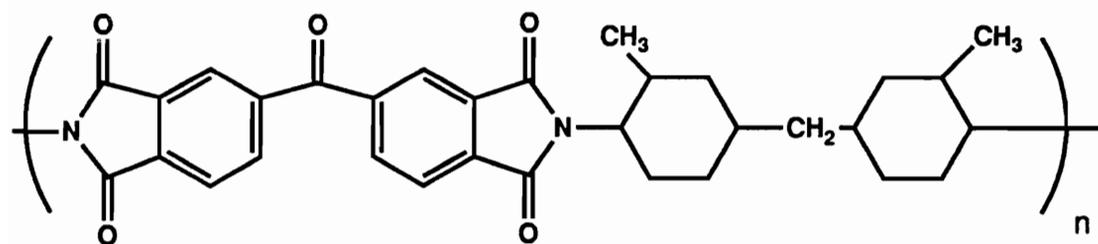
The fluorene substituent is another important group which has recently been incorporated in polyimides displaying very high T_g 's and excellent solubility. The diamine 9,9-bis-(4-aminophenyl)-fluorene (FDA) is currently available commercially, and Sillion and coworkers have reported T_g 's over 360°C and solubility in amide solvents for polyimides synthesized from BTDA and FDA.¹²⁴ Synthetic variations of FDA have also appeared such 9,9-bis[4-(*p*-aminophenoxy)phenyl] fluorene, 2,7-diaminofluorene, N-phenyl-3,3-bis[4-(*p*-aminophenoxy)phenyl]phthalimidine, and 2,7-diamino-9-fluorenone.^{125,126} Polymer repeat units and T_g 's based on several pendant-substituted monomers is shown Table 2.3.2.1.

Several attempts to design dianhydrides for improved polyimide solubility have focused on nonconventional systems. Polyimides based on 1,6,7,12-tetrakis(4-*tert*-butyloxy)-3,4:9,10-perlenedianhydride,¹²⁷ bis(phenylmaleic anhydride),^{128,129} 2,2'-dichloro-4,4',5,5'-benzophenone tetracarboxylic dianhydride¹³⁰ and spirobisindane dietheranhydride¹³¹ monomers have been successfully synthesized are indeed soluble in organic solvents. Dianhydrides are illustrated in Figure 2.3.2.6.

2.3.3 Hydrolytic Stability/Water Adsorption



BTDA/bis(4-amino-3-methylcyclohexyl) methane



BTDA/bis(4-amino-3-ethylphenyl) methane

Figure 2.3.2.5 Methyl-substituted Benzophenone Based Polyimides ¹²⁰

Table 2.3.2.1 Pendant Fluorene Based Polyimides ¹²⁴⁻¹²⁶

Polyimide	T _g (°C)
	> 360
	351
	291
	289
	292

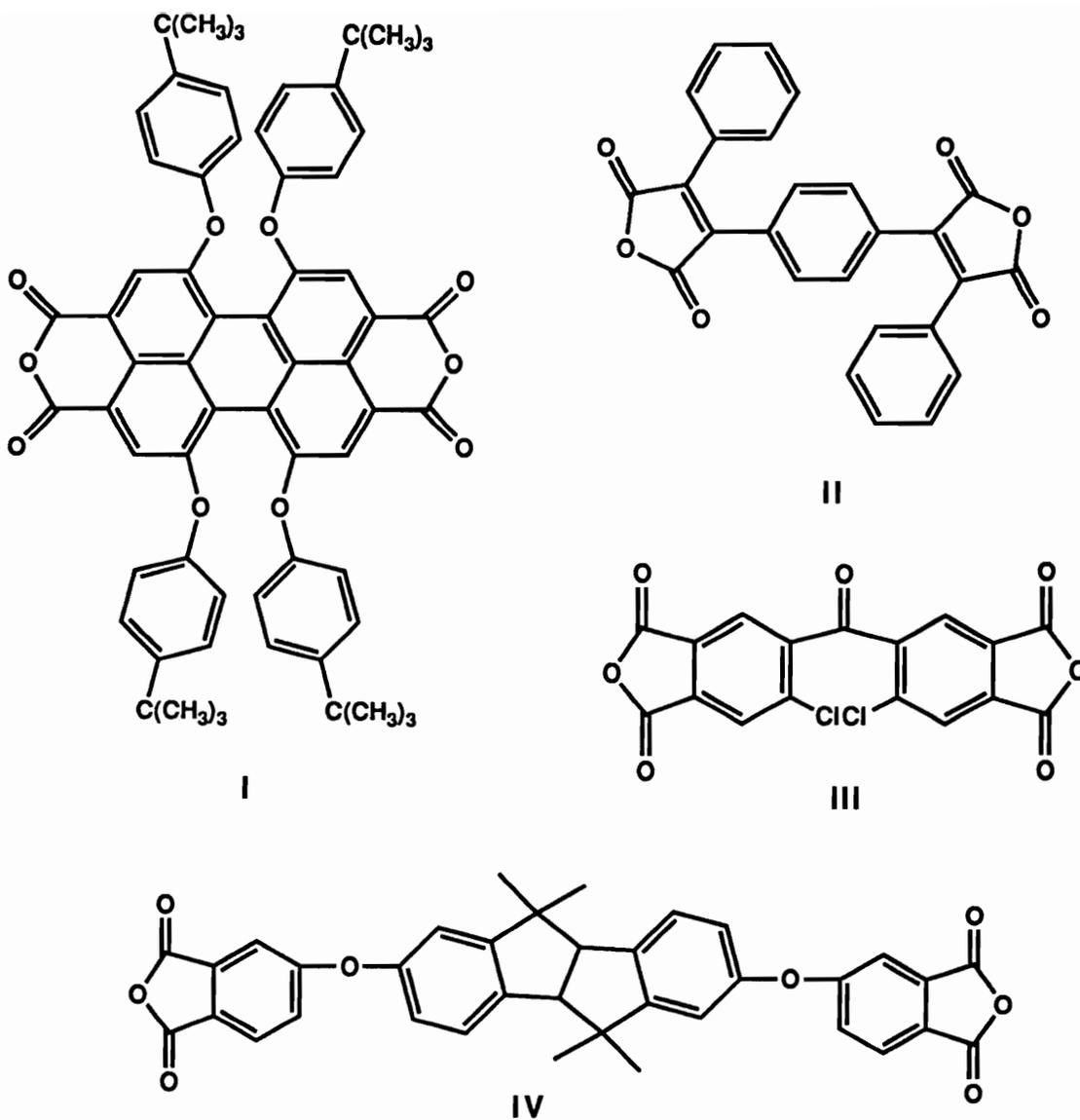


Figure 2.3.2.6 Dianhydrides Giving Soluble Polyimides: (I) 1,6,7,12-Tetrakis(4-*tert*-butyloxy)-3,4,9,10-perylene dianhydride, (II) Bis(phenylmaleic anhydride), (III) 2,2'-Dichloro-4,4',5,5'-benzophenone Tetracarboxylic Dianhydride, and (IV) Spirobisindane Dietheranhydride ¹²⁷⁻¹³¹

Polyimides are known for their stability towards acid hydrolysis. Kapton, for example, can be dissolved in concentrated sulfuric acid for extended periods of time with no apparent decrease in molecular weight.^{109,110} However, strong aqueous bases will readily hydrolyze the imide moiety.¹³²

Polyimides are generally considered to be hygroscopic materials. In fact, two imide rings can reportedly hydrogen bond up to seven water molecules.^{133,134} Water absorption may be as high as several percent of the polyimide's weight; Kapton absorbs as much as 3 to 4 percent by weight.^{135,136} This water uptake can have detrimental effects on the mechanical properties of properties.¹³⁷

2.3.4 Gas Transport Properties

The potential use of polyimides as gas separation membranes on an industrial scale have recently spawned many investigations in the gas transport properties of polyimides.¹³⁸⁻¹⁴⁴ Significant energy savings could be realized if effective gas separations could be performed via membrane technology as opposed to expensive cryogenic processes. Separation of carbon dioxide from methane, nitrogen purification, and recovery of hydrogen gas from industrial processes could be potential applications.

Several factors contribute to the separation of gases by polyimides. These include: (1) total free volume (2) distribution of free volume (3) intersegmental resistance to chain motions, and (4) intrasegmental resistance to chain motions.¹⁴⁴ Generally, increasing the free volume increases gas solubility (gas permeation), but lowers selectivity among penetrant gases (separation is lowered).¹⁴³ The effect of fractional free volume on the permeability of CO₂ for several fluorine containing polyimides is shown in Figure 2.3.4.1. The fractional free volume agrees well with permeability for the *para*-connected 6FDA- and 6FpDA-based polyimides. The highest permeability is seen for the open 6FDA-6FpDA and the lowest permeability in the most densely packed BTDA-6FpDA.¹⁴⁴

The polyimides based on monomers containing the hexafluoro isopropylidene (i.e. 6FDA) tend to give the best overall separation (highest permeation and selectivity) of gases.¹⁴²

Another recent development in gas separation using polyimide membranes has been the synthesis of polyimide-polydimethylsiloxane copolymers.^{139,145} Increasing the siloxane content generally improves the gas permeability. The increase in permeability of imide-siloxane copolymers is shown in Figure 2.3.4.2. However, the increase permeability is not simply a linear relationship with siloxane content. Instead, the resulting polyimide morphologies play an important role in the permeation behavior which is correlated to the copolymer structure.^{138,139}

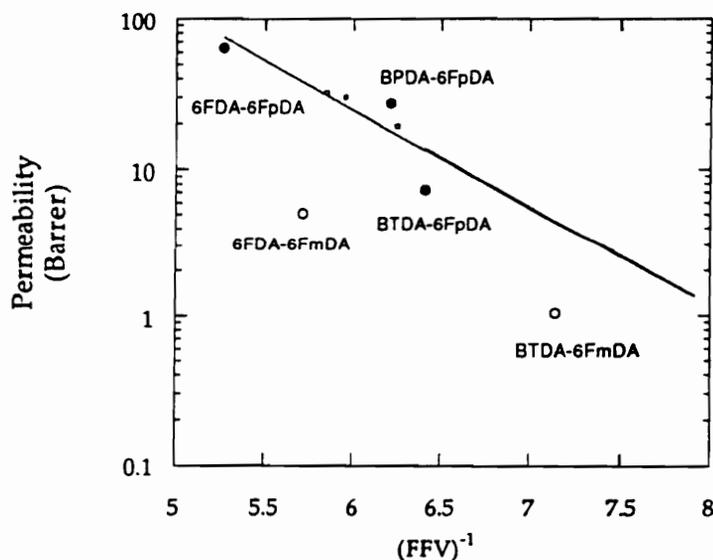


Figure 2.3.4.1 Effect of Fractional Free Volume on the Permeability of CO₂ for Several Fluorine Containing Polyimides at 10 atm and 35°C¹⁴⁴

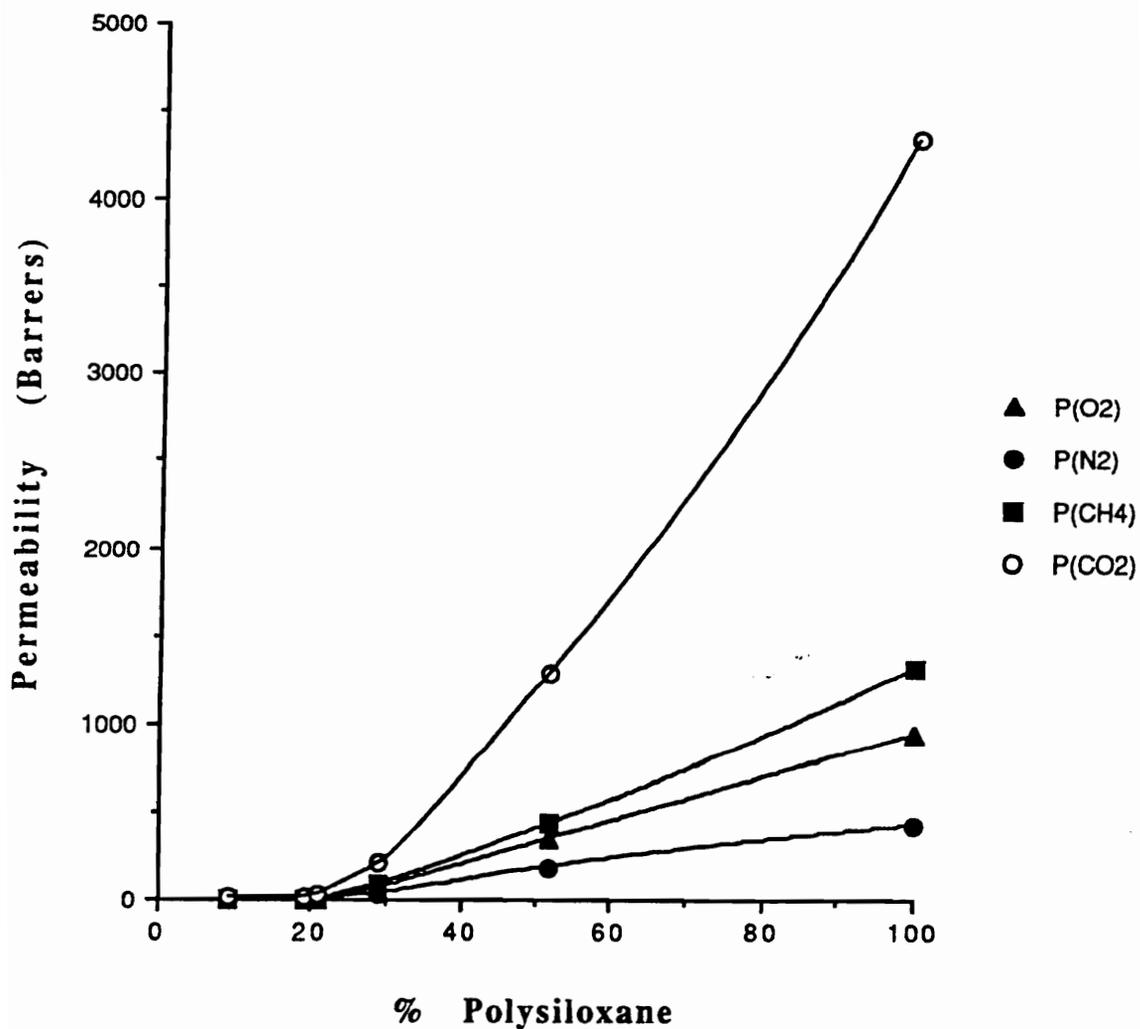


Figure 2.3.4.2 Influence of Siloxane Content on Permeability for Imide-siloxane Copolymers ^{138,139}

2.4 PROPERTIES OF PHOSPHORUS CONTAINING POLYIMIDES

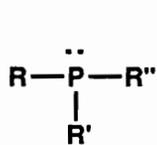
2.4.1 Introduction

The incorporation of different forms of phosphorous into otherwise all organic polymers has been of interest to polymer scientists for many years primarily due to the enhanced fire-resistance it imparts.¹⁴⁶⁻¹⁵¹ Several forms of organophosphorus links have been available for chemists to utilize; however, the phosphine oxide based polymers exhibit superior thermal and hydrolytic stability over for example, the phosphines, phosphites and phosphine sulfides. In fact, the P-C bond is more stable than the C-C bond linkage in terms of resistance to hydrolysis. Phosphine oxide based polymeric systems offer excellent thermal stability, improved solubility, and the ability to complex with selective metals.¹⁵²⁻¹⁵⁵ Table 2.4.1.1 illustrates the most common form of organophosphorus compounds useful to polymer synthesis. Phosphorus in its lowest oxidation state, the phosphine, to its high oxidation state, the phosphate, have all been incorporated into polymeric systems. As would be expected, those polymers with phosphorus in its lower oxidation states (lone pair of electrons on phosphorus) have been found to be more prone to oxidation, as are the lower molecular weight analogs.

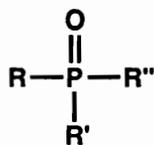
2.4.2 Phosphorus Containing Polyimides

Phosphorus has been successfully incorporated into many different monomers including diamines and dianhydrides for use in polyimide synthesis. Monomers of the generic type illustrated in Figure 2.4.2.1 have been used in synthesis of polyesters, polyamides, polycarbonates, poly(arylene ether)s, polyimides, and polybenzoxazoles. For example, the incorporation of bis(4-carboxyphenyl)phenyl (or methyl) phosphine oxide into high performance thermally stable polybenzoxazoles of moderate molecular weight by solution polycondensation techniques was successful.^{156,157}

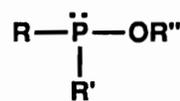
Table 2.4.1.1 Types of Organophosphorus Moieties



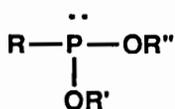
Phosphine



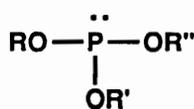
Phosphine Oxide



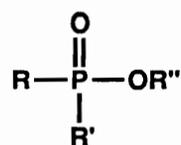
Phosphinite



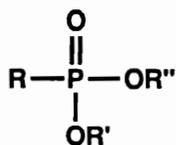
Phosphonite



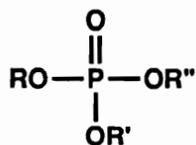
Phosphite



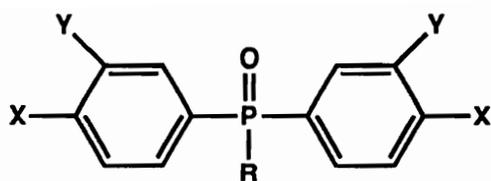
Phosphinate



Phosphonate



Phosphate



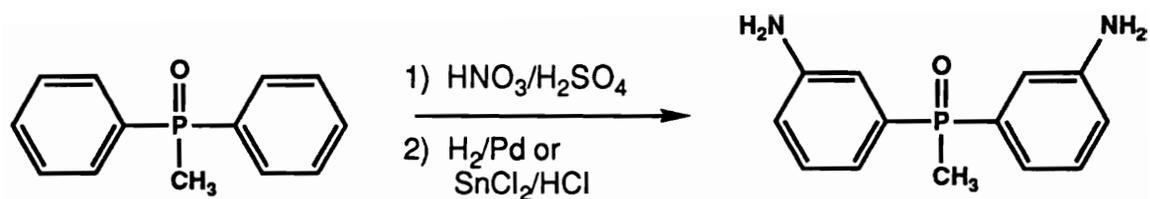
X = H, F, OH, NH₂, OPhNH₂, COOH
 Y = H, OH, NH₂, COOH, CO
 R = CH₃, or phenyl

Figure 2.4.2.1 Phosphine Oxide Containing Monomers

The incorporation of phosphorus into polyimides is an area where the enhanced solubility and thermal stability characteristics observed due to the bulky phosphine oxide moiety could be widely exploited. As discussed earlier in this literature review, the insolubility/intractability and processability of polyimides can be greatly enhanced by the introduction of bulky pendant groups such as a triphenylphosphine oxide group in the polymer backbone. Diamine and dianhydride monomers incorporating the phosphine oxide moiety will be discussed.

The first reported preparation of a diamine of the aryl phosphine oxide family was in 1963^{158,159} by the nitration of diphenylmethylphosphine oxide followed by reduction to the diamine. This procedure gave good yields for the methyl substituted phosphine oxide as shown in Scheme 2.4.2.1; however, polyimides were not reported until much later.¹⁶⁰ Nevertheless, this diamine has recently been synthesized by an alternate route¹⁶¹ and has successfully been incorporated into high molecular weight polyimides.

Diamine functional phenyl substituted phosphine oxides were less mentioned in the literature than any other phosphine oxide containing monomer, due to the nature of P-C bond formation. A low yield route was performed by Schiennz in 1971 yielding bis(3-aminophenyl)phenyl phosphine oxide. In addition, in 1971, Russian scientists claimed to

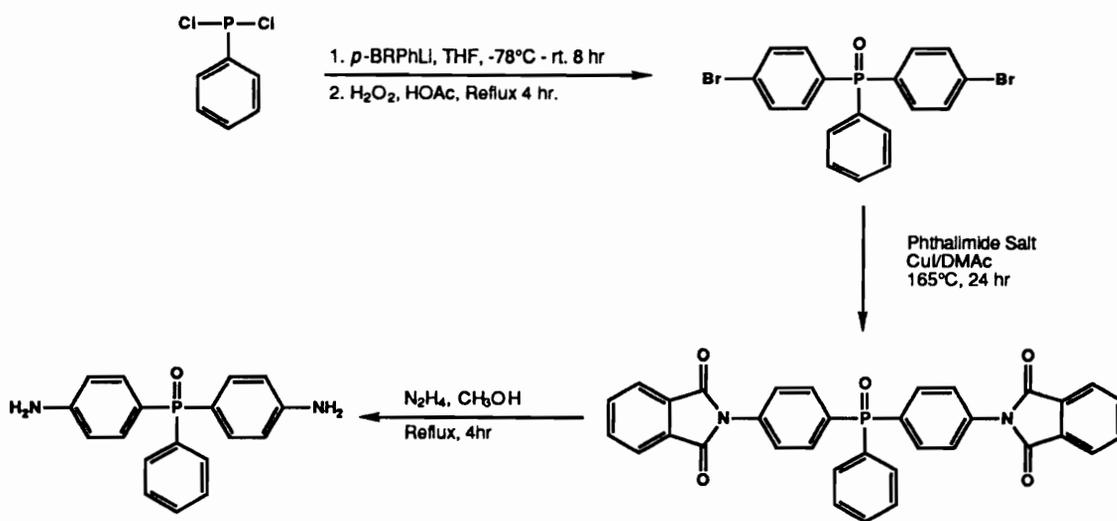


Scheme 2.4.2.1 Bis(3-aminophenyl) Phenyl Phosphine Oxide Synthesis ^{158,159}

have synthesized the same diamine via a simple one step route.^{162,163} In the presence of excess aniline hydrochloride at high temperatures, phenylphosphonic dichloride was suggested to undergo a Friedel Crafts type reaction, affording monomer grade diamine in low yields after recrystallization from ethanol. However, the polyimides prepared from such diamines^{164,165} were brittle and much less thermally stable than other polyimides synthesized with the same methods without phosphorus.¹⁶⁶ The process was probably unsuccessful.¹⁵⁴

The synthesis of bis(4-aminophenyl)phenyl phosphine oxide has recently been reported by Grubbs¹⁶⁷ and by Yang and McGrath¹⁶⁸ in much higher yields and purity. Bis(4-aminophenyl)phenyl phosphine oxide was prepared by a four step process as shown in Scheme 2.4.2.2. In the first step, *para*-bromophenyllithium prepared from 1,4-dibromobenzene and *n*-butyllithium, was quenched with phenyldichlorophosphine at low temperature to afford an intermediate. The intermediate was subsequently oxidized to the phosphine oxide and then subjected to Gabriel reaction to afford the diimide which was treated with hydrazine to afford bis(4-aminophenyl)phenyl phosphine oxide in 92% yield. Polyimides prepared from bis(4-aminophenyl)phenyl phosphine oxide with various dianhydrides to produce soluble polyimides that were all film forming. These polyimides exhibited very high glass transition temperatures in some cases and all were very thermo-oxidatively stable with values approaching 600°C for 5% weight loss in air. The solution and thermal properties of polyimides prepared from bis(4-aminophenyl)phenyl phosphine oxide are shown in Table 2.4.2.1.

A significant advancement in phosphorous containing polyimides was the synthesis of an ether-linked phenylphosphine oxide diamine, bis(4-aminophenoxy-4'-phenyl)phenylphosphine oxide also known as *m*-BAPPO. Gungor and coworkers successfully



Scheme 2.4.2.2 Improved Synthesis of Bis(4-aminophenyl)phenyl Phosphine Oxide ¹⁶⁸

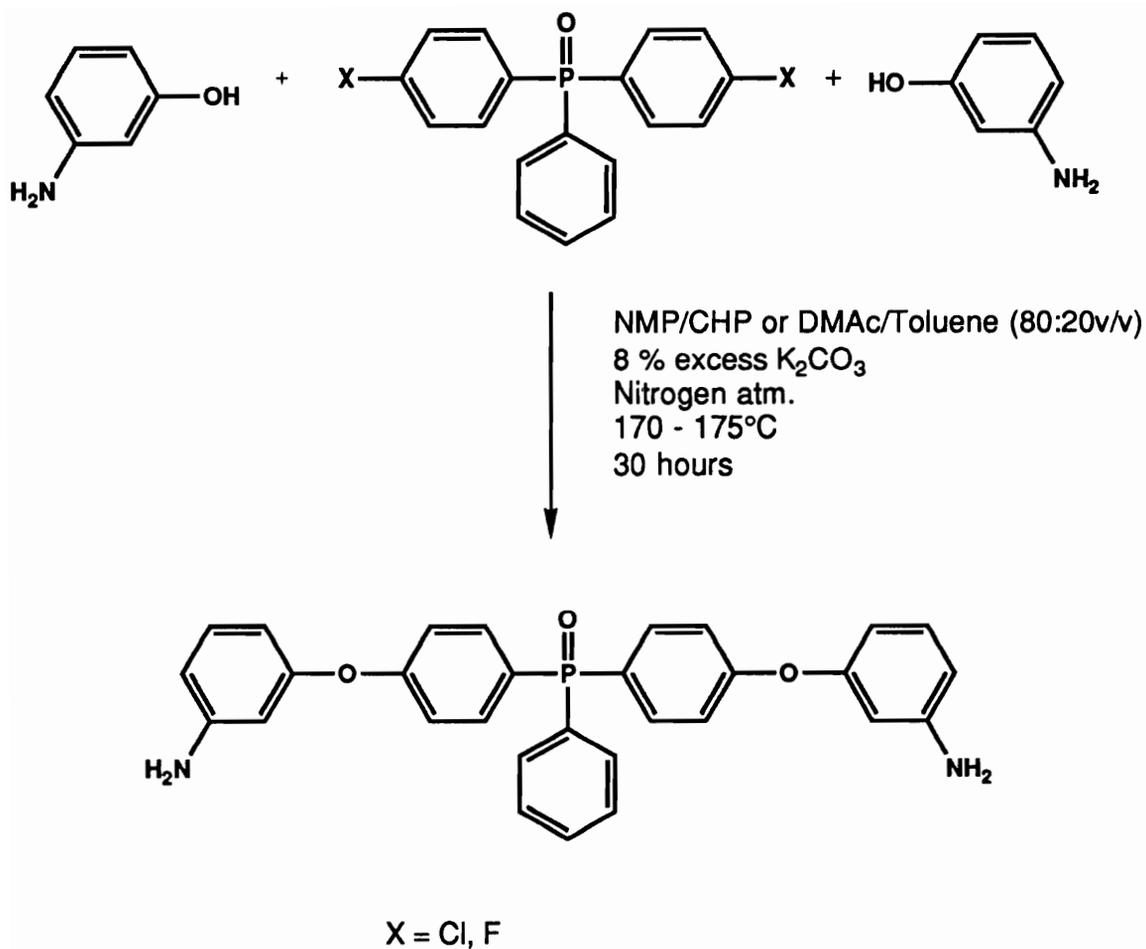
Table 2.4.2.1 Solution and Thermal Properties of Polyimides Prepared from Bis(4-aminophenyl)phenyl Phosphine Oxide ¹⁶⁸

Dianhydride	[η] (dL/g)	T_g (°C)	TGA (°C) (5% Wt. Loss, air)
6FDA	0.46	345	592
BPDA	0.55	371	578
PMDA	0.41	425	584
BTDA	0.46		577
DSDA	0.35		529
ODPA	0.54	311	588

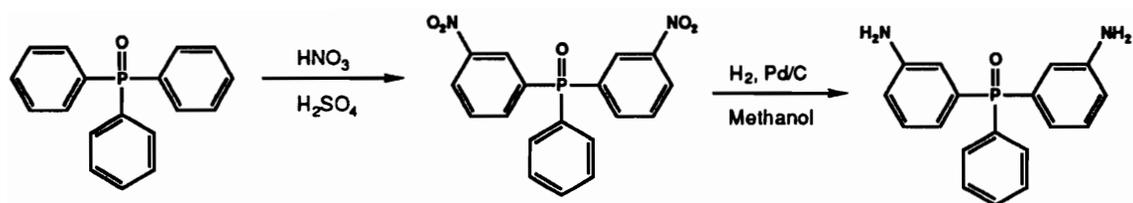
synthesized *m*-BAPPO by the Grignard reaction of dichlorophenylphosphine oxide and 4-bromofluorobenzene. Bis-(fluorophenyl)phenyl phosphine oxide was then reacted with *m*-aminophenol in DMAc/toluene solvent mixture in the presence of potassium carbonate (nucleophilic aromatic substitution conditions) to form *m*-BAPPO. Polymer forming material was obtained after successive recrystallizations from DMAc and precipitation of ethanol solutions from water.¹⁶⁹ The reaction scheme for the synthesis of *m*-BAPPO is shown in Scheme 2.4.2.3. Completely soluble polyimides were synthesized using *m*-BAPPO with various dianhydrides with moderately high T_g's (220°C - 254°C) and char yields in air as high as 35% at 750°C.

Hergenrother and Havens have used an isomer of *m*-BAPPO, bis(4-aminophenoxy-4'-phenyl) phenylphosphine oxide or *p*-BAPPO to synthesize high molecular weight polyimides as well.¹⁷⁰ *p*-BAPPO was synthesized from bis(4-fluorophenyl)phenyl phosphine oxide and 4-aminophenol. Wescott has also successfully synthesized *p*-BAPPO.¹⁷¹ This route involves reacting *p*-aminophenol with bis(4,4'-fluorophenyl)phenyl phosphine oxide. To obtain pure monomer, it was crucial that the *p*-aminophenol was sublimed immediately prior to use. The *p*-BAPPO was obtained in 70% yield.

Martinez-Nunez and coworkers have recently reported the synthesis of and utilization of bis(3-aminophenyl)phenyl phosphine oxide (*m*-DAPPO) in high yields and purity.¹⁷² This route entails the nitration of commercially available triphenylphosphine oxide and subsequent reduction to the diamine. The synthesis of bis(3-aminophenyl)phenyl phosphine oxide is shown in Scheme 2.4.2.4. The amount of nitric acid used for nitration is crucial to reduce the amount of trinitro compound formed. The diamine may be recrystallized from ethanol to obtain pure product. High molecular weight polyimides were also successfully prepared with excellent thermal stability.¹⁷²



Scheme 2.4.2.3 Synthesis of *m*-BAPPO ¹⁶⁹



Scheme 2.4.2.4 Synthesis of *m*-DAPPO ¹⁷²

Another route to polyimides containing the phosphine oxide moiety in the backbone was by synthesizing the triphenyl phosphine oxide tetracarboxylic dianhydride.¹⁷³⁻¹⁷⁷ By reacting either 4-lithiated *ortho*-xylene or the Grignard reagent of 4-bromo-*ortho*-xylene with phenylphosphonic dichloride in THF, followed by oxidation of the tetramethyl compound, the tetraacid of the phosphine oxide containing monomer was isolated in approximately 30% yields. Quantitative ring closure procedures resulted in the desired dianhydride. Improved reaction pathways and yields were recently reported for this triaryl phosphine oxide dianhydride.¹⁷⁸

Lin and coworkers greatly enhanced the yields of the triphenyl phosphine oxide dianhydride and successfully incorporated it into high molecular weight, soluble polyimides.¹⁷⁸ Lin's procedure entailed a Friedel-Crafts acylation reaction between phenylthiophosphonic dichloride with *o*-xylene which was then oxidized with hydrogen peroxide to the oxide form. The bis(3,4-dimethylphenyl)phenyl phosphine oxide was then oxidized using KMnO₄ and finally refluxed in acetic acid and acetic anhydride to form the anhydride. Polyimides utilizing this dianhydride were synthesized with various diamines to produce soluble, high molecular weight polymers. T_g's ranged from 317 to 366°C and char yields in air at 750°C as high as 42%.

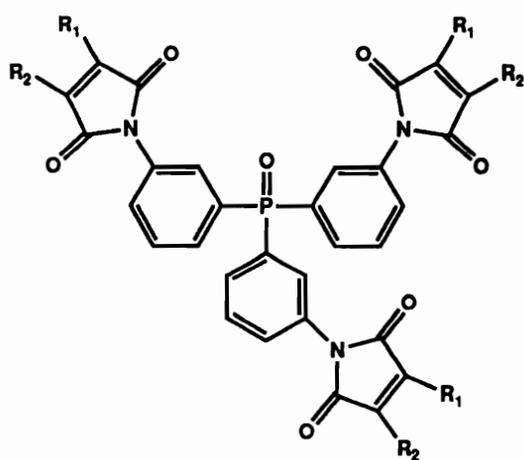
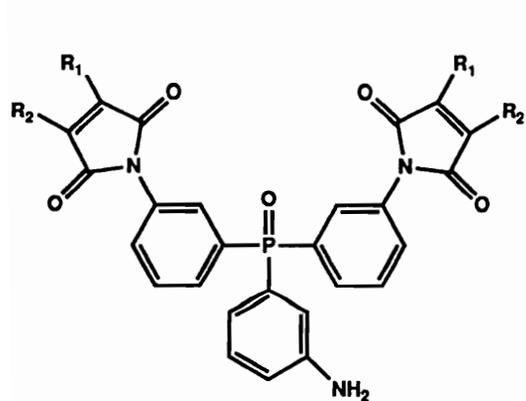
Phosphine oxide materials have also been utilized in the synthesis of many thermosetting resins. In particular, the nitrated triphenyl phosphine oxide^{160,179-182} has been reduced to tris(3-aminophenyl) phosphine oxide and reacted with different stoichiometric ratios of maleic or nadic anhydride as shown in Figure 2.4.2.2. These maleimide and nadimide resins exhibited cure temperatures of ~ 280°C by DSC analysis. Composite fabrication and flame retardant properties were evaluated. Bismaleimides based *m*-BAPPO were also investigated by Wood and McGrath.¹⁸³⁻¹⁸⁵ These bis[bis(maleimido)phenoxy]phenylphosphine oxide materials exhibited melting points as low as 92°C and increased adhesion to metal and carbon fibers compared to commercial

bismaleimides.^{186,187} Pak has also shown recently that poly(arylene ether sulfone)s which contain the triphenylphosphine oxide moiety with a pendent amine could be prepared.¹⁸⁸ These pendent amines were converted to maleimides¹⁸⁹ or phenylethynylphthalimides^{190,191} and thermally cured to give tough insoluble networks. The poly(arylene ether sulfone) copolymers were also utilized for the curing of epoxy resins along with diaminodiphenyl sulfone.¹⁸⁹

2.4.3 Characteristics of Phosphorus Containing Polymers

Phosphorus containing high performance polymers have some common characteristics. Phosphorus containing engineering thermoplastics tend to be much more flame-retardant than their non-phosphorus containing counterparts. Reduction in thermal stability does not occur when phosphorus was incorporated into otherwise thermally stable polymers. By incorporating the flame retardant (phosphorus) directly into the polymer backbone, the processing and stability concerns of using additives are almost nonexistent. The flame retardancy in phosphine oxide based polymers has been studied both quantitatively and qualitatively compared to those with no phosphorus.^{146,154,167,192-194}

It has been postulated that a nonvolatile char is formed which then severely limits oxygen penetration into the polymer and thereby reducing its flammability. Furthermore, phosphine oxide based polymers will self-extinguish upon removal of a flame and the heat release rate is much lower than non-phosphorous containing polymers. This is illustrated in Figure 2.4.3.1 where polyamides containing phosphine oxide are compared to those with no phosphorous. However, as a result of a much lower heat release rate (less burning), the smoke formation increased in the case of phosphine oxide containing systems. The inherent flame retardancy of phosphorous containing polymers is a tremendous advantage



$R_1 = R_2 = H$
 or
 $R_1 = R_2 = Cl$
 or
 $R_1 = H, R_2 = CH_3$

Figure 2.4.2.2 Phosphine Oxide-Containing Bismaleimides 160,179-182

over systems in which additives must be added. These additives must be stable under polymer processing conditions, be compatible with the polymer structure while not detracting from mechanical properties and retaining flame retardant properties over long periods of time.

Phosphine oxide containing poly(arylene ether)s and polyimides also exhibit very high resistance to oxygen plasma.¹⁹⁵ Oxygen plasma is used to simulate exposure of polymeric materials to atomic oxygen (AO) found while in low earth orbit (LEO). These phosphorus based polymers displayed weight losses 1-2 orders of magnitude lower than Kapton ® HN when exposed to oxygen plasma.^{196,197} These materials may have applications in spacecraft and as reactive ion etch barriers used in the fabrication of microelectronic circuitry.

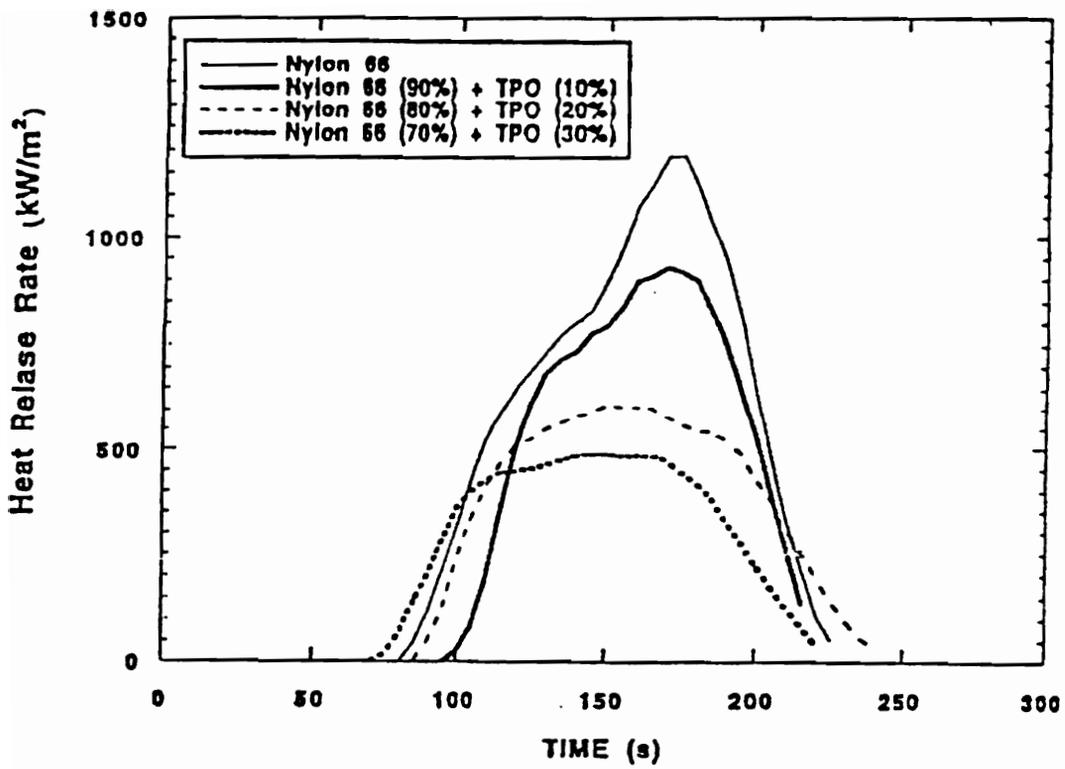


Figure 2.4.3.1 Heat Release Rate of Triaryl Phosphine Oxide Containing Nylon 6,6 Copolymers ¹⁹⁴

2.5 THERMOSETTING IMIDES

2.5.1 Introduction

Recent years have seen a rapid growth in the area of temperature-resistant thermosets. In particular, polyimides are gaining wide acceptance by industry because they combine a number of excellent properties such as retention of physical properties at elevated temperatures and in wet environments, almost constant electrical properties over a wide range of temperatures, low density, high T_g 's, thermo-oxidative stability and non-flammability. However, polyimides still carry misconceptions of being difficult to process. Yet with the many advancements on enhancing solubility and processability discussed earlier without sacrificing thermal stability, polyimides are becoming the material of choice for high temperature adhesive and composite manufacturing. As a consequence, processing via hot melt prepregging, wet- and tow-preg filament winding and resin transfer molding is mandatory. These processing techniques require very specific rheological properties and cure kinetics (ability to be processed to give high-quality, low void content laminates). By controlling molecular weight and the chemistry of the backbone structure between the reactive crosslinking terminations in thermosetting polyimide resins, these specific properties can be met.

The major driving force for the use of composite materials is reduced weight manifested by the high stiffness/weight and high strength/weight ratios and the potential for lower component cost.¹⁹⁸ Figure 2.5.1.1 illustrates the value of weight saved in aircraft and spacecraft. For a Boeing 747, 1 kilogram of weight saved is worth about \$450, while a similar weight saved on the space shuttle is worth about \$30,000. The need also exists for high performance polyimides for use in composite and adhesive applications to withstand high temperatures (600-700°C) (see Figure 2.5.1.2) to replace conventional systems.

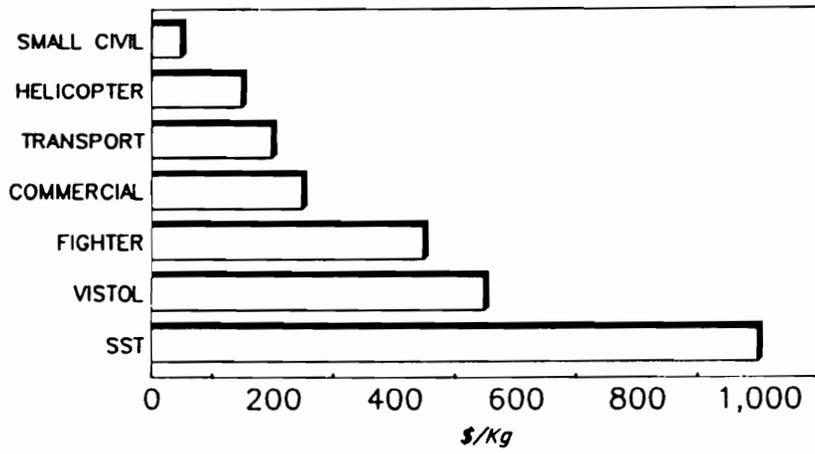


Figure 2.5.1.1 Value of Weight Saved in Aircraft and Spacecraft ¹⁹⁸

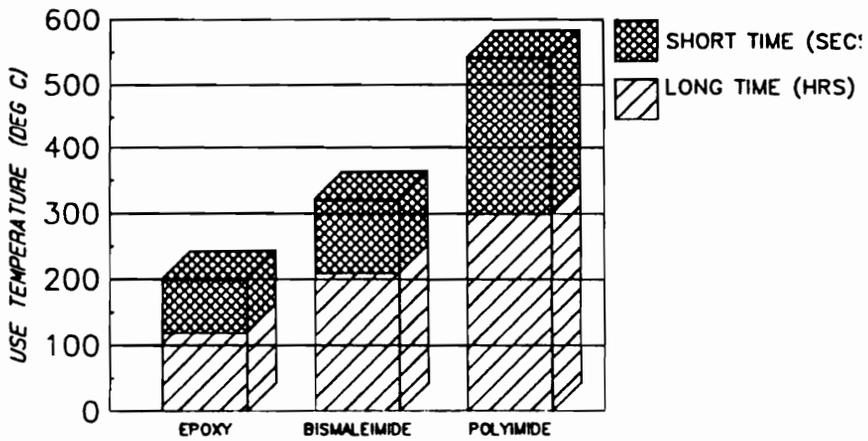


Figure 2.5.1.2 Use Temperatures for Resin Matrix Composites ¹⁹⁸

Thermosetting polyimides are best defined as low molecular weight, at least difunctional monomers or prepolymers, or mixtures thereof, which carry imide moieties in their backbone structure.¹⁹⁹ Such materials are terminated by reactive groups which undergo homo- and/or copolymerization by thermal or catalytic means. Thermosetting polyimides may be pre-imidized and therefore, can cure without generating volatiles. Examples are the maleimides and acetylene terminated polyimides which polymerize via multiple carbon-carbon bonds. Other resins where the imide containing backbone structure is synthesized *in situ* during processing of the thermosetting imide resin (PMR-concept) are also available. These systems and additional imide structures with reactive endgroups such as nadimide substituted acetylene endgroups, paracyclophane, and biphenylene endgroups will be discussed in the following sections.

2.5.2 Bismaleimides

Bismaleimides (BMI's) are a leading class of thermosetting polyimides. Their excellent processability and balance of thermal and mechanical properties have made them extremely popular in advanced composites and electronics. The chemical structure of bismaleimides is shown Figure 2.5.2.1. Bismaleimides are synthesized from the reaction of a diamine and excess maleic anhydride in low boiling organic solvents such as chloroform or acetone or aromatic solvents such as toluene.²⁰⁰ The intermediate bis(amic acid) may be cyclodehydrated to the final bismaleimide by heating in N,N-dimethylformamide (DMF) or acetic acid.²⁰¹⁻²⁰³ Alternatively, cyclodehydration may be effected by a low temperature imidization utilizing sodium acetate in acetic anhydride.²⁰⁴⁻²⁰⁷ The synthesis of a bismaleimide is shown in Scheme 2.5.2.1.

Bismaleimides readily polymerize upon heating without the presence of a catalyst. The reactivity of the carbon-carbon double bond is due to the electron-withdrawing nature

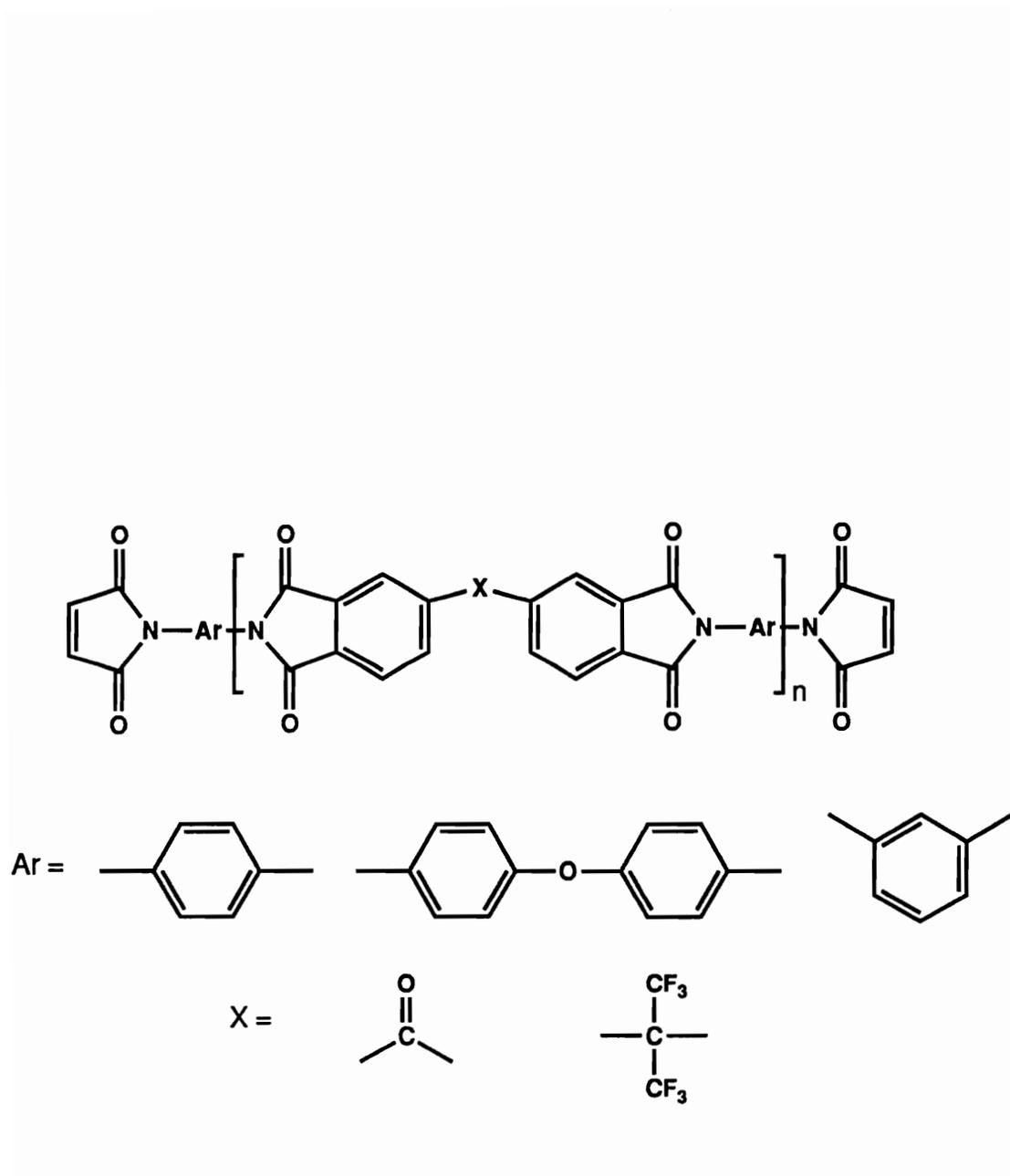
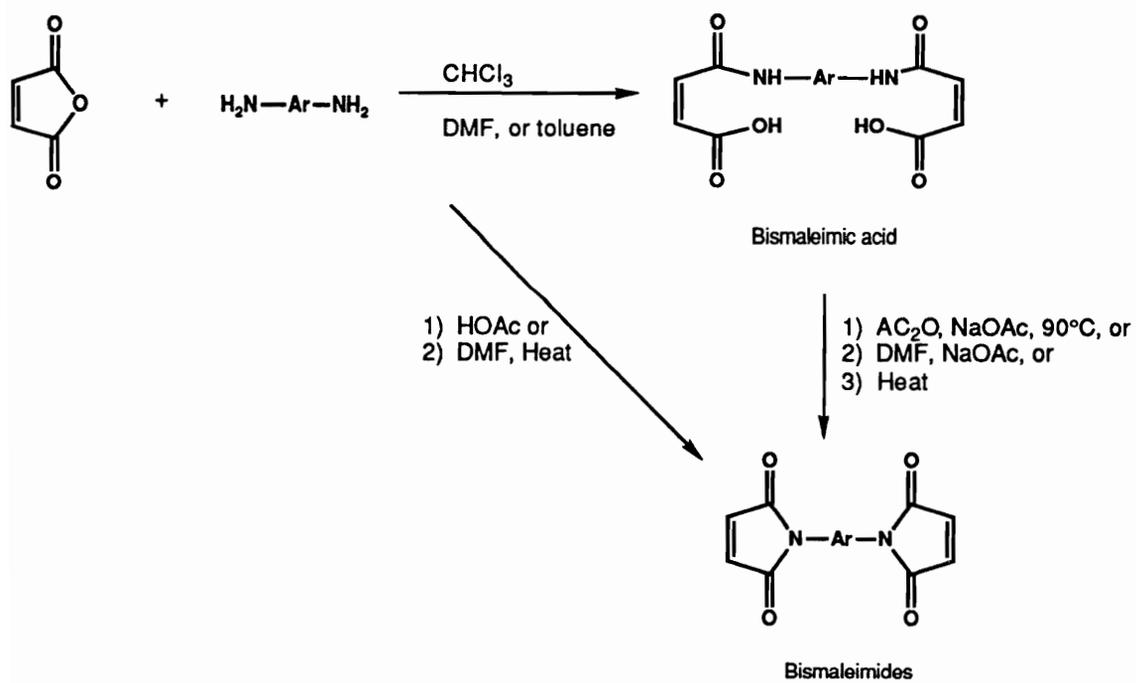


Figure 2.5.2.1 General Formula for Bismaleimide



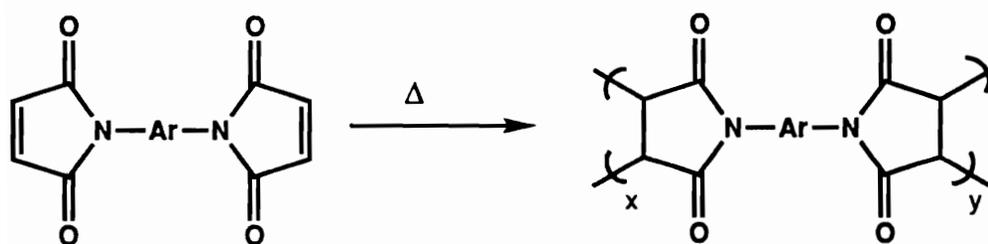
Scheme 2.5.2.1 Synthesis of Bismaleimides

of the two adjacent carbonyl groups. The crosslinking of the bismaleimide is shown in Scheme 2.5.2.2. Perhaps less widely recognized is the potential that bismaleimides offer for the synthesis of high molecular weight, step-growth polymers. The double bond is especially labile to nucleophilic attack and yields Michael type adducts with both amines and thiols.²⁰⁷⁻²⁰⁹ This Michael type of addition with aromatic diamines is shown in Scheme 2.5.2.3.

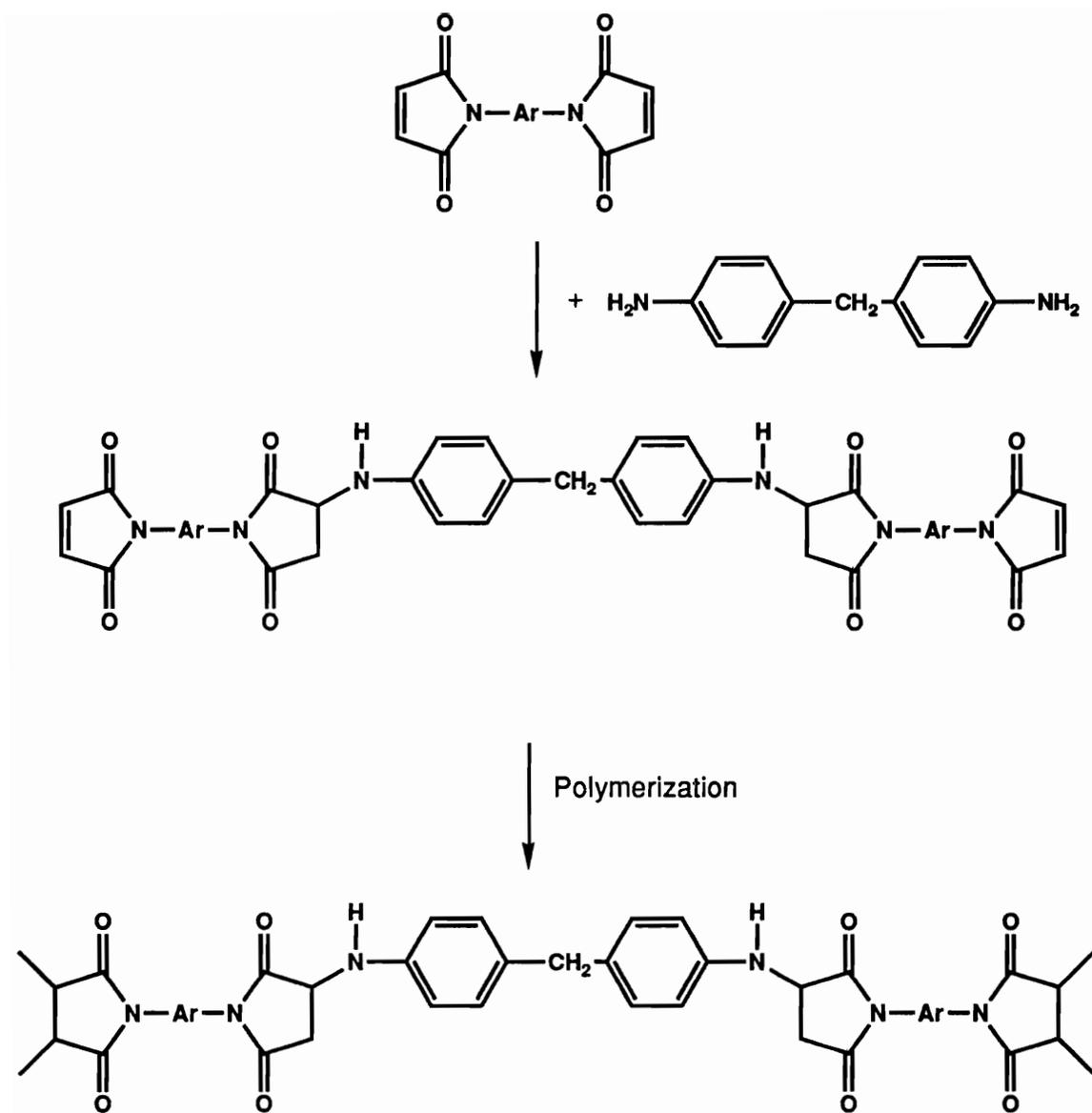
BMI's are attractive for several reasons, including ease of synthesis, relatively low cost and well-defined molecular weight. However, the major drawbacks include inherent brittleness due to the high degree of crosslink density and the relatively low curing temperatures (small processing window); onset of curing usually occurs at 200-210°C.²¹⁰

Many improvements in the mechanical properties and the processing window have been reported. Blending BMI's with reactive thermoplastic tougheners such poly(arylene ether sulfone)s, poly(arylene ether phosphine oxide)s and polyimides greatly enhanced their mechanical properties.^{211,212} BMI's synthesized from long chain sulfone-ether diamines²¹³ and poly(arylene ether sulfone)s and poly(arylene ether ketone)s^{214,215} give systems with high T_g 's and moduli with low stress cracking. Additionally, BMI's may be blended with nonreactive thermoplastic polyimides to form semi-interpenetrating networks. The BMI acts as a plasticizer prior to crosslinking, depressing the T_g of the thermoplastic polyimide and thus aiding in processing.^{216,217} Curing of the semi-interpenetrating network results in properties intermediate between those of the individual starting materials.

Attempts to lower the melting temperatures of the uncured BMI's has also facilitated the processing procedures. Wood and coworkers have utilized a flexible phosphine oxide diamine to synthesize soluble, lowering melting BMI's with improved thermo-oxidative stability.¹⁸³ Goldfarb and coworkers also prepared BMI's from oxyalkyl-linked diamines with aliphatic pendant substituents with melting points in the range of 20-215°C



Scheme 2.5.2.2 Crosslinking of Bismaleimides



Scheme 2.5.2.3 Bismaleimide/Aromatic Diamine Copolymerization (Michael Addition)
207-209

and final T_g 's ranging from 340-395°C.²¹⁸

2.5.3 In-Chain Maleimide Polyimides

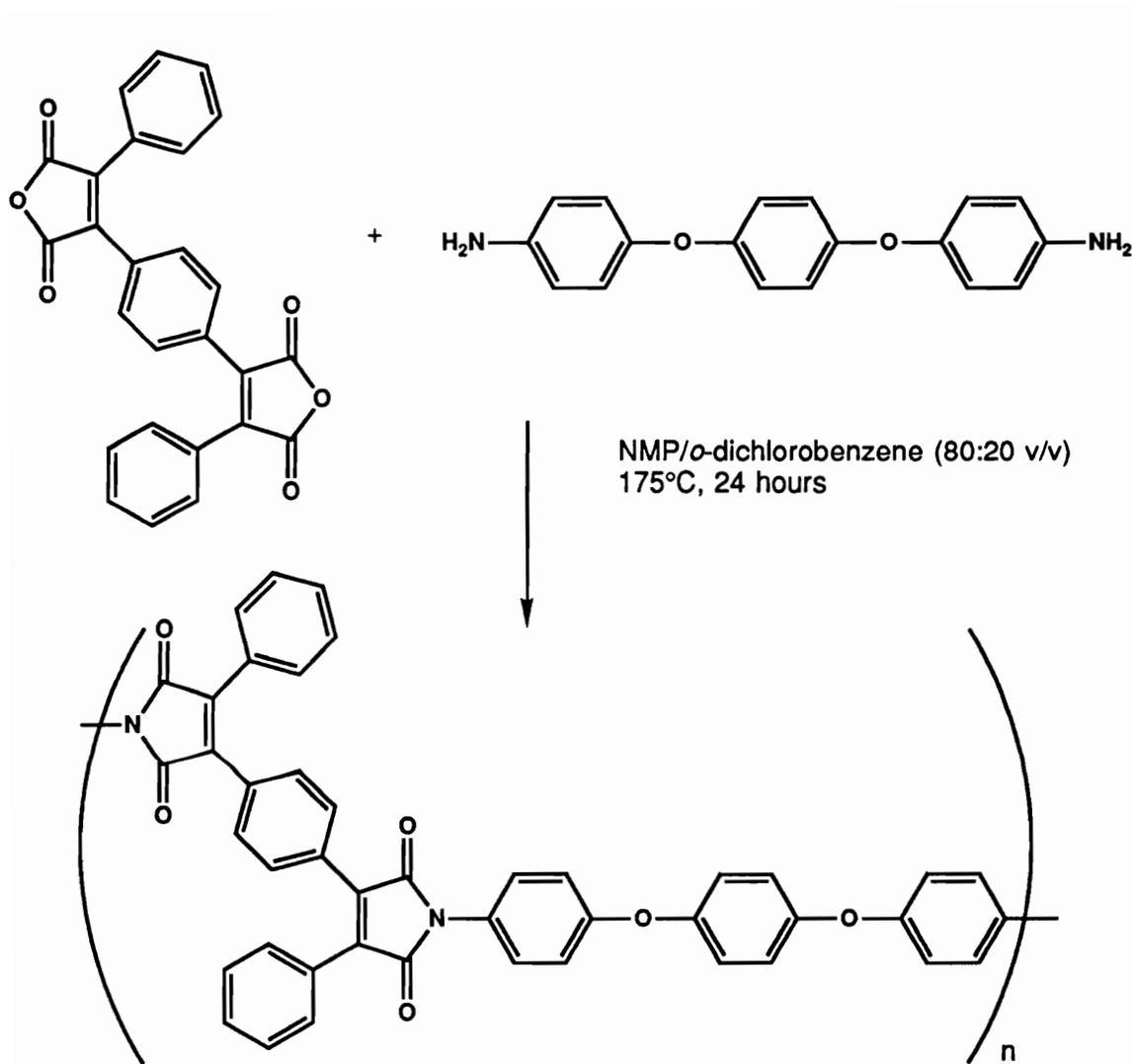
Polyimides synthesized from 1,4-bis-(phenylmaleic anhydride)-benzene affords maleimide groups in the polymer backbone.^{128,129} Moy reported that thermal crosslinking of these unsaturated sites was possible when films of the polyimides were heated at 350°C. The pendant phenyl substituents apparently provide a steric barrier to crosslinking, thereby increasing the cure temperature sufficiently (above conventional bismaleimides) that imide networks could easily be generated from linear, non-reactive endcapped polyimides without the evolution of volatiles. The synthesis of polyimides based on 1,4-bis-(phenylmaleic anhydride)-benzene is depicted in Scheme 2.5.3.1.

Bismaleimides having nadimide endgroups (PMR-type polymers) functionalities were synthesized from either 4,4'-methylenedianiline or *p*-phenylene diamine and 1,4-bis-(phenylmaleic anhydride)-benzene.²¹⁹ These materials showed good solubility and flow characteristics with T_g 's as much as 70°C higher than PMR-15. However, the thermo-oxidative stability was reported lower than PMR-15 resins. This decreased stability was probably due to incomplete imidization and high polydispersity of the polyimide oligomers used.

2.5.4 PMR Resins

2.5.4.1 Nadimides

The polymerization of monomeric reactants (PMR) is a unique approach to temperature-resistant crosslinked polymers. Most polyimide thermosets have a totally imidized backbone molecule which carries terminal polymerizable endgroups with no



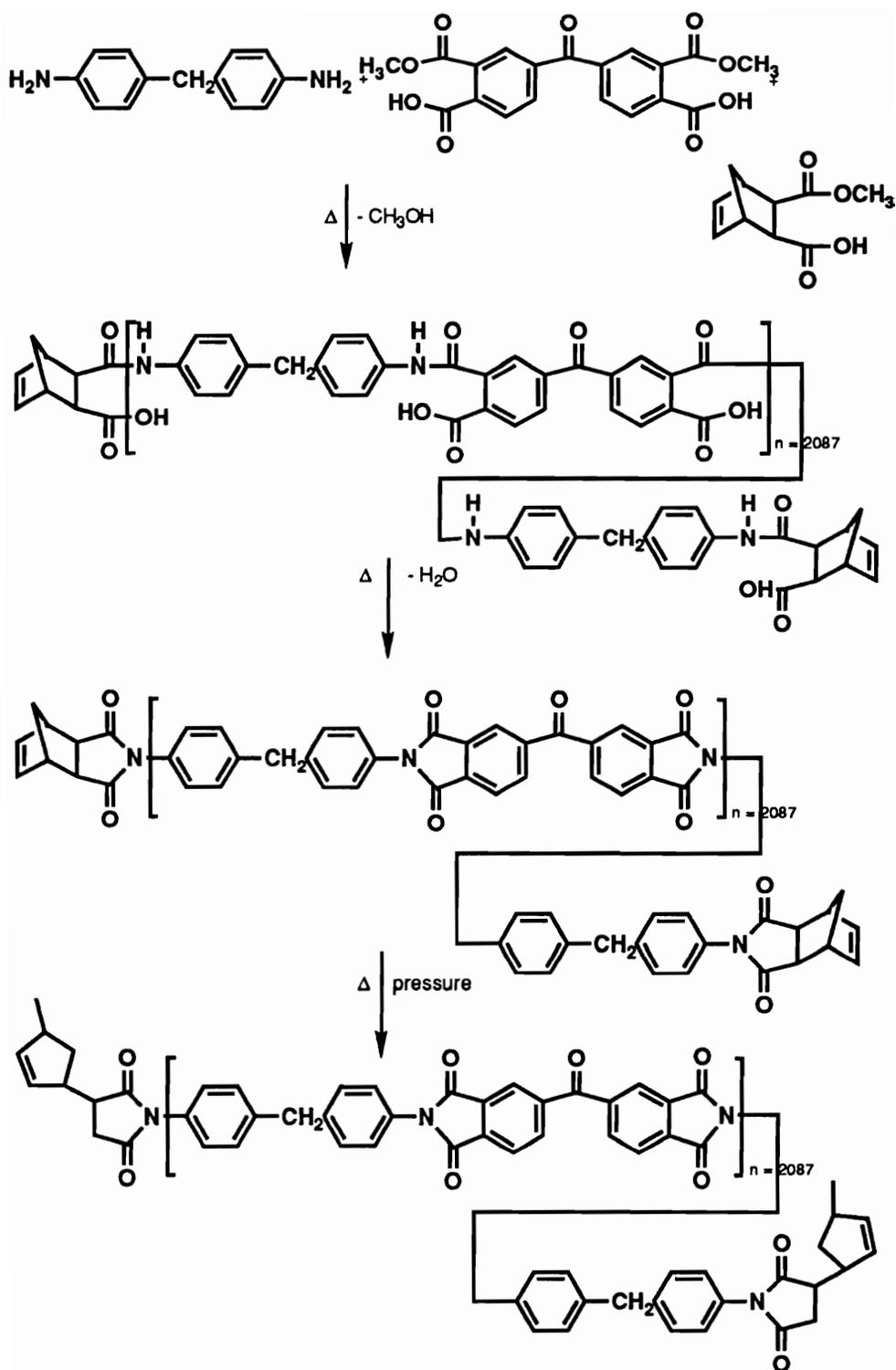
Scheme 2.5.3.1 Synthesis of Polyimides Based on 1,4-bis-(phenylmaleic anhydride)-Benzene ^{128,129}

volatile evolution during the final reaction step. The PMR approach, in contrast, is unique because the imide prepolymer is synthesized *in situ* during the processing of the resin.

Endomethylenetetraphthalimides (nadic or norbornene endcapped imide resins) were first patented and published in 1970 and 1971 respectively.^{61,62} Lubowitz discovered that bisnadic imides undergo a reverse Diels-Alder reaction in the temperature range of 250-270°C, releasing cyclopentadiene followed by an almost simultaneous polymerization of the maleimide formed. This reaction is also referred to as pyrolytic polymerization because the initial step in the cure reaction sequence is the decomposition of the norbornene groups.

The norbornene resin most widely accepted by the aerospace industry in PMR-15.²²⁰ Usually 4,4'-methylene dianiline (MDA) is reacted with a dialkylester of benzophenonetetracarboxylic acid (BTDE) and the monoalkylester of norbornene 2,3-dicarboxylic acid (NE) in such a molar ratio that a prepolymer with a molecular weight of 1500 is obtained. The reaction is usually carried in an alkyl alcohol; this solution is then used to impregnate the reinforcing fibers for composite manufacturing. The synthesis of PMR-15 is shown in Scheme 2.5.4.1.1. Upon heating, the reactive endgroups polymerize via a reverse Diels-Alder reaction to form a crosslinked system.

The cure reaction of nadimides has been studied by numerous investigators.²²¹⁻²³⁰ Cyclopentadiene is released during cure and can react with nadimide to form a 1:1 adduct which can subsequently be involved in addition reactions with maleimide of nadimide. Wilson also found similar results by polymerizing N-phenylnadimide under high pressure and analyzed the soluble part of the polymer via ¹H-NMR, ¹³C-NMR and FTIR spectroscopy.²³⁰ Wilson's proposed mechanism of polymerization (crosslinking) is shown in Figure 2.5.4.1.1. A variation of the mechanism has also been proposed by the original researchers in this area (BP/Rolls-Royce) seemed to support the conventional



Scheme 2.5.4.1.1 PMR-15 Resin Chemistry ²²⁰

crosslinking mechanism as well. However recent studies utilizing NMR and EPR techniques^{221,223} also suggests the presence of two major structures. One is nonimidized BTDE moieties and the endo-exo isomerization reactions. The possible structures are shown in Figure 2.5.4.1.2. All of these proposed structures may possibly contribute to increased microcracking observed for high -temperature-cured resins.

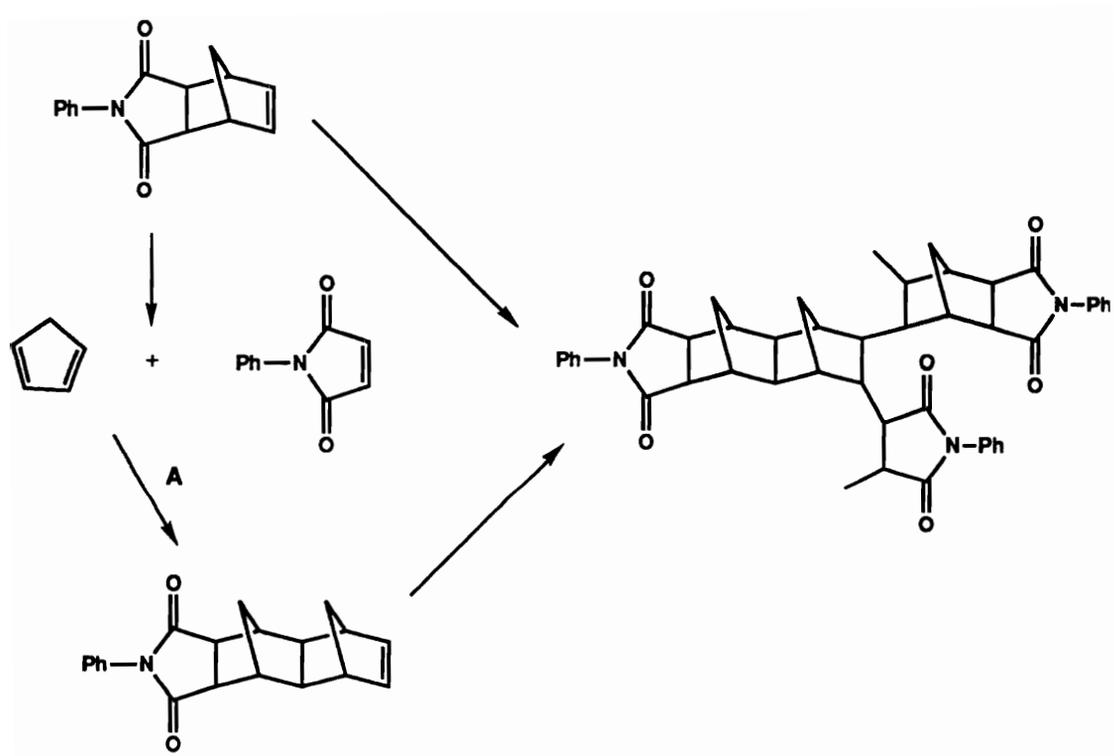
The desirable properties of PMR-15 include good processability (wide processing window), physical and mechanical properties, acceptable thermal stability at 316°C (600°F) applications, an established data base, cost competitiveness, and availability from multiple sources.⁷

Nevertheless, PMR-15 suffers from many disadvantageous attributes as well. Blisters and voids may form in finished composites due to the evolution of cyclopentadiene during cure.²²² Furthermore, the nadic endcap has been associated with the high temperature decomposition of PMR-15. NASA has confirmed that long-term isothermal stability improves with decreased nadic endgroup concentration (molecular weight between crosslinks increases).²³¹⁻²³⁴

2.5.4.2 Additional PMR Resins

Attempts to improve the processability and final properties of PMR resins have focused on replacement of either or both monomers and/or endgroups with more stable substituents. Alston²³⁵ and Sillion²³⁶ have reported on the synthesis of a PMR resin analog in which 6F dianhydride was used in place of the usual benzophenone tetracarboxylic dianhydride. The oligomers showed improved solubility in organic solvents prior to crosslinking and after crosslinking thermal oxidative stability improved.

Other attempts to alter PMR-15 by changing the diamine moiety include the use of a liquid isomeric mixture of di- and trifunctional amines (Jeffamine 22) in place of MDA.²³⁷



Scheme 2.5.4.1.1 Proposed Polymerization of N-Phenylmaleimide by Wilson ²³⁰

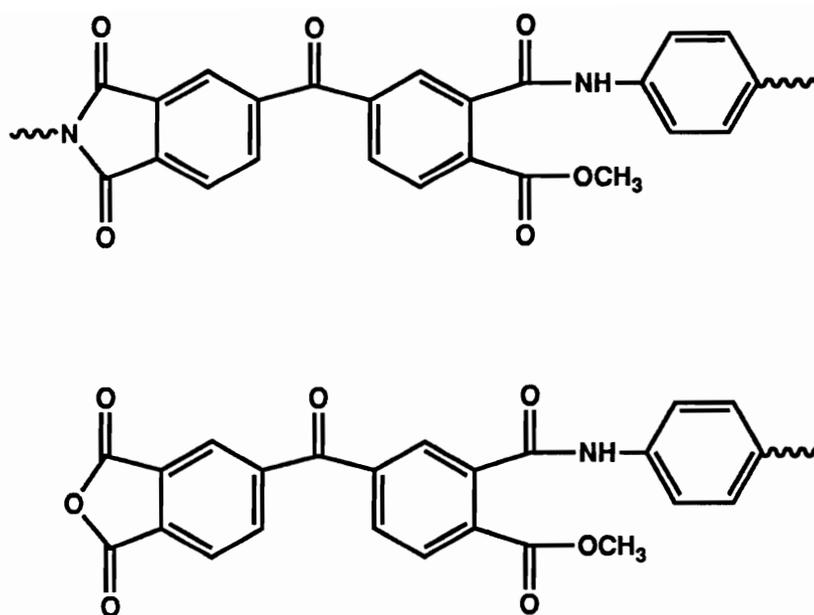


Figure 2.5.4.1.2 Proposed Structures of Cured PMR-15 Polymers ^{221,223}

This substitution provides a mixture of monomeric reactants which was tacky at room temperature and could be processed almost like an epoxy. However, the thermal oxidative stability of the cured resin was lower than PMR-15. Recently, researchers have used variations of diaminoanthraquinone in place of MDA which exhibited good thermo-oxidative stability and higher T_g values than PMR-15.²³⁸

Recently, the synthesis of PMR-type resins utilizing 6F dianhydride and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (BTDB) has been reported.²³⁹ Other researchers have utilized the Avimide N® backbone [6FDA with (95:5) *p*-PDA:*m*-PDA] that produces resins with T_g values well over 300°C.²⁴⁰ In addition, *p*-aminostyrene replaced the nadic ester (NE) as the endgroup in some cases. These 12F prepolymers displayed lower melting temperatures by DSC analysis and higher melt flow in rheological studies than conventional PMR resins. Long-term isothermal aging studies showed improved thermo-oxidative stability over PMR-15 and the resins with *p*-aminostyrene endcaps exhibited the best promise for long-term, high temperature application at 343°C (650°F).

The employment of substituted norbornene endcaps has resulted in a new class of thermosetting imides related to the PMR resins. Allylnadic imides are imide oligomers endcapped with allylnadic anhydride. The bisimides prepared with this endcapper are usually viscous liquids at room temperature and can be polymerized thermally at temperatures around 250°C.^{241,242} Glass transition temperatures over 360°C were obtained that exhibited good thermal stability. Bridgehead substitution of nadic anhydride with a methoxycarbonyl group has produced PMR resins with cure temperatures approximately 25°C lower than unsubstituted nadimides.²⁴³ Glass transition temperatures were slightly lower than those of PMR-15 and isothermal thermal stability at 316°C was comparable to PMR-15.

The substitution of benzonorbornadienyl for norbornenyl endgroups in PMR systems has also been reported.²⁴⁴ PMR resins utilizing this endcap were found to soften and cure at temperatures approximately 50°C higher than the corresponding values for commercial PMR-15 (225°C and 300°C, respectively). Isothermal weight loss after 1000 hours at 316°C was lower than PMR-15. The benzonorbornadienyl endcap may offer several advantages over nadic or norbornenyl endgroups; the higher cure temperature affords a wider processing window for the conventional BTDE-MDA based resins and may allow for the preparation of higher T_g systems. Miscellaneous PMR systems are illustrated in Figure 2.5.4.2.1.

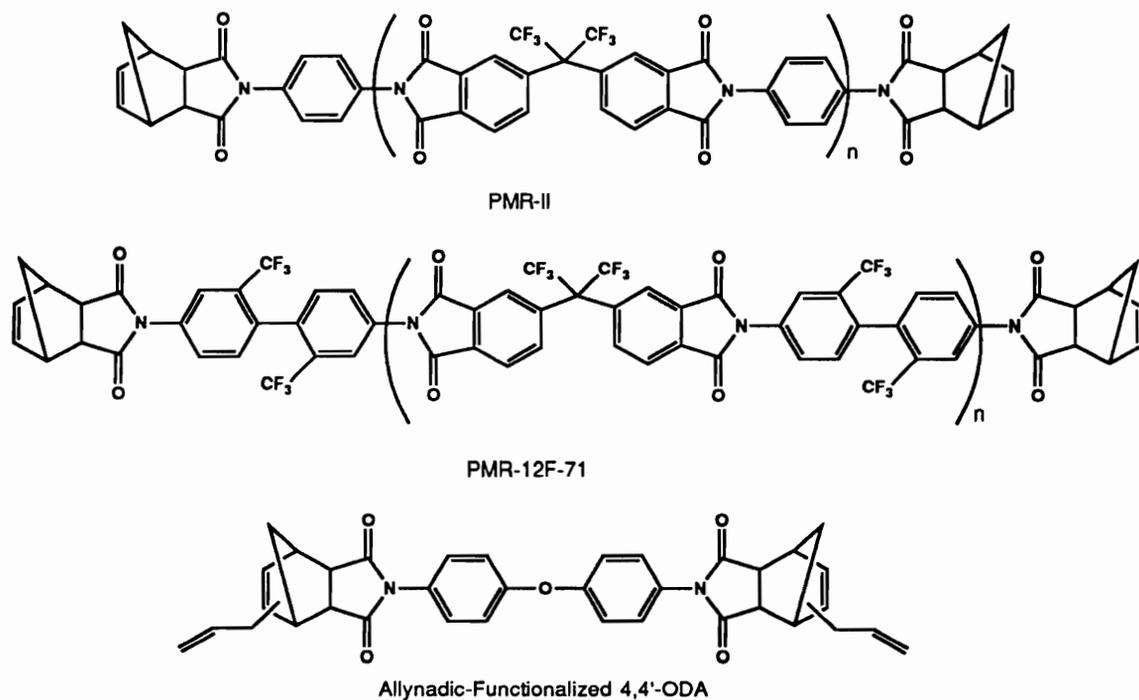


Figure 2.5.4.2.1 Miscellaneous PMR Resins ^{235,236,239,241,242}

2.5.5 Acetylene Functionalized Imides

Acetylene or ethynyl functional groups have been incorporated into a number of high performance polymers as pendant, terminal, or internal reactive functionalities. These polymers include poly(arylene etherketone)s,^{245,246} poly(arylene ethersulfone)s²⁴⁷⁻²⁴⁹ polyquinoxalines and polyphenylquinoxalines,^{250,251} poly(iminolactone)s,^{60,252} polyaspartimides,²⁵³ polyamides^{254,255} and aromatic polyimides.²⁵⁶⁻²⁷⁴ Landis et al. synthesized acetylene-terminated polyimides of the chemical structure given in Figure 2.5.5.1.²⁶⁸

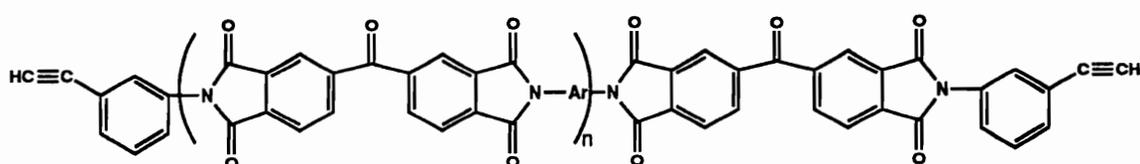


Figure 2.5.5.1 Chemical Structure of Acetylene Terminated Polyimides²⁶⁸.

Of high importance to the end user of ethynyl-terminated polyimides is the influence of chemical structure on the melting transition of the prepolymer and the glass transition temperature of the fully cured product. Lowering the uncured T_g means increasing flow and, in most cases, a widening of the processing window. One resin that has become commercially available out of this family through Gulf Chemical and now National Starch is Thermid 600 (Figure 2.5.5.2) which utilized 3-aminophenylacetylene (3-ethynylaniline) as the endcapping agent. However, one drawback of this material is its high melting point (195-200°C) and the start of polymerization immediately after becoming molten and therefore it has a very narrow processing window.

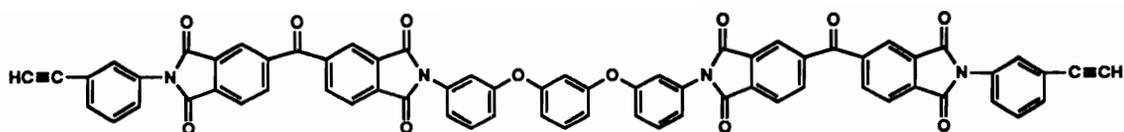


Figure 2.5.5.2 Thermid 600 Acetylene Terminated Polyimide

Ethynyl-terminated polyimides cure without the evolution of volatiles and this is advantageous in composite applications. However, the narrow processing window caused processing problems; good flow and wetting behavior of the resin was hampered by preliminary reactions of the endgroups during cure, preventing adequate contact with substrates.

Two synthetic approaches have been utilized to circumvent these processing problems. The first approach involves the use of acetylene-functionalized iminolactone (isoimide) oligomers. Isoimides display lower T_g 's and increased solubility resulting in better flow than their imide analogs and undergo both crosslinking and isomerization to imide at elevated temperatures.^{60,252,274} National Starch and Chemical Company produces such resins as Thermid IP-600. The second approach involves phenylsubstituted acetylene (phenylethynyl) derivatives. These crosslinking systems will be discussed in the following section.

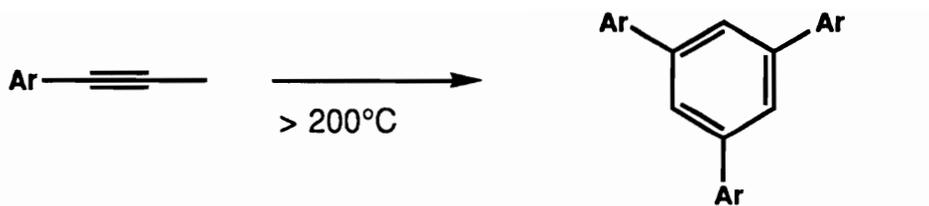
Another approach to acetylene-terminated polyimides is to use 4-ethynylphthalic anhydride as an endcapping agent.^{262,275} This involves the synthesis of an amino-terminated amide acid prepolymer, by reacting 2 moles of tetracarboxylic acid dianhydride with 2 moles of diamine, which subsequently is endcapped with 4-ethynylphthalic anhydride. The properties of the resin endcapped with 4-ethynylphthalic anhydride are similar from those prepared from 3-ethynylaniline.

Acetylene-terminated polyimides were first reported almost twenty years ago; however, the chemistry involved in the crosslinking reaction is still not very well

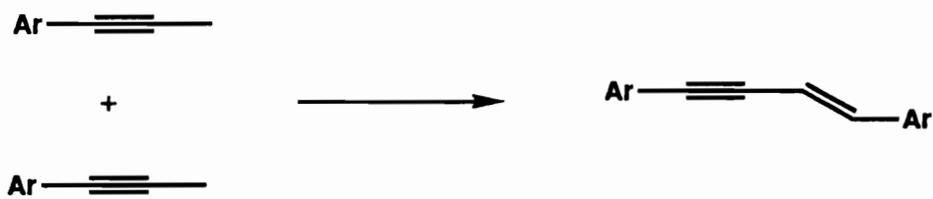
understood. Early studies indicated that crosslinking occurred by cyclotrimerization of the acetylene groups to form a benzene ring, as shown in Scheme 2.5.5.1.²⁶⁸ Nevertheless, further studies have proven that the crosslinking reaction is a very complex mixture of reactions taking place. Investigators have found evidence of increased aromatic character after cure; however, it was estimated that no more than 30% of the endgroups underwent cyclotrimerization, while the remainder underwent other reactions.^{262,264,276} Alkene endgroups intermediates have been claimed,²⁶³ and endgroups coupling to form ene-yne and yne-yne structures, followed by rearrangement and aromatization, have been proposed as curing reactions.^{264,266,269} The proposed structures are shown in Figure 2.5.5.3.

Hergenrother et al. have studied the thermal crosslinking reaction of N-(3-ethynylphenyl)phthalimide (EPPI) using DSC, mass spectrometry, HPLC and infrared spectrometry.²⁶⁹ As shown in Figure 2.5.5.4, the thermal reaction of EPPI can yield a very complex mixture composed of 2 dimers, 3 trimers, a tetramer as the minor components and high molecular weight polymeric material being the major component. However, model compound work can only serve as a guide and not a direct correlation to the products formed from the thermal polymerization of acetylene-terminated imide oligomers.

Recently, studies using ¹³C Magic-Angle Spinning NMR on isotopically labeled ethynyl functionalized imides revealed several cure products, including aromatic groups, polycyclic aromatic structures (naphthalene and phenanthrene), and bridged structures presumably resulting from electrophilic addition of ethynyl groups to backbone aromatic rings.²⁵⁹ FTIR cure studies of ethynyl-functionalized imide oligomers found no apparent cyclotrimerization or aromatization. Instead, crosslinking occurred exclusively by electrophilic addition of ethynyl endgroups to backbone aromatic rings as illustrated in Scheme 2.5.5.2.²⁵⁸ Many other studies investigating the curing mechanism and kinetics of ethynyl-terminated resins have been performed.²⁷⁷⁻²⁸⁶



Cyclotrimerization

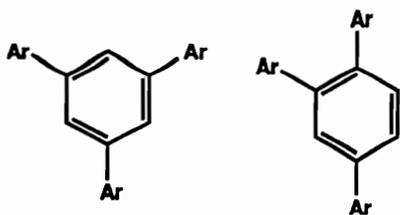


Formation of Ene-Yne Intermediates

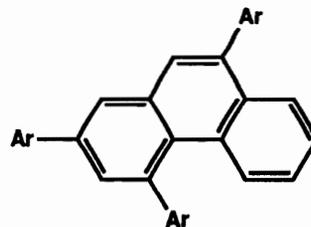
Scheme 2.5.5.1 Proposed Crosslinking Reactions of Ethynyl Endgroups ²⁶⁸

Reaction Mechanism and Products

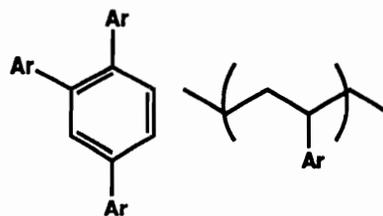
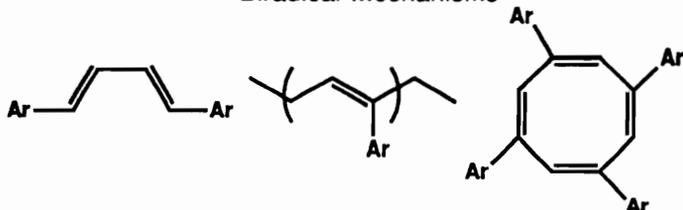
Cyclotrimerization



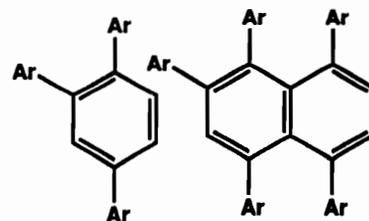
Further Reaction or Degradation Products



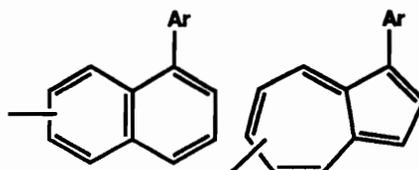
Biradical Mechanisms



Glasser Coupling



Strauss Coupling



Electrophilic Addition

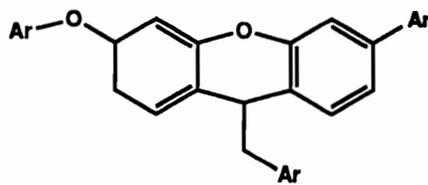
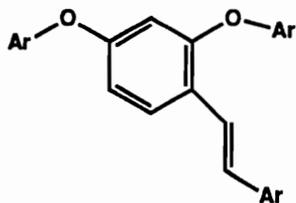
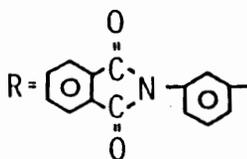
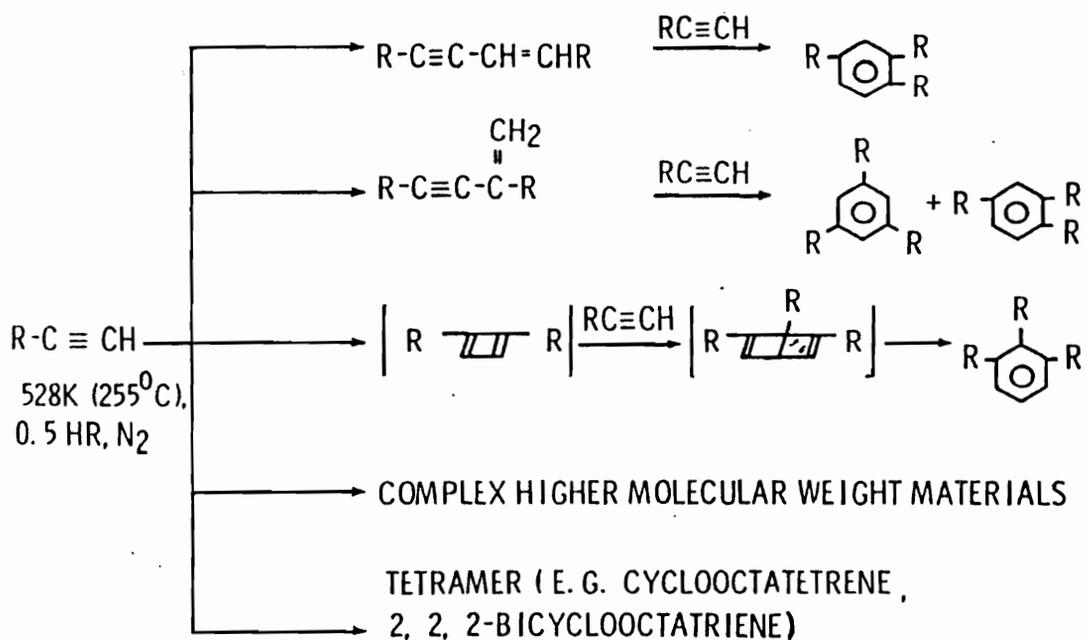


Figure 2.5.5.3 Acetylene Cure Reactions and Products ^{263,264,266,269}



COMPOUND	MOL. WT.
DIMER	494
TRIMER	741
TETRAMER	988

Figure 2.5.5.4 Products Found from Cured N-(3-ethynylphenyl)phthalimide (EPPI) ²⁶⁹

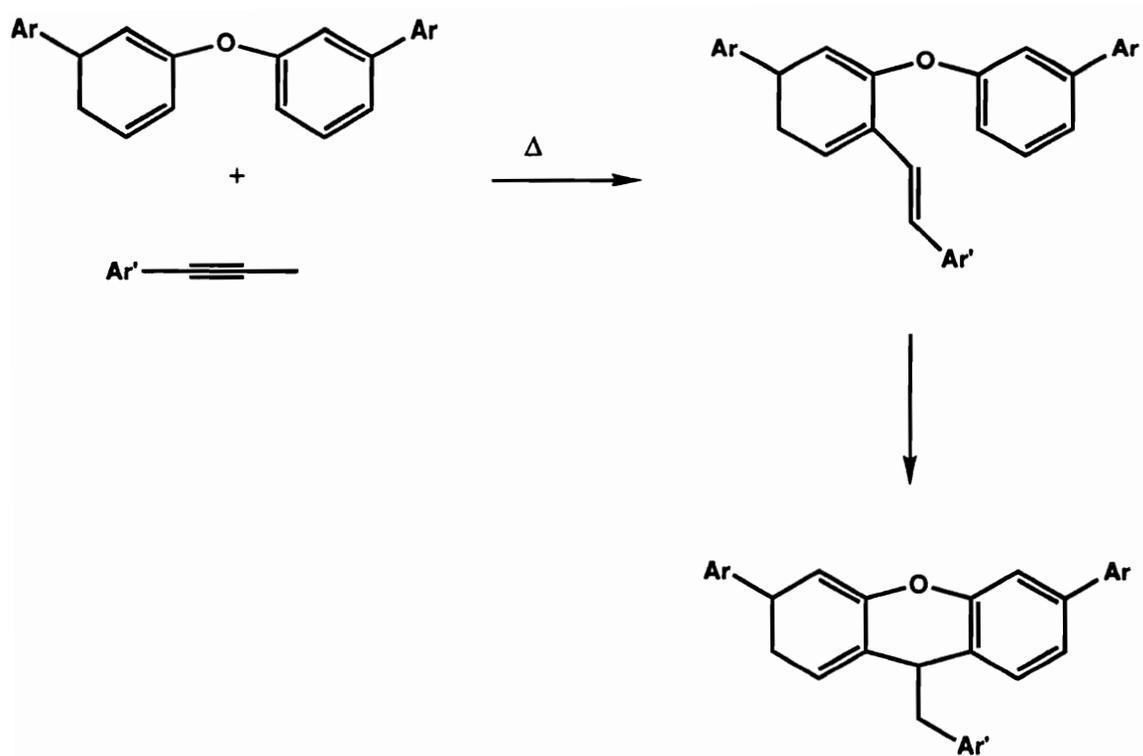
2.5.6 Phenylethynyl Functionalized Imides

Phenylethynyl-terminated polymers are a fairly recent development in thermosetting resin technology. Substitution of the terminal hydrogen on the acetylenic bond in monofunctional ethynyl endcapping agents with a phenyl group greatly increases the cure temperature (100°C or more) of polymers bearing this functionality. Polymers functionalized with either phenylethynyl pendant or terminal groups include polyphenylene,²⁸⁷ poly(phenylquinoxalines),²⁸⁸⁻³⁰⁰ polyamides,³⁰¹⁻³⁰⁵ poly(arylene ether)s,³⁰⁶⁻³¹³ polybenzoxazoles³¹⁴ and polyimides.^{190,191,309,315-334}

Through the last decade, the majority of polyimides endcapped with phenylethynyl groups were done so with the use of 3-phenylethynylaniline.^{190,191,309,315,316,318,319,325,329,330,333,334} Derivatives of 3-ethynylaniline utilizing phenyl or substituted phenyl substituents in place of the ethynyl proton exhibited cure temperatures as high as 343°C,^{315,334} insuring solvent removal prior to crosslinking, affording a wider processing window and permitting the use of higher T_g imide backbones. Some derivatives of 3-ethynylaniline are shown in Table 2.5.6.1.

The study conducted by workers at National Starch and Chemical Company raised several points. Phenyl substitution increases cure temperature by well over 100°C; the terminal phenyl substituent certainly hinders mutual endgroup reactions. In addition, incorporation of a flexible link into the endgroup as in 3-(3-(phenylethynyl)-phenoxy)aniline serves to lower the cure temperature. Furthermore, phenyl substituents bearing electron withdrawing groups raises the cure temperature relative to the unsubstituted phenyl substituent.

Harris and coworkers were the first to report on the synthesis of 3-phenylethynylaniline.³³³ The synthetic method involved a two-step method where 3-bromonitrobenzene was reacted with phenylacetylene in the presence of a palladium catalyst



Scheme 2.5.5.2 Electrophilic Addition of an Ethynyl Endgroup to an Aromatic Polymer Backbone²⁵⁸

[PdCl₂(PPh₃)₂], copper iodide and triphenylphosphine. Hydrogenation of 1-phenyl-2-(3-nitrophenyl)ethyne over a ruthenium catalyst afforded 3-phenylethynylaniline.

More recently, the focus has been directed towards the use of 4-phenylethynylphthalic anhydride as the endcapper of choice for imide oligomers.^{322,324,326,327,331,332} The phenylethynylphthalic anhydrides are prepared from a coupling reaction of 4-bromo or 4-iodophthalic anhydride with phenylacetylene or substituted phenylacetylene. Imide oligomers endcapped with 4-phenylethynylphthalic anhydrides tend to give cure temperatures 30 to 70°C higher than imides capped with phenylethynylaniline endcappers. In addition, substitution of the phenyl group pendant to the acetylenic bond affects the cure temperature as was noted with the phenylethynylaniline imide oligomers. The addition of electron withdrawing groups on the pendant phenyl groups significantly lowers the cure temperature as compared to 4-phenylethynylphthalic anhydride. This trend is opposite to that observed by the electron withdrawing groups attached to 3-phenylethynylaniline.^{315,334} Similarly, the introduction of electron donating groups raise the cure temperature slightly above that found for 4-phenylethynylphthalic anhydride. The structure and cure onset temperatures for phenylethynylphthalic anhydrides is shown in Table 2.5.6.2.

Cured phenylethynyl terminated imide oligomers display high fracture energies and high unoriented thin film elongations more typical of high molecular weight polymers than a conventional thermoset material.^{190,322,324} The thermal curing of imide oligomers terminated with phenylethynyl groups appears to be a very complex process and probably proceeds through a free-radical process. The exceptional mechanical properties of the cured materials indicate that a polyene may initially form, but probably concurrent with its formation, branching and subsequently crosslinking also occur. Cyclotrimerization of the phenylethynyl groups is sterically unfavorable and is expected to be significantly different

Table 2.5.6.1 Derivatives of 3-Ethynylaniline^{315,334}

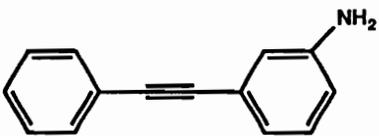
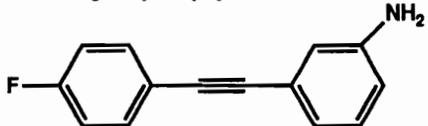
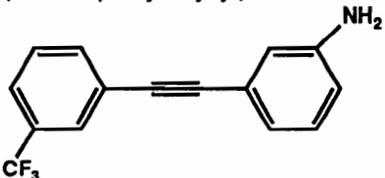
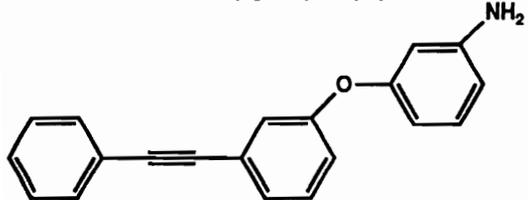
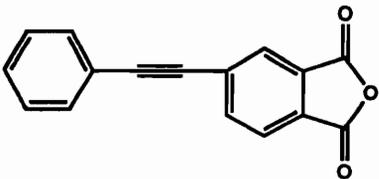
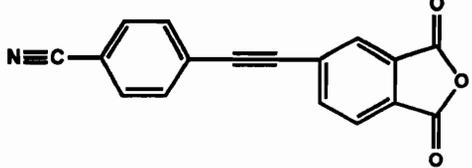
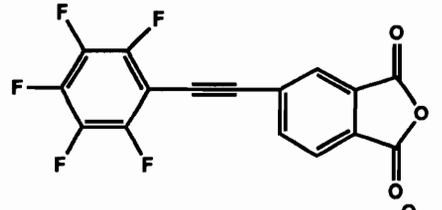
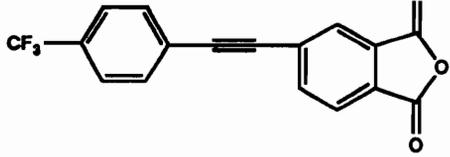
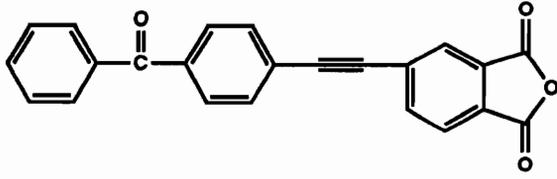
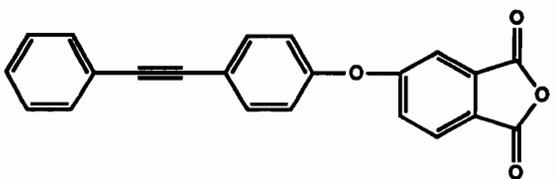
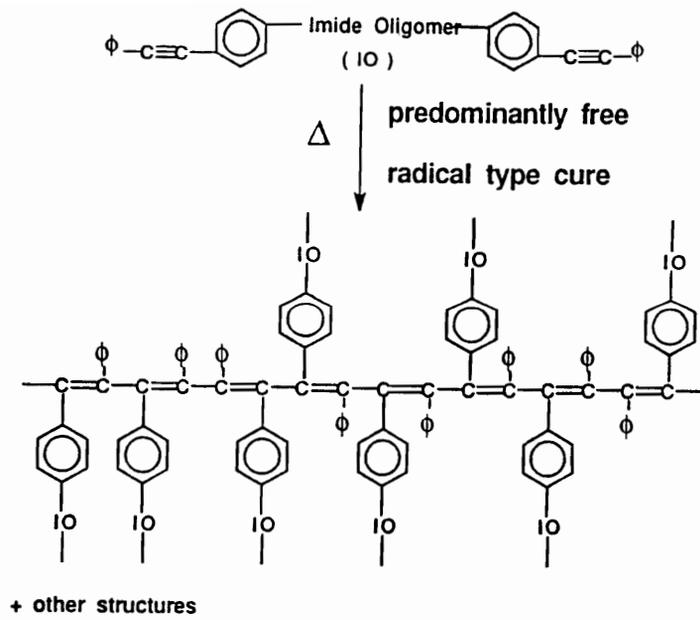
	Cure Temperature (°C)
 <p>3-phenylethynylaniline</p>	332
 <p>3-(4-fluorophenylethynyl)aniline</p>	343
 <p>3-(3-(trifluoromethyl)phenylethynyl)aniline</p>	343
 <p>3-(3-phenylethynylphenoxy)aniline</p>	303

Table 2.5.6.2 Phenylethynylphthalic Anhydride Endcapping Agents ^{322,324}

	Cure Temperature (°C)*
	436
	434
	430
	425
	424
	421

* = Heating rate of 20°C/min in nitrogen by DSC.



Scheme 2.5.6.1 Proposed Curing Reaction Structures of Phenylethynyl Terminated Polyimides ³²²

from that of the ethynyl groups. A proposed view of the type of chemical structures expected upon curing is illustrated in Scheme 2.5.6.1.³²²

2.5.7 Benzocyclobutene Functionalized Imides

Curing chemistry utilizing a strained four-membered ring fused to an aromatic system (benzocyclobutene) has appeared in the literature.^{335,336} High performance polymers including polyimides, polyaramids and poly(aryl ether ketone)s have been synthesized that have utilized the benzocyclobutene reactive groups to prepare crosslinked resins with excellent high temperature properties.³³⁷ Researchers at the Air Force Materials Laboratory were able to synthesize 4-aminobenzocyclobutene which has made possible the synthesis of benzocyclobutene terminated imide oligomers. The structure of a bisbenzocyclobutene imide is shown in Figure 2.5.7.1. The polymerization is believed to proceed through the thermally initiated ring opening of the benzocyclobutene to yield the *o*-xylene (*o*-quinodimethane) as an intermediate which polymerizes to form the crosslinked polymer. Although the exact cure mechanism of benzocyclobutenes is not yet fully understood, the polymerization proceeding through *o*-xylene as a 1,4 addition process is depicted in Scheme 2.5.7.1 at temperatures around 250°C.³³⁸ Similarly, *o*-xylene can undergo a Diels-Alder reaction to form crosslinked resins with various dienophiles as acetylene and maleimide groups. Benzocyclobutene functionalized imides cure without the generation of volatiles and without the need for a catalyst. Cured benzocyclobutene imides show very low moisture absorption and good thermal stability for potential use in high temperature structural composites.

2.5.8 Other Reactive Functionalized Imides

2.5.8.1 Biphenylene Functionalized Imides

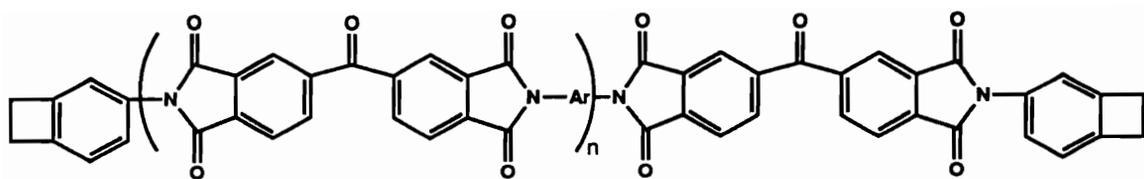
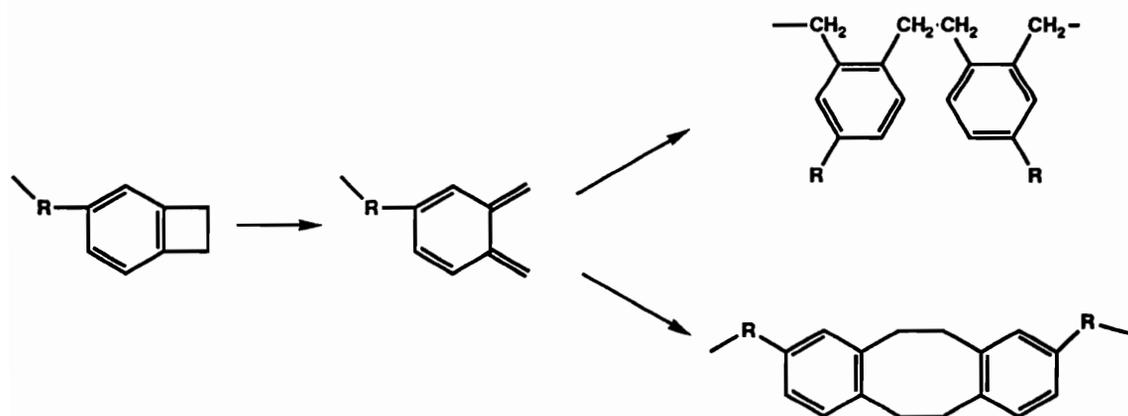


Figure 2.5.7.1 Chemical Structure of Benzocyclobutene Terminated Polyimides



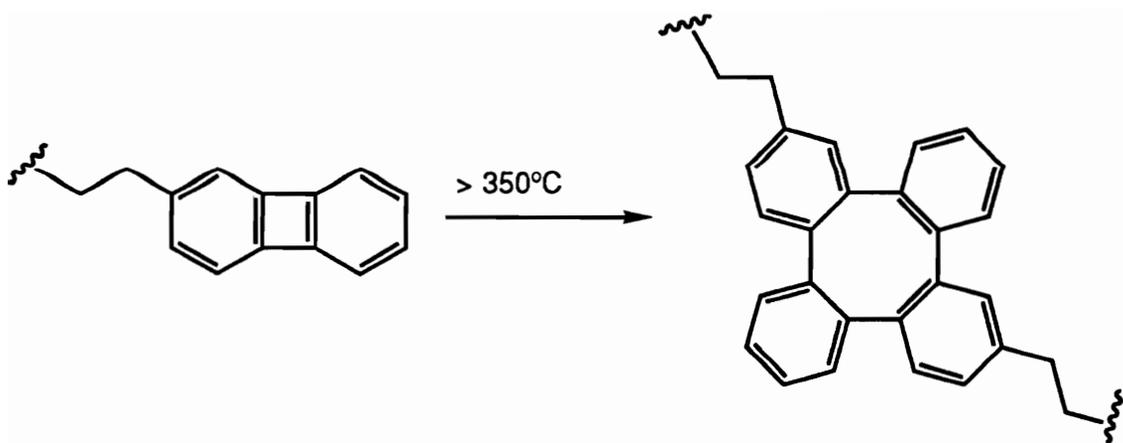
Scheme 2.5.7.1 Proposed Polymerization Sequence for Benzocyclobutene Imides ³³⁸

Biphenylene has been successfully employed as a reactive endgroup in polyimides^{272,339-341} and poly(phenylquinoxaline)s.³⁴² When heated above 350°C, biphenylene undergoes thermal ring opening to form primarily its cyclic dimer, tetrabenzocyclooctatetraene without the evolution of volatiles. In the presence of aromatic polymers, it reacts to form biphenylated aromatics as major products; however, crosslinking efficiency is low. The crosslinking is shown in Scheme 2.5.8.1.1. Increased curing has been achieved by co-curing blends of biphenylene-functionalized polyimides with polyimides containing in-chain (internal) acetylene linkages.³³⁹ The terminal biphenylene groups and internal acetylenes coreact at temperatures of 350-400°C to form phenanthrene crosslinks.

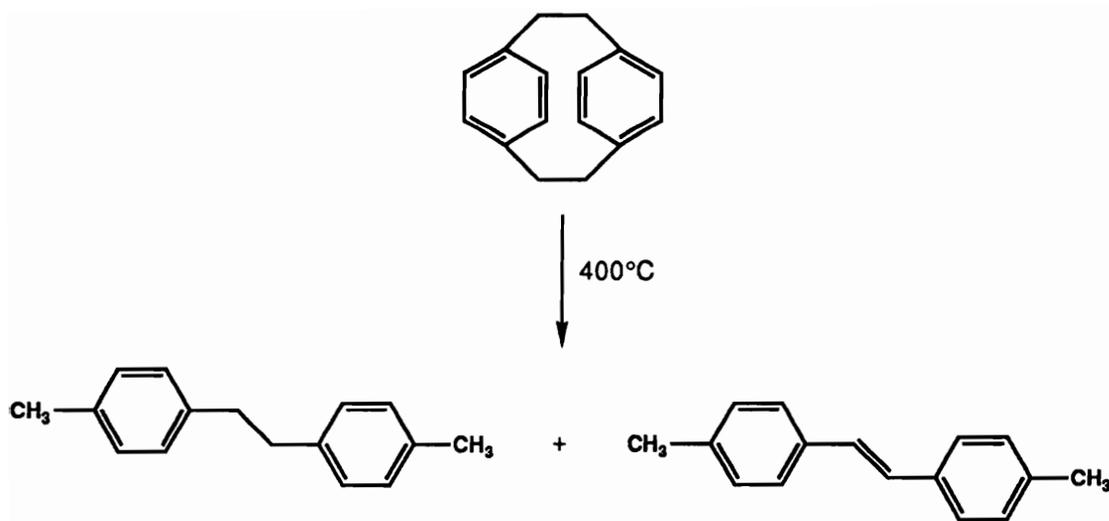
2.5.8.2 Paracyclophane Functionalized Imides

Paracyclophane has also been used as a potential high temperature curing end groups for polyquinolines^{343,344} and polyimides.^{345,346} Amino[2.2]paracyclophane has been used as the endcapping agent for polyimide synthesis. Paracyclophane reportedly crosslinks at temperatures in excess of 250°C without the evolution of volatiles.³⁴⁶⁻³⁵⁰

The crosslinking mechanism of paracyclophane-functionalized imides is not fully understood, but thermolysis studies of [2.2]-paracyclophane provide some possible structures of reactive intermediates. Cram found that when [2.2]-paracyclophane was heated at 400°C, two monomeric products were observed: 4,4'-dimethylbibenzyl and 4,4'-dimethylstilbene as illustrated in Scheme 2.5.8.2.1. The formation of methyl carbons resulting from the homolytic cleavage of an ethylene bridge of the cyclophane endcap followed by hydrogen abstraction by the methylene radical to form a methyl group may account for these products. Crosslinking via coupling of radical endgroups has been proposed regarding the cyclophane-functionalized imide³⁵¹; however, reaction of unsaturated endgroups generated at high temperatures is also possible.



Scheme 2.5.8.1.1 Biphenylene Dimerization



Scheme 2.5.8.2.1 Thermal Decomposition of [2.2]-Paracyclophane

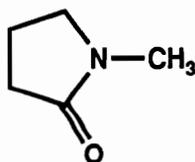
CHAPTER 3 - EXPERIMENTAL

3.1 PURIFICATION OF REAGENTS AND SOLVENTS

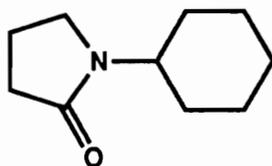
The utilization of pure reagents, solvents, and monomers is important in the synthesis of monomers, model compound studies, and for the synthesis of high molecular weight polyimides and controlled molecular weight functionalized oligomers. Therefore, the monomers and reagents were carefully purified and dried before use. Polymerization solvents were distilled from dehydrating agents using the apparatus shown in Figure 3.1.1. The distilled solvents (constant boiling middle fraction) were collected in round bottom flasks and sealed under a dry nitrogen atmosphere with a rubber septum. The solvents were transferred to reaction vessels using syringe techniques.

3.1.1. Solvent Purification

3.1.1.1 1-Methyl-2-pyrrolidone (NMP: Fisher) was dried over P_2O_5 for at least 12 hours and then distilled under reduced pressure generated by a vacuum pump to avoid solvent decomposition prior to use. (b.p. $205^{\circ}C/760$ mm)



3.1.1.2 N-Cyclohexyl-2-pyrrolidone (CHP: Aldrich) was dried over P_2O_5 for at least 12 hours and then distilled under reduced pressure (vacuum pump). (b.p. $290^{\circ}C/760$ mm)



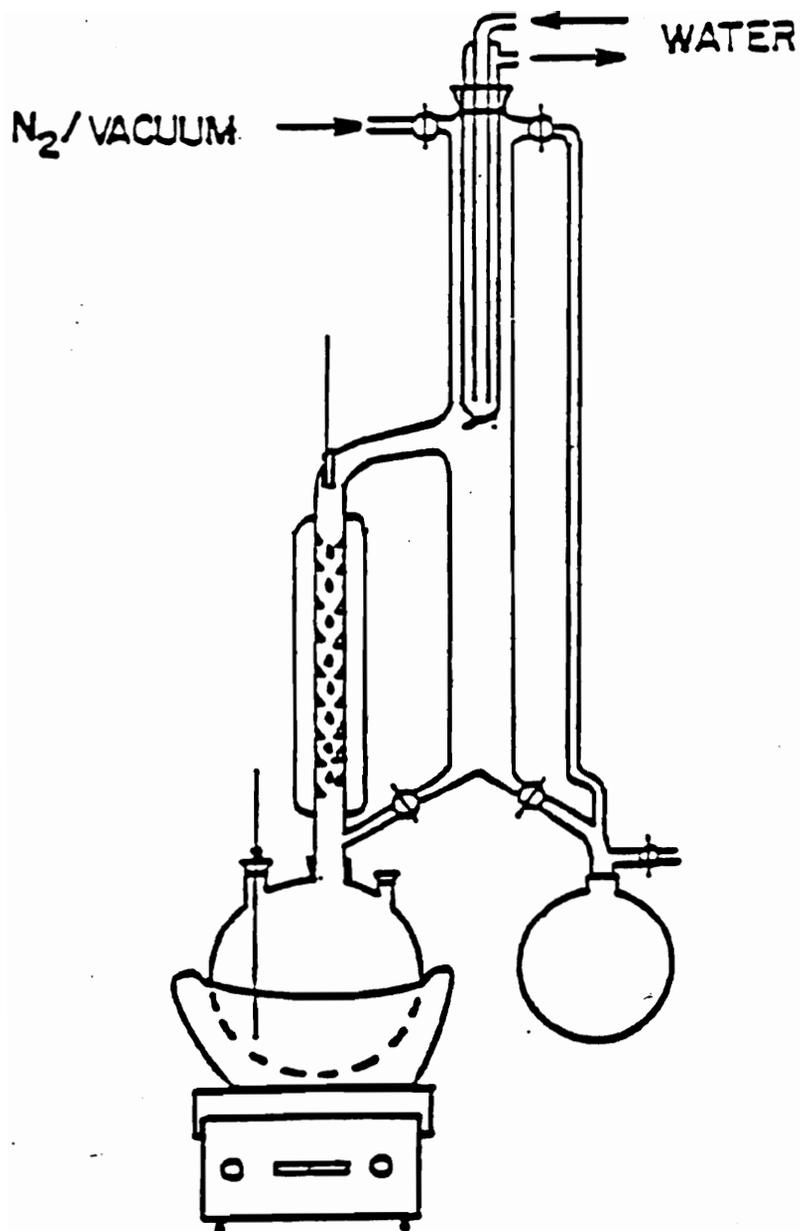
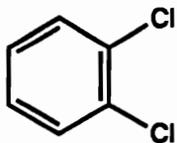
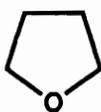


Figure 3.1.1 Distillation Apparatus

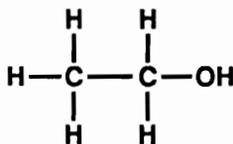
3.1.1.3 *o*-Dichlorobenzene (*o*-DCB) was dried over crushed calcium hydride for at least 12 hours and then distilled prior to use under reduced pressure (vacuum pump). (b.p. 180°C/760 mm)



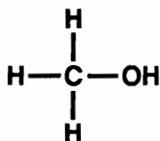
3.1.1.4 Tetrahydrofuran (THF; Fisher) was dried over sodium for at least 18 hours and distilled at atmospheric pressure under an argon gas purge. (b.p. 76°C/760 mm)



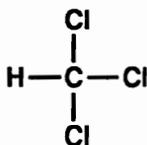
3.1.1.5 Ethanol (Absolute) (AAEPR Alcohol and Chemical) was used as received. (b.p. 78.5°C/760 mm)



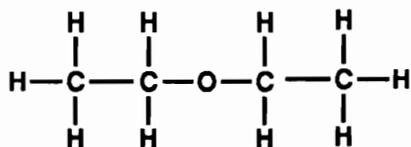
3.1.1.6 Methanol (Fisher) was received as an HPLC grade solvent and was not further purified. (b.p. 64.7°C/760 mm)



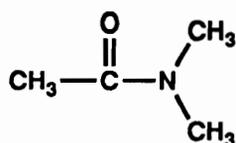
3.1.1.7 Chloroform (Fisher) was used as received. (b.p. 61-62°C/760 mm).



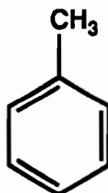
3.1.1.8 Diethyl Ether (Fisher) was used as received. (b.p. 34.6°C/760 mm)



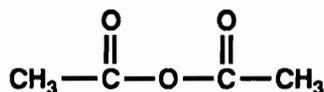
3.1.1.9 N,N-Dimethylacetamide (DMAc: Fisher) was dried over crushed calcium hydride for at least 12 hours and was then distilled under reduced pressure (vacuum pump). (b.p. 163-165°C/760 mm)



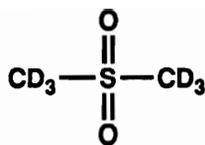
3.1.1.10 Toluene (Fisher) was distilled at atmospheric pressure prior to use. (b.p. 110.6°C/760 mm)



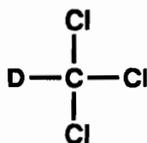
3.1.1.11 Acetic Anhydride (Fisher) was dried over crushed calcium hydride for at least 12 hours and was then distilled under reduced pressure (water aspirator). (b.p. 138-140°C/760 mm)



3.1.1.12 Deuterated Dimethyl Sulfoxide (DMSO-d₆: Cambridge Isotope Laboratories) 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)



3.1.1.13 Deuterated Chloroform (CDCl₃; Cambridge Isotope Laboratories) was dried over molecular sieves for at least 24 hours. The CDCl₃ was not distilled prior to use. (b.p. 61°C/760 mm)

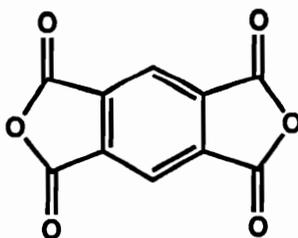


3.1.2 Monomers and Reagents

3.1.2.1 Pyromellitic Dianhydride (PMDA)

Supplier:	Allco
Molecular Formula:	C ₁₀ H ₂ O ₆
Molecular Weight:	218.12
Melting Point (pure), °C	286

Structure



Purification: Polymer forming PMDA was obtained as fine white granular crystals and was dried at 180°C for at least 12 hours under vacuum prior to use.

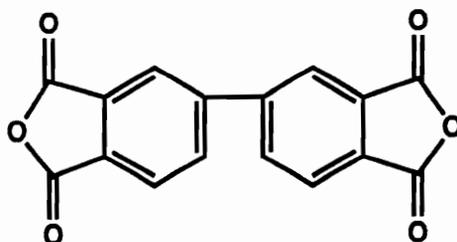
3.1.2.2 3,4,3',4'-Biphenyltetracarboxylic Dianhydride (BPDA)

Supplier:	Chriskev
Molecular Formula:	C ₁₆ H ₆ O ₆

Molecular Weight: 294

Melting Point (pure), °C 300

Structure



Purification: Polymer forming BPDA was obtained as fine white powder and was dried at 180°C for at least 12 hours under vacuum prior to use.

3.1.2.3 4,4'-Oxydiphthalic Anhydride (ODPA)

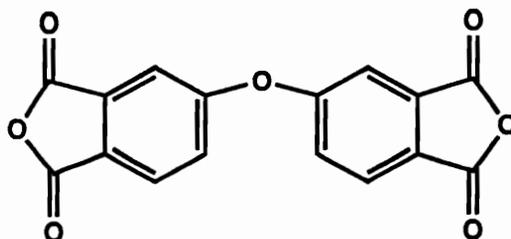
Supplier: Occidental Chemical Corporation

Molecular Formula: $C_{16}H_6O_7$

Molecular Weight: 310.23

Melting Point (pure), °C 228

Structure



Purification: Polymer forming ODPA was obtained as fine white powder and was dried at 180°C for at least 12 hours under vacuum prior to use.

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

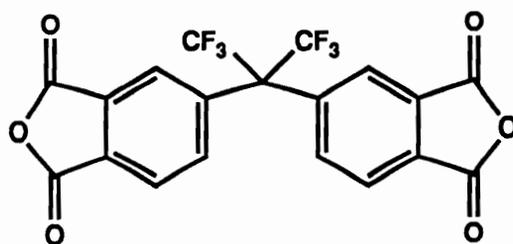
Supplier: Hoechst Celanese Corporation

Molecular Formula: $C_{19}H_6F_6O_6$

Molecular Weight: 444

Melting Point (pure), °C 247

Structure

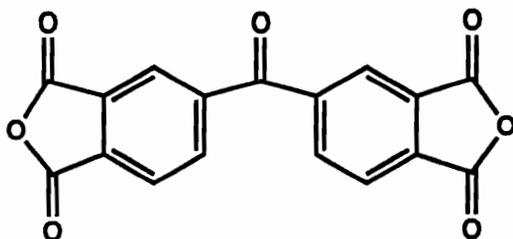


Purification: Ultra pure electronic grade 6FDA was obtained as fine white powder and was dried at 180°C for at least 12 hours under vacuum prior to use.

3.1.2.5 3,3',4,4'-Benzophenonetetracarboxylic Dianhydride (BTDA)

Supplier:	Allco
Molecular Formula:	C ₁₇ H ₆ O ₇
Molecular Weight:	322.23
Melting Point (pure), °C	224-226

Structure

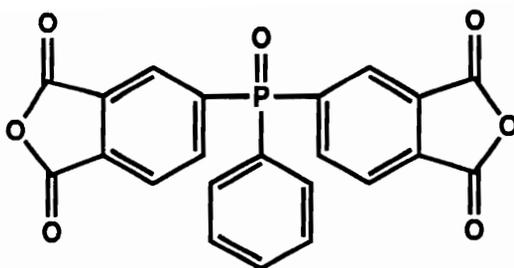


Purification: Polymer forming BTDA was obtained as fine white powder and was dried at 150°C for at least 12 hours under vacuum prior to use.

3.1.2.6 Bis(3,4-dicarboxyphenyl) Phenyl Phosphine Oxide Dianhydride (Phosphine Oxide Dianhydride or PPODA)

Supplier:	Synthesized in house
Molecular Formula:	C ₂₂ H ₁₁ O ₇ P
Molecular Weight:	418.30
Melting Point (pure), °C	287-288

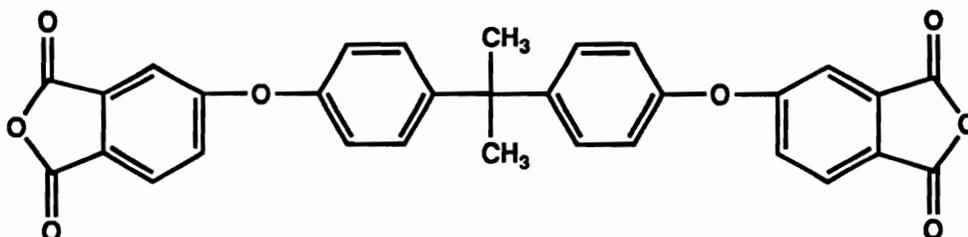
Structure



Purification: The synthesis of the PPODA was prepared by the reported procedure.¹⁷⁸ The synthesis and purification of phosphine oxide dianhydride is credited to Dr. Yin Lin. His work can be consulted for further details.¹⁷⁸

3.1.2.7 2,2'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane Dianhydride (Bisphenol A Dianhydride or BPA-DA)

Supplier:	General Electric Company
Molecular Formula:	C ₃₁ H ₂₁ O ₈
Molecular Weight:	520.49
Melting Point (pure), °C	193
Structure	

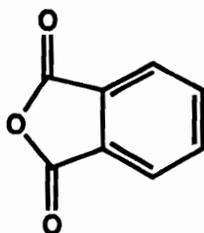


Purification: Polymer forming BPA-DA was obtained as fine yellow-white powder and was dried at 160°C for at least 12 hours under vacuum prior to use.

3.1.2.8 Half-ester derivatives were prepared in situ in by dissolving monomer grade dianhydride in refluxing ethyl alcohol. Esterified bis(phthalic anhydride) derivatives were obtained as viscous oils or syrups. In addition, esterification times were significantly reduced by adding a stoichiometric amount of triethylamine; the resulting bis(ester-triethylammonium carboxylate) could be used as a monomer directly without conversion to the parent ester-acid.

3.1.2.9 Phthalic Anhydride (PA)

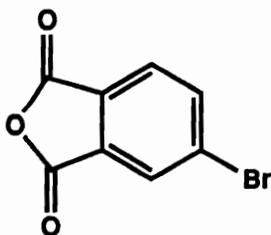
Supplier:	Aldrich Chemical Company
Molecular Formula:	$C_8H_4O_3$
Molecular Weight:	148.12
Melting Point (pure), °C	134
Structure	



Purification: Pure PA was obtained by sublimation under full vacuum at a temperature of ~125°C.

3.1.2.10 4-Bromophthalic Anhydride (Br-PAN)

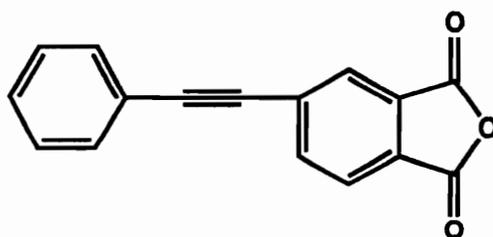
Supplier:	Ameribrom/Bromine Compounds Ltd.
Molecular Formula:	$C_8H_3O_3Br$
Molecular Weight:	227.01
Melting Point (pure), °C	280-282
Structure	



Purification: Pure Br-PAN was obtained and was not further purified before use.

3.1.2.11 4-Phenylethynylphthalic Anhydride (4-PEPA)

Supplier:	Synthesized in house
Molecular Formula:	$C_{16}H_8O_3$
Molecular Weight:	248.24
Melting Point (pure), °C	150-151
Structure	



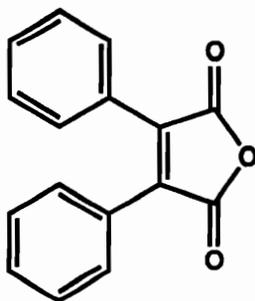
In a typical experiment 4-PEPA was synthesized via the palladium-catalyzed coupling reaction of 4-bromophthalic anhydride (4-BrPAN) and phenylacetylene in the presence of anhydrous triethylamine and DMAc as the cosolvents. For example, 2.202×10^{-2} mole (5.000 grams) of 4-BrPAN was charged to a round bottom flask equipped with a condenser, N_2 purge, and a magnetic stir bar, followed by the addition of 1.773×10^{-4} mole (0.0465 grams) of triphenylphosphine. Phenylacetylene 2.202×10^{-2} mole, (2.250 grams) was then syringed into the flask with 10 mL of DMAc.

Bis(triphenylphosphine)palladium(II) chloride ($Pd(Cl_2)(PPh_3)_2$) 3.320×10^{-5} mole, (0.0233 grams) was washed in with 10 mL of triethylamine. The flask was slowly heated to $60^\circ C$ and then 4.857×10^{-5} mole (0.00925 grams) of copper(I) iodide (CuI) was added with 15 mL of dried and distilled triethylamine. The reaction temperature was raised to $80^\circ C$ and the reaction was continued for ~12 hours.

The reaction mixture was next filtered to remove by product inorganic salts and the triethylamine was vacuum distilled using a rotary evaporator. The solution was then added to water and the aqueous solution was acidified with dilute HCl to a pH of 4. A light yellow solid precipitated out of solution which was extracted with ether. The ethereal solution was treated with charcoal, dried over $MgSO_4$, and filtered through Celite. The ether was removed under vacuum by a rotary evaporator and crude 4-PEPA was obtained. The crude product was dried in vacuo at $85^\circ C$ for 24 hours and then sublimed under vacuum at $160^\circ C$, to afford an off-white yellow solid. The overall yield was high (4.59g, 84%). Crude 4-PEPA can also be recrystallized directly in acetic anhydride. The compound was characterized by FTIR, 1776, 1847 (anhydride, C-O), 3050 (aromatic C-H), 2214 ($-C\equiv C-$), and 1506 cm^{-1} (aromatic, C-C); 1H NMR (DMSO - d_6) 7.4-7.5 (m, 3H, aromatic), 7.6 (m, 2H, aromatic), 8.1 (s, 2H, aromatic), 8.2 (s, 1H, aromatic); MS m/z (relative intensity %): 248 (M^+ , 100) and a melting point of $146 - 148^\circ C$ (capillary) was observed. The material could also be sublimed or recrystallized from acetic anhydride to afford a melting point peak (DSC) of $151^\circ C$.

3.1.2.12 Diphenylmaleic anhydride (DPMA)

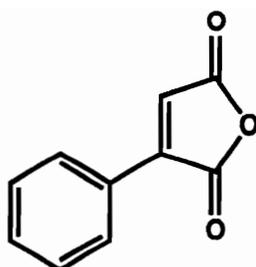
Supplier:	Synthesized in house
Molecular Formula:	C ₁₆ H ₁₀ O ₃
Molecular Weight:	250.25
Melting Point (pure), °C	156-158
Structure	



The synthesis of diphenylmaleic anhydride is based on the procedure reported by Fields et al.³⁵² In a typical experiment 1.566 g (1.043×10^{-2} mole) of benzoylformic acid was added to 80 mL of water. Subsequently, 0.417 g (1.04×10^{-2} mole) of NaOH was dissolved in 200 mL of water and this solution was added to the benzoylformic acid solution with stirring to form the sodium salt of benzoylformic acid. The water was then removed under vacuo. Phenylacetic acid (1.420 g, 1.043×10^{-2} mole) was added to the flask with 10 mL of acetic anhydride and was allowed to reflux for 2 hours. The solution was allowed to cool to room temperature. A yellow solid precipitated from solution upon standing and was placed in a refrigerator overnight. The solid was then poured into 150 mL of water with stirring for 5 minutes. The solid was filtered and washed with excess water. The yellow solid was dried at 90°C for at least 18 hours. Dark yellow crystals were obtained in 95% yield. The crude material was sublimed under reduced pressure at ~115°C to give a bright yellow solid.

3.1.2.13 Phenylmaleic Anhydride (PMA)

Supplier:	Synthesized in house
Molecular Formula:	C ₁₀ H ₆ O ₃
Molecular Weight:	174.16
Melting Point (pure), °C	118-120
Structure	

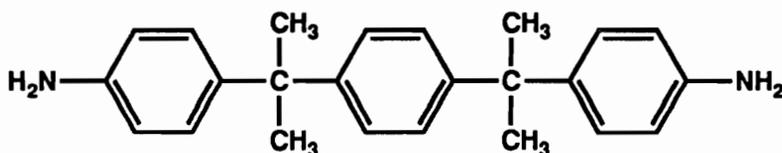


The synthesis is based a modification of the procedures reported by Hill and Paquette.^{353,354} In a typical experiment, 5.164×10^{-2} mole (10.028 g) of phenylsuccinic acid was charged to a 100 mL round bottom flask equipped with a condenser, N_2 purge, and a magnetic stir bar, and was washed in with 15 mL of acetic anhydride. Selenium dioxide (6.093×10^{-2} mole, 6.761 g) was then added and washed in with 16 mL of acetic anhydride. The reaction flask was immersed into an oil bath set at 155°C and the reaction was allowed to reflux ~ 9 hours.

The reaction mixture was filtered to remove the selenium salts formed. Most of the acetic anhydride was removed under vacuum by a rotary evaporator. The solution was then allowed to sit overnight in a refrigerator. The solution was then poured into water and stirred. A dark yellow solid precipitated out of solution. The solid was filtered and dried under vacuo at 60°C for 12 hours. The crude PMA was then sublimed under vacuum at $\sim 100^\circ\text{C}$ which afforded a light yellow solid. Overall yield (8.27 g, 92%), mp $119\text{-}120^\circ\text{C}$, FTIR- cm^{-1} 1766, 1842 (anhydride, C-O), 3077 (aromatic C-H), 1508 (aromatic, C-C); ^1H NMR (DMSO - d_6) 7.5-7.6 (m, 3H, aromatic), 7.75 (s, 1H, aromatic), 8.05 (d, $J = 8.0$ Hz, 2H, aromatic); MS m/z (relative intensity %): 175 (M^+ , 100).

3.1.2.14 4, 4'-[1, 4-Phenylene-bis-(1-methylethylidene)]bisaniline (Bis P)

Supplier:	Air Products and Chemicals, Inc. or Kennedy and Klim
Molecular Formula:	$\text{C}_{24}\text{H}_{28}\text{N}_2$
Molecular Weight:	344
Melting Point (pure), $^\circ\text{C}$	165
Structure	

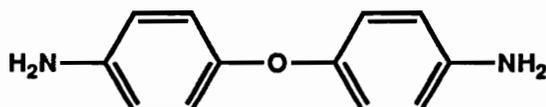


Purification: Bis P was dried at 110°C for at least 12 hours in a vacuum oven prior to use.

3.1.2.15 4, 4'-Oxydianiline (4, 4'-ODA)

Supplier: Aldrich Chemical Company or Kennedy and Klim
Molecular Formula: C₁₂H₁₂N₂O
Molecular Weight: 200.24
Melting Point (pure), °C: 192

Structure



Purification: 4,4'-ODA was sublimed under vacuum (50 millitorr) at ~170°C.

3.1.2.16 1,4-Phenylenediamine (*p*-PDA)

Supplier: Aldrich Chemical Company
Molecular Formula: C₆H₈N₂
Molecular Weight: 108.14
Melting Point (pure), °C: 145

Structure

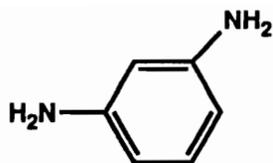


Purification: *p*-PDA was sublimed under vacuum (50 millitorr) at ~130°C. *p*-PDA oxidizes readily in air and must be used soon after sublimation and stored under vacuum away from light.

3.1.2.17 1, 3-Phenylenediamine (*m*-PDA)

Supplier: Aldrich Chemical Company
Molecular Formula: C₆H₈N₂
Molecular Weight: 108.14
Melting Point (pure), °C: 66

Structure



Purification: *m*-PDA was sublimed under vacuum (50 millitorr) at ~50°C. *m*-PDA oxidizes readily in air and must be used soon after sublimation and stored under vacuum away from light.

3.1.2.18 3, 3'-Diaminodiphenyl Sulfone (*m*-DDS)

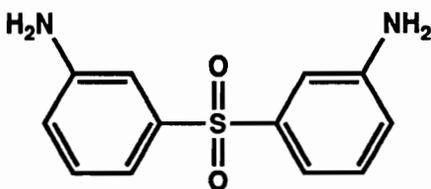
Supplier: Aldrich Chemical Company

Molecular Formula: C₁₂H₁₂N₂O₂S

Molecular Weight: 248.3

Melting Point (pure), °C 173

Structure



Purification: *m*-DDS was received as a fine white powder of 97% purity and was recrystallized from deoxygenated ethanol to yield polymer forming material. *m*-DDS was dried under vacuum at 70°C for at least 12 hours.

3.1.2.19 Bis-(3-aminophenoxy-4'-phenyl) Phenylphosphine Oxide (*m*-BAPPO)

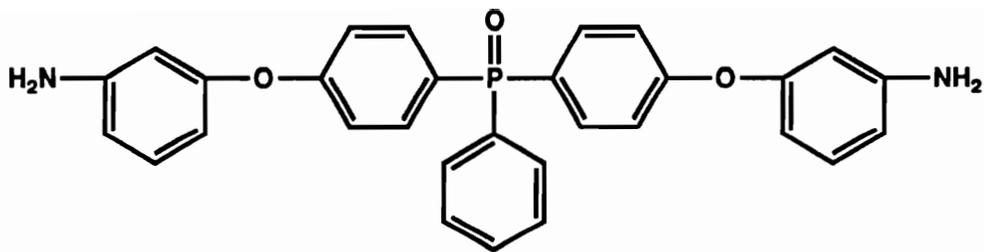
Supplier: Synthesized in house

Molecular Formula: C₃₀H₂₃N₂O₃P

Molecular Weight: 492.52

Melting Point (pure), °C 72-74

Structure

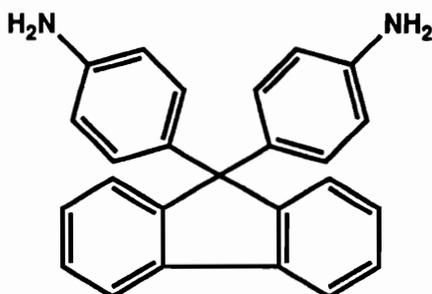


Purification: The synthesis of the *m*-BAPPO was prepared by the reported procedure. The synthesis and purification of *m*-BAPPO is credited to Dr. A. Gungor. His work can be consulted for further details.¹⁶⁹

3.1.2.20 9,9-Bis(4-aminophenyl)fluorene (FDA)

Supplier:	Kennedy and Klim
Molecular Formula:	C ₂₅ H ₂₀ N ₂
Molecular Weight:	348.16
Melting Point (pure), °C	235-237

Structure

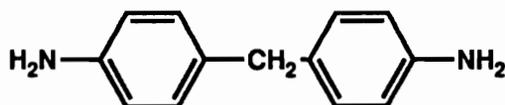


Purification: Polymer forming FDA was obtained and was used without any further purification.

3.1.2.21 4,4'-Diaminodiphenylmethane (4,4'-Methylene Dianiline, 4,4'-MDA)

Supplier:	Aldrich Chemical Company
Molecular Formula:	C ₁₅ H ₁₈ N ₂
Molecular Weight:	198.27
Melting Point (pure), °C	89-91

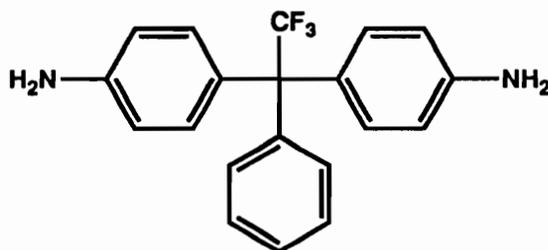
Structure



Purification: 4,4'-MDA was received as impure dark yellow pellets. 4,4'-MDA was recrystallized from benzene and was vacuum dried at 50°C.

3.1.2.22 1, 1-Bis(4-aminophenyl)-1-phenyl-2, 2, 2-trifluoroethane (3F Diamine or 3FDAM)

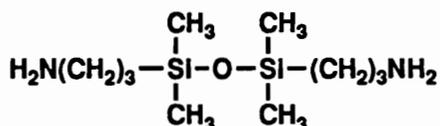
Supplier: Synthesized in house or Maxdem Corporation
Molecular Formula: C₂₀H₁₇N₂F₃
Molecular Weight: 342.37
Melting Point (pure), °C: 218-220
Structure



Purification: The synthesis of the 3FDAM was prepared by the reported procedure. The synthesis and purification of 3FDAM is credited to Dr. Harvey Grubbs. His work can be consulted for further details.^{167,355}

3.1.2.23 Aminopropyl Terminated Polydimethylsiloxane (Amine Terminated PDMS)

Supplier: Synthesized in house
Molecular Weight: 1090
Structure



Purification: The amine terminated PDMS was prepared by the reported procedure. The synthesis and purification of amine terminated PDMS is credited to Sue Mecham. Her work can be consulted for further details.^{138,356}

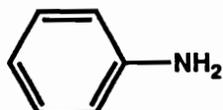
3.1.2.24 Aniline (An)

Supplier: Aldrich Chemical Company
Molecular Formula: C₆H₇N₁

Molecular Weight: 93.13

Boiling Point (pure), °C 184

Structure



Purification: An was dried over crushed calcium hydride for at least 12 hours and then distilled under reduced pressure (water aspirator).

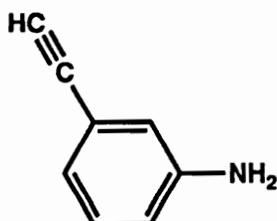
3.1.2.25 3-Ethynylaniline (*m*-Aminophenylacetylene or *m*APA)

Supplier: Eastman Kodak

Molecular Formula: C₈H₇N

Molecular Weight: 117

Structure



Purification: *m*APA was received as an impure yellow liquid, which was readily purified by vacuum distillation at ~ 90°C and 50 millitorr.

3.1.2.26 3-Phenylethynylaniline (3-PEA)

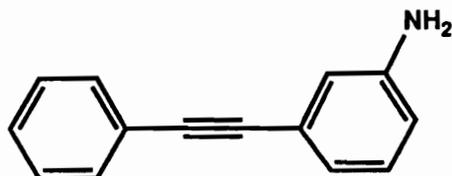
Supplier: Synthesized in house

Molecular Formula: C₁₄H₁₁N

Molecular Weight: 193.25

Boiling Point (pure), °C 46-48

Structure



Purification: The 3-phenylethynylaniline endcapping agent was synthesized via the palladium-catalyzed coupling reaction of *m*-aminophenylacetylene and bromobenzene.³⁰⁹

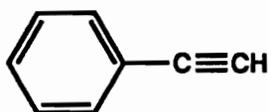
A typical example of the synthesis of the 3-phenylethynylaniline follows : 44.71 mL (0.4274 mole, 66.67g) of bromobenzene (distilled) was charged to a 1 L round bottom flask equipped with a stir bar and a condenser which was fitted with a septa with nitrogen purge. 50.00 grams (0.4274 mole) of *m*-aminophenyl acetylene (distilled) was then charged to the flask and washed in with 50 mL of triethylamine (distilled and purged with nitrogen 30 minutes). 1.554 grams (5.925×10^{-3} mole) of triphenylphosphine was then added and washed in with 40 mL of triethylamine. 0.776 grams of $\text{PdCl}_2(\text{PPh}_3)_2$ (1.105×10^{-3} mole) was charged to the flask and washed in with 40 mL of triethylamine. An additional 80 mL of triethylamine was charged to the flask. DMAc was used as a cosolvent and 150 mL (distilled and purged with nitrogen 30 minutes) was charged to the reaction flask. This latter component appears to be the main reason for the significantly improved yield, relative to the literature³³³. The reaction flask was then warmed to $\sim 60^\circ\text{C}$ with an oil bath and 0.309 grams (1.62×10^{-3} mole) of copper iodide was then added. Finally the reaction was warmed to 80°C where it was maintained overnight (~ 12 hours). The entire reaction setup was covered with aluminum foil and the reaction was allowed to proceed in the dark.

The following day the salts that formed were filtered from the reaction solution and washed with DMAc. The triethylamine was then removed by a rotary evaporator. The solution was then added into ~ 1200 mL of water to afford a total volume of 1800 mL. Sodium chloride was added with stirring to break-up the emulsion that had formed. This was allowed to stir for approximately 30 minutes, and then the 3-phenylethynylaniline product was extracted with 3 - 4 aliquots with diethyl ether. The ether solution was then washed with water, dried over MgSO_4 and treated with charcoal. The solution was filtered through Celite and the ether was then removed by a rotary evaporator. The flask was placed on a vacuum line fitted with a stir bar where it crystallized slowly over a period of about 12 hours.

This material was then sublimed at $\sim 90^\circ\text{C}$ to afford a yellowish-white solid. This product may also be vacuum distilled with a short-neck distillation head at $\sim 160^\circ\text{C}$ and 50 millitorr. Overall yield was $\sim 80\%$, mp $46\text{-}48^\circ\text{C}$, FTIR- cm^{-1} 3448, 3375 (amine, N-H), 3050 (aromatic C-H), 2213 ($\text{—C}\equiv\text{C—}$), 1506 (aromatic, C-C); ^1H NMR (DMSO - d_6) 5.2 (s, 2H, NH_2), 6.6 (d, $J = 8.2$ Hz, 1H, aromatic), 6.7 (d, $J = 7.6$ Hz, 1H, aromatic), 6.75 (s, 1H aromatic), 7.4 - 7.6 (broad, 5H, aromatic), 7.1 (t, $J = 7.8$ Hz, 1H, aromatic); MS m/z (relative intensity %): 193 (M^+ , 100).

3.1.2.27 Phenylacetylene (Ethylnylbenzene)

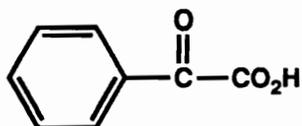
Supplier:	Aldrich Chemical Company
Molecular Formula:	C_8H_6
Molecular Weight:	102.14
Boiling Point (pure), °C	142-144
Structure	



Purification: Phenylacetylene was received as an impure yellow liquid, which was readily purified by vacuum distillation at $\sim 100^\circ C$ and 50 millitorr.

3.1.2.28 Benzoylformic acid

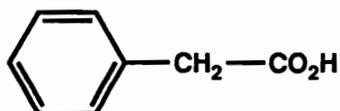
Supplier:	Aldrich Chemical Company
Molecular Formula:	$C_8H_6O_3$
Molecular Weight:	150.13
Melting Point (pure), °C	65-67
Structure	



Purification: Benzoylformic acid was received as a white-tan solid which was used as received.

3.1.2.29 Phenylacetic acid

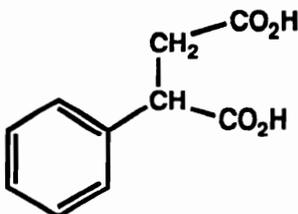
Supplier:	Aldrich Chemical Company
Molecular Formula:	$C_8H_8O_2$
Molecular Weight:	136.15
Melting Point (pure), °C	77-78.5
Structure	



Purification: Phenylacetic acid was received as a white solid which was used as received.

3.1.2.30 Phenylsuccinic acid

Supplier:	Aldrich Chemical Company
Molecular Formula:	$C_{10}H_{10}O_4$
Molecular Weight:	194.19
Melting Point (pure), °C	167-169
Structure	



Purification: Phenylsuccinic acid was received as a white solid which was used as received.

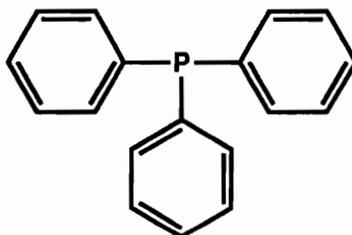
3.1.2.31 Bis(triphenylphosphine)palladium(II) Chloride

Supplier:	Aldrich Chemical Company
Molecular Formula:	$C_{18}H_{15}P_2PdCl_2$
Molecular Weight:	701.89
Structure	$[(C_6H_5)_3P]_2PdCl_2$

Purification: Bis(triphenylphosphine)palladium(II) chloride was received as a yellow solid which was used as received.

3.1.2.32 Triphenylphosphine

Supplier:	Aldrich Chemical Company
Molecular Formula:	$C_{18}H_{15}P$
Molecular Weight:	262.29
Melting Point (pure), °C	79-81
Structure	



Purification: Triphenylphosphine was received as a white solid which was used as received.

3.1.2.33 Copper (I) Iodide

Supplier: Aldrich Chemical Company

Molecular Formula: CuI

Molecular Weight: 190.44

Melting Point (pure), °C 605

Structure

Purification: CuI was received as a brown solid which was used as received.

3.1.2.34 Selenium (IV) Oxide (Selenium Dioxide)

Supplier: Aldrich Chemical Company

Molecular Formula: SeO₂

Molecular Weight: 110.96

Melting Point (pure), °C 315

Structure



Purification: Selenium dioxide was received as a white solid which was used as received.

3.3 POLYMER SYNTHESIS

The high molecular weight polyimides and polyimide oligomers studied in this research were synthesized by first forming the ester-acid of the dianhydride and then combining the ester-acid with a diamine. Reactive or non-reactive monofunctional endcapping agents were usually added after the formation of the ester-acid to control the endgroup composition. The starting materials were then cyclodehydrated in solution in the presence of an azeotroping agent.

The polyimides synthesized in this research were made in a three or four-neck, round bottom flask pictured in Figure 3.3.1.1. The size employed was usually 100 mL in volume but the size varied depending on the amount of polymer being made. The flasks were equipped with a nitrogen purge, an overhead stirrer or magnetic stir bar and a reverse Dean Stark trap (wrapped with heat tape) to which a condenser was attached. The reverse Dean Stark trap was filled with *o*-DCB to maintain a constant amount of azeotroping agent in the reaction solution. Synthetic procedures will be summarized for the synthesis of high molecular weight polyimides, randomly segmented polyimide siloxane copolymers endcapped with 3-ethynylaniline or 3-phenylethynylaniline and polyimide oligomers endcapped with 3-phenylethynylaniline, 4-phenylethynylphthalic anhydride and phenylmaleic anhydride.

3.3.1 Molecular Weight Control and Determination of Monomer Stoichiometry

Molecular weight control techniques were used to obtain well defined functionalized, processable polyimide oligomers. The techniques of molecular weight control and endgroup control in step growth condensation polymers are based on the stoichiometric imbalance of monomers with a calculated amount of a monofunctional molecular weight limiting reagent derived from the Carothers equation.¹⁰³

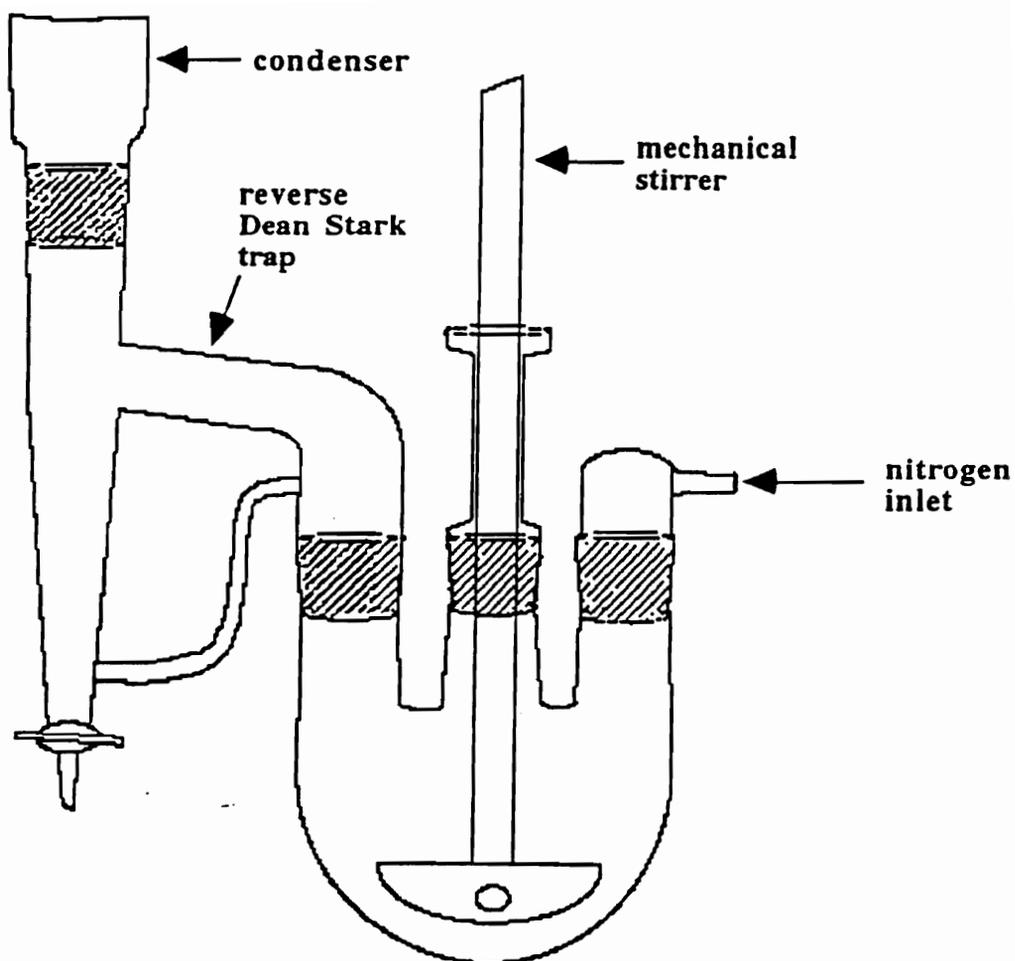


Figure 3.3.1.1 Reaction Flask Apparatus

The stoichiometric imbalance of monomers or monofunctional monomer must be carefully controlled to obtain desired molecular weights. Sample calculations for controlling molecular weight in polyimides with monofunctional endgroups are now described.

Based on the Carothers equation,¹⁰³ the number average degree of polymerization, X_n or D_p , is correlated to the extent of reaction, p , and the average functionality, f_{avg} , of the polymer.

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

D_p is related to the polymer molecular weight by

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

where M_d is the desired molecular weight of the polymer and M_{ru} is the repeat unit molecular weight. The molecular weight is also related to the stoichiometric imbalance, r , which is normally defined to be less than 1.

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

One factor in molecular weight and endgroup control that is often forgotten is the contribution of endgroups to the targeted molecular weight. The contribution of endgroups in low molecular weight polymer chains (< 15,000 g/mole) can have a pronounced effect on the desired molecular weight and must be accounted for in the calculation of the degree of polymerization, D_p . The desired molecular weight is more accurately given by M_d'

$$(3-4) \quad M_d' = M_d - M_{teg}$$

where M_{teg} is the total molecular weight of both endgroups. As a result, the degree of polymerization for low molecular weight polymers is given by

$$(3-5) \quad D_p = 2 \frac{M_d'}{M_{ru}}$$

The number average molecular weight of a polymer can be controlled by offsetting the stoichiometry of two mutually reactive difunctional monomers in favor of one of the monomers. The polymer will have the same endgroup functionality as the monomer used in excess. The stoichiometric imbalance, r , may be defined as

$$(3-6) \quad r = \frac{N_a}{N_b}$$

where N_a is the number of moles of "A" functional groups and N_b is the number of moles of "B" functional groups in a polymer using monomer AA with "A" functional groups and excess of monomer BB with "B" functional groups.

The molecular weight can also be controlled by adding a monofunctional endgroup. The monofunctional endgroup, B, has the same functionality as monomer BB. In this instance, the number of moles of "A" functional groups in the difunctional monomer, AA is given by N_a and the moles of AA is $\frac{1}{2} N_a$. The number of moles of "b" functional group in the difunctional monomer, BB, is given by N_b and the number of moles of BB is $\frac{1}{2} N_b'$ which is also equal to the number of moles of B. The total number of moles containing "B" functional groups is $\frac{1}{2} N_b + N_b'$. As a result, r is defined as

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

3.3.2 Example of Monomer Amount Calculations

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

MW_{6FDA}: molecular weight of 6FDA = 444.243

MW_{ODA}: molecular weight of 4,4'-ODA = 200.242

MW_{PEA}: molecular weight of 3-Phenylethynylaniline = 193.250

X_n is found from equation 3-2 where M_d is 3,000 g/mole and M_{ru} is given by

$$(3-6) \quad M_{ru} = MW_{6FDA} + MW_{ODA} - 36.03 = 444.243 + 200.242 - 36.03 = 608.455$$

The molecular weight of 2 moles of water (36.03) is subtracted from the combined molecular weight of 6FDA and ODA since 2 moles of water is given off for every repeat unit that is formed. M_d' is calculated to be

$$(3-8) \quad M_d' = 3,000 \text{ g/mole} - 177.227 - 614.485 = 2,208$$

D_p is then calculated by

$$(3-9) \quad D_p = 2 \frac{M_d'}{M_{ru}} = 2 \frac{(2,208)}{(608.455)} = 7.26$$

The stoichiometric imbalance, r , is found by using equation 3-3

$$(3-10) \quad r = \frac{D_p - 1}{D_p + 1} = \frac{7.26 - 1}{7.26 + 1} = 0.76$$

N_b' is given by a value of 0.10 mole. Therefore, using equation 3-5

$$r = \frac{N_a}{N_b + 2N_b'}$$

N_a and N_b may be calculated. The reactant quantities are listed below:

<u>Monomer</u>	<u>MW</u>	<u>Moles</u>	<u>grams</u>
6FDA	444.243	0.18	79.963
ODA	200.242	0.13	26.031
3-PEA	193.250	0.10	19.325

3.3.3 High Molecular Weight Polyimides

High molecular weight polyimides were typically made by the solution imidization starting with the combination the diester-diacid of a dianhydride and a diamine which was heated directly to $\sim 180^\circ\text{C}$ to form the polyimide. No poly(amic acid) was formed. The molecular weight of the polyimides was controlled by offsetting the stoichiometry of the dianhydride and the diamine. Ordinarily, the monofunctional nonreactive endcapping agent phthalic anhydride was added to endcap the polyimide. However, uncontrolled molecular weight polyimides were also synthesized where an equal stoichiometry (1:1) was used; this resulted in polymer chains with both anhydride and amine functionalities.

The following procedure is a representative example of the synthesis of high molecular weight polyimide polymerization. The polyimide prepared was BPA-DA/*m*-PDA/PA polyimide with a targeted number average molecular weight of 30,000 g/mole. The BPA-DA (6.713×10^{-3} mole, 3.494 grams) and 2.65×10^{-4} mole (0.0393 grams) of

phthalic anhydride were charged to a 3-neck round bottom flask equipped with a magnetic stirrer, nitrogen inlet, thermometer, reverse Dean-Stark trap and reflux condenser which was heated in an oil bath. Absolute ethanol, 7-10 mL per gram of dianhydride and ~ 3 mL of triethylamine were then introduced and the mixture was refluxed with stirring until a clear solution was obtained. When the distillation of ethanol ceased, the trap was filled with *o*-DCB. Next, the diamine, *m*-PDA, 6.85×10^{-3} mole (0.740 grams) was then added into the reaction vessel, followed by NMP (19 mL) and *o*-DCB (5 mL) (80:20 vol.:vol.) to provide a solids content of 15 % wt. to vol. The reaction mixture was then heated at 170-185°C for 20 hours, after which time the polymer solution was precipitated by slowly dripping the cooled polyimide solution into methanol in a high speed blender. The polymer was collected by vacuum filtration, washed with excess methanol and then with excess anhydrous diethyl ether. It was then air dried 6-8 hours and vacuum dried at ~160°C for 24 hours. If the samples were semi-crystalline, they were dried an additional 12 hours at 250°C under vacuum.

3.3.4 Polyimide Oligomers Endcapped with 3-Phenylethynylaniline

This section describes the synthesis of a PMDA/*m*-BAPPO/PEA polyimide oligomer with a target $\langle M_n \rangle$ of 9,000 g/mole. PMDA, 74.96 grams (3.437×10^{-1} mole) was charged to a 2000 mL 3-neck round bottom flask equipped with an overhead stirrer, nitrogen inlet, thermometer, reverse Dean-Stark trap and reflux condenser and the reactor was heated with a silicone oil bath. Absolute ethanol (7-10 mL per gram of dianhydride) was then introduced. The mixture, was then refluxed with stirring until a clear solution was obtained. When the distillation of ethanol ceased, the trap was filled with *o*-dichlorobenzene. Next, 9.7943 grams (5.0682×10^{-2} mole) of 3-phenylethynylaniline was charged to endcap the oligomer as a solution in 100 mL of NMP. The diamine, *m*-BAPPO, 156.74 grams (3.1825×10^{-1} mole), was then dissolved in 200 mL NMP and

charged into the reaction vessel. An additional 280 mL of NMP was subsequently added to the reaction vessel. An azeotroping solvent, *o*-dichlorobenzene, 145 mL, was then added to provide a solids content of 25% wt.:vol. The reaction mixture was then slowly heated to 170-185°C and held for ~15 hours, after which time the viscous polymer solution was cooled to room temperature and precipitated by slowly dripping the polyimide solution into an excess of methanol in a high speed blender. The polymer was collected by vacuum filtration, washed with excess methanol and excess anhydrous diethyl ether, air dried 6-8 hours and vacuum dried at ~170°C for 24 hours.

3.3.5 Randomly Segmented Polyimide Siloxane Copolymers Endcapped with 3-Phenylethynylaniline or 3-Ethynylaniline

The random segmented polyimide siloxane copolymers were prepared by a one-step solution imidization method similar to the previously reported procedure by Wescott³⁵⁷ and Rogers.⁷⁰ The $\langle M_n \rangle$ was controlled to 30,000 g/mole. The synthesis of a ODPa/Bis P/21 % PSX1090/PEA was conducted as follows: ODPa, 8.328 grams (2.6843×10^{-2} mole) was charged to a 250 mL 4-neck round bottom flask equipped with an overhead stirrer, nitrogen inlet, thermometer, reverse Dean-Stark trap and reflux condenser and the reactor was heated with a silicone oil bath. Absolute ethanol (7-10 mL per gram of dianhydride) was then introduced. The mixture, was then refluxed with stirring until a clear solution was obtained. When the distillation of ethanol ceased, the trap was filled with *o*-dichlorobenzene. Next, 4.200 grams (3.853×10^{-3} mole) of amine terminated PSX1090 was charged with 40 mL of *o*-DCB and 4 mL of NMP. The solution was allowed to react for 45 minutes at 160°C. Bisaniline P, 7.679 grams (2.232×10^{-2} mole), was then added with 25 mL *o*-DCB. The reaction was stirred at 160°C for 30 minutes. Finally, 0.156 grams (1.33×10^{-3}) of *m*APA was added to the reaction vessel with 15 addition mL of *o*-DCB to give a solids content of 20 wt % (an appropriate molar amount of

3-phenylethyneylaniline may be substituted in place of *m*APA). The reaction mixture was then heated at 160°C and held for ~24 hours, after which time the viscous polymer solution was cooled to room temperature, diluted to 15 wt % solids with additional *o*-DCB and precipitated by slowly dripping the polyimide solution into an excess of methanol in a high speed blender. The polymer was collected by vacuum filtration, washed with excess methanol and excess anhydrous diethyl ether, air dried 6-8 hours and vacuum dried at ~170°C for 24 hours.

3.3.6 Polyimide Oligomers Endcapped with 4-Phenylethyneylphthalic Anhydride

Polymerizations were conducted as follows for the synthesis of 6FDA/*p*-PDA/PEPA oligomers with a number average molecular weight $\langle M_n \rangle$ of 10,000 g/mole provided as an example: 9.679×10^{-3} mole (4.300 grams) monomer grade 6FDA was charged to a 100 mL 3-neck, round-bottom flask equipped with a magnetic stirrer, nitrogen inlet, thermometer, reverse Dean-Stark trap and reflux condenser which was heated in an oil bath. Absolute ethanol, 7-10 mL per gram of dianhydride was then introduced and the mixture was refluxed with stirring until a clear solution was obtained. When the distillation of ethanol ceased, the trap was filled with *o*-DCB. Next, 1.06×10^{-3} mole (0.263 grams) of 4-phenylethyneylphthalic anhydride in 9 mL of NMP was then charged to control molecular weight. The diamine, *p*-PDA, 1.021×10^{-2} mole (1.103 grams) was then added into the reaction vessel, followed by NMP (9 mL) and *o*-DCB (5 mL) (80:20 vol.:vol.) to provide a solids content of 20 % wt.:vol.. The reaction mixture was then heated at 170-185°C for 20 hours, after which time the polymer solution was precipitated by slowly dripping the cooled polyimide solution into methanol in a high speed blender. The polymer was collected by vacuum filtration, washed with excess methanol and then with excess anhydrous diethyl ether. It was then air dried 6-8 hours and vacuum dried at ~160°C for 24 hours.

3.3.7 Polyimide Oligomers Endcapped with Phenylmaleic Anhydride

Polymers endcapped with phenylmaleic anhydride were synthesized via three methods in order to study molecular weight control using PMA as the endcapping agent.

3.3.7.1 Ester-Acid High Temperature Solution Imidization: The first method of polymerization was high temperature solution imidization through the ester-acid route. A polymerization with a number average molecular weight $\langle M_n \rangle$ of 3,000 g/mole as an example was conducted as follows: 4.9560 g (1.1156×10^{-2} mole) of 6FDA was charged to a 100 mL 3-neck round bottom flask equipped with an overhead stirrer, Dean-Stark trap, nitrogen purge and a condenser heated in an oil bath. The 6FDA was washed in with 20 mL of ethanol. Then 0.9296 g (5.338×10^{-3} mole) of PMA was washed in with an additional 20 mL of ethanol and 3 mL of triethylamine was added and the solution refluxed at $\sim 100^\circ\text{C}$ until the ethanol was removed by distillation at which time the trap was drained. When the distillation of ethanol ceased, the trap was filled with *o*-DCB. Next, 2.7683 g (1.3825×10^{-2} mole) of ODA was added with 17 mL of NMP and 4 mL of *o*-DCB to make a 30% solid solution. The reaction mixture was then heated at $170\text{-}185^\circ\text{C}$ for 20 hours, after which time the polymer solution was precipitated by slowly dripping the polyimide solution into methanol in a high speed blender. The polymer was collected by suction filtration, washed with excess methanol and then excess anhydrous diethyl ether. The polymer was then air dried 6-8 hours and vacuum dried at $\sim 170^\circ\text{C}$ for 24 hours.

3.3.7.2 Amic Acid Chemical Imidization: The second method of polymerization was chemical imidization through the amic acid precursor. A polymerization with a number average molecular weight $\langle M_n \rangle$ of 3,000 g/mole as an example was conducted as follows: 1.819 g (9.086×10^{-3} mole) of ODA was added with 8 mL of NMP to a 100 mL 3-neck

round bottom flask heated in an oil bath equipped with an overhead stirrer, Dean-Stark trap, nitrogen purge and a condenser. Next, 0.611 g (3.51×10^{-3} mole) of PMA which was washed in with an additional 5 mL of NMP followed by 3.257 g (7.332×10^{-3} mole) of 6FDA was charged and washed in the vessel with 4 mL of NMP. The mixture was allowed to stir at room temperature for 3 hours. After which, 3.4 mL of acetic anhydride and 4.4 mL of triethylamine was charged to the flask. The reaction mixture was then heated to 60°C for 6 hours, after which time the polymer solution was precipitated by slowly dripping the polyimide solution into methanol in a high speed blender. The polymer was collected by suction filtration, washed with excess methanol and then excess anhydrous diethyl ether. The polymer was then air dried 6-8 hours and vacuum dried at ~170°C for 24 hours.

3.3.7.3 Variable Temperature Solution Imidization: The third method of polymerization was a two step method that involved forming an amine-terminated polyimide using the high temperature solution imidization ester-acid route and then endcapping the polyimide with PMA at a lower temperature. A polymerization with a number average molecular weight $\langle M_n \rangle$ of 3,000 g/mole as an example was conducted by the same procedure reported in the ester-acid high temperature solution imidization section except the PMA was not charged to the reaction mixture so to form an amine-terminated imide oligomer due to the offset in stoichiometry in favor of the diamine. At this point the polymer was a) precipitated by slowly dripping the polyimide solution into methanol in a high speed blender. The polymer was collected by suction filtration, washed with excess methanol and then excess anhydrous diethyl ether. The polymer was then air dried 6-8 hours and vacuum dried at ~170°C for 24 hours. The amine-terminated imide oligomer (2.022 g, 6.738×10^{-4} mole) was then redissolved in 2.1 mL of DMAc in the reaction setup previously described and 0.235 g (1.35×10^{-3} mole) of PMA was added and washed in the flask with 2.1 mL of

DMAc and 1.1 mL of toluene. The reaction was heated in an oil bath at 140°C for 6 hours at which time the polymer solution was precipitated by slowly dripping the polyimide solution into methanol in a high speed blender, isolated and dried as previously described. Alternatively, the polymer solution was b) lowered in temperature to 135°C by lowering the oil bath temperature and then the appropriate amount of PMA was added with NMP. The polymerization was allowed to proceed for 4-6 hours, after which time the polymer was precipitated and dried as in section a).

3.4 CURING OF REACTIVE POLYIMIDES

The reactive polyimide oligomers were usually cured by one of two methods. The first method involved the melt fabrication of films by placing ~ 1-2 grams of the imide powder between steel platens coated with either aluminum foil or Release-All #100 high temperature mold release agent. The steel platens were then placed between preheated Tetrahedron Press platens. The temperature of the Smart Press ranged from 350°C to 380°C and the samples were held at the respective temperatures between 60 to 90 minutes. Pressure ranging from contact to 40 psi was applied to the sample. The steel platens containing the sample was then removed and placed in a Pasadena Hydraulics, Inc. (phi) press with flowing water through the press platens to quench the sample to room temperature with ~ 5 minutes.

The second method of curing involved placing 0.5-1.0 gram of the imide powder in a 10 cm aluminum pan which was placed in a Thermolyne Type 47900 Furnace. Alternatively, the imide powder was cold pressed in a 28 mm diameter cylindrical mold with 10,000 psi pressure. This procedure formed a disc which was cured in the aluminum pan. The oven was purged with either nitrogen or air. The samples were placed in the oven preheated to temperatures ranging from 350°C to 380°C and the samples were held at

the respective temperatures between 60 to 90 minutes after which time they were removed and cooled to room temperature within ~ 2 minutes.

3.5 MODEL STUDY

3.5.1 Synthesis of Model Phenylethynyl Imides

Model compounds were synthesized as follows, using the reaction of 3-phenylethynylaniline (PEA) with 4-PEPA as an illustrative example: PEA, 1.271×10^{-2} mole (3.316 grams) was charged with 7 mL of DMAc to a 3-neck, round-bottom flask equipped with a magnetic stirrer, nitrogen inlet, thermometer, reverse Dean-Stark trap and reflux condenser which was heated in a silicone oil bath. An equimolar amount of 4-PEPA was then introduced as a solution in toluene (7 mL). The reaction mixture was then heated to $\sim 150^{\circ}\text{C}$ for 6 hours, after which time the solution was allowed to cool. The model compound was observed to precipitate from solution upon cooling. The imide product was washed with excess anhydrous diethyl ether and then air dried for 6-8 hours and vacuum dried at $\sim 120^{\circ}\text{C}$ for 24 hours to afford an 87% yield. Model compounds based on PEA-PA, An-PEPA and 6FDA-PEA were also prepared in the manner described.

3.5.2 Synthesis of Model Phenylmaleic Imides

A model compound based on PMA/An was synthesized as follows: PMA, 2.4266×10^{-2} mole (4.2259 grams) was charged with 10 mL of THF to a 3-neck, 100 mL flame-dried round-bottom flask equipped with an overhead stirrer, nitrogen inlet, thermometer, and reflux condenser which was heated in a silicone oil bath. An equimolar amount of An (2.2109 grams) was then introduced with 5 mL of THF. The reaction mixture was then allowed to stir at room temperature for 1 hour. The compound precipitated out of solution at this point. An additional 15 mL of THF was added with 12 mL of triethylamine and 9 mL of acetic anhydride. The solution was then heated to $\sim 60^{\circ}\text{C}$ at which point the

compound became soluble and was heated for 3 hours, and allowed to cool. The model compound was observed to precipitate from solution upon cooling and washed with excess water and then air dried for 6-8 hours and vacuum dried at $\sim 100^{\circ}\text{C}$ for 24 hours.

3.5.3 Model Study - Curing of Phenylethynyl Imide Compounds

Approximately 0.40 grams of the model compound (PEPA/An or PA/PEA) was placed in a 6.9 mm diameter 6 cm long capillary tube which was then sealed. The sealed capillary tubes were placed in a salt bath (10 parts KNO_3 and 8.5 parts NaNO_2) heated to 350°C for times ranging from 5-60 minutes. The individual capillary tubes were removed from the salt bath, allowed to cool ~ 2 minutes and then immersed in a water bath to cool completely to room temperature. The capillaries were then broken and the sample was analyzed by FTIR, mass spectroscopy, proton and carbon solution NMR. NMR samples were dissolved in 3.0 mL of either deuterated DMSO or deuterated CHCl_3 .

3.6 CHARACTERIZATION OF POLYMERS AND MONOMERS

3.6.1 Intrinsic Viscosities

Intrinsic viscosities were determined on all of the soluble polyimide and oligomer systems as a qualitative measure of the molecular weights. Measurements were obtained using Cannon-Ubbelohde viscometers with various capillary sizes. The samples were generally dissolved in NMP at 25°C ; however, polyimide siloxane copolymers were run in chloroform at 25°C . The intrinsic viscosity values were obtained by using four different concentrations and the results were linearly extrapolated to zero concentration.

3.6.2 Gel Permeation Chromatography (GPC)

Gel permeation chromatography measurements provided a more accurate measure of polymer and oligomer molecular weights and determined the molecular weight

distributions of the various polyimide and imide oligomer samples. GPC measurements were performed in NMP/LiBr at 60°C using a Waters 150-C ALC/GPC with a refractive index (RI) detector and Viscotek Model 100 viscosity detector. $\langle M_n \rangle$ and $\langle M_w \rangle / \langle M_n \rangle$ values were determined using universal calibration techniques.^{358,359} Alternatively, a Waters R401 GPC was used with an RI detector and chloroform as the mobile phase operating at 30°C.

3.6.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton nuclear magnetic resonance (¹HNMR) spectra were obtained using a Varian Unity 400 MHz instrument to obtain chemical composition information of both polymers and monomers synthesized. Samples were dissolved in deuterated solvents such as deuterated DMSO or deuterated CHCl₃ at concentrations of 1 to 10 % solids. Carbon 13 nuclear magnetic resonance (¹³CNMR) was also run on the Varian Unity 400 MHz NMR. ¹³CNMR were also run in either deuterated DMSO or chloroform. Solid state ¹³CNMR experiments were used to follow the curing of model phenylethynyl compounds in real time using a programmable high temperature probe. Solid state NMR experiments were conducted using a Bruker MSL 300 with Magic Angle Spinning (MAS). A Doty High Temperature probe was used in conjunction with the Bruker MSL 300.

3.6.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to obtain IR spectra of the final polymers and monomers using either a MX-1 spectrometer or a Nicolet Impact 400 FTIR spectrometer. High molecular weight polymer samples were analyzed as thin films or by casting thin films on salt plates. Monomers, low molecular weight oligomers and model compounds were run as KBr pellets. FTIR bands occurring at approximately 1780, 1730, 1375 and 720 cm⁻¹ confirmed the presence of imide heterocycles in polymers and oligomers.

3.6.5 Mass Spectroscopy (MS)

Mass spectroscopy analysis for the determination of monomer molecular weights and to follow the molecular weight changes for the model compound studies were performed on either a VG 7070 E-HF or a Fisons VG Quattro mass spectrometer. Both spectrometers were normally operated in the Liquid Secondary Ion Mass Spectrometry (LSIMS) also known as Fast Atom Bombardment (FAB) mode.

3.6.6 Differential Scanning Calorimetry (DSC)

DSC was used to determine the glass transition and melting transition temperatures of the polymers and oligomers. DSC was conducted on a Perkin Elmer DSC 7. Scans were run under a nitrogen atmosphere at 10°C per minute. Samples were scanned at least twice to accurately determine T_g values. The T_g values were obtained from a second heating cycle after rapid cooling from above the T_g of the polymer and the values were taken as the midpoint of the change in slope of the baseline.

3.6.7 Thermogravimetric Analysis (TGA)

3.6.7.1 Dynamic Thermogravimetric Analysis

Dynamic TGA was performed to assess the relative thermal stability of polyimide and imide oligomer samples using a Perkin Elmer TGA 7 thermogravimetric analyzer. Thin films or powder samples were placed in a platinum pan connected to an electric microbalance. The samples were heated at a rate of 10°C per minute in a flowing air atmosphere. Weight loss of the sample was measured as a function of time and temperature. The thermal stability of the polymers was generally reported as the 5 weight % loss values.

3.6.7.2 Isothermal Thermogravimetric Analysis

Isothermal TGA could also be run on the Perkin Elmer TGA 7 under an air atmosphere to assess the long term thermal stability of several samples at 371°C (700°F). The samples were held at the 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. Compression molded crosslinked films were dried to a constant weight and heated in the Blue M oven to the test temperature. The samples were aged under a flowing air atmosphere of 25 cubic feet per hour. The films were periodically removed and weighed on an analytical balance.

3.6.8 Mechanical Testing

Compression molded samples were typically pressed at 370°C for 1 hour or 380°C for 90 minutes under pressures of 0 to 40 psi depending on the molecular weight and backbone structure of the polyimide. An Instron model 1123 was used to determine the room temperature mechanical properties of the polyimide samples. Dogbone shaped specimens were cut from the compression molded crosslinked films using a steel run die (ASTM-638V). The specimen gauge length was 10 mm and the width was 2.76 mm. The strain rate was 0.05 inch per minute. Reported values are an average of 3 to 5 samples. Tensile shear specimens were prepared by solution coating an adhesive tape (112 glass) containing 2 percent volatiles which was cured for 1 hour at 350°C at 50 psi or 90 minutes at 380°C at various pressures in between titanium tensile shear specimens (6A1-4V). All values are the average of 4-5 runs per specimen.

3.6.9 Solvent Extractions

Cured thermosetting imides were extracted with chloroform to determine the gel content in crosslinked polyimide films. Films were prepared as described in Section 3.4. The cured films were then placed into dried, pre-weighed cellulose thimbles. The thimbles were previously soaked in chloroform for at least 18 hours and then dried at ~ 120°C for 2 days. The combined weight of the sample and thimble was recorded and the assembly was placed in a Soxhlet extractor under refluxing chloroform for 5 days. Sample weight was determined by subtracting the thimble weight from their combined weight. After the extraction period, the thimble and sample were removed from the extractor, air dried for 24 hours and then vacuum dried at ~ 120°C for 5 days. The gel fraction weight was found by subtracting the thimble weight from their combined weight, and their percent gel fraction was calculated as described below:

$$(3-11) \text{ \% gel fraction} = (wt_f/wt_i) \times 100$$

where wt_f is the sample weight after extraction and wt_i is the sample weight prior to extraction.

3.6.10 Rheological Properties - Melt Viscosity and Flow

Rheological properties such melt viscosity, storage and loss moduli in the melt were performed using a Bohlin VOR rheometer. The imide powder was cold pressed in a 15 mm or a 28 mm diameter cylindrical mold with 10,000 psi pressure. The size of the mold used was determined by the type of polyimide backbone being studied. This procedure formed a disc which was then inserted in between 2 parallel steel plates which oscillated at a frequency of typically 1.0 or 0.1 Hz. Flowing nitrogen or air was used as the purge gas during the runs. For dynamic runs, a heating rate of 3°C per minute was utilized and for isothermal runs, temperatures ranging from 300°C to 380°C were studied. Melt viscosity

values may be interpreted only semi-quantatively since the value of the melt viscosity is dependent upon the type of torque bar used in the rheometer. The measurements reported in this dissertation were obtained using a 12.55 g-cm torsional resistance torque bar which allowed sufficient range over the temperatures studied. Absolute values for very low melt viscosities can only be compared between samples, and not be taken as precise values.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

Results and discussion covering seven sections will be addressed in this chapter. The first section reports the synthesis of monofunctional high temperature reactive compounds used as endcapping agents for thermosetting polyimide systems. The second section reports the synthesis and characterization of high molecular weight soluble, nonreactive polyimide homopolymers synthesized by the ester-acid route. The next four sections explore the synthesis and characterization of high temperature thermosetting polyimide systems. These systems include polyimides endcapped with 3-phenylethynylaniline, randomly segmented polyimide siloxane copolymers endcapped with either 3-phenylethynylaniline or *m*-aminophenylacetylene, polyimides endcapped with 4-phenylethynylphthalic anhydride and polyimides endcapped with phenylmaleic anhydride. The last section covers model reactions of phenylethynyl and phenylmaleic imides to explore the chemistry taking place during the synthesis and curing of these reactive systems.

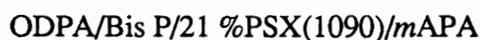
In order to discuss clearly the polyimides in this section, a clear identification of each polyimide system must be set forth. The nomenclature to describe high molecular weight nonreactive polymer systems will consist of a listing of the monomers and oligomers used in its synthesis, starting with the dianhydrides, then the diamines, followed by nonreactive monofunctional reagents. For example, a polyimide synthesized from bisphenol A dianhydride (BPA-DA), *m*-phenylene diamine (*m*-PDA) and phthalic anhydride (PA) is designated as:

BPA-DA/*m*-PDA/PA

The designations for reactive functionalized polyimide oligomers will list the dianhydrides, then the diamines, followed by the reactive monofunctional reagents with the theoretical number average molecular weight ($\langle M_n \rangle$) in parenthesis. A polyimide oligomer made from 6F dianhydride (6FDA), oxydianiline (ODA), 4-phenylethynylphthalic anhydride (4-PEPA) and a $\langle M_n \rangle$ of 3,000 g/mole is listed as:



Polyimide systems 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. Randomly segmented polyimide siloxane copolymers will be listed with the dianhydride first, then the diamine, followed by the weight % of the polydimethylsiloxane (PSX) oligomer, the $\langle M_n \rangle$ of PSX oligomer, and the monofunctional endcapper. A copolymer made with ODPA, Bis P and 21 weight % PSX(1090) endcapped with *m*-aminophenyl acetylene (*m*APA) is given by:



4.2 MONOFUNCTIONAL ENDCAPPER SYNTHESIS

The synthesis of four monofunctional compounds for use as polyimide endcapping agents was performed. The four monofunctional compounds include 3-phenylethynylaniline (3-PEA), 4-phenylethynylphthalic anhydride (4-PEPA), diphenylmaleic anhydride (DPMA) and phenylmaleic anhydride (PMA). The synthesis and characterization of each monofunctional compound will be discussed in the following sections.

4.2.1 3-Phenylethynylaniline (3-PEA)

3-Phenylethynylaniline was synthesized by a palladium-catalyzed coupling reaction³⁰⁹ of *m*-aminophenylacetylene (*m*APA) with bromobenzene in the presence of triethylamine as solvent and DMAc as the cosolvent shown in Scheme 4.2.1.1. The use of DMAc greatly enhanced the yield of 3-PEA over the previously reported synthetic approaches to this compound.³³³ 3-PEA was obtained as a light orange waxy solid after isolation from diethyl ether extractions. Upon standing under vacuum, a yellow-orange solid was isolated. Yields as high as 81% were obtained after sublimation under reduced pressure at ~ 60°C. The ¹HNMR of the 3-PEA is shown in Figure 4.2.1.1 where the four different aromatic protons and the amino protons are labeled.

4.2.2 4-Phenylethynylphthalic Anhydride (4-PEPA)

Phenylethynylphthalic anhydride (4-PEPA) was successfully synthesized in our laboratory via the palladium-catalyzed coupling³³² reaction of 4-bromophthalic anhydride (4-BrPAN) and phenylacetylene in the presence of anhydrous triethylamine and DMAc as the cosolvents as shown in Scheme 4.2.2.1. Upon completion of the coupling reaction, a quantitative yield of the 4-PEPA was recovered.

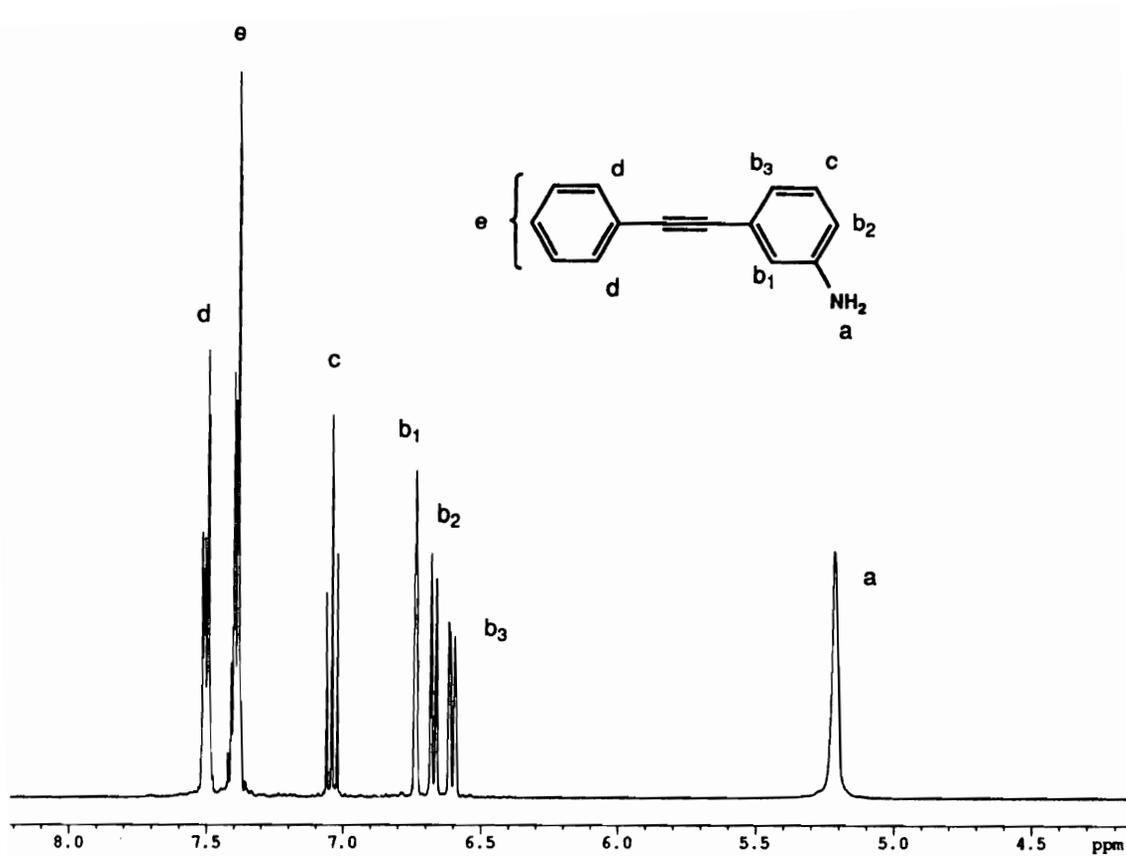
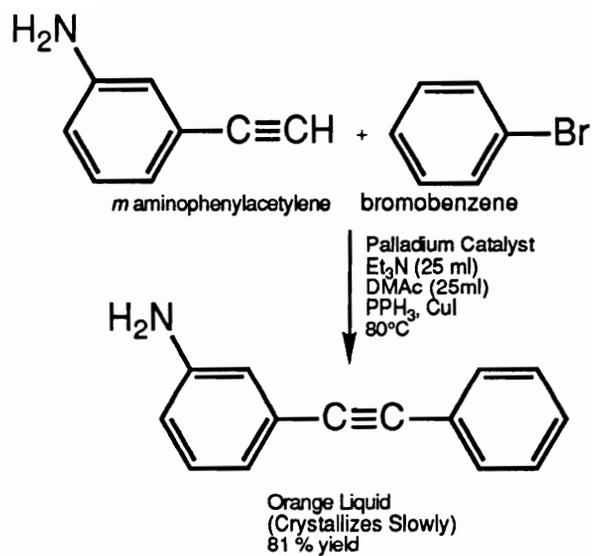
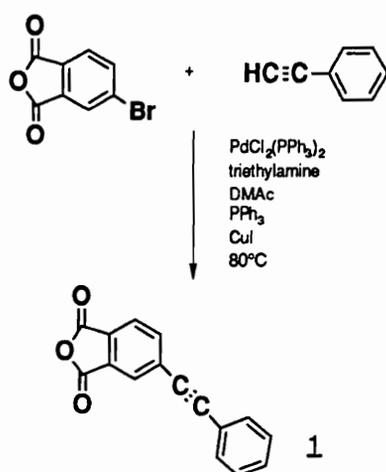


Figure 4.2.1.1 ^1H NMR Spectrum of 3-Phenylethynylaniline in DMSO-d_6 (400 MHz)



Scheme 4.2.1.1 Synthesis of 3-Phenylethynylaniline



Scheme 4.2.2.1 Synthesis of 4-Phenylethynylphthalic Anhydride

The 4-PEPA is much easier to purify than 3-PEA since upon addition to water of the reaction solution, an easily isolated solid is formed. The solid 4-PEPA can be sublimed under reduced pressure or may be recrystallized directly from acetic anhydride to give pure yields of at least 84%. The 4-PEPA is possibly less toxic than the earlier reported 3-phenylethynylaniline. The ^1H NMR spectrum of 4-PEPA is shown in Figure 4.2.2.1 and the ^{13}C NMR spectrum is shown in Figure 4.2.2.2. In the ^1H NMR spectrum, the 4 different aromatic protons are clearly labeled at 7.4-7.5, 7.6 and 8.1 ppm exhibiting the proper integration for each different kind of proton. The ^{13}C NMR spectra reveals the acetylenic carbons at 88.3 and 92.4 ppm and the carbonyl carbons at 168.1 ppm occurring in the expected regions. In addition, the FTIR spectra is shown in Figure 4.2.2.3 where the acetylenic stretching band is found at 2214 cm^{-1} and the carbon-oxygen anhydride stretch is shown at 1776 and 1847 cm^{-1} .

Several attempts were made to synthesize 4-PEPA from 4-chlorophthalic anhydride and phenylacetylene since 4-chlorophthalic anhydride is less expensive than 4-bromophthalic anhydride. Reaction conditions both similar to the procedure using 4-bromophthalic anhydride as well as increased reaction temperatures of 120°C (versus 80°C) were tried. However, in all cases a mixture of 4-PEPA and starting material (phenylacetylene) with the majority of the mixture being unreacted phenylacetylene was obtained.

4.2.3 Diphenylmaleic Anhydride (DPMA)

Diphenylmaleic anhydride was synthesized by the procedure reported by Fields et. al.³⁵² where the sodium salt of benzoyl formic acid was reacted with phenylacetic acid in refluxing acetic anhydride as shown in Scheme 4.2.3.1. The reaction proceeds in a quantitative manner through a Perkin condensation mechanism to give the DPMA. The DPMA may be sublimed at $\sim 115^\circ\text{C}$ under reduced pressure or it may be

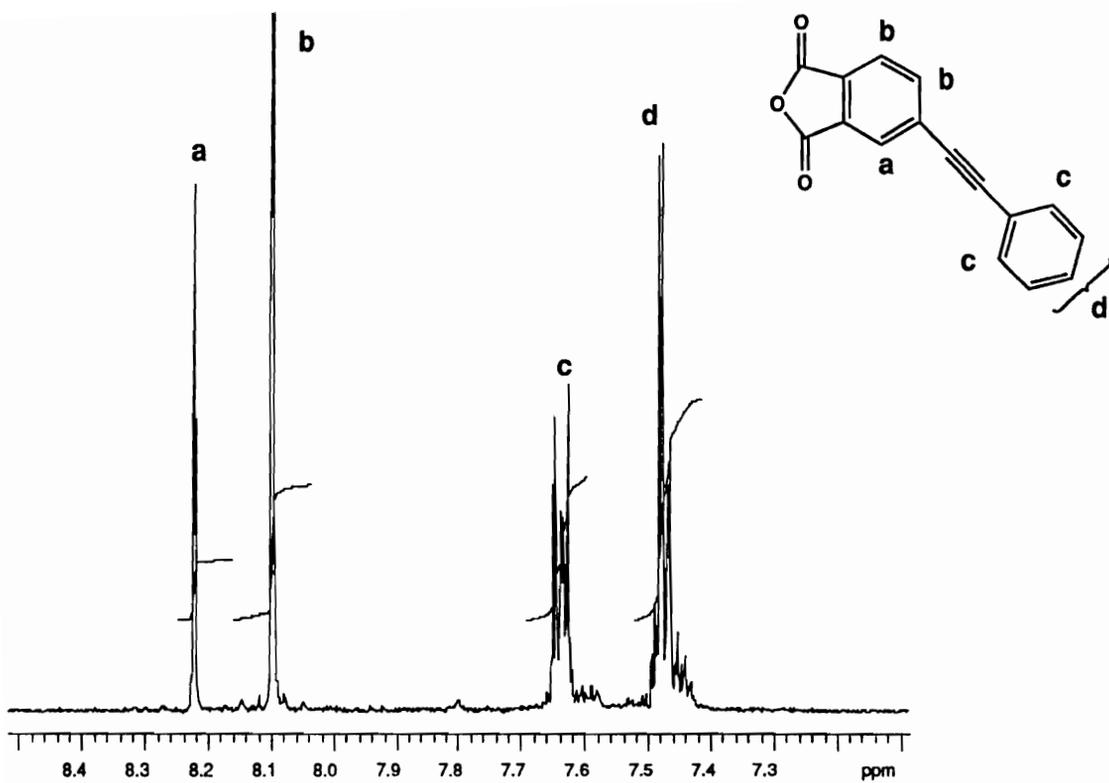


Figure 4.2.2.2 ^1H NMR Spectrum of 4-Phenylethynylphthalic Anhydride in DMSO-d_6 (400 MHz)

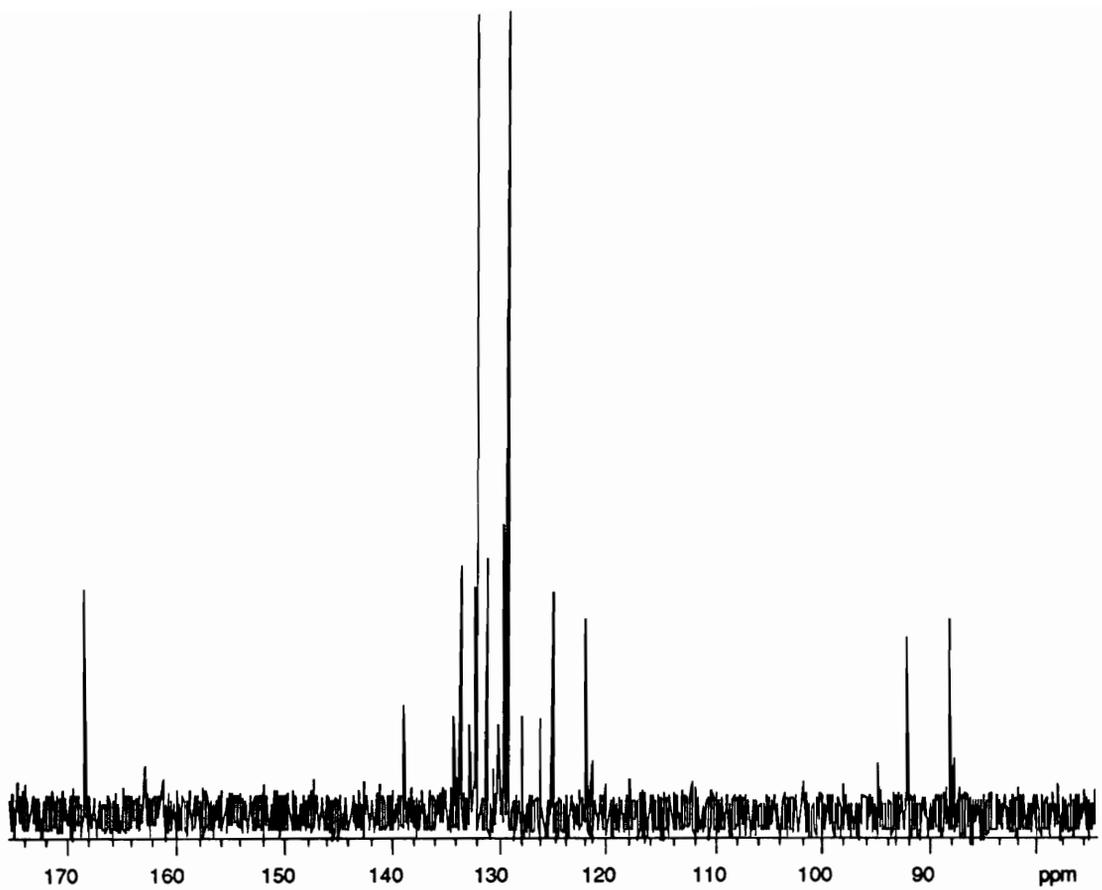


Figure 4.2.2.2 ^{13}C NMR Spectra of 4-Phenylethynylphthalic Anhydride in DMSO-d_6 (400 MHz)

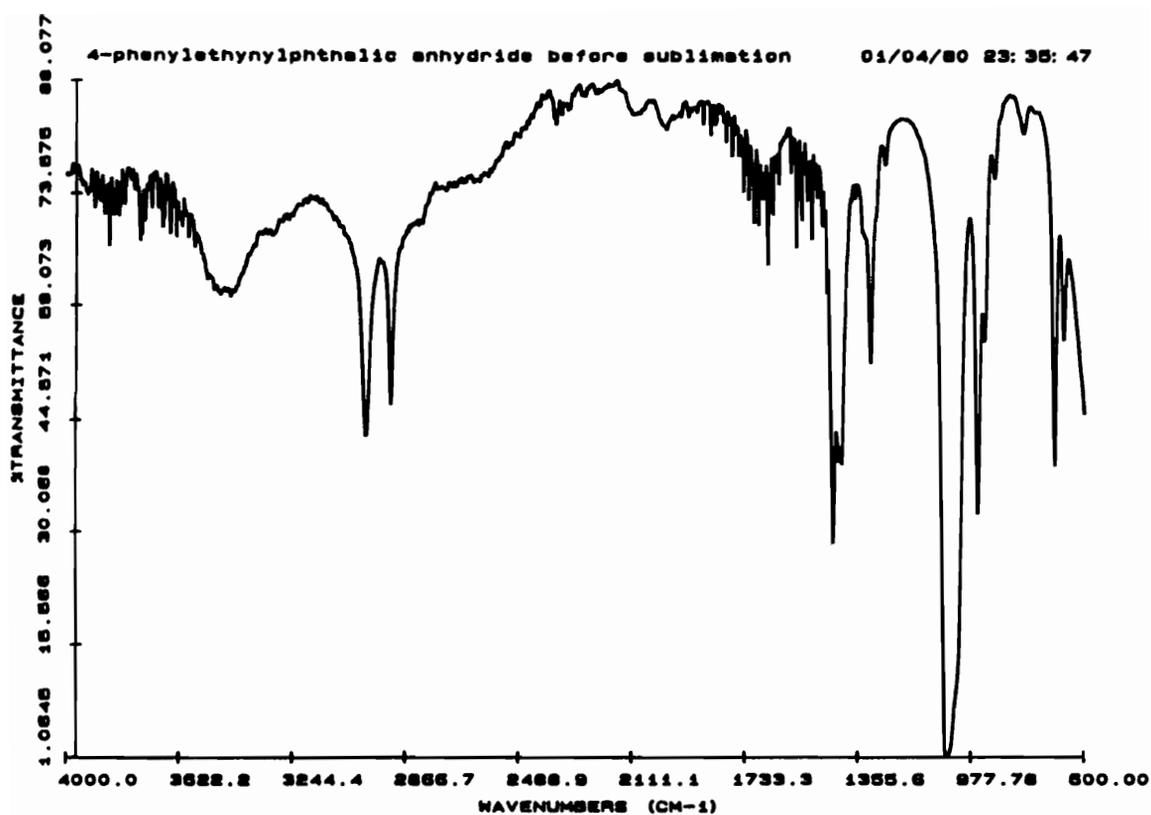
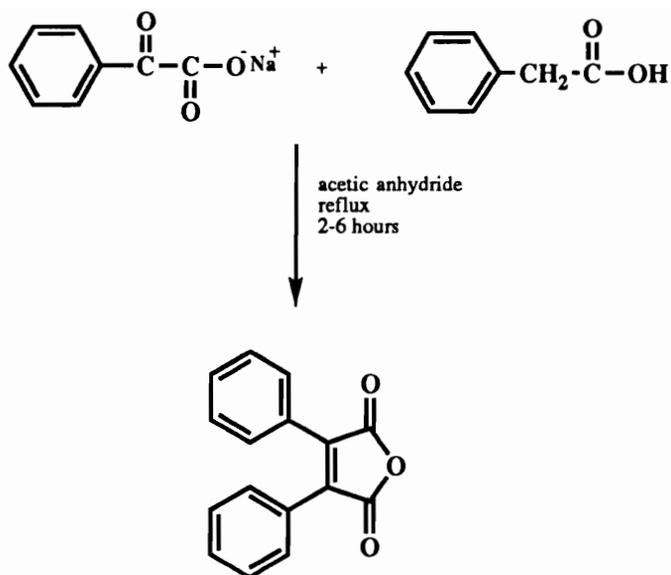


Figure 4.2.2.3 FTIR Spectrum of 4-Phenylethynylphthalic Anhydride in KBr



Scheme 4.2.3.1 Synthesis of Diphenylmaleic Anhydride

recrystallized from acetic acid to give pure material in 95 % yield. The ^1H NMR of DPMA is shown in Figure 4.2.3.1 and the ^{13}C NMR is shown in Figure 4.2.3.2. The proton NMR exhibits only aromatic protons as would be expected with DMSO-d_6 occurring at 2.49 ppm and water at 3.3 ppm. The ^{13}C NMR exhibits the carbonyl carbons at 165.6 ppm and shows the carbon double bond carbons at 138.8 ppm.

4.2.4 Phenylmaleic Anhydride (PMA)

Phenylmaleic anhydride was prepared by a combination of the procedures reported by Hill³⁵⁴ and Paquette.³⁵³ Phenylsuccinic acid was refluxed in acetic anhydride in the presence of a stoichiometric amount of selenium dioxide as illustrated in Scheme 4.2.4.1. PMA was easily isolated by precipitation in water and was purified by sublimation under reduced pressure at $\sim 100^\circ\text{C}$ in 92% yield. The proton NMR spectrum of the PMA is shown in Figure 4.2.4.1. The *meta* and *para* aromatic protons attached to the pendent phenyl group are seen as a multiplet at 7.5-7.6 ppm and the *ortho* protons are found at 8.0-8.5 ppm, while the lone proton attached to the carbon-carbon double bond is seen at 7.75 ppm. The FTIR spectrum is also shown in Figure 4.2.4.2 where the anhydride stretches are observed at 1766 and 1842 cm^{-1} .

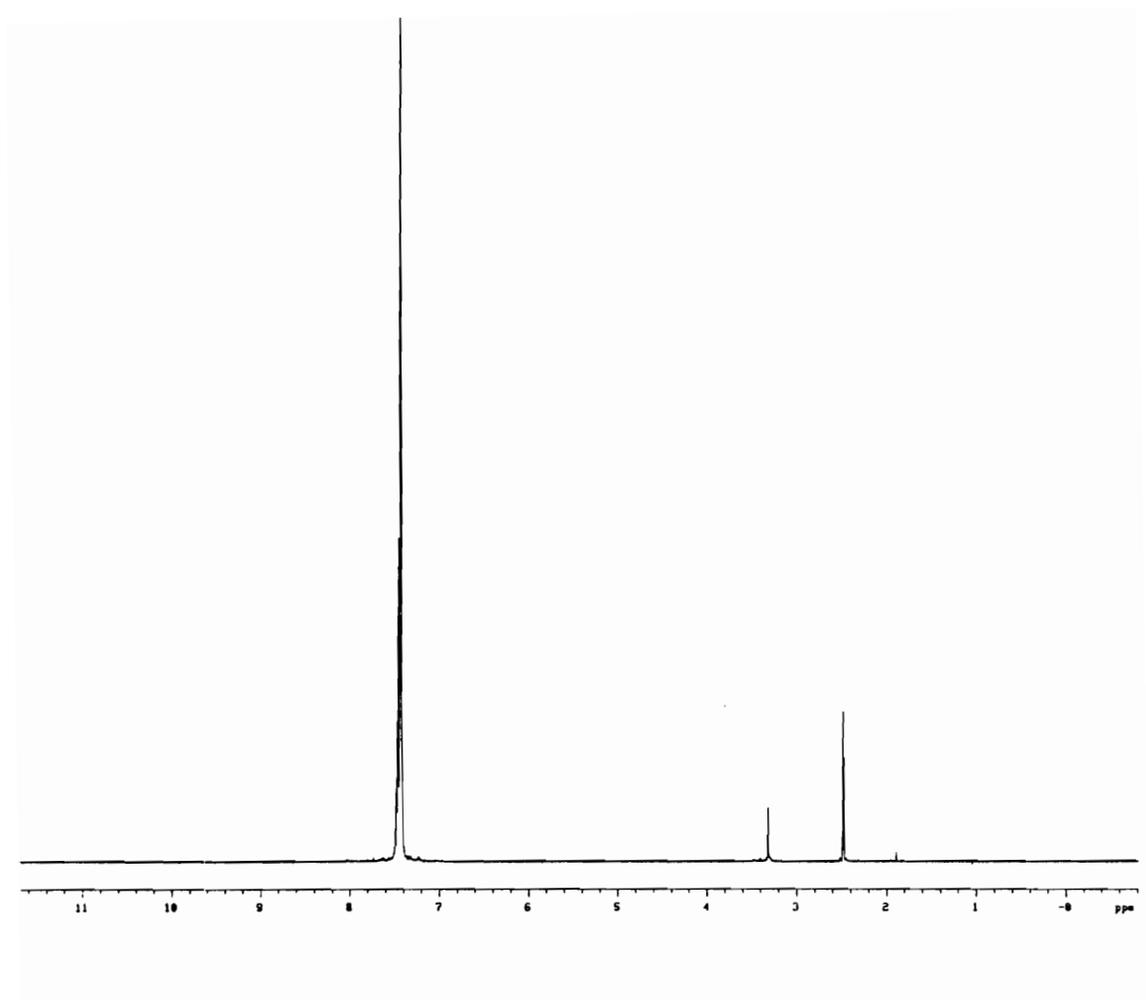


Figure 4.2.3.1 ¹H NMR Spectrum of Diphenylmaleic Anhydride in DMSO-d₆ (400 MHz)

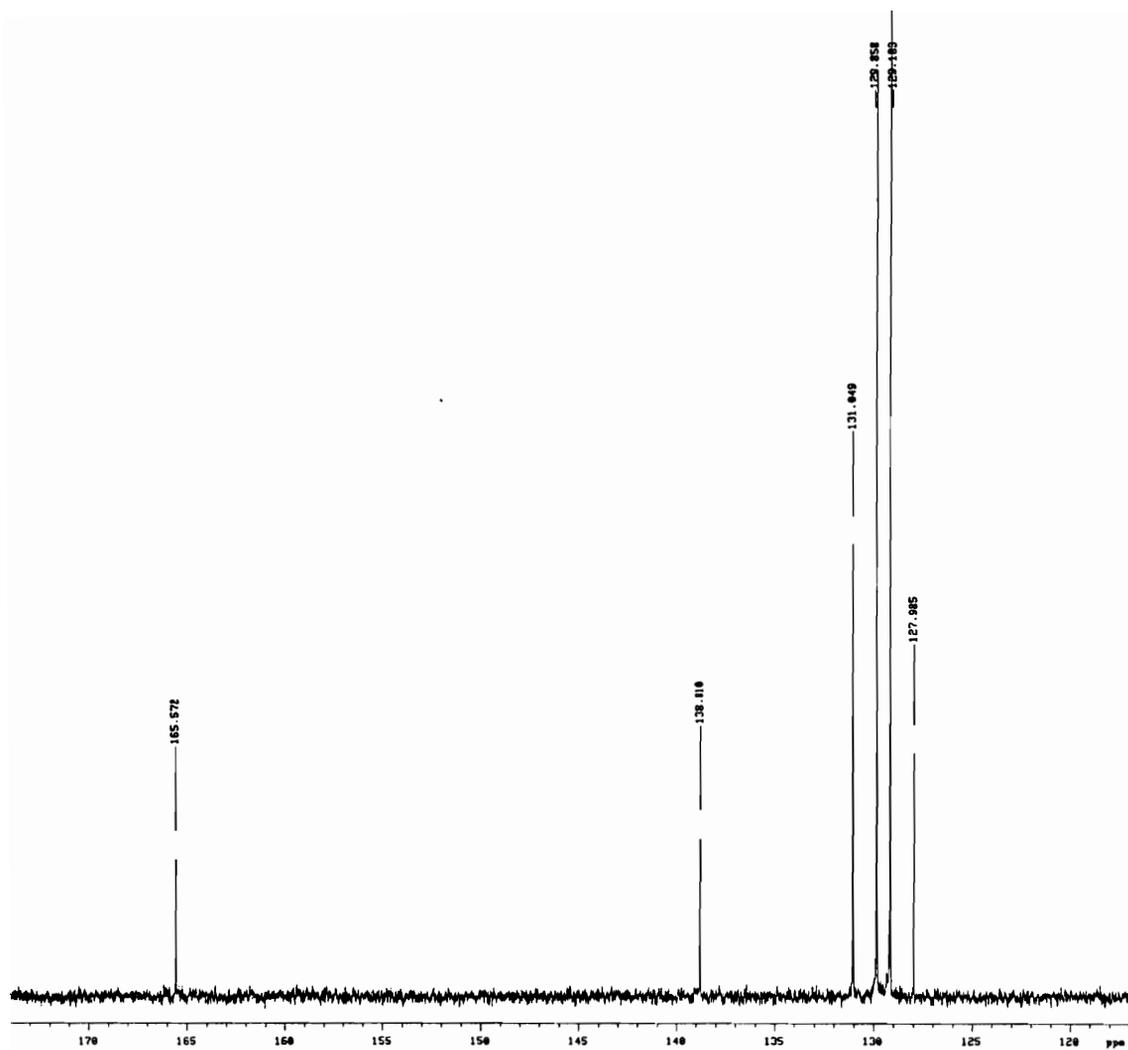
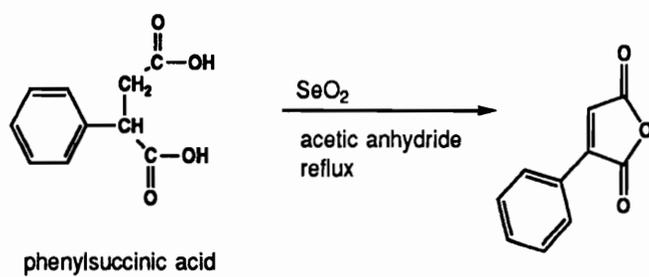


Figure 4.2.3.2 ^{13}C NMR Spectrum of Diphenylmaleic Anhydride in DMSO-d_6 (400 MHz)



Scheme 4.2.4.1 Synthesis of Phenylmaleic Anhydride

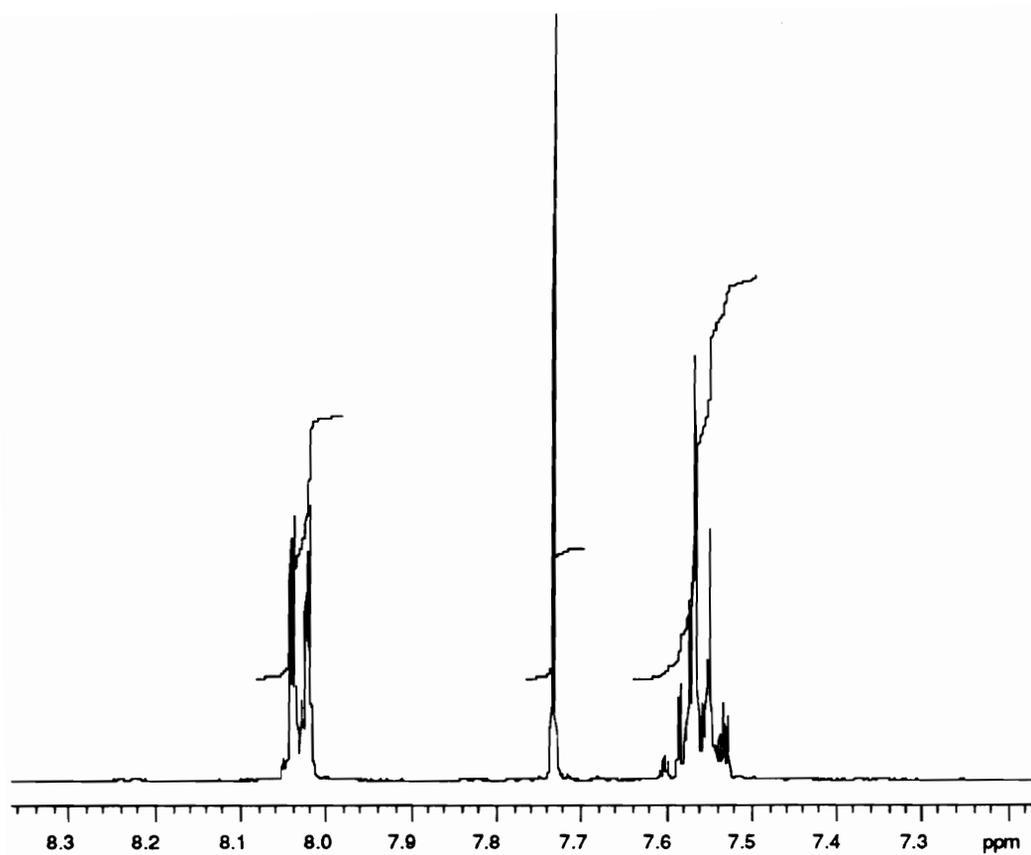


Figure 4.2.4.1. ^1H NMR Spectrum of Phenylmaleic Anhydride in DMSO-d_6 (400 MHz)

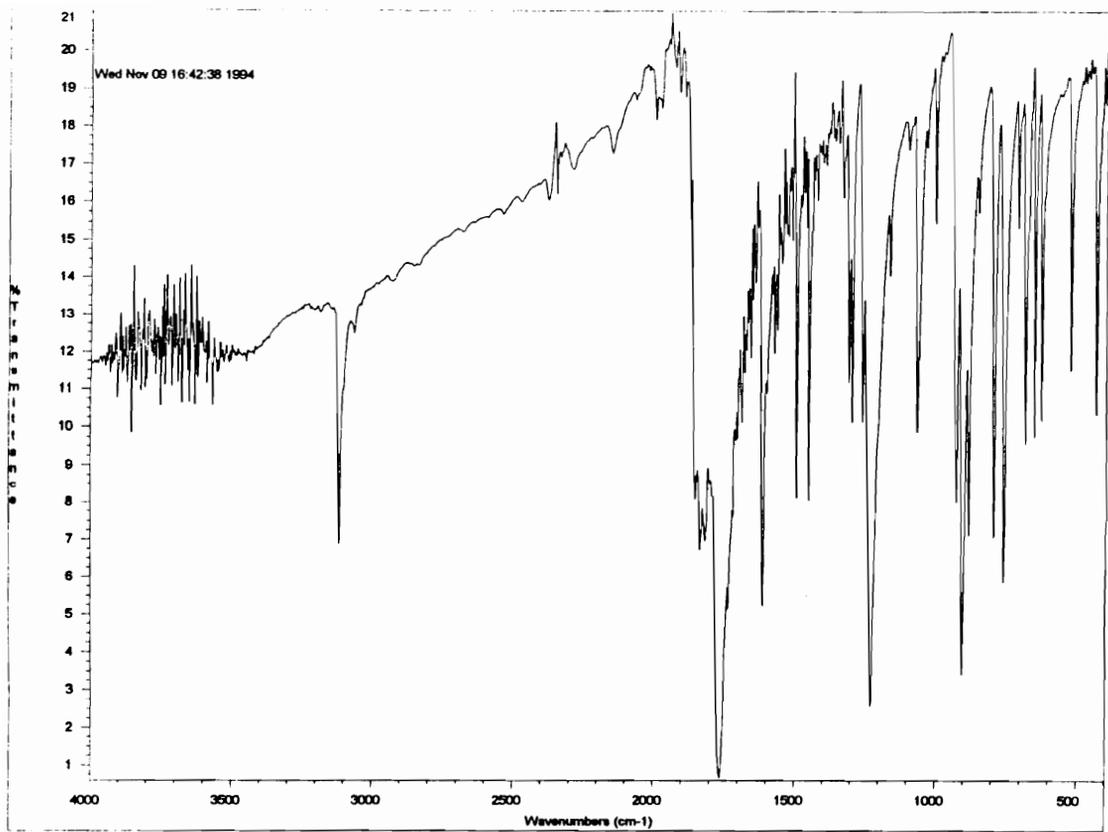
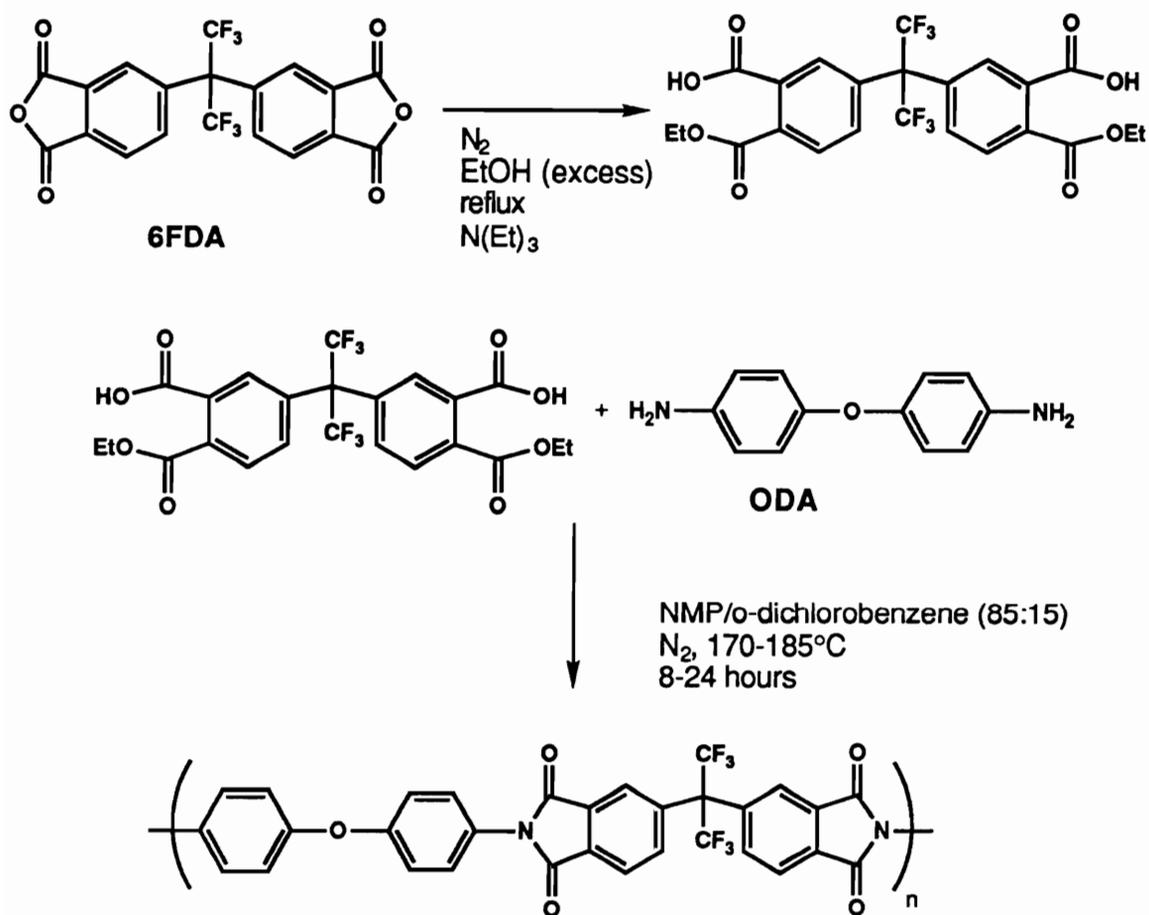


Figure 4.2.4.2 FTIR Spectrum of Phenylmaleic Anhydride in KBr

4.3 LINEAR HIGH MOLECULAR WEIGHT POLYIMIDES

Various high molecular weight soluble polyimides were synthesized using the ester-acid route.^{63,64} First, the diacid-diester derivative of the dianhydride was formed by refluxing the dianhydride in an alcoholic solvent such as ethanol in the presence of a base such as triethylamine. The ester-acid form of the dianhydride was usually a very viscous syrup-like substance with an off-white to yellow color. Next, a diamine was added in a polar aprotic solvent such as NMP, after which an azeotroping agent (usually *o*-DCB) was added and the reaction was heated at 170-185°C to affect polymerization and complete imidization. An azeotroping agent such as *o*-DCB was used to remove the water that was generated during the reaction and to ensure complete cyclization. An 8:2 or 8.5:1.5 mixture of NMP/*o*-DCB was sufficient for the efficient removal of water which was formed during the polymerization. The reaction times ranged from 8 to 24 hours in which the most probable molecular weight distribution could be obtained.^{63,64} During this time, water was seen collecting in the reverse Dean-Stark trap. The polyimide solution also turned from a light yellow to a dark brown which was likely due to imide formation and also degradation of NMP. An example of the synthesis of an uncontrolled molecular weight 6FDA/ODA polyimide prepared by the ester-acid route is shown in Scheme 4.3.1.

At the end of the polymerization, the solution was cooled. The polyimide was isolated by slowly pouring the reaction mixture into methanol which was rapidly stirred in a blender. Methanol was a nonsolvent for the polyimide but was miscible with NMP and *o*-DCB, so the polyimide precipitated when the solution was added to the methanol. About a 10 fold excess of methanol was used to one part polyimide. The polyimide solutions were often diluted with additional NMP before precipitating in methanol to decrease the solution viscosity. The polyimide was collected by suction filtration and dried in a vacuum oven at ~ 180°C for 24 hours.



Scheme 4.3.1 Synthesis of Uncontrolled Molecular Weight 6FDA/ODA Polyimide by the Ester-Acid Route

These high molecular weight polyimides were synthesized as a direct comparison with reactive low molecular weight imide oligomers in terms of molecular weight control and thermal characteristics. Polyimides according to subgroups, either dianhydride or diamine type, will be discussed with regard to structure- T_g and structure-solubility relationships.

The ester-acid route has been demonstrated to be a practical alternative to the conventional two-step route for synthesizing soluble polyimides.^{63,64} Usually moderate to high molecular weight polyimides (intrinsic viscosities in the range of 0.37 to 0.78 dL/g in NMP at 25°C) could be attained. The high molecular weight polyimides are typically soluble in NMP and DMAc at 25°C at concentrations of 15 percent (wt/vol); in addition, some systems also show solubility in common solvents such as chloroform, methylene chloride and THF. Characteristic imide FTIR stretches at 1770, 1730, 1370 and 720 cm^{-1} as shown in Figure 4.3.1 are observed.

4.3.1 Polyimides Derived from 6F Dianhydride

The flexibility imparted to polyimides containing the hexafluoroisopropylidene or 6F linkage affords a high degree of flexibility in the polyimide backbone and allows for the synthesis of various soluble polyimides. Repeat units, intrinsic viscosities and T_g 's of 6FDA-based polyimide are shown in Table 4.3.1.1. The intrinsic viscosities of the various 6FDA-containing polyimides were all relatively high and indicated that high molecular weight was obtained for all of the polyimides. The ester-acid solution imidization method was effective in obtaining fully cyclized, high molecular weight polyimides.

Table 4.3.1.2 indicates the solubility (15 percent wt/vol) of the 6FDA-based polyimides. All of the polymers were soluble in the polar aprotic solvents, NMP and DMAc. 6FDA/*p*-PDA exhibited poor solubility in methylene chloride, chloroform and

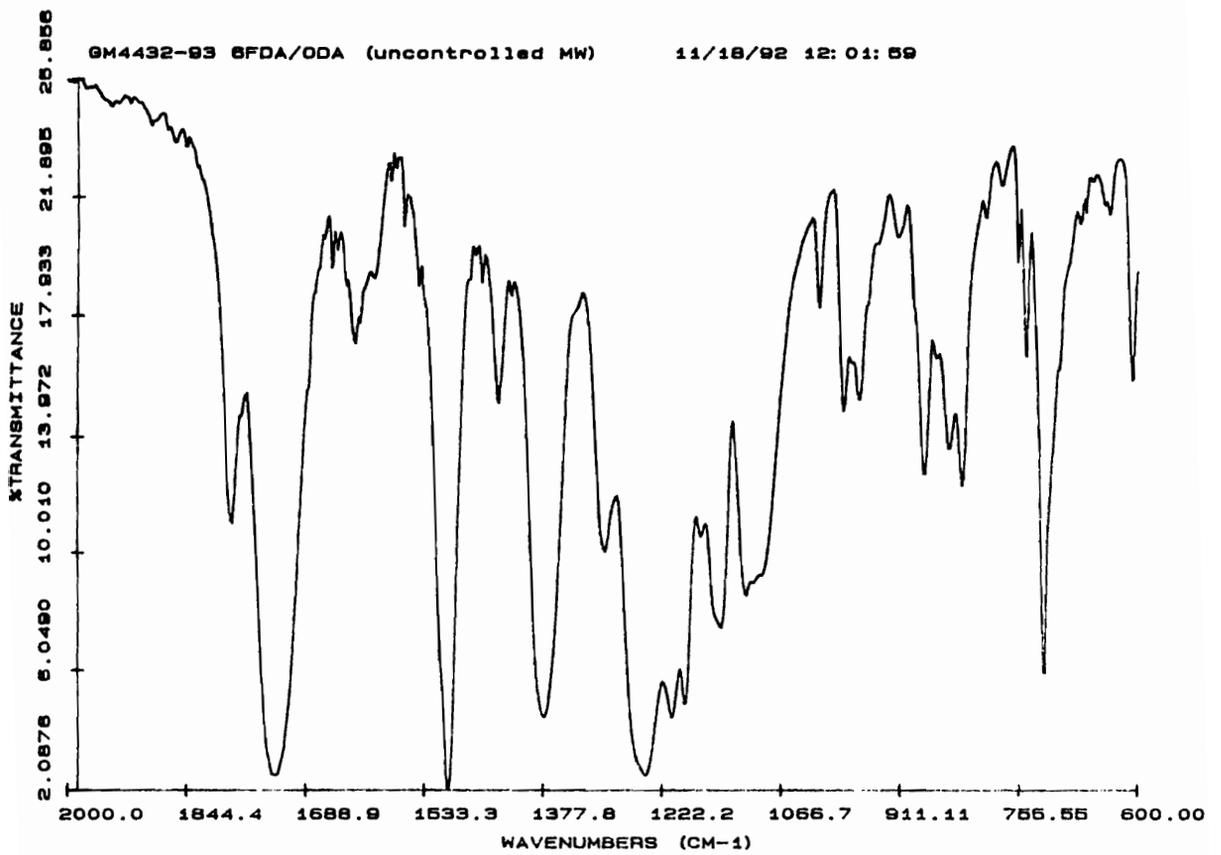
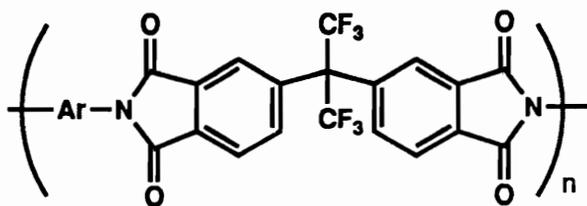


Figure 4.3.1 FTIR Spectrum of 6FDA/ODA Polyimide Film

Table 4.3.1.1 Polyimides Derived From 6F Dianhydride



Ar	$[\eta]_{25^\circ\text{C.NMP}}$	$T_g(^{\circ}\text{C})$
<p>p-PDA</p>	0.78	349
<p>4,4'-ODA</p>	0.58	303
<p>FDA</p>	0.49	370

Table 4.3.1.2 Solubility of 6F Dianhydride Polyimides

Polyimide	Target $\langle M_n \rangle$ g/mole	NMP	DMAc	CHCl ₃	CH ₂ Cl ₂	THF
6FDA/ <i>p</i> -PDA	not controlled	S	S	I	I	I
6FDA/ODA	not controlled	S	S	S	S	S
6FDA/FDA	not controlled	S	S	S	S	S

THF. As the more flexible diamines were used in place of *p*-PDA, the solubility of the 6FDA containing polyimides increased. The 6FDA/ODA and 6FDA/FDA polyimides were soluble in chloroform, methylene chloride and THF.

The T_g 's of the 6FDA containing polyimides are listed in Table 4.3.1.1. The 6FDA/FDA polyimide exhibited glass transition temperatures as high as 370°C. The bulky fluorenone moiety which contributes to the solubility of the polyimide also affected the T_g . The fluorenone groups limited the rotation of the polymer chain, thus, making it rather stiff which resulted in a high T_g . Replacing FDA with a less hindered but still stiff diamine, *p*-PDA lowered the glass transition temperature and the solubility. The 6FDA/*p*-PDA polyimide had a T_g of 349°C. However, when the diamine moiety was replaced with a more flexible, less bulky diamine, 4,4'-ODA, the T_g was lowered to 303°C and the solubility improved.

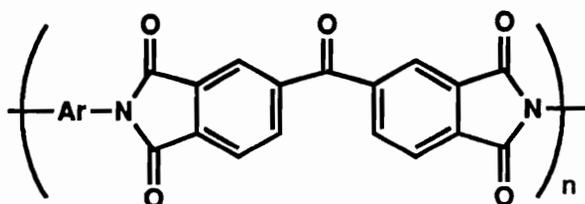
4.3.2 Polyimides Derived from 3,3',4,4'-Benzophenonetetracarboxylic Dianhydride

The ketone bridge in 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) affords high mobility in the polyimide backbone and allows for the synthesis of various soluble polyimides. Repeat units, intrinsic viscosities and T_g 's of BTDA-based polyimides are shown in Table 4.3.2.1. The intrinsic viscosities of the various BTDA-containing polyimides were all moderately high and indicated that moderately high molecular weight was obtained for all of the polyimides.

All of the BTDA-based polyimides were soluble in the polar aprotic solvents, NMP and DMAc. BTDA/Bis P exhibited enhanced solubility even in methylene chloride, chloroform and THF. The BTDA/FDA polyimide exhibited similar solubility as the BTDA/Bis P system, except that it swells but does not dissolve in THF. The polyimide based on BTDA/*p*-BAPS was not soluble in any of the solvents tested.

Table 4.3.2.1 Polyimides Derived from Benzophenonetetracarboxylic Dianhydride

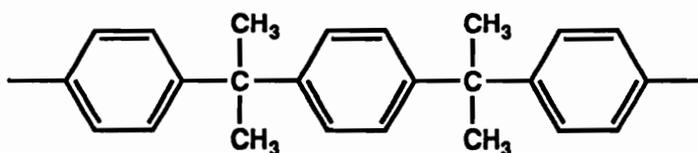
(BTDA)



Ar

$[\eta]_{25^\circ\text{C, NMP}}$

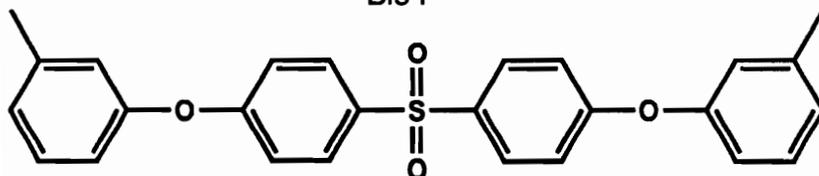
T_g (°C)



1.2

267

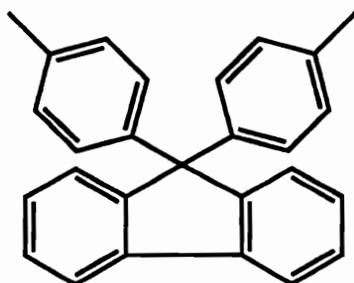
Bis P



0.78

232

m-BAPS



0.48

376

FDA

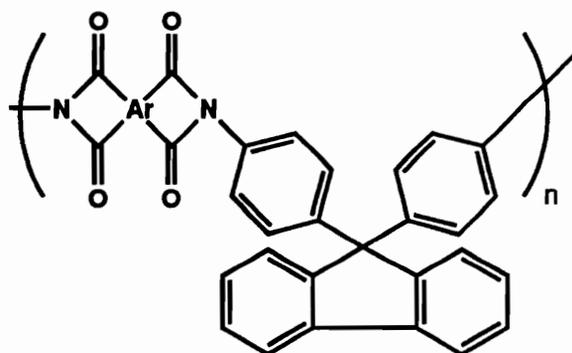
The T_g 's of the BTDA containing polyimides are listed in Table 4.3.2.1. The BTDA/FDA polyimide exhibited glass transition temperatures as high as 376°C, which was the highest in the series probably due to the bulky fluorenone moiety. Replacing FDA with Bis P, which no doubt exhibits increased flexibility afforded by the 2,2-isopropylidene linkages and non-polar hydrocarbon character of the diamine residue, gave a reasonably high glass transition temperature with enhanced solubility. The T_g of the BTDA/Bis P polyimide was 267°C. In addition, when the diamine moiety was replaced with an even more flexible diamine, *m*-BAPS, the T_g was lowered to 232°C. Overall, the BTDA based polyimides show the expected T_g order: *m*-BAPS < Bis P < FDA.

4.3.3 Polyimides Derived from 9,9-Bis-(4-Aminophenyl)fluorene

The polyimides derived from 9,9-bis-(4-aminophenyl)fluorene (FDA) exhibit excellent solubility and high T_g 's. Polyimides based on FDA were synthesized from the following dianhydrides: benzophenonetetracarboxylic dianhydride (BTDA), biphenyl dianhydride (BPDA), diphenylsulfone dianhydride (DSDA) and 6F dianhydride (6FDA). Repeat units, intrinsic viscosities and T_g 's of FDA-based polyimide are shown in Table 4.3.3.1. The intrinsic viscosities of the various FDA-containing polyimides were all moderately high and indicated that moderately high molecular weight was obtained for all of the polyimides. In general, FDA affords very high T_g polyimides which are readily soluble in a number of solvents, including NMP, DMAc, DMSO, THF, chloroform and methylene chloride. Only in the case of DSDA with the polar sulfone linkage does the polyimide not dissolve in THF, methylene chloride and chloroform.

The T_g 's of the BTDA containing polyimides are listed in Table 4.3.3.1. The FDA-based polyimides exhibited glass transition temperatures in all cases in excess of 370°C. The structure of the fluorene group seems to dominate the properties of these

Table 4.3.3.1 Polyimides Derived from 9,9-bis(4-aminophenyl)fluorene (FDA)



Ar	$\eta_{inh}^{25^\circ\text{C, NMP}}$	T_g ($^\circ\text{C}$)
<p>BTDA</p>	0.48	376
<p>BPDA</p>	0.62	388
<p>DSDA</p>	0.29	392
<p>6FDA</p>	0.49	370

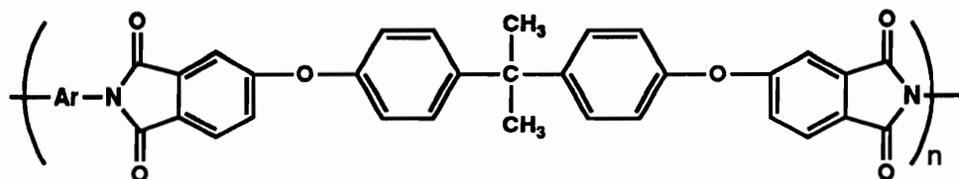
polyimides, since review of the T_g values reveals little dependence of T_g on dianhydride structure.

4.3.4 Polyimides Derived from 2,2'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane Dianhydride

The polyimides derived from 2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPA-DA) were only evaluated with phenylene diamines, so as to have a comparison to the commercially available polyimide Ultem® which is produced from BPA-DA and *m*-PDA and a molecular weight of approximately 20,000 g/mole. Repeat units, intrinsic viscosities and T_g 's of BPA-DA-based polyimide are shown in Table 4.3.4.1. Only the BPA-DA/*m*-PDA/PA(30,000) polyimide was soluble in NMP, DMAc and chloroform; whereas the *p*-PDA polyimide was only partially soluble in hot NMP. The intrinsic viscosity of the BPA-DA/*m*-PDA/PA(30,000) polyimide was 0.47 dL/g and indicated that moderately high molecular weight was obtained.

The T_g 's of the BPA-DA containing polyimides are listed in Table 4.3.4.1. The BPA-DA/*p*-PDA/PA(40,000) polyimide exhibited glass transition temperatures as high as 219°C. Replacing *p*-PDA with a less stiff *m*-PDA lowered the glass transition temperature but greatly increase the solubility. The T_g of the BPA-DA/*m*-PDA/PA(30,000) polyimide was 211°C.

Table 4.3.4.1 Polyimides Derived from 2,2'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane Dianhydride (BPA-DA)



Ar	$[\eta]_{25^\circ\text{C. NMP}}$	$T_g(^\circ\text{C})$	5% Wt. Loss ($^\circ\text{C}$)
 <i>p</i> -PDA	insol.	219	542
 <i>m</i> -PDA	0.47	211	539

4.4 CONTROLLED MOLECULAR WEIGHT THERMOSETTING POLYIMIDES

Controlled molecular weight polyimides were synthesized under the conditions reported above for high molecular weight systems, except a calculated excess of diamine or dianhydride with a calculated amount of a monofunctional reactive molecular weight limiting reagent was employed. The molecular weights were limited according to the well-known Carothers equation. Demonstration of effective molecular weight and endgroup control was essential with the ester-acid route to prove this route to be a viable alternative to the conventional two-step synthesis of soluble polyimides.

4.4.1 3-Phenylethynylaniline Functionalized Polyimides

Phenylethynyl functionalized soluble imide oligomers are of great interest as potential high temperature adhesives and matrix resins. The use of soluble precursors offers the advantages of being able to isolate fully imidized polymers at relatively low temperatures without crosslinking compared to bulk PMR type syntheses. The solubility of these resins permits molecular weight characterization and its distribution, which is critical in designing high temperature thermosetting materials. In addition, controlling the molecular weight of the imide oligomers to values of $\langle M_n \rangle \leq 15,000$ g/mole allows for much greater ease in processing due to lowered bulk viscosity and enhanced solubility.

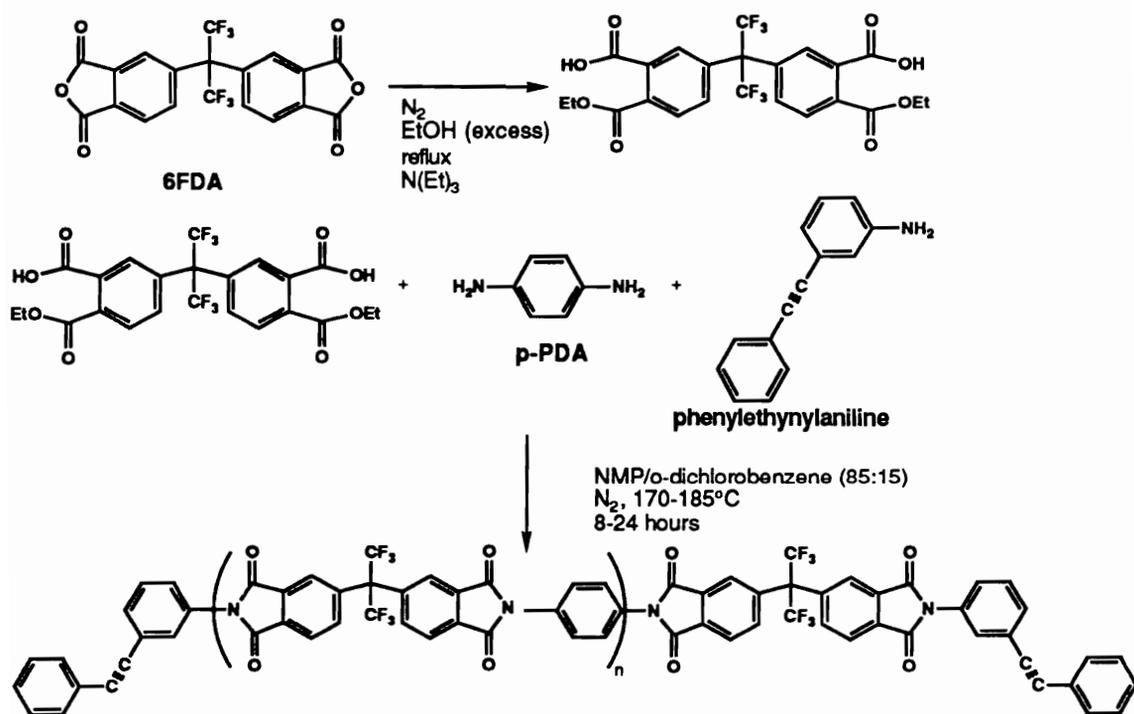
Considerable work on polyimides has focused on the incorporation of acetylenic or ethynyl moieties on the ends of imide oligomers^{267,268} and pendent along the polymer backbone. Acetylene-terminated imide oligomers designated as Thermid™ are also commercially available. This resin, however, does not undergo sufficient flow before the initiation of the cure process. In the past, acetylene-functionalized oligomers endcapped with *m*-aminophenylacetylene that cure upon heating to give a highly crosslinked network that is highly solvent resistant, and that shows exceptional thermo-oxidative stability^{63,64} have been explored. However, the *m*-aminophenylacetylene endcapped polyimides,

analogous to the Thermid™ system and other recent work²⁵⁸ cure at ~220°C. Therefore, this low curing point limits its use either to solvent cast films or to polyimide systems that have T_g's below 220°C. As a consequence, this work has focused on the incorporation of 3-phenylethyneylaniline as the endcapping agent, which cures at ~ 380 - 420°C.

The 3-phenylethyneylaniline terminated polyimide matrix resins have been synthesized in an analogous manner as described in the earlier section concerning high molecular weight polyimides using the ester-acid route. However, an excess of the dianhydride was used to offset the stoichiometry so as to have an have free anhydride groups present to react with a calculated amount of the 3-phenylethyneylaniline (3-PEA). After formation of the diester-diacid derivative of the dianhydride, a calculated amount of the 3-PEA was added with NMP and the reaction mixture was allowed to react at ~ 175°C for approximately 15 minutes. Next, a diamine was added with NMP, after which, an azeotroping agent (usually *o*-DCB) was added and the reaction was continually heated to 170-185°C to affect polymerization and complete imidization. A solids concentration of 25 to 30% (wt/vol) was usually employed for polymerizations since high solution viscosities were not obtained due to the low molecular weight of the polymer. An example of the synthesis of a controlled molecular weight 6FDA/*p*-PDA/PEA polyimide prepared by the ester-acid route is shown in Scheme 4.4.1.1.

At the end of the polymerization, the solution was cooled. The polyimide was isolated by slowly pouring the reaction mixture into methanol which was rapidly stirred in a blender. The polyimide was collected by suction filtration and dried in a vacuum oven at ~ 180°C for 24 hours.

Attempts were made to synthesize 3,000 g/mole PEA terminated resins via a PMR approach where the ethyl ester was synthesized from either BTDA or 6FDA. The PEA was then added with excess ethanol followed by addition of the diamine 1,4-bis-(4-



Scheme 4.4.1.1 Synthesis of 6FDA/*p*-PDA/PEA Polyimide by the Ester-Acid Route

aminophenoxy)benzene (TPE-Q) with excess ethanol. The ethanol was allowed to distill off at $\sim 120^{\circ}\text{C}$. After concentration of the monomeric reactants, the viscous solution was placed in a vacuum oven at 70°C for 16 hours. A foam material was obtained that was ground to a powder that was then placed in a forced air convection oven heated to 100°C for 1 hour, 200°C for 1 hour and then 300°C for 1 hour to effect polymerization and cyclization. An insoluble polyimide was obtained after heating and was somewhat unexpected since the phenylethynyl groups were not expected to react until 350°C in the solid state. The insolubility may also be attributed to crosslinking caused by imine formation.^{45,104,105} As a result of the insolubility, no further attempts were performed to synthesize polyimides by the PMR approach.

The materials based on 6FDA, *p*-PDA, and ODA were synthesized and three different molecular weights ranging from 3,000 to 10,000 g/mole were generated. No solid precipitated and no turbidity was observed except in one polymerization (which will be addressed in a latter section), indicating that no crosslinking occurred. Furthermore, the isolated oligomers completely redissolve in NMP and DMAc. The phenylethynyl endgroups could be detected by ^1H NMR as seen in Figure 4.4.1.1, and these materials become insoluble after heating to 375°C , swelling but not dissolving in DMAc.

As shown in Table 4.4.1.1, molecular weight control was achieved utilizing 3-phenylethynylaniline as an endcapping agent and this afforded $\langle M_w \rangle / \langle M_n \rangle$ values of ~ 2.0 as determined by GPC using a viscosity detector in conjunction with a universal calibration curve for the 6FDA/*p*-PDA and 6FDA/ODA polyimide systems. These results indicate that the ester-acid route is a suitable method for the synthesis of controlled-molecular-weight phenylethynyl terminated polyimides. These materials appeared to be completely imidized, showing strong infrared imide absorptions at 1780 cm^{-1} , 1730 cm^{-1} , 1370 cm^{-1} , and 710 cm^{-1} , and absence of absorptions attributable to amic-acid. However,

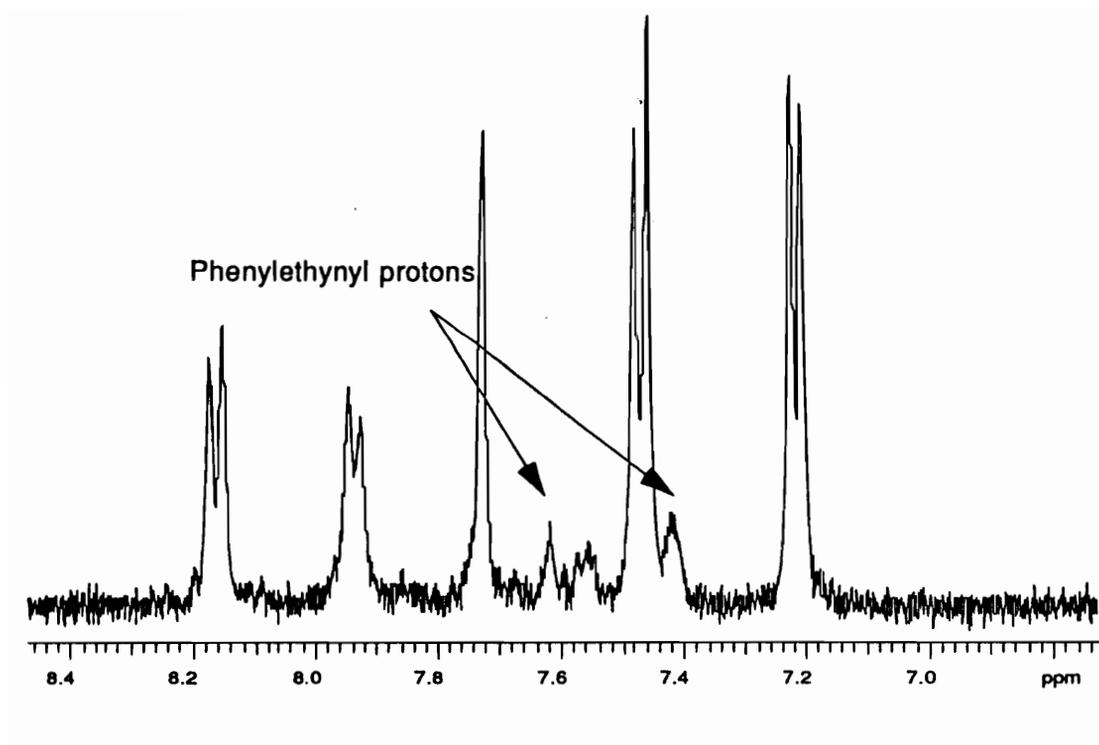


Figure 4.4.1.1 ¹H NMR Spectrum of 3-Phenylethynylaniline Terminated 6FDA/ODA Polyimide in DMSO-d₆ (400 MHz)

Table 4.4.1.1 Molecular Weight Data for 3-Phenylethynylaniline Terminated Polyimides

System	Target $\langle M_n \rangle$ (g/mole)	$[\eta]$ (dL/g) [†]	$\langle M_n \rangle$ by GPC* (g/mole)	$\langle M_w \rangle / \langle M_n \rangle$
6FDA/ODA	3,000	0.22	3930	2.0
	5,000	0.24	5200	2.0
	10,000	0.45	9800	2.1
6FDA/ <i>p</i> -PDA	3,000	0.19	3490	1.9
	5,000	insol.	insol.	insol.
	10,000	0.30	9900	2.0

[†] = Run in NMP, 25°C

* = Obtained using Universal Calibration methods.

for all of these systems, the ethynyl carbon-carbon bond could not be detected by FTIR spectroscopy.

Table 4.4.1.2 lists the glass transition temperatures before curing (239-366°C) (taken from first heat) and after curing (265-382°C) which is consistent with the T_g of the high molecular weight linear systems. In addition, the cure exotherm maxima ranged from 342 to 379°C. The 6FDA/*p*-PDA/PEA(5,000) system did precipitate out of solution during the polymerization reaction. This system surprisingly appears to be semi-crystalline, as shown by the DSC melting transition and by Wide Angle X-ray studies. The Wide Angle X-ray diffractogram of the 6FDA/*p*-PDA/PEA(5,000) polymer is shown in Figure 4.4.1.2 and exhibits intense peaks indicating significant amounts of crystallinity in the polymer. This polymer was not compression molded due to its high melting transition. This phenomenon has, no doubt, been observed by others since Avimide-N® is known to contain ~ 5% of *m*-phenylene diamine which would likely disrupt the semi-crystallinity. However, as illustrated in Table 4.4.1.1, the 3,000 g/mole oligomer and 10,000 g/mole oligomer were amorphous in nature. A 6FDA/*p*-PDA(5,000) polyimide was synthesized with anhydride endgroups using excess 6FDA. The change in endgroups to anhydride again resulted in a semi-crystalline polyimide as seen by the intense melting transition at 451°C as seen in Figure 4.4.1.3. Yet, when 4-phenylethynylphthalic anhydride endgroups were employed, the molecular weight at which crystallinity occurred was 3,000 g/mole as discussed in a later section. All of the polyimides formed tough, flexible films upon curing at 375°C for 1 hour by compression molding the isolated oligomeric powders between two steel plates pretreated with a high temperature mold release agent in a Tetrahedron press. These reactive oligomers thermally cure without the evolution of volatile byproducts.

Several other PEA endcapped imide oligomers were synthesized by the ester-acid route. These systems include: BPDA/3FDAM/PEA(3,000), ODPDA/3,3'-

DDS/PEA(3,000), BTDA/3,3'-DDS/PEA(3,000), 6FDA/FDA/PEA(3,000), BPDA/FDA/PEA(3,000), 6FDA/4,4'-MDA/PEA(3,000). The intrinsic viscosities, $\langle M_n \rangle$ determined by GPC, molecular weight distribution, and T_g 's are shown in Table 4.4.1.3. Good molecular weight control was achieved in all of these 3,000 g/mole oligomeric systems. Only the 6FDA/4,4'-MDA/PEA(3,000) and BPDA/3FDAM/PEA(3,000) number average molecular weights were slightly higher than the targeted values. In addition, molecular weight distributions were all very close to 2.0 as would be expected for step-growth condensation polymers. Furthermore, the glass transition temperatures increased as the rigidity of the polyimide backbone increased with the ODPA/3,3'-DDS/PEA(3,000) polymer exhibiting the lowest T_g of 228°C and the most rigid system, BPDA/FDA/PEA(3,000), exhibiting the highest T_g of 371°C.

The thermal stability of the 6FDA/ODA and 6FDA/*p*-PDA phenylethynylaniline terminated polyimides was also investigated before and after curing by Thermogravimetric Analysis (TGA). The phenylethynylaniline functionalized polyimides exhibit 5% weight loss values for the uncured polymers ranging from 485°C to 559°C which is consistent for polyimide systems. In order to identify polyimide systems for potential candidates for 700°F (371°C) applications, cured films were evaluated for long term isothermal stability in air. Although isothermal thermogravimetric analysis is not a true measure of a material's performance it is currently an accepted and convenient means of assessing long term, high temperature thermo-oxidative stability of polymeric materials. The cured polymers were subjected to two isothermal thermal gravimetric experiments; one was an analysis for 24 hours at 371°C in the TGA and another was an extended isothermal aging of the polymers in a forced air oven under an air atmosphere for 100 hours. Weight loss data with values

Table 4.4.1.2 Thermal Analysis Data for 3-Phenylethynylaniline Terminated Polyimides

System	Target $\langle M_n \rangle$ (g/mole)	5% Wt. Loss ($^{\circ}\text{C}$)*	T _{g1} ($^{\circ}\text{C}$)	T _{g2} ($^{\circ}\text{C}$)	TGA ₁ ($^{\circ}\text{C}$)	TGA ₂ ($^{\circ}\text{C}$)
6FDA/ODA	3,000	553	280	302	1.7	12.1
	5,000	559	286	297	1.2	9.1
	10,000	541	288	298	3.1	12.8
6FDA/p-PDA	3,000	548	365	382	0.7	4.9
	5,000	549	352 T _M = 451	---	---	---
	10,000	485	366	381	6.3	17.4

* = Heating rate of 10 $^{\circ}\text{C}/\text{min}$ in air, TGA of oligomer

T_{g1} = T_g before cure, heating rate of 10 $^{\circ}\text{C}/\text{min}$ in nitrogen

T_{g2} = T_g after cure, heating rate of 10 $^{\circ}\text{C}/\text{min}$ in nitrogen

TGA₁ = Isothermal TGA % Weight Loss after cure (in air 371 $^{\circ}\text{C}$ for 24 hours)

TGA₂ = Isothermal TGA % Weight Loss after cure (in air 371 $^{\circ}\text{C}$ for 100 hours in Blue M Electric Oven)

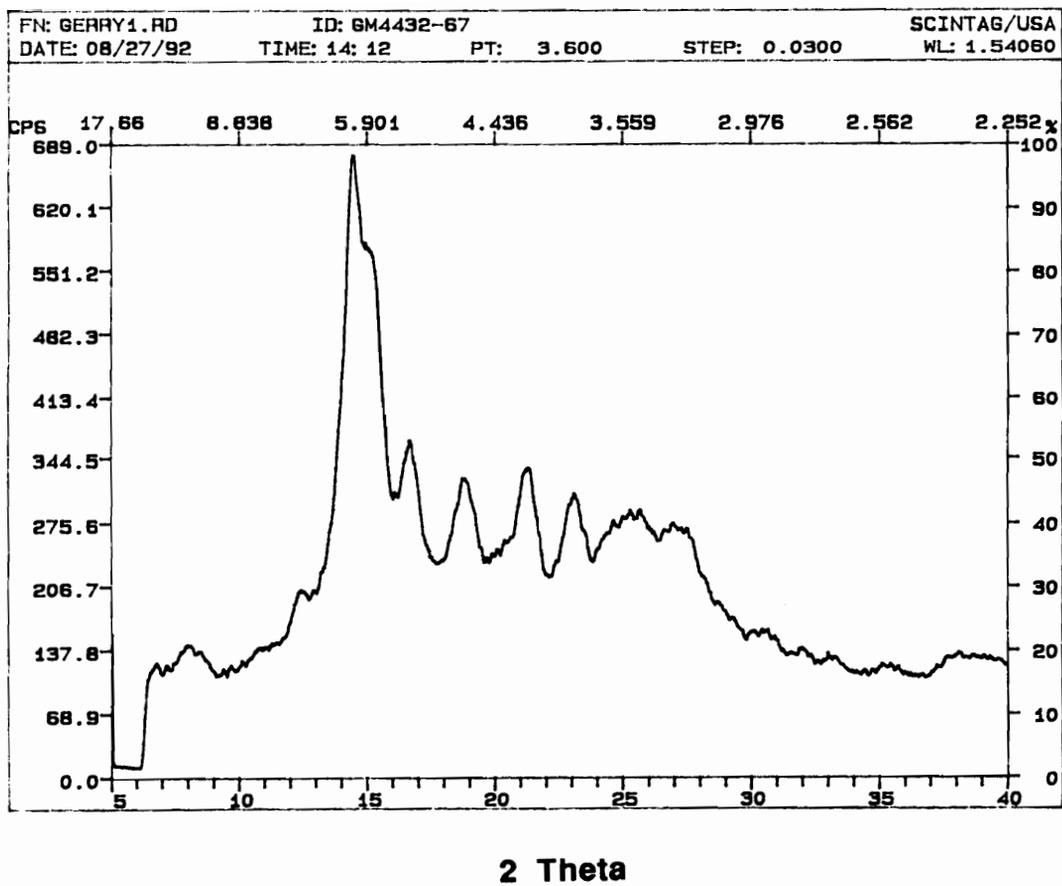


Figure 4.4.1.2 Wide Angle X-Ray Diffraction of 6FDA/*p*-PDA/PEA(5,000) Polyimide

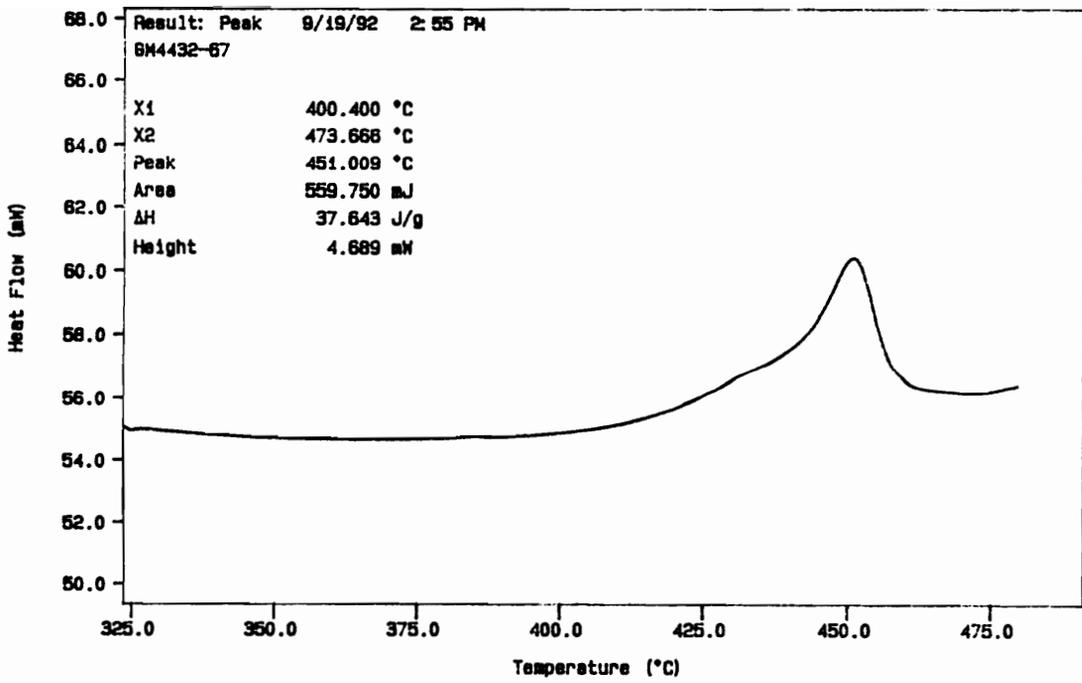


Figure 4.4.1.3 DSC of 6FDA/*p*-PDA(5,000) Semi-Crystalline Polyimide with Excess 6FDA

Table 4.4.1.3 Characterization of Additional Phenylethyneylaniline Terminated Polyimides

System	$[\eta]^\dagger$	$[\eta]^*$	$\langle M_n \rangle \Delta$ (g/mole)	$\langle M_w \rangle / \langle M_n \rangle$	T_g (°C)
ODPA/3,3'-DDS	0.13	0.12	3350	2.2	228
BTDA/3,3'-DDS	0.15	0.13	3490	2.2	248
6FDA/4,4'-MDA	0.14	0.14	3810	2.0	282
6FDA/FDA	0.12	0.11	3170	2.1	340
BPDA/3FDAM	0.17	0.15	3620	2.0	325
BPDA/FDA	0.19	0.17	3590	1.9	371

† = Run in NMP, 25°C

* = Obtained by GPC

Δ = GPC values obtained using universal calibration methods

of 0.7-6.3% by TGA is shown in Table 4.4.1.2. An isothermal TGA thermogram of the 3,000 g/mole polymers is shown in Figure 4.4.1.4. From Figure 4.4.1.4, it can be seen that the cured phenylethynylaniline functionalized polyimides exhibit exceptional thermal stability. Films prepared by compression molding were also subjected to an aggressive oxidative environment oven chamber for 100 hours and show weight loss values ranging from 5.0 to 17.0 % as shown in Table 4.4.1.2. The results are shown graphically in Figure 4.4.1.5. In all cases, 6FDA/*p*-PDA displayed the best stability of the 6FDA-based materials probably due to the more rigid backbone of the polymer as compared to the more flexible ODA-based polymer.

Thermally cured samples also displayed good solvent resistance (samples would swell but not dissolve) when immersed in DMAc. Samples of polyimide in film form that had been cured for 1 hour at 375°C by compression molding were immersed in DMAc solvent for 15 days. The swelling data is shown in Figure 4.4.1.6, where again the lower molecular weight sample exhibited the best solvent resistance due the higher crosslink density formed upon curing.

Rheological melt properties were examined by parallel plate methods for the BPDA/3FDAM/PEA(4,000) imide oligomer. The melt viscosity and the storage and loss moduli were observed as a function of temperature as shown in Figure 4.4.1.7 and Figure 4.4.1.8. The melt viscosity and the moduli steadily decreased after the T_g to a minimum and then increased as curing proceeded. The gel point (cross over of storage and loss moduli) was ~ 420°C. Additionally, the polymer held isothermally at 325°C resulted in a ~ 10-12 minute window before crosslinking began.

Carbon fiber composite specimens were manufactured by an electrostatic powder prepregging procedure. Imide oligomers of the type 6FDA/ODA/PEA of molecular weights of 3,000 and 7,000 g/mole were used to produce the composite specimens with

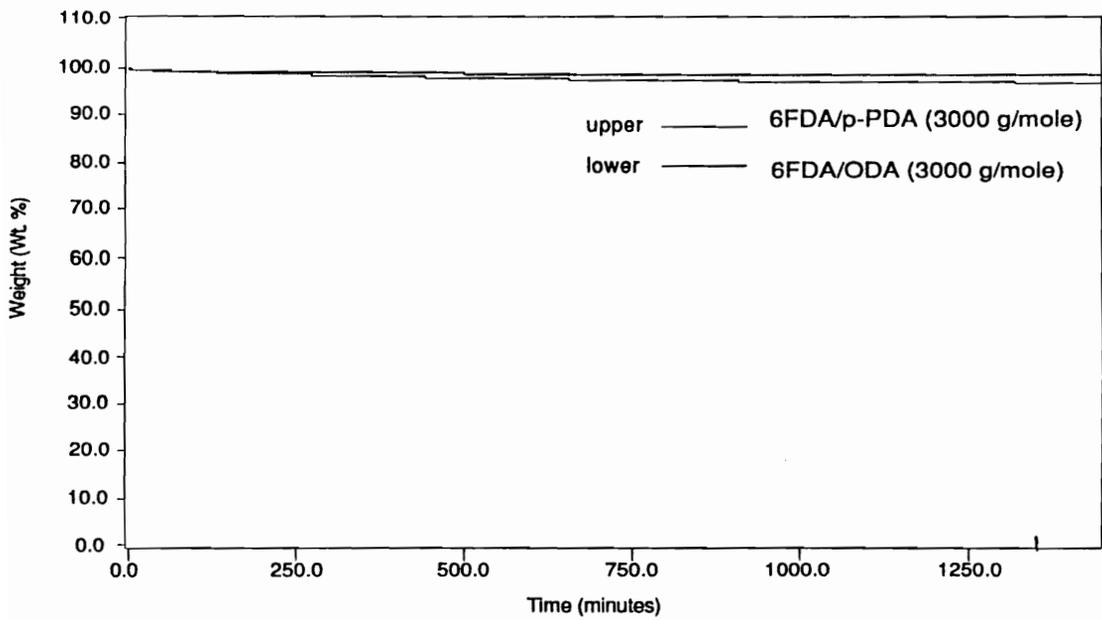


Figure 4.4.1.4 Isothermal TGA Thermogram of 3,000 g/mole 6FDA-Based Phenylethynylaniline Terminated Polyimides Aged at 371°C

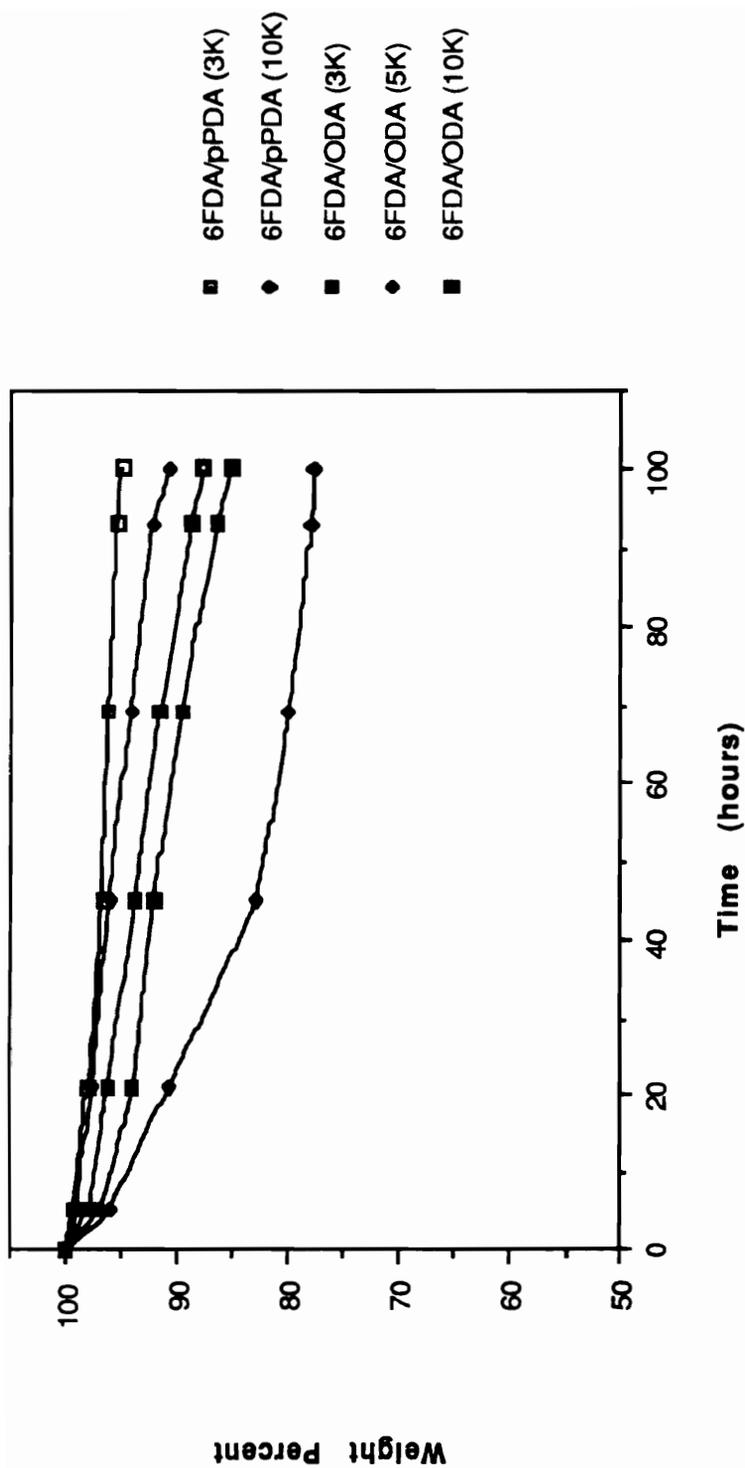


Figure 4.4.1.5 Long-term Isothermal Aging (371°C, 700°F) of Phenylethynylaniline Terminated Polyimides

G30 carbon fibers. The imide oligomers exhibited particle diameters of 12.7 μm and 14.2 μm determined by centrifugal, gravimetric particle size analysis. The particle size distribution analysis is shown in Figure 4.4.1.9. These average particle sizes were also confirmed using Scanning Electron Microscopy (SEM) where a random sampling of particle sizes was taken and averaged. The values of particle size diameters ranged from 15 to 20 μm by SEM analysis. The polyimide carbon fiber prepreg was then consolidated in a mold placed in a computer controlled hot press at a maximum temperature of 380°C and consolidation pressure of 400 psi for the 3,000 g/mole oligomer and 500 psi for the 7,000 g/mole system. A typical consolidation process cycle for the 6FDA/ODA/PEA(7,000) oligomer is shown in Figure 4.4.1.10. The 6FDA/ODA/PEA(3,000) showed excellent consolidation by C-scan analysis; however, the 6FDA/ODA/PEA(7,000) system had poorer consolidation.

The composite specimens were evaluated by Iosipescu shear strength and shear modulus analysis. The cured imide composites showed Iosipescu shear moduli practically equal to or greater than the specimens prepared from poly(ether ketone ketone) (PEKK) as seen in Figure 4.4.1.11. The Iosipescu shear modulus values were 5.31 ± 0.63 GPa and 5.10 ± 0.33 GPa respectively for the 3,000 and 7,000 g/mole imide specimens. While the PEKK specimens exhibited values of 4.33 GPa and 5.58 GPa. However, as illustrated in Figure 4.4.1.12, the cured imide specimens exhibited Iosipescu shear strengths in the same range as composite specimens prepared in a similar manner from commercially available PEKK utilizing two different carbon fibers, G30 and AS-4. The carbon fibers differ by manufacturer. G30 was produced by BASF and AS-4 was produced by Hercules. Both fiber specimens were surface treated; however, sizing and specific surface treatment is proprietary information. The 7,000 g/mole oligomer showed lower Iosipescu

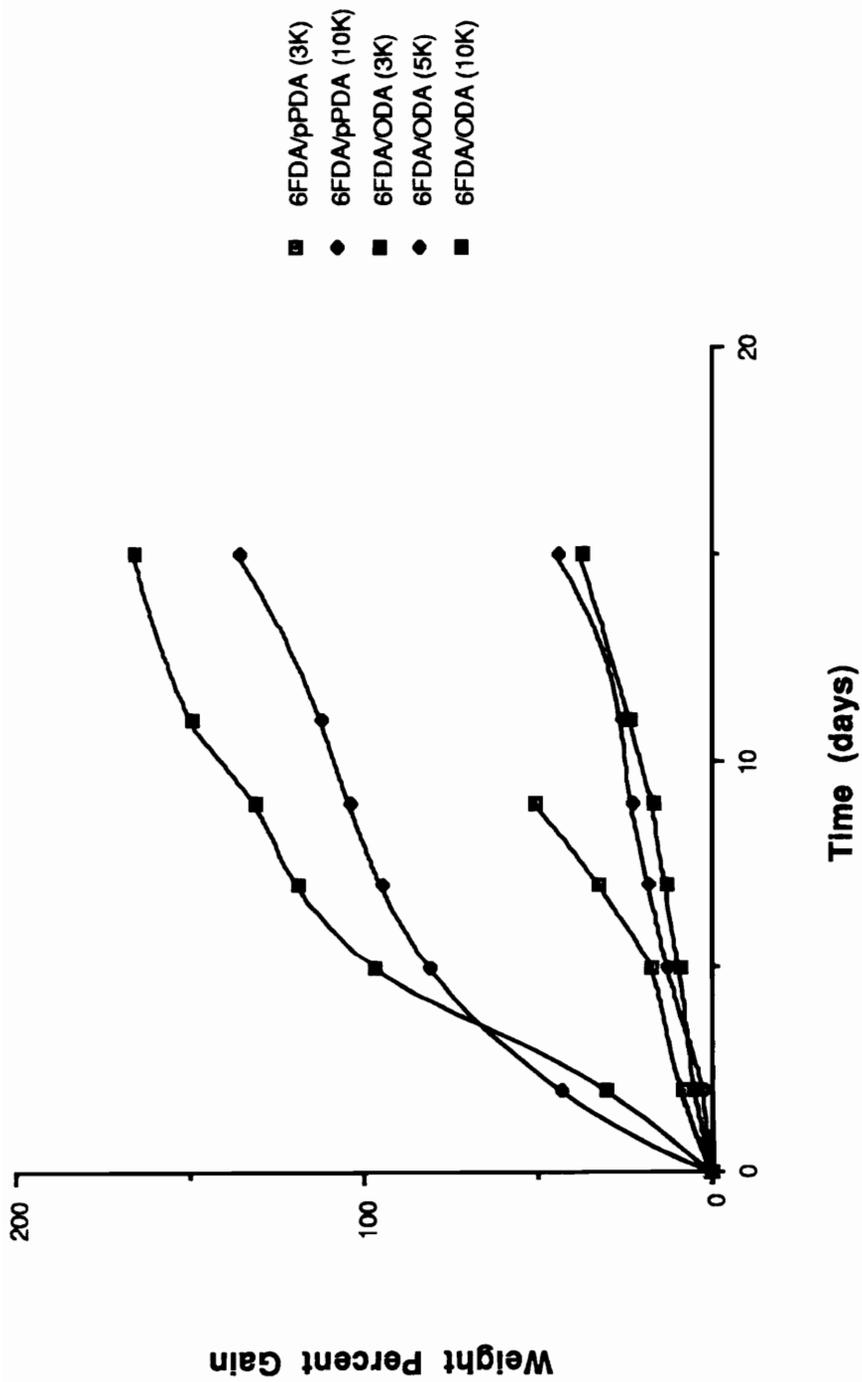


Figure 4.4.1.6 Solvent (Chloroform) Resistance of Phenylethyne/laniline Terminated Polyimides

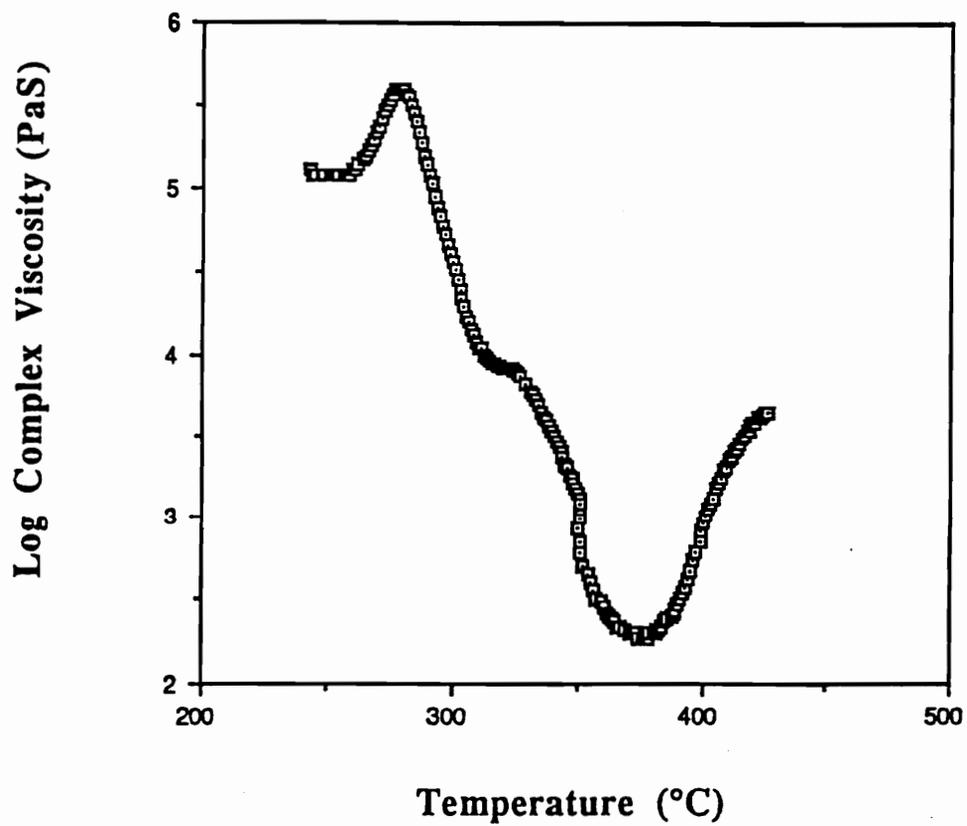


Figure 4.4.1.7 Viscosity vs. Temperature Profile of BPDA/3FDAM/PEA(4,000) Polyimide

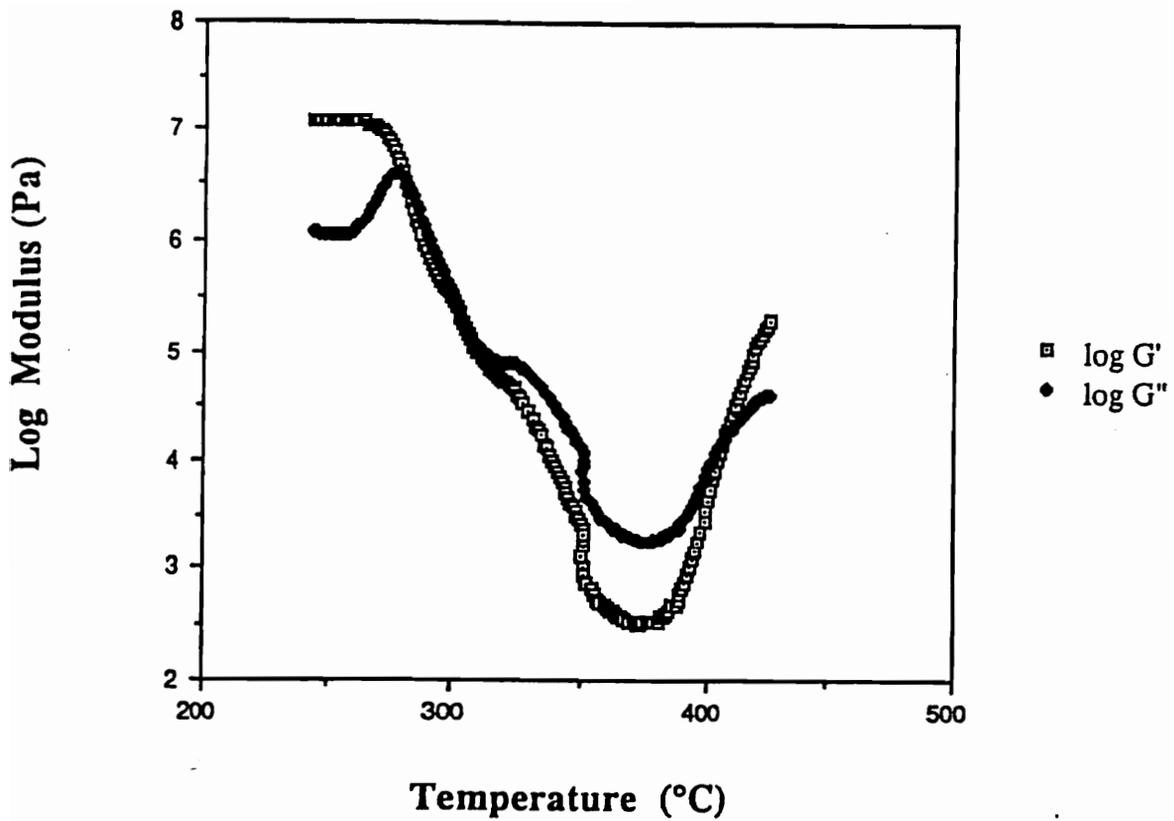
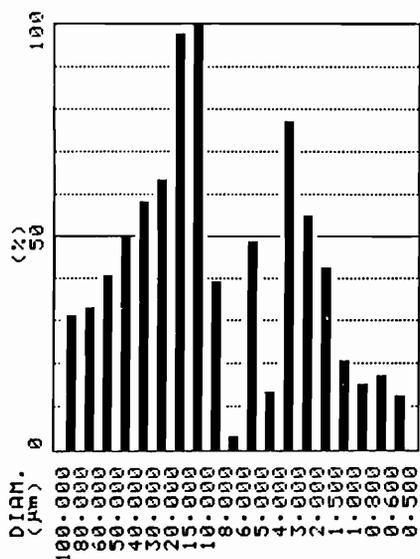
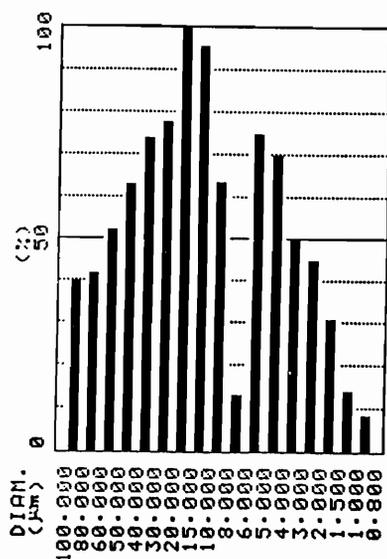


Figure 4.4.1.8 Influence of Temperature on the Loss and Storage Moduli for BPDA/3FDAM/PEA(4,000) Polyimide



3000 g/mole
 Median particle diameter = 12.7µm



7000 g/mole
 Median particle diameter = 14.2µm

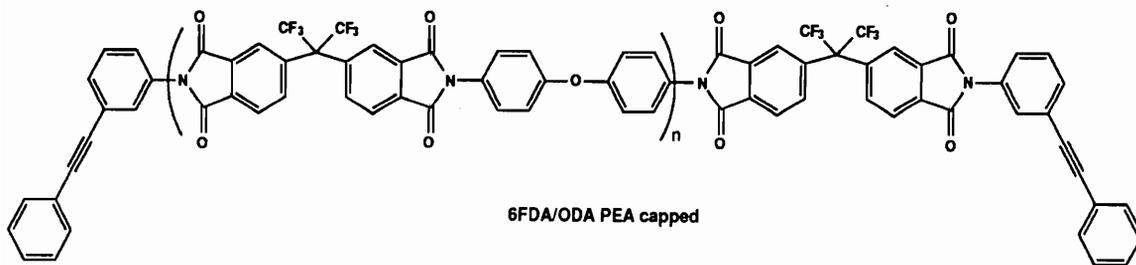


Figure 4.4.1.9 Partical Size Analysis of 6FDA/ODA/PEA Polyimides

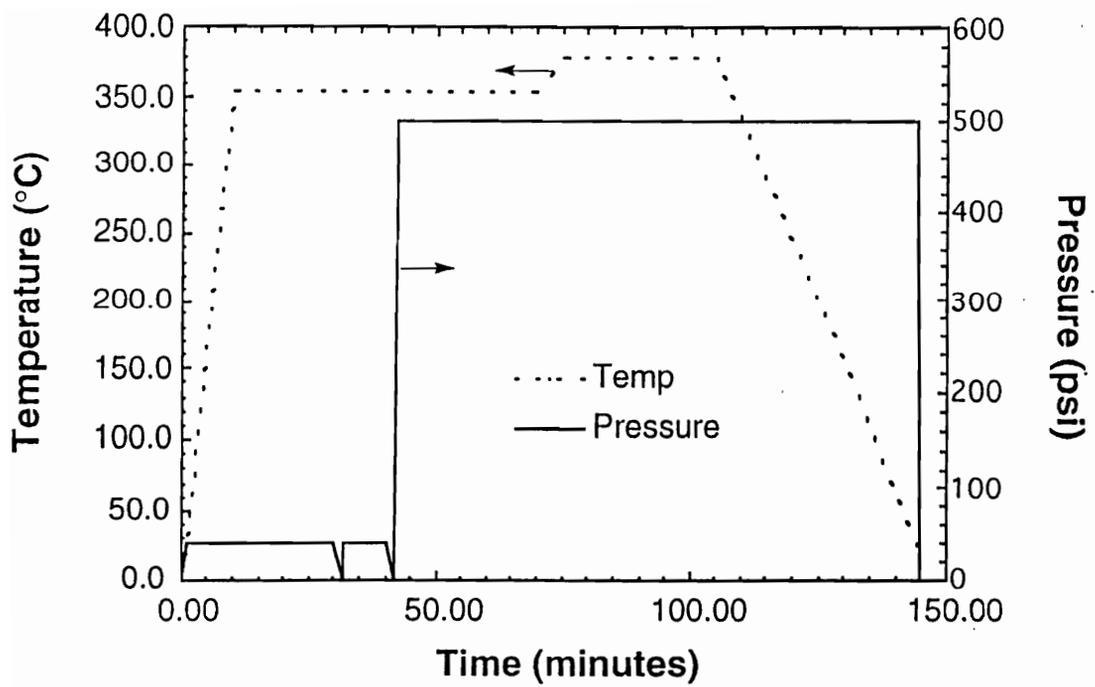


Figure 4.4.1.10 Consolidation Process Cycle for 6FDA/ODA/PEA(7,000) Polyimide

shear strength (24.1 ± 5.2 MPa) than the 3,000 g/mole system (49.9 ± 13.9 MPa) probably due to poorer consolidation of the composite specimen. From these promising results, PEA terminated resins were established as candidates for powder processing systems displaying excellent composite properties.

4.4.1.2 Phosphine Oxide Containing 3-Phenylethynylaniline Functionalized Polyimides

Phenylethynyl terminated phosphine oxide-containing imide oligomers have been synthesized using the ester-acid route previously used for the 6FDA-containing PEA endcapped imide oligomers. The oligomeric materials were based on pyromellitic dianhydride (PMDA), phosphine oxide dianhydride (PPODA), bis-(3-aminophenoxy-4'-phenyl)phenylphosphine oxide (*m*-BAPPO), 3FDAM and *p*-PDA. The majority of polyimides were derived from the PMDA/*m*-BAPPO system where the resulting polyimides have been controlled to the targeted number average molecular weight, $\langle M_n \rangle$, of $\sim 7,000$ and $10,000$ g/mole. The intrinsic viscosities in NMP at 25°C for the PMDA/*m*-BAPPO(7,000) and PMDA/*m*-BAPPO(10,000) systems were 0.17 and 0.20 dL/g respectively and $\langle M_n \rangle$, as determined by GPC using NMP and 0.06 M LiBr at 60°C was 6,700 g/mole for the 7,000 g/mole sample. The GPC chromatogram of the 7,000 g/mole PMDA/*m*-BAPPO system is shown in Figure 4.4.1.2.1. Scheme 4.4.1.2.1 illustrates the general synthetic scheme for the phenylethynyl terminated phosphine oxide polyimides.

The T_g values of the polyimides were determined by DSC before and after network formation, as shown in Table 4.4.1.2.1. The T_g of the 7,000 g/mole polymer before curing on the first scan was 236°C . Curing the polyimide for 90 minutes at 380°C , increased the T_g to 264°C . The thermal stability was also investigated by thermogravimetric analysis (TGA) in air by comparing the polymer before cure, after 90 minutes

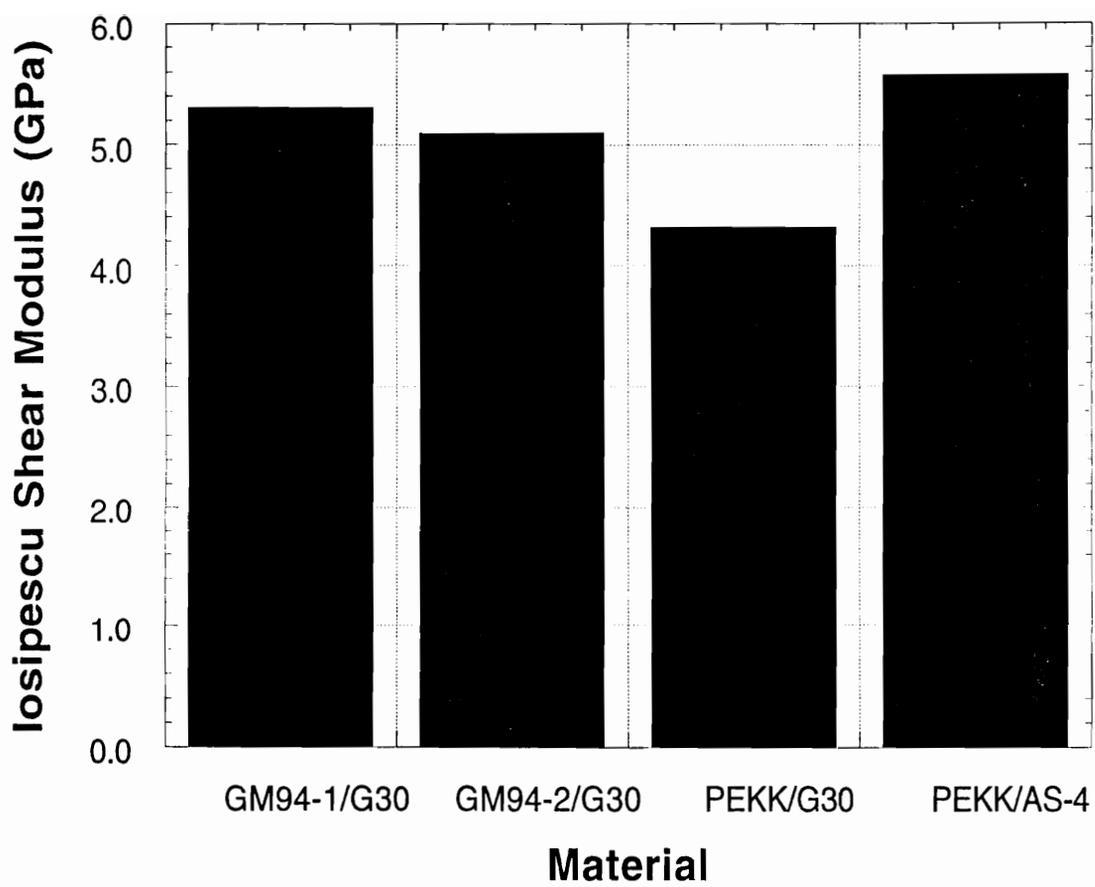


Figure 4.4.1.11 Iosipescu Shear Moduli of Composites Prepared by Powder Prepregging

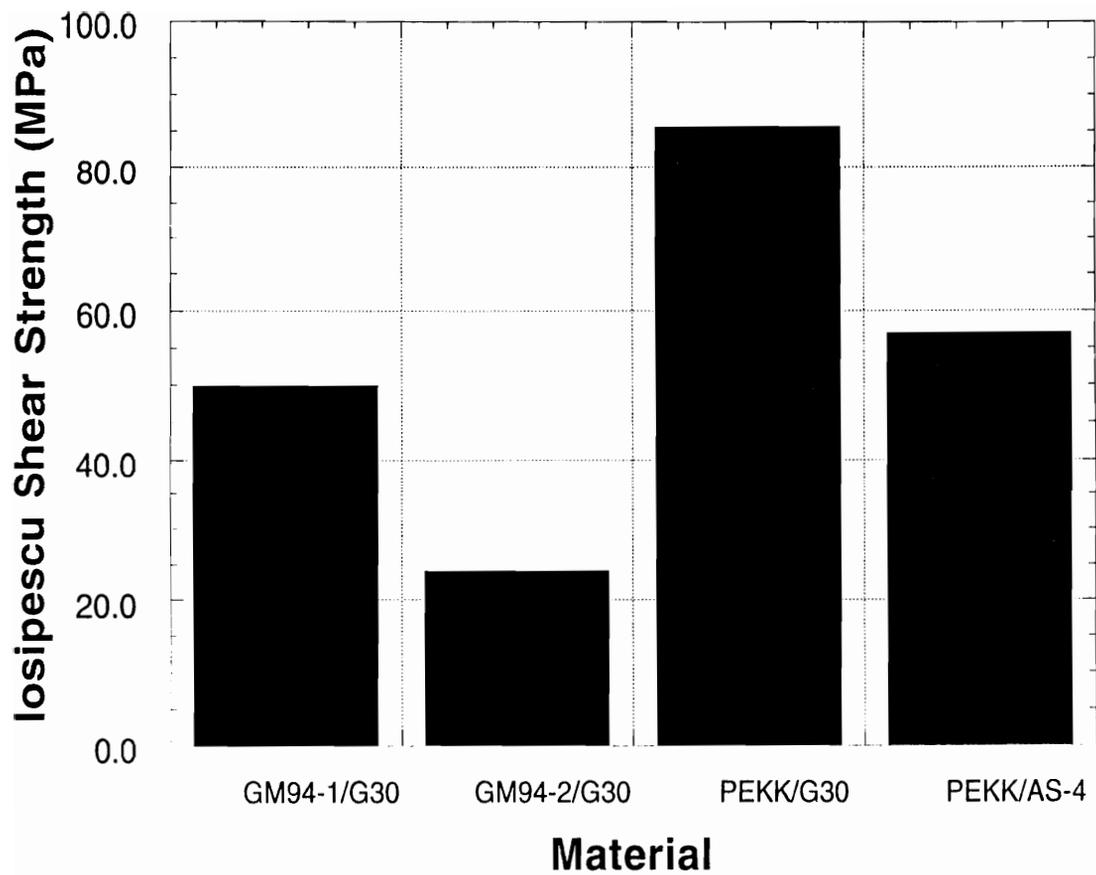


Figure 4.4.1.12 Iosipescu Shear Strengths of Composites Prepared by Powder Prepregging

at 350°C and after 90 minutes at 380°C. As seen in Figure 4.4.1.2.2, the initial weight loss is unchanged by the thermal treatment. However, the char yield, (which is often correlated with flame resistance) determined at 700°C for each of the three curing schedules was influenced. The char yield after curing for 90 minutes at 380°C, increased substantially to 49 weight percent. These initial results suggest that the polymer network exhibited better char formation when cured for 90 minutes at 380°C.

The thermal properties of the other phosphine oxide based systems have also been examined. The phosphine oxide dianhydride based polyimides exhibit even higher T_g 's and higher thermo-oxidative stability than the *m*-BAPPO systems. Thus, the T_g values range from 277 to 334°C and the temperature of 5% weight loss range from 492 to 531°C for the cured systems as illustrated in Table 4.4.1.2.1.

To further optimize the curing cycle for these phenylethynylaniline terminated polyimide oligomers, a cure study was conducted. The PMDA/*m*-BAPPO/PEA(7,000) system was chosen since this system exhibited the largest difference in T_g and the onset of cure. By comparing the thermal stability and the storage modulus [determined by Dynamic Mechanical Analysis (DMA)] of the polymer cured at different times and temperatures, a optimum cycle was chosen. The thermal stability was investigated by comparing the polymer cured at 350°C for 60 minutes, 350°C for 120 minutes, after 60 minutes at 380°C and after 90 minutes at 380°C. As seen in Figure 4.4.1.2.3 and Figure 4.4.1.2.4, the thermal stability is enhanced and the highest storage modulus is achieved after curing for 90 minutes at 380°C.

Studies to examine the gel fraction of the cured samples were also performed. Films cured at various times and temperatures were extracted with chloroform (which is a solvent for the linear material) for 5 days. They were then dried for 5 days at 100°C under vacuum. As Table 4.4.1.2.2 shows, the sample cured at 380°C for 90 minutes had the

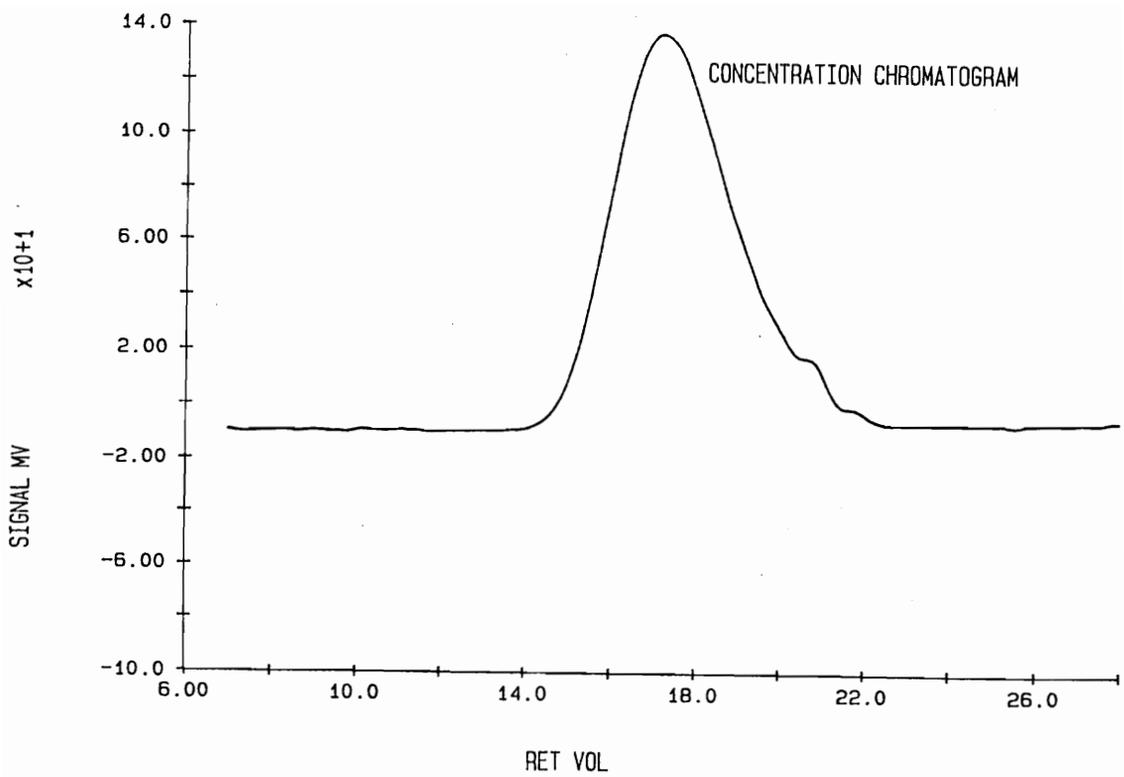
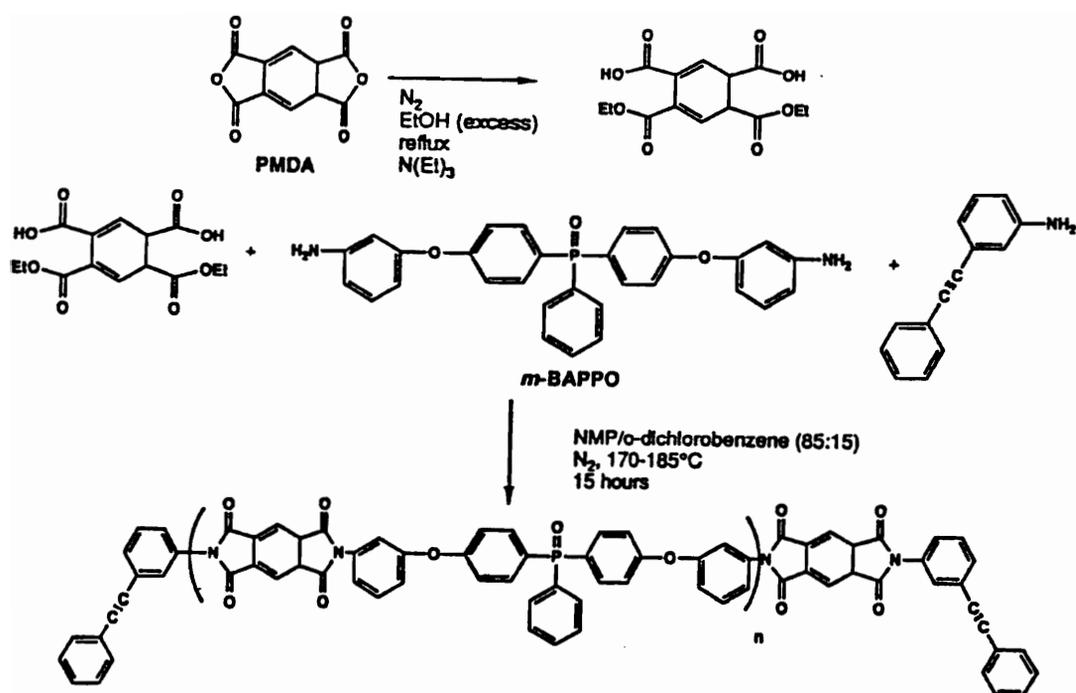


Figure 4.4.1.2.1 GPC Chromatogram of PMDA/*m*-BAPPO/PEA(7,000) Polyimide in NMP and 0.06 M LiBr at 60°C



Scheme 4.4.1.2.1 Synthesis of Phenylethynyl Terminated Phosphine Oxide Polyimides

Table 4.4.1.2.1 Thermal Analysis of Triarylphosphine-Containing Polyimides Endcapped with Phenylethynylaniline

System	Target $\langle M_n \rangle$ (g/mole)	T _{g1} (°C)	T _{g2} (°C)	5% Wt. Loss (°C)*
PMDA/ <i>m</i> -BAPPO	7,000	236	264	529
	10,000	247	274	537
PPODA/ <i>p</i> -PDA	3,000	232	277	510
PPODA/3FDAM	3,000	247	334	547

* = Heating rate of 10°C/min, TGA of the insitu cured oligomer

T_{g1} = T_g before cure, heating rate of 10°C/min in nitrogen

T_{g2} = T_g after cure, heating rate of 10°C/min in nitrogen

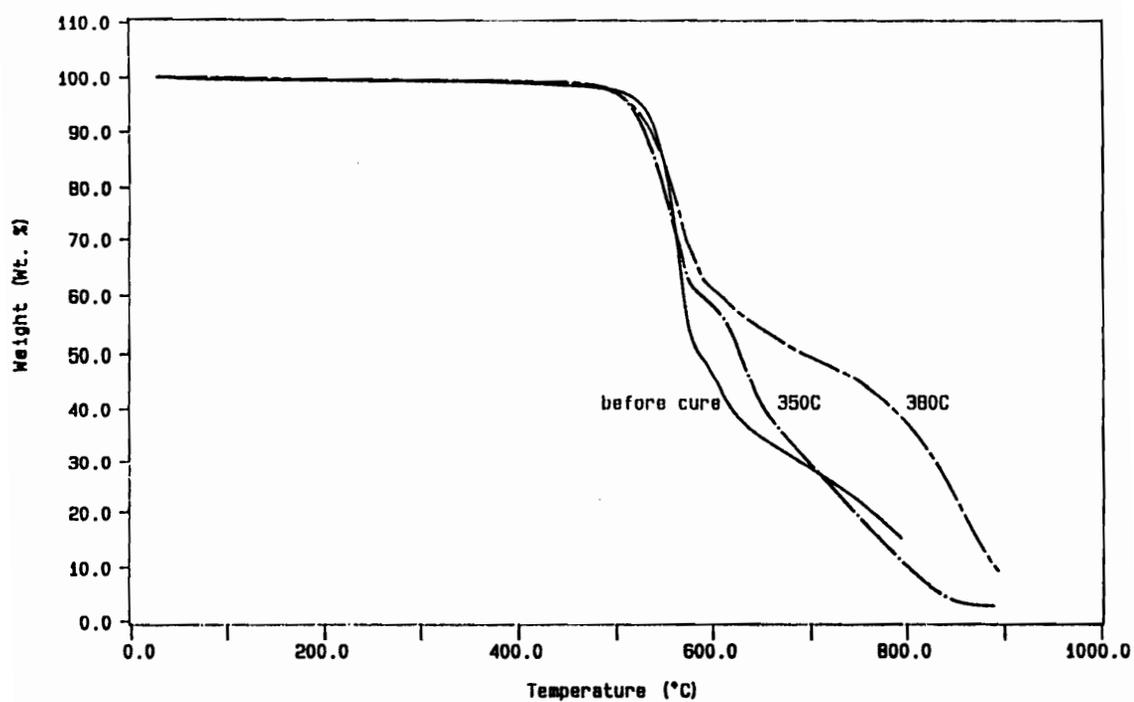


Figure 4.4.1.2.2 TGA Thermograms (10°C/min, Air) of PMDA/*m*-BAPPO/PEA Polyimide Cured Under Different Cure Schedules

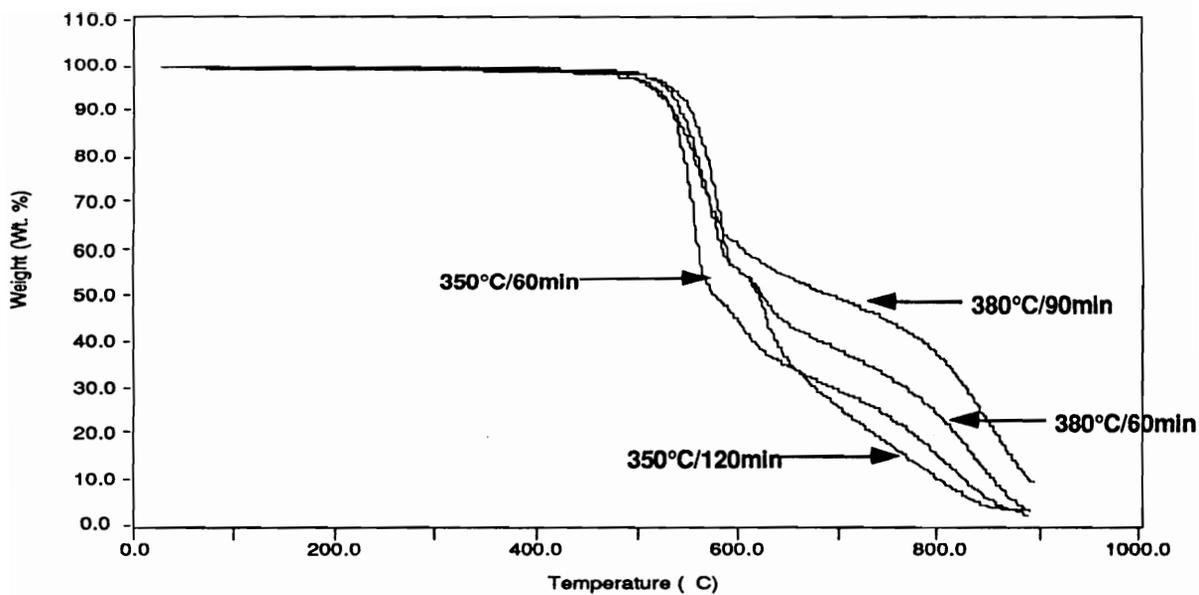


Figure 4.4.1.2.3 Influence of Curing Schedule on Thermo-oxidative Stability of PMDA/*m*-BAPPO/PEA(7,000) Polyimide (10°C/min, Air)

highest gel fraction at 98%. By contrast, samples cured for 90 minutes at 350°C exhibited a high, but significantly lower gel fraction of 89%.

Mechanical testing has also been performed to measure the tensile properties of the cured PMDA/*m*-BAPPO polyimide. Some data based on samples cured at 350°C for 90 minutes are in the general range expected for polyimides, and are shown in Table 4.4.1.2.3. Furthermore, initial evaluation of the composite materials based on this polyimide system have been provided by NASA Langley and these results are shown in Table 4.4.1.2.4 where the reactive polyimide oligomers were cured at 350°C for 1 hour. The Ti/Ti tensile shear strengths at room temperature and 177°C were very good, with values of near 5000 psi and 4000 psi respectively. The unidirectional composite flexural properties were also very promising with values of ~ 220 ksi (RT) and 143 ksi (177°C) for flexural strength and modulus values of ~ 21.0 Msi and 18.0 Msi were observed. Additional evaluation of Ti/Ti tensile shear strengths at room temperature and 177°C were performed after exposing the adhesive specimens to various solvents for 3 days. As depicted in Figure 4.4.1.2.5, there was virtually no affect of solvent exposure on the tensile lap shear values. The water boil sample did show slightly lower values; however, this is believed to be due to degradation of the Pasagel surface treatment of the Ti coupons and not a result of poor resin performance.

The flow properties and cure window, or processing window, defined as the interval between T_g and T_{gel} have been examined by rheological parallel plate studies. The viscosity and modulus have been plotted against temperature for the PMDA/*m*-BAPPO/PEA(7,000) system as shown in Figures 4.4.1.2.6 and 4.4.1.2.7. The gel point may be established to be ~380°C as judged from the crossover point of the real and imaginary (loss and shear moduli), G' and G'' . As seen from Figures 4.4.1.2.6 and 4.4.1.2.7, the processing window is greatly increased compared to the commercially

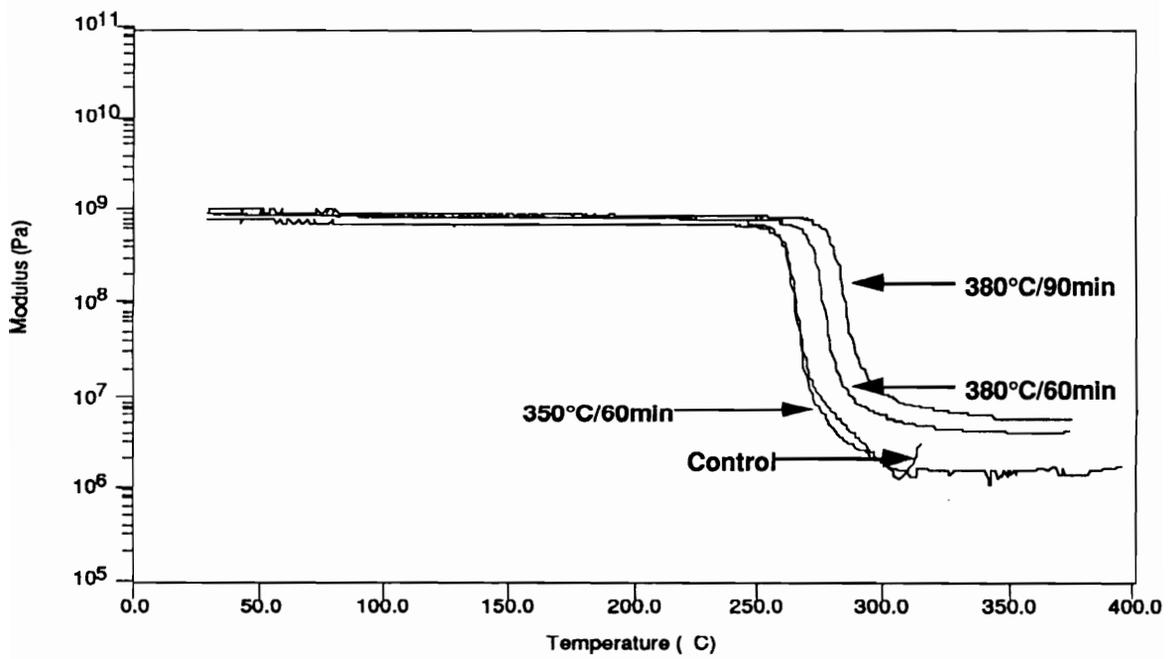


Figure 4.4.1.2.4 Influence of Curing Schedule on Storage Modulus of PMDA/*m*-BAPPO/PEA(7,000) Polyimide

Table 4.4.1.2.2 Influence of Time and Temperature of the Gel Fraction of PMDA/*m*-BAPPO/PEA(7,000) Cured Imide Networks

Temperature (°C)	Time (minutes)	Gel Content %
350	60	67
350	90	89
380	30	90
380	60	94
380	90	98

Solvent Extraction Experiments - Each sample was extracted with chloroform for 5 days, then dried 5 days at 100°C under vacuum

Table 4.4.1.2.3 Tensile Behavior of Cured Polyimide Networks

Modulus (ksi) (MPa)	403 (2780)
Yield Stress (ksi) (MPa)	11.1 (76.5)
Yield Strain (%)	4.0

Samples were cured at 350°C for 90 minutes.

Table 4.4.1.2.4. Mechanical Testing of PMDA/*m*-BAPPO/PEA(7,000) Oligomer^(a)

Ti/Ti Tensile Shear Strength (cure conditions of 1 hour at 350°C, 50 psi)

<u>Test Temperature</u>	<u>Strength (psi) (MPa)</u>
RT	4760 (32.8)
177°C	3930 (27.1)

IM-7 Unidirectional Composite Flexural Properties

(cured 0.5 hr at 300°C--150 psi, 1 hr at 375°C, 100 psi)

<u>Test Temperature</u>	<u>Flexural Strength (ksi) (MPa)</u>	<u>Modulus (Msi) (MPa)</u>
RT	219 (1510)	21.4 (148,000)
177°C	143 (986)	18.2 (125,000)

<u>Test Temperature</u>	<u>Compression Strength (psi)</u>
RT	182

(a)Data courtesy of NASA Langley/William and Mary

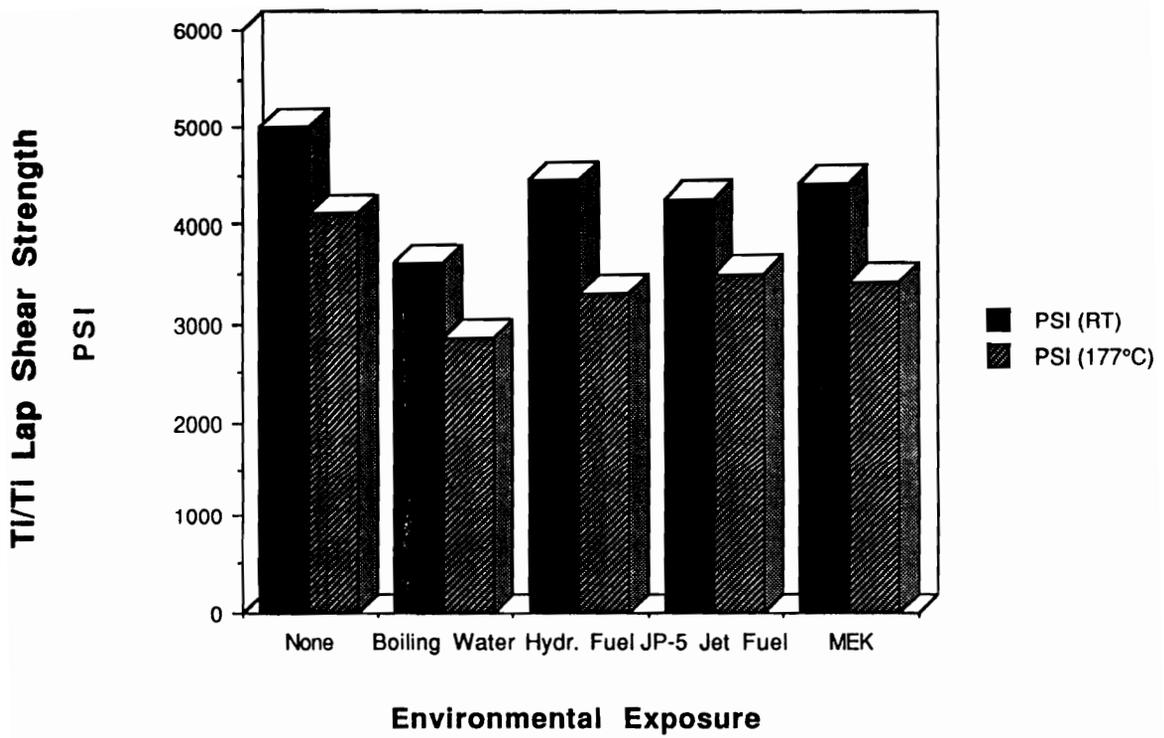


Figure 4.4.1.2.5 Ti/Ti Single Lap Shear Results after Solvent Exposure for PMDA/*m*-BAPPO/PEA(7,000) Polyimide

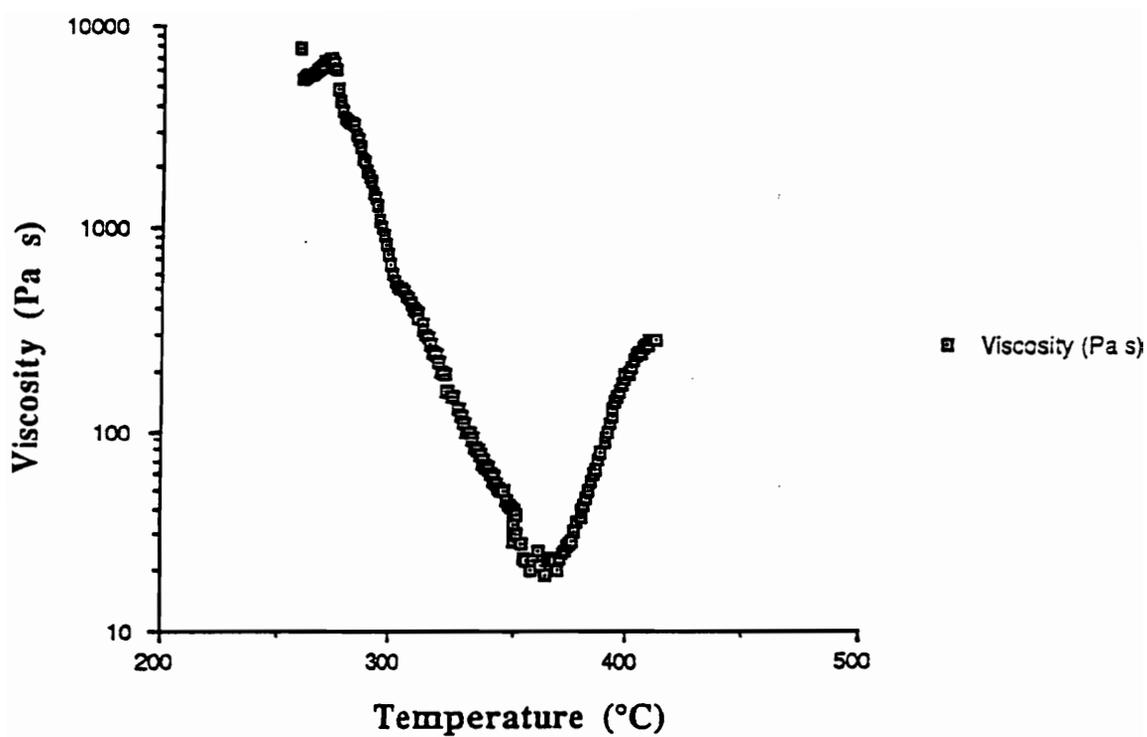


Figure 4.4.1.2.6 Viscosity vs. Temperature Profile of PMDA/*m*-BAPPO/PEA(7,000)
Polyimide

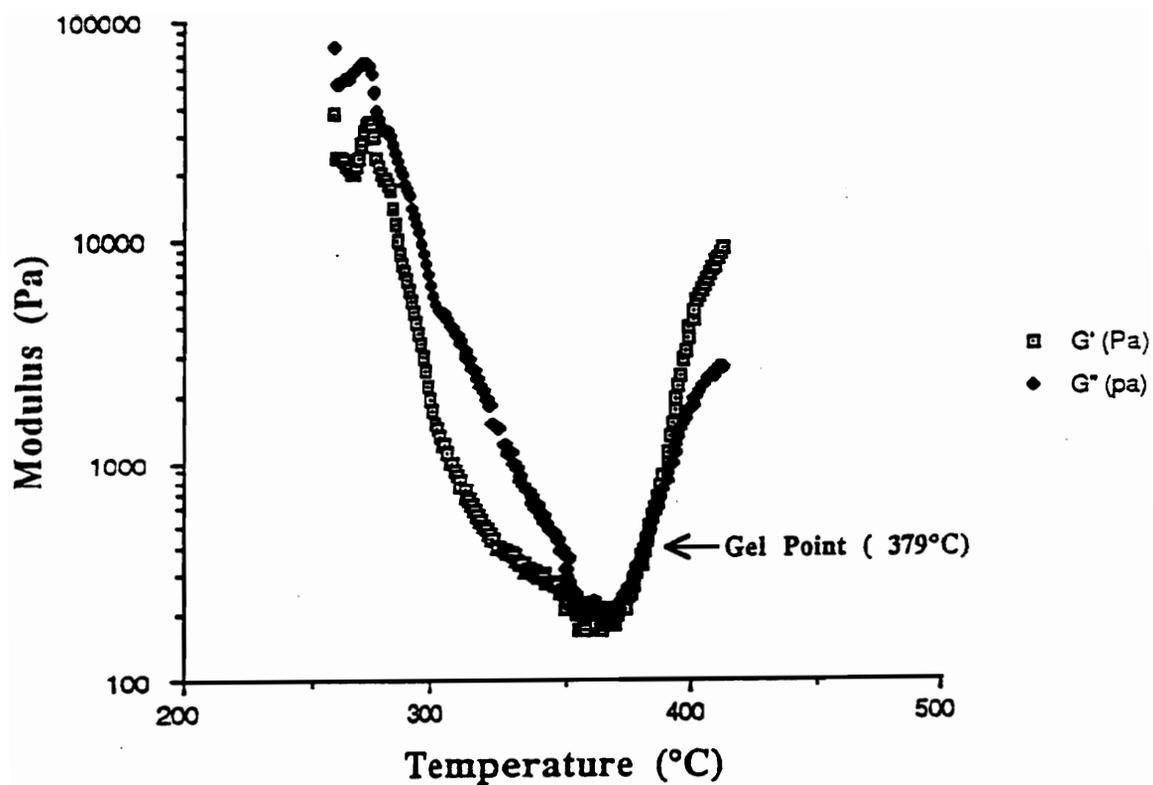


Figure 4.4.1.2.7 Influence of Temperature on the Loss and Storage Moduli of PMDA/*m*-BAPPO/PEA(7,000) Polyimide

available systems. These reactive oligomers possess relatively low melt viscosities above their T_g .

4.4.2 Randomly Segmented Polyimide Siloxane Copolymers Endcapped with 3-Phenylethynylaniline or *m*-Aminophenylacetylene

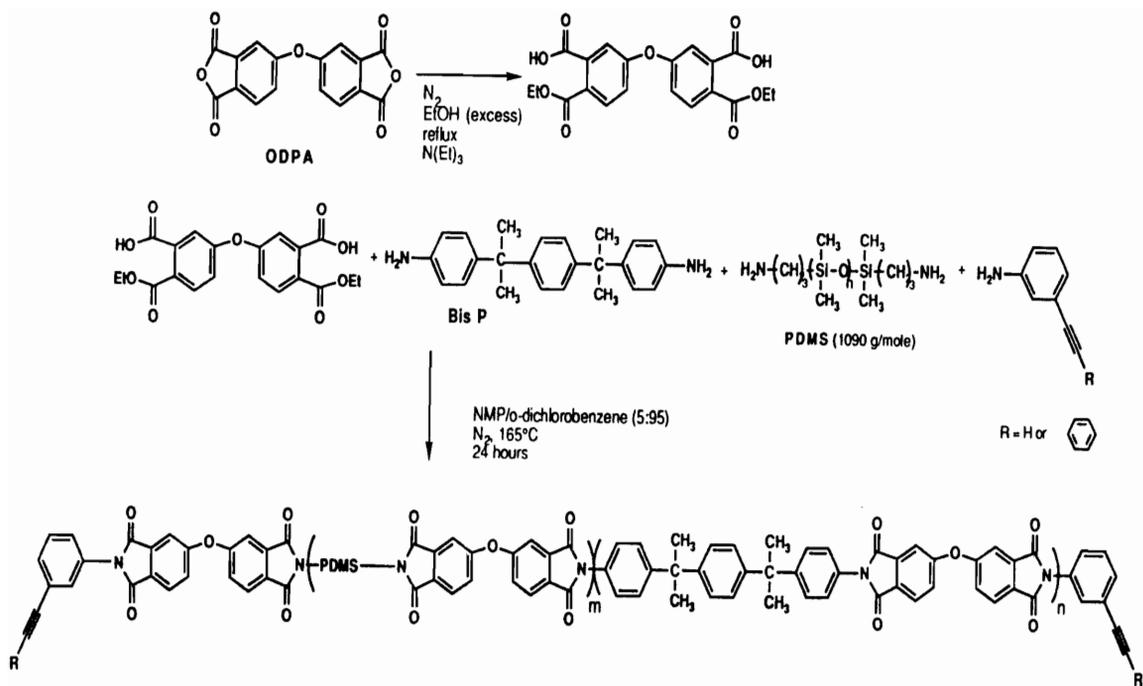
Randomly segmented polyimide siloxane copolymers were synthesized by a one-step solution imidization route as used by Wescott et. al.³⁵⁷ and Rogers et. al.⁷⁰ The ODPa/Bis P/PSX randomly segmented polyimide copolymers endcapped with either 3-phenylethynylaniline or *m*-aminophenylacetylene were synthesized as shown in Scheme 4.4.2.1. The ester-acid of ODPa was made and then PSX was slowly added with 40 mL of *o*-DCB and 4 mL of NMP slowly over a fifteen minute period. The reaction was allowed to stir at 160°C for 45 minutes to give an anhydride capped PSX. This insured random incorporation of the PSX in to the polyimide siloxane copolymer. Bis P was added with 25 mL NMP and was stirred for another 30 minutes before either 3-phenylethynylaniline or *m*-aminophenylacetylene was added. The monomers were rinsed in with *o*-DCB to give a final concentration of 20 weight % solids. The target molecular weight was 30,000 g/mole. The reaction was allowed to proceed for 24 hours at 160°C. During this time, water was observed collecting in the reverse Dean-Stark trap. After the reaction was completed, the solution was cooled, diluted to 15 weight % solids with additional NMP and then precipitated in methanol. The polymer was dried at ~ 180°C for 24 hours under vacuum. Films of the randomly segmented copolymers were cast from chloroform and dried at a final temperature of ~ 220°C.

Six ODPa/Bis P/PSX acetylene-type endcapped randomly segmented polyimide siloxane copolymers are listed in Table 4.4.2.1. The intrinsic viscosities of the randomly segmented copolymers were in the range of 0.32 to 0.48 dL/g. The ODPa/Bis P/21

%PSX1090/PEA(30,000) polyimide exhibited a lower intrinsic viscosity than was expected as compared to the other copolymers. However, the remaining polymers exhibited intrinsic viscosity values corresponding very well with the targeted $\langle M_n \rangle$ values.

The T_g 's of the random polyimide siloxane acetylene-type endcapped copolymers before and after curing are listed in Table 4.4.2.1. The PEA endcapped copolymer films were cured in a forced nitrogen atmosphere oven at 350°C for 1 hour. The *m*APA endcapped copolymer films were cured at 180°C for 10 minutes, 210°C for 10 minutes, 240°C for 60 minutes and 280°C for 30 minutes. Glass transition temperatures before curing were higher for the 30,000 g/mole systems than the 15,000 g/mole systems as would be expected. Furthermore, increases in T_g 's were highest for the lowest molecular weight copolymers due to the highest concentration of reactive endgroups. For example, the T_g increased as much as 37°C in the ODPa/Bis P/9 %PSX1090/*m*APA(15,000) polyimide after curing.

The crosslinking of these randomly segmented polyimide siloxane copolymers could have interesting topological effects and should alter their gas separation properties. Polyimide membranes have been studied extensively for gas separation applications particularly for use in separating CO₂/CH₄ mixtures as well as N₂/CH₄ mixtures. Most polyimides show an inverse selectivity for nitrogen over methane from most other available materials which makes them attractive materials for these types of separations. However, an inherent problem with many polyimides which exhibit excellent permselectivity ratios is low permeation rates. Therefore, it is desirable to have both high selectivity and permeability in order to obtain the most economical and efficient separations. By crosslinking the polyimide siloxane copolymers, relatively high permeation *and* permselectivity may be achieved. In addition, crosslinking improves chemical and solvent resistance which is beneficial since many gas separations employed in industrial



Scheme 4.4.2.1 Synthesis of Randomly Segmented Polyimide Siloxane Copolyimides
Endcapped with 3-PEA or *m*APA

Table 4.4.2.1 Characterization of Randomly Segmented Segmented Polyimide Siloxane Copolymers

Polyimide	$[\eta]^*$ (dL/g)	T _{g1} (°C)	T _{g2} (°C)
ODPA/Bis P/21 % PSX(1090)/PEA/(30,000)	0.37	200	227
ODPA/Bis P/9 % PSX(1090)/PEA/(30,000)	0.48	229	241
ODPA/Bis P/21 % PSX(1090)/mAPA/(30,000)	0.48	232	241
ODPA/Bis P/9 % PSX(1090)/mAPA/(30,000)	0.42	232	244
ODPA/Bis P/21 % PSX(1090)/mAPA/(15,000)	0.32	225	246
ODPA/Bis P/9 % PSX(1090)/mAPA/(15,000)	0.37	198	235

* = Run in CHCl₃ at 25°C

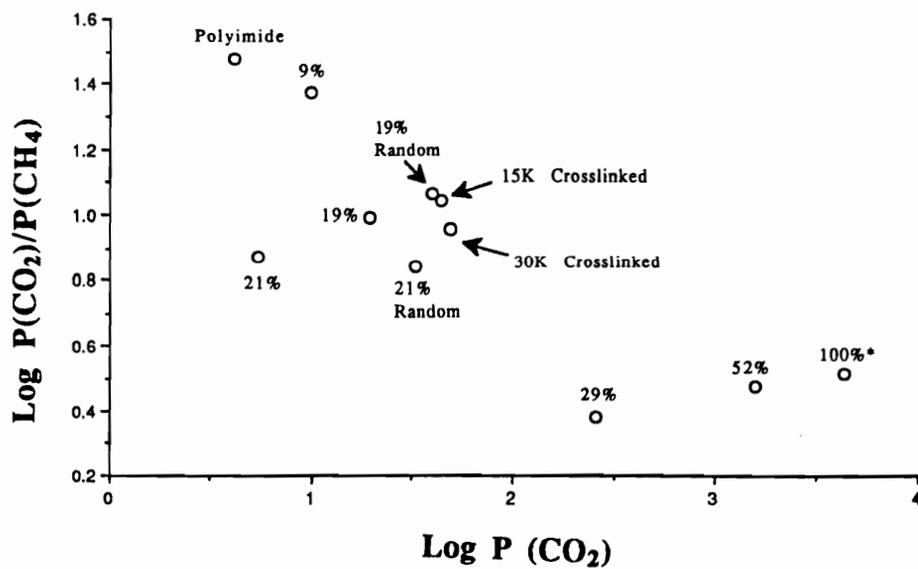
T_{g1} = T_g before cure, heating rate of 10°C/min in nitrogen

T_{g2} = T_g after cure, heating rate of 10°C/min in nitrogen

downstream processes often encounter aggressive gases such as hydrogen sulfide in petroleum refineries. These aggressive gases would vigorously attack and destroy most membranes.

Polyimide siloxane copolymers inherently exhibit relatively good permeability and permselectivity in CO₂/CH₄ and N₂/CH₄ separations.³⁶⁰ The ODPA/Bis P/21 %PSX1090/*m*APA(15,000) and the ODPA/Bis P/21 %PSX1090/*m*APA(30,000) copolyimides were chosen to evaluate their gas separation properties since their nonreactive counterparts had shown excellent results in previous studies.^{138,139} In addition, the *m*APA endcapped polymers were investigated instead of the 3-PEA endcapped polymers because of concern that the polymer backbone may undergo some degradation at the curing temperatures necessary to cure the phenylethynyl groups.

The crosslinked randomly segmented copolymers exhibited higher selectivity values than corresponding thermoplastic randomly and perfectly alternating segmented copolymers without significantly lowering the permeability of the faster permeating gases. These results were encouraging since an increase in selectivity usually results in a decrease in permeability. Furthermore, as might be expected the 15,000 g/mole crosslinked polyimide siloxane copolymer exhibited higher permselectivity than the 30,000 g/mole copolymer probably due to its increased crosslinked density of the cured polymer film. These results are depicted in Figure 4.4.2.2 where the permselectivity of carbon dioxide from methane with respect to carbon dioxide permeation in a series of ODPA/Bis P/PSX copolymers is shown. The values corresponding to thermoplastic copolymers were derived from another study conducted in our laboratory.^{138,139} A summary of the comparison of the permeability and selectivity characteristics of the linear and the ODPA/Bis P/21 %PSX/*m*APA(15,000) crosslinked analogs is presented in Table 4.4.2.3. The selectivity of the randomly segmented crosslinked polyimide siloxane copolymers was increased as much as 61 % in the case of CO₂/CH₄ without any significant decrease in permeability.



*100 % PSX values: Stern et. al., Journal of Polymer Science: Part B: Polymer Physics, Vol. 25, 1263-1298 (1987)

Figure 4.4.2.2 Permselectivity of Carbon Dioxide from Methane with Respect to Carbon Dioxide Permeation in ODPA/Bis P/PSX Copolymers

Table 4.4.2.3 Gas Separation Characteristics of Linear and Crosslinked ODPA/Bis P/PSX
Copolyimides

	15K Crosslinked	Linear Random Copolymer
P(O ₂)	11.6	8.8
P(N ₂)	3.6	3.6
P(CH ₄)	4.0	4.7
P(CO ₂)	44.5	32.5
P(O ₂)/P(N ₂)	3.2	2.4
P(CO ₂)/P(CH ₄)	11.1	6.9

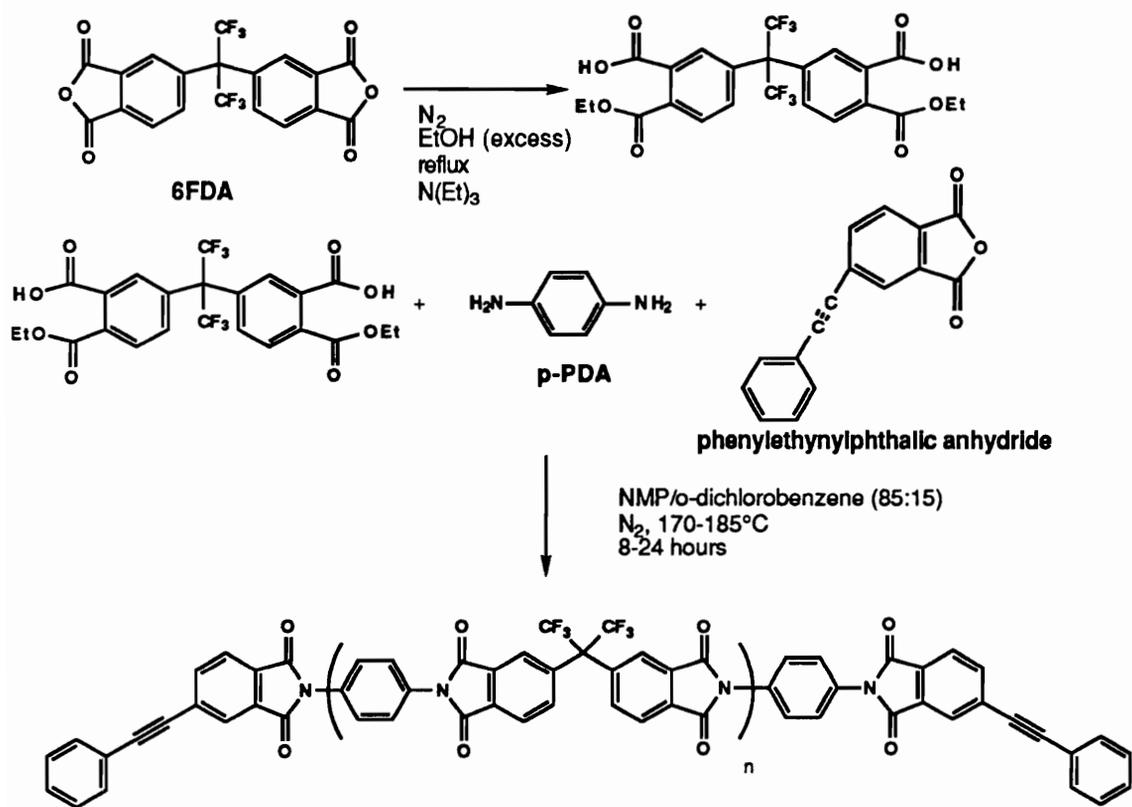
Measurements were taken at 30°C and $\Delta P = 1$ atm.

4.4.3 Polyimide Oligomers Endcapped with 4-Phenylethynylphthalic Anhydride

Phenylethynyl-functionalized oligomers endcapped with 3-phenylethynylaniline cure upon heating to afford a highly crosslinked network that is highly solvent resistant and that show exceptional thermo-oxidative stability. However, as an alternative to the 3-PEA endcapped systems, 4-phenylethynylphthalic anhydride (4-PEPA) as the endcapping agent has been investigated. The later is more easily purified and possibly less toxic than the aromatic amine version. The utilization of 4-phenylethynylphthalic anhydride results in a much larger processing window between T_g and T_{cure} than polyimides capped with the more widely studied 3-ethynylphthalic anhydride, which shows a reaction exotherm at about 230-250°C.²⁷⁵

The 4-phenylethynylphthalic anhydride terminated polyimide matrix resins have been synthesized in an analogous manner as described in the earlier section concerning controlled molecular weight polyimides endcapped with 3-PEA. The stoichiometry was offset in favor of the diamine and 4-phenylethynylphthalic anhydride was used as a endcapping agent to control molecular weight. After formation of the diester-diacid derivative of the dianhydride and 4-PEPA, a calculated amount a diamine was added with NMP, after which, an azeotroping agent (usually *o*-DCB) was added and the reaction was continually heated to 170-185°C to affect polymerization and complete imidization. A solids concentration of 25 to 30% (wt/vol) was usually employed for polymerizations since high solution viscosities were not obtained due to the low molecular weight of the polymer. An example of the synthesis of a controlled molecular weight 6FDA/ODA/PEPA polyimide prepared by the ester-acid route in shown in Scheme 4.4.3.1.

At the end of the polymerization, the solution was cooled. The polyimide was isolated by slowly pouring the reaction mixture into methanol which was rapidly stirred in a blender. The polyimide was collected by suction filtration and dried in a vacuum oven



Scheme 4.4.3.1. Synthesis of Phenylethynylphthalic Anhydride-Terminated Polyimides

at ~ 180°C for 24 hours.

The 4-phenylethynylphthalic anhydride terminated polyimide matrix resins were synthesized using the ester-acid route in high yields and purity. The materials were based on 6FDA, *p*-PDA, and ODA and three different molecular weights were generated ranging from 3,000 g/mole oligomers to 15,000 g/mole.

Molecular weight control was achieved utilizing 4-phenylethynylphthalic anhydride as a endcapping agent, as shown in Table 4.4.3.1. The intrinsic viscosity values listed correspond very well with the theoretical calculated molecular weight of the 6FDA/*p*-PDA and 6FDA/ODA polyimide systems.³⁵⁹ These materials appeared to be completely imidized, as judged by the strong infrared imide absorptions at 1780 cm⁻¹, 1730 cm⁻¹, 1370 cm⁻¹, and 710 cm⁻¹ and absence of absorptions attributed to poly(amic-acids).^{2,5} All of the polyimide oligomers (even the 3,000 g/mole system) formed tough, creasable films after curing (380°C, 90 minutes, 40-400 psi). This appears to be due to considerable chain extension, prior to the gel point.

Table 4.4.3.2 lists the glass transition temperatures before curing (255-288°C) and after curing (289-310°C) which were consistent with the T_g (~300°C) of the high molecular weight linear systems. The T_g's of the 15,000 g/mole oligomers exhibited very little increase upon curing probably due to the low crosslink density formed upon curing. The onset of exothermic crosslinking occurred at ~380-420°C, as judged by DSC (10°C/minute) measurements. These exothermic maxima are approximately 40°C higher than those observed for the PEA endcapped polyimides indicating an even wider window between T_g and T_{cure} of the oligomers. The 3,000 g/mole 6FDA/*p*-PDA oligomer system appears to be crystalline, as shown by the DSC melting transition which explains why it is insoluble. This phenomenon was also observed in the 6FDA/*p*-PDA/PEA(5,000) polyimide discussed earlier. This polymer was not compression molded due to its high melting transition (T_m = 452°C). Due to the semi-crystalline nature of the 3,000 g/mole oligomer, curing at 380°C

Table 4.4.3.1 Molecular Weight Characterization of 4-Phenylethynylphthalic Anhydride Terminated Polyimides

System	Calculated $\langle M_n \rangle$ (g/mole)	$[\eta]$ (dL/g)*
6FDA/ODA	3,000	0.15
	10,000	0.32
	15,000	0.41
6FDA _p -PDA	3,000	insol.
	10,000	0.30
	15,000	0.40

* = Run in NMP at 25°C

Table 4.4.3.2 Thermal Analysis of 4-Phenylethynylphthalic Anhydride Functionalized Polyimides

System	Target $\langle M_n \rangle$ (g/mole)	T _{g1}	T _{g2}	TGA ₁	TGA ₂
6FDA/ODA	3,000	255	310	555	587
	10,000	275	308	551	577
	15,000	288	289	546	---
6FDA/ _p -PDA	3,000	324 T _m = 452	325	540	---
	10,000	340	362	537	---
	15,000	352	358	543	---

T_{g1} = T_g before cure, heating rate of 10°C/min in nitrogen

T_{g2} = T_g after cure, heating rate of 10°C/min in nitrogen

TGA₁ = 5% weight loss before cure, heating rate of 10°C/min in air

TGA₂ = 5% weight loss after cure(380°C for 90 minutes), heating rate of 10°C/min in air

did not increase the T_g of the oligomer probably since very little crosslinking takes place until the melting transition is reached.

The thermal stability of the 6FDA/ODA and 6FDA/*p*-PDA 4-phenylethynylphthalic anhydride terminated polyimides was also investigated before and after curing at 380°C for 90 minutes by Thermogravimetric Analysis (TGA). The phenylethynylphthalic anhydride functionalized polyimides exhibit 5% weight loss values in air for the cured polymers ranging from 537-555°C, (Table 4.4.3.2) which is consistent for polyimide systems. A TGA thermogram of the 3000 g/mole oligomer before and after curing is shown in Figure 4.4.3.1. In order to identify polyimide systems for potential candidates for 700°F (371°C) applications and to compare the 4-PEPA endcapped polyimides with 3-PEA endcapped polyimide systems, cured films were evaluated for long term isothermal stability in air. The cured polymers were subjected to an extended aggressive oxidative environment in a forced air oven for 200 hours. Weight loss data with values of 11.3-80.9 % were observed and the results are shown graphically in Figure 4.4.3.2. The 6FDA/*p*-PDA displayed the best stability of the 6FDA-based materials as was similarly observed with the PEA endcapped cured polyimides. Overall, the PEA endcapped materials exhibited slightly better high temperature (371°C) thermo-oxidative performance over the PEPA endcapped systems.

Thermally cured samples displayed excellent solvent resistance when immersed in DMAc, as judged by stress-crack resistance and short term swelling resistance. In addition, Soxhlet extractions on the cured polyimide films in refluxing chloroform showed gel contents as high as 98% as shown in Table 4.4.3.3.

4.4.3.1 Phenylethynylphthalic Anhydride Terminated Poly(Ether Imides)

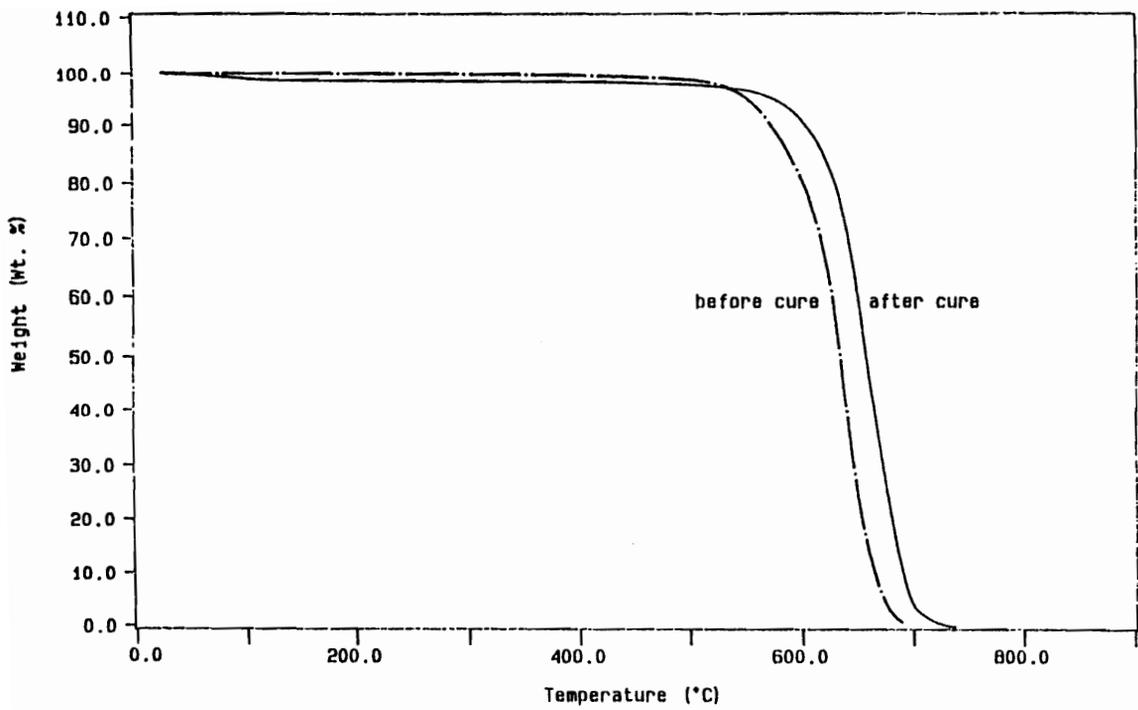


Figure 4.4.3.1 TGA Thermogram (10°C/min, Air) of 4-Phenylethynylphthalic Anhydride Terminated Polyimides Before and After Cure

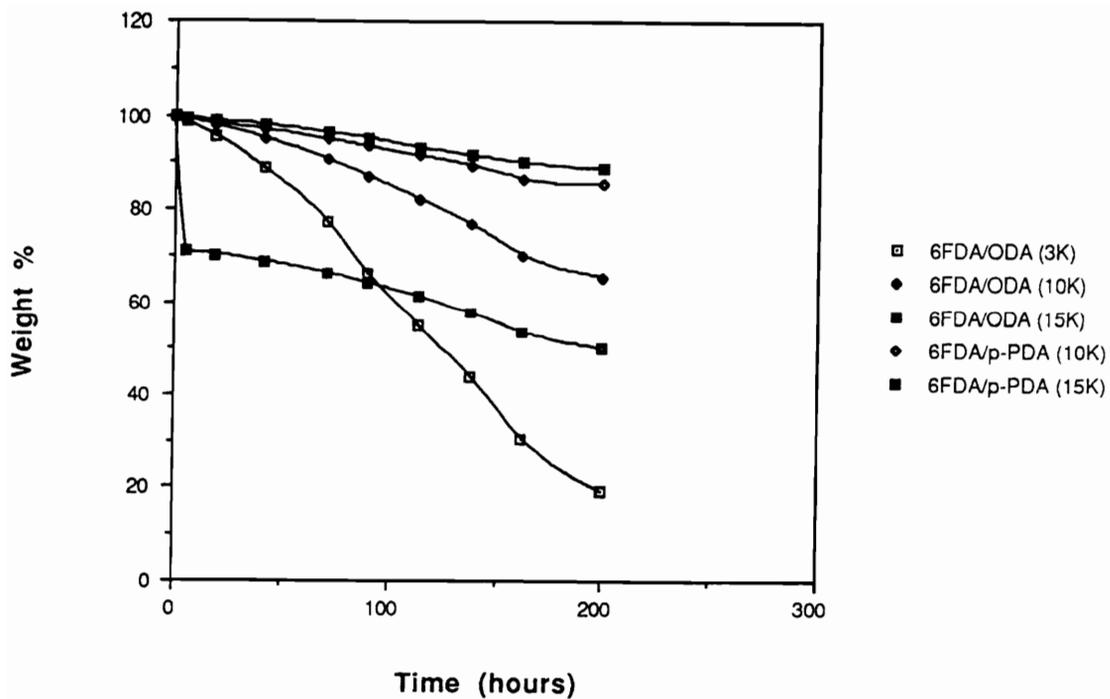


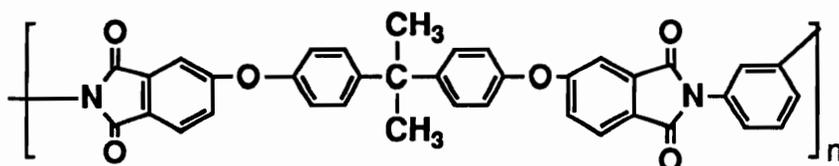
Figure 4.4.3.2 Long Term Isothermal Aging (371°C, 700°F, Air) of 6FDA-Based Phenylethynylphthalic Anhydride Endcapped Polyimides

Table 4.4.3.3 Gel Content of Cured 4-Phenylethynylphthalic Anhydride Functionalized Polyimides

System	Target $\langle M_n \rangle$ (g/mole)	% Gel Content
6FDA/ODA	3,000	95.6
	10,000	95.7
	15,000	96.2
6FDA/ <i>p</i> -PDA	10,000	98.1
	15,000	96.3

Samples were cured for 90 minutes at 380°C and refluxed in chloroform for 4 days. Samples were subsequently dried at 100°C under vacuum for 8 days.

Ultem® 1000 produced by General Electric is an injection-moldable high performance thermoplastic polyetherimide based on Bisphenol A dianhydride and *meta*-phenylene diamine⁸⁰ with a number average molecular weight of approximately 19,000 g/mole and is shown below.

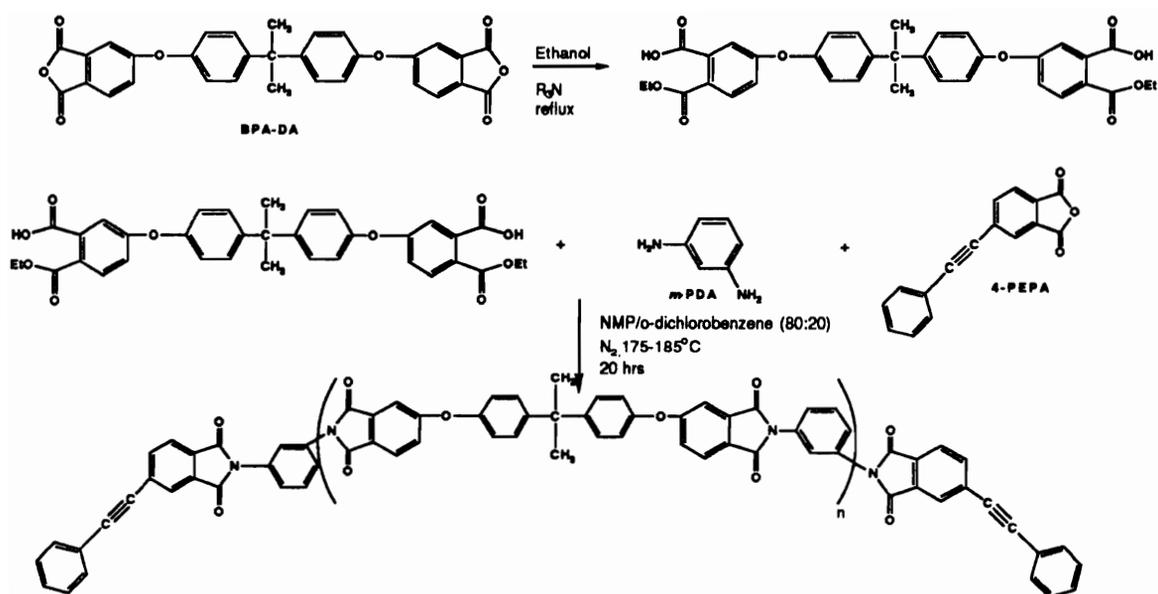


Ultem® 1000

It is considered to have good moldability, high mechanical strength, good ductility, and non-flammability characteristics as well as outstanding electrical properties. However, a trade-off for this material's excellent processability is the relatively poor chemical and solvent resistance to be expected for an amorphous thermoplastic. Thus it is only slightly resistant to salt solutions, dilute bases, gasoline and alcohol.³⁶¹ This section focuses on the development of processable ductile and durable high glass transition thermosetting poly(ether imide) oligomers endcapped with 4-PEPA.

Poly(ether imides) of various molecular weights were successfully synthesized using the ester-acid route in high yields and purity. The procedures employed were exactly the same as those described in the previous section. The only differences were that BPA-DA was used as the dianhydride and *m*-PDA was used as the diamine. Molecular weights were generated ranging from 3,000 to 30,000 g/mole. Scheme 4.4.3.1.1 illustrates the general synthetic scheme using phenylethynylphthalic anhydride to prepare phenylethynylphthalimide-terminated poly(ether imides).

Meta-phenylenediamine was the only diamine employed in the phenylethynylphthalic anhydride terminated polyimide systems, so that a direct comparison could be made with



Scheme 4.4.3.1.1. Synthesis of Phenylethynylphthalic Anhydride-Terminated Poly(ether imides)

the linear system in terms of increased glass transition temperatures and solvent resistance after curing of phenylethynyl endgroups. Molecular weight control was achieved by offsetting the stoichiometry in favor of the diamine and utilizing 4-phenylethynylphthalic anhydride as an endcapping agent, as shown in Table 4.4.3.1.1 with molecular weights ranging from 3,000 to 30,000 g/mole. The intrinsic viscosity values listed correspond well with the anticipated molecular weight of the BPA-DA/*m*-PDA systems with values ranging from 0.18 to 0.47 dL/g.

Glass transition temperatures before curing increased with increasing molecular weight with values increasing from 192 to 218°C as shown in Table 4.4.3.1.2. Films of the imide oligomers were formed by melt pressing the oligomers between steel platens (~20-40 psi pressure) and curing for 90 minutes at 380°C. After the thermal cure, the glass transition temperatures increased significantly up to a maximum of 233°C for the 3,000 g/mole system and this molecular weight oligomer also displayed the largest increase in T_g after curing. The DSC curves of the 3,000 g/mole oligomer before and after thermal curing are shown in Figure 4.4.3.1.1. The onset of exothermic crosslinking occurred at ~380-420°C as reported by the previous 4-PEPA functionalized polyimides. This high temperature cure exotherm may be identified with a wide window for these Ultem-based polyimides to be fabricated by processes such hot melt or resin transfer molding.

The cured polymers also exhibited excellent thermal stability in air as shown in Table 4.4.3.1.2. The TGA plot of the 3,000 g/mole cured phenylethynylphthalic anhydride poly(ether imide) is shown in Figure 4.4.3.1.2. All of the imide oligomers (even the 3,000 g/mole system) formed tough, creasable films after curing.

Refluxing chloroform extractions in a Soxhlet extractor were also performed on the cured polymers to evaluate their solvent resistance after network formation. As shown in Table 4.4.3.1.3, high (> 95%) gel fractions were obtained upon thermally curing the phenylethynylphthalic anhydride-terminated poly(ether imide)s. Even the 30,000 g/mole

Table 4.4.3.1.1. Molecular Weight Characterization of Phenylethynylphthalic Anhydride
Poly(Ether Imides)

System	Target $\langle M_n \rangle$ (g/mole)	$[\eta]$ dL/g (NMP, 25°C)
BPA-DA/ <i>m</i> -PDA	3,000	0.18
	7,000	0.28
	30,000	0.47

Table 4.4.3.1.2. Thermal Characterization of Phenylethynylphthalic Anhydride
Poly(Ether Imides)

System	Target $\langle M_n \rangle$ (g/mole)	$T_{g\text{before cure}}$ (°C)*	$T_{g\text{after cure}}$ (°C)*	TGA 5% Wt. Loss (°C)
BPA-DA/ <i>m</i> -PDA	3.0	192	233	547
	7.0	205	227	540
	30.0	218	218	539

* = Heating rate of 10°C/min in nitrogen

TGA = 5 % Wt. Loss after cure, measured in air at 10°C/minute

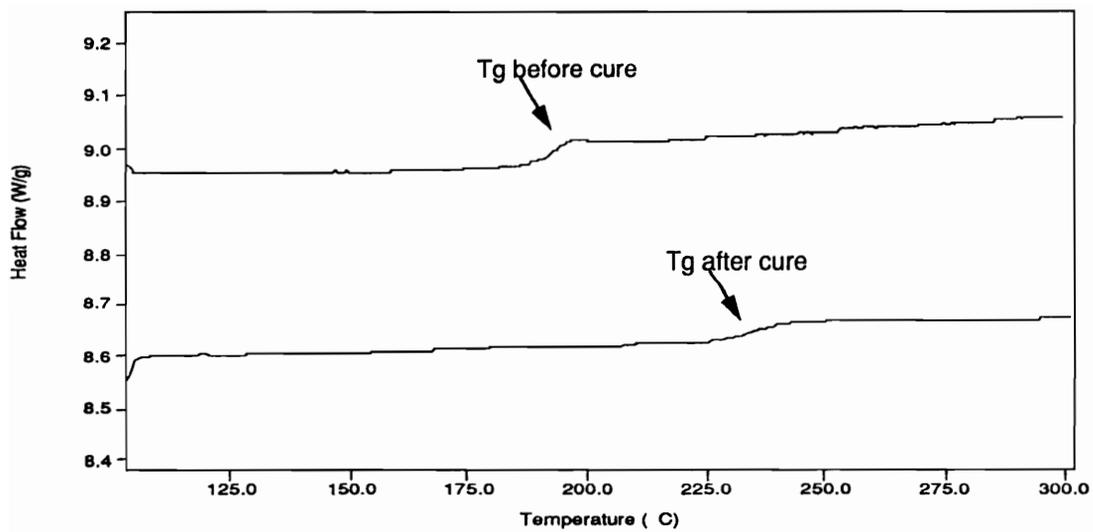


Figure 4.4.3.1.1 DSC (10°C/min) of BPA-DA/*m*-PDA/PEPA(3,000) Imide Oligomer Before and After Curing

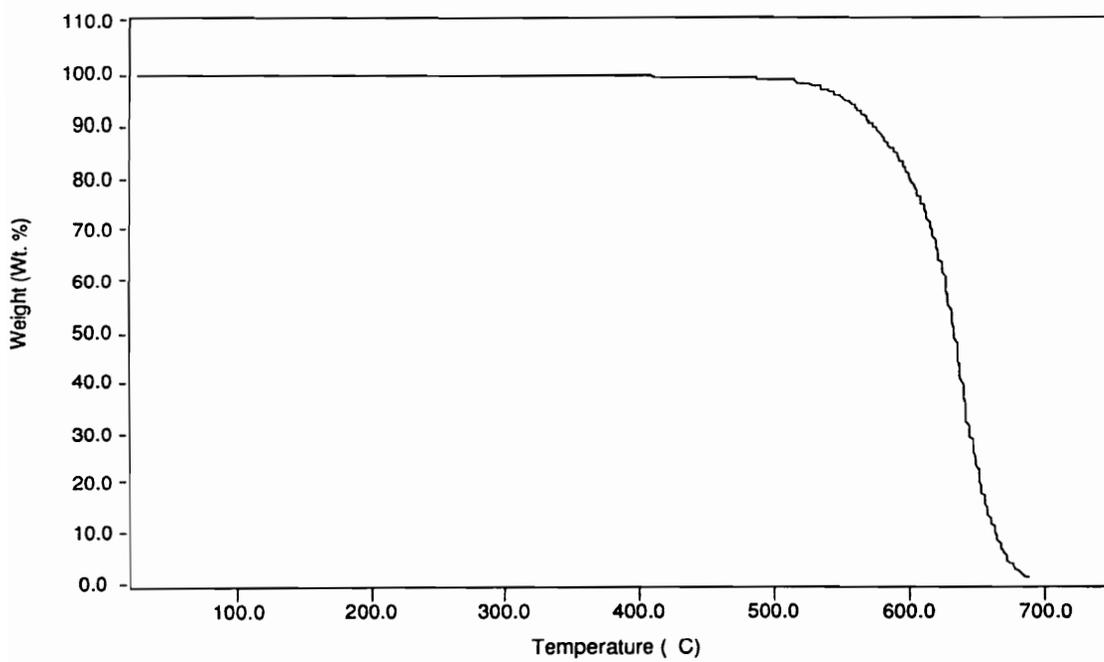


Figure 4.4.3.1.2 TGA Chromatogram (10°C/min, Air) of BPA-DA/*m*-PDA/PEPA(3,000) Imide Oligomer After Curing

4-PEPA terminated polymer was substantially crosslinked as demonstrated by a 78% gel fraction.

4.4.4 Polyimide Oligomers Endcapped with Phenylmaleic Anhydride

The development of high temperature appropriate cure sites for polyimides and other high performance thermosetting systems remains a challenging issue. This research has demonstrated that 3-phenylethynylaniline or 4-phenylethynylphthalic anhydride endcapped polyimides have a wide curing window with reasonable rates of network formation at 350°C or higher. These endcapping agents are very attractive but at the present time may be considered somewhat expensive. As an alternate system, phenylmaleic anhydride (PMA) has been synthesized and appears to be more easily prepared and perhaps less expensive than analogous ethynyl systems. Maleimide-terminated high performance polymers, especially poly(arylene ethers), can be thermally cured at 230°C to produce crosslinked networks that give high gel contents and low stress cracking.²¹⁴ By substituting one of the olefinic protons on maleic anhydride with a phenyl moiety, experiments have been performed to determine if the curing temperature of conventional maleimide sites could be increased from ~220°C to well over 300°C. PMA has been utilized as an alternate high temperature crosslinking endgroup for polyimides.

Polymers endcapped with phenylmaleic anhydride were synthesized via three methods in order to study molecular weight control using PMA as the endcapping agent. The three synthetic methods employed to prepare the PMA endcapped polyimides were the ester-acid route as previously discussed, the chemical imidization route, and a two step route where an amine-terminated polyimide was first formed and then subsequently functionalized with PMA. These different routes were explored in detail in order to determine

Table 4.4.3.1.3. Soxhlet Extraction Data in Chloroform of Phenylethynylphthalic Anhydride Endcapped Poly(Ether Imides)

Polymer System	Target $\langle M_n \rangle$ (g/mole)	% Gel Fraction*
BPA-DA/ <i>m</i> -PDA	3,000	96
	7,000	84
	30,000	78

* = Samples were extracted for 5 days and then dried for 4-5 days at 100-150°C.

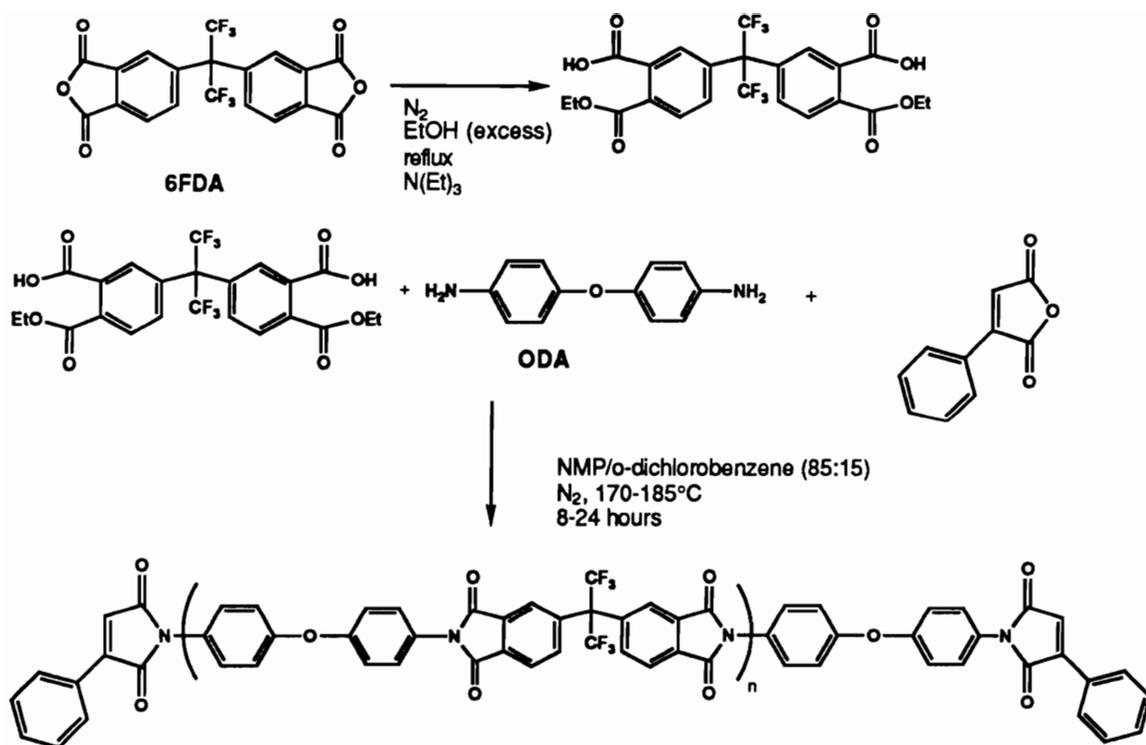
appropriate reaction conditions to prepare controlled molecular weight PMA endcapped imide oligomers.

4.4.4.1 Phenylmaleic Anhydride Endcapped Polyimides Prepared by the Ester-Acid Route

Phenylmaleic anhydride terminated polyimide matrix resins have been synthesized in an analogous manner as described in the earlier section concerning controlled molecular weight polyimides endcapped with 4-PEPA. The stoichiometry was offset in favor of the diamine and PMA was used as a endcapping agent in an attempt to control molecular weight. After formation of the diester derivative of the dianhydride or the dianhydride and PMA, a calculated amount a diamine was added with NMP, after which, an azeotroping agent (usually *o*-DCB) was added and the reaction was continually heated to 170-185°C to affect polymerization and complete imidization. A solids concentration of 25 to 30% (wt/vol) was usually employed for polymerizations since high solution viscosities were not expected. An example of the synthesis of a 6FDA/ODA/PMA polyimide prepared by the ester-acid route is shown in Scheme 4.4.4.1.1.

At the end of the polymerization, the solution was cooled and diluted with additional NMP since high solution viscosities were obtained from high molecular weight build-up. The polyimide was isolated by slowly pouring the reaction mixture into methanol which was rapidly stirred in a blender. The polyimide was collected by suction filtration and dried in a vacuum oven at ~ 180°C for 24 hours.

The phenylmaleic anhydride terminated polyimide matrix resins based on 6FDA and ODA synthesized using the three routes were all targeted to a number average molecular weight of 3,000 g/mole. In all attempts to use the ester-acid route, surprisingly high molecular weight, fibrous, creasable film forming polymer upon workup resulted that



Scheme 4.4.4.1.1 Attempted Synthesis of Phenylmaleic Anhydride Endcapped Polyimides

exhibited intrinsic viscosity values of 0.46 to 0.57 dL/g or higher. Many variations were executed by varying the sequence of monomer and endcapper addition and using poly(amic acid) precursors to imidize at $\sim 180^{\circ}\text{C}$. In all cases, the molecular weight was not controlled to 3,000 g/mole as evidenced by the high intrinsic viscosity values illustrated in Table 4.4.4.1.1. In as little as two hours, the polymerization solution became very viscous and difficult to stir. Also somewhat surprising, the molecular weight distribution of these high molecular weight polyimides was very near 2.0 as shown by the unimodal narrow molecular weight distribution GPC curve. One may expect a broad distribution of molecular weights since molecular weight was not successfully controlled. The T_g values determined by DSC of $> 290^{\circ}\text{C}$ (Table 4.4.4.1.1) also indicated high molecular weight polymer since the T_g of high molecular weight 6FDA/ODA polyimide is $\sim 300^{\circ}\text{C}$. These polymers exhibited 5% weight loss values of 542°C and 570°C , attesting to the thermal stability of the polymers.

A film cast from chloroform of the 6FDA/ODA/PMA polymer exhibited a T_g of 291°C . After thermally curing at 350°C for 1 hour, the T_g increased to $\sim 305^{\circ}\text{C}$ and the 5% weight loss temperature was 570°C indicating that some crosslinking had taken place even in these high molecular weight polyimides.

A polymerization was conducted to synthesize a BPA-DA/*m*-PDA/PMA polyimide controlled to a $\langle M_n \rangle$ of 3,000 g/mole to determine if the lack of molecular weight control was inherent to the 6FDA/ODA/PMA system. As shown in Table 4.4.4.1.1, the intrinsic viscosity was again abnormally high at 0.45 dL/g. In addition, the polyimide could be cast from solution to form a tough, ductile film indicating that high molecular weight resulted.

4.4.4.2 Phenylmaleic Anhydride Endcapped Polyimides Prepared by Chemical Imidization

Table 4.4.4.1.1 Intrinsic Viscosities for Phenylmaleic Anhydride Endcapped Polyimides
Prepared at High Reaction Temperatures

Reaction Conditions	$[\eta]$ (dL/g)*	T _g (°C)	5% Wt. Loss (°C)
Ester-acid of 6FDA & PMA-then diamine	0.57	303	551
amine-term. PI then PMA at 180°C	0.46	291,305†	548,570†
amic acid-6FDA, ODA, PMA all in pot-raise to 180°C	0.54	295	553
amic acid of ODA & PMA-raise to 180°C w/6FDA	0.51	292	542
BPA-DA, <i>m</i> -PDA, PMA at 150°C	0.45		

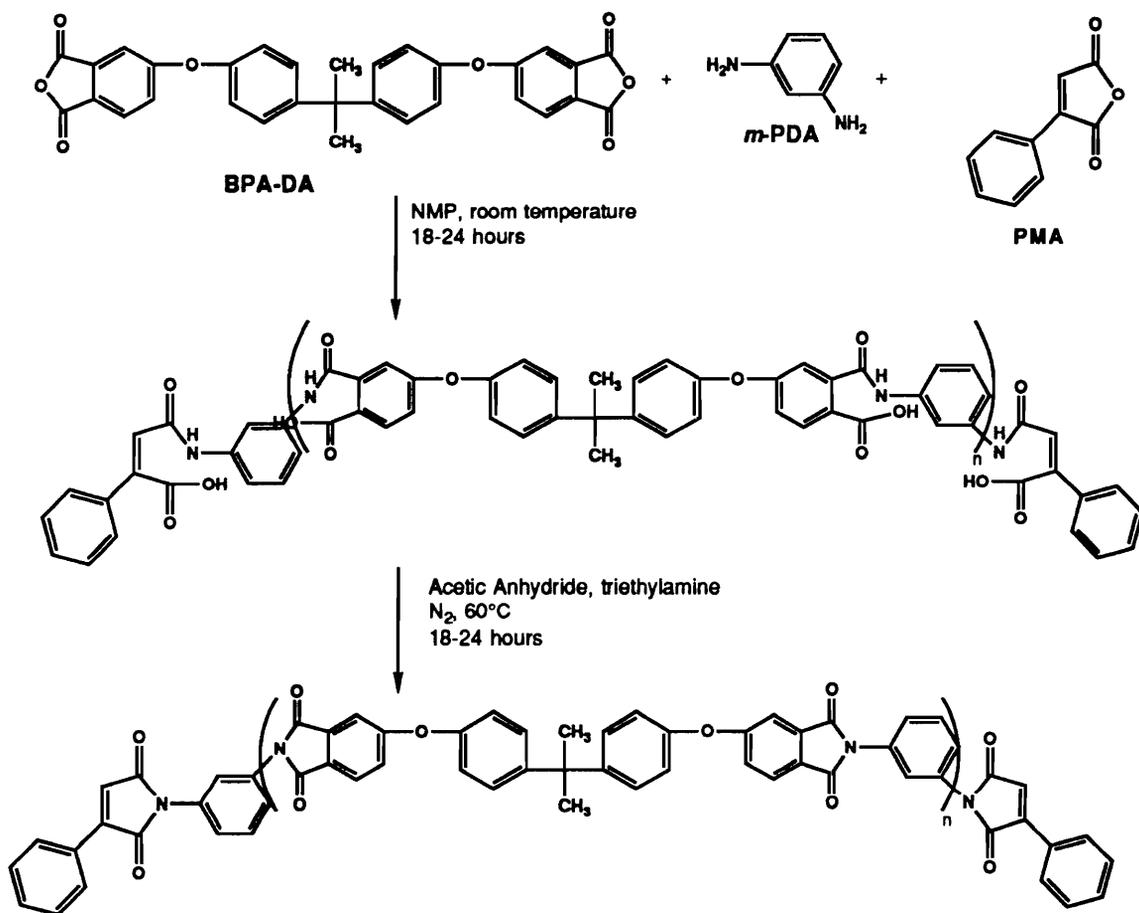
* = Run in NMP at 25°C

† = value obtained after curing at 350°C for 1 hour

The phenylmaleic anhydride terminated polyimide matrix resins synthesized by chemical imidization means were performed by offsetting the stoichiometry in favor of the diamine and PMA was used as an endcapping agent in an attempt to control molecular weight. The dianhydride, PMA and diamine were dissolved in NMP and was allowed to stir at room temperature for 2 to 24 hours to form the poly(amic acid). After formation of the poly(amic acid), acetic anhydride and triethylamine were added to the reaction and the solution was continually heated to 60°C to affect polymerization and complete cyclization. A solids concentration of 25 to 30% (wt/vol) was usually employed for polymerizations since high solution viscosities were not expected. An example of the synthesis of a BPA-DA/*m*-PDA/PMA polyimide prepared by the chemical imidization route is shown in Scheme 4.4.4.2.1.

At the end of the polymerization, the solution was cooled. The polyimide was isolated by slowly pouring the reaction mixture into methanol which was rapidly stirred in a blender. The polyimide was collected by suction filtration and dried in a vacuum oven at ~180°C for 24 hours.

Molecular weight control was achieved utilizing phenylmaleic anhydride as an endcapping agent and chemical imidization techniques. This route afforded an intrinsic viscosity value of 0.18 dL/g for a 6FDA/ODA/PMA(3,000) polyimide that corresponded very well with 3,000 g/mole 6FDA/ODA polyimide systems. A series of polyimides based on BPA-DA/*m*-PDA (Ultem-like) endcapped with PMA was synthesized to controlled molecular weights ranging from 2,000 to 15,000 g/mole using chemical imidization to imidize the poly(amic acid). This series was synthesized so we could have a direct comparison with the imide oligomers obtained by a two-temperature route that will be described in a latter section. Again molecular weight control was achieved as seen by the progressive increase in intrinsic viscosity values in Table 4.4.4.2.1. The intrinsic



Scheme 4.4.4.2.1. Synthesis of Phenylmaleic Anhydride-Terminated Polyimides by Chemical Imidization

viscosity values increased from 0.18 dL/g for the 2,000 g/mole polyimide up to 0.40 dL/g for the 15,000 g/mole polymer.

Glass transition temperatures of the 6FDA/ODA/PMA polyimide increased from 245°C before curing to 290°C after curing at 350°C for 45 minutes which is consistent with the T_g of the high molecular weight linear system. A curing study was performed at various temperatures and times in a convection oven. After curing for 30 minutes at 310°C in a nitrogen atmosphere, the system was completely soluble in chloroform. After 30 minutes at 350°C the system was mostly crosslinked or insoluble, but still had a soluble portion as seen by the coloration of chloroform indicating a sol portion. However when cured at 350°C for 45 minutes, the system was completely insoluble. The 5% weight loss was seen at 526°C before curing, indicating thermal stability, and at 558°C after cure. These results indicate that PMA endcapped imide oligomers thermally crosslink at 350°C or higher to produce an insoluble network. The thermal stability of the 3,000 g/mole oligomer synthesized by chemical imidization was subjected to an isothermal TGA scan at 350°C for 6 hours as illustrated in Figure 4.4.4.2.1. Only 0.36% weight was lost, indicating no volatiles were released during the curing process.

The glass transition temperatures for the BPA-DA/*m*-PDA/PMA polyimides before curing ranged from 192°C for the 2,000 g/mole oligomer to 205°C for the 15,000 g/mole as shown in Table 4.4.4.2.1. T_g values increased upon curing at 380°C for 90 minutes as expected as seen in Table 4.4.4.2.1. Furthermore, peak maximum for cure exotherms occurred at ~ 430°C which is even higher than values observed for 3-PEA and 4-PEPA endcapped imide oligomers. These systems were all thermo-oxidatively stable as shown by the 5% weight loss values by TGA in air ranging from 515°C to 525°C.

Table 4.4.4.2.1 Characterization of BPA-DA/*m*-PDA PMA Endcapped Polyimides
Synthesized by Chemical Imidization

Target $\langle M_n \rangle$ (g/mole)	$[\eta]_{25^\circ\text{C}, \text{NMP}}$	$T_{g(\text{uncured})}(\text{°C})^*$	$T_{g(\text{cured})}(\text{°C})^*$	5% Wt. Loss(°C)†
2,000	0.18	192	223	522
7,000	0.21	205	215	518
10,000	0.35	205	221	525
15,000	0.40	205	220	515

* = T_g 's were run under nitrogen at heating rate of 10°C/min and values were taken from the second heat after quench cooling.

† = TGA's were run in air at a heating rate of 10°C/min

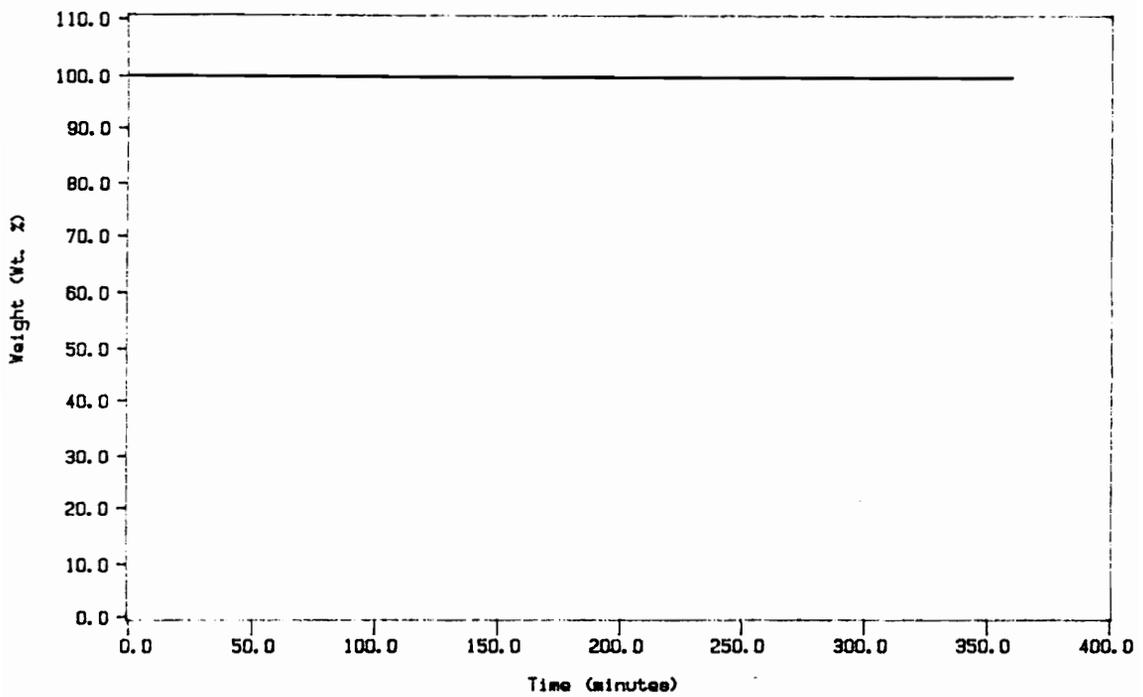


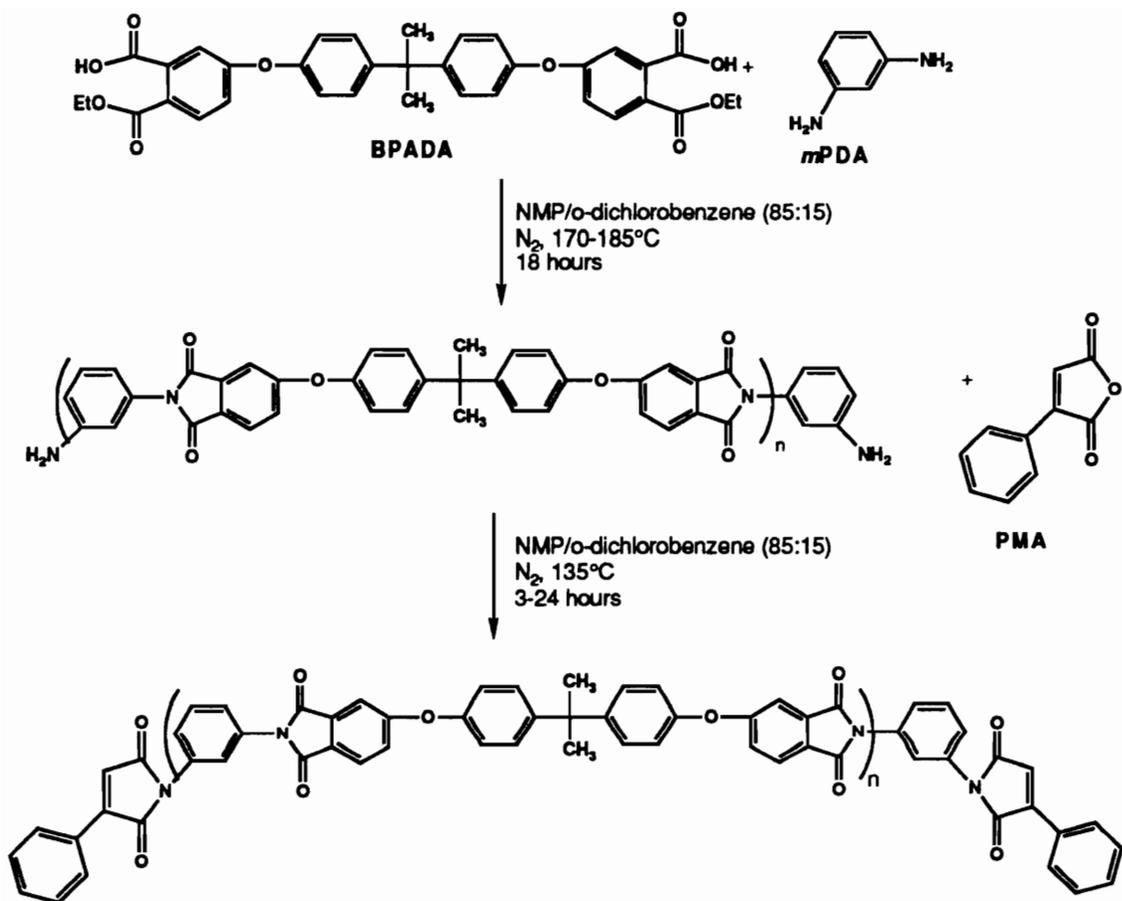
Figure 4.4.4.2.1 Isothermal TGA Thermogram (350°C, Air, 6 Hours) of
6FDA/ODA/PMA(3,000) Polyimide

4.4.4.3 Phenylmaleic Anhydride Endcapped Polyimides Prepared by a Two-Step Route

The third route employed to synthesize PMA terminated polyimides was a two-step route where an amine-terminated polyimide was first formed and then subsequently functionalized with PMA. The phenylmaleic anhydride terminated polyimide matrix resins synthesized by this two-step route were performed by offsetting the stoichiometry in favor of the diamine and PMA was used as an endcapping agent in an attempt to control molecular weight. The ester-acid of the dianhydride and a diamine were dissolved in NMP after which, an azeotroping agent (usually *o*-DCB) was added and the reaction was continually heated to 170-185°C to affect polymerization and complete imidization. A solids concentration of 25 to 30% (wt/vol) was usually employed for polymerizations since high solution viscosities were not expected. The amine-terminated imide oligomer in some cases was then isolated in methanol, dried under vacuum and redissolved in DMAc and toluene which permits imidization to take place at lower temperature (~145°C) than NMP/*o*-DCB and was allowed to react with the calculated amount of PMA. Alternatively, the amine-terminated oligomer was formed in NMP/*o*-DCB at ~180°C and then reaction temperature was lowered to 135°C and the PMA was added and allowed to react for 2 to 24 hours. An example of the synthesis of a BPA-DA/*m*-PDA/PMA polyimide prepared by the two-step (two-temperature) route is illustrated in Scheme 4.4.4.3.1.

At the end of the polymerization, the solution was cooled. The polyimide was isolated by slowly pouring the reaction mixture into methanol which was rapidly stirred in a blender. The polyimide was collected by suction filtration and dried in a vacuum oven at ~180°C for 24 hours.

The intrinsic viscosity values for the 6FDA/ODA(3,000) amine-terminated oligomer and the 6FDA/ODA/PMA(3,000) oligomer are 0.18 dL/g and 0.22 dL/g, respectively, indicating that molecular weight was controlled in both steps when the amine terminated



Scheme 4.4.4.3.1 Synthesis of Phenylmaleic Anhydride Terminated Polyimides by a Two-Temperature Route

oligomer was isolated and endcapped at 145°C using DMAc/toluene. When the reaction temperature was lowered to 135°C and the PMA was added and allowed to react, again the intrinsic viscosity value of 0.18 dL/g confirms that molecular weight was achieved. Reaction times of 2, 12 and 24 hours at 135°C were used to endcap the amine-terminated oligomer with PMA. In all instances, complete endcapping was achieved. Proton NMR confirmed the presence of the protons of the amine endgroups in the first step and the disappearance of amino protons after PMA functionalization as depicted in Figure 4.4.4.3.1.

An additional experiment was run where the reaction solvent system NMP/*o*-DCB was replaced with NMP/CHP to maintain a reaction temperature of ~ 150-155°C. Once again, high molecular weight polyimide was obtained as demonstrated by the relatively high intrinsic viscosity value of 0.47 dL/g. These findings indicate that reaction temperature has a pronounced effect on whether controlled molecular weight polyimides can be synthesized using PMA as the endcapping agent. At reaction temperatures below ~ 135-140°C, molecular weight can be successfully controlled, whereas above ~ 135-140°C, high molecular weight film forming polymer is obtained. Possible explanations for these observations will be discussed in a subsequent section.

A second series of polyimides based on BPA-DA/*m*-PDA (Ultem-like) endcapped with PMA were synthesized to controlled molecular weights ranging from of 2,000 to 15,000 g/mole using the two-temperature route where the amine-terminated polyimide was formed at 180°C in NMP/*o*-DCB and then the reaction temperature was lowered to 135°C at which point the PMA endcapping agent was added to the flask to endcap the polyimide chains. Again molecular weight control was achieved as seen in the progressive increase in intrinsic viscosity values in Table 4.4.4.3.1. The intrinsic viscosity values increased from 0.18 dL/g for the 2,000 g/mole polyimide up to 0.34 dL/g for the 15,000 g/mole polymer.

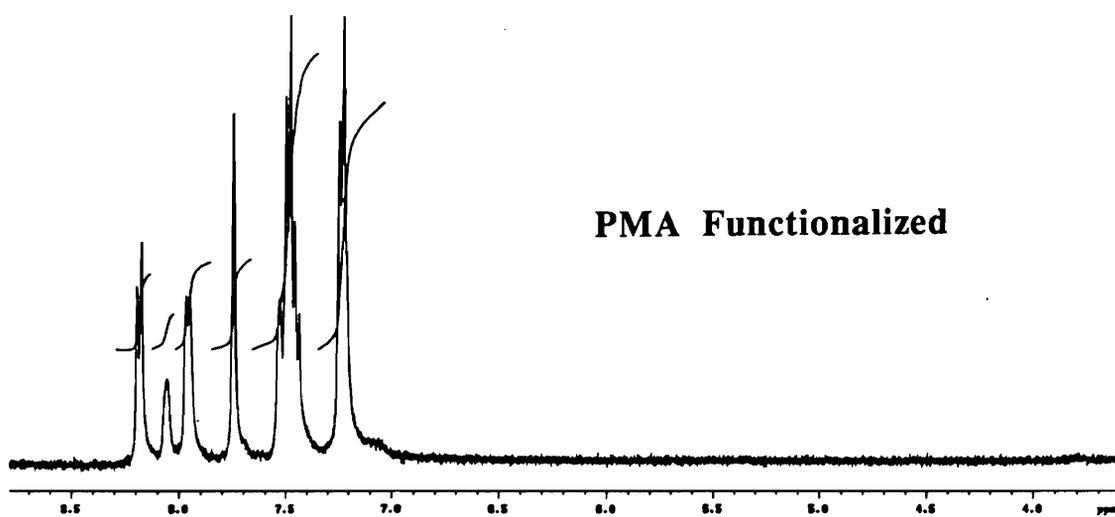
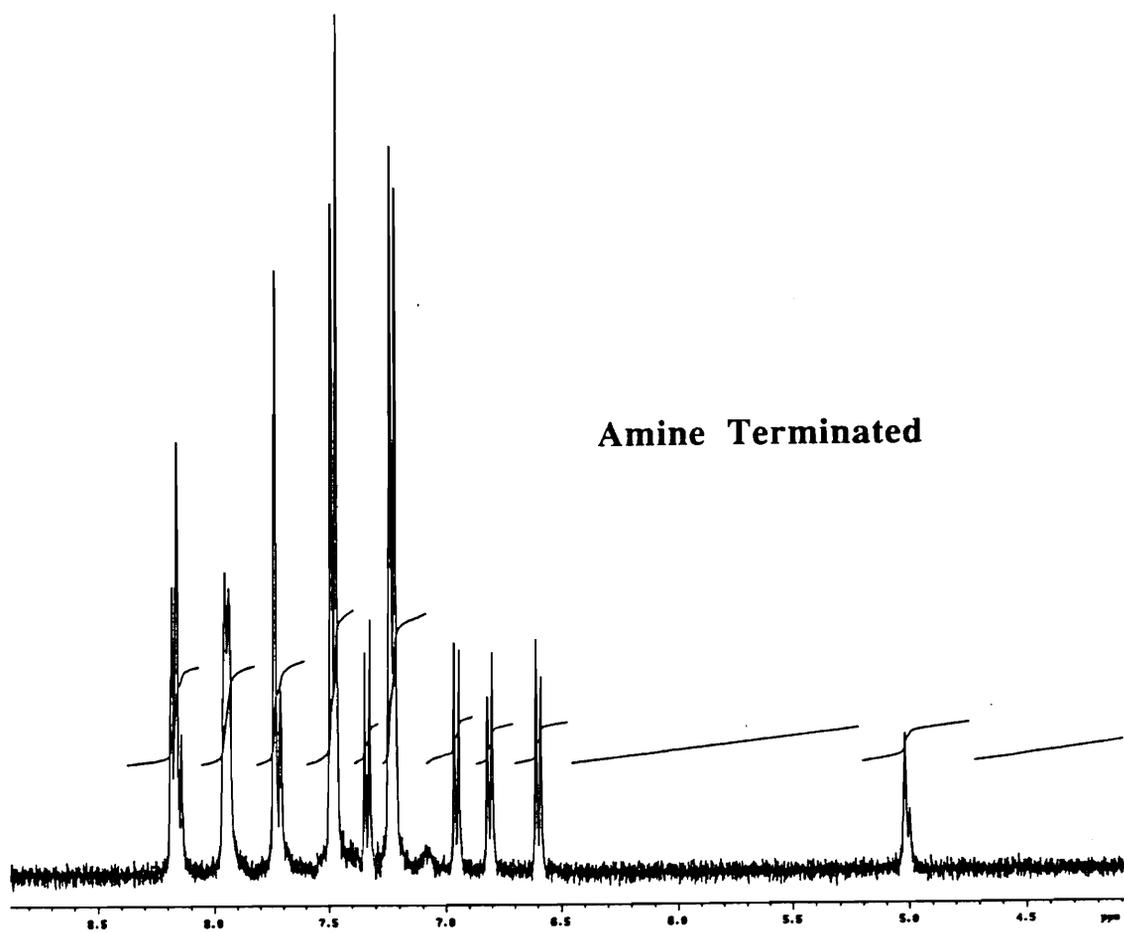


Figure 4.4.4.3.1 ^1H NMR Spectra of an Amine Terminated and PMA Functionalized Imide Oligomer in DMSO-d_6 (400 MHz)

Table 4.4.4.3.1 Characterization of BPA-DA/*m*-PDA PMA Endcapped Polyimides
Synthesized by Two-Temperature Route

Target $\langle M_n \rangle$ (g/mole)	$[\eta]_{25^\circ\text{C}, \text{NMP}}$	$T_{g(\text{uncured})}(\text{°C})^*$	$T_{g(\text{cured})}(\text{°C})^*$	5% Wt. Loss(°C)†
2,000	0.18	200	227	504
7,000	0.24	208	219	522
10,000	0.26	212	219	524
15,000	0.34	213	221	525

* = T_g 's were run under nitrogen at heating rate of 10°C/min and values were taken from the second heat after quench cooling.

† = TGA's were run in air at a heating rate of 10°C/min

Comparison of the intrinsic viscosity values of the polyimides prepared by either chemical imidization or the two-temperature route illustrated virtually no difference in molecular weight control capability by the different methods.

The T_g 's for the polyimides before curing ranged from 200°C for the 2,000 g/mole oligomer to 213°C for the 15,000 g/mole as shown in Table 4.4.4.3.1. After curing the oligomers at 380°C for 90 minutes under nitrogen in a convection oven, the T_g 's raised substantially to as high as 227°C for the 2,000 g/mole oligomer.

These systems were all thermo-oxidatively stable as shown by the 5% weight loss values by TGA in air ranging from 504°C to 525°C. In order to evaluate these polyimide systems for long-term isothermal thermo-oxidative stability, cured films were subjected to an extended aggressive oxidative environment in a forced air oven under an air atmosphere for 1000 hours at 232°C (450°F). Weight retention values 98.4 - 99.5 % were observed for the BPA-DA/*m*-PDA/PMA polyimides synthesized by the two-temperature route and the results are shown graphically in Figure 4.4.4.3.2. The polyimides prepared by the chemical imidization method exhibited weight retention values of 98.7-99.2 % as is illustrated in Figure 4.4.4.3.3. Both series were compared to commercially produced Ultem 1000® which is a nonreactive thermoplastic. The commercial Ultem performed the best showing virtually no weight loss over 1000 hours at 232°C. For the PMA functionalized polyimides, as the molecular weight between crosslinks (M_c) increased, the thermo-oxidative stability declined. This phenomenon is probably due to lower crosslink density in the higher molecular weight samples, which may allow more aggressive oxygen penetration into the sample and more facile degradation. Over the 1000 hour aging period, ultimate weight retention values were very similar between the BPA-DA/*m*-PDA/PMA polyimides prepared by the two different methods.

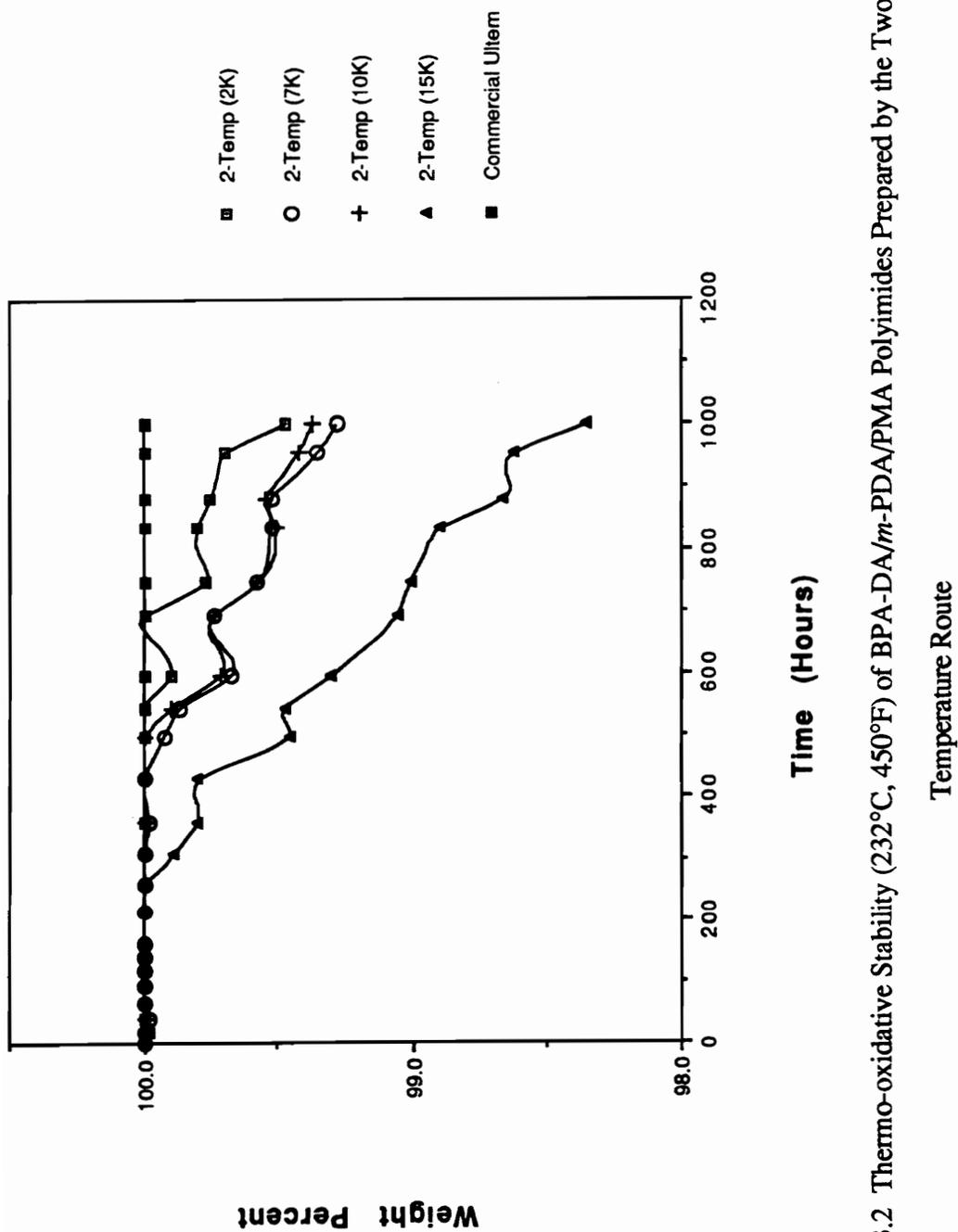


Figure 4.4.4.3.2 Thermo-oxidative Stability (232°C, 450°F) of BPA-DA/*m*-PDA/PMA Polyimides Prepared by the Two-

Temperature Route

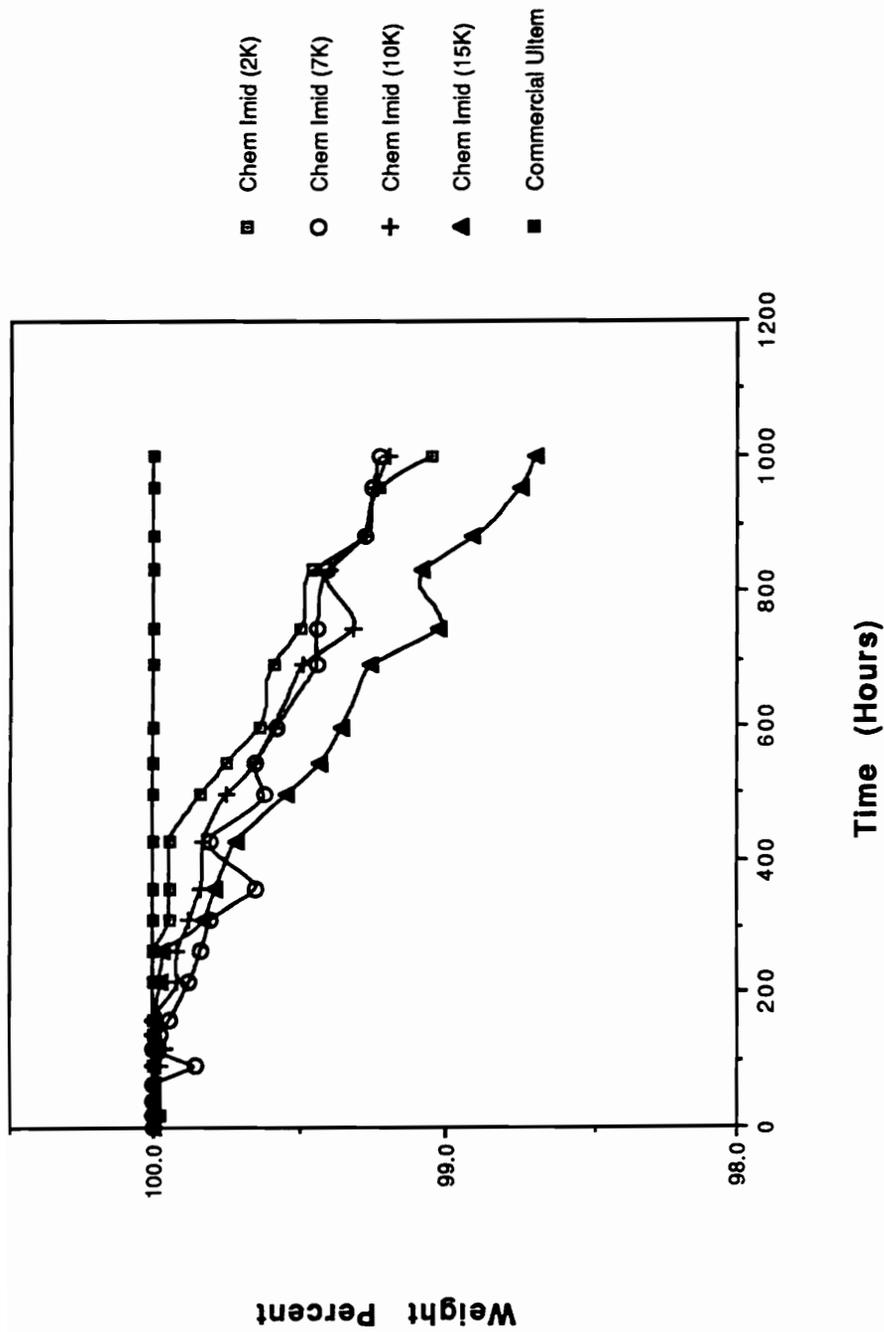


Figure 4.4.4.3.3 Thermo-oxidative Stability (232°C, 450°F) of BPA-DA/*m*-PDA/PMA Polyimides Prepared by the Chemical Imidization Route

In addition to long-term isothermal aging of the PMA endcapped polymers, a comparison was made between polyimides of the same molecular weight, backbone structure and curing conditions, only differing in the reactive endcapping agent employed. Polyimide oligomers each 3,000 g/mole in number average molecular weight with a 6FDA/ODA backbone with 3-PEA, 4-PEPA and PMA endgroups were compared by dynamic thermogravimetric analysis. Figure 4.4.4.3.4 illustrates that the 3-PEA endcapped polyimide was slightly more thermally stable than the polyimide endcapped with 4-PEPA. Furthermore, the two phenylethynyl functionalized resins were noticeably more stable above ~ 550°C than the PMA endcapped polyimide; however, all three were virtually identical in thermo-oxidative stability below ~ 550°C.

Refluxing chloroform Soxhlet extractions were also performed on the cured PMA functionalized polymers to evaluate their solvent resistance after network formation. Thermally cured samples displayed moderate solvent resistance as shown in Table 4.4.4.3.2, moderately high (> 63 %) gel fractions were obtained upon thermally curing the phenylmaleic anhydride-terminated poly(ether imide)s. These values were significantly lower than those obtained from poly(ether imides) endcapped with 4-PEPA. The lower gel fractions may possibly be due to incomplete endcapping of the oligomers; however, ¹HNMR indicate that complete endcapping is achieved. More likely, the phenyl group on PMA may cause significant steric barrier not only increasing cure temperatures but also decreasing crosslinking efficiency.

The melt flow properties of these PMA endcapped systems were also examined by parallel plate rheology studies. The 6FDA/ODA/PMA(3,000) imide oligomer held isothermally at 350°C under a nitrogen atmosphere exhibited a melt viscosity below 5.0 PaS for approximately 30 minutes at which point the viscosity began to rapidly increase indicating curing or network formation as shown in Figure 4.4.4.3.5. A dynamic scan

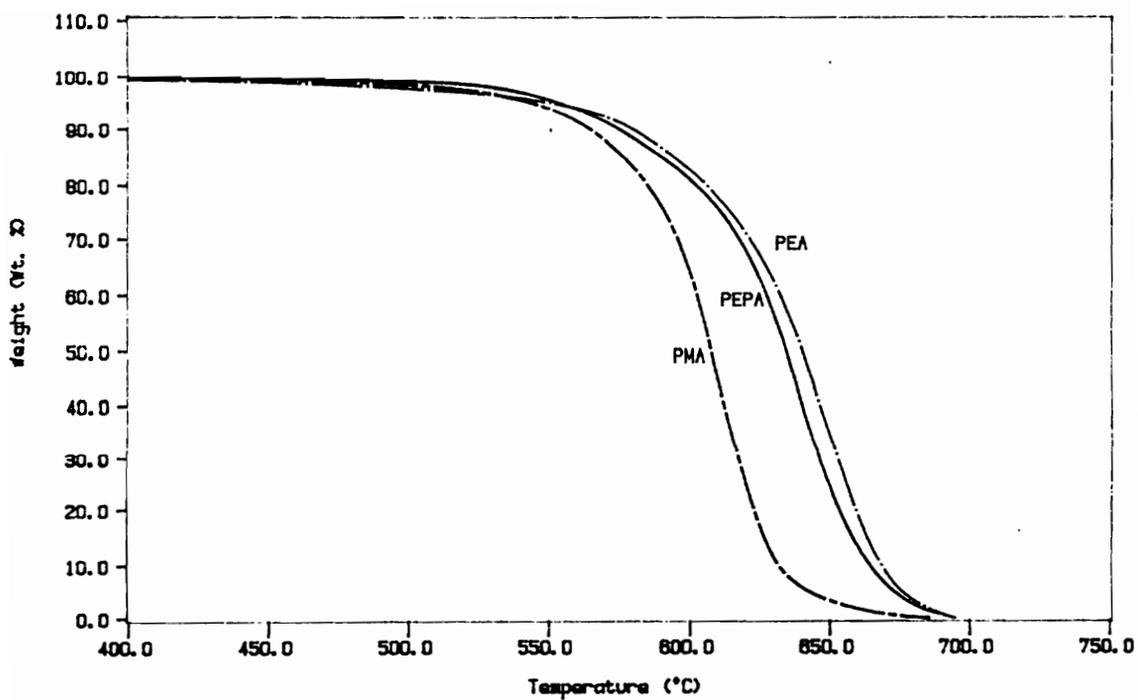


Figure 4.4.4.3.4 Thermo-oxidative Comparison (10°C/min) of Different High Temperature Reactive Endgroups

Table 4.4.4.3.3 Gel Content of Cured BPA-DA/*m*-PDA/PMA Polyimides

System	Target $\langle M_n \rangle$ (g/mole)	% Gel Content
BPA-DA/ <i>m</i> -PDA	2,000	68
	7,000	65
	10,000	63
	15,000	---

Samples were refluxed in chloroform for 5 days and then dried under vacuum for 5 days at ~100°C.

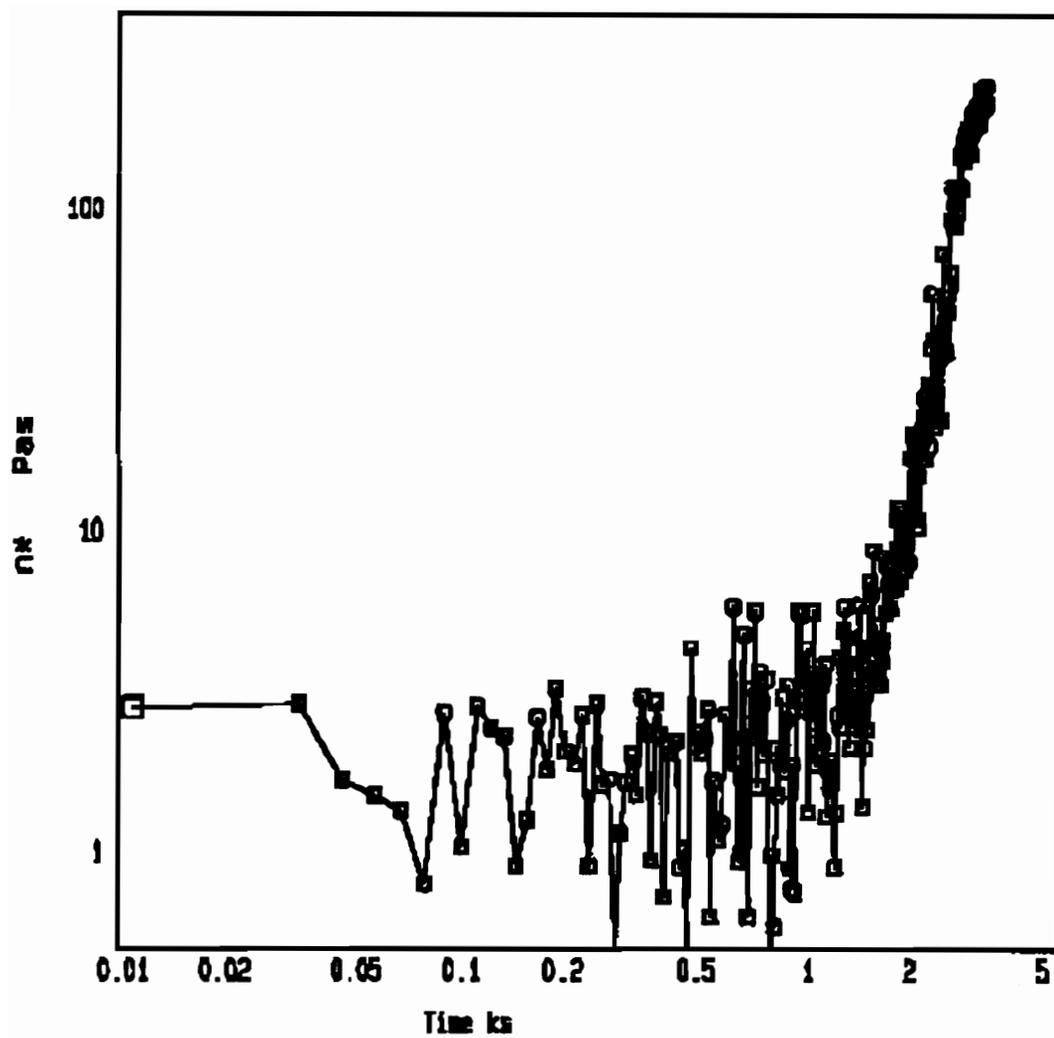


Figure 4.4.4.3.5 Isothermal Melt Viscosity of 3,000 g/mole 6FDA/ODA/PMA(3,000) Polyimide Held at 350°C Under Nitrogen

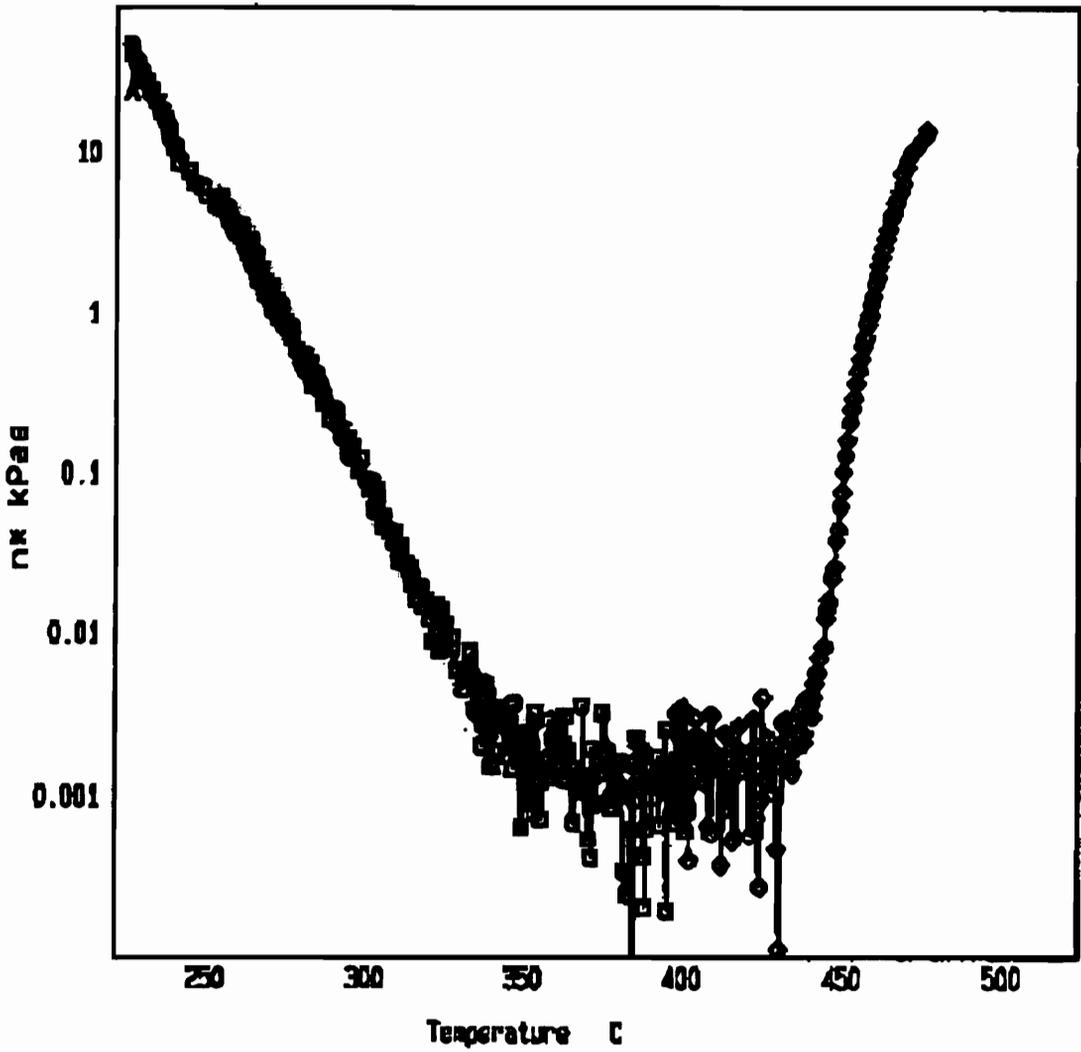


Figure 4.4.4.3.6 Influence of Temperature on Melt Viscosity of 6FDA/ODA/PMA(3,000)

Polyimide

from 225°C to 470°C at 3°C/minute and 0.1 Hz also showed that after the T_g , the viscosity dropped to below 10 PaS and at approximately 440°C, the viscosity began to increase indicating the onset of curing as illustrated in Figure 4.4.4.3.6.

More detailed studies were performed using the BPA-DA/*m*-PDA/PMA(2,000) imide oligomer synthesized by the two-temperature method. Isothermal scans were conducted at 350°C and 380°C under both air and nitrogen atmospheres. At 380°C under a nitrogen purge, a melt viscosity below 100 PaS was observed for ~ 25 minutes before crosslinking began as observed in Figure 4.4.4.3.7. However, at 380°C under an air purge, crosslinking started almost immediately as illustrated in the sharp rise in melt viscosity from the onset of the experiment (Figure 4.4.4.3.8). Moreover, a sample held at 350°C under a nitrogen atmosphere displayed a melt viscosity of ~ 200 PaS for ~ 42 minutes before a rise in melt viscosity was observed. Lowering the scan temperature 30°C resulted in an increase of melt stability without crosslinking of ~ 17 minutes. Nevertheless, when the sample was exposed to an air atmosphere, again a sharp increase in melt viscosity was observed immediately upon starting the scan. The results obtained at 350°C are overlaid in Figure 4.4.4.3.9. Finally, a dynamic scan was performed in air from ~ 190°C to 450°C. Again, a significant window (~ 200°C) was observed between T_g and T_{cure} . These measurements indicate that in a inert atmosphere such as nitrogen, a wide processing window of ~ 30 to 40 minutes can be achieved and differences in air and nitrogen melt viscosity behavior may indicate that oxygen plays a significant role in the curing mechanism of the PMA endcapped polyimides.

Upon curing of these BPA-DA/*m*-PDA/PMA imide oligomers, films displaying good mechanical integrity were formed, even for the 2,000 g/mole system. Adhesive properties the two series were evaluated using Ti/Ti lap shear specimens conforming to ASTM-D1002 methods. Lap shear specimens were prepared by coating 112-E glass

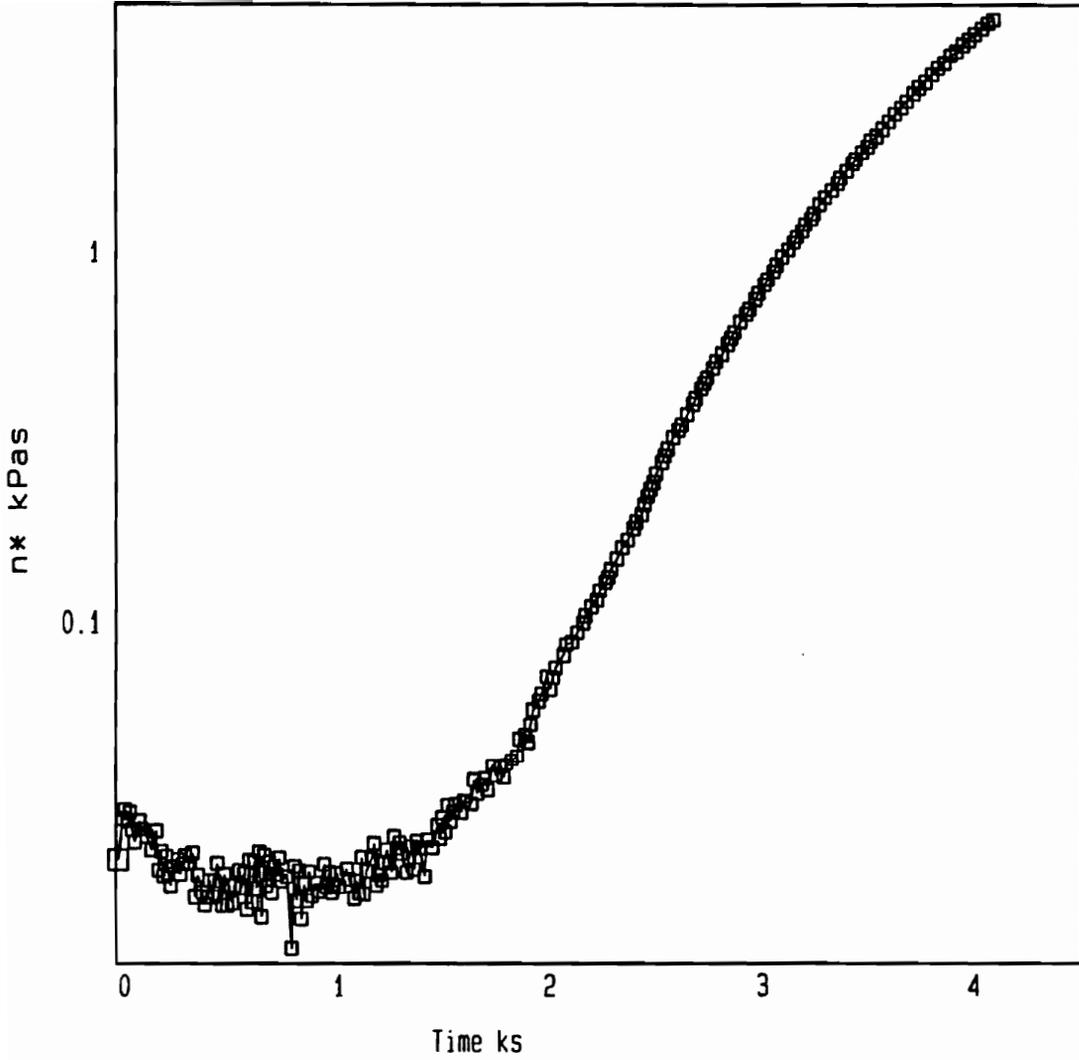


Figure 4.4.4.3.7 Isothermal Melt Viscosity of BPA-DA/*m*-PDA/PMA(2,000) Imide Oligomer at 380°C in Nitrogen

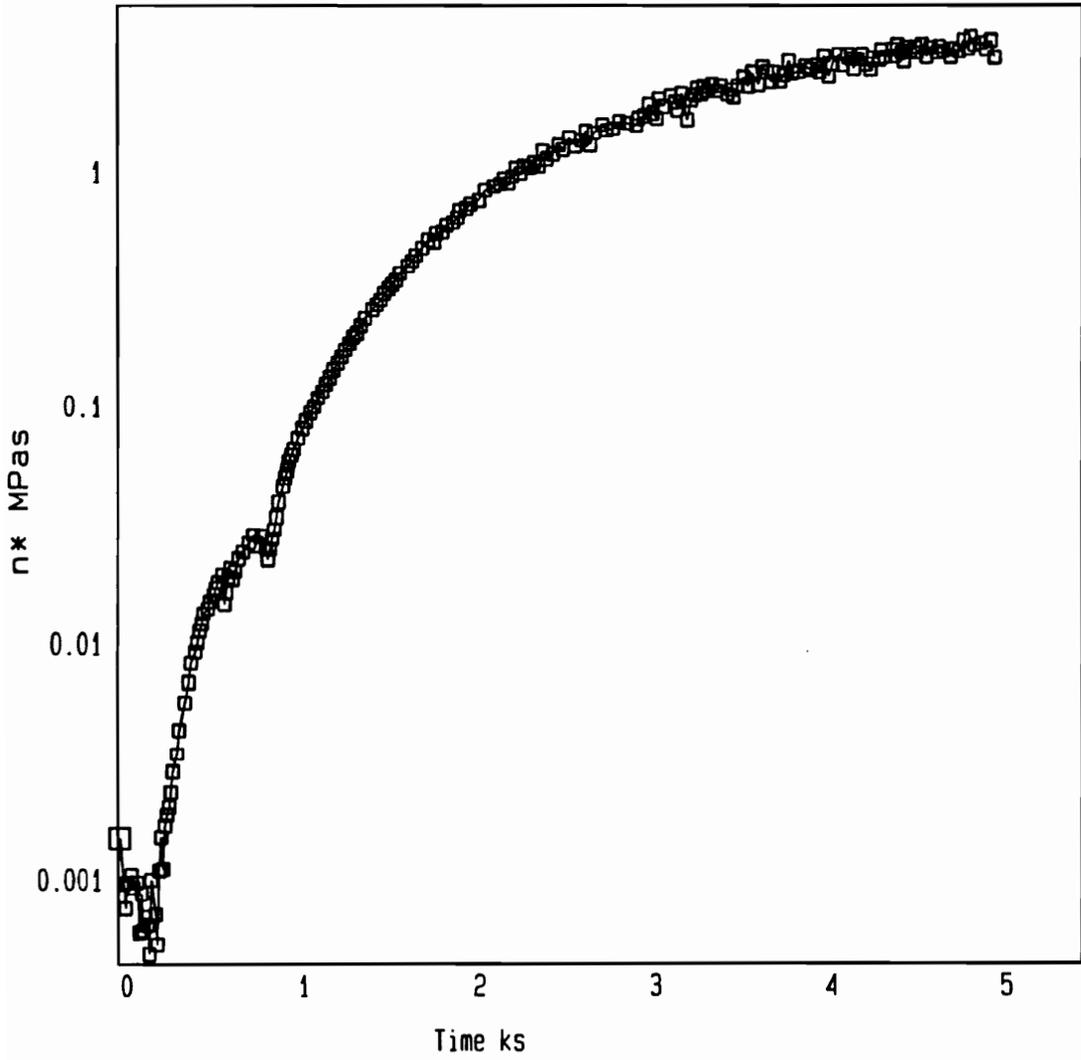


Figure 4.4.4.3.8 Isothermal Melt Viscosity of BPA-DA/*m*-PDA/PMA(2,000) Imide Oligomer at 380°C in Air

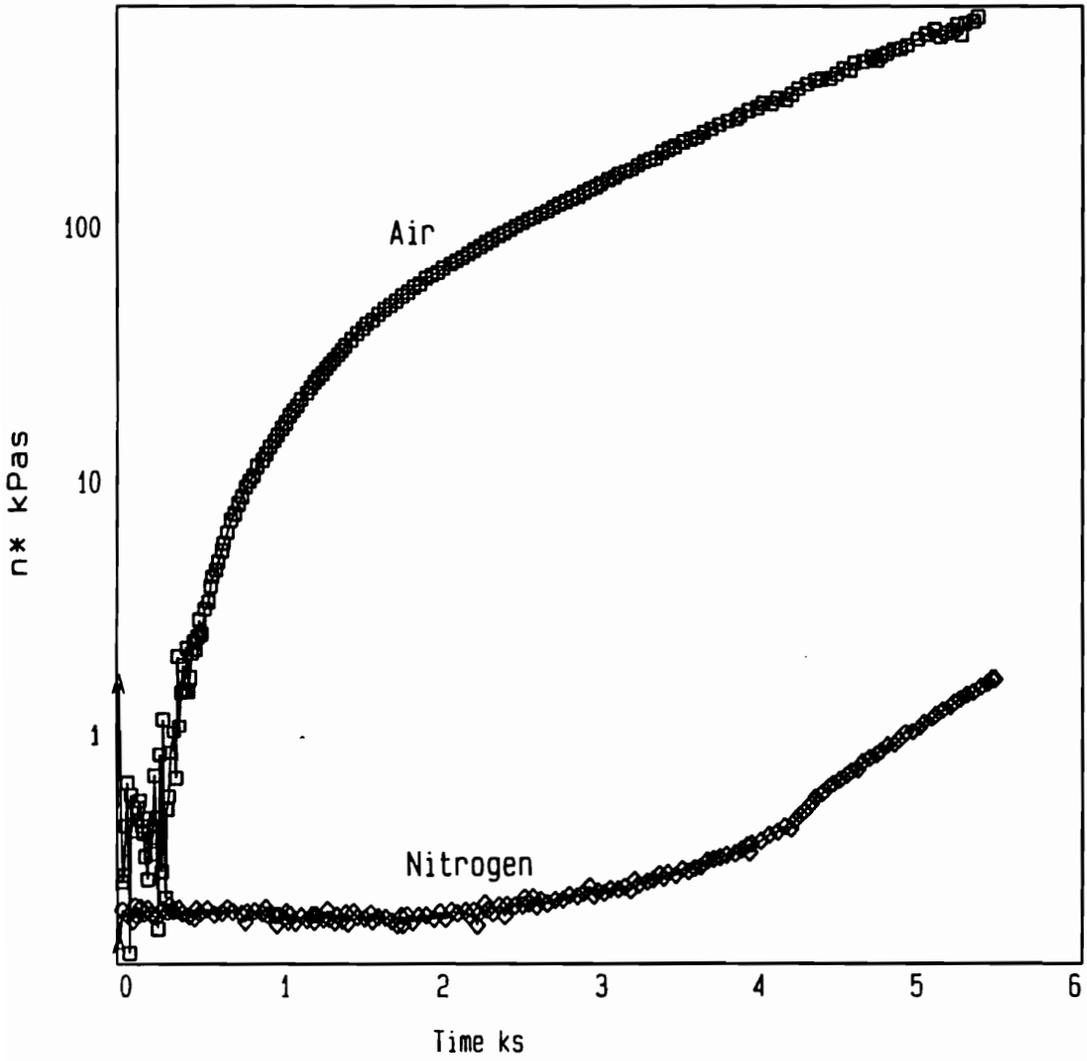


Figure 4.4.4.3.9 Isothermal Melt Viscosity of BPA-DA/*m*-PDA/PMA(2,000) Imide Oligomer at 350°C in Nitrogen and Air

scrim cloth with the resin dissolved in chloroform. The glass cloth was coated several times with the 15 wt. % polymer solution to provide an adhesive tape with a 10 to 12 mil thickness. The Ti coupons were bonded in a Tetrahedron press with pressures of 75 psi and a temperature ramp of 10°C/min from 25°C to 380°C where they were held isothermally for 90 minutes and then cooled to 200°C at 10°C/min. As seen in Table 4.4.4.3.4 commercial Ultem 1000® exhibited an average value of 4420 ± 300 psi. The PMA endcapped samples exhibited values ranging from 3330 to 5070 psi. All of the samples failed cohesively, except the 15,000 g/mole sample which failed at the Ti/scrim cloth interface (adhesive failure). The molecular weight range for optimal adhesive properties appears to be 7,000 to 10,000 g/mole according the results found in Table 4.4.4.3.4.

Note: 6FDA/ODA 3,000 g/mole oligomers endcapped with diphenylmaleic anhydride (DPMA) were successfully synthesized at ~ 180°C using the ester-acid route. However, attempts to thermally cure the DPMA endcapped oligomers at temperatures up to 400°C, always resulted in soluble uncrosslinked polymers. These results, successful high temperature synthesis and the failure to thermally cure, indicate that the protonated olefinic carbon in PMA may play a major role in unsuccessful molecular weight control.

Table 4.4.4.3.4 Ti/Ti Lap Shear Adhesive Data for BPA-DA/*m*-PDA/PMA Polyimides

Polyimide	$\langle M_n \rangle$ (g/mole)	Ti/Ti Lap Shear (psi)
Commercial Ultem	20,000	4420 ± 300
PMA Capped Ultem-Like	2,000	4420± 320
	7,000	5070± 580
	10,000	4750± 590
	15,000	3330± 180

4.4.5 Model Studies of Phenylethynyl and Phenylmaleic Imides

4.4.5.1 Phenylethynyl Imides

Model phenylethynyl imide compounds were synthesized and used to follow and attempt to elucidate the nature of the products formed from the phenylethynyl curing by using high temperature Magic-Angle ^{13}C Nuclear Magnetic Resonance (MAS NMR), FTIR, solution ^1H NMR and ^{13}C NMR and mass spectrometry.

The first model phenylethynyl imide compound studied was synthesized from 6FDA and 3-PEA. This compound was simply prepared by reacting 3-PEA in a 2:1 ratio with 6FDA in DMAc/chlorobenzene (75:25) at 135°C for 9 hours. The product was isolated in water and dried under vacuum at $\sim 170^\circ\text{C}$ for ~ 24 hours. The overall yield of the model compound was $> 90\%$ and exhibited a melting point of $202\text{-}203^\circ\text{C}$. The 6FDA/PEA compound (Figure 4.4.5.1.1) was chosen for high temperature solid state ^{13}C NMR experiments since it exhibited sufficient thermal stability and would not sublime from the NMR rotor used to hold the sample.

A high resolution MAS NMR spectra of the phenylethynyl terminated system was obtained when scanned at 220°C shown in Figure 4.4.5.1.2. The acetylenic carbons can easily be seen at 89.6 and 91.7 ppm. In addition, the curing reaction was followed from melting to beginning of the cure exotherm by slowly increasing the probe temperature as seen in Figure 4.4.5.1.3. From 220°C to 280°C , a scan was taken every 7 minutes, and from 280°C to 330°C a scan was taken every 15 minutes. The spectra obtained at 220°C is considered time (t) = zero. As illustrated in Figure 4.4.5.1.3, the acetylenic carbons are unreacted up to a probe temperature of 330°C . However, after holding the probe at 330°C for 30 minutes, one can detect the disappearance of the carbon-carbon triple bond. As curing proceeded, the formation of broader lines indicated more rigidity in the cured structure. As a result, the assignment of new peaks was not feasible. The nature of the

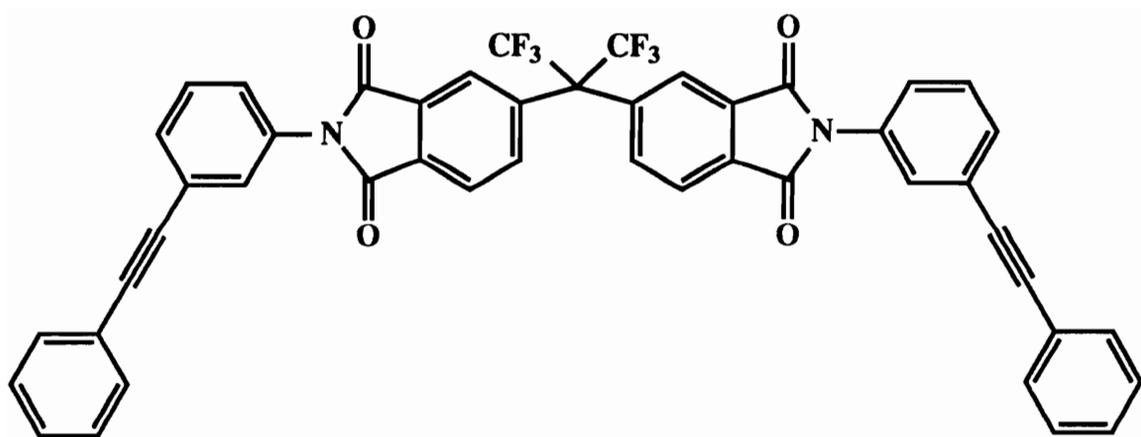


Figure 4.4.5.1.1 6FDA/PEA Model Compound

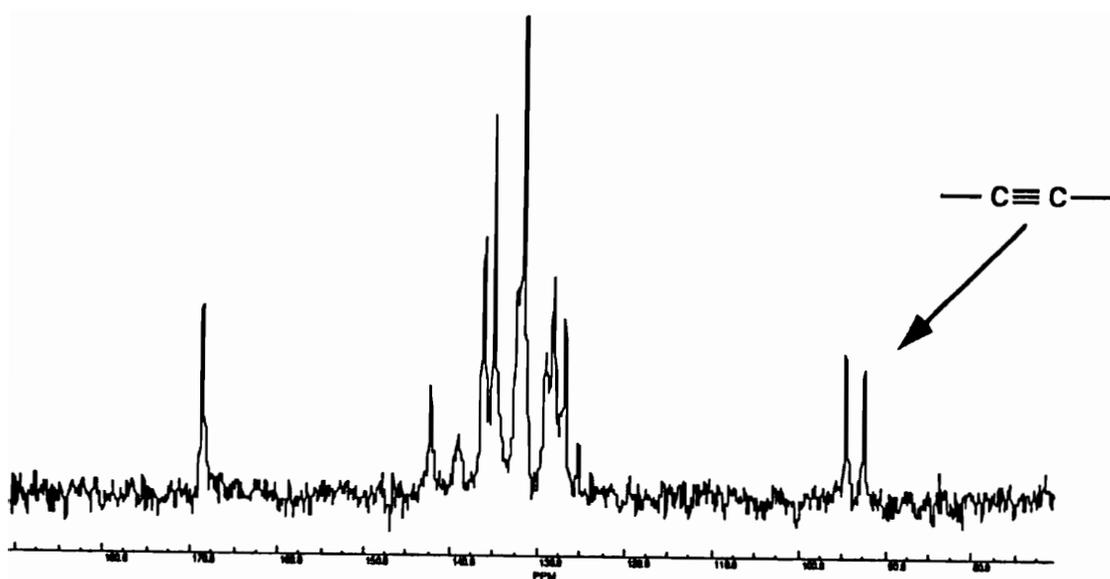


Figure 4.4.5.1.2 High Temperature MAS NMR spectra of the 6FDA/PEA Model Compound at 220°C

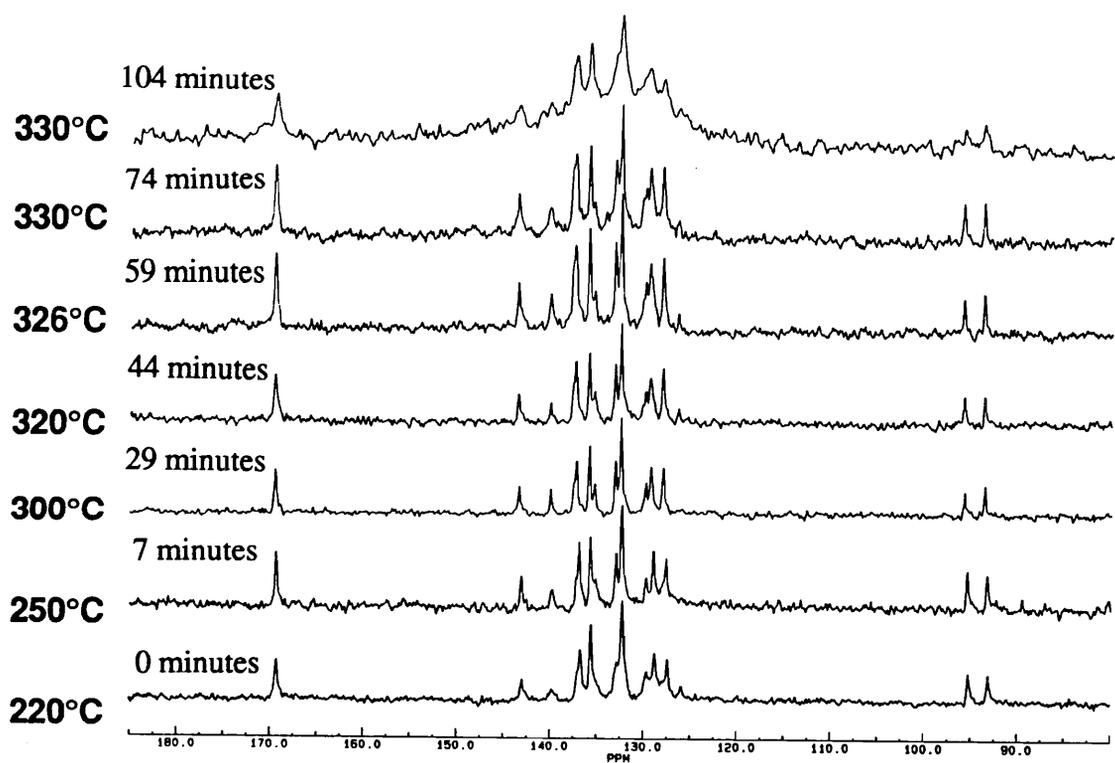
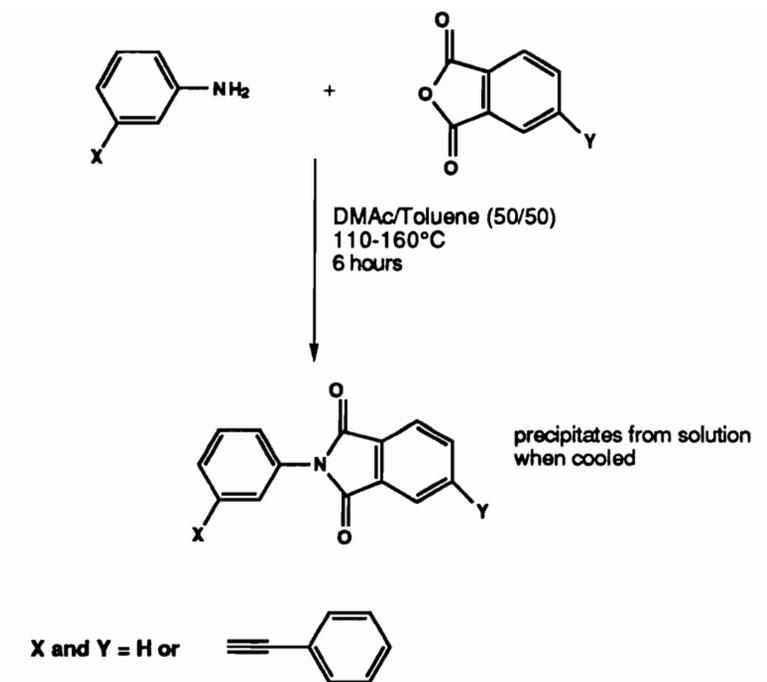


Figure 4.4.5.1.3 Phenylethynyl Cure Studies Using High Temperature MAS NMR

products being formed during the curing process is difficult to determine by the solid state Magic-Angle ^{13}C NMR alone, and as a result, additional work using mass spectra analysis and solution NMR was performed to further quantify the curing process.

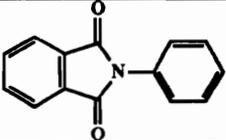
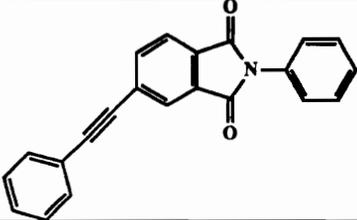
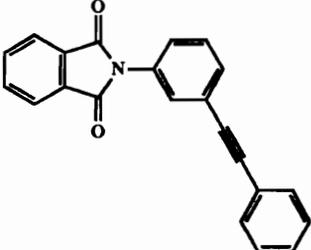
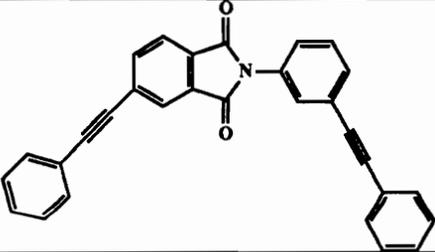
Model compounds based on PA/An, PA/PEA, 4-PEPA/An, and 4-PEPA/PEA were synthesized in yields ranging from 54 to 87% by the reaction of the monofunctional anhydride with the monofunctional amine in a 50:50 mixture of DMAc and toluene at temperatures ranging from 110 - 160°C. The products crystallized upon cooling of the reaction mixture and were washed with water and dried under vacuum. Scheme 4.4.5.1.1 illustrates the general synthetic scheme for phenylethynyl model imides. These model imide compounds were all crystalline in nature and exhibited melting points ranging from 169 to 211°C as shown in Table 4.4.5.1.1. The melting and exothermic transitions via DSC are shown in Figure 4.4.5.1.4 for the PEPA/PEA model imide. The DSC trace clearly shows that the model system does indeed melt and displays a wide window before the strong cure exotherm is observed. Thermal stability of these model compounds was also evaluated by TGA and values for 5% weight loss are listed in Table 4.4.5.1.1. The 5% weight loss values include vaporization as well as degradation. Spectroscopic studies involving the model phenylethynyl compounds were conducted only on the PA/PEA and PEPA/An systems since these contained only one phenylethynyl moiety which resulted in soluble products after curing. Whereas, curing of PEPA/PEA with two phenylethynyl groups resulted in an insoluble system.

The model phenylethynyl compounds were cured by placing ~ 0.40 grams of the model compound (PEPA/An or PA/PEA) in a 6.9 mm diameter 6 cm long capillary tube which was then sealed. The sealed capillary tubes were placed in a 350°C salt bath for times ranging from 5-60 minutes. The resulting cured products were analyzed by FTIR, mass spectroscopy, proton and carbon solution NMR. NMR samples were dissolved in 3.0 mL of either deuterated DMSO or deuterated CHCl_3 .



Scheme 4.4.5.1.1 Synthesis of Phenylethynyl Model Imides

Table 4.4.5.1.1 Thermal Characterization of Model Phenylethynyl Imides

<u>Model Compound</u>	<u>5% Wt. Loss (°C)*</u>	<u>Melting Point (°C)**</u>
	289	210-211
	296	204-205
	297	169-170
	380-Uncured 584-Cured	183-184 DSC = 185

* = Run in air at 10°C/min. Includes vaporization as well as degradation.

** = Capillary flow, unless otherwise noted.

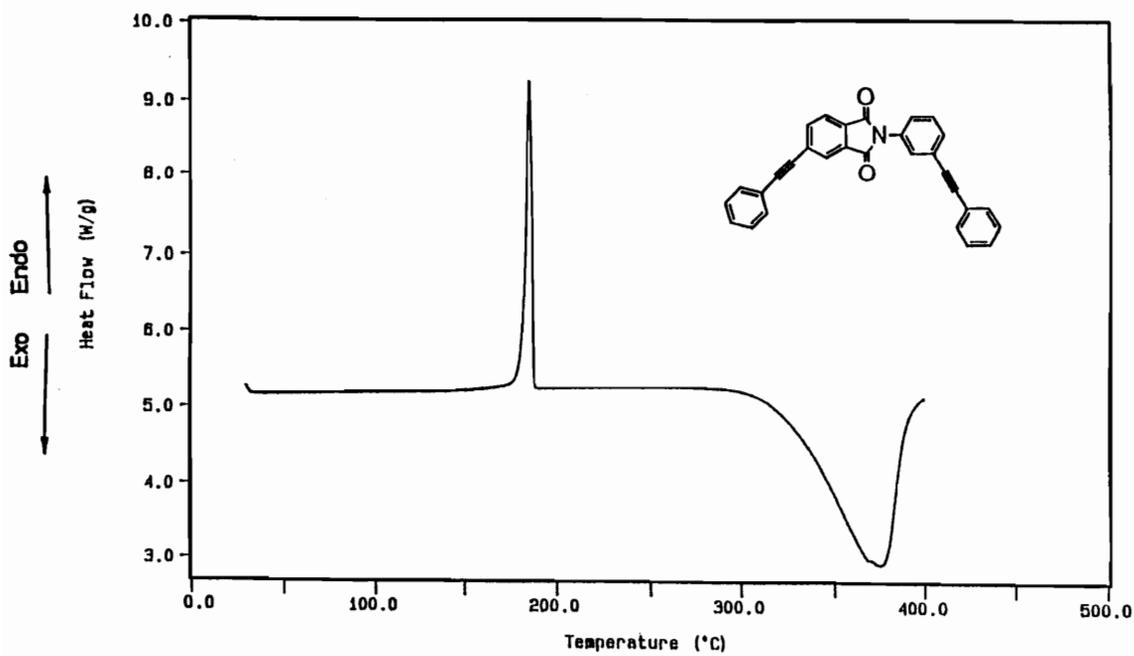


Figure 4.4.5.1.4 DSC (10°C/min) of PEPA/PEA Model Compound

FTIR was used to monitor the disappearance of the acetylenic carbon-carbon triple bonds as a function of curing time. The model compound cured at 350°C for 1 hour was assumed to be fully cured so a percentage of ethynyl groups could be calculated for each curing time. The peak height of the ethynyl stretch occurring at 2215 cm⁻¹ was normalized to a internal standard peak that should not change during the curing process. The standard peak chosen was the asymmetric C=O stretch occurring at 1730 cm⁻¹ denoted by H(C=O). The percent phenylethynyl groups remaining were found by dividing the peak heights of the normalized phenylethynyl stretch at time, t, denoted by H(PE_t) by the normalized phenylethynyl stretch at time = 0 minutes (no curing), denoted by H(PE₀). The equation for the percent phenylethynyl groups remaining is given by Equation 4-1

$$(4-1) \text{ \% Phenylethynyl Groups} = \frac{H(PE_t)/H(C=O_t)}{H(PE_0)/H(C=O_0)} \times 100$$

Figure 4.4.5.1.5 illustrates the FTIR spectra of the PEPA/An model compound focusing on the acetylenic stretch at 2215 cm⁻¹ as a function of cure time. The stretch is very intense before curing and gradually decreases in intensity with longer cure times. The corresponding plot for the PA/PEA model system showed a similar trend; however, the acetylenic stretch became harder to distinguish after 15 minutes of curing time. The extent of cure for the two systems is plotted in Figure 4.4.5.1.6. In addition, the PEPA/An model compound exhibited second-order reaction kinetics with a rate constant of 3.5 x 10⁻¹ s⁻¹ and a half-life (t_{1/2}) of ~ 7 minutes as shown in Figure 4.4.5.1.7. For the PA/PEA model compound, a second-order plot of the data is shown in Figure 4.4.5.1.8 with a rate constant of 7.5 x 10⁻² s⁻¹ and t_{1/2} ~ 13 minutes. From these results, the PEPA/An model compound is observed to cure approximately twice as fast as

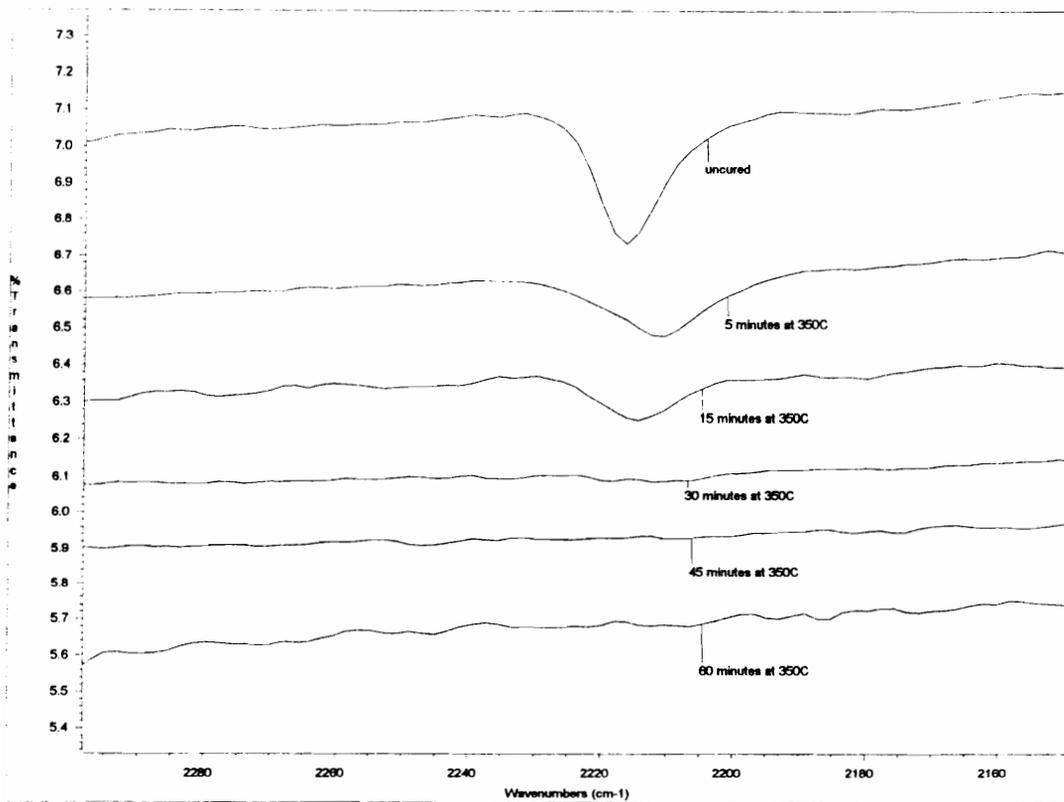


Figure 4.4.5.1.5 Following Phenylethynyl Cure in PEPA/An Model Compound with FTIR

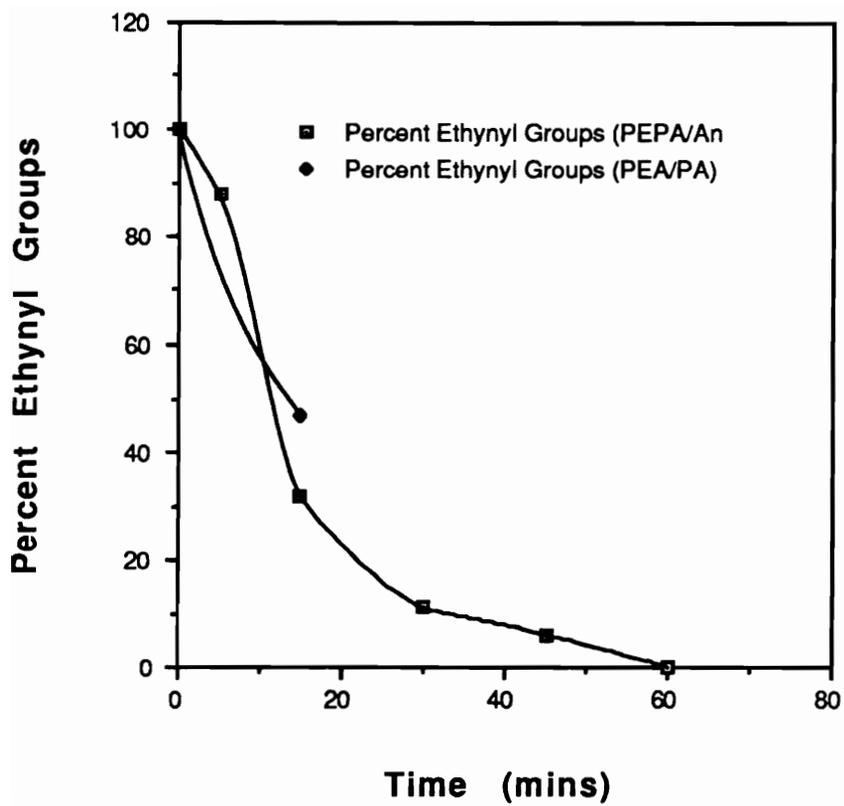


Figure 4.4.5.1.6 Extent of Phenylethynyl Cure as Determined by FTIR

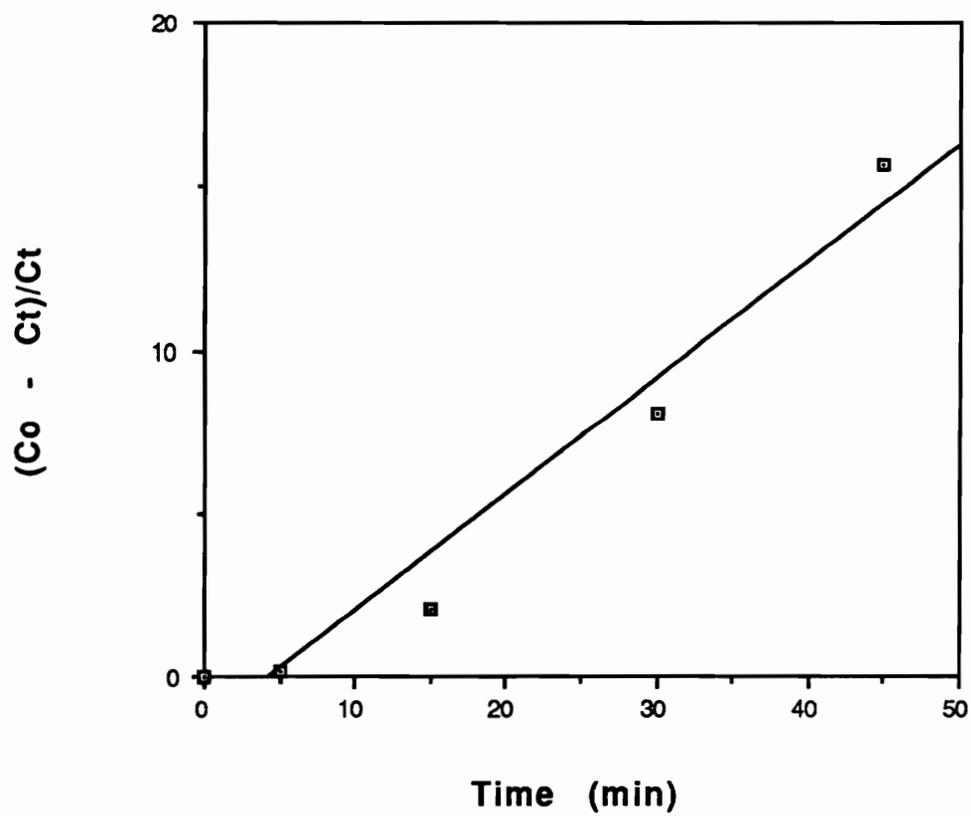


Figure 4.4.5.1.7 Second-Order Reaction Plot for PEPA/An Model Compound

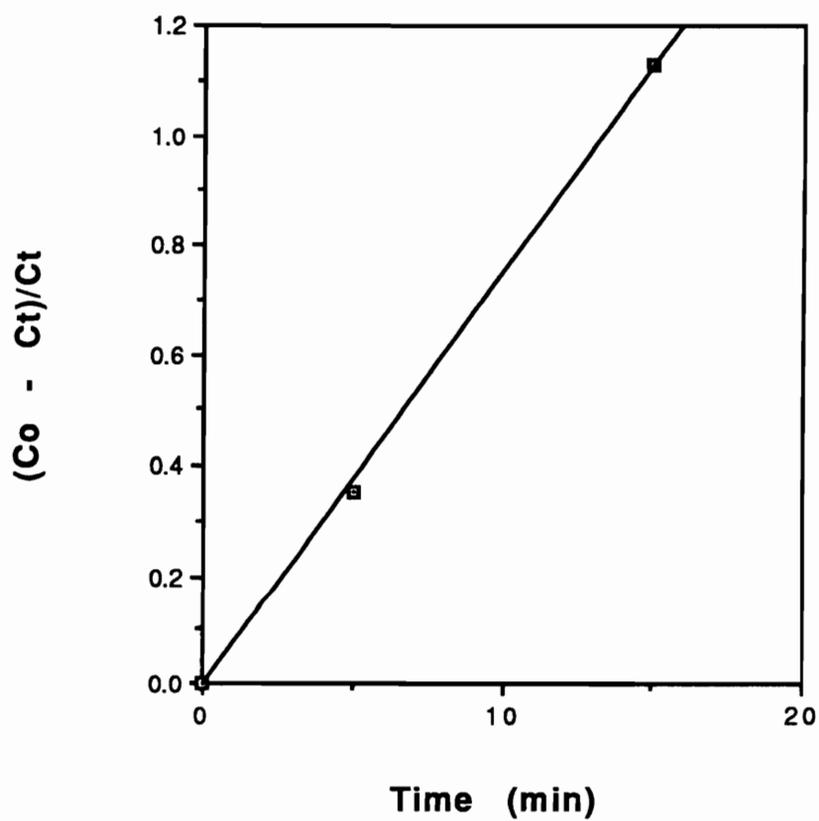


Figure 4.4.5.1.8 Second-Order Reaction Plot for PA/PEA Model Compound

the PA/PEA model compound. This data reaffirms the faster curing experienced in the BPDA/3FDAM/PEPA polyimide as compared to the BPDA/3FDAM/PEA polyimide.

Fast Atom Bombardment (F.A.B.) mass spectrometry was utilized to examine the reaction products formed during the curing of the phenylethynylphthalimides at 350°C. The expected or primary reaction products attributed to the PEPA/An model ($M_w = 323$) compound cured at 350°C for 45 minutes were obtained, i.e. dimers, trimers, tetramers and even pentamers as shown in Figures 4.4.5.1.9 - 4.4.5.1.10. These fragments supports the hypothesis that linear chain extension is a major product of cured phenylethynyl imide oligomers. However, several additional products appeared which were attributed to fragmentation products arising from primary products or intermediates rather than direct addition products themselves. Mass peaks at $m/e = 879$ and 1203 (1202) may be the result of loss of $C_6H_5-CH^+$ ($M_w = 90$) or tropylium $C_7H_7^+$ ($M_w = 91$) from the trimer ($m/e = 969$), tetramer ($m/e = 1292$) and pentamer ($m/e = 1615$), respectively. In addition, another series of fragmentation products with $m/e = 734$, 1055 (1057) and 1380 may arise from the loss of the fragments shown in Figure 4.4.5.1.11 from the trimer, tetramer and pentamer respectively. From the above fragments, the results indicate that the primary mode of thermal degradation may be the scission of acetylenic bonds. Even more likely, the fragments may be secondary products expelled from the primary addition products.

The mass spectrum of the thermal reaction products of the PA/PEA phenylethynylphthalimide are shown in Figures 4.4.5.1.12 - 4.4.5.1.13. The degradation pattern was very similar to the PEPA/An model compound since the two are isomeric structures of one another. The major cleavage again occurred at the acetylenic C-C bond. The fragmentation products of model compound PA/PEA may have the structure shown in Figure 4.4.5.1.14.

Quantitative ^{13}C NMR was performed on the thermal reaction products of the model

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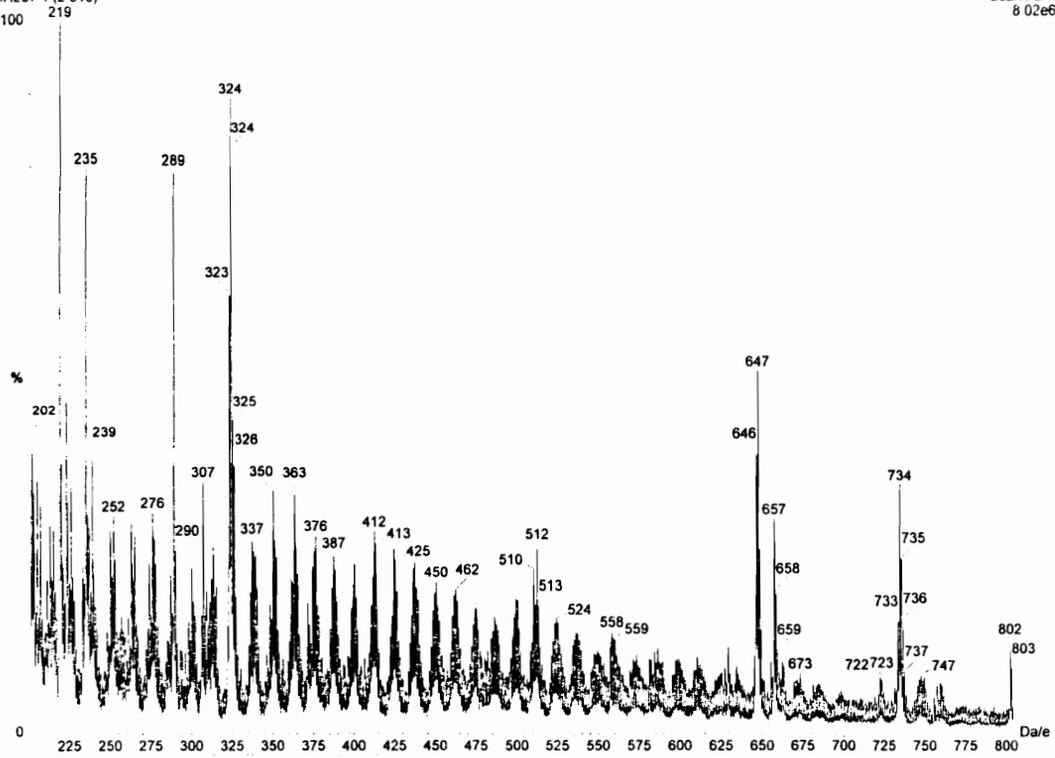


Figure 4.4.5.1.9 Mass Spectrum of PEPA/An Model Compound Cured at 350°C for 45
Minutes

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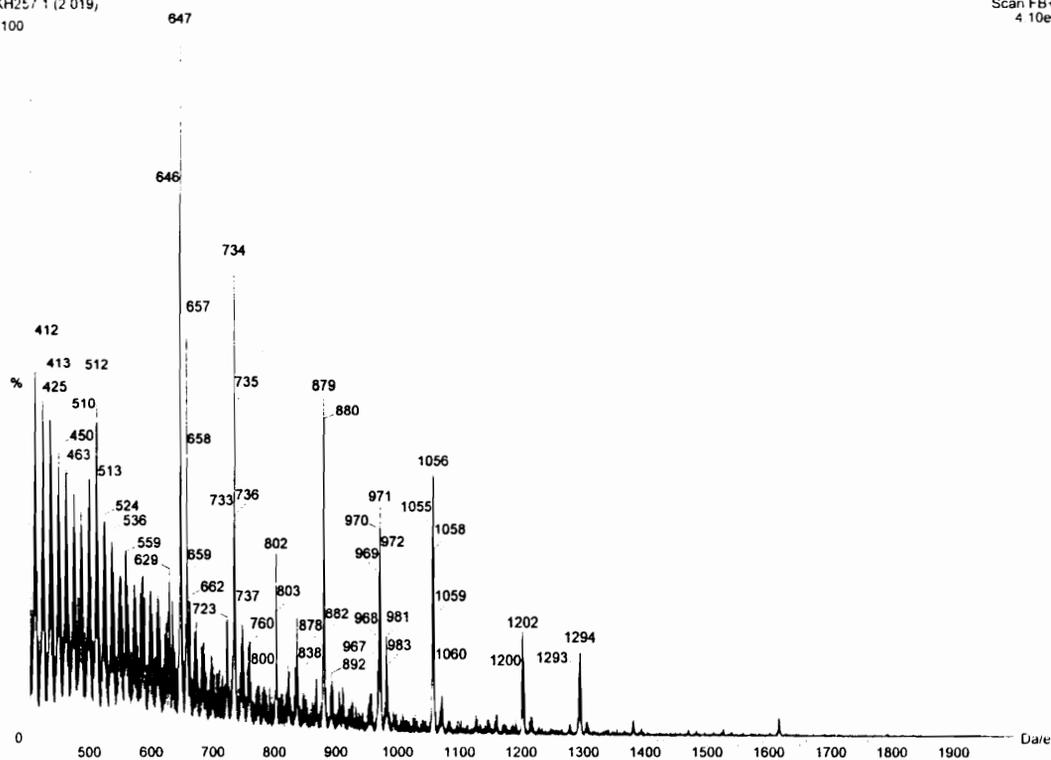


Figure 4.4.5.1.10 Mass Spectrum of PEPA/An Model Compound Cured at 350°C for 45
Minutes

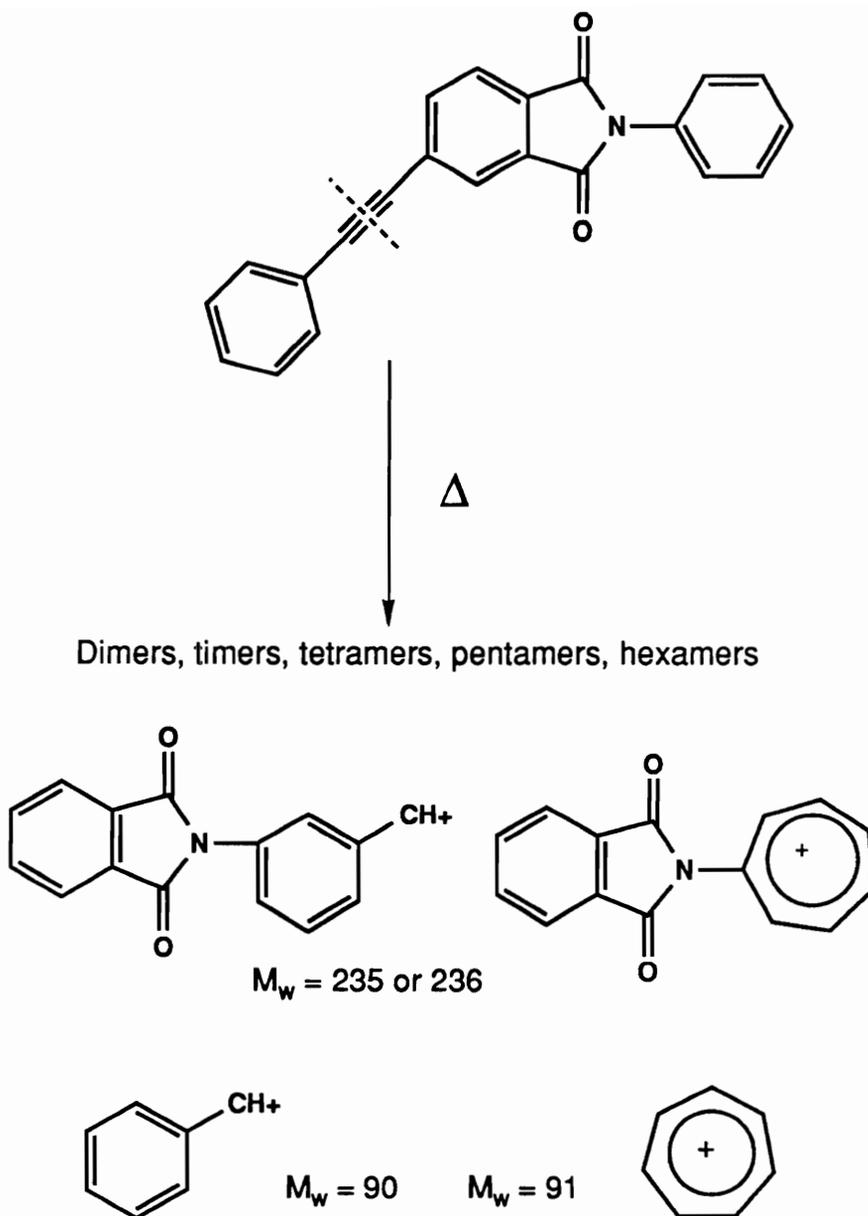


Figure 4.4.5.1.11 Possible Fragmentation Products of PEPA/An Model Compound Cured at 350°C for 45 Minutes

GM3-16-60mins in NBA
Analytical Services

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1.37e8

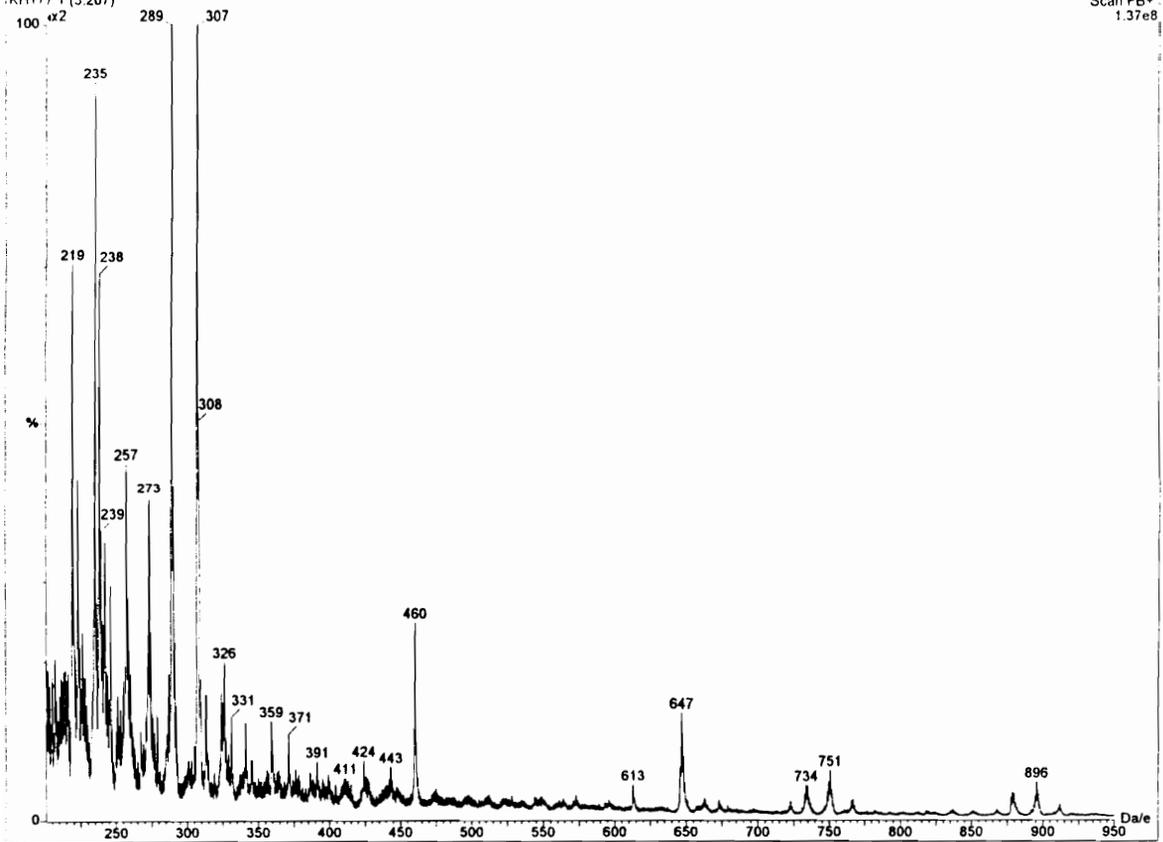


Figure 4.4.5.1.12 Mass Spectrum of PA/PEA Model Compound Cured at 350°C for 1 Hour

GM3-16-60mins in NBA
Analytical Services

VG Quattro

17-Oct-1994
14:06:52
Scan FB-
6.63e6

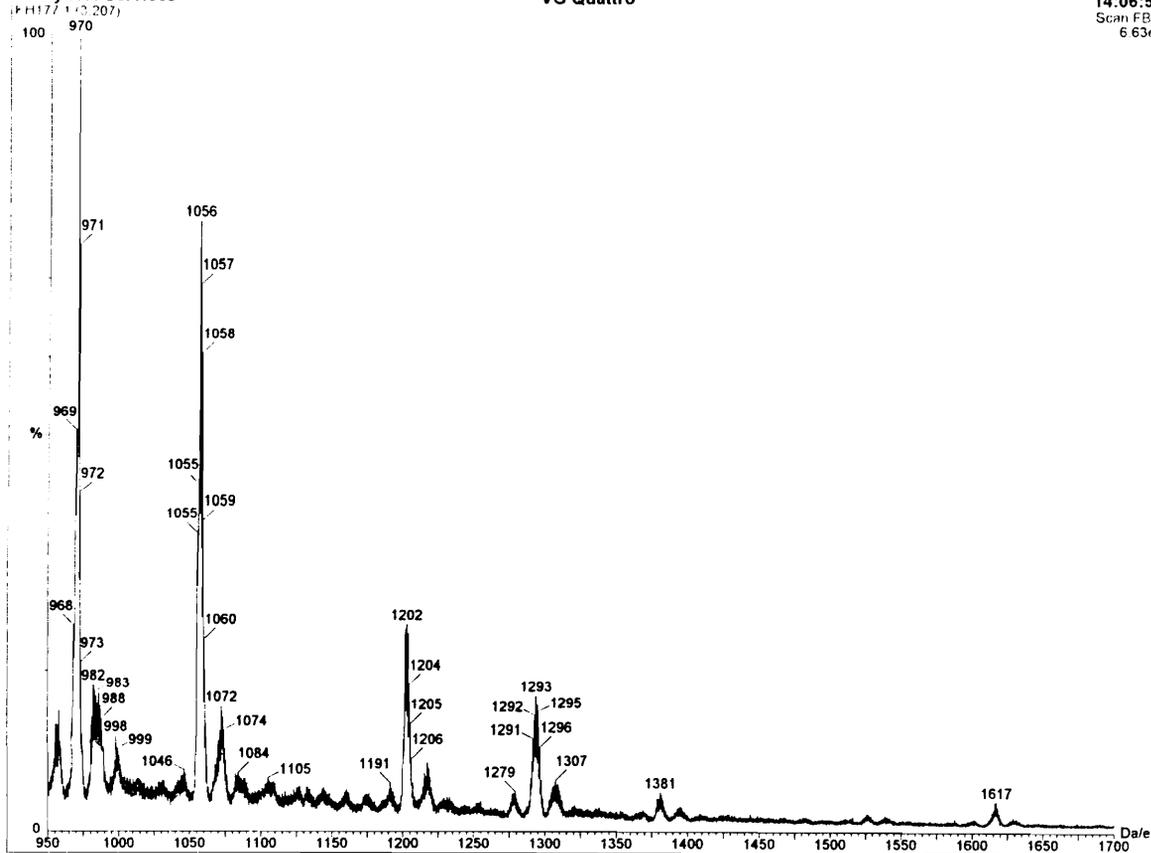


Figure 4.4.5.1.13 Mass Spectrum of PA/PEA Model Compound Cured at 350°C for 1 Hour

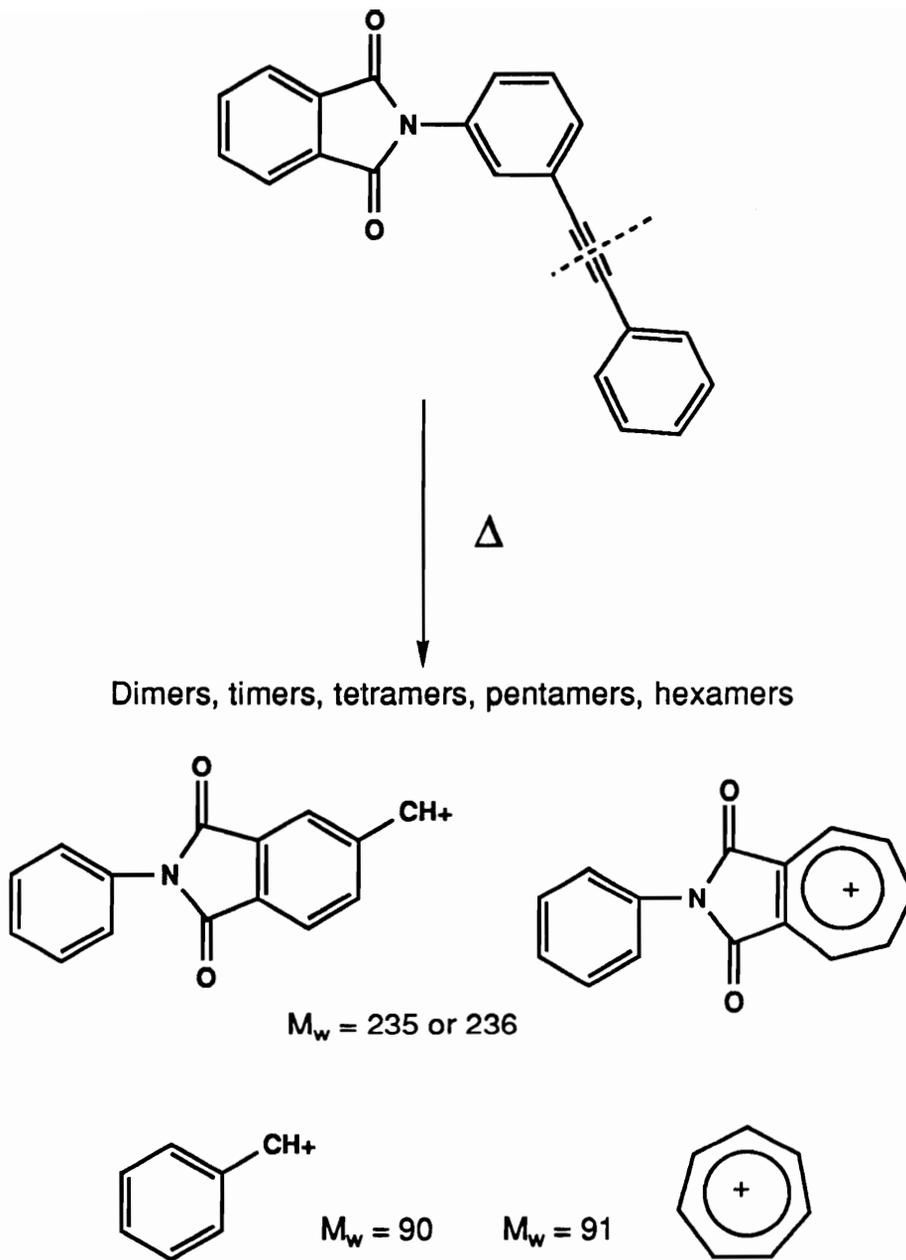


Figure 4.4.5.1.14 Possible Fragmentation Products of PA/PEA Model Compound Cured at 350°C for 1 Hour

phenylethynylphthalimides. The ^{13}C NMR spectra of the uncured PEPA/An model compound is shown in Figure 4.4.5.1.15 where the acetylenic carbons are clearly observed at 87.6 and 93.2 ppm, the aromatic carbons from 121-137 ppm and the carbonyl carbon at 165.8 ppm. An expansion of the aromatic region is given in Figure 4.4.5.1.16 where the carbons are all seen as well defined peaks. As curing at 350°C progressed, the acetylenic carbons were observed to decrease in intensity as would be expected and the aromatic region broadened with various peaks growing in intensity at 120-125 ppm and in the olefinic region at 136 and 144 ppm as shown in Figure 4.4.5.1.17. A blown-up of the aromatic and olefinic region after curing for 45 minutes at 350°C is shown in Figure 4.4.5.1.18. The growth of peaks at 136 and 144 ppm indicated that olefinic carbons perhaps associated with protonated carbon-carbon double bonds (polyene structure) form upon thermal curing. However, the significant growth of peaks occurring in the aromatic region suggests that aromatization (possibly cyclotrimerization) is also a significant reaction product. Nevertheless, the amount of aromatization is probably much smaller in cured imide oligomers due to increased steric factors and polymer melt viscosity.

Similar spectral changes were observed from the thermal reaction products of PA/PEA. The quantitative ^{13}C NMR spectra of the PA/PEA model compound cured for 60 minutes at 350°C is pictured in Figure 4.4.5.1.19. Similar to the PEPA/An results, the acetylenic carbons disappear with longer curing times and the aromatic region shows significant overlap and broadening. In addition, the formation of olefinic-type carbons was also observed occurring in the 136 - 141 ppm range.

The ^1H NMR spectra of the uncured PEPA/An model compound with the assignment of peaks is shown in Figure 4.4.5.1.20. Upon curing at 350°C, the aromatic protons broadened and began to overlap indicating that significant aromatic character was developing during the curing process. A blown-up of the aromatic region is illustrated in

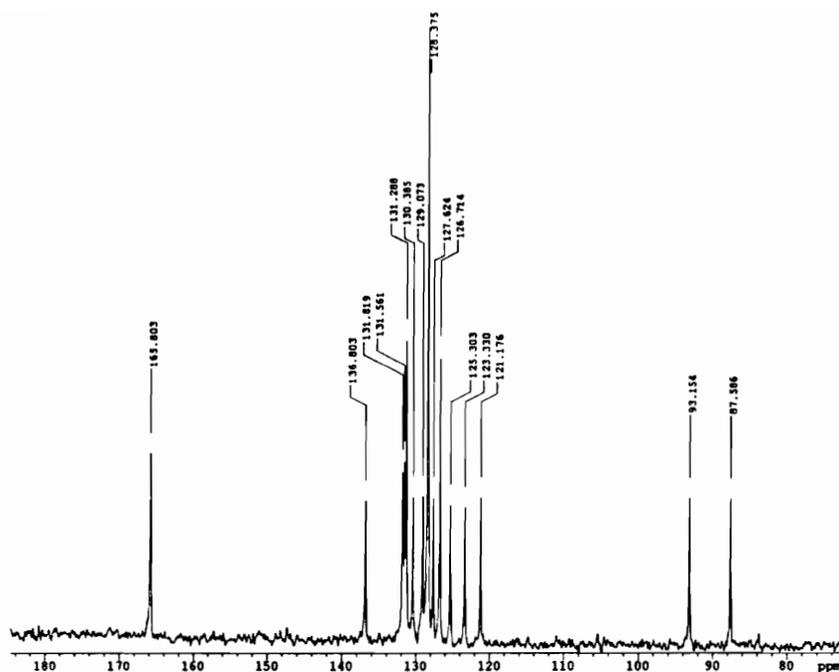


Figure 4.4.5.1.15 ^{13}C NMR Spectrum of Uncured PEPA/An Model Compound in CDCl_3

(400 MHz)

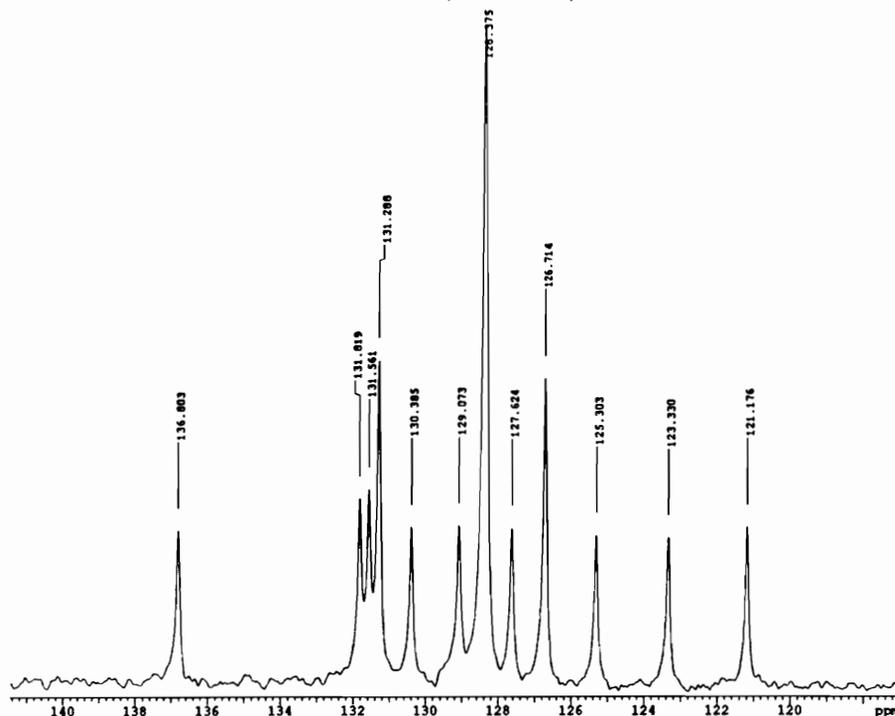


Figure 4.4.5.1.16 ^{13}C NMR Spectrum of Uncured PEPA/An Model Compound in CDCl_3

(400 MHz)

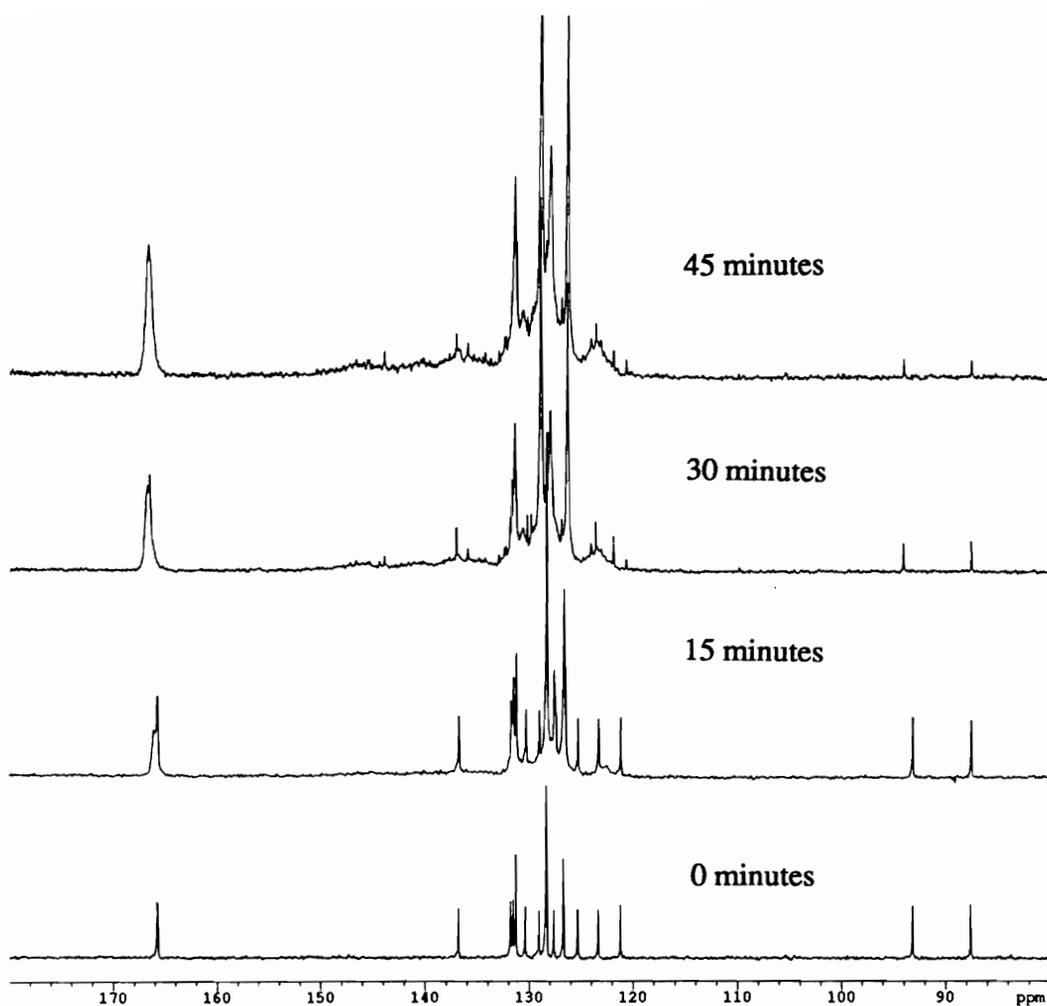


Figure 4.4.5.1.17 ^{13}C NMR Spectra of PEPA/An Model Compound after Curing at 350°C for 0 Minutes, 15 Minutes, 30 Minutes and 45 Minutes (CDCl_3 , 400 MHz)

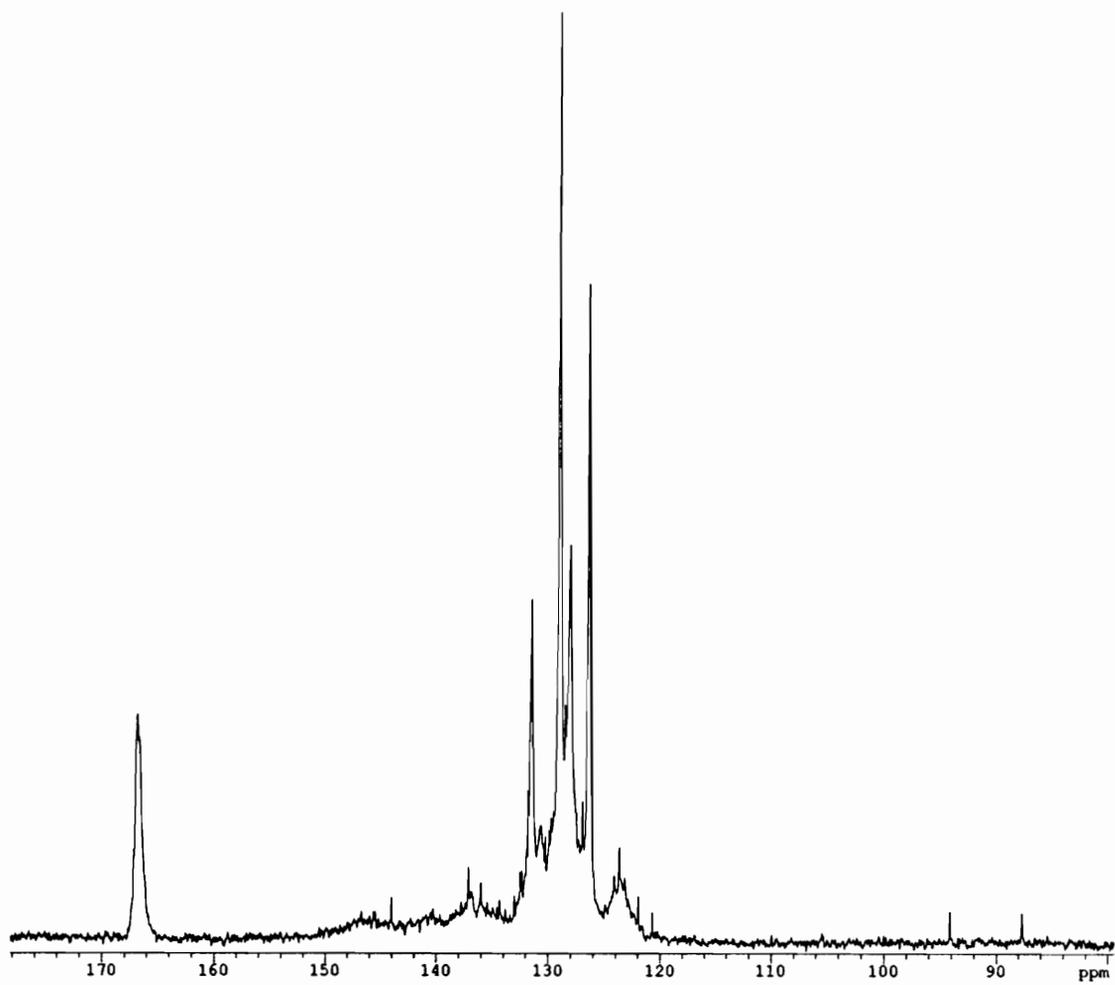


Figure 4.4.5.1.18 ^{13}C NMR Spectrum of PEPA/An Model Compound Cured at 350°C for 45 Minutes (CDCl_3 , 400 MHz)

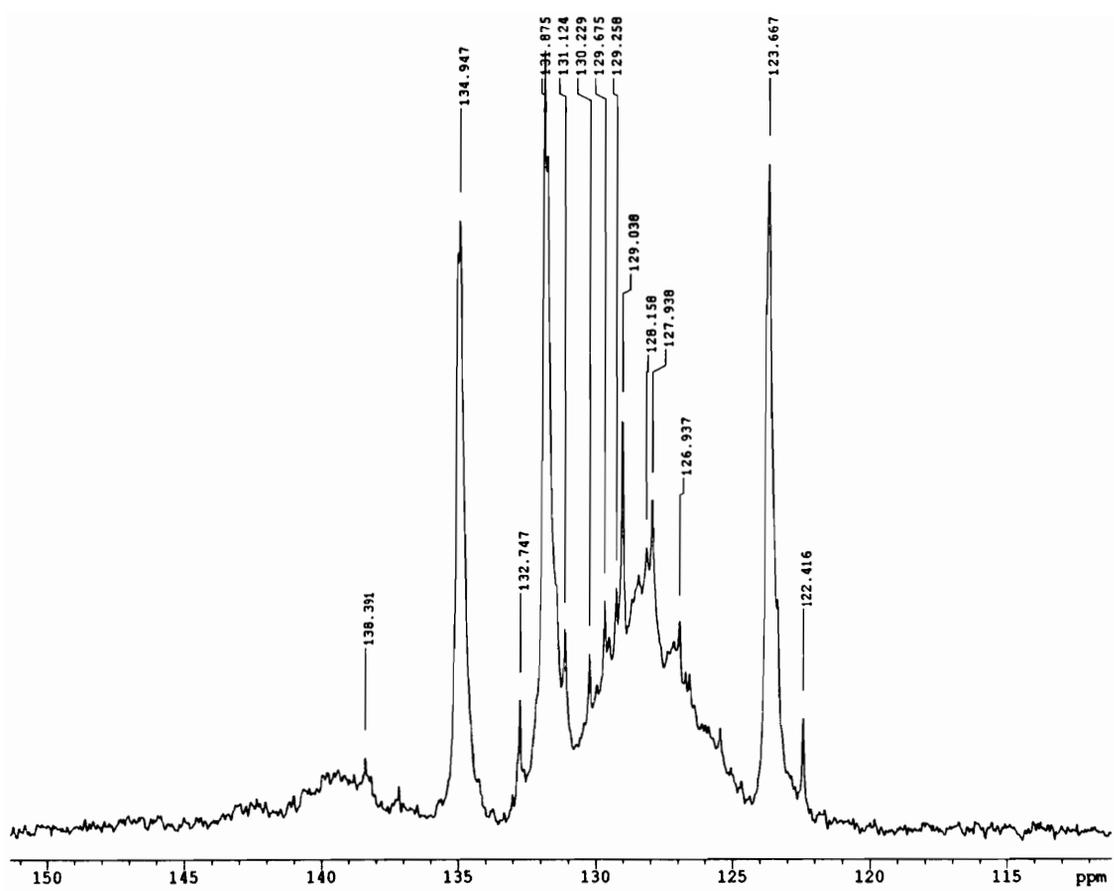


Figure 4.4.5.1.19 ¹³CNMR Spectrum of PA/PEA Model Compound Cured at 350°C for 1 Hour (DMSO-d₆, 400 MHz)

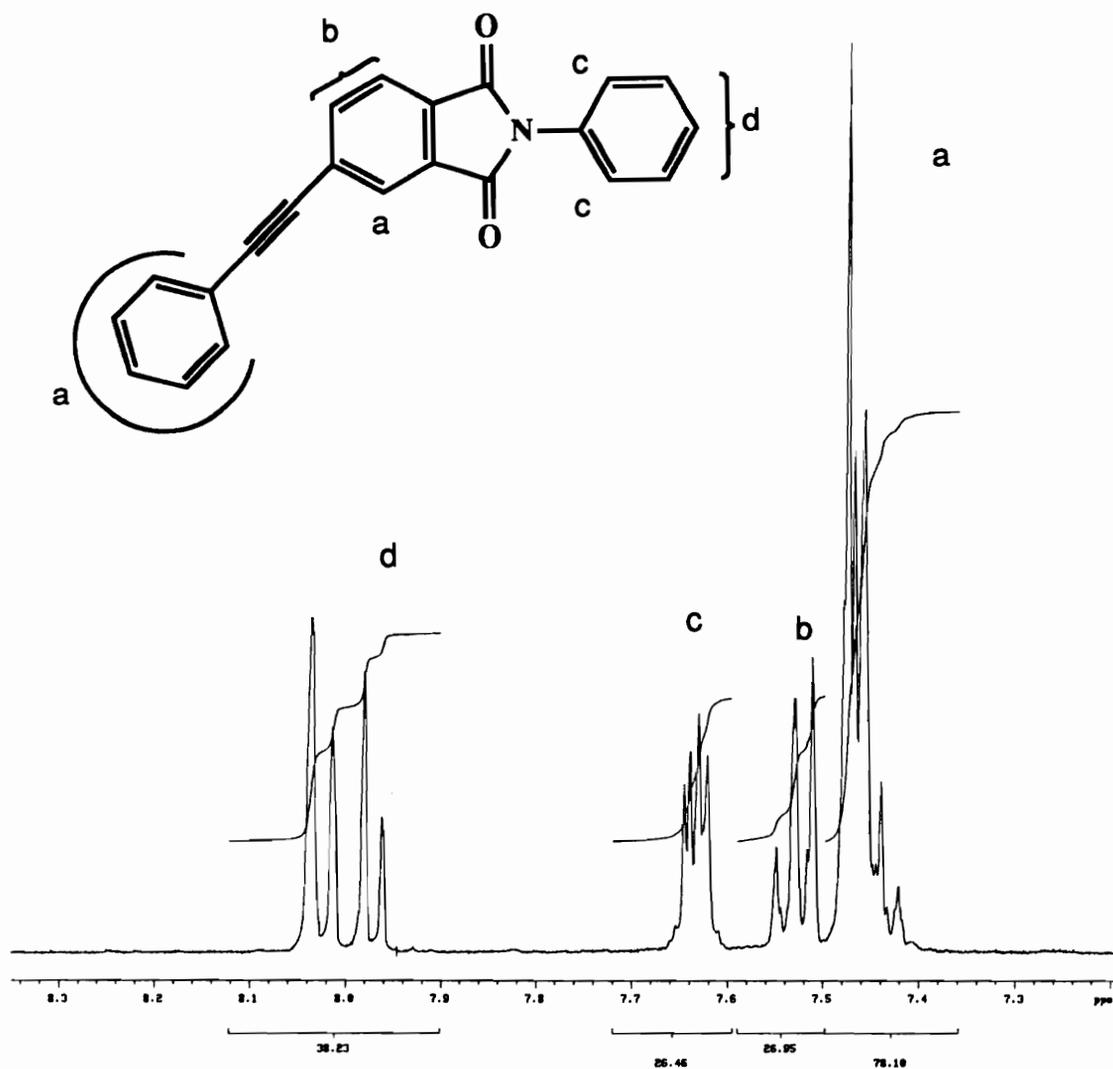


Figure 4.4.5.1.20 $^1\text{H NMR}$ Spectrum of Uncured PEPA/An Model Compound in $\text{DMSO-}d_6$ (400 MHz)

Figure 4.4.5.1.21. In this spectrum, the aromatic protons have almost completely overlapped and in addition, olefinic protons are detectable. These olefinic protons are detectable as early as 15 minutes curing time, and they increase in amount from 0.41 % to 0.88 % of the total protons present from 15 to 45 minute curing time at 350°C. Furthermore, these olefinic protons originate in the range of α , β protonated double bonds. Analogous spectral changes occur for the PA/PEA model compound with significant broadening and overlap. Olefinic protons also appear and progress from 0.51 % of the total protons at 15 minutes curing time to a maximum of 0.79 % and then begin to decrease to 0.54 % at 60 minutes curing time. The apparent formation of carbon-carbon protonated double bonds again suggests that a linear chain extension occurs along with crosslinking (possibly aromatization) during the curing of phenylethynyl functionalized imide polymers.

A molecular weight study was performed to provide further evidence that linear chain extension/branching may be occurring during curing. The increase in $\langle M_w \rangle$ of a BPDA/3FDAM/PEA(4,000) imide oligomer was monitored by GPC using polystyrene standards as a function of cure time. Samples of the phenylethynyl terminated oligomer were cured in a convection oven at 350°C and 380°C under a nitrogen atmosphere for various times. The cured samples that remained soluble in chloroform were then evaluated by GPC. Figure 4.4.5.1.22 illustrates a significant increase in $\langle M_w \rangle$ as a function of cure time. $\langle M_w \rangle$ was seen to increase over four fold at 350°C from 9,200 to 40,700 g/mole while at 380°C $\langle M_w \rangle$ increased by nearly a factor of seven from 9,200 to 60,300 g/mole. Furthermore, the molecular weight distribution, $\langle M_w \rangle / \langle M_n \rangle$, or polydispersity increased significantly as curing progressed. The polydispersity of the phenylethynyl terminated oligomer nearly doubled from 2.1 to 3.8 when cured at 350°C, while it over tripled from 2.1 to 6.9 when cured at 380°C. The increase in polydispersity again suggests that crosslinking along with chain extension/branching may be occurring during the curing process.

GM3-16 cured 45 mins at 350C in chloroform
OBSERVE H1
FREQUENCY 399.951 MHz
SPECTRAL WIDTH 5000.0 Hz
ACQUISITION TIME 3.744 sec
RELAXATION DELAY 1.000 sec
PULSE WIDTH 4.1 usec
AMBIENT TEMPERATURE
NO. REPETITIONS 32
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
LINE BROADENING 3.0 Hz
FT SIZE 65536
TOTAL ACQUISITION TIME 2 minutes
Jan 6 95
Virginia Tech STC NMR Facility

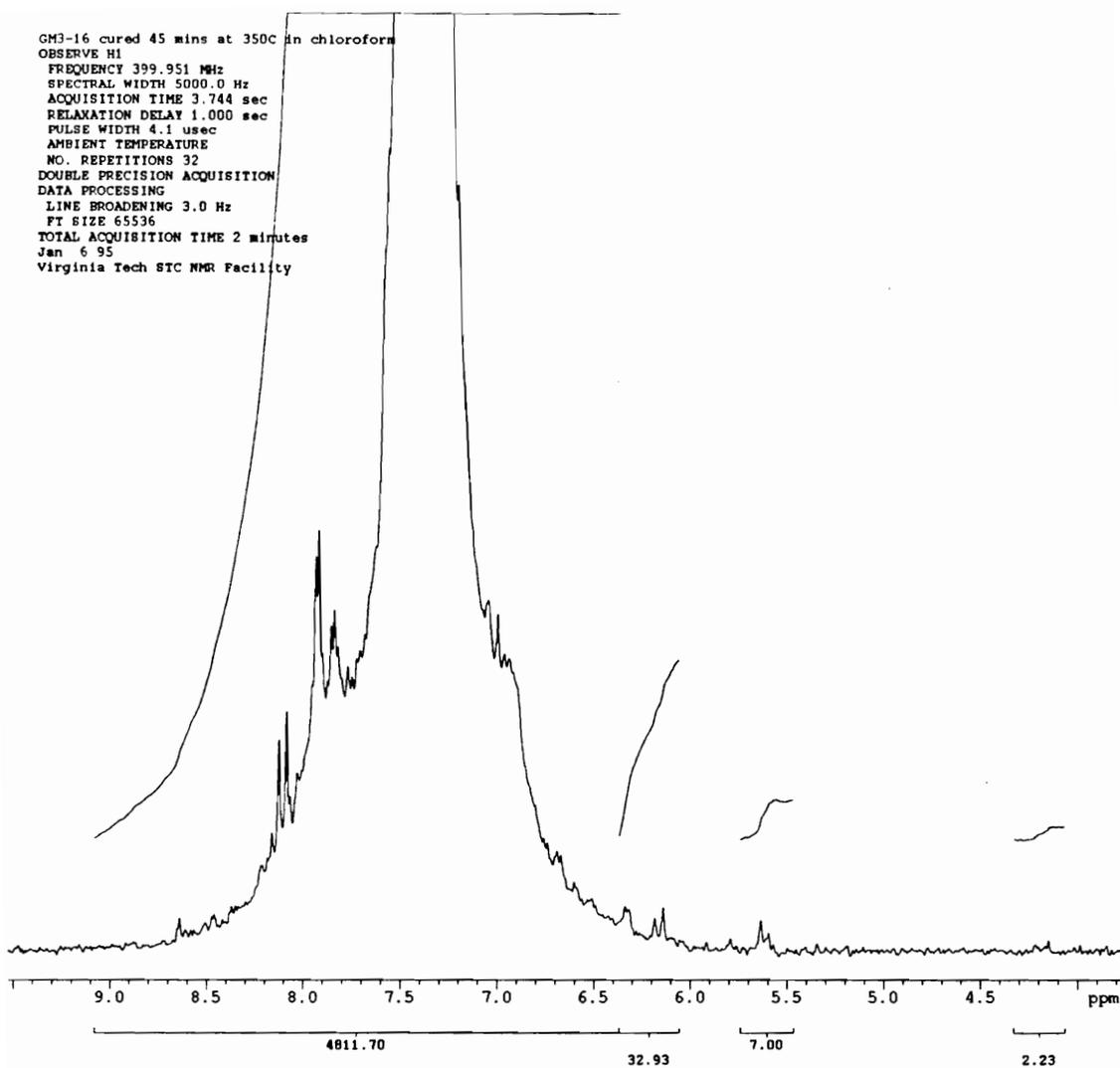


Figure 4.4.5.1.21 ¹H NMR Spectrum of PEPA/An Model Compound Cured at 350°C for 45 Minutes (CDCl₃, 400 MHz)

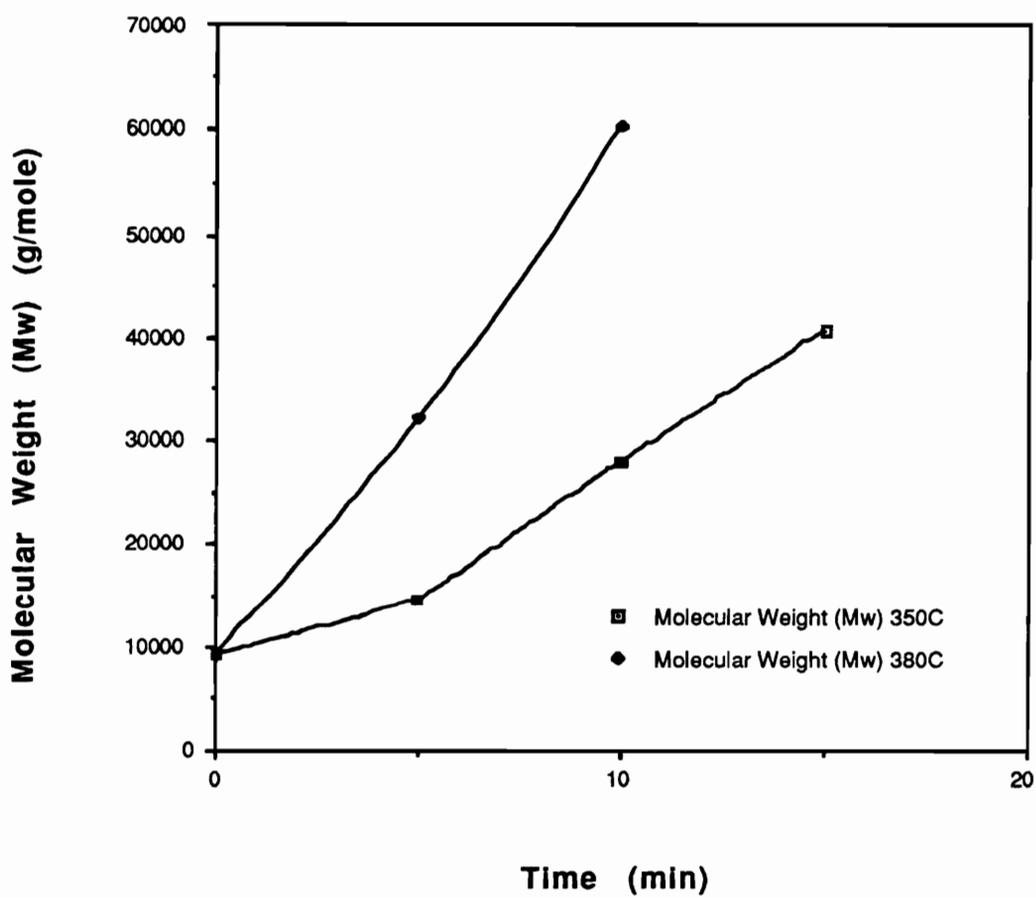


Figure 4.4.5.1.22 Molecular Weight ($\langle M_w \rangle$) Increase with Curing Time of BPDA/3FDAM/PEA(4,000) Imide Oligomer (Referenced to Polystyrene Standards)

These findings may serve as a guide to the thermal curing of phenylethynyl terminated imide oligomers. However, it must be emphasized that the model compound work serves only as a guide and not a direct correlation to the products formed from the thermal crosslinking of a phenylethynyl terminated imide oligomer. The latter could exhibit significant differences in reactivity relative to a model compound due to differences such as molecular mobility and phenylethynyl density.

4.4.5.2 Phenylmaleic Imides

In order to have a better understanding as to why molecular weight control was unsuccessful during the polymerization of imide oligomers endcapped with phenylmaleic anhydride at temperatures above $\sim 150^{\circ}\text{C}$, a model study was performed. A model compound based on PMA/An was synthesized by first forming the amic acid which was then subsequently imidized at high temperatures ($\sim 180^{\circ}\text{C}$) using NMP/*o*-DCB as the reaction solvents. The ^1H NMR of the amic acid compound formed at room temperature is shown in Figure 4.4.5.2.1. The protons observed at 12.8 ppm due to the carboxylic acid, at 10.2 ppm corresponding to the amide linkage and the olefinic protons at 6.3 and 6.5 ppm as well as the aromatic protons confirm the formation of the amic acid occurring in its two isomeric forms. Therefore, room temperature formation of the amic acid is not affected by the presence of the phenylmaleic anhydride groups. However, as the reaction is heated to $\sim 180^{\circ}\text{C}$, unexpected peaks appear in the ^1H NMR spectra.

Aliquots taken from the reaction solution at various times clearly reveal the formation of two doublets at 4.4 ppm and 4.6 ppm as early as 30 minutes reaction time and a significant reduction in the olefinic protons relative to the aromatic protons as illustrated in Figure 4.4.5.2.2. ^{13}C NMR results also indicate significant formation of signals occurring at 131.7 ppm and at 35.4, 39.9, 50.6 and 57.6 ppm. Based on Heteronuclear Chemical Shift Correlation (HETCOR), Heteronuclear

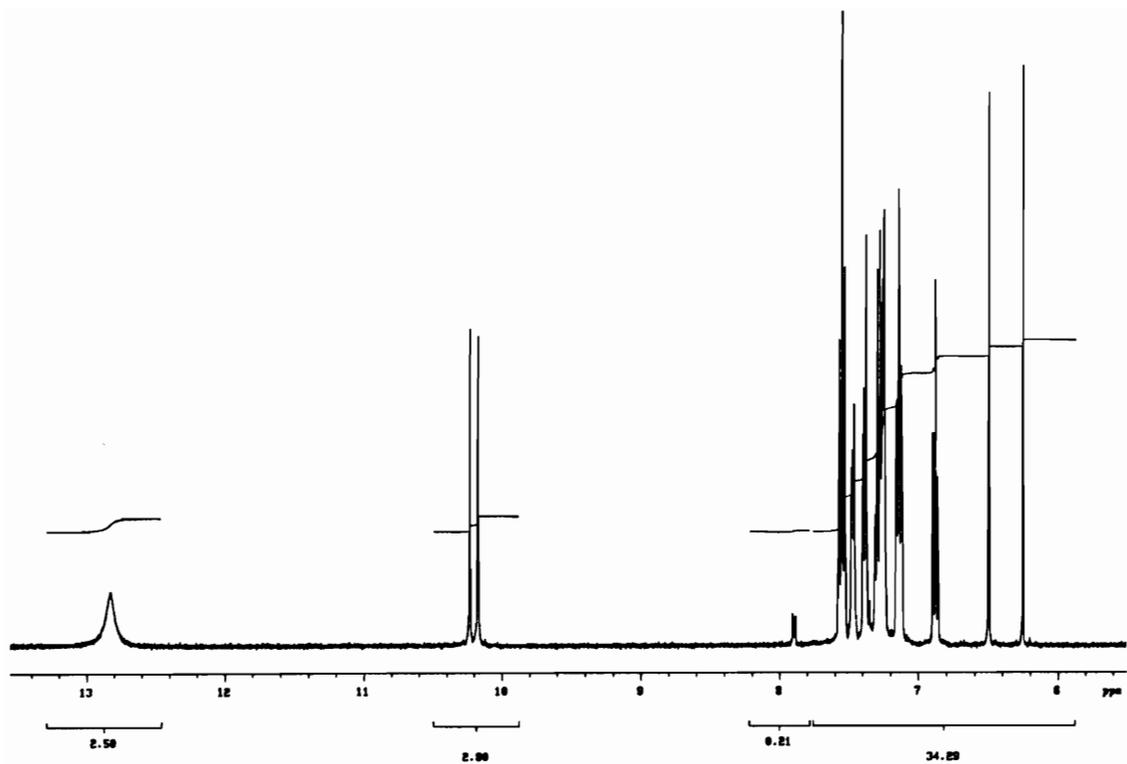


Figure 4.4.5.2.1 ^1H NMR Spectrum of PMA/An Amic Acid in DMSO-d_6 (400 MHz)

Multiple Quantum Coherence (HMBC) and Distortionless Enhancement by Polarization Transfer (DEPT) NMR analysis, the carbon at 131.7 ppm is correlated to the proton occurring at 8.0 ppm indicating that a protonated nitrogen is attached to the carbon arising from the olefinic bond as seen in Figure 4.4.5.2.3. In addition, the aliphatic protons occurring at 4.4 ppm are correlated only to two carbons at 50.6 and 35.4 ppm and the protons at 4.6 ppm are correlated to three carbons occurring at 57.6, 39.9 and 35.4 ppm as shown in Figure 4.4.5.2.4. Furthermore, protonated carbons are only observed at 35.4, 39.9 and 50.6 ppm indicating that a quaternary carbon is present. This seems highly unlikely since a reaction would have to be occurring at the phenyl substituted olefinic carbon which is highly hindered. A proposed structure of the reaction product is shown in Figure 4.4.5.2.5 where the arylamine may attack the olefinic bond and this compound may then couple through another olefinic bond. These results seem to suggest that the amic acid structure is partially hydrolyzed to yield free amine and anhydride groups as Kim⁵⁰ has proposed for polyimide formation from polyamic acid. The free amine groups, instead of recombining to form imide, may act a nucleophile and attack the carbon-carbon double bond through a Michael addition.

This Michael addition process is known to occur with bismaleimides and is even a method for formation of high molecular weight step-growth polymers.²⁰⁰ Arylamines can add rapidly and quantitatively to maleimides in solution (> 60°C) via the proposed mechanistic pathway shown in Figure 4.4.5.2.6.²⁰⁰ It is conceivable that phenylmaleimide systems impose more steric barrier due to the pendent phenyl moiety and as a result, higher reaction temperatures are needed to cause this Michael-type addition. Therefore, at polymerization temperatures above ~ 150°C, polyimides endcapped with phenylmaleic anhydride may undergo this Michael addition to produce high molecular weight polymer. However, again the model compound work serves only as a guide and not a direct

correlation to the products formed from the polymerization of phenylmaleic anhydride terminated imide oligomers.

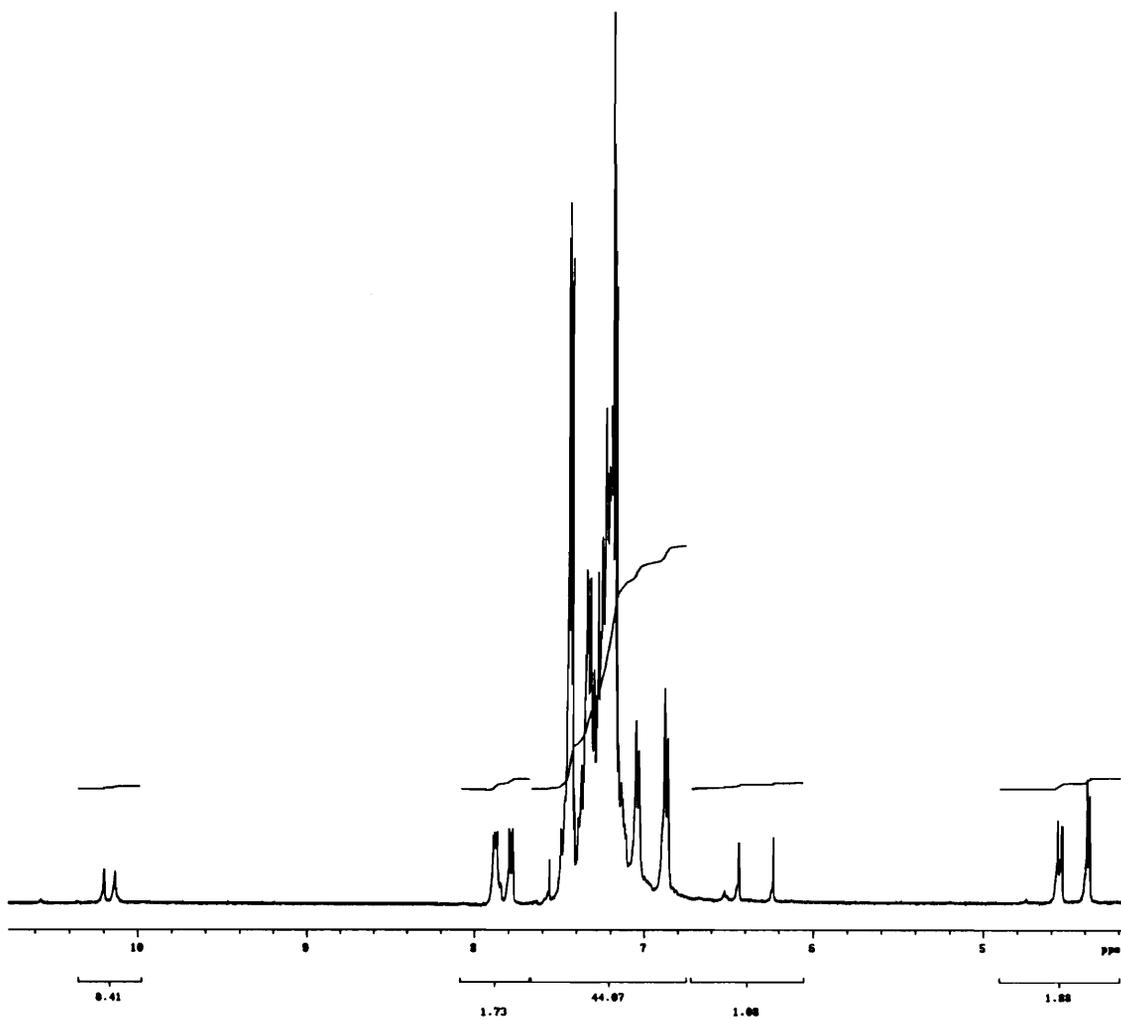


Figure 4.4.5.2.2 ^1H NMR Spectrum of PMA/An after 30 Minutes Imidization at 180°C
(DMSO- d_6 , 400 MHz)

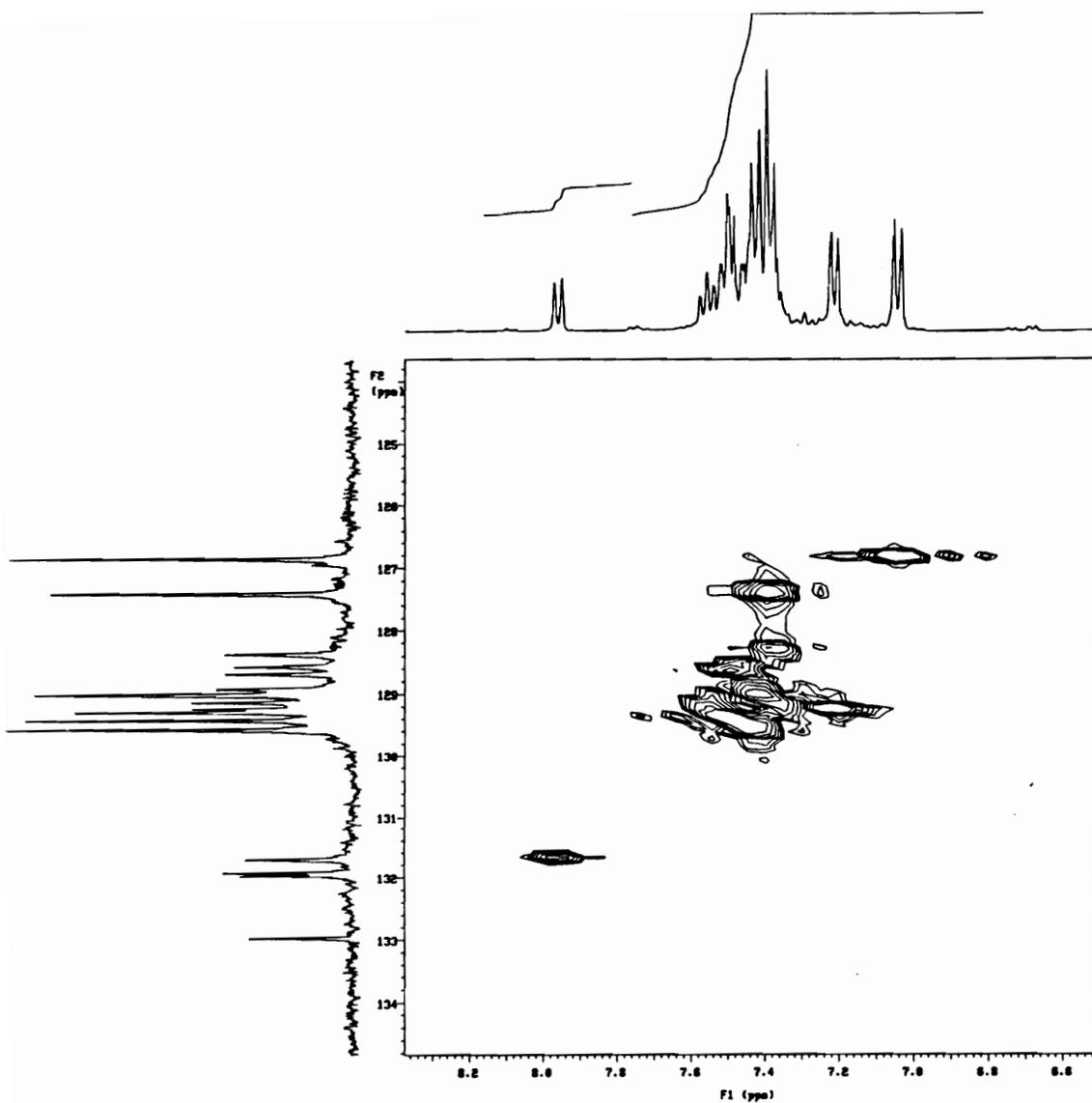


Figure 4.4.5.2.3 HETCOR NMR Spectrum of PMA/An Model Compound in Aromatic Region (DMSO-d₆, 400 MHz)

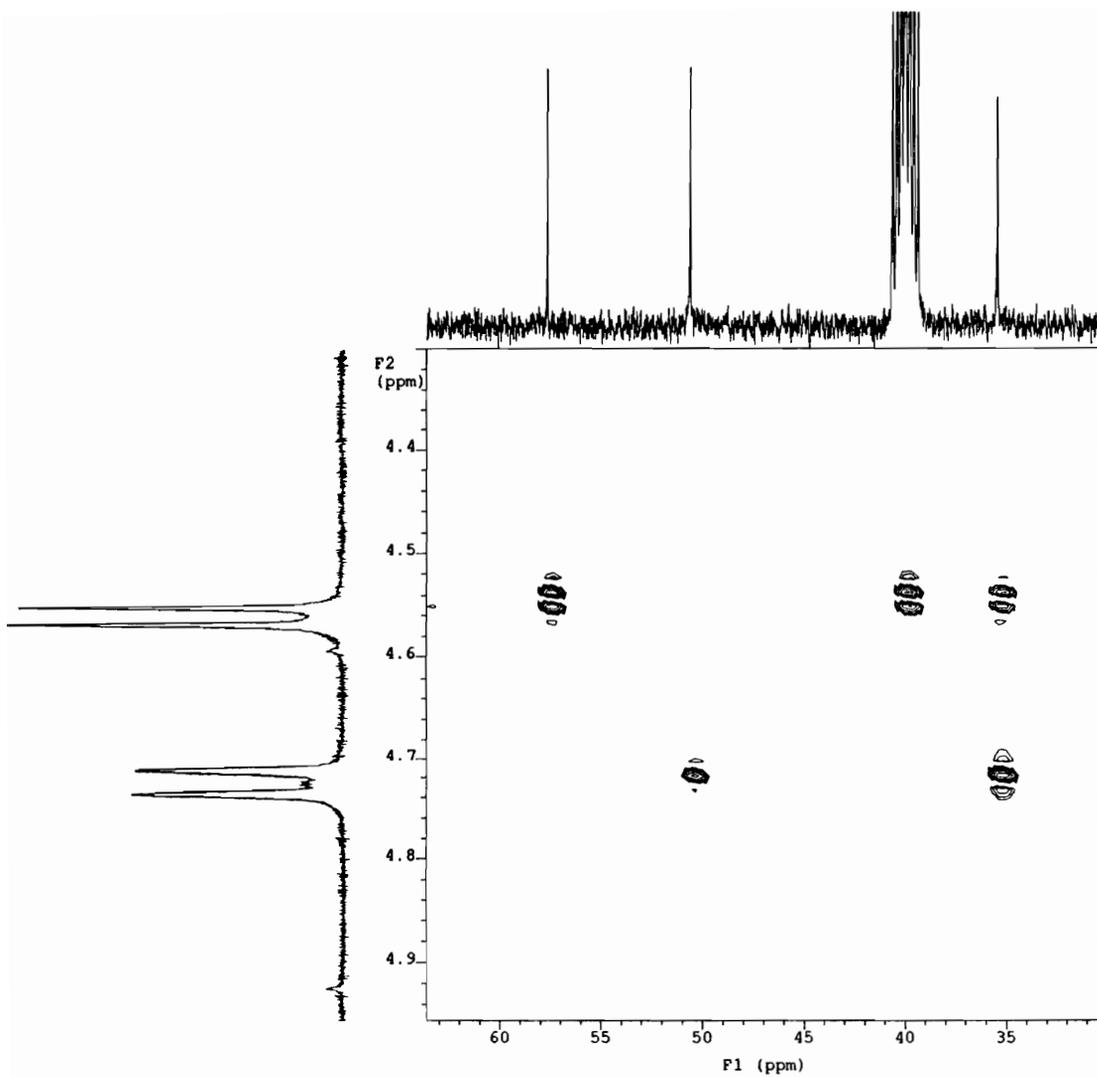


Figure 4.4.5.2.4 HMBC NMR Spectrum of PMA/An Model Compound in Aliphatic Region (DMSO-d₆, 400 MHz)

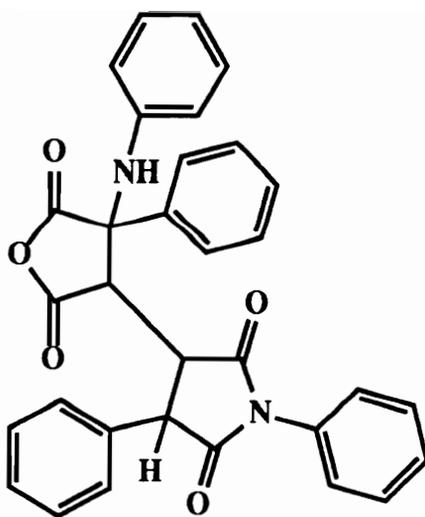


Figure 4.4.5.2.5 Proposed Reaction Product of PMA/An Imidized at 180°C

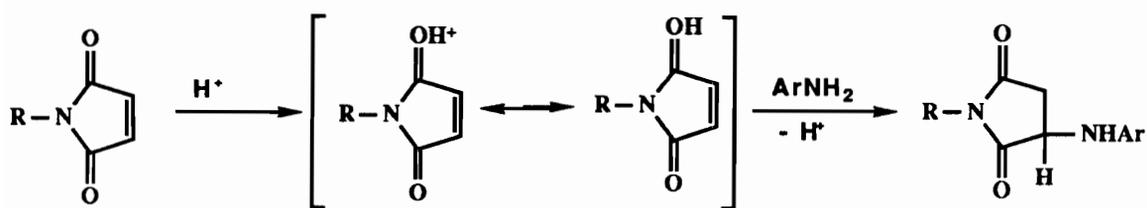


Figure 4.4.5.2.6 Proposed Mechanistic Pathway for Michael Addition

CHAPTER 5 - CONCLUSIONS

The goals of the research presented in this dissertation were directed towards the synthesis and characterization of soluble, processable high temperature linear and thermosetting polyimides which would be suitable for new structural matrix resins, adhesives and gas separation membranes. Several new high temperature curing monofunctional endcapping agents were employed to produce the desired reactive thermosetting polyimides.

High molecular weight amorphous aromatic polyimides were successfully prepared from the ester-acid of many dianhydrides and diamines in polar aprotic solvents such as *N*-methylpyrrolidone and *o*-dichlorobenzene. The resulting polyimides were soluble in *N*-methylpyrrolidone and *N,N*-dimethylacetamide at 25°C at concentrations of 15 to 20 percent (wt/vol), and many were also soluble in common solvents such as tetrahydrofuran, chloroform and methylene chloride. Moderate to high glass transition temperatures and thermo-oxidative stability were demonstrated by thermal analysis.

3-Phenylethynylaniline, 4-phenylethynylphthalic anhydride and phenylmaleic anhydride were used as high temperature reactive endcapping cure sites for soluble imide thermosetting (reactive) oligomers. The phenylethynyl endcapping agents were synthesized by a palladium-catalyzed coupling reaction of brominated starting materials with phenylacetylene derivatives in purified yields greater than 80 %. Phenylmaleic anhydride was also synthesized and was investigated as a novel high temperature reactive site for polyimide systems. The polyimide oligomers were synthesized via the ester-acid route and the "one pot" procedure reproducibly exhibit fully imidized soluble polyimides with $\langle M_w \rangle / \langle M_n \rangle$ values of ~ 2.0 determined by gel permeation chromatography.

Polyimide oligomers endcapped with 3-phenylethynylaniline were synthesized to yield highly imidized, controlled molecular weight phenylethynyl functionalized polyimides.

Glass transition temperature values increased with increasing molecular weight of the oligomer. Upon thermal curing at temperatures greater than 350°C, insoluble, highly crosslinked films with the anticipated T_g values were obtained that exhibited excellent thermo-oxidative stability. Matrix materials were also synthesized by the incorporation of triaryl phosphine oxide moieties into the polyimide backbone which displayed char yields as high as 80% in air by dynamic TGA analysis and mechanical properties equal to or exceeding high molecular weight polyimides.

Polyimide siloxane copolymers endcapped with either *m*-aminophenylacetylene or 3-phenylethynylaniline were synthesized to controlled molecular weights. Films were prepared for gas separation membranes from these reactive imide siloxane copolymers by thermally crosslinking the copolymers. The crosslinked membranes exhibited enhanced selectivity compared to the linear random copolymers (as much as 61 % increase in the case of CO₂/CH₄) without any significant decrease in permeability.

Polyimide and (ether imide) oligomers endcapped with 4-phenylethynylphthalic anhydride were also synthesized to yield controlled molecular weight, phenylethynyl functionalized polyimides. Thermal curing at 380°C produced insoluble, crosslinked, solvent resistant but yet creasable films, with high T_g 's and good thermo-oxidative stability. The 4-phenylethynylphthalic anhydride endcapped imides exhibited cure exotherm maxima as much as 40°C higher than the 3-phenylethynylaniline endcapped oligomers; however, their thermo-oxidative stability was slightly lower compared to the 3-PEA systems. These oligomers were highly processable which was related to the wide processing window between T_g and T_{cure} (> 150°C) afforded by the phenylethynyl endcap.

Thermally cured phenylethynyl imide films displayed excellent solvent resistance with gel contents of 95 % or higher in most cases. Several systems exhibited excellent thermal stability at temperatures up to 700 °F (371°C) aged in air determined by dynamic and isothermal thermal gravimetric analysis. Composite specimens prepared from these

reactive imide systems by conventional and "powder prepregging" techniques displayed moduli equal to or greater than specimens prepared from commercial state of the art materials.

Controlled molecular weight polyimide oligomers endcapped with phenylmaleic anhydride were synthesized via chemical imidization or a 2-step amine-terminated lower temperature imidization route. However, typical high temperature solution imidization techniques surprisingly produced high molecular weight polymer. Upon curing, insoluble, crosslinked films with the anticipated T_g values were obtained that exhibit good thermo-oxidative stability at 232°C for 1000 hours. The phenylmaleic anhydride endcapped oligomers displayed lower gel contents and slightly lower thermo-oxidative stability as compared to the phenylethynyl functionalized systems under comparable curing conditions. These oligomers were easily processable and exhibited a wide curing window of ~200°C determined by parallel plate rheological studies, indicating that phenylmaleic anhydride may be a viable, economically attractive alternative for phenylethynyl systems for structural adhesives and polymer matrix composites.

Model phenylethynyl and phenylmaleic compounds were studied with a variety of spectroscopic techniques. The results indicated that crosslinking (possibly including cyclotrimerization) and chain-extension/branching may both occur concurrently during the thermal curing of the model phenylethynyl groups. This chain-extension/branching phenomena has far reaching consequences since no other thermosetting system has been reported to yield extremely tough, ductile materials with outstanding mechanical properties as the phenylethynyl endcapped systems. Furthermore, the phenylethynyl groups allow for the melt processing of high T_g imide systems before premature curing and result in a thermally stable crosslink junction point upon high temperature curing. Phenylmaleic model imide studies indicated that Michael addition side reactions at > 140°C may be a

significant factor in successful molecular weight control in phenylmaleic anhydride endcapped imide oligomers.

The phenylethynyl terminated imide oligomers are currently considered to be the material of choice for use in applications that require processable, thermally stable, solvent resistant resins. However, the drawback to the phenylethynyl systems is their high cost since the starting materials and the palladium catalyst are relatively more expensive than traditional thermosetting material systems. This research has shown that the phenylmaleic anhydride endcapped imides may be a less expensive, perhaps industrially viable, alternative to the phenylethynyl endcapped systems. These systems offer processability and reasonable high temperature stability at a lower cost to prepare than the phenylethynyl systems.

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Vitae

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