SYNTHESIS AND CHARACTERIZATION OF PHENYLETHYNYL ENDCAPPED POLYETHERIMIDE OLIGOMERS

by

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(ABSTRACT)

Fully cyclized, soluble phenylethynyl-terminated ether imide oligomers of 2.0-10.0 kg/mole (M_n) were prepared in high yield by the reaction of 2,2'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]-propane dianhydride (Bisphenol-A Dianhydride, BPADA) with a stoichiometric excess of *p*-/*m*- phenylene diamine and phenylethynylphthalic anhydride (4-PEPA) endcapper. The lower (M_n) oligomers displayed attractive low melt viscosity properties, and were successfully processed via thermal curing at 350-380°C for 30-90 minutes. The 3.0 kg/mole oligomers had a cured glass transition temperature (T_g) of 267°C and produced tough, solvent-resistant films. Excellent adhesion values to surface treated titanium alloys were produced by single lap shear measurements. Resin infusion molding has been conducted that permitted low void graphite fabric composite panels to be prepared.

The diamine monomer bis(*m*-aminophenyl) methyl phosphine oxide (DAMPO) was synthesized via nitration and the reduction of diphenyl methyl phosphine oxide. Rigorous purification of this monomer enabled it to be used for the synthesis of high molecular weight polyetherimides. Both thermoplastic materials and thermosetting systems endcapped with either

phthalic or phenylethynylphthalic anhydride, respectively, have been produced. Major emphasis has been placed on polyimides derived from 2,2'-bis(4-(3,4-dicarboxyphenoxy) phenyl) propane dianhydride (BPADA). High molecular weight homo- and copolyimides based on BPADA/DAMPO exhibited glass transition temperature values in the range of 215-223°C, and were completely amorphous. They displayed higher modulus and tensile strength values than the polyetherimide control based on *meta*-phenylene diamine, and also generated high TGA char yields in air. Phenylethynyl crosslinkable materials were effectively cured at 380°C to produce solvent resistant networks that were ductile, and which also generated high char yields, suggesting their possible utilization in fire resistant matrix systems.

Key Words: Phenyl ethynyl imides thermosetting matrix, structural adhesives, composite, bis(*m*-aminophenyl) methyl phosphine oxide, high char yield

Dedicated to my wife,

Cindy Yao, for her great love and support

to the memory of my grandmother,
Pan Yu-huang, and to my parents
for their love

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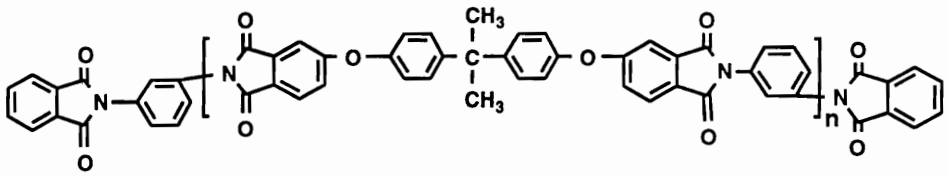
Chapter 1. INTRODUCTION

Polyimides are well known for excellent thermal stability, as well as for good mechanical and electrical properties. Many common applications are known for these materials, such as high-temperature coatings, structural adhesives and matrix resins for high performance composites [3-7]. For example, a thermoplastic polyetherimide produced by General Electric based on bisphenol-A dianhydride and *meta*-phenylene diamine [92-94], as identified in the repeat unit shown below, has a glass transition temperature of 217 °C.



Ultem™-1000

This material possesses good melt processability, high mechanical strength, ductility, moderate self-extinguishing characteristics and outstanding electrical properties. On the other hand, it displays relatively poor chemical and solvent resistance, which is characteristic of an amorphous thermoplastic. For instance, it is only moderately resistant to salt solutions, dilute bases, gasoline, hydraulic fluid, etc.

Recent studies have demonstrated that imide oligomers terminated with phenylethynyl functional groups can result in excellent solvent resistance, good processability and durability [218-222]. One important application for these materials is the High-Speed-Civil-Transport (HSCT) airplane, for which candidate materials should have a wide processing window, T_g values higher

than 250°C, good adhesive properties in relation to the titanium alloy substrates, as well as excellent solvent resistance [146,147]. Composite matrix systems are also required that demonstrate good stiffness, strength, fracture resistance and similar T_g values.

The physical addition or chemical incorporation of phosphorus into polymeric materials is a long-standing industrial approach for improving fire resistance, and this is detailed in previous work describing the synthesis of such materials [224] and the preparation of novel monomers [225,226] and new functionalized oligomers/polymers [227-230]. In particular, several important features of the hydrolytically stable phosphorus carbon containing materials have been identified, including oxygen plasma resistance [231-233], plasma supported catalysis [234], structural adhesives [235], radiation resonance [236], and polymer blends [237].

Thus, the combination of phenylethynyl reactive groups, polyetherimide backbone and increased phosphine oxide moiety will result in an excellent combination of the desired characteristics mentioned above. However, further research is needed to investigate the synthesis, characterization and structure-property relationships of this new class of materials.

A major objective of this dissertation research was to synthesize and characterize a polyetherimide type of melt-processable polymer with the 4-phenylethynyl phthalic anhydride endcapping agent in order to develop networks that are easily melt processable, exhibit high glass transition temperatures, and are sufficiently ductile, thermo-oxidatively stable and solvent-resistant. These polyimides were also expected to possess excellent

physical and mechanical properties, as well as improved fire resistance. The specific objectives that were set forth in this research are as follows:

1. The synthesis and characterization of controlled molecular weight polyetherimide homo- or copolymers with non-reactive phthalic anhydride endcappers, with emphasis on the synthetic procedures, molecular weight control and thermal analysis of this type of polymer.
2. The synthesis and characterization of controlled molecular weight polyetherimide homo- or copolymer with reactive 4-phenylethynyl phthalic anhydride endcapper. The synthesis of several related poly(amic) acid system on a relatively large scale was also conducted.
3. The characterization of 4-phenylethynyl phthalic anhydride endcapped oligomers using tensile measurements, gel fractions, single lap shear tests, FTIR, DSC and melt viscosity etc., to better understand their structure-property relationships. Blending thermoset materials with thermoplastic materials was also investigated to further improve processability.
4. The synthesis and characterization of both linear and phenylethynyl terminated crosslinkable diphenyl methyl phosphine oxide containing polyimides. It was anticipated that the presence of the phosphine oxide group in the backbone would improve fire resistance. An important monomer, bis(*m*-aminophenyl) methyl phosphine oxide (DAMPO), was also prepared through a modification of the standard literature method [248]. Furthermore, controlled molecular weight thermoplastics and high gel fraction

containing thermosetting network systems based on this diamine were produced to explore new polyimide systems that could offer even better fire resistance.

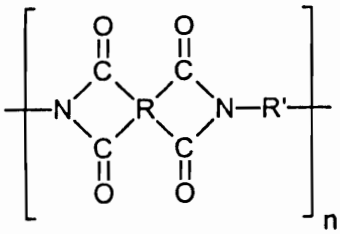
The literature review that follows in Chapter 2 contains discussions of polyimide synthesis methods, structure-property relationships, various types of thermosetting polyimides and the synthesis of phosphorus containing polyimides. Chapter 3 describes the experimental procedures that have been conducted in this research. Experimental results are discussed in Chapter 4, followed by the conclusions in Chapter 5.

Chapter 2. LITERATURE REVIEW

2.1 Introduction

Polyimides are condensation or step polymers that have cyclic imide functionalities in their repeat unit, as shown in Figure 2.1.1. They are generally derived from the reaction of organic diamines and organic tetracarboxylic acid or derivatives thereof [1,2]. Excellent thermal and mechanical properties can be obtained from fully aromatic structures and these aromatic polyimides can be utilized for many high performance applications, providing the backbone is properly designed. Many books and reviews discussing polyimides are available in the literature [3-7].

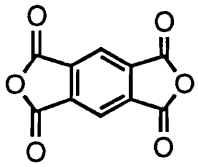
This chapter provides a background to the experimental section that follows, and emphasizes the most recent developments. Section 2.2 will discuss the common synthetic methods used to prepare polyimides, while the next two sections deal with the structure-property relationship of thermoplastics polyimides and thermosetting polyimides, respectively. The final section reviews phosphorus-containing polyimides systems. The most commonly utilized dianhydrides and diamines for polyimides synthesis are listed in Table 2.1.1. Accepted abbreviations will be used throughout the remainder of the thesis.



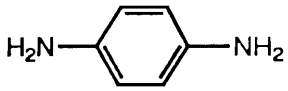
where R = cycloaliphatic, aromatic
R' = aliphatic, aromatic

Figure 2.1.1. Structure of a polyimide.

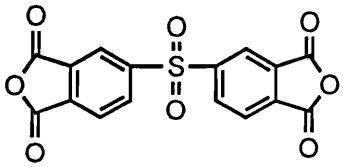
Table 2.1.1 Commonly used dianhydrides and diamines.



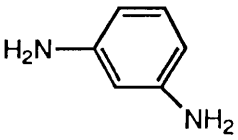
PMDA



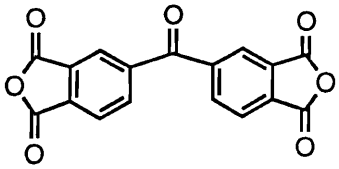
p-PDA



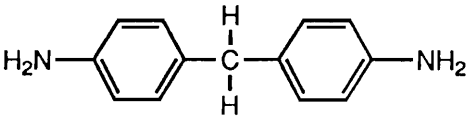
DSDA



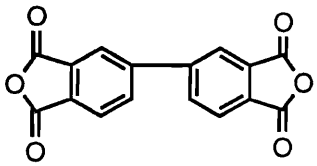
m-PDA



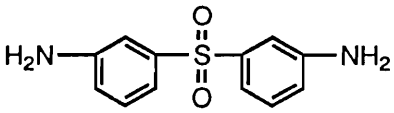
BTDA



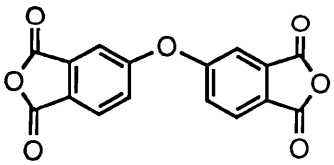
MDA



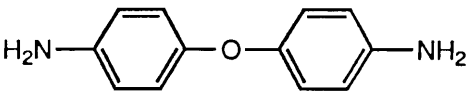
BPDA



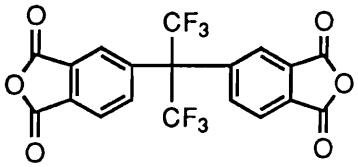
m-DDS



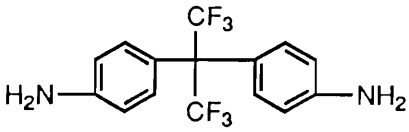
ODPA



4,4'-ODA



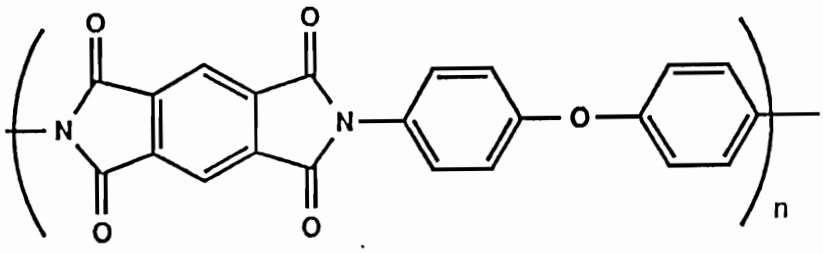
6FDA



6F Diamine

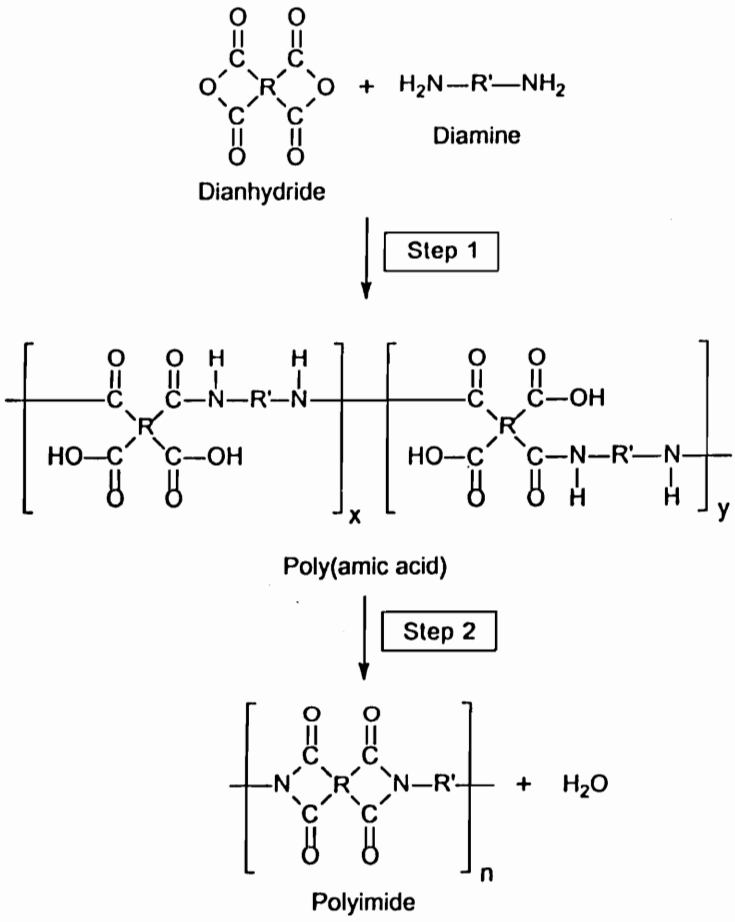
2.2 Synthesis of polyimides

The first commercially produced polyimide (Tradename: Kapton®, with repeat units shown below) was introduced by DuPont [8-12] over three decades ago, and extensive research has been reported since that time that has resulted in a much better understanding of the synthesis, characterization, and structure property behavior of polyimides. The following sections provide a summary of the most important polyimide synthetic procedures.



2.2.1 Classical 2-step route.

The most common method of preparing aromatic polyimides involves the reaction of an aromatic tetracarboxylic acid anhydride with an aromatic diamine. The first step involves the formation of a soluble, processable poly(amic) acid intermediate, followed by the generation of an aromatic polyimide through dehydration and cyclization of the poly(amic) acid (Scheme 2.2.1). This method is representative of the initial work on aromatic polyimides [13-16] and remains the most practical way to synthesize high performance polyimides. This approach is based on the reaction of a suitable diamine with a dianhydride in a dry polar, aprotic solvent such as N-methylpyrrolidone (NMP), dimethylacetamide (DMAc), dimethylsulfoxide



Scheme 2.2.1 Polyimide synthesis via the classical two step route.

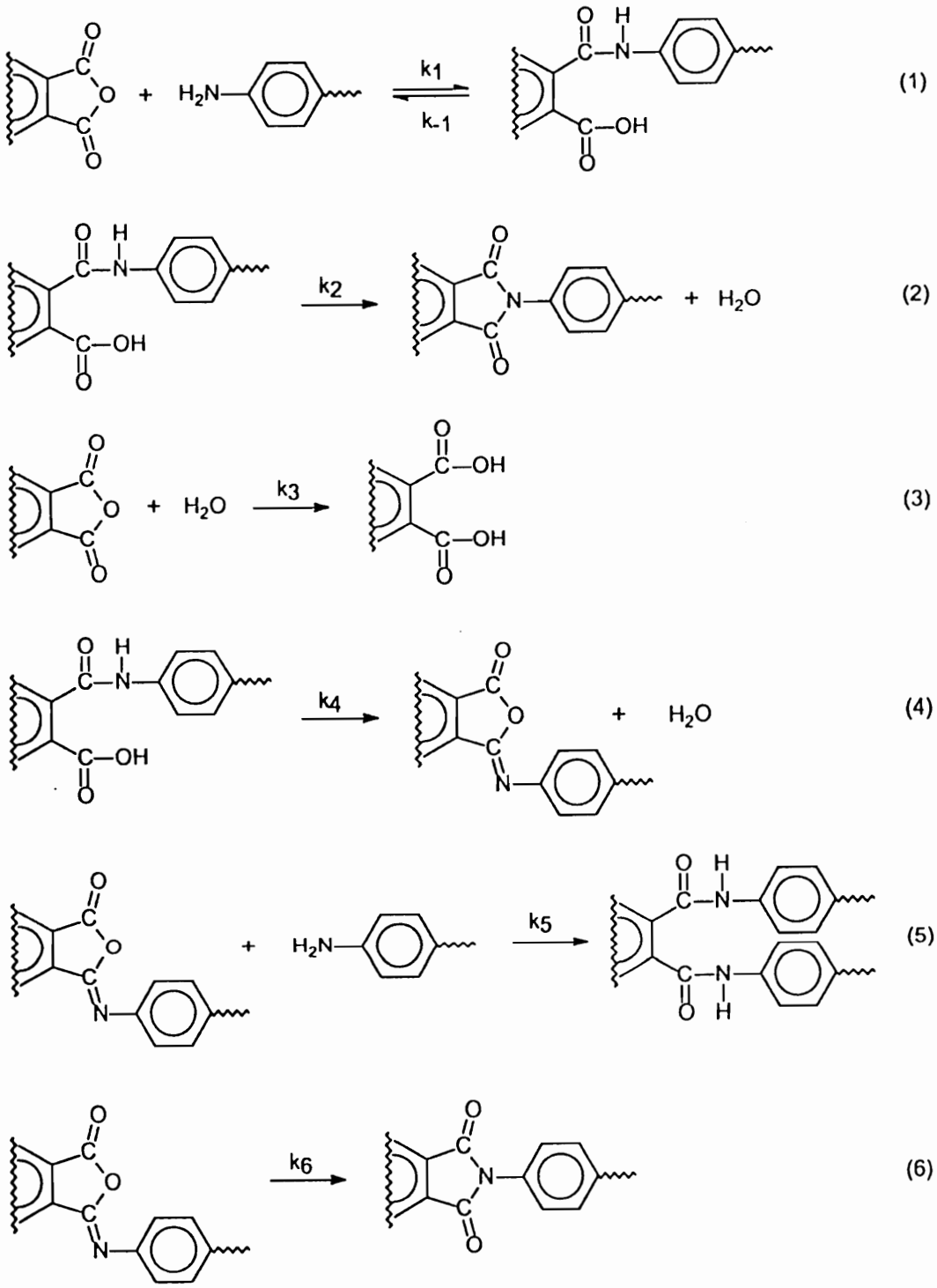
(DMSO) or dimethylformamide (DMF). The stirred reaction proceeds at ambient temperature to procedure poly(amic) acid within 24 hours or less, depending on the reactivity of the component. The poly(amic) acid is then cyclized via thermal, chemical or via solution imidization. The reason for this two-step method is that many of the resulting polyimides (e.g., Kapton®) are insoluble and infusible due to their rigid aromatic repeat unit. On the other hand, the soluble and processable poly(amic) acid intermediates facilitate the generation of films via spin coating procedures.

2.2.2.1 Poly(amic) acid formation:

In the classical two-step reaction of poly(amic) acid formation, any aliphatic, cyclo-aliphatic, or aromatic dianhydride can generally be used with a suitable diamine. The soluble poly(amic) acid contains at least two structural isomers, depending on the symmetry of the initial dianhydride [17]. The reactive nature of the diamine is very important for successfully producing a high molecular weight poly(amic) acid. Highly basic diamines (e.g., aliphatic diamines) will react with the preformed poly(amic) acid linkage, which prevents the reaction of the protonated amine groups with the anhydride. This changes the stoichiometry of the initial monomer ratio, and thus, these diamines are not suitable for polyimide synthesis. Diamines with low basicity are considered less suitable for poly(amic) acid synthesis since they may not exhibit sufficient nucleophilic characteristics in order to rapidly react with the dianhydride. It has been suggested that an optimal diamine should have a pK_a of 4.5-6 [18]. Of course, the basicity and the reactivity of the second amine

group depends on the exact chemical structure of the diamine. Reactivity of this amine is also influenced as a result of the reaction of the first amine-group due to the electronic nature of the amide linkage formed [18,19].

Poly(amic) acid formation is a typical step growth polymerization, which requires high purity monomers and the elimination of side reactions [20]. The most significant such side reaction involves the interaction of the water derived from the non-polar, aprotic solvents (e.g., NMP) with the dianhydride. Scheme 2.2.2 shows the poly(amic) acid formation reactions involved in the classical 2-step route [21-25]. In addition to the propagation reaction, five other potential reaction pathways are also listed here. The rate data from various literature references are listed in Table 2.2.1. It is generally believed that the propagation step involves an equilibrium between the amic acid and the initial dianhydride and diamine groups. The hydrolysis reactions in the PMDA/ODA system are suggested to be attribued to the hydrolysis of phthalic anhydride and not necessarily due to the amide groups. Scheme 2.2.2 and Table 2.2.1 outline the main reaction pathways. Even in the presence of water, the anhydride-amine reaction is five times faster than the corresponding hydrolysis of anhydride by water. However, once the diamine concentration has decreased, the competing reaction with water becomes significant. Hydrolysis of an anhydride group would lead to the formation of diacid moieties, which are inert when further reacted with the aromatic amines. Thus, the utilization of a dry solvent in a completely dry apparatus is extremely important in the synthesis of poly(amic) acids. The rate data illustrate that reactions 1 and 3 are of key importance, followed by reaction 2, and then reactions 4-6. Since no data has been published for reaction set 4-6



Scheme 2.2.2 Reactions involved in poly(amic) acid synthesis [21-25].

Table 2.2.1 Relative rate constants for reaction shown in Scheme 2.2.2 [21-27].

REACTION	RATE CONSTANT (s^{-1})
Propagation (k_1)	0.1–0.5
Depropagation (k_{-1})	10^{-5}–10^{-6}
Spontaneous Imidization (k_2)	10^{-8}–10^{-9}
Hydrolysis (k_3)	10^{-1}–10^{-2}
Isoimide Formation (k_4)	—
Diamide Formation (k_5)	—
Isomerization (k_6)	—

* Rate constants are estimated for a typical polymerization at ca. 10 wt% concentration, i.e. 0.5 M.

under poly(amic) acid formation, one can only expect that if isoimidization should occur in a significant amount, then reaction 6 would be the dominant pathway since the free amine concentration in reaction 5 should be very low [26,27].

The review described above indicates that polymerization should be conducted at high monomer purity and under very dry conditions. The monomer purity can easily be achieved by recrystalization or sublimation of the monomers. To do so, polar, aprotic solvents are generally dried by vacuum distillation over phosphorus pentoxide, which also aids in the removal of low levels of amine impurities present in this class of solvents [25,28-30]. It is interesting to note that Volksen and Cotts [31] (Table 2.2.2) demonstrated that the monomer concentration and the addition sequence had no effect on the resulting molecular weight of the poly(amic) acid prepared from highly purified PMDA and ODA in freshly distilled NMP in dry atmospheric conditions.

Regrettably, the solution behavior of poly(amic) acids is still poorly understood. Earlier, it was discovered that the PMDA/ODA solution viscosity increases in the initial stage of polymerization [19,32,33]. Subsequently, the viscosity decreases and this was generally believed to be a result of hydrolytic molecular weight degradation. Later research based on light scattering techniques of the resulting poly(amic) acid solutions attributed the initially high viscosity to the fact that the weight average molecular weights were higher than anticipated by the monomer stoichiometry [34,35]. These high molecular weights then decreased via equilibration over time and temperature until reaching the weight average molecular weight predicted by

the Carother's equation and the most probable molecular weight distribution (Figure 2.2.1). The explanation for the re-equilibration of the molecular weight was attributed to the presence of the monomer-polymer equilibrium, allowing for fragmentation and recombination of the polymer chains to attain the theoretical molecular weight distribution. It has also been suggested that the high reactivity of the PMDA/ODA system produced a heterogeneous system, possibly allowing reactions to occur at the solid-liquid interface, which is reminiscent of an interfacial-type polymerization [36,37].

Table 2.2.2 Effect of synthetic variables on the molecular weight of PMDA/ODA based poly(amic) acid [31].

PMDA/ODA	%Solids	$\bar{M}_w$ (calculated)	$\bar{M}_w$ (exp.)
0.8182	9.27	11,000	10,000
0.9804	0.31	42,000	37,000
0.9921	7.55	115,000	80,000
Addition of Solid PMDA to ODA Solution			
0.9259	9.55	10,800	9,000
0.9804	9.31	42,000	37,000
Addition of Solid ODA to PMDA Solution			
0.9259	9.58	10,000	10,500
0.9804	9.32	42,000	35,000
Additional of Solid PMDA to ODA Solution			
0.9725	18.6	30,000	29,000

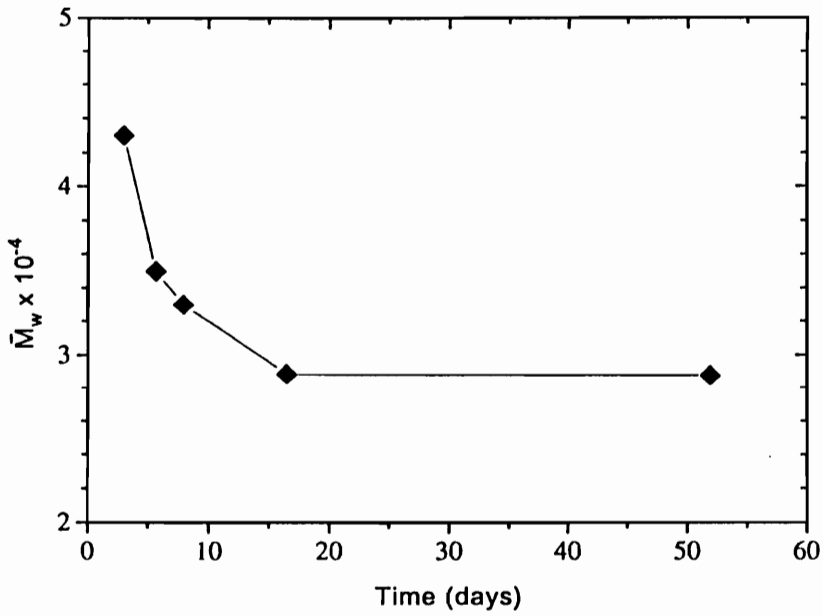


Figure 2.2.1 Re-equilibration of the weight average molecular weight of PMDA/ODA based poly(amic) acid as a function of time in NMP at ambient temperatures [34,35].

2.2.2.2 Imidization Methods:

Thermal imidization:

In the thermal imidization pathway, a programmed time and temperature treatment of the poly(amic) acid solution is believed to have been developed at NASA Langley, as seen below [61].

25°C: 1hr, heat to 100 °C within 1 hr

100°C: 1hr, heat to 200°C within 1 hr

200°C: 1hr, heat to 300°C within 1 hr

300°C: 1hr, cool to 25°C

The imidization is generally accomplished in an inert atmosphere or under vacuum to remove all traces of solvent and water. Normally, the temperature at the final stage should be higher than the product's T_g. This is by far the most common method used with insoluble polyimides to cast films from poly(amic) acid solution because it is relatively cost-effective and can be readily instituted and easily controlled in industrial settings [38,39,152].

Examination by mass spectrometry of a typical poly(amic) acid/NMP consolidation profile from ambient temperature to 350°C [40] is shown in Figure 2.2.2. Much of the resulting solvent is produced during temperatures ranging from ambient temperature to approximately 150°C. Both solvent and maximum evolution of water from imidization takes place between 150°C to 250°C, while solvent removal and final imidization is completed at 250°C and higher. Since solvent removal and maximum imidization occurs simultaneously, tremendous shrinkage and the resulting maximum stress in the polymer film can commonly occur [41-43].

Chemical imidization:

The chemical imidization of poly(amic) acid is conducted by using chemical reagents as catalysts for cyclodehydration at ambient tmperature or below the temperature at which thermal imidization occurs. The reagent most widely used is an equamolar mixture of pyridine/acetic anhydride [44-47]. The reaction mechanism for this chemical imidization is shown in Scheme 2.2.3 [48-50]. Using pyridine or triethylamine as the base catalyst, the amic acid reacts with acetic anhydride to form a mixed anhydride. Pathway A, it should be pointed out, is thermodynamically favorable. However for kinetically favorable isoimidization products (pathway B), it is also possible for the isoimide to isomerize to the thermodynamically more stable imide form (pathway C), which is supported by the fact that stronger amines, such as triethylamine, promote acetate formation and thus increase the back reaction leading to exclusive imide formation. This type of imidization is less attractive for the manufacture of commercial polyimides because of the need for additional reactants and the complexity of the process. Nevertheless, this approach eliminates the potential of hydrolytic molecular weight degradation during thermal consolidation. It has been reported [51] that a PMDA/ODA system prepared by chemical imidization has better elongation-at-break values than those resulting from thermal imidization. This knowledge could possibly offer a potential pathway to toughen otherwise brittle polyimides.

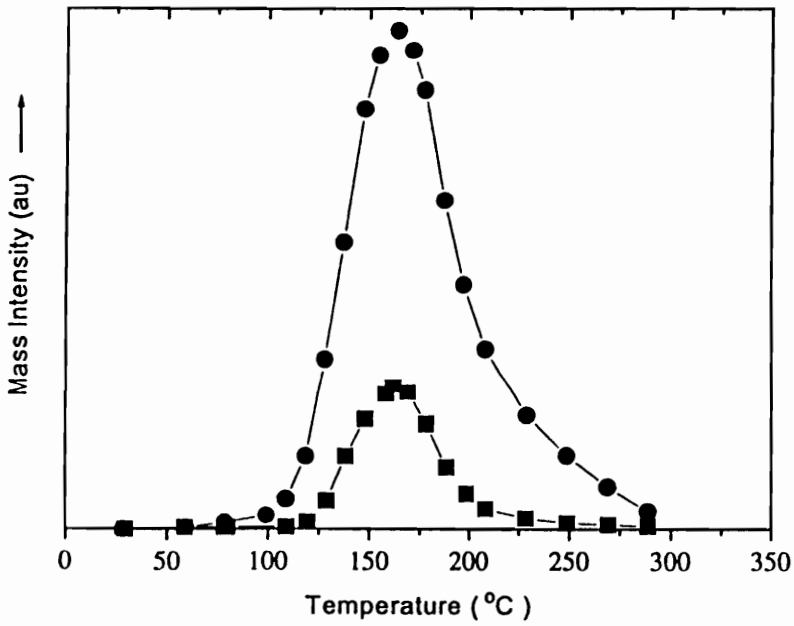
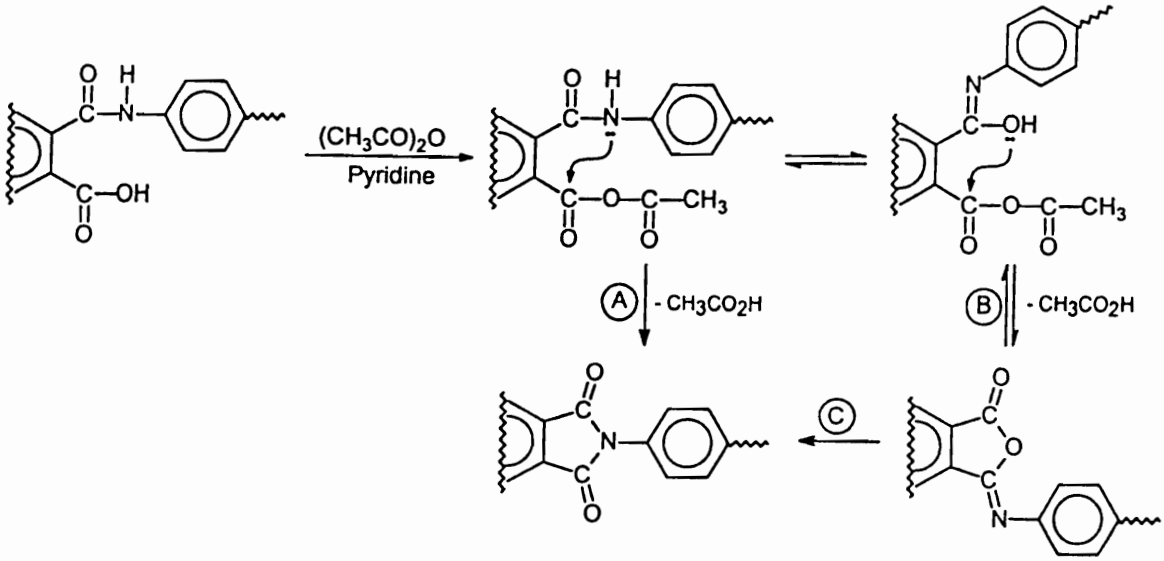


Figure 2.2.2 Evolution of volatiles during the thermal cure of PMDA/ODA poly(amic) acid. (●) Mass 18-water and (■) mass 99-NMP. Sample was predried at 90°C for 1 hour [40].



Scheme 2.2.3. Chemical imidization [48-50].

Solution imidization:

The solution imidization method was developed as result of the improved of the solubility of new aromatic polyimide systems. Depending on the molecular design of the monomers, it is possible to create fully imidized, high molecular weight, high T_g, polyimides that are soluble. This will be discussed in more detail in a later section. This solubility feature will allow much more flexibility in choosing the reaction media. In addition, a lower reaction temperature also avoids many degradation and side reactions that might occur at more elevated temperature.

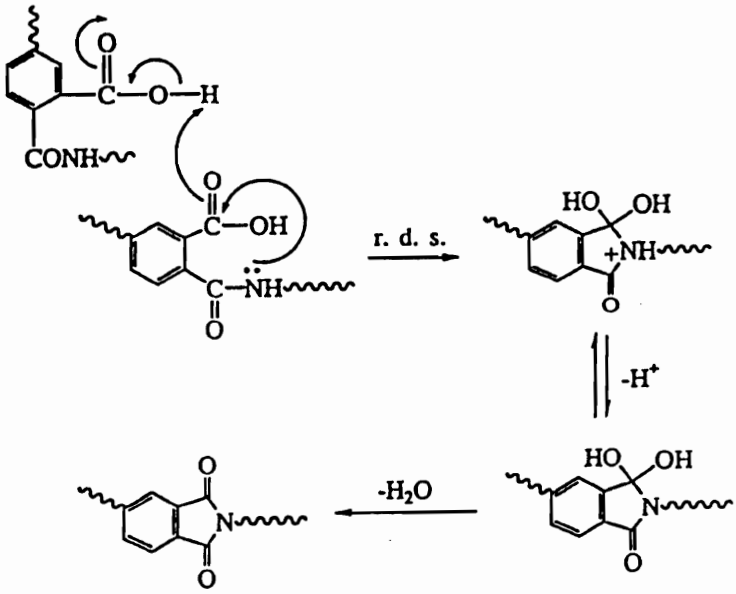
The key component of solution imidization is the utilization of an azeotroping agent as the solvent or co-solvent [52-54,151]. The imidization of poly(amic) acid can be conducted through the addition of an azeotroping agent such as *o*-DCB, xylene or cyclohexylpyrrolidone (CHP). At elevated temperatures (150-180°C), water generated from cyclodehydration was removed using such azeotroping agents. Complete imidization can be achieved within 16-24 hours. It is interesting to note that insoluble polyimides (e.g. exhibiting semi-crystalline morphology) will precipitate from the solution before the imidization is complete. This can actually be beneficial in the formation of submicron polyimide particles for composite fabrication [55,56].

Kim, et. al. [43,57] has demonstrated that the imidization mechanism is an acid-catalyzed second order process which may possibly permit lower reaction temperatures and shorter reaction times, as shown in Scheme 2.2.4. The rate determining step (r.d.s.) is the nucleophilic substitution of the carboxyl carbon by the amide nitrogen. The kinetic data was obtained by FT-

IR and non-aqueous titration of the residual amic acid. ^1H-^1H COSY spectra clearly showed partial degradation of poly(amic) acid chains due to initial water release. As the reaction proceeded, the endgroups recombined or the chains "healed" to form polyimides of higher molecular weight. Figure 2.2.3 is an example of this behavior, and may be indicative of similar patterns reported by others during thermal imidization [43,58-64].

2.2.2 Polyimides from poly(amic) acid salts

One important reason to form poly(amic) acid derivatives is to prevent theback reaction of poly(amic) acid to anhydride and amine by blocking the proton transfer, which occurs in a internal acid catalyzed manner, as shown in Scheme 2.2.5 [65]. The simplest approach is to neutralize the pendant carboxylic acid group with amines to form a polyelectrolyte (Scheme 2.2.6) [66,67]. Secondary and tertiary amines are preferable as shown in Scheme 2.2.6 (reaction 1&2). It should be pointed out that primary amines should be avoided since they can result in competitive transamidation reactions during further thermal imidization (Scheme 2.2.6, reaction 3). This method has been successfully utilized in preparing photo sensitive polyimide formulations, in which the polyimide precursor is a poly(amic) acid neutralized with suitable unsaturated aliphatic amines [66]. One recent application [68] for this approach is to precipitate the poly(amic) acid prior to neutralization. It is then readily formulated in aqueous amine solutions. The resulting solution is used as a carbon fiber coating to form a polyimide interface between the fiber and composite matrix upon thermal imidization. This provides a



Scheme 2.2.4. Possible reaction mechanism for the solution imidization process [43].

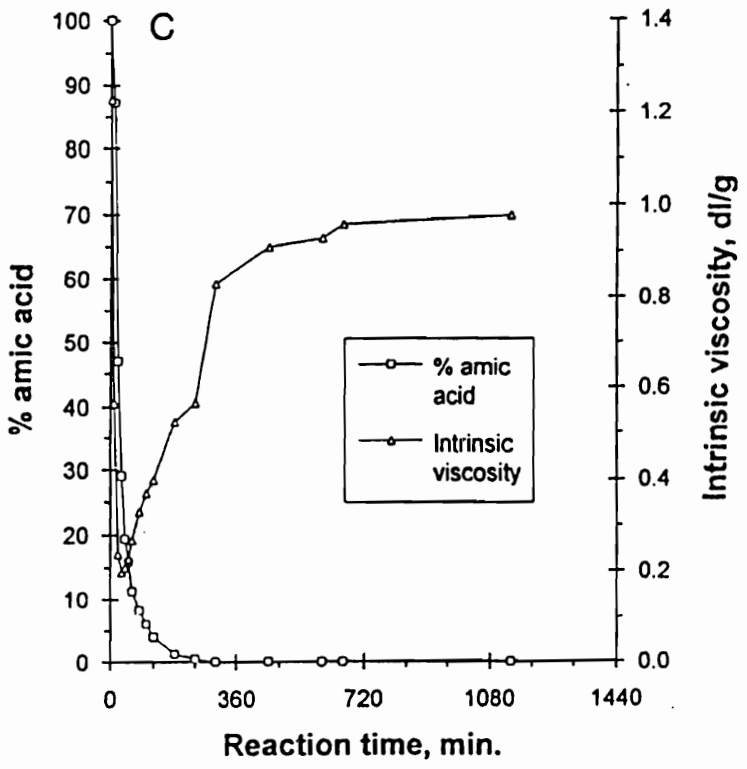
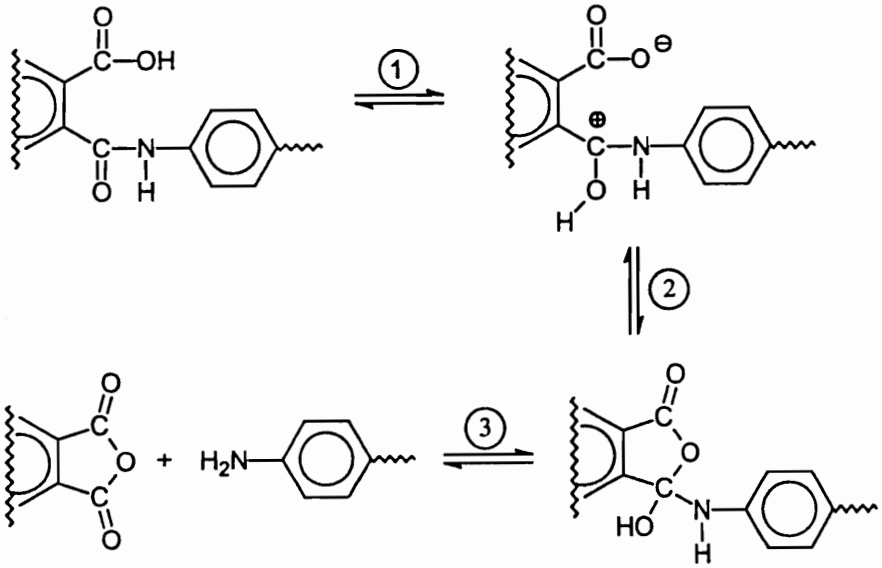
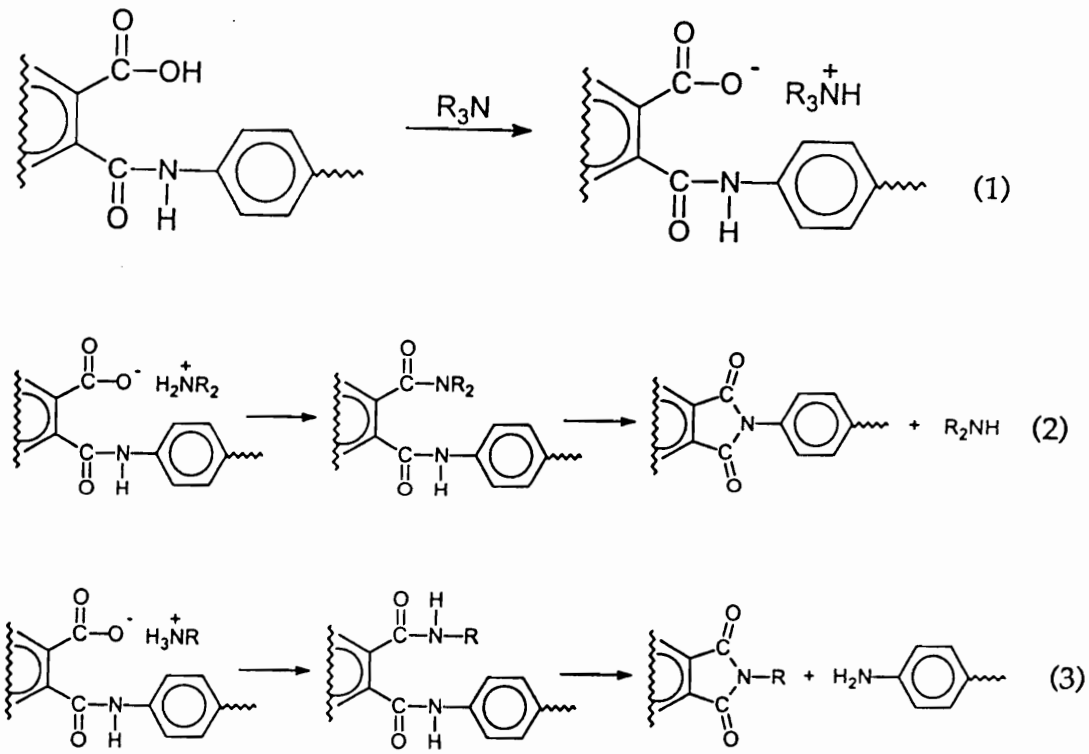


Figure 2.2.3. Remaining amic acid content and intrinsic viscosity as a function of reaction time at 180°C [43].



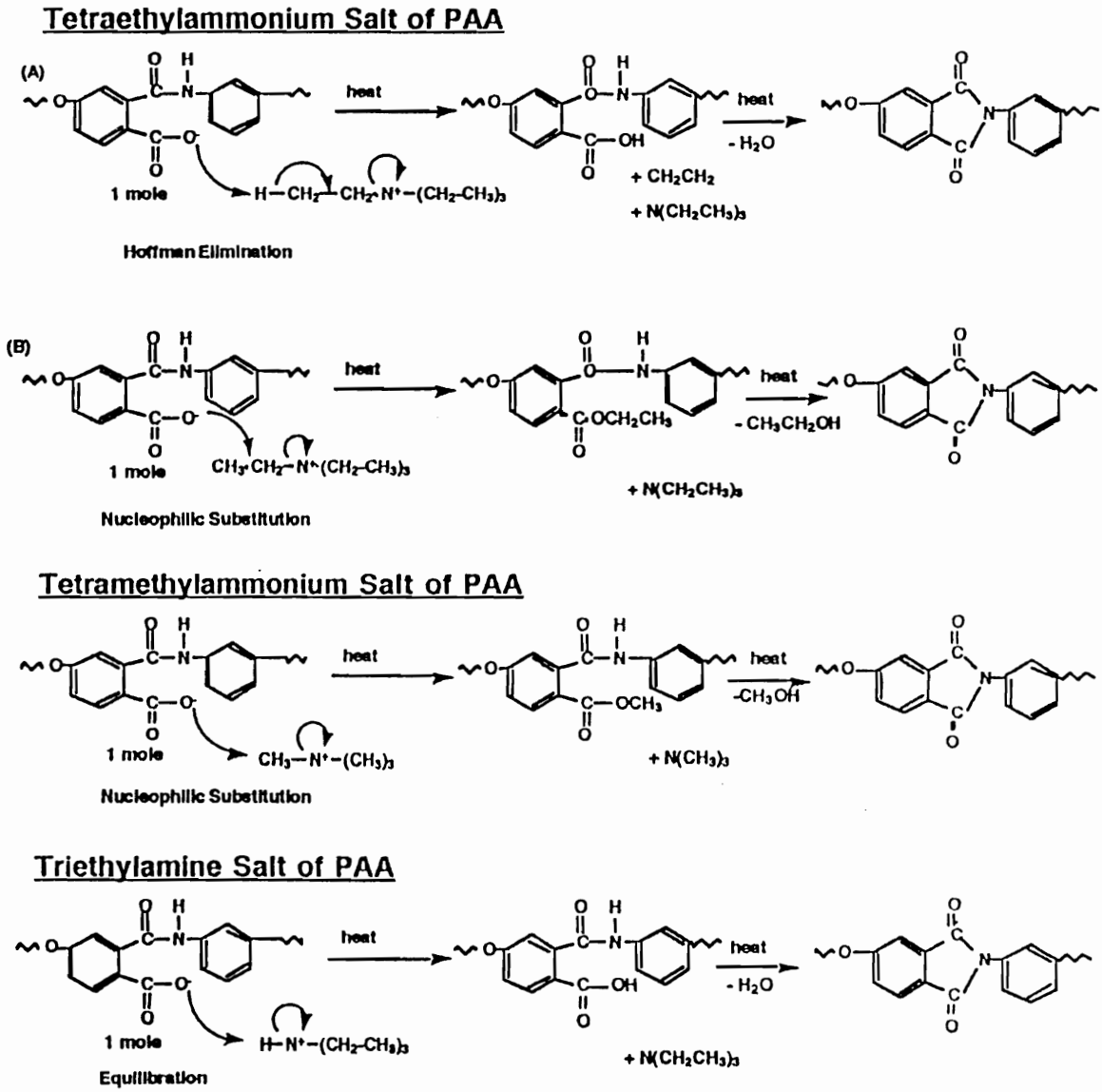
Scheme 2.2.5 Poly(amic) acid back reaction [65].



Scheme 2.2.6 Poly(amic) acid salt formation [66,67].

environmentally friendly approach for the processing of carbon fiber composites.

Poly(amic) acid salts solution display relatively high solution viscosity due to typical polyelectrolyte behavior [65]. Moreover, at very high dilution conditions, the viscosity dramatically increased because of counter ion diffusion and concomitant chain expansion. For comparable concentrations, the poly(amic) acid salt solution viscosity is about 5 times higher than the corresponding free acid in a typical polar, aprotic solvent. However, these salts imidize with greater ease than do the corresponding free acids. Some experimental data show that certain tertiary amines promote ring closure of the polyimide precursor with rates that can be an order of magnitude faster than the free acid [67]. Facinelli and Riffle [68] reported that polyimides prepared from melt imidization of the triethylammonium salts of poly(amic) acid retained their original molecular weight without crosslinking. Chain healing was observed from poly(amic) acid salts imidized at 300°C for 60 minutes by SEC methods. The proposed imidization pathway is shown in Scheme 2.2.7 and the results from GC-MS analyses suggest that the nucleophilic substitution route to form the poly(amic) ester, followed by the polyimide, is the predominant route of imidization for all of the quaternary ammonium poly(amic) acid salts studied.

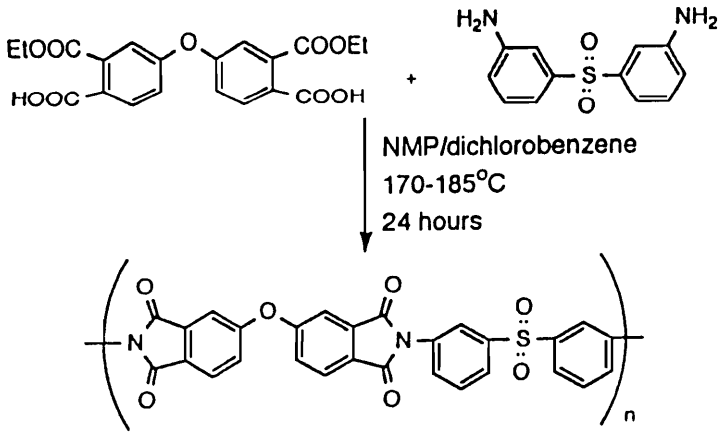


Scheme 2.2.7 Proposed mechanism for melt imidization of poly(amic) acid salts [68].

2.2.3 Polyimides from acid-ester route

The acid-ester route is an example of the so called "PMR" method. PMR refers to polymerization of monomeric reactants [69-72]. PMR commences with relatively stable monomers, i.e. hydrolytically stable, which then react at elevated temperatures to form a polyimide of sufficient molecular weight. The advantage of this type of synthesis is that it is relatively simple and can afford the possibility of preparing high solids content coating formulations. Some early commercial examples that use this approach are the Monsanto Skybond series of polyimide precursors [73], as well as PMR-15 [74], a resin developed for the aerospace industry. The latter will be addressed in more detail in the following sections dealing with thermosetting polyimides.

Polyimides synthesized from the diester-diacid derivatives of aromatic tetracarboxylic dianhydrides and aliphatic diamines or aromatic diamines in solution is called acid-ester route [71,75]. This approach is shown in Scheme 2.2.8. It has several real and potential advantages over the more conventional "two-step" synthesis. For example, the presence of even a small amount of moisture in glassware or in the polymerization solvents is not problematic since the acid-ester, rather than the dianhydride, is used for the polymerization. Furthermore, the acid-esters are generally more soluble in polymerization solvents than are the corresponding dianhydride or tetraacids. The initial solution viscosity of the acid-ester is low and provides better fiber wetting in composite applications. The acid-ester also anticipated



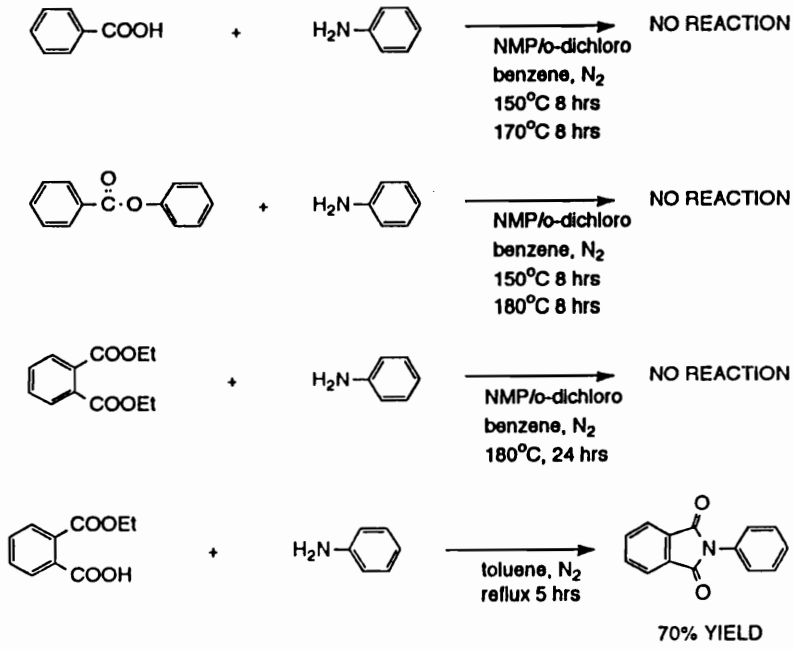
Scheme 2.2.8 Polyimide synthesis by ester-acid route [75].

to be less toxic and the polymerization could be conducted using a "one-pot" solution imidization method [76,77].

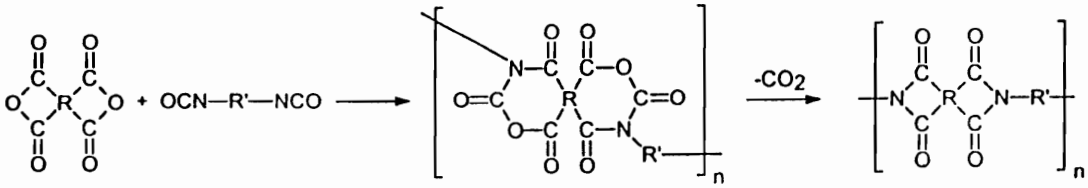
Moy and others [78] recently investigated the possible conversion of diester-diacid to dianhydride by model compounds, as shown in Scheme 2.2.9. Their results clearly indicate that anhydride can indeed be regenerated from ester-acids in solution at temperatures substantially lower than those required for quantitative imidization. Based on the model compounds study results, it was suggested that a solvent system using NMP/*o*-dichlorobenzene at temperatures of 170-180°C would be suitable for polyimide synthesis. Acetylene-terminated ODPA/3,3'-DDS imide oligomers of controlled molecular weight were successfully synthesized by this route and evaluated as a model system.

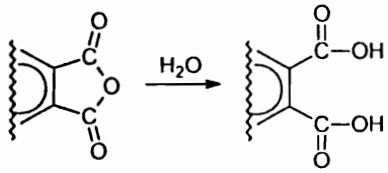
2.2.4 Polyimides from aromatic dianhydride and diisocyanate

Imide formation from the reaction of isocyanates with anhydrides has been known for a long time [79]. However, applying this process to polyimide synthesis began around 1960s and this mechanism is much less understood than classical two-step route. The reaction of aromatic dianhydrides with aliphatic or aromatic diisocyanates is believed to form a cyclo seven-member intermediate, which then gives off CO_2 to form the polyimide (Scheme 2.2.10, top reaction) [80]. It has been reported that the addition of water would accelerate the anhydride/isocyanate reaction, and some possible water-related modifications are also shown in Scheme 2.2.10, reactions 1-5 [81-85]. In general, the synthesis is initiated at low temperatures (0-10°C) to minimize

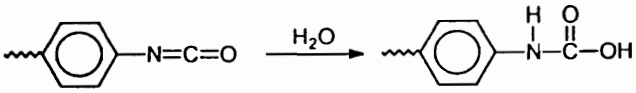


Scheme 2.2.9 Model investigations of the ester-acid route [78].

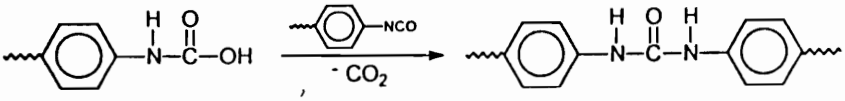




(1)



(2)



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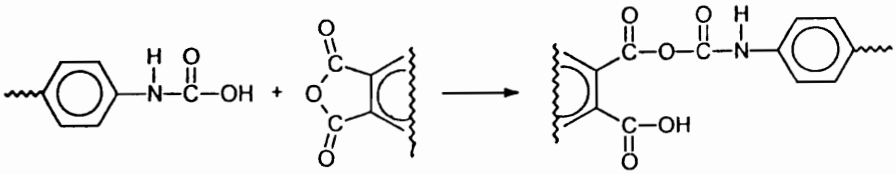

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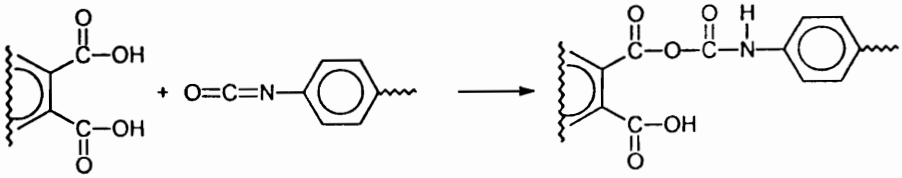


(5)

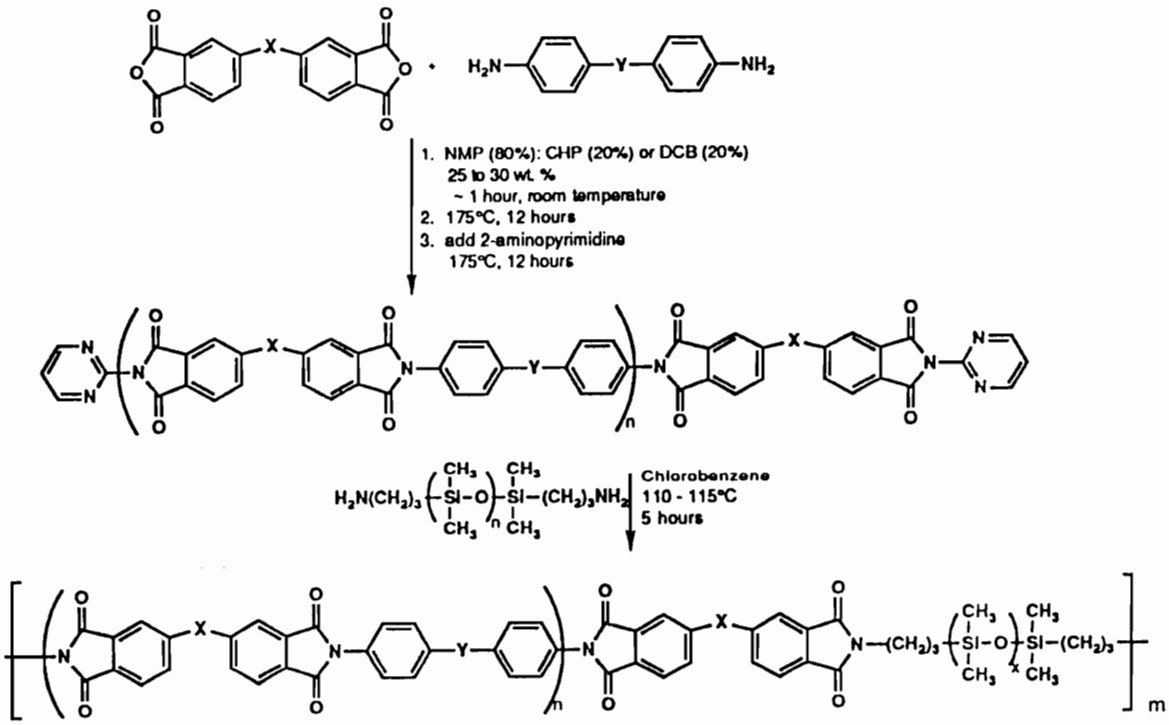
Scheme 2.2.10 Polyimides from dianhydrides and diisocyanates [85].

the reactions of the diisocyanate with the solvent. CO_2 gas is evolved when the polymerization mixture is heated to 50-100°C. This approach is useful for preparing polyimide foams since the evolution of carbon dioxide can be utilized as a blowing agent [82].

2.2.5 Polyimides from transimidization (amine-imide exchange)

The chemistry of preparing N-alkyl imides by the exchange reaction of an alkyl amine is well documented [86]. The formation of amine-imide exchange reaction, also referred to as transimidization, involves the high temperature equilibrium of an imide in the presence of a different amine [87,88]. The diamine used for this exchange should be more basic or nucleophilic than the monoamine that is exchanged. The monoamine 2-aminopyridine in combination of a pK_a of 6.8 has been widely used [89]. This approach has been particularly successful when utilizing transition metal catalysis in the preparation of polyetherimides. Polyimides of sufficient molecular weights have been obtained when the reaction was conducted at a temperature well above the T_g of the polymer, and where vacuum was applied to remove volatile amine [87,88].

Rogers [90,91] reported that transimidization can be utilized to synthesize perfectly alternating segmented imide siloxane copolymers (Scheme 2.2.11). Their approach utilized a less toxic 2-aminopyrimidine to enhance the reactivity even further than the 2-aminopyridine. Imide oligomers endcapped with 2-aminopyrimidine were reacted with aminopropyl terminated (dimethyl siloxane) oligomers. Under relatively



Scheme 2.2.11 Synthesis of perfectly alternating segmented imide siloxane copolymers [91].

mild conditions (3 hours at 75°C), nearly quantitative yields of high molecular weight, fully imidized perfectly alternating segmented imide siloxane copolymers were obtained

2.2.6 Polyimides from nucleophilic aromatic substitution

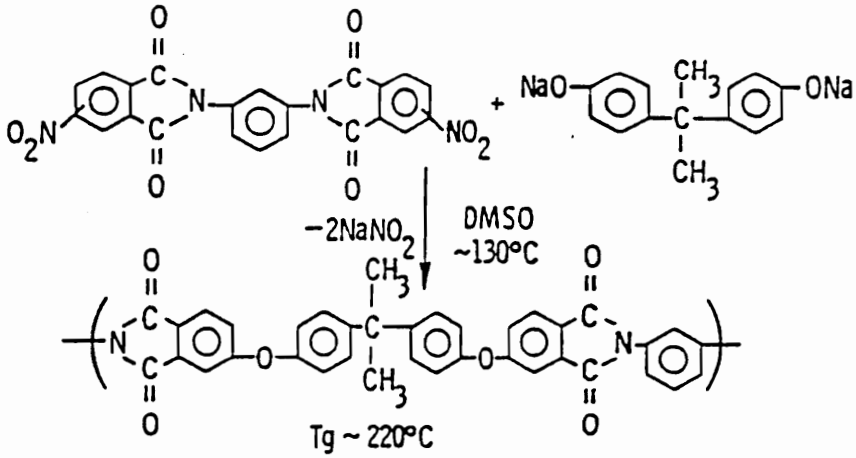
A typical example of synthesizing polyimides from nucleophilic aromatic substitition is by displacing the activated nitro group with a phenoxide anion at the formation of the polyetherimide, which was developed by the General Electric Company [92] (Scheme 2.2.12). The polymerization is carried out at 80-130°C in a polar solvent (NMP, DMAc), and it is believed that the Ultem™ precursor, BPADA, was derived in this manner [93,94].

Davies, et al. [95] reported a series of new diether dianhydrides from common bisphenols and halophthalic anhydrides by two different aromatic nucleophilic substitution routes, as shown in Scheme 2.2.13 & 2.2.14. Synthesis via the dianhydride route is limited by the ease of isolation of the dianhydride, while the nucleophilic aromatic substitution polymerization method results in polymers of limited molecular weight.

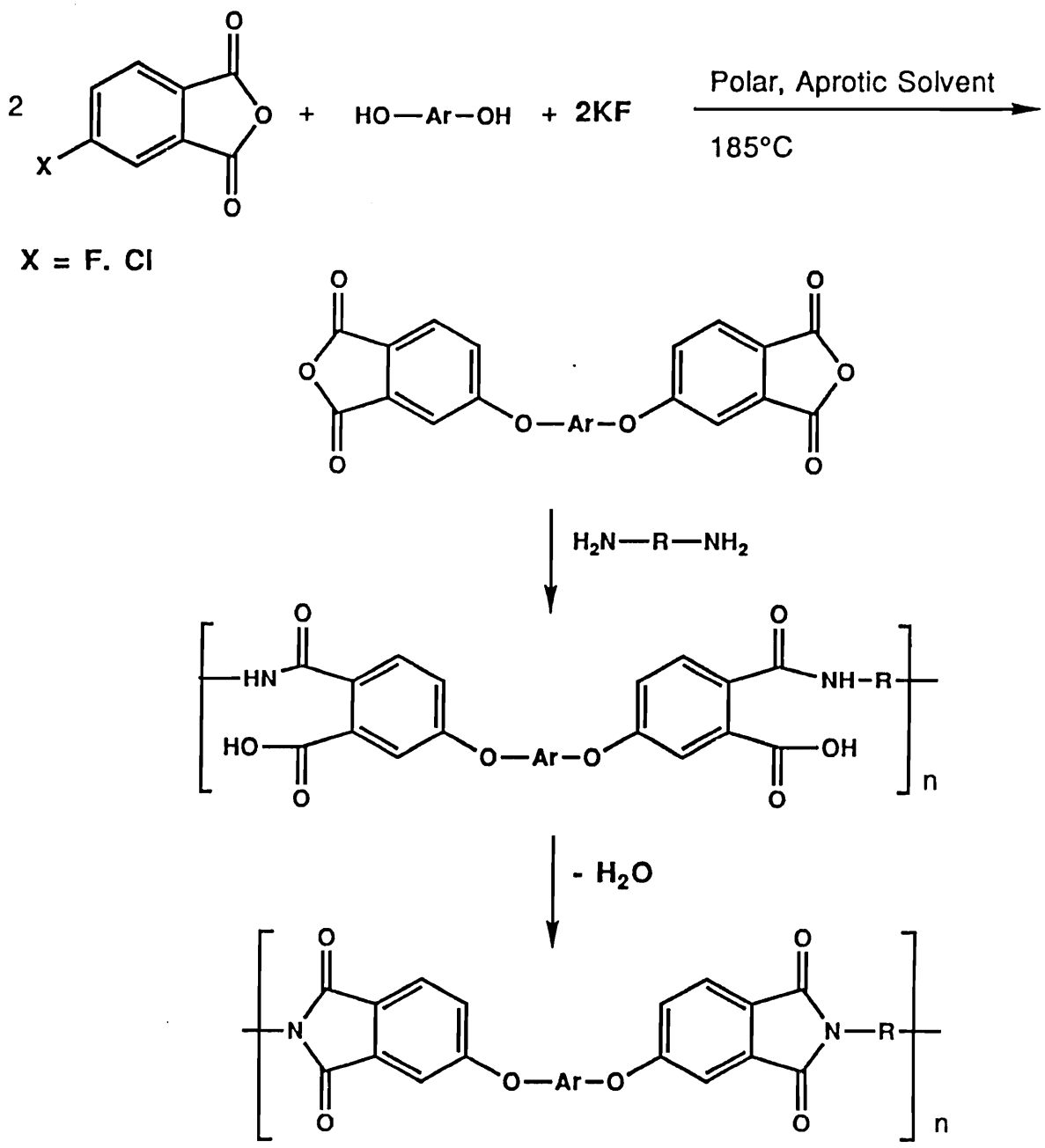
2.2.7 Other methods of polyimide synthesis

Many other methods have been reported for polyimides synthesis. For example, polyimides can be synthesized via phthalide derivatives, which permits a low temperature approach [96,97]. Harris, et al. reported that high

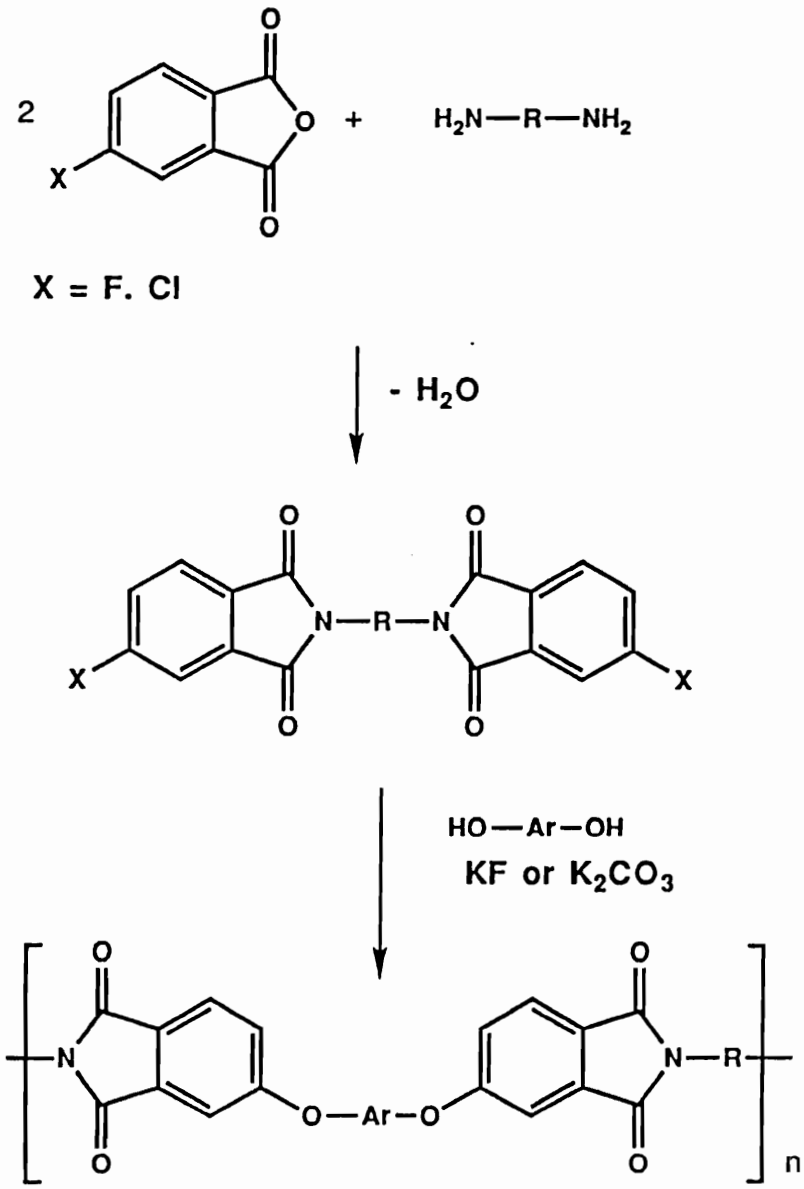
molecular weight polyimides in refluxing m-cresol without azeotroping agents via a "one-step" route in which no poly(amic) acid formation was needed [98,99]. Diels-Alder reactions have also been reported for the preparation of polyimides [100-102]. In addition, polyimides prepared by palladium-catalyzed coupling reaction of diaryl halide monomers have been reported [103-106].



Scheme 2.2.12 Polyimide via nitro displacement [92].



Scheme 2.2.13 Schwartz route for synthesizing polyetherimides [95].



Scheme 2.2.14. Reverse Schwartz route for synthesizing polyetherimides [95].

2.3 Structure-property relationship of polyimides

2.3.1 Introduction

Thermally stable polymers have been defined as polymers containing high aromatic content and/or heterocyclic units with relatively rigid segments that impart high glass transition temperatures, good thermooxidative stability and desirable mechanical properties [107]. Polyimides are one of the most important class of these high performance materials, and if properly designed, they can retain their useful properties during and even after short or long-term exposure to various single or combined conditions (e.g. temperature, time, atmosphere, stress, chemical action, electrical action, solvent, etc.). The structure factors which contribute to the heat resistance of polyimides can be summarized as follows:

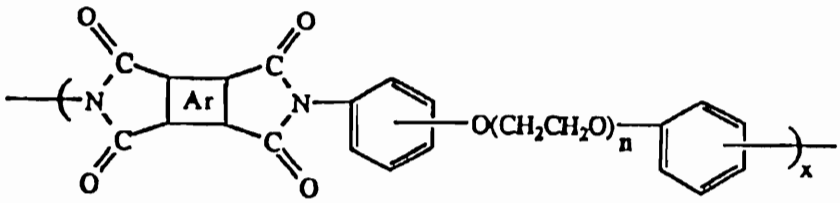
- Primary bond strength
- Secondary bonding forces (hydrogen bonding 6-10 Kcal/mole, polar interactions, Van Der Waals forces, etc.)
- Resonance stabilization (40-70 Kcal/mole)
- Mechanism of bond cleavage (recombination, unzipping)
- Molecular weight and distribution
- Molecular symmetry (regularity of structure)
- Rigid intrachain structure
- Close packing (order of crystallinity)
- Crosslinking and branching
- Purity

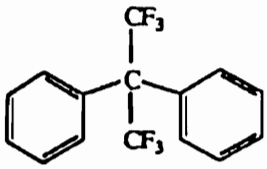
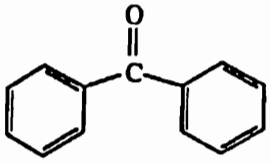
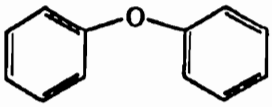
Thus, polyimides can be often be specifically designed for precise applications that require high chemical, physical, electrical or mechanical properties. There are, however, limitations. For example, the structures that impart thermal stability typically also result in intractability and infusibility. Therefore, the development of high molecular weight polyimides that are both heat resistant *and* processable is very challenging. Understanding the structure-property relationships are critical to the appropriate molecular design of the polyimide. This section, then, will focus on designing polyimide structures by introducing a flexible spacer, bulky side groups or asymmetry. Several commercial polyimides will be used as examples. Molecular weight control and polyimide blends will also be addressed.

2.3.2 Introduction of a flexible spacer

In order to improve processability, much work has been done with the introduction of flexible spacers in the polyimide backbone [108-112,150]. Harris, et al. utilized an aliphatic oxyethylene based diamine with a variety of dianhydrides to form the polyimides listed in Table 2.3.1 [111,113,114]. As expected, the increase in chain length resulted in lower glass transition temperatures and enhanced solubility and processability. However, lower bond strength from the aliphatic units resulted in decreased thermal oxidative stability. The only structures that retained their excellent thermal stability were those that did not contain any aliphatic units. Inoue, et al. [115] also reported that greater aromaticity in the pyromellitimides increased

Table 2.3.1 Glass transitions of polyimides containing oxyethylene units [111,113,114].



-Ar- DIANHYDRIDE	META or PARA	n	Tg	Tm	TGA
	p	1	255	---	460
	p	2	180	---	425
	p	3	175	---	425
	p	4	140	---	385
	p	1	246	460	438
	p	2	235	410	425
	p	3	200	395	430
	m	1	192	290, 315	455
	m	2	154	243	430
	p	1	330	505	436
	p	2	320	465	444
	p	3	320	450	415
	m	1	134	---	----
	m	2	128	---	----
	p	1	184	470	----
	p	2	164	370	----

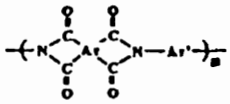
thermal oxidative stability in both air and nitrogen, according to the following order: tolan>stilbene>bibenzyl.

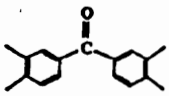
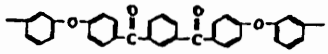
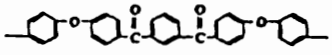
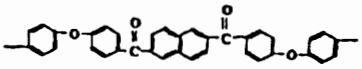
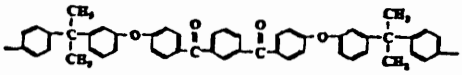
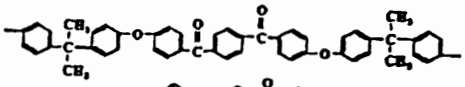
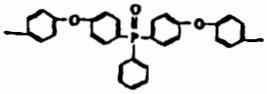
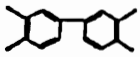
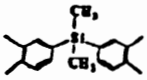
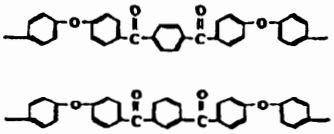
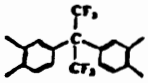
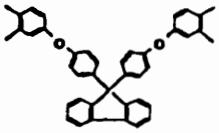
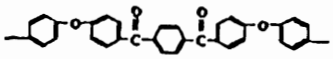
Dianhydride or diamine monomers containing ether, sulfone, sulfide, carbonyl, phosphine oxide, or dimethylsilyl bridge units have also been investigated. The polyimides containing phosphine oxide groups have many unique properties and will be addressed in detail in a later section. Hergenrother, et al. [116-118] investigated a series of polyimides containing ether and carbonyl connecting groups (Table 2.3.2). Many of these were semicrystalline in nature and some of them exhibited excellent tensile and adhesive properties, exceptional resistance to solvents and strong base, and high thermal oxidative stability. It has been reported that the thermal resistance of various dianhydrides as measured by thermal gravimetric analysis follows the sequence shown in Scheme 2.3.1 [110]. On the other hand, the effect of variations of the bridging moiety in the diamine portion of a BTDA based polyimide is shown in Table 2.3.3.

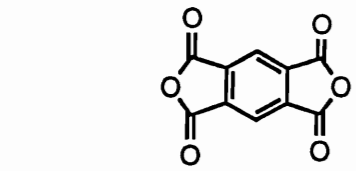
2.3.3 Introduction of a bulky side group

Polyimides have been synthesized with large pendant groups in order to improve their solubility by reducing the charge-transfer complex formed between polyimide chains through steric hindrance [149]. For example, 3,6-diphenylpyromellitic dianhydride was polymerized with various aromatic diamines in refluxing *m*-cresol containing isoquinoline by a one-step procedure to yield phenylated pyromellitimides [119]. By introducing

Table 2.3.2 Thermal transitions of polyimides containing ether and carbonyl connecting groups; ND: not detected [117].



Ar	Ar'	Polyamide acid η_{inh} (dl/g)	Tg - Tm °C
		0.67	207 - ND
		0.81	222 - 350
		0.42	246 - 424
		0.55	164 - ND
		0.65	222 - ND
		0.64	258 - ND
		1.25	222 - ND
		0.41	245 - 414
		1.10	206 - ND
		1.40	236 - ND
		0.64	235 - ND
		1.26	253 - ND



PMDA

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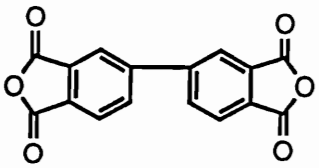

BPDA

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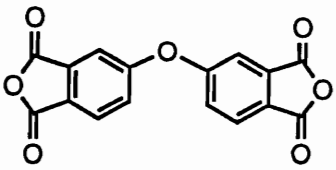
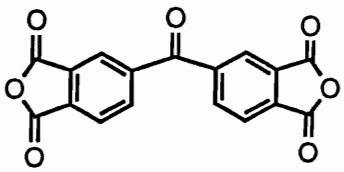


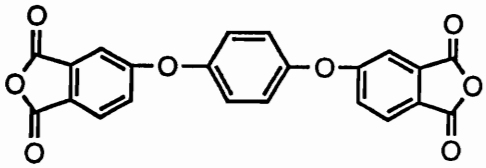
ODPA

>



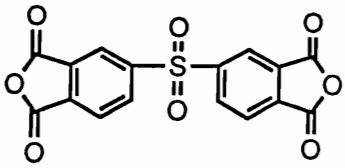
BTDA

>



O-phenyl-O

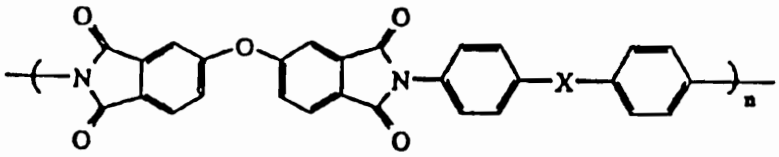
>



DSDA

Scheme 2.3.1 Thermal resistance of dianhydrides [110].

Table 2.3.3. The influence of bridging group of the diamine portion on the glass transition [110].



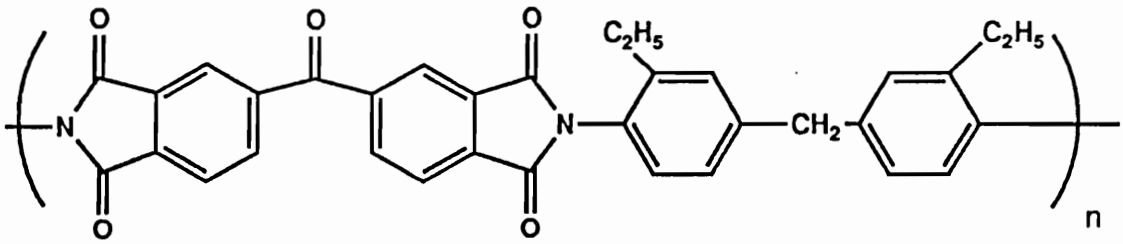
-X-	Glass Transition, °C
	200
	250
-S-	265
-O-	270
-CO-	280
$-SO_2-$	310

aromatic phenyl side groups, the solubility increased without substantially decreasing the rigidity of the polyimide backbone.

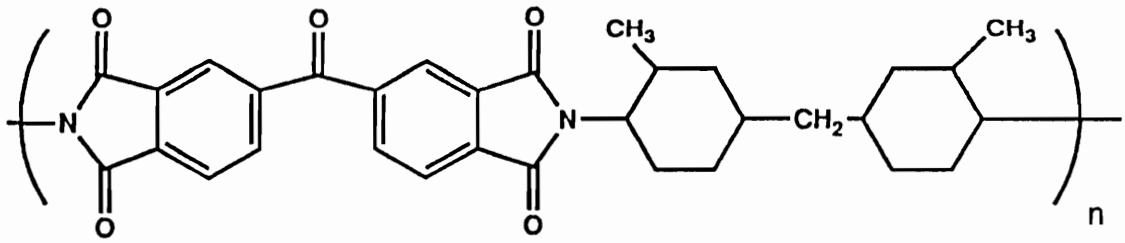
Pendant alkyl groups in the polyimide repeat units have also been reported [120]. BTDA polymerized with methyl or ethyl-substituted diamines result in soluble polyimide with the structures shown in Figure 2.3.1. Incorporating different pendant alkyl groups and the resulting effect on glass transition temperature is depicted in Figure 2.3.2 [110,121]. The presence of pendant isobutyl, isopropyl, methyl, hydroxyl, and methoxy groups on the diamine or dianhydride also impart solubility in conventional organic solvents to high molecular weight bis(phthalic anhydrides)s and polypyromellitimides.

2.3.4 Introduction of asymmetry

Electronic interactions, and in some cases polyimide crystallinity, can be reduced by introducing kinks or asymmetry into the polymer backbone (through ortho- or meta- linkages). Bell, et al. investigated isomeric diamines with BTDA or PMDA, as illustrated in Table 2.3.4 [122-125]. The results indicate that glass transition temperatures decreased by about 30°C for polyimides based upon BTDA, and about 100°C for PMDA. St. Clair, et al. also reported similar trends using isomeric diamines reacted with 6FDA and ODPA anhydrides as shown in Table 2.3.5 [126,127]. Processability and solubility improved, although at the expense of lowering the glass transition temperature.

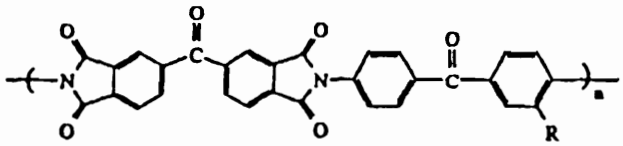


BTDA/bis(4-amino-3-methylcyclohexyl) methane



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

Figure 2.3.1 Methyl- and ethyl-substituted benzophenone based polyimides [120].



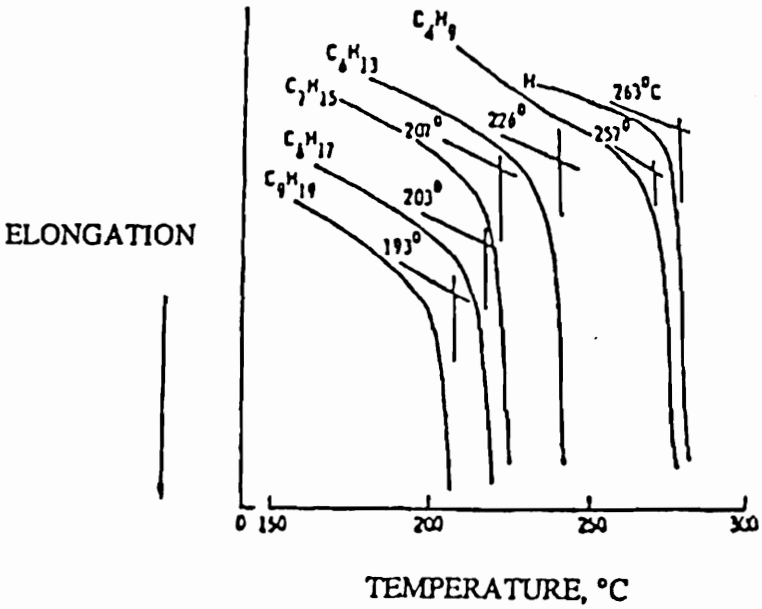


Figure 2.3.2 Thermomechanical analysis of polyimides with pendant alkyl groups [121].

Table 2.3.4 Glass transitions of polyimides from isomeric diamines of diaminobenzophenone (DABP), diamino biphenyl (DABiP), methylene dianiline (MDA), or oxydianiline (ODA) and benzophenone tetracarboxylic dianhydride (BTDA) or pyromellitic dianhydride (PMDA) [122].

Dianhydride	Diamine	Glass Transition, °C
BTDA	p, p-DABP	295
BTDA	m, p-DABP	283
BTDA	m, m-DABP	264
BTDA	o, p-DABP	289 (N, TBA)
BTDA	o, m-DABP	259
BTDA	o, o-DABP	289
PMDA	p, p-DABP	380
PMDA	m, p-DABP	339
PMDA	m, m-DABP	321
BTDA	m, p-MDA	259
BTDA	m, m-MDA	234
BTDA	o, p-MDA	289
BTDA	o, m-MDA	258
BTDA	o, o-MDA	285 (N, TBA)
BTDA	p, p-ODA	279
BTDA	o, p-ODA	278
PMDA	p, p-ODA	361 (A, TBA)
PMDA	o, p-ODA	386 (A, TBA)
BTDA	p, p-DABiP	382 (A)
BTDA	o, p-DABiP	305

Imidization environment: constant temperature of 300°C and vacuum, unless noted (N) for nitrogen or (A) for air; TBA: glass transition determined by torsional braid analysis.

Table 2.3.5 Glass transitions of polyimides from isomeric diamines of oxydianiline (ODA) or aminophenoxybenzene (APB) and oxydianhydride (ODPA) or hexafluoroisopropylidene (6F) dianhydride [127].

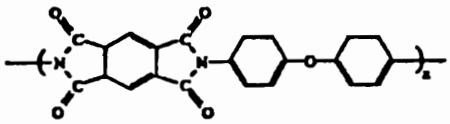
Polymer	η_{inh} (dl/g)	Tg, oC	Refractive Index (n)
6F + 3,3'-ODA	1.00	244	1.60
6F + 2,4'-ODA	0.75	276	--
6F + 3,4'-ODA	0.79	280	1.60
6F + 4,4'-ODA	1.11	326	1.60
ODPA + 3,3'-ODA	1.09	186	1.69
ODPA + 2,4'-ODA	0.77	264	1.67
ODPA + 3,4'-ODA	0.61	245	1.69
ODPA + 4,4'-ODA	0.34	273	1.69
6F + 1,4(4)-APB	1.82	281	1.60
6F + 1,3(4)-APB	1.58	255	1.62
6F + 1,4(3)-APB	1.19	230	1.61
6F + 1,3(3)-APB	1.02	209	1.61
ODPA + 1,4(4)-APB	1.46	245	1.67
ODPA + 1,3(4)-APB	1.29	217	1.69
ODPA + 1,4(3)-APB	1.06	204	1.68
ODPA + 1,3(3)-APB	0.98	182	1.68

2.3.5 Commercial polyimides

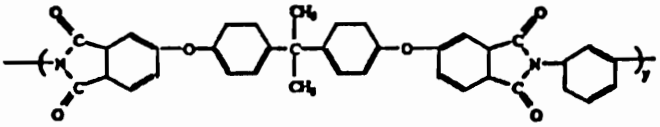
Several commercial polyimides are listed in Table 2.3.6 [128]. The structure-property relationship of these commercial samples is also highlighted here. The rigid structure of the classic, fully imidized Kapton™ polyimide has a weak transition near 380°C, indicated by torsional braid analysis, and is only soluble in sulfuric acid. Thus, it can only be processed using a solution containing a poly(amic) acid intermediate. However, as previously discussed, the poly(amic) acid is hydrolytically unstable with a limited shelf life. Other limitations of the solution technique include the necessity of maintaining a high temperature for the quantitative imidization and the elimination of water as the byproduct. Thus, this type of polyimide can only be utilized for films, coatings, and film adhesives, and not for structural parts.

Using fully imidized polyimides would alleviate many of the difficulties associated with processing poly(amic) acid precursors into polyimides. Therefore, employing structural modifications such as incorporating flexible spacers, bulky side groups, and asymmetry will greatly improve solubility. This allows the polyimides to be synthesized easily into their fully imidized form and thus will improve processability. Examples of using this approach include General Electric's Ultem™ polyetherimide, Ciba-Geigy's XU 218, Upjohn's 2080 and Mitsui-Toatsu's or Rogers's LARC-TPI.

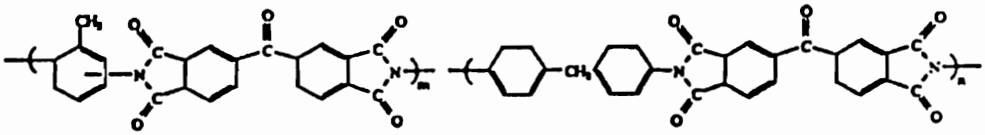
Table 2.3.6 Representative structures of some commercially available polyimides [128].



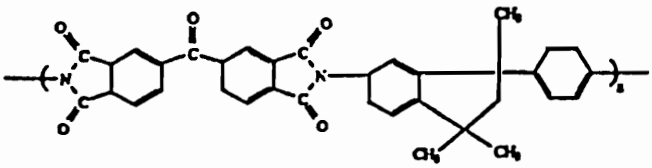
DuPont's Kapton: Tg by TBA ~380°C, rigid and intractable



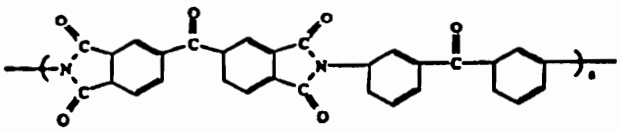
General Electric's Ultem polyetherimide: Tg ~220°C, flexible link and asymmetry



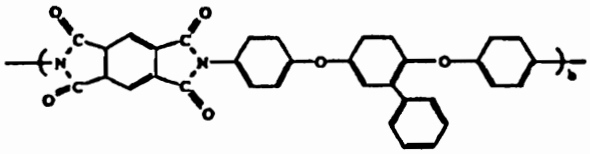
Upjohn's 2080: m ~ 80%, n ~ 20%, Tg ~310°C, asymmetry approach



Ciba Geigy's XU 218: Tg ~320°C, bulky side groups and asymmetry



Mitusi Toatsu's and Rogers Corp. LARC-TPI: Tg ~ 260°C, asymmetry approach



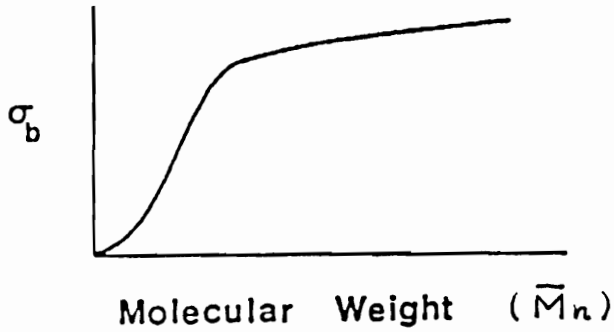
DuPont's Avimid K-III Proposed Structure: Tg ~ 294°C, bulky side group approach

2.3.6 Molecular weight control of polyimides

One critical factor for obtaining processable polyimides is molecular weight control. For linear polyimides, the minimum molecular weight required to attain good physical and mechanical properties occurs near the onset of entanglements. Many commercial step growth thermoplastic polymers report molecular weight values around 20,000 to 30,000 g/mole. One example of the relationship between number average molecular weight and physical properties including glass transition temperature, tensile strength, density, and heat capacity is shown in Figure 2.3.3 [129,130]. The following equation can serve as a guideline:

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

The rheological behavior of a polymer is directly related to its weight average molecular weight. As shown in Figure 2.3.3, the melt viscosity vs. weight average molecular weight has two regions. Before the polymer chain is long enough to generate entanglements, its exhibits inferior physical properties; melt viscosity is given by $\eta = K\langle M_w \rangle$. Above the chain entanglement molecular weight, the melt viscosity corresponds to $\eta = K'\langle Mw \rangle^{3.4}$. Therefore, molecular weight control is critical in promoting good processability.



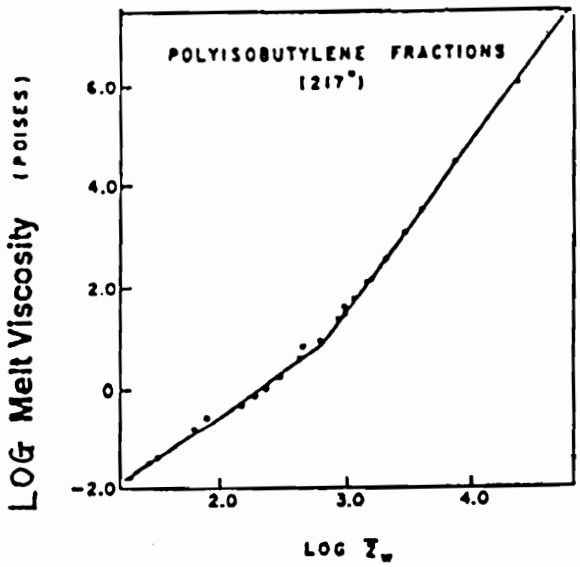


Figure 2.3.3. Upper: Effect of polymer number average weight ($\overline{M}_n$) on tensile strength (σ_b) [129].

Lower: Effect of weight-average nubmer of chain atoms in polymer ($\overline{Z}_w$) on melt viscosity [130].

Molecular weight control can be achieved by incorporating monofunctional reagents such as phthalic anhydride as endcappers. Alternatively, a polyimide oligomer endcapped with a reactive monofunctional anhydride or amine can produce thermoset polyimide precursor. Subsequently, the curing of such precursors will generate thermoset network, and this will be addressed in the next section. Thus, molecular weight control is critical in both linear and addition imide oligomer synthesis.

2.3.7 Polyimide blends

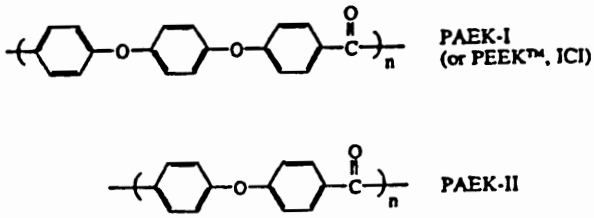
Many polyimides properties can be modified through polymer-polymer blends. For a blend to exhibit thermodynamic stability, the Gibbs free energy of mixing must be negative, $\Delta G=\Delta H-T\Delta S<0$ [131]. Miscibility is usually a rare occurrence among polymer blends, because the required negative Gibbs free energy of mixing is difficult to obtain for high molecular weight components. Many interactions influence miscibility and these may be nonpolar-polar, hydrogen bonding, charge-transfer, electronic, acid-base, or dipole-dipole [132-134].

Many miscible blend systems have been reported in literature [132,135-137]. For example, the PAEK with polyetherimide (PEI) blends offer an interesting balance of properties (Table 2.3.7) [138,139]. All the blends display a single, sharp glass transition, indicative of miscibility. The annealed and crystallized blends, however, exhibit a significant increase in strength and modulus accompanied by a decrease in ultimate elongation, with maximum

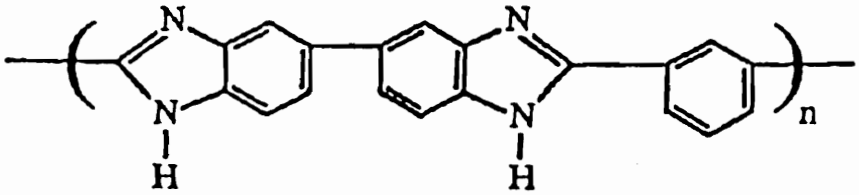
toughness occurring at intermediate compositions. Blending also improves the environmental stress crack resistance of PEI in toluene and trichloroethylene. The PBI (Figure 2.3.4) with PEI blend has also been investigated as a means of generating polymeric matrix resins for advanced aerospace fiber reinforced composite, and adhesive applications [140-142]. They are readily processable by conventional techniques, yet stable to 700°F (371°C).

A rigid polyimide can be blended with a more flexible one at the poly(amic) acid stage. However, the presence of an amic acid/anhydride-amine back reaction greatly complicates this system, as shown in Scheme 2.3.2 [143,144]. In this manner, segmented block copolymers are ultimately formed. If the back reaction can be blocked in one of the components, the re-equilibration of the two homopoly(amic) acids may be eliminated [145].

Table 2.3.7 Glass and melting transitions of miscible blends of poly(aryl ether ketone) with polyetherimide [138].



Weight % PAEK-I	Tg. °C	TM, °C
100	142	343
80	155	340
70	161	340
60	168	340
50	176	340
40	183	340
0	215	340



Poly[2, 2'-(m-phenylene)-5, 5'-bibenzimidazole] (PBI)

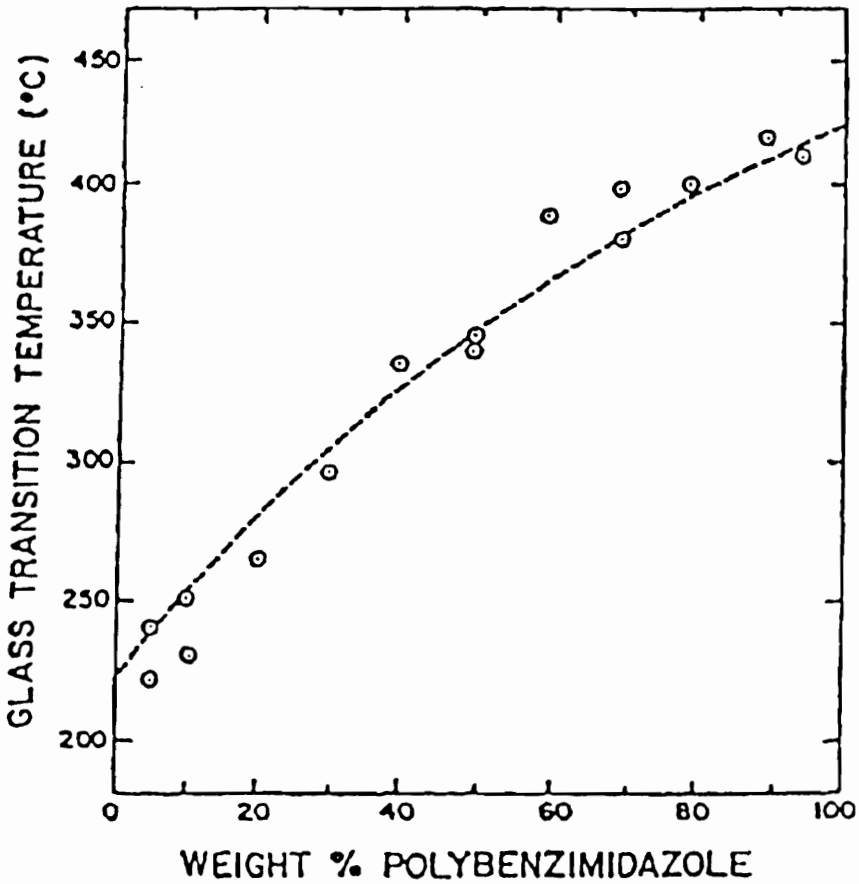
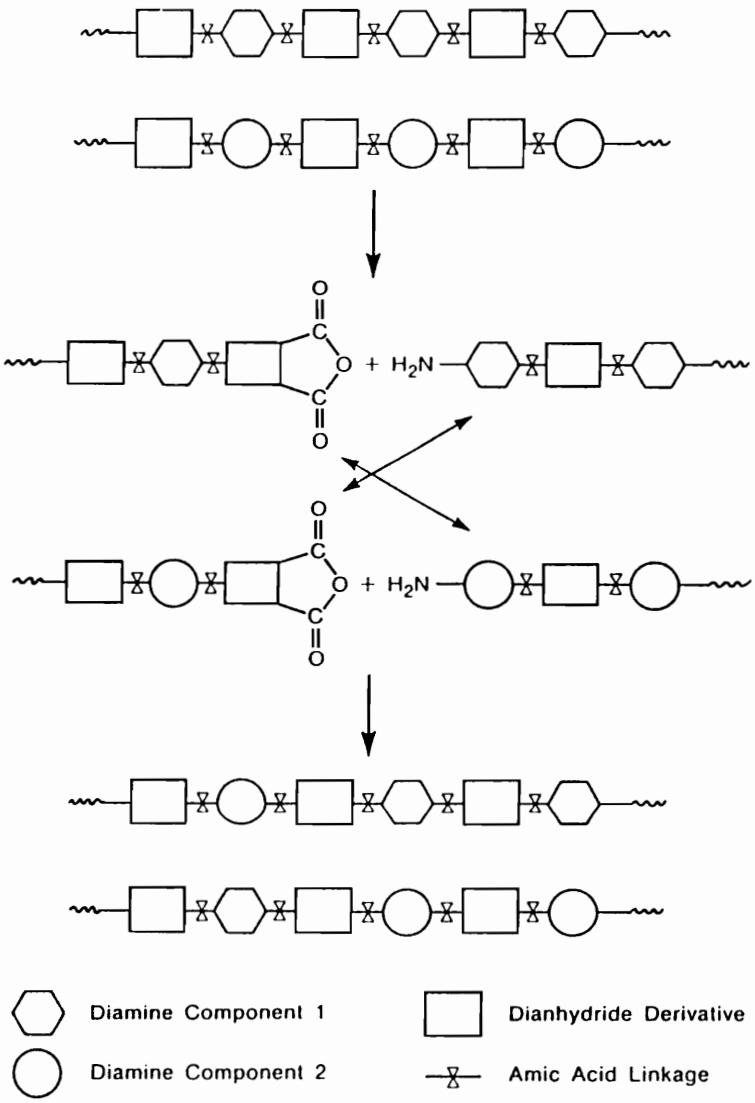


Figure 2.3.4 Glass transitions of miscible blends of polybenzimidazole with Ultem™-1000 [142].



Scheme 2.3.2 Idealized scheme of the re-equilibration reaction of poly(amic) acid mixtures [144].

2.4 Thermosetting Polyimides

2.4.1 Introduction

Thermosetting polyimides, which are primarily referred to as "addition" polyimide oligomers, are used as matrix resins for high performance composites based on glass, carbon, and aramide fibers. Addition polyimides are becoming increasingly popular, especially for use as electronic/electrical materials in printed circuit boards and insulators, as well as structural composites in aircraft and thermal insulation materials. The possible emergence of the High Speed Civil Transport program (HSCT) may offer more opportunities for the development and use of these polyimides [146,147].

Addition polyimides are usually based on low molecular weight and/or difunctional monomers or prepolymers (or mixtures thereof) that carry functional reactive termination and imide functions on their backbone. The functional endgroups can be maleimides, nadimides, acetylene, phenylethynyl, benzocyclobutene, etc. These endcappers are susceptible to polymerization, copolymerization or crosslinking by thermal or catalytic means. Addition polyimides can be synthesized by the same, well established polyimide synthesis procedures. Thus, molecular weight and molecular weight distribution of the imide backbone can also be tailored by manipulating the stoichiometry of the monomers, as well as the synthetic conditions.

An early 1964 patent [148] describes crosslinked polyimides obtained through homo- and/or copolymerization bismaleimides (BMI). Soon after that a number of bismaleimide resins based on this chemical concept became commercially available for their application in printed circuit boards and molding compounds [153]. Imide oligomers terminated with nadimide were developed by NASA Lewis Research Center in late 1960s [154,155], and then further refined for use as so-called PMR resins. Early research work involving these materials concentrated on improved processability, low viscosity resin flow and shrinkage, and solution stability of the amic-acid prepolymer, among other improvements. PMR-15, a resin developed in the early 70s, is still the most widely used addition imide resin for advanced composites [156]. At this time, acetylene (ethynyl) terminated imide oligomers (EIs) were developed by the U.S. Air Force [157,158], and these cured thermoset network demonstrated high thermal oxidative stability. Commercially available products based on this chemistry first appeared in 1975.

The three addition polyimides described above are the most significant representatives of this type of material. Much research has focused on the development of prepreg systems for tow pressure autoclave molding, i.e. modification of resin chemistries to achieve flow, tack and non-volatile cure. These important requirements were dictated by the industry to meet the processing techniques already in place for epoxy and polyester resins. However, other functional imides have developed in more recent years. For example, benzocyclobutene imides showed very low moisture absorption and

good thermal stability [159-162]. In addition, biphenylene and paracyclophane are suitable as reactive endgroups [163-166].

The following section will provide a brief review of bismaleimides, and PMR and acetylene terminated resins. The acetylene (ethynyl) containing polyimides will be discussed in more details since they are directly related to this research.

2.4.2 Bismaleimides

Bismaleimides are well known for their excellent processability and desirable balance of thermal, electrical and mechanical properties. They can be used as advanced composites for electronic applications, such as multilayer and printed circuit boards. Figure 2.4.1 shows the general structure of a bismaleimide building block. The double bond of endcapped maleimide is susceptible to homo- and copolymerizations due to the adjacent carbonyl groups. The electron withdrawing nature of these two carbonyl groups create a double bond that is quite electron-deficient. It is also a very reactive dienophile and can therefore be employed in a variety of Diels Alder reactions.

BMI based on N,N'-arylene can be synthesized by the cyclodehydration of N,N'-arylene bismaleamic acids with acetic anhydride in the presence of a catalyst [167]. The relative low yield is due to the formation of isoimides, acetanilides, amleimide-acetic acid adducts and products with mixed functionalities [168]. Scheme 2.4.1 demonstrates the mechanism by which the chemical imidization is thought to occur. Much research [168-171] has shown

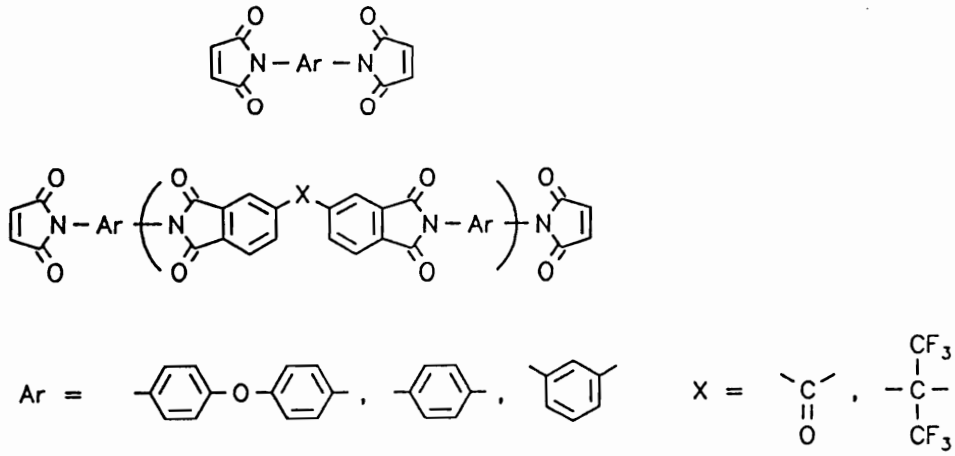


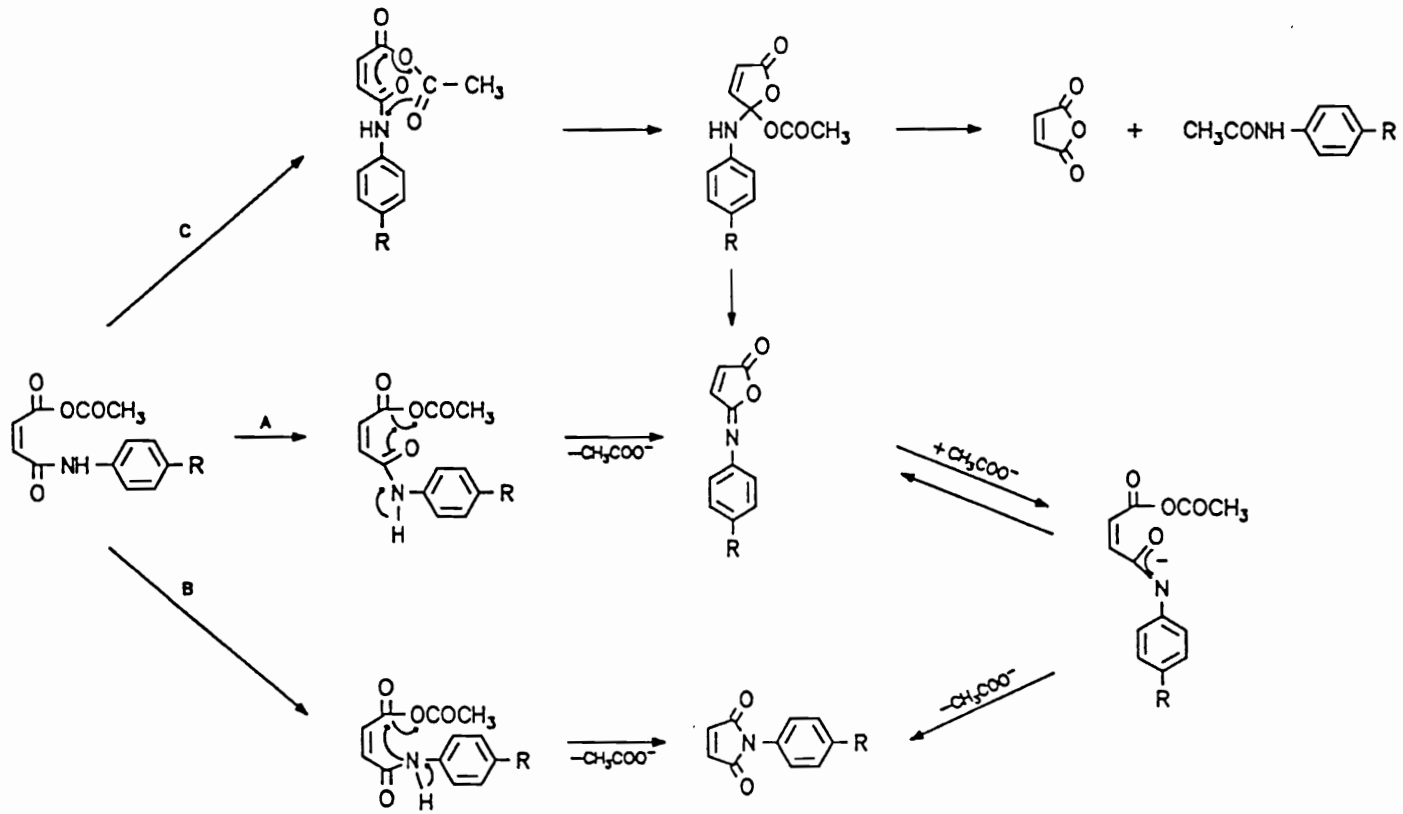
Figure 2.4.1. Chemical structure of a bismaleimide.

that the isoimide is the kinetically favored product and that isomerization yields the thermodynamically stable imide when sodium acetate is used as the catalyst. Possible isoimidization is shown as pathway A and C.

4,4'-bismaleimidodiphenylmethane (MDA) is the most widely used BMI building block since the precursor diamine is readily available and relatively inexpensive. Other aromatic amine or diamine building blocks have also been used since they can be converted to the corresponding maleimide or bismaleimide, respectively, via similar procedures. Table 2.4.1 [172,173] shows the structures of the various BMI's that have been investigated. The reactivity of the BMI is influenced by the chemical nature of the residue between the maleimide groups. Electron donation groups, such as alkyl groups, reduces the BMI reactivity. On the other hand, electron withdrawing groups such as sulfone, carbonyl and so on, have the opposite effect.

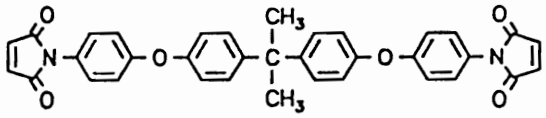
Maleimide terminated oligomers (Figure 2.4.2) were developed for molding, adhesive and composite applications. Most oligomer synthesis involves the key step of preparing an amino terminated intermediate for late modification with the maleimide groups [174]. Other synthetic methods, such as utilizing maleic anhydride as an endcapping agent utilizing the classic two-step method, have been reported [175]. The stoichiometry of monomers can be modified to produce controlled molecular weight oligomers.

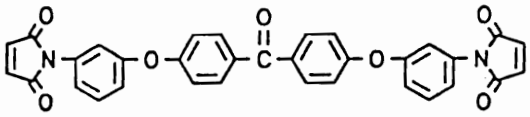
The drawback of BMI resins are their inherent brittleness due to the high degree of crosslink density and the relatively low cure temperature, which results in a small processing window. The onset of curing usually occurs at 200-210°C. Toughness can be improved by modifying the BMI with

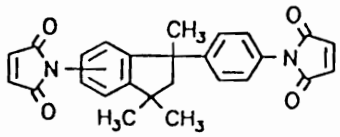


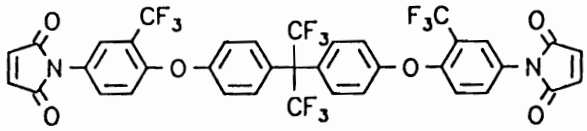
Scheme 2.4.1 Chemistry involved in the base catalyzed cyclodehydration on N,N'-bismaleamic acids [167,168,170].

Table 2.4.1 Bismaleimides structures [172,173].

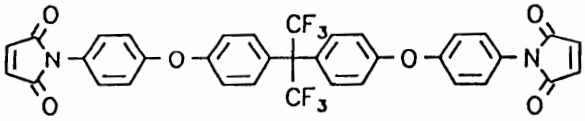




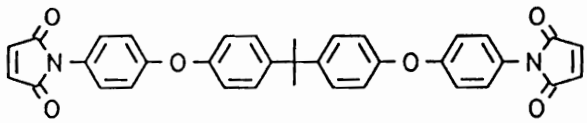




Mol.wt. = 815, Mp = 112°C, DC(polymer) = 2.8



Mol.wt. = 679, Mp = 136°C, DC(polymer) = 3.0



Mol.wt. = 571, Mp = 142°C, DC(polymer) = 3.2

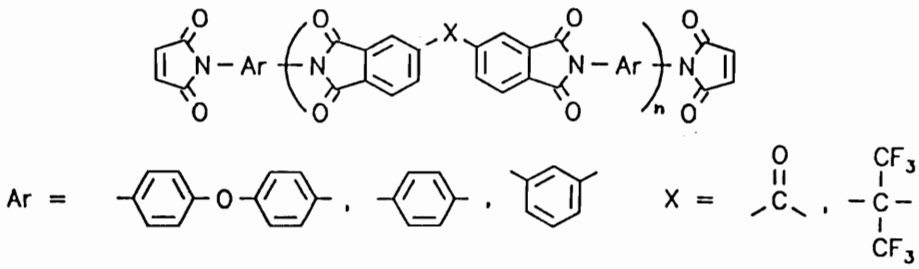
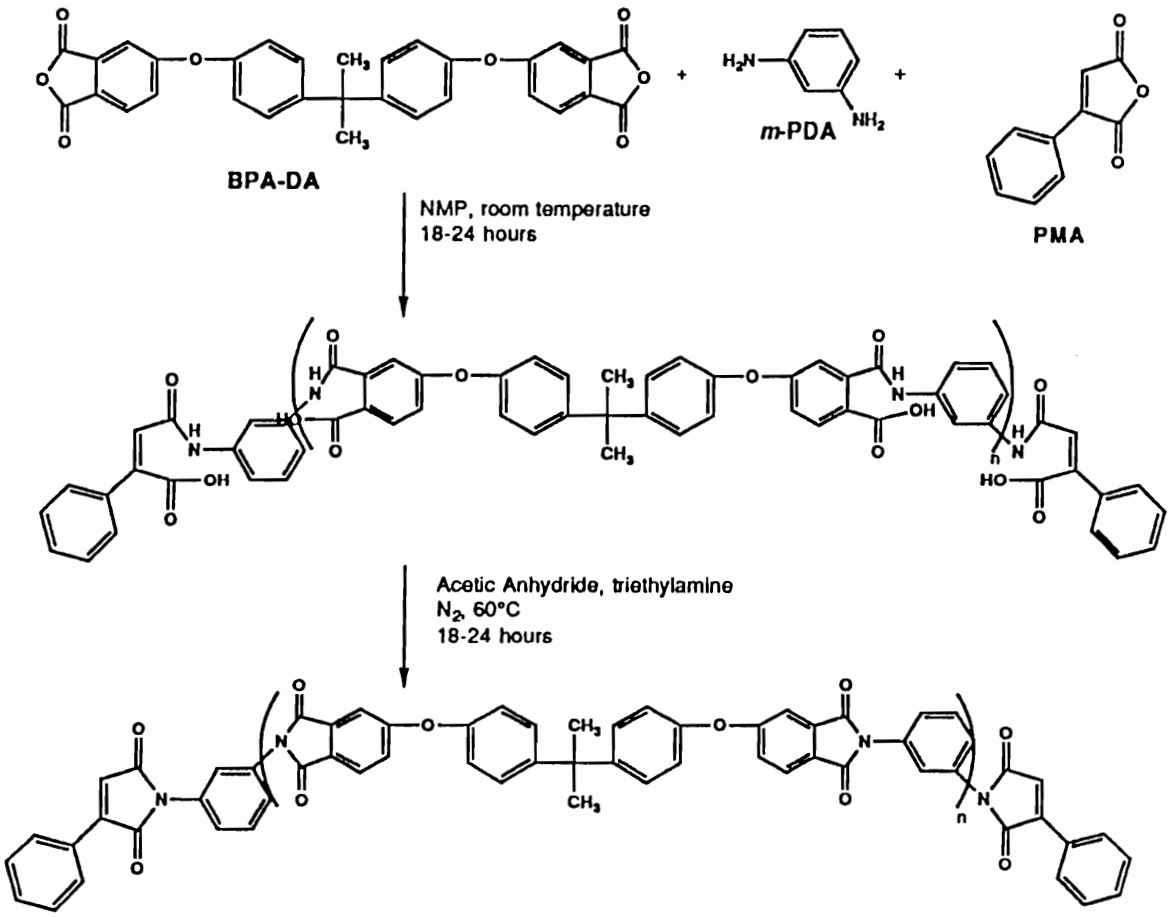


Figure 2.4.2 Chemical structure of maleimide-terminated imide oligomer [174,175].

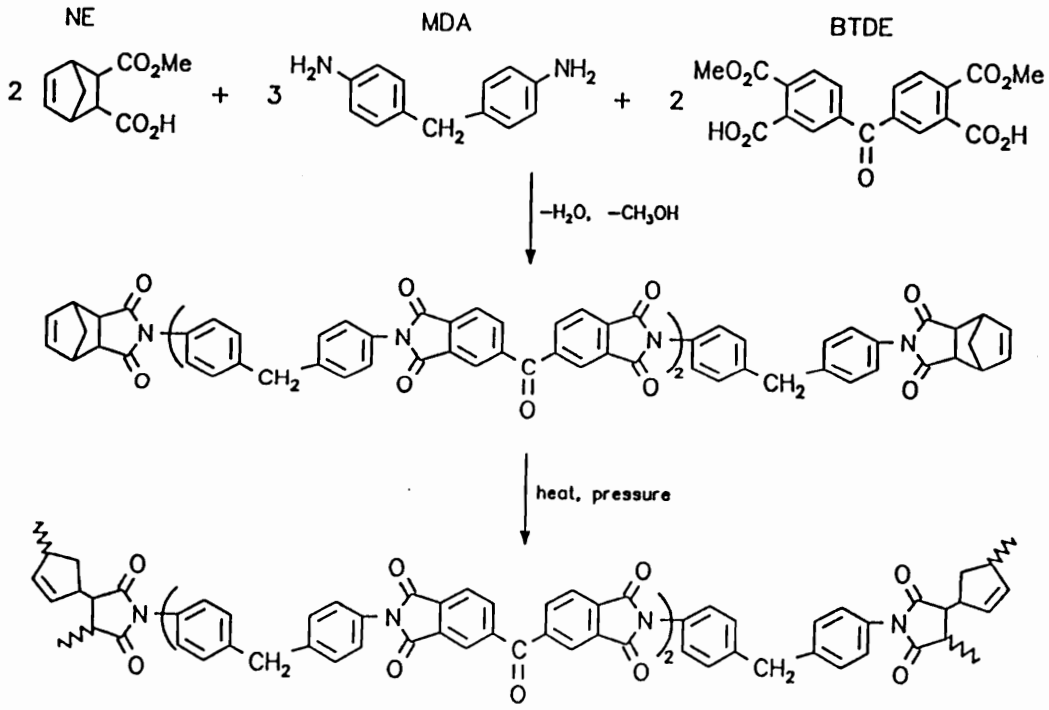
CTBN rubber, although at the expense of their desirable high temperature properties [176,177]. However, blending BMI with thermoplastics will improve toughness without compromising other important properties, such as T_g and modulus of elasticity [178-180]. In some cases, semi-interpenetrating networks are formed with properties that can combine those of the individual starting materials [181,182]. Meyer, et al. [183,263] reported using phenylmaleic anhydride as an endcapping agent, which resulted in oligomers (Scheme 2.4.2) with greatly improved processability due to high onset cure temperature. With the pendant phenyl group, the cure onset increased to 370°C which ensured a large processing window.

2.4.3 PMR resin

As previously noted, PMR refers to *polymerization of monomeric reactants*, and is a unique approach to temperature-resistant crosslinked polyimides. The most widely used resin of this family is PMR-15, which is depicted in Scheme 2.4.3 [156]. The synthesis of PMR-15 involves dissolving BTDE, MDA and NE monomers in a low boiling alkyl alcohol, and the resulting low viscosity solution is subsequently used to impregnate prepreg fibers. After removing the solvents, the prepreg contains the monomeric reactants. The monomers then undergo an "in situ" condensation reaction to form the norbonene-endcapped imide prepolymer at temperatures around 150-200°C. The prepolymer can have nadimide endcaps with a molecular weight of 1,500 g/mole by controlling the stoichiometry of the monomeric reactants. The final cure is performed at 250-320°C.



Scheme 2.4.2 Synthesis of phenylmaleic anhydride-terminated polyimides by chemical imidization [263].

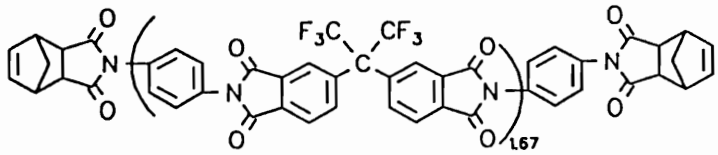


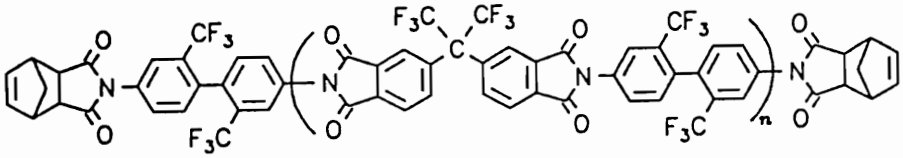
Scheme 2.4.3 PMR-15 resin chemistry [156].

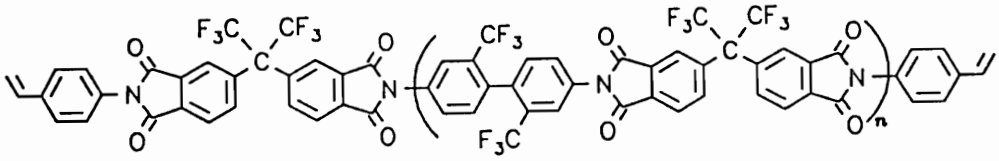
Several later PMR resins are listed in Table 2.4.2 [184-188]. The fluoro-containing PMR-II possesses significantly improved thermal-oxidative stability at 316°C. The further improvement of the PMR-II resin was achieved by increasing the prepolymer molecular weight in order to reduce the aliphatic endgroup content. Instead of using a nadic endgroup, a styrene endgroup was utilized as so called V-cap-12F-71 by modification of the PMR-12F-71 (Table 2.4.2). This V-cap version can undergo comparatively longer thermal oxidative stability testing.

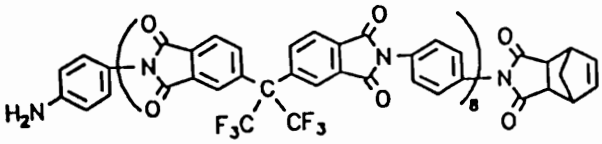
The most important aspect in PMR resin chemistry is processability. The impregnation of fibers to produce a prepreg and the subsequent molding of the prepreg layup into a component is made possible through PMR technology. The current state-of-the-art practice of employing a resin solution to impregnate the reinforcement can be utilized; however, other techniques such as hot melt impregnation or powder prepregging may become more important in the future as environmental issues associated with using solvents and solutions become important. Thus, the use of fully imidized prepolymer fine powder is preferred, especially for dry powder impregnation methods.

Table 2.4.2 PMR resins [184-188].







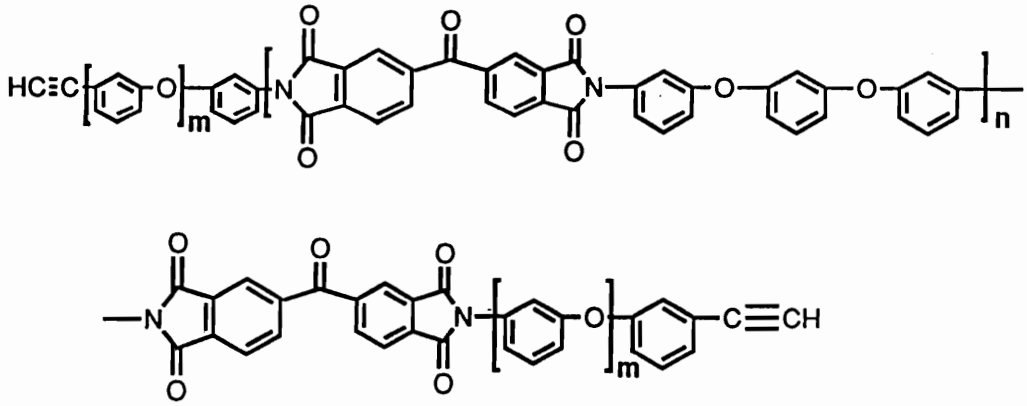


2.4.4 Ethynyl-containing polyimides

Ethynyl containing imide oligomers (EIs) have received attention over the past two decades since these thermosetting prepolymers can be crosslinked at high temperature without generating volatile byproducts. The properties of crosslinked polymer networks formed in this way depend primarily on the backbone structure, crosslink density, and cure temperature. Oligomers and polymers containing ethynyl groups have excellent shelf lives, can be cured under moderate conditions, and provide resins with solvent resistance and a desirable combination of physical and mechanical properties.

The ethynyl-containing imide oligomers were first prepared by Hughes Aircraft Company, under the sponsorship of the U.S. Airforce Materials Laboratory (AFML) [158], and marketed under the trade name Thermid-600 [189]. Currently, Thermid™ resins are manufactured and marketed by National Starch and Chemical Corporation (Figure 2.4.3) [190,191]. These prepolymers are capable of being chain extended and cured at 200°C or above – even in the absence of a catalyst – to yield void-free polymer networks [192]. Modified Thermid-600 with 6F (Figure 2.4.4) results in resins with unique properties, such as improved solubility in a variety of solvents. These solutions are also stable in high concentrations.

The synthesis of these oligomers is achieved via the classic "two step" polyimide polymerization [197-199]. For example, 2 moles of an aromatic tetracarboxylic acid dianhydride with 1 mole of aromatic diamine in a polar solvent to form an anhydride-terminated amic acid oligomer. This oligomer can then be treated with an ethynyl-substituted aromatic amine, followed by



Where m=0,1 and n=1,2,3

Figure 2.4.3 Backbone structure of Thermid™ [189].

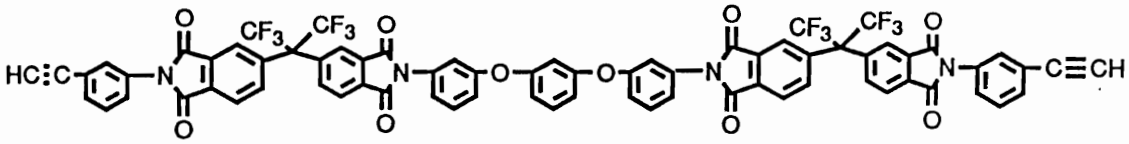
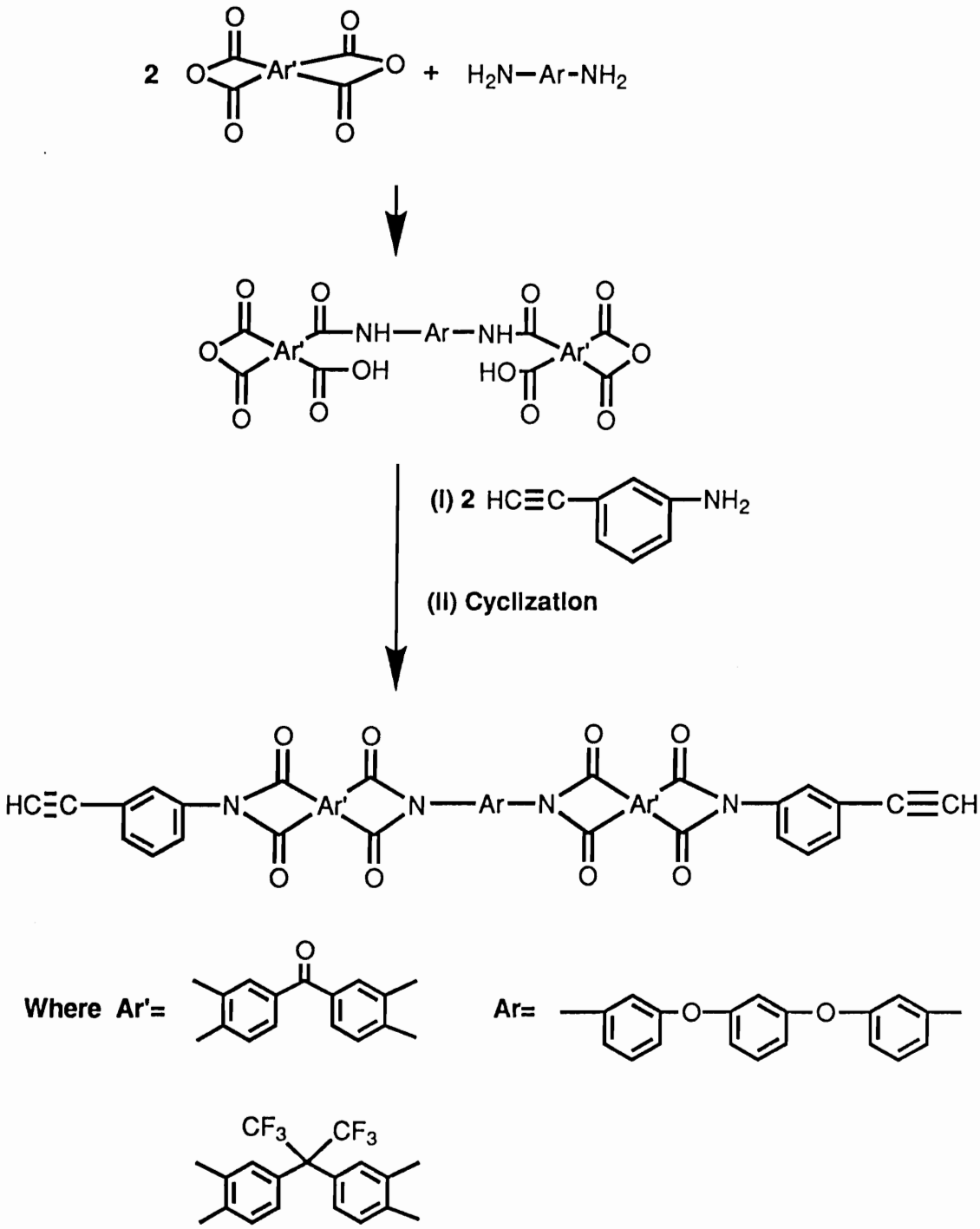


Figure 2.4.4 Thermid FA-700™ [189].

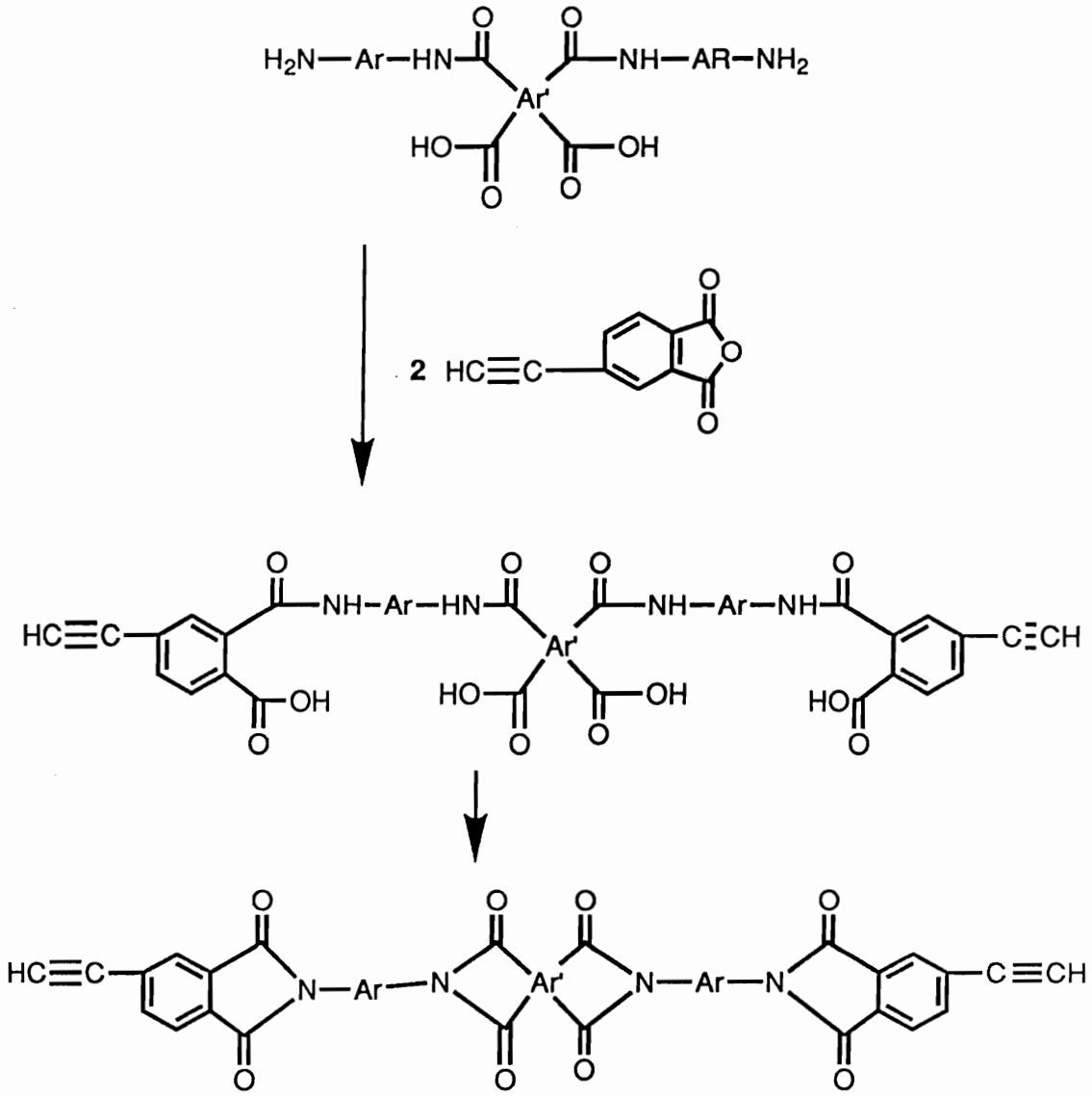
chemical or thermal cyclodehydration, which converts the amic acid to an ethynyl-terminated imide oligomer (Scheme 2.4.4). The model compound study can be useful in selection the optimum reaction conditions [193]. Alternatively, ethynyl-terminated imide resins can also be prepared by reacting 4-ethynyl phthalic anhydride with an amine-terminated amide acid or imide resin (Scheme 2.4.5) [194]. If the ethynyl containing diamine is used in the first step of the polymerization, an internal acetylene group in the backbone of polyimide can be obtained [195,204].

Ethynyl-terminated amic acid oligomers are converted to isoimides via chemical cyclodehydration using dicyclohexyl carbodiimide (Figure 2.4.5) [200]. The only structural difference between the isoimide and imide oligomers is in the arrangement of atoms in the heterocyclic rings. The isoimide changes into the normal imide structure as it is cured, and the cured resin properties should resemble those of normal polyimides. The advantage, however, is that these oligomers demonstrate better solubility and processability.

In short, the polymerization of ethynyl-containing imides involves a free radical propagation of the ethyne moiety to a linear conjugated polyene [201]. The kinetic chain length of this reaction is unusually short (6-8 ethynyl units) and termination is first order. The crosslink reaction mechanism is complex. Early investigators believed that crosslinking occurred by simple cyclotrimerization to form an aromatic crosslink [202]. Subsequent studies, however, suggest that aromatic content increases after cure. However, it was estimated that no more than 30% of the endgroups underwent



Scheme 2.4.4 Preparation of EIs [193].



Scheme 2.4.5 Alternative reaction route for preparation of EIs [194].

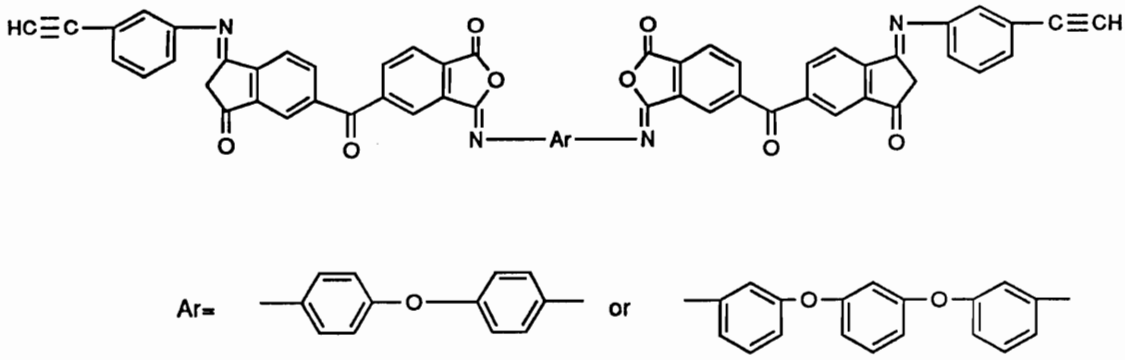


Figure 2.4.5 Isoimides with acetylene termination [200].

cyclotrimerization, while the reminder experienced other addition reactions, such as eyn-yne formation by Strauss coupling [203].

The resulting cured polymers are crosslinked and insoluble, making solution spectroscopic analysis difficult. The actual cure chemistry, therefore, has been subject to conjecture and uncertainty [204]. Recently, however, the cure states of acetylene-terminated polymers have been studied using several solid-state techniques including FTIR, NMR and ESR. The model compound study results from solid-state ^{13}C cross-polarization magic-angle spinning (CPMAS) NMR shows that several cure products can be detected and these results are summarized in Table 2.4.3 [205].

Two major deficiencies have been encountered in EIs: its high melting temperature and its high rate of cure. As a consequence, EIs have a very short gel time at cure temperature and this factor has restricted its use in several applications. In addition, the material's high T_g permits only a very small processing window between softening and cure, but recent developments have been undertaken to address this problem. For example, research is underway to design new polymer systems, which use novel endcaps like 4-phenylethynylphthalic anhydride or 3-phenylethynyl aniline.

The main thrust of this research is the investigation of phenylethynyl endcapped polyimides, which is a fairly recent development. Early work [210-216] focused on using 3-phenylethynylaniline (3-PEA) as endcapping agent. Harris [217] reported that the endcapper was synthesized from 3-bromonitrobenzene reacted with phenylacetylene in the presence of a palladium coupling catalyst. Hydrogenation of 1-phenyl-2-(3-

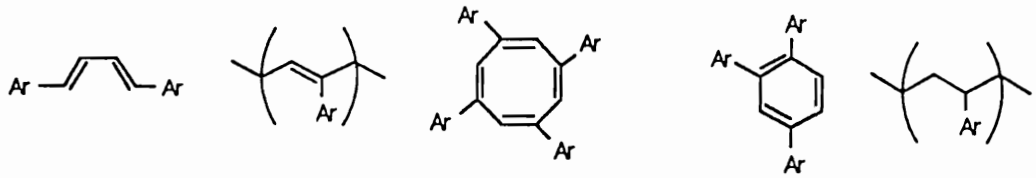
Table 2.4.3 Acetylene cure reactions and products [205].

Reaction mechanism and products

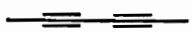
Further reaction or degradation products

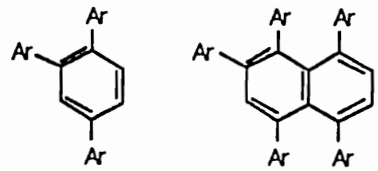
Cyclotrimerization

Biradical Mechanisms

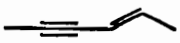


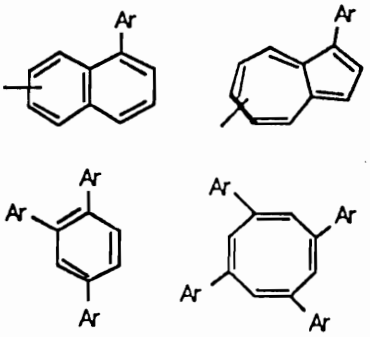
Glaser Coupling





Strauss Coupling





Electrophilic Addition

nitrophenyl)ethyne over a ruthenium catalyst afforded 3-phenylethynyl-aniline. More recently, focus has been directed towards the use of 4-phenylethynyl phthalic anhydride (4-PEPA) as an endcapper [218-222]. 4-PEPA can be synthesized by similar coupling reaction as used for the 3-PEA [221]. Imide oligomers endcapped with 4-PEPA tend to result in cure temperatures 30-70°C higher than the imides capped with 3-PEA. The higher onset cure temperature ensures a wider processing window and thus complete removal of the remaining solvents before cure.

Although a detailed study of ethynyl endgroup structure vs. cure temperature was not conducted for these compounds, several trends are apparent. First, phenyl substitution increases cure temperature well over 100°C; the bulk of the terminal phenyl substituent undoubtedly hinders mutual endgroup reaction. Secondly, incorporation of a "flexible link" into the endgroup, as in 3-(3-(phenylethynyl)phenoxy)aniline, serves to further lower cure temperature. Such a structure provides additional mobility to the endgroups, thus promoting a favorable orientation for crosslinking. Thirdly, it appears that phenyl substituents bearing electron withdrawing groups further raise the cure temperature relative to the unsubstituted phenyl control [219]. However, the temperature increase is small – on the order of 10°C. Thus, it cannot be claimed with sufficient certainty that electron donation groups would lower cure temperature, as no such compounds have yet been reported.

Cured phenylethynyl endcapped imide oligomers displayed high fracture energies and high unoriented thin film elongations [218,219]. As such, their properties are more typical of high molecular weight polymers

than conventional thermoset materials. Unfortunately, the curing mechanism is not well understood. A model compound curing study based on mono-phenylethynyl functionality suggest that very complex cure process may be due to the degradation of small molecular weight compounds [223]. Research is needed to explore structure-properties of these phenylethynyl endcapped imide oligomers and their curing chemistry.

2.5 Phosphorus containing polyimides

2.5.1 Introduction

Physical addition or chemical incorporation of phosphorus into polymeric materials is a long-standing industrial approach for improving fire resistant properties [264]. Extensive research has been conducted investigating these synthesis procedures [224], the preparation of novel monomers [225,226], and new functionalized oligomers and polymers [227-230]. In particular, several important aspects of hydrolytically stable phosphorus carbon containing materials have been identified, including oxygen plasma resistance [231-233], plasma supported catalysis [234], structural adhesives [235], radiation resonance [236], and polymer blends [237]. One of the thrusts of this research is to develop candidate adhesive and composite material systems based on polyimides with phosphine oxide moiety. Such polyimides are thought to possess excellent physical and mechanical properties, and show good solvent- and fire-resistance. Thus, the related research is summarized in the following sections.

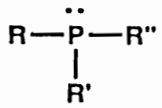
2.5.2 Properties of phosphorus containing polymers

Phosphorus containing polymers are distinguished by two important characteristics; they are flame-retardant and self-extinguishing [238]. Phosphorus containing polymers can be generated by either blending the polymer with phosphorus additives, or incorporating phosphorus functionality into the polymer backbone. This research concentrates on the latter approach to investigating the chemistry of new polyimide systems. As previously mentioned, introducing flexible spacers into the polyimide backbone will result in many desirable properties. Compared with other phosphine containing functionalities (Table 2.5.1), phosphine oxide groups have the advantage of containing hydrolytically stable phosphorus-carbon bonds. This results in high thermal oxidative stability, enhanced solubility, and improved polymer-polymer miscibility and fire resistance.

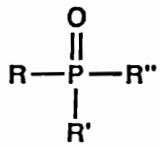
Phosphine oxide containing polymers produce very high char yield in air. Such char formation is considered to be very important for fire-resistance since the char can insulate the underlying polymer and restrict flammable volatiles from diffusing through and feeding the flame. This may explain the apparent excellent self-extinguishing properties of these phosphine oxide containing polyimides relative to other engineering thermoplastics.

These fire-resistant properties have traditionally been measured by Limited Oxygen Index (LOI) methods, but cone calorimetry is now preferred since it provides more basic information on the material's behavior. One example of these measurement results is shown in Figure 2.5.1 [239]. The triarylphosphine oxide containing nylon 6,6 copolymers demonstrated much

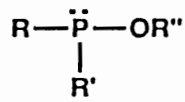
Table 2.5.1 Types of organophosphorus moieties.



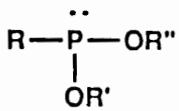
Phosphine



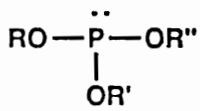
Phosphine Oxide



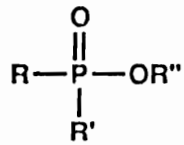
Phosphinite



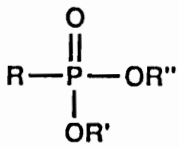
Phosphonite



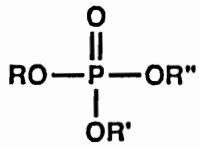
Phosphite



Phosphinate



Phosphonate



Phosphate

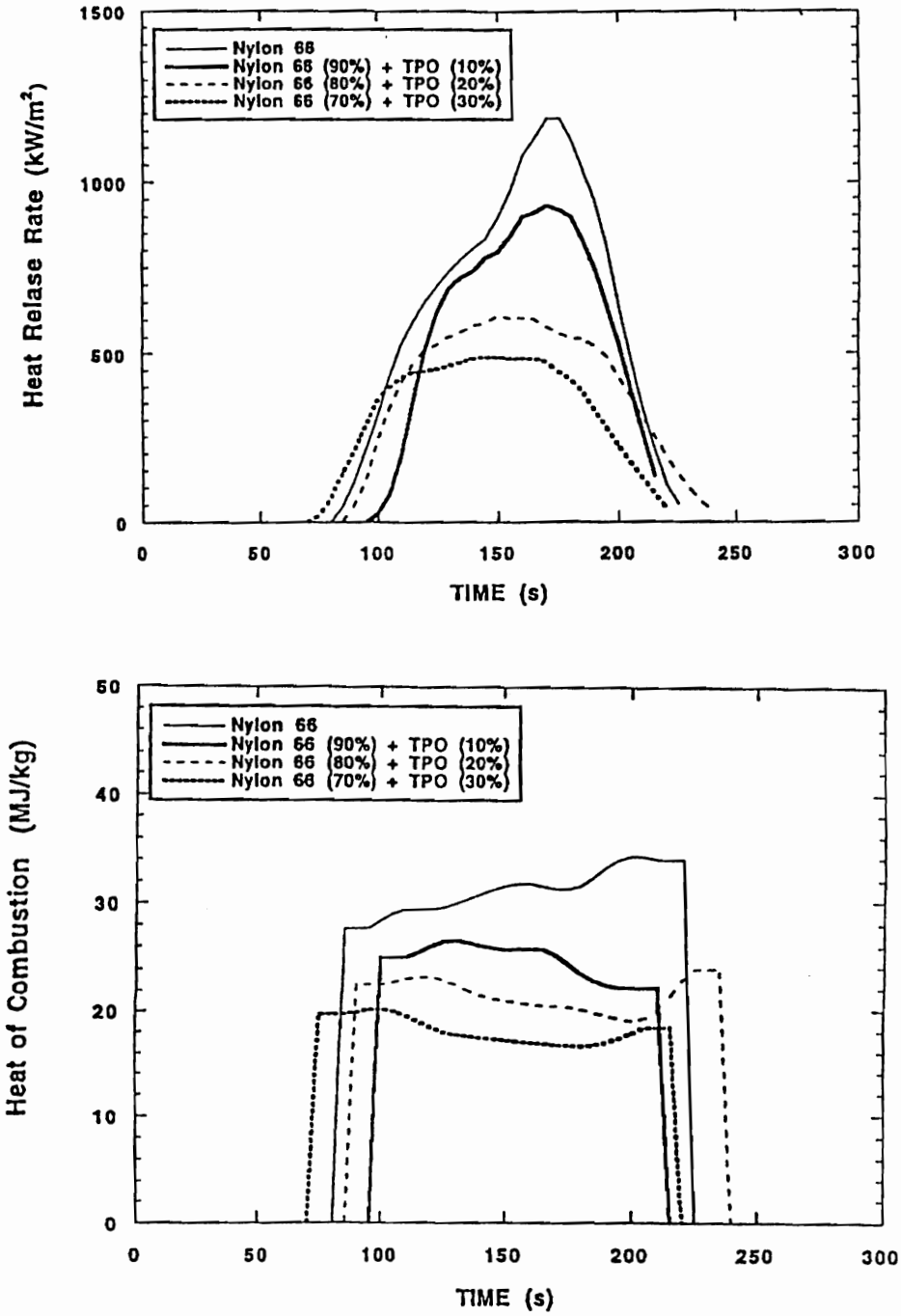


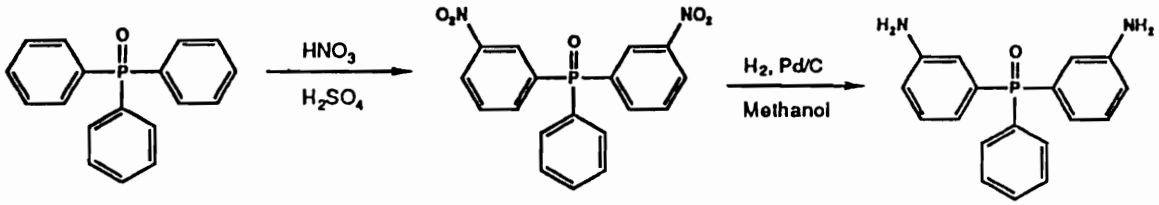
Figure 2.5.1 Heat release rate and heat of combustion of triarylphosphine oxide containing nylon 6,6 copolymers [239].

lower heat release rates and heat of combustion rates than did the control nylon 6,6, which indicates that the phosphine oxide group greatly reduced the flammability of the pure homopolymer. On the other hand, toxic CO generation was higher than the nylon 6,6 control.

2.5.3. Commonly used phosphine oxide containing polyimide monomers

Phosphine oxide has been successfully incorporated into diamines or dianhydrides for use in polyimide synthesis. Several examples of these diamines are described below.

In the early 70's, Schiemnz and others [240-242] reported a synthetic route which could allegedly make a bis(3-aminophenyl)phenyl phosphine oxide (m-DAPPO). Phenylphosphonic dichloride was treated with excess aniline hydrochloride at high temperatures and underwent a Friedel Crafts type reaction, which resulted in low yield products. However, additional polyimide synthesis was unsuccessful. Subsequent research revealed that their procedures produced an unstable amide between the phosphorus and benzene which could not produce a polymer [243]. More recently, the same monomer was successfully synthesized by Martinez-Nunez and Ghassemi [226] in high yields and purity (Scheme 2.5.1). The key step in their synthesis was improving the reaction conditions for nitration. The amount of nitric acid, as well as time and temperature control, is crucial to form dinitro products that contain minimal amounts of mono- and tri-nitro byproducts.



Scheme 2.5.1 Synthesis of *m*-DAPPO [226]

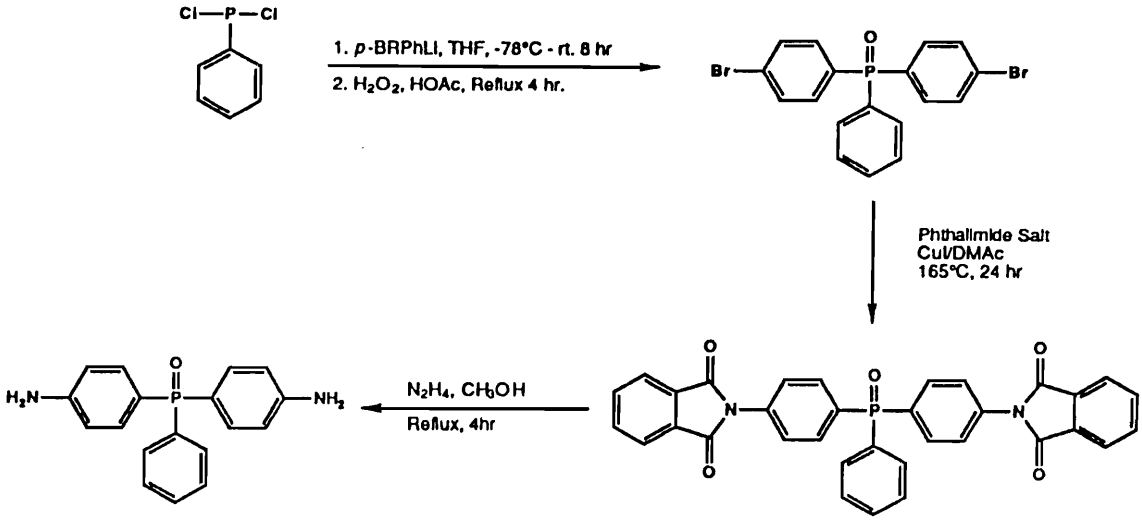
Grubbs and Yang [225,243] reported the synthesis of bis(4-aminophenyl)phenyl phosphine oxide in high yield and purity. The reaction is shown in Scheme 2.5.2. A series of high molecular weight polyimides based on this diamine and 6FDA, BPDA, PMDA, BTDA, DSDA and ODPA have been successfully prepared and creasable films were obtained. Good solubility and thermal stability have been reported for these polyimides.

Ether-linked phenylphosphine oxide diamines are known to be more reactive in polyimide synthesis. The synthesis of bis(3-aminophenoxy-4'-phenyl)phenylphosphine oxide diamine (m-BAPPO) by Gungor, et al. [244] is shown in Scheme 2.5.3. Completely soluble polyimides were prepared from this diamine with high Tg (220-254°C) and char yield. Isomers of m-BAPPO, bis(4-aminophenoxy-4'-phenyl)phenylphosphine oxide (p-BAPPO) have also been reported [245,246]. This diamine synthesis involves the reaction of p-aminophenol with bis(4,4'-fluorophenyl)phenyl phosphine oxide and 4-aminophenol.

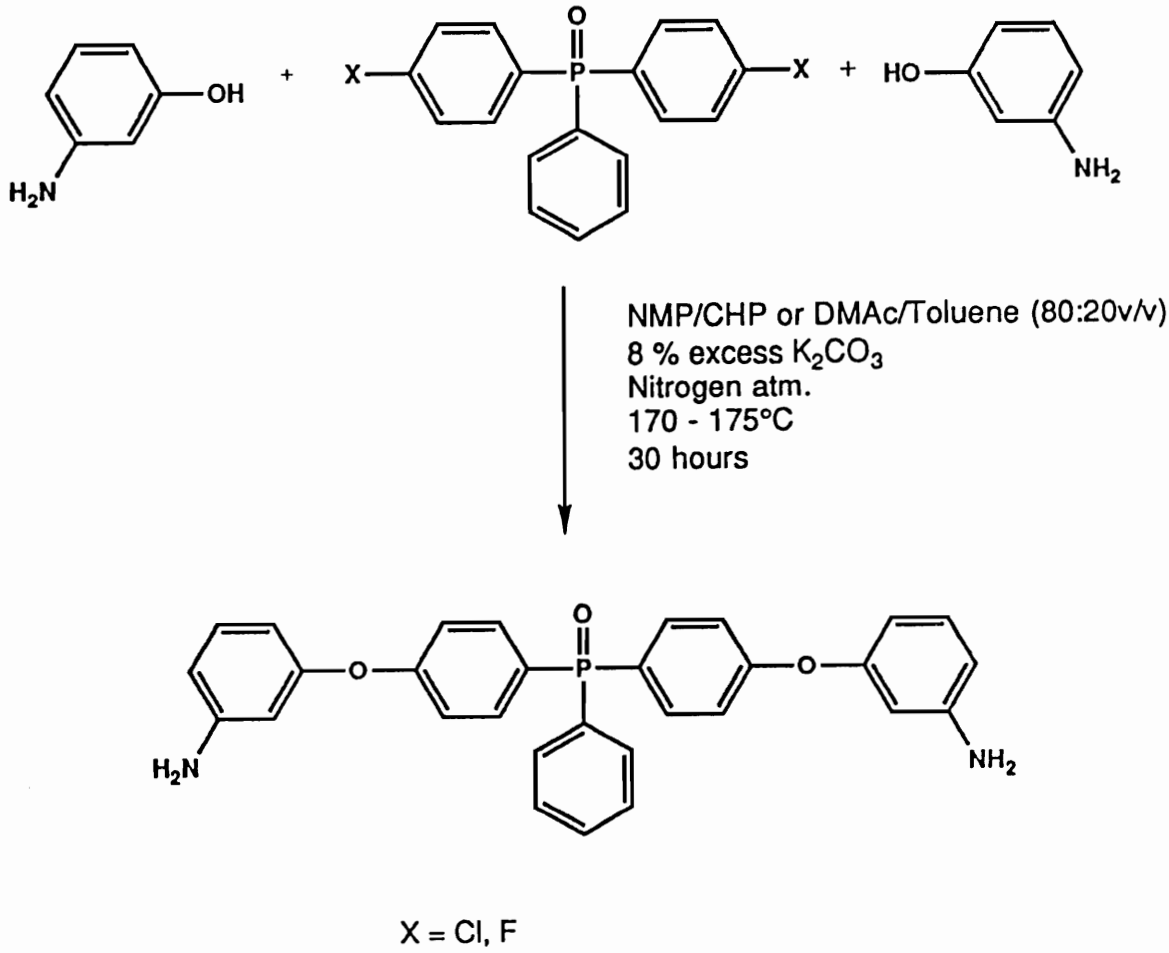
The preparation of bis(3-aminophenyl)methyl phosphine oxide (m-DAMPO) has also been reported [247-249]. However, very little work has been done to utilize this diamine for polyimide synthesis. This research, however, explored improved methods for monomer and polyimide synthesis involving this diamine and the results will be reported later.

Dianhydrides containing a phosphine oxide group has also been investigated. Early reports on the synthesis of triphenyl phosphine oxide tetracarboxylic dianhydride offered low yields [250-252]. Recently, Lin, et al. [253] reported a improved route, which is shown in Scheme 2.5.4. The

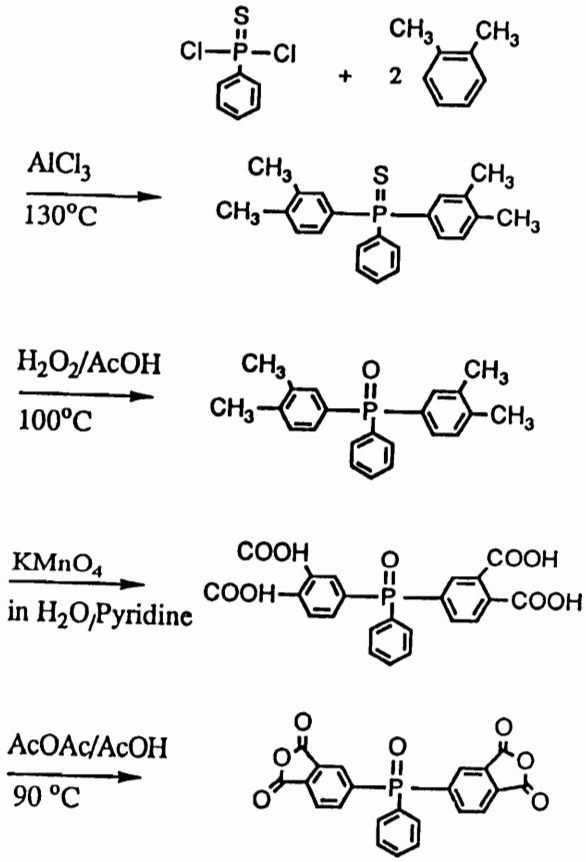
resulting dianhydride has high purity and resulted in high molecular weight polyimides. T_g values from 317 to 366°C were reported.



Scheme 2.5.2 Improved synthesis of Bis(4-aminophenyl)phenyl phosphine oxide [225].



Scheme 2.5.3. Synthesis of *m*-BAPPO [244].



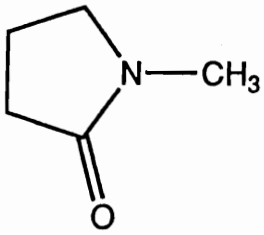
Scheme 2.5.4 Synthesis of dianhydride of bis(3,4-dicarboxyphenyl)phenyl phosphine oxide [253].

Chapter 3. EXPERIMENTAL

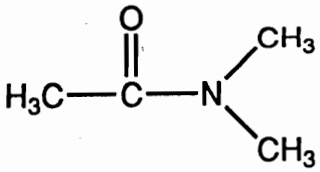
3.1 Synthesis

3.1.1 Solvents

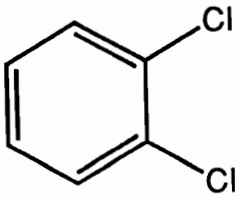
1-Methyl-2-Pyrrolidinone (NMP: Fisher Scientific) was dried over calcium hydride for at least 12 hours and then vacuum distilled prior to use (b.p. 205°C/760mm, 82°C/10mm).



N,N-Dimethylacetamide (DMAc: Fisher Scientific) was dried over calcium hydride for at least 12 hours and then vacuum distilled prior to use (b.p. 163-165°C/760mm).



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



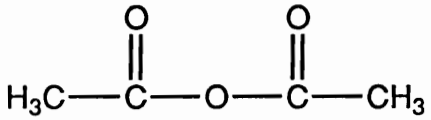
Methanol (Fisher Scientific) was received as a HPLC grade solvent and was used without purification (b.p. 64.7°C/760mm).

Ethanol (100%, AAPER Alcohol and Chemical) was used as received (b.p. 78.5°C/760mm).

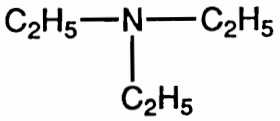
Chloroform (Fisher Scientific) was received as a HPLC grade solvent and was used without purification (b.p. 61-62°C/760mm).

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

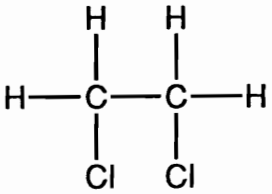
Acetic Anhydride (Fisher Scientific) was dried over calcium hydride for at least 12 hours and then vacuum distilled prior to use (b.p. 138-140°C/760mm).



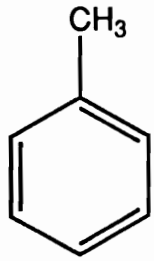
Triethylamine (Et_3N: Fisher Scientific) was dried over sodium for at least 12 hours and then vacuum distilled prior to use (b.p. 88.8°C/760mm).



1,2 dichloroethane (Fisher Scientific) was used as received (b.p. 83°C/760mm).

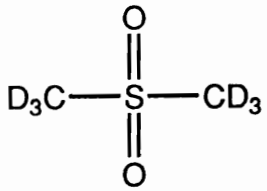


Toluene (Fisher Scientific) was used as received (b.p. 110.6°C/760mm).



Hexanes (EM Chemicals) were used as received (b.p. 68-70°C/760mm).

Deuterated Dimethyl Sulfoxide (DMSO-d6: Cambridge Isotope Laboratories) was dried over molecular sieves for at least 24 hours. (b.p. 55°C/5mm).



Deuterated Chloroform ($CDCl_3$: Cambridge Isotope Laboratories) was dried over molecular sieves for at least 24 hours (b.p. 61°C/760mm).

3.1.2 Monomer synthesis and purification

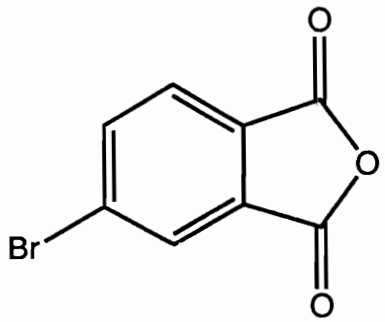
3.1.2.1 Chemicals and reagents used for monomer synthesis and purification

Magnesium sulfate ($MgSO_4$, 99%, Aldrich), Celite (Fisher) and charcoal (activated carbon, 4-12 mesh, Aldrich) were purchased and used as received. Calcium hydride (CaH_2, Aldrich) and phosphorus pentoxide (P_2O_5, 98+%, Aldrich) were crushed to a fine powder prior to use. Sodium (Na in paraffin, 40 wt.% dispersion, Aldrich) was carefully cut into small pieces prior to use.

4-Bromophthalic Anhydride (Br-PAN)

Supplier:	Ameribrom/Bromine Compounds Ltd.
Molecular Formula:	$C_8H_3O_3Br$
Molecular Weight (g/mole):	227.01
Boiling Point, °C:	280-282

Structure:

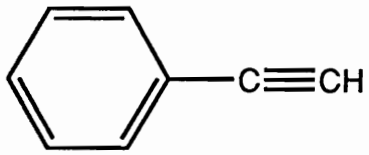


Purification: used as received.

Phenylacetylene (Ethynylbenzene)

Supplier:	Aldrich
Molecular Formula:	C_8H_6
Molecular Weight (g/mole):	102.14
Boiling Point, °C:	142-144

Structure:



Purification: vacuum distillation at ~100 °C and 50 millitorr.

Triphenylphosphine

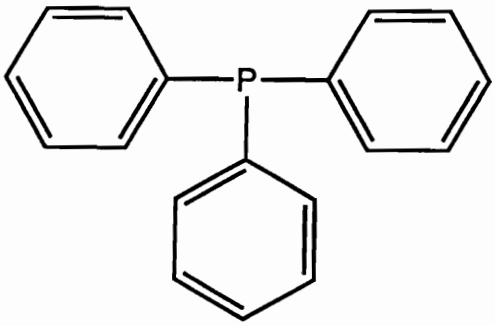
Supplier: Aldrich

Molecular Formula: $C_{18}H_{15}P$

Molecular Weight (g/mole): 262.29

Melting Point, °C: 79-81

Structure:



Purification: used as received.

Bis(triphenylphosphine)palladium(II) Chloride

Supplier: Aldrich

Molecular Formula: $C_{18}H_{15}P_2PdCl_2$

Molecular Weight (g/mole): 701.89

Structure: $[(C_6H_5)_3P]_2PdCl_2$

Purification: used as received.

Copper (I) Iodide

Supplier: Aldrich

Molecular Formula: CuI

Molecular Weight (g/mole): 190.44

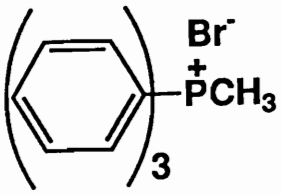
Melting Point, °C: 605

Purification: used as received.

Methyl Triphenyl Phosphonium Bromide

Supplier:	Aldrich, 98%
Molecular Formula:	$C_{19}H_{18}PBr$
Molecular Weight (g/mole):	357.24
Melting Point, °C:	230-234

Structure:



Purification: used as received.

Sodium Hydroxide

Supplier:	Mallinckrodt
Molecular Formula:	NaOH
Molecular Weight (g/mole):	40.00

Purification: used as received.

Sulfuric Acid

Supplier:	Mallinckrodt, 96%
Molecular Formula:	H_2SO_4
Molecular Weight (g/mole):	98.08

Purification: used as received.

Nitric Acid

Supplier: Fisher, 69.3-71.0%

Molecular Formula: HNO_3

Molecular Weight (g/mole): 63.01

Purification: used as received.

Hydrazine

Supplier: Aldrich, 98%

Molecular Formula: H_4N_2

Molecular Weight (g/mole): 32.05

Boiling Point, °C: 113.5

Structure: $H_2N\text{-}NH_2$

Purification: used as received.

Palladium on Activated Carbon (Pd/C)

Supplier: Aldrich

Molecular Formula: Pd 5%, +C

Purification: used as received.

3.1.2.2 Dianhydrides

Pyromellitic Dianhydride (PMDA)

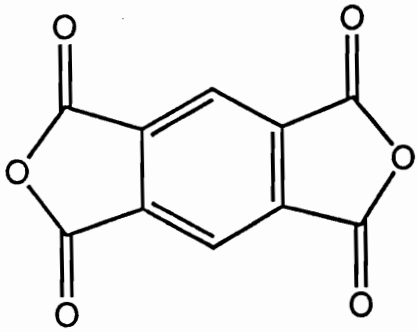
Supplier: Allco

Molecular Formula: $C_{10}H_2O_6$

Molecular Weight (g/mole): 218.12

Melting Point, °C: 286

Structure:



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

2,2'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (Bisphenol-A dianhydride or BPADA)

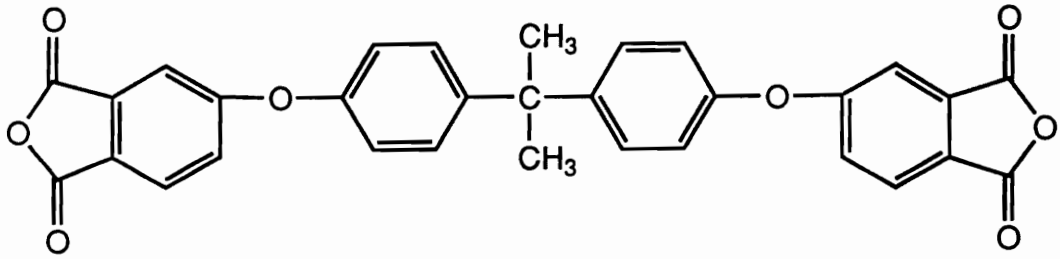
Supplier: General Electric Company

Molecular Formula: $C_{31}H_{21}O_8$

Molecular Weight (g/mole): 520.49

Melting Point, °C: 193 (pure); 188-191 (plant grade)

Structure:



Purification: BPADA was received as a fine white powder and was dried at 150°C for at least 12 hours under vacuum prior to use. Some samples of

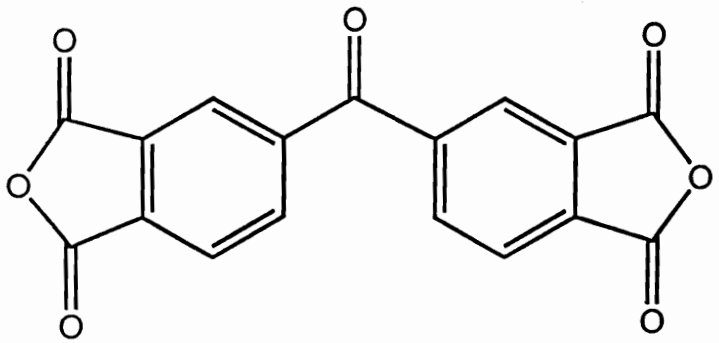
BPADA were plant grade (about 98% pure) flakes and they were purified as follows:

A 1L 3-neck round bottom flask equipped with condenser, mechanical stirrer and nitrogen inlet was charged with plant grade BPADA (100 g), toluene (500 g) and acetic anhydride (50 g). The mixture was heated to reflux (completely dissolved) under nitrogen for 1 hour. The mixture was allowed to cool to 20°C overnight, filtered, and washed with toluene. The BPADA was returned to the flask without drying, along with toluene (500 g) and acetic anhydride (10 g). The mixture was heated to reflux to complete dissolution, cooled to 20°C, filtered and washed with toluene, followed by *n*-heptane. The product was vacuum dried at 120°C overnight. The whole procedure was repeated again to generate a purified product in about 70% yield (m.p.=191-193°C).

<u>3,3',4,4'-Benzophenonetetracarboxylic Dianhydride</u> (BTDA)

Supplier:	Allco
Molecular Formula:	$C_{17}H_6O_7$
Molecular Weight (g/mole):	322.23
Melting Point, °C:	224-226

Structure:



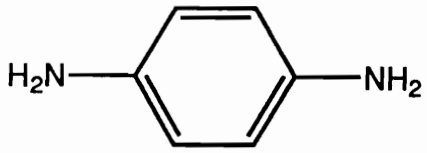
Purification: BTPA was obtained as fine white granular crystals and was dried at 180°C for at least 12 hours under vacuum prior to use.

3.1.2.3 Diamines

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

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

Structure:

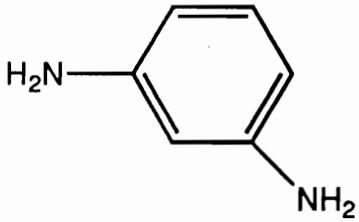


Purification: *p*-PDA was sublimed under vacuum (50 millitorr) at 140 °C. *p*-PDA oxidizes readily in air and must used soon after sublimation and stored under vacuum in darkness.

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

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

Structure:

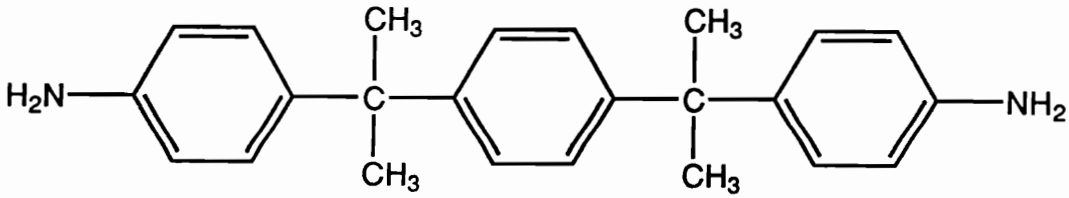


Purification: *m*-PDA was sublimed under vacuum (50 millitorr) at 140 °C. *m*-PDA oxidizes readily in air and must be used soon after sublimation and stored under vacuum in darkness.

<u>4,4'-[1,4-Phenylene-bis-(1-methylethylidene)]bisaniline</u> (Bis P)

Supplier:	Air Products and Chemicals, Inc.
Molecular Formula:	$C_{24}H_{28}N_2$
Molecular Weight (g/mole):	344
Melting Point, °C:	165

Structure:



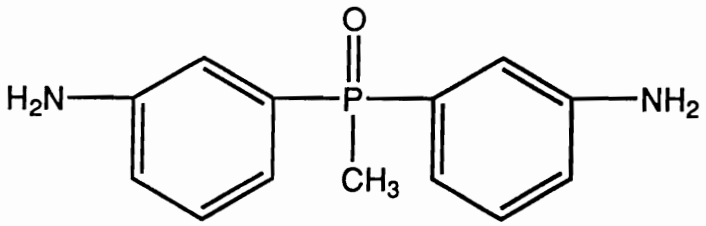
Purification: Bis P was dried at 110°C for at least 12 hours in a vacuum oven prior to use.

<u>Bis(*m*-aminophenyl) methyl phosphine oxide</u> (DAMPO)

Supplier:	Synthesized in house
Molecular Formula:	$C_{13}H_{15}N_2PO$
Molecular Weight (g/mole):	246.25

Melting Point, °C: 155-156

Structure:



Synthesis and purification:

Bis(*m*-aminophenyl) methyl phosphine oxide (DAMPO) was prepared following a modified literature method [248]. This synthesis was refined by Mr. C.N. Tchatchoua (Scheme 3.1.1).

Synthesis of Diphenyl methyl phosphine oxide 2*:*

Methyl triphenyl phosphonium bromide 1 (200 g, 0.56 mole, 98%), which can be derived from commercially available triphenyl phosphine, was transferred into a 5 L round bottom three neck flask fitted with a reflux condenser and a nitrogen inlet. Water (2 L) was then added and the mixture was stirred and heated to reflux (~100°C) for about 30 minutes which produced a cloudy suspension. Sodium hydroxide (112 g, 2.80 mole, 5 times the stoichiometric amount) was dissolved with 1 L water in a beaker and then charged to the cloudy methyl triphenyl phosphonium bromide suspension. Immediately after the addition of the sodium hydroxide solution, a clear layer formed (benzene) on top of the reaction mixture. The reaction was monitored by TLC (chloroform:methanol=9:1) and allowed to reflux for 2 hours. The crude product was extracted with chloroform, washed several times with water, dried over magnesium sulfate and dried again in a vacuum

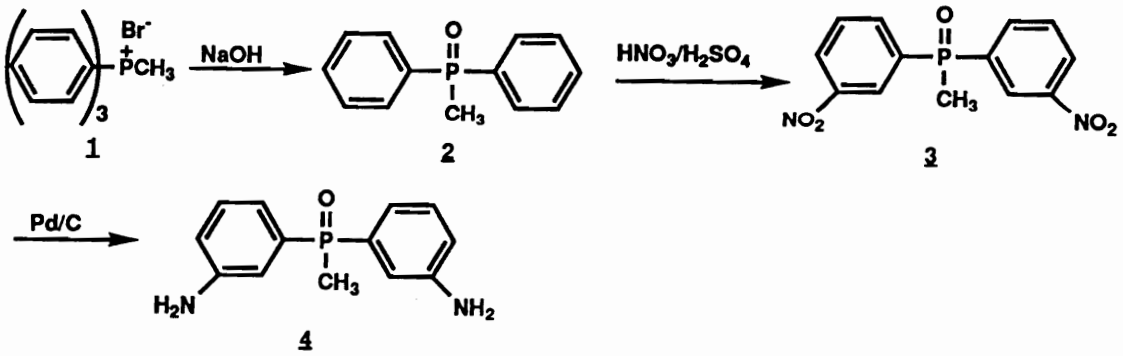
oven for 24 hours. The final product exhibited a melting point of 113-115°C (lit. m.p.: 110-112°C) and the yield was quantitative.

Synthesis of Bis(m-nitrophenyl) methyl phosphine oxide **3**:

Diphenyl methyl phosphine oxide **2** (287 g, 1.33 mole) was charged into a 5 L round bottom flask equipped with a 200 ml dripping funnel, a reflux condenser and a mechanical stirrer. The flask was placed in an ice bath and concentrated (96%) sulfuric acid (1.5 L) was carefully added to the flask. The mixture was stirred for about 30 minutes until the starting material dissolved. In a separate flask placed in an ice bath, concentrated sulfuric acid (500 ml) was added very slowly to nitric acid (252 g, 70% per weight solution (a 5% excess of stoichiometric amount). The mixture of acids was allowed to cool to 0-5 °C and was then added dropwise from a funnel to the reaction solution. The reaction was then allowed to proceed for 2 hours at 0-5°C, and for 3 hours at room temperature (RT), over which time the mixture turned progressively yellowish green. The reaction mixture was then precipitated into ice water, filtered, and dried for 3 days in an oven. The yellowish product was recrystallized twice from ethanol to yield greenish crystals (m.p. 204-205°C, lit. m.p.: 199-202°C) in an overall yield of 85%.

Synthesis of Bis(m-aminophenyl) methyl phosphine oxide **4**:

Bis(3-nitrophenyl)methyl phosphine oxide **3** (115 g, 0.37 mole) and 400 ml of absolute ethanol were charged into a 3 L 4 neck round bottom flask fitted with an addition funnel and a reflux condenser. The mixture was carefully purged with nitrogen and heated to reflux. Hydrazine (175 g, 3.50



Scheme 3.1.1 Synthesis of Bis(*m*-aminophenyl) methyl phosphine oxide (DAMPO)

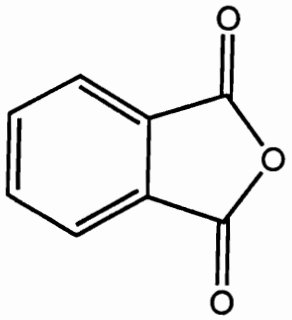
mole, about 3 times of the stoichiometric amount) was added dropwise to the mixture while 200 mg of Pd/C catalyst was simultaneous introduced into the flask. The hydrazine and catalyst addition was repeated two more times for a period of about 2 hours. The resulting black mixture obtained was filtered through Celite using a Buchner funnel to afford a relatively clean product that was washed with acetone and dried for 24 hours in a vacuum oven. The product was recrystallized in 80% yield from 1,2-dichloroethane and has a melting point of 155-156°C. No impurities were detected by silica gel TLC (ethanol). ^{1}H NMR (400 MHz, *d*-DMSO): δ1.79(3H,d), 5.38(4H,s), 6.66(2H,d), 6.75(2H,t), 6.87(2H,d), 7.08(2H,t). ^{31}P NMR (400 MHz, *d*-DMSO): δ 29.11(s). GC/MS (M^+ calcd for $C_{13}H_{15}N_2PO$ 246.25 g/mole) *m/z* (%): 246(28), 245(100), 122(14), 106(18), 93(12), 92(26), 66(15), 65(28). Anal. calcd for $C_{13}H_{15}N_2PO$ (found): C, 63.41(63.55); H, 6.14(6.20); N, 11.38(11.52); P, 12.58(12.71).

3.1.2.4 Endcaps

Phthalic Anhydride (PA)

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

Structure:

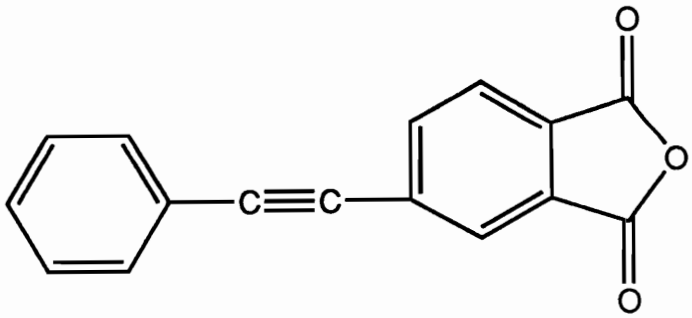


Purification: Pure PA was obtained by sublimation at a temperature of ~125°C.

4-phenylethynylphthalic anhydride (4-PEPA)

Supplier:	Synthesis in house
Molecular Formula:	$C_{16}H_8O_3$
Molecular Weight (g/mole):	248.24
Melting Point, °C:	150-151

Structure:



Synthesis and purification:

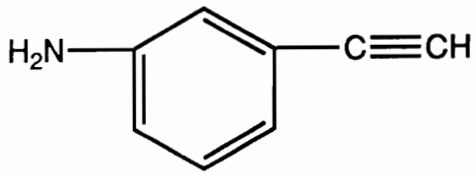
A flame dried 1L, 3 neck round bottom flask fitted with a condenser, mechanical stirrer and nitrogen inlet was used. The procedure involved charging 4-BrPAN (70 g, 0.309 mole), PPh_3 (0.651 g, 2.48×10^{-3} mole) and phenylacetylene (31.494 g, 0.309 mole) into the flask and washing with 140 ml

DMAc. Next, $PdCl_2(PPh_3)_2$ (0.3262 g, 4.648×10^{-4} mole) was added to the flask along with 300 ml Et_3N. The mixture was then stirred and slowly heated to 60 °C under nitrogen. After the reaction mixture reached 60°C, CuI (0.1295 g. 6.8×10^{-4} mole) was charged with 50 ml Et_3N. The flask was slowly heated again to 80°C and stirred for another 12 hours under nitrogen. The reaction was stopped by filtration to remove the salt. The salt was washed with DMAc before discarding and the filtrate was combined with the product solution. Et_3N and most of the DMAc were removed from solution by vacuum distillation using a rotary evaporator. The solution was then added to 2200 ml H_2O, while stirred. The aqueous solution was acidified with dilute HCl to a pH of 4, producing a light yellow precipitate which was extracted with ether. The ethereal solution was treated with charcoal, dried over $MgSO_4$, and filtered through Celite. Crude 4-PEPA was obtained by evaporation of the ether and recrystallized from acetic anhydride to obtain a 84% yield of purified product. ^1H NMR (d-DMSO): 7.4-7.5 (3H, m), 7.6 (2H, m), 8.1 (2H, s), 8.2 (1H, s). GC/MS (M+ calcd for $C_{16}H_8O_3$ 248.24) *m/z* (%): 248(100) and m.p. 150-151°C.

<u>3-Ethynylaniline</u> (*m*-Aminophenylacetylene, *m*-APA or 3-APA)

Supplier:	Eastman Kodak
Molecular Formula:	C_8H_7N
Molecular Weight (g/mole):	117

Structure



Purification: *m*-APA was purified by vacuum distillation at ~90°C and 50 millitorr

3.1.3 Polymer Synthesis

Successful polyimide synthesis with endgroups and good molecular weight control depends on the purification of the starting material, the stoichiometry control, and the synthesis method of choice. Our target number average molecular weight ranged from 2,000 to 40,000 g/mole. Stoichiometric control of the molecular weight will be addressed in the Section 3.1.3.1. The synthesis method of choice and reaction conditions depend on the activity of the monomers and the nature of the intermediates and final products. Thus, the classic two-step route, an acid-ester route, and a modified scale-up procedure will be addressed here.

3.1.3.1 Molecular weight control in polymer synthesis

The number average molecular weight (M_n) and endgroup control of step growth polymerization can be achieved using the Carothers equation as follows:

$$< X_n >= \frac{N_0}{\frac{1}{2}(2N_0 - N_0 p f_{av})} = \frac{2}{2 - p f_{av}} = \frac{2}{2 - f_{av}} \quad \text{(When p=1)} \qquad \text{Eq. 3-1}$$

where $<X_n>$ is the number average degree of polymerization of the reaction mixture, p is the extent of reaction of the functional groups, and f_{av} is the

average number of functional groups per monomer molecule. Since the polymerization reaction must be allowed to proceed to near completion ($p \rightarrow 1$), the $<X_n>$ is controlled by changing the number average functionality, f_{av}, which is:

$$f_{av} = \frac{\text{number of useful equivalents of functional groups}}{\text{number of moles of monomers}} = \frac{\sum N_i f_i}{\sum N_i} \qquad \text{Eq. 3-2}$$

where N_i is the number of moles of species i, and f_i is the number of functional groups of species i. The concept of useful equivalents was introduced here since an excess of the opposing group is, of course, not capable of reacting. In the case of monomer AA and BB type of polymerization which form A-B links and BB is used as an excess component, then B functional end groups will be produced. Then f_{av} is given by:

$$f_{av} = \frac{4N_A}{N_A + N_B} = \frac{4r}{r+1} \qquad \text{Eq. 3-3}$$

where the stoichiometric imbalance is defined as $r=N_A/N_B$, ($NA<NB$). The combination of Eq. 3-1 and Eq. 3-3 gives:

$$< X_n > = \frac{1+r}{1-r} \qquad \text{Eq. 3-4}$$

In another case, when N_B' of monofunctional B endcapper is used to control molecular weight,

$$f_{av} = \frac{\text{number of useful equivalents of functional groups}}{\text{number of moles of monomers}}$$
$$= \frac{\text{number of useful equivalents of A functional groups}}{\text{number of moles of monomers}} + \frac{\text{number of useful equivalents of B functional groups}}{\text{number of moles of monomers}} \qquad \text{Eq. 3-5}$$
$$= \frac{2N_A}{N_A + N_B + N_B'} + \frac{2N_A}{N_A + N_B + N_B'}$$
$$= \frac{4N_A}{N_A + N_B + N_B'} = \frac{4r}{r+1}$$

with redefined stoichiometric imbalance by $r=N_A/(N_B+N_B')$, $(2N_A<2N_B+N_B')$. The same results as in Eq. 3-4 can be obtained, except for the redefined r.

Sample calculation for the synthesis of an endcapped polyimide

The Carothers equation was utilized to calculate the composition of the polymerization recipe for the synthesis of a Mn=40,000 g/mole, BPADA/*p*-PDA PA capped polyimide. We designate the diamine monomer, the dianhydride monomer and phthalic anhydride as BB, AA, and A, respectively. The product has the structure as **A(BBAA)nBBA**. Thus,

$$\langle X_n \rangle = 2n+1$$

In order to derive $\langle X_n \rangle$, n is calculated as follows:

$$n = \frac{\text{Target MW} - 2 \times \text{Endgroup(A)} - MW_{BB}}{\text{Repeat Unit MW}} \qquad \text{Eq. 3-6}$$

where: Target MW=40,000

Endgroup (A)=148.117-O+N=146.125

$MW_{BB}=C_6H_4=79.0976$

Repeat Unit MW=520.491+108.143-$2H_2O$=592.604

in which 520.491, 108.143 and 148.117 are the MW of BPADA, *p*-PDA and PA, respectively. Therefore, values of n=66.872 and <Xn>=134.744 are obtained. Application of Eq. 3-4 gives r=0.9853.

From Eq. 3-5, we know that $r=N_B/(N_A+N_A')$. Eq. 3-6 and the structure of the final product results in the relationship: $N_A/N_B=n/n+1=66.872/67.872$. If we assume $N_A=1$ mole, then the N_B and N_A' can be solved and the reaction concentration for the synthesis can be generated as follows:

	moles[1]	scaled moles[2]	M W	grams
BPADA	1	1×10^{-2}	520.491	5.2049
p-PDA	1.015	1.015×10^{-2}	108.143	1.0977
PA	0.03	3×10^{-4}	148.117	0.0444

1: normalized moles based on BPADA

2: scaled moles for a polymerization batch size of 6~7 grams.

A simple method can also be utilized to calculate the recipe. The final product structure and Eq. 3-6, allow one to observe that with 66.872 moles of BPADA, (66.872+1) moles of *p*-PDA and 2 moles of PA, the target M_n of 4.0 kg/mole can be obtained. Thus, the BPADA:*p*-PDA:PA=66.872:67.872:2 (in moles) can be used to calculate the amount of reagents. The results are analgous to those obtained using the Carothers equation.

3.1.3.2 Classic two step route

The classic two-step route utilizes polyamic acid in the first step, while the second step involves imidization via cyclodehydration of the polyamic acid. The latter step can be performed either by thermal, chemical or solution methods. The following is an example of the classic two-step synthesis used in this research. The target polyimide was based on PMDA/DAMPO reacted in 1:1 stoichiometry.

Polyamic acid formation:

To a flame dried flask under nitrogen, DAMPO (5.0846 g, 0.02 mole) was added with 9 ml NMP. The diamine dissolved within 30 minutes via mechanical stirring. PMDA (4.5067 g, 0.02 mole) was then transferred into the flask along with 20 ml NMP. The dianhydride gradually dissolved and the mixture was stirred for another 20 hours under nitrogen, at which time the mixture was viscous and trapped many small gas bubbles. The reaction was stopped and the solution was placed in vacuum for few minutes, which produced a clear, yellow, viscous polyamic acid/NMP solution.

Thermal imidization:

The above solution was cast onto a clean glass plate in a film-like precursor form. The glass plate was then placed on a hot plate fitted with a temperature controller and a glass cover, and the material was slowly purged with nitrogen. The glass plate was then heated according to the following schedule:

25°C: 1hour, heat to 100 °C within 1 hour

100°C: 1hour, heat to 200°C within 1 hour

200°C: 1hour, heat to 300°C within 1 hour

300°C: 1hour, cool to 25°C

In general, a brownish film was then collected which could be peeled from the glass plate.

Other polyamic acid systems synthesized by this route were based on BTDA/Bis P and BPADA/*m*-PDA systems. The latter will be detailed in a subsequent section addressing scale up synthesis

3.1.3.3 Acid-ester route

The acid-ester route for the synthesis of polyimides was the primary method used in this research, which also requires two steps. The first step is to form the acid-ester intermediate from the reaction of the anhydride with ethanol. The second step employs an elevated temperature reaction of the acid-ester intermediate with the diamine, in the presence of azeotropic agent, which permits formation of fully imidized amorphous polyimides. The reaction apparatus is show in Figure 3.1.1. Both homo- and copolyimides can be synthesized by this procedure.

<u>Example of homopolyimide synthesis</u>

Polymerizations were conducted as follows for the synthesis of BPADA/DAMPO 4-PEPA capped oligomers with a number average molecular weight (M_n) of 3.0 kg/mole. For example, 9.075×10^{-3} mole (4.7236

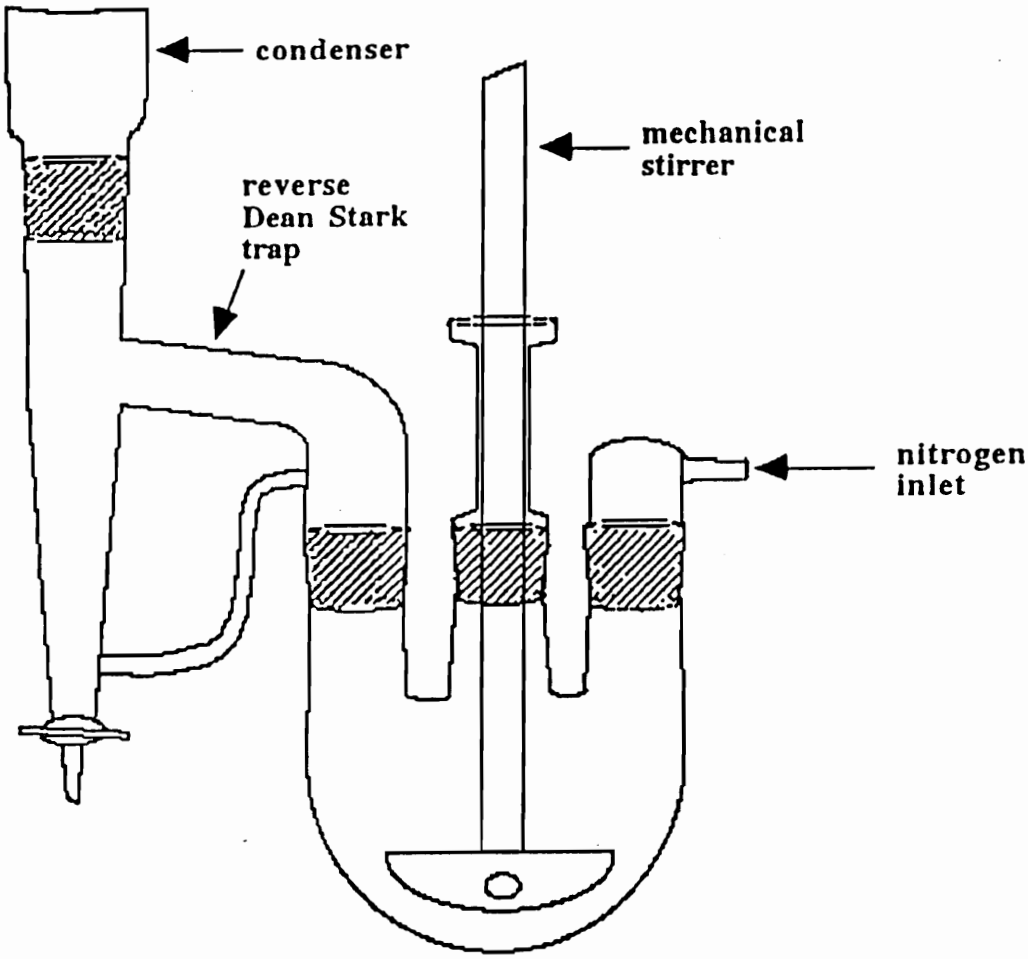


Figure 3.1.1. Reaction flask apparatus.

g) monomer-grade BPADA and 5.7832×10^{-3} mole (1.4356 g) of 4-PEPA were charged to three-neck round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, thermometer, reverse Dean-Stark trap and reflux condenser, and was heated in a silicone oil bath. Absolute ethanol, 7-10 ml per gram of dianhydride, and ~2 ml of a triethylamine catalyst were then introduced and the mixture was refluxed with stirring for about one hour until a clear solution was obtained. When the distillation of ethanol ceased, the trap was filled with *o*-DCB and the diamine DAMPO, 1.1967×10^{-2} mole (2.9468 g) was added to the reaction vessel, followed by NMP (16 ml) and *o*-DCB (4 ml) (80:20 vol:vol) to provide a solids content of 30% wt./vol. The reaction mixture was then heated to 170-185°C for 20 hours, which was sufficient time to complete the reaction (e.g. P, the fractional extent of the functional group conversion was > 0.99). Then the polymer was coagulated 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 with excess anhydrous diethyl ether. It was then air dried for 6-8 hours and vacuum dried at ~160°C for 24 hours.

Other homopolyimide systems synthesized by the same method include BPADA/*p*-PDA and BPADA/*m*-PDA systems that were endcapped with PA, 4-PEPA or *m*-APA endcappers.

Example of copolyimide synthesis

Copolyimides were synthesized according to similar procedure described above, except where a mixture of dianhydrides or diamines were used instead of pure monomers.

Polymerization was conducted as follows for the synthesis of BPADA/*p*-:*m*-(7:3)PDA 4-PEPA capped oligomers with a number average molecular weight (M_n) of 3,000 g/mole as an example: 3.436×10^{-2} mole (17.8824 g) monomer-grade BPADA and 1.677×10^{-2} mole (4.1624 g) of 4-PEPA were charged to three-neck round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet, thermometer, reverse Dean-Stark trap and reflux condenser, and was heated in an oil bath. Absolute ethanol, 7-10 ml/g of dianhydride, and ~3 ml of triethylamine were then introduced and the mixture was refluxed via stirring until a clear solution was obtained. When the distillation of ethanol ceased, the trap was filled with *o*-DCB. Next, the diamines, *p*-PDA, 2.992×10^{-2} mole (3.2355 g) and *m*-PDA, 1.282×10^{-2} mole (1.3866 g) were added to the reaction vessel, followed by NMP (50.0 ml) and *o*-DCB (12.5 ml) (80:20 vol:vol) to provide a solids content of 30% wt.%. The reaction mixture was then heated to 170-185°C for 20 hours, after which time the polymer solution was coagulated 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 with excess anhydrous diethyl ether. It was then air dried for 6-8 hours and vacuum dried at ~160°C for 24 hours. The samples were semicrystalline when high *para*-phenylene diamine isomer contents was utilized, and these were dried for an additional 12 hours at 250°C under vacuum.

Other copolyimides system that were synthesized by the same procedure include BPADA/PMDA/DAMPO and BPADA/DAMPO/*p*-PDA with PA as the endcapper.

3.1.3.4 Scale up synthesis

A simplified method was also used to synthesize all *m*-PDA based oligomers: *m*-PDA, followed by BPADA and 4-PEPA were charged into the reactor with *o*-dichlorobenzene (*o*-DCB) at 120°C. The mixture was stirred for 1 hour until a homogenous solution was obtained. The reaction mixture was then heated to 180°C for 20 minutes, followed by 170°C for 24 hours. The workup of the polymer was the same as described above. This method was used for scale up synthesis using a 10-gallon reactor in the General Electric Corporate Research and Development Laboratory. Detailed procedures are described below.

Synthesis of M_n=2.0 kg/mole BPADA/*m* -PDA 4-PEPA Capped Polyimide

The procedure charged 1,181 g *m*-PDA into a 10-gallon reactor equipped with a stirrer, nitrogen inlet, thermometer, reflux condenser and trap. The *m*-PDA was rinsed with 5.4 L *o*-DCB. It was necessary to heat the reactor to 120°C to dissolve the *m*-PDA. BPADA (4,069 g) was then added to the reactor and rinsed with 8.3 L *o*-DCB. The temperature dropped to 100°C shortly after charging. The reaction mixture at that stage was milky and water formed quickly on the sight glass of the reactor. The water was distilled upon subsequent heating, resulting in a clear solution. It took about 20 minutes to dissolve the BPADA to form a clear, yellow solution. Next, 4-PEPA (1,572 g) was charged into the reactor, which was rinsed with 2.3 L *o*-DCB. This immediately produced a solution. Next, 1 L *o*-DCB was added as an extra diluent and the reaction mixture was kept at 120°C for 1 hour. The water that

formed was removed by distillation. The reaction mixture was then heated to 180°C and refluxed for 20 minutes at that temperature. The water was collected, along with a large amount of *o*-DCB in the trap (0.31 L water was collected, while theoretically it should have been 0.4 L). The distilled *o*-DCB was collected and a calculated amount of freshly distilled *o*-DCB was added back to the reactor, to bring the total amount of *o*-DCB to 16.0 L. The reaction mixture was cooled to 164°C and held at that temperature for 24 hours. After this time, it was cooled to 50°C and precipitated by slowly dripping the polymer solution into methanol (polymer solution : methanol = 1:5 by vol.) in a low-speed blender. The polymer was isolated by filtration, air dried for 6-8 hours and vacuum dried for 72 hours, initially at ambient temperature, followed by heating to 160°C.

The same procedure was used to synthesize a M_n=3.0 kg/mole oligomer.

Synthesis of M_n=10.0 kg/mole BPADA/*m*-PDA(excess) Polyamic Acid

The reaction charged 1,521 g *m*-PDA into a 10-gallon reactor equipped with a stirrer, nitrogen inlet and reflux condenser. The *m*-PDA was rinsed with 18.9 L NMP and stirred to dissolve. Then, BPADA (7,007 g) was added to the reactor and rinsed with 1.0 L NMP. It took about 30 minutes to dissolve most of the BPADA, and this resulted in a yellowish, viscous solution. The reaction mixture was then stirred at 40°C for 24 hours. The ensuing clear, viscous, yellow solution was collected into sealed bottles.

The same procedures were used to synthesize the following systems:
M_n=20.0 kg/mole BPADA/*m*-PDA PA Capped Polyamic Acid.
M_n=3.0 kg/mole BPADA/*m*-PDA 4-PEPA Capped Polyamic Acid.

3.2 Preparation of Polymer Blends

A BPADA/DAMPO thermoplastic and Ultem™-1000 polyetherimide were blended at different ratios (0:100, 25:75, 50:50, 75:25, 100:0 by weight) and dissolved with chloroform to form solutions of 15% wt./vol. concentrations. Clear solutions were obtained after stirring for 2-3 hours. At this point the solution can be directly used to cast films or can be coagulated by slowly dripping into methanol in a high speed blender. The coagulated polymer was then collected and dried at 170°C under reduced pressure for 24 hours.

The same procedure was used to prepare blend of M_n=3.0 kg/mole BPADA/*m*-PDA 4-PEPA capped imide oligomer with an Ultem™-1000 polyetherimide.

3.3 Characterization

Intrinsic Viscosity

Intrinsic viscosity measurements were conducted in NMP or $CHCl_3$ at 25°C using a Canon-Ubbelohde viscometer. The intrinsic viscosity values were obtained by using four different concentrations and the results were linearly extrapolated to zero concentration.

Differential Scanning Calorimetry (DSC)

Glass transition temperatures and cure exotherms were determined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-7 Differential Scanning Calorimeter. Scans were run under nitrogen at a

heating rate of 10°C/minute; reported values were obtained from a second heating, except where noted, after quick cooling.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed dynamically on a Perkin Elmer TGA-7 Thermogravimetric Analyzer at 10°C/minute in air. Char yields at designated temperatures and 5% weight loss temperatures were recorded.

Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance (^{1}H, ^{13}C and ^{31}P NMR) spectra were obtained using a Varian Unity 400 spectrometer, which confirmed the monomer and polymer structures and the number average molecular weights of the oligomers using end group analysis. Samples were dissolved in a deuterated solvent, such DMSO-d_6 or $CDCl_3$, at concentrations of 1 to 10% solids. The solid state ^{31}P NMR spectra was obtained with a Brucker MSL 300 spectrometer to determine the char composition of the degraded polymers.

Mass Spectroscopy (MS)

Mass spectroscopy analysis was conducted using a Fisons VG Quattro mass spectrometer to determine compound molecular weight.

Gel Permeation Chromatography (GPC)

GPC measurements were performed on a Waters 150-C ALC/GPC instrument, which was equipped with a viscosity detector; M_n and M_w/M_n

values for the polyimide samples were determined using the universal calibration procedure previously developed [254].

Solubility Test

The solubility of various synthesized polyimides was determined using several solvents. The dried polymer powder was mixed with the appropriate solvent to a concentration of 10 wt./vol.%. The mixture was then stirred at RT for 8 hours. Solubility was assessed by visual observation. In some cases, the solubility was recorded at elevated solvent temperatures under reflux.

Melting Point (m.p.) Measurement

The melting points of purified compounds were determined by a Lab Devices Melt-Temp II at a heat rate of <1°C/min.

Thin Layer Chromatography (TLC)

Thin layer chromatography was then performed to determine the purity of the various compounds prepared in this research. A sealed developing chamber, a silica gel plate, and appropriate solvents were used.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was used to determine the presence of ethynyl groups in the polyimide oligomers; spectra were obtained with a Nicolet Impact 400 FT i.r. spectrometer. For kinetic studies, dilute solutions (5 w/v% in $CHCl_3$) of the 4-PEPA endcapped imide oligomers were deposited on a NaCl IR disc. The solvent was evaporated and the disc

was dried (~100 °C) for at least 12 hours to produce a thin oligomer layer on the disc surface. The disc was then put into a pre-heated furnace at a designated temperature (300-345°C) under nitrogen flow. The oligomer was then allowed to cure for a certain time, after which reaction was quenched by cooling the disc at room temperature. FTIR spectra were then used to monitor the disappearance of the ethynyl peak and to generate reaction kinetic data.

Parallel Plate Rheology

Samples for melt viscosity measurements were prepared by compression molding at temperatures 20°C above T_g. Vacuum dried polymers were used to prepare 2.5 cm diameter samples of about 0.2 cm thickness. Samples were kept under vacuum prior to measuring. Parallel plate scans were performed using a Bohlin Rheometer in both nitrogen and air at various temperatures. Tests were conducted using parallel plates at a frequency of 1 Hz, at either a constant temperature or using a dynamic temperature scan of 3°C/minute at 10% amplitude.

Refractive index measurement

To prepare the samples of the solvent cast films on a clean class plate, a polymer solution of 15% wt./vol. in chloroform was used. The glass plate was then air dried for 2 hours and slowly heated to 170°C (2 hours) and dried for another 12 hours. Films were carefully peeled off the glass plate and were used for refractive index measurements.

The refractive indices of thin polyimides films were measured using a Metricon™ Model 2010 prism coupler thin film thickness/refractive index measurement system, with index accuracy of ±0.001, and index resolution of ±0.0005. Measurements were based on solution cast films with an operating wave length of 633 nm and prism type 200-P-4.

Solvent extraction measurements

Sample preparation: Dry reactive imide oligomer powders (0.3-0.5 g) were deposited on a 5 cm aluminum pan, which was then placed in a Thermolyne Type 47900 Furnace. The furnace was preheated to designated curing temperatures (350-380°C). Samples were held at the cuer temperature for 30-90 minutes under air or nitrogen. After curing, the film sample was cooled to room temperature and isolated.

The pre-weighed cured thermoset films (0.2 g) were placed in a cellulose extraction thimble and extracted with a Soxhlet extraction apparatus using chloroform as the solvent. The extraction was conducted for 4 days and the thimble was then dried in air for 2 hours, followed by additional drying under reduced pressure at 120°C for 3 days, then at 180°C for 1 day. The dried sample weight after extraction was identified as the network gel; the gel fraction was then calculated as a ratio of the network gel to the total sample weight.

3.4 Mechanical Properties Investigation

3.4.1 Tensile properties

To produce samples by compression molding, the polymer powder was placed between two steel plates that were wrapped with aluminum foil and treated with release agents (fluorocarbon based). The plates were then placed into pre-heated (250°C) smart press and 0.2 kpsi contact pressure was applied for 10-15 minutes. A pressure of 1.2 kpsi was then applied for another 1 minute, after which the plates were cooled in a cooling press for 1-2 minutes. A film with a thickness of 10-15 mils. was obtained, which was cut into dogbone specimens for use in tensile tests.

Tensile property measurements were determined using an Instron Model 1123, using the ASTM D638 method at a strain rate of 0.05 in./minute at RT. Samples were cut with a dogbone die conforming to ASTM D368 type V. All values are the average of 4-5 runs per specimen.

3.4.2 Adhesive properties by single lap shear measurements

The Ti-Ti single lap shear specimens were prepared and tested according to ASTM-D1002. A solution of the oligomer [15%(w/v)] in chloroform was coated onto a glass scrim cloth (112E) and dried at 180°C for 6-12 hours under reduced pressure. This procedure was repeated (~ 4 times) until the scrim contained 85 wt.% oligomer. The scrim was then cut into rectangles slightly larger than 1.27 cm × 2.54 cm.

Titanium coupons were sandblasted, washed with water and dipped in a Pasa-Jell surface treatment for 20 minutes, then washed with water and dried at 100°C. Next, the coupons were primed with the same polymer solution and dried at 180°C under reduced pressure. A piece of scrim was placed between two titanium plates placed end-to-end with a horizontal overlap of 1.27 cm × 2.54 cm. The specimens were placed in a melt press and the temperature was then raised from 25°C to cure temperature (350-380°C) at a rate of 10°C/minute. After reaching cure temperature, the specimens were then cured for 45-90 minutes at 25-75 psi.

The Ti-Ti lap shear specimens were mounted between two grips of an Instron model 1123 and tested in tension with a crosshead speed of 0.05 in./minute.

Chapter 4. RESULTS AND DISCUSSION

4.1 Introduction

This chapter is divided into four major sections. The first section will report the synthesis and characterization of non-reactive phthalimide-terminated polyetherimides. The second section will discuss the synthesis and characterization of reactive endcapped polyetherimides – especially 4-phenylethynyl phthalimide-terminated oligomers, including a scale up of several related systems. The third section will explore the properties of several reactive endcapped oligomers. Characterization of the cured oligomers to ascertain their mechanical, adhesive and composite properties will also be reported using rheology testing, DSC and FTIR. The last section will cover the synthesis and characterization of arylene ether imide reactive oligomers and polymers containing diaryl alkyl phosphine oxide groups.

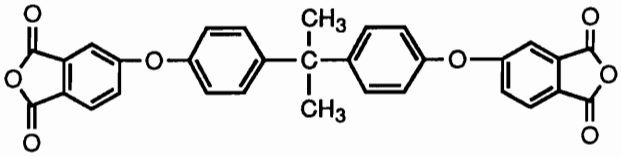
The monomers (and their corresponding IUPAC names) utilized for polyetherimide synthesis are listed in Table 4.1.1. Abbreviations for monomers will be used hereafter. The polymer systems will be written as:

dianhydride/diamine endcap

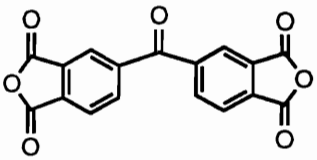
For example, a polymer synthesized from BPADA dianhydride and *p*-PDA diamine with PA endcap agent is described as a BPADA/*p*-PDA PA endcapped polyimide.

Table 4.1.1. Polyimide monomers.

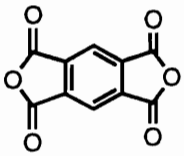
Dianhydrides:



2,2'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]-propane dianhydride (BPADA)

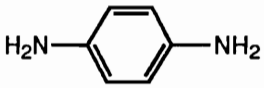


3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA)

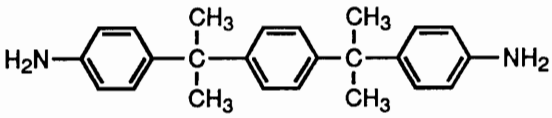


Pyromellitic dianhydride (PMDA)

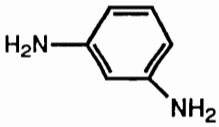
Diamines:



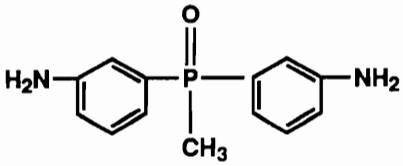
1,4-Phenylenediamine (*p*-PDA)



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

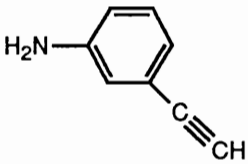


1,3-Phenylenediamine (*m*-PDA)

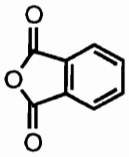


Bis(*m*-aminophenyl) methyl phosphine oxide (DAMPO)

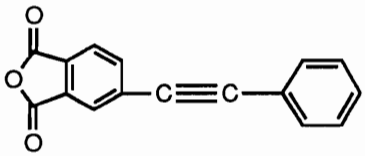
Endcappers:



m-Aminophenylacetylene (3-APA)



Phthalic anhydride (PA)



4-Phenylethynylphthalic anhydride (4-PEPA)

4.2 Synthesis of non-reactive phthalimide-terminated polyetherimides

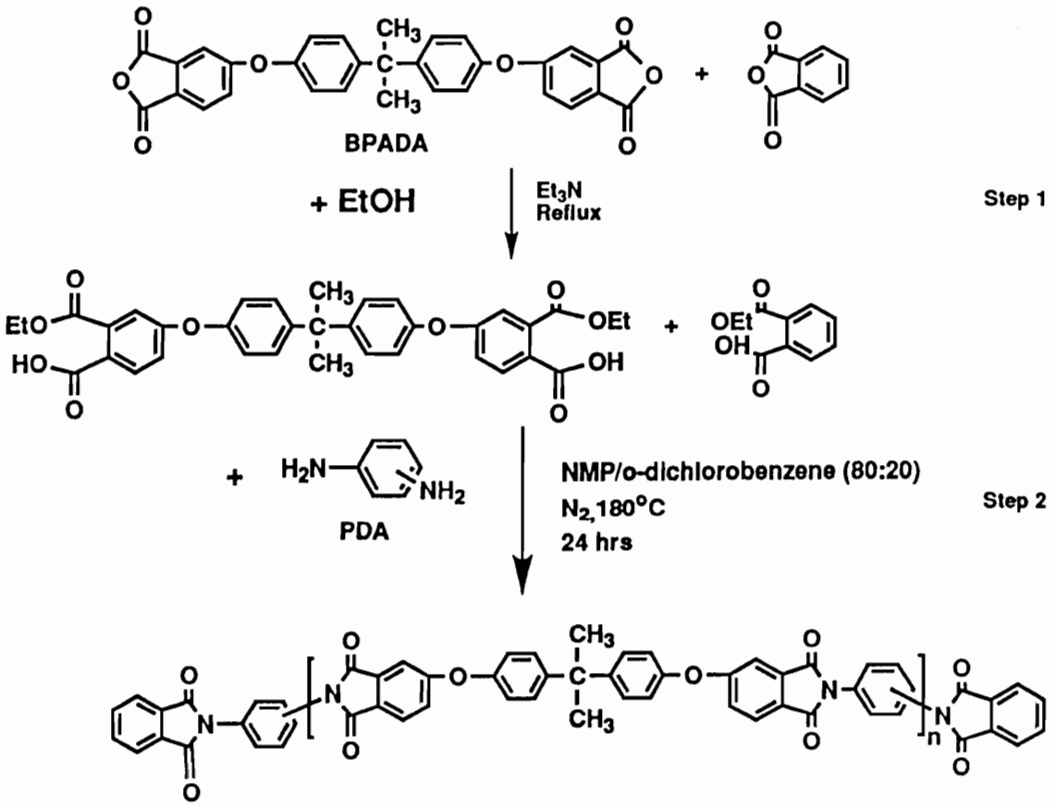
4.2.1 Synthesis of polyetherimides based on *m* -PDA

Phthalimide-terminated polyimides based on *m*-PDA with 20.0 and 30.0 kg/mole target molecular weight were synthesized using the ester acid route [224] with high yield and purity (Scheme 4.2.1). The purpose of this synthesis was to generate a direct comparison with the commercial available polyetherimide (Ultem™-1000) and to determine if the synthetic procedure utilized was appropriate.

Most of polymerizations were conducted via the acid-ester route, primarily because of the solubility of the fully cyclized polyetherimides and the procedure's relative simplicity. The mechanisms and advantages of this synthetic route have already been summarized in previous review sections.

Characterization of the BPADA/*m*-PDA PA endcapped polyimides are listed in Table 4.2.1. The glass transition temperature of the polymer with M_n=30.0 kg/mole was 217°C and the 5% weight loss in air was reported at 539°C, as determined by TGA. The intrinsic viscosity of this polymer was measured at 0.47 dL/g in NMP, indicating that high molecular weight was achieved, which is consistent with published values [218]. All these polymers were completely amorphous and were soluble in organic solvents including NMP, DMAc, chloroform and methylene chloride.

In order to verify reaction conditions, molecular weight growth as a function of time was measured by GPC. An online viscosity detector along with universal calibration was used to determine absolute molecular weight. The second step of the acid-ester route polymerization reaction (Scheme 4.2.1)



Scheme 4.2.1 Synthesis of BPADA/PDA PA capped polyetherimide by acid-ester route

Table 4.2.1. Thermal analysis characterization of BPADA/*m*-PDA PA endcapped polyetherimides.

Target M_n (kg/mole)	η (dL/g)	T_g (°C)[a]	TGA[b] 5% weight loss (°C)
30.0	0.47	217	539
20.0	0.42	215	525

a: Heating rate of 10°C/minute in nitrogen

b: Measured in air at 10°C/minute

was monitored by GPC. Time zero was identified as the point where the diamines were added to the previously formed acid-ester dianhydrides at 180°C. The concentration of the reaction solution was 25 wt.% and molecular weight results are shown in Figure 4.2.1. The target number average molecular weight (20.0 kg/mole) was achieved after about 20 reaction hours, indicating that the ester-acid reaction route was successful.

4.2.2 Synthesis of polyetherimides based on *p*-phenylene diamine (*p*-PDA)

A synthetic variations using *p*-PDA in place of *m*-PDA was employed to examine isomer effect on glass transition temperature. Number average molecular weights ranging from 5.0 to 40.0 kg/mole were synthesized with phthalic anhydride as the endcapping agent. As expected, the T_g of the *para*-linked systems increased from 211 to 231°C, as shown in Table 4.2.2.

The all-*para*-linked systems were somewhat surprisingly semicrystalline in nature, as evidenced by DSC melting endotherms on the first heat, where T_m values varied from 291 to 321°C (Table 4.2.2). However, these melting endotherms were only observed during the first heat. A typical DSC trace of a 40.0 kg/mole *para*-linked polyimide is shown in Figure 4.2.3. The 5.0 kg/mole material displayed two melting endotherms, at 285°C and 321°C (Figure 4.2.2). However, it is not considered unusual for a semicrystalline polyimide to display two T_ms because of the differing thicknesses of the crystalline lamellae. Interestingly, these polyimides remained soluble during the entire polymerization process at elevated temperatures, and precipitated out as fine particles only after cooling to <100°C, which suggests their possible utility in powder prepregging systems. These semicrystalline samples were

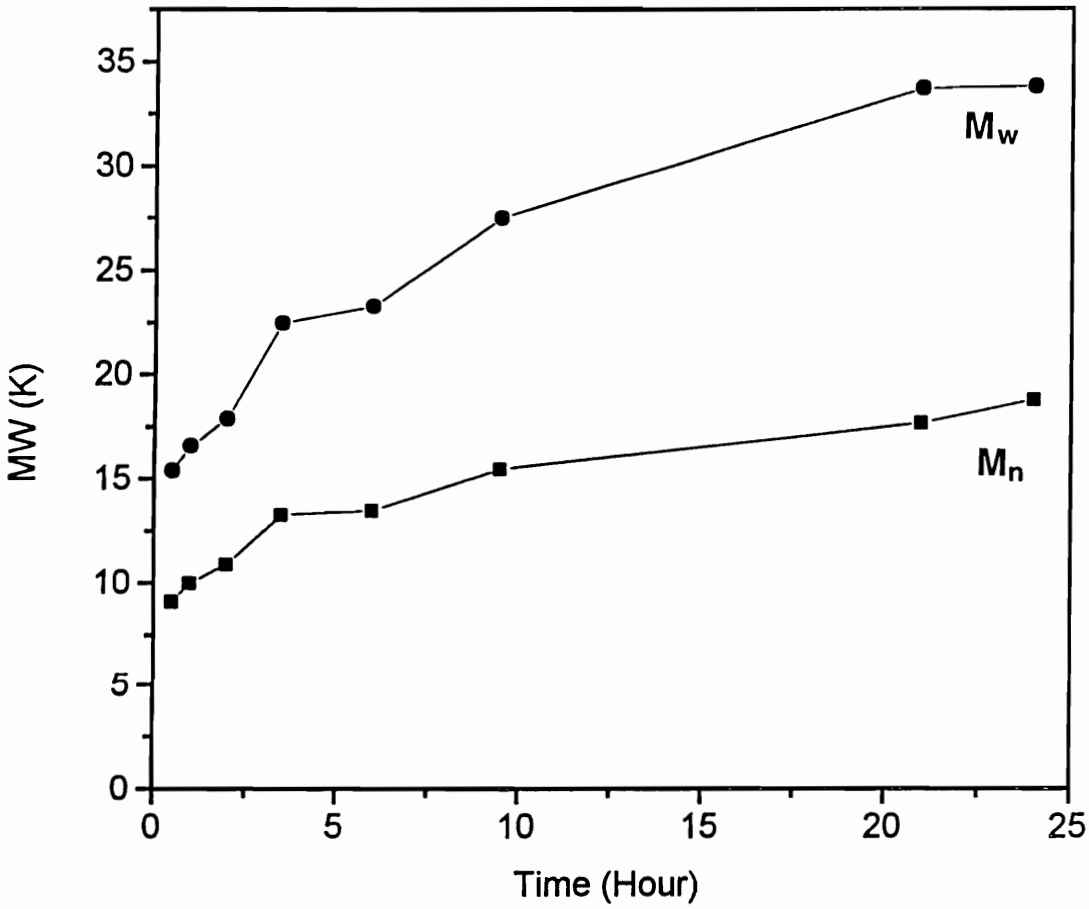


Figure 4.2.1. Following the polymerization reaction of M_n=20.0 kg/mole BPADA/*m*-PDA PA endcapped polyimides by GPC.

Table 4.2.2. Thermal analysis characterization of BPADA/*p*-PDA PA endcapped polyetherimides.

Target M_n (kg/mole)	T_g (°C)[a]	T_m (°C)[b]	TGA[c] 5% weight loss (°C)
40.0	231	291	525
15.0	225	285	558
5.0	211	285, 321	554

a: Heating rate of 10°C/minute in nitrogen

b: T_m values observed on first heating only

c: Measured in air at 10°C/minute

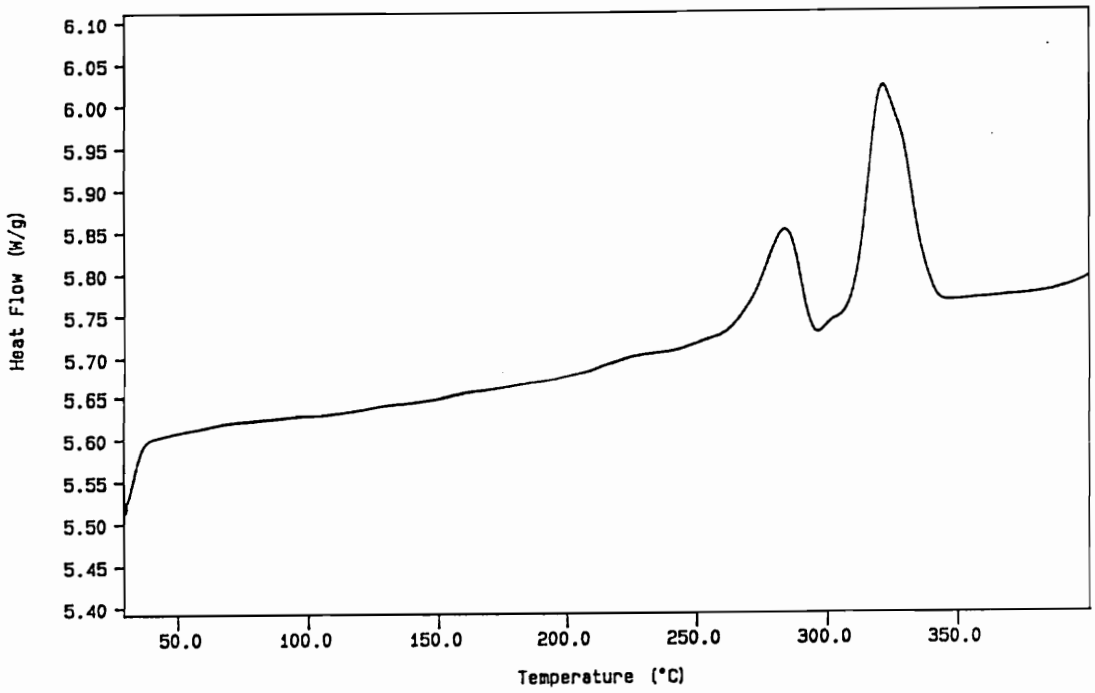


Figure 4.2.2. DSC thermogram (1st heating) of M_n=5.0 kg/mole BPADA/*p*-PDA PA endcapped polyetherimides.

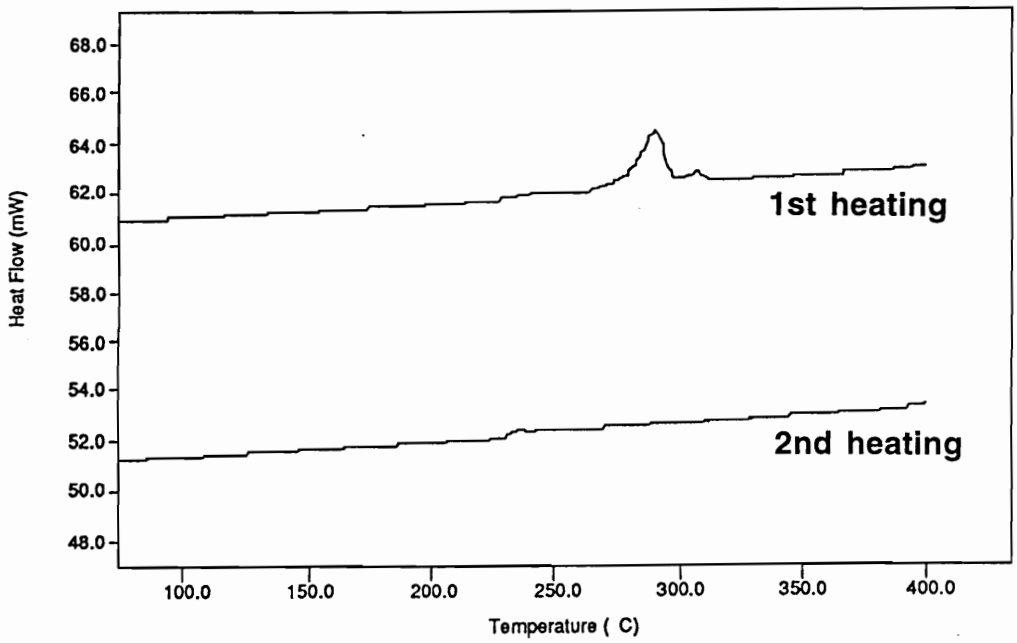
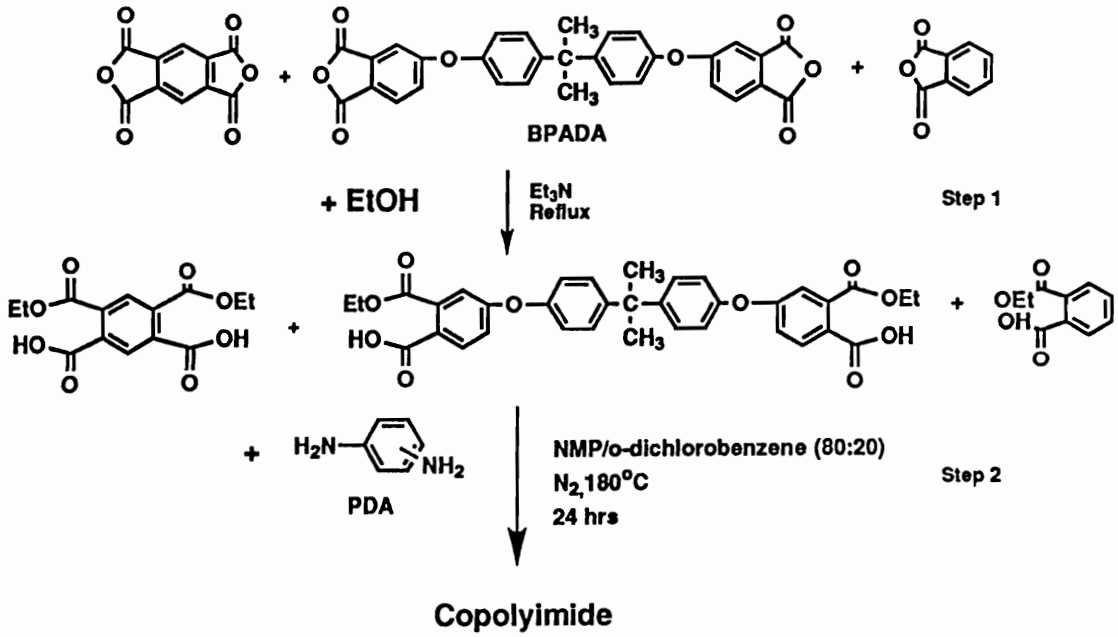


Figure 4.2.3. DSC thermogram of M_n=40.0 kg/mole BPADA/*p*-PDA PA endcapped polyetherimides.

insoluble in most organic solvents. All of the systems exhibited high thermo-oxidative stability in air as indicated by dynamic TGA (5% weight loss values of 525–558°C).

4.2.3 Synthesis of copolyimides based on BPADA and PMDA

Our research objective was to prepare polyetherimides with the reactive phenylethynyl endgroups, which possess high cure temperatures, in order to ensure a wider processing window. The semi-crystalline nature of all *para*-linked polymer systems described herein possess high T_m values, which reduce the processing window and are thus undesirable. Therefore, copolyimides based on BPADA/PMDA/*p*-PDA with a phthalimide endgroup were synthesized at a target number average molecular weight of 15.0 kg/mole in order to evaluate its effect on crystallinity. PMDA copolyimides of 5, 10 and 50 mole% were synthesized (Scheme 4.2.2) and characterized (Table 4.2.3). The glass transition of the polymer rose as PMDA content increased. Crystallinity also increased with higher levels of PMDA due to the rigid nature of this copolyimide. During solution polymerization, precipitation during imidization was observed with increased amount of PMDA. It was not surprising, then, that BPADA:PMDA (50:50) had a broad T_g interval due to the semicrystalline nature of this systes. Therefore, introducing PMDA increases both the percent crystallinity and the glass transition temperature.



Scheme 4.2.2. Synthesis of BPADA/PMDA/*p*-PDA, M_n=15.0 kg/mole copolyimide.

Table 4.2.3. Thermal analysis characterization of BPADA/PMDA/*p*-PDA PA endcapped, M_n=15.0 kg/mole copolyimides.

PMDA (mole %)	T_g (°C)[a]	T_m (°C)[b]	TGA[c] 5% weight loss (°C)
5	225	281, 312 low intensity	532
10	236	303 low intensity	548
50	250 (broad)	none	418

a: Heating rate of 10°C/minute in nitrogen

b: T_m values observed on first heating only

c: Measured in air at 10°C/minute

4.2.4. Synthesis of copolyimides based on *p*-PDA and *m*-PDA

Another approach to reduce crystallinity is to synthesize copolyimides based on BPADA and a mixture of *para*- and *meta*-PDA. Copolyimides with M_n= 15.0 kg/mole and phthalic anhydride endcapper were successfully synthesized. The characterization of 10-40 mole%*m*-PDA copolyimides is listed in Table 4.2.4. Incorporating the *m*-PDA did not greatly reduce T_g values. For example, the 9:1 and 8:2 (*p*-PDA:*m*-PDA/BPADA) systems exhibited melting points of 265°C and 257°C, respectively. However, incorporating higher amounts of *m*-PDA (30 mole% or higher), suppressed crystallinity in the 15.0 kg/mole systems, and no melting endotherm was observed by DSC. Furthermore, the copolyimides based on *m*-PDA and *p*-PDA exhibited excellent thermal stability in air with 5% weight loss values in the range of 536°C to 549°C. The solubility of the copolyimides improved as the *m*-PDA content increased, which is listed in Table 4.2.5. Therefore, incorporating *m*-PDA can effectively suppress the crystallinity of all *para*-linked system without significantly lowering glass transition temperatures.

4.3. Synthesis of reactive endcapped polyetherimides

4.3.1. Synthesis of 4-phenylethynyl phthalic anhydride (4-PEPA) endcapper

4-phenylethynyl phthalic anhydride (4-PEPA) was applied as a reactive endcapper and was successfully synthesized via the palladium-catalyzed coupling reaction [221] of 4-bromophthalic anhydride and phenylacetylene, as

Table 4.2.4. Thermal analysis characterization of BPADA/*m*-PDA/*p*-PDA PA endcapped, M_n=15.0 kg/mole copolyimides.

Ratio of *p*-PDA:*m*-PDA	T_g (°C)[a]	T_m (°C)[b]	TGA[c] 5% weight loss (°C)
9:1	226	265	548
8:2	218	257, 284	549
7:3	225	none	545
5:5	217	none	536

a: Heating rate of 10°C/minute in nitrogen

b: T_m values observed on first heating only

c: Measured in air at 10°C/minute

Table 4.2.5. Solubility of BPADA/*m*-PDA/*p*-PDA PA endcapped, M_n=15.0 kg/mole copolyimides.

Ratio of *p*-PDA:*m*-PDA	$CHCl_3$	DMAc	NMP	THF
9:1	PD	N	SD	N
8:2	PD	N	SD	N
7:3	D	N	SD	N
5:5	D	D	D	PD

D-completely dissolved

PD-partially dissolved

SD- slightly dissolved

N-non dissolved

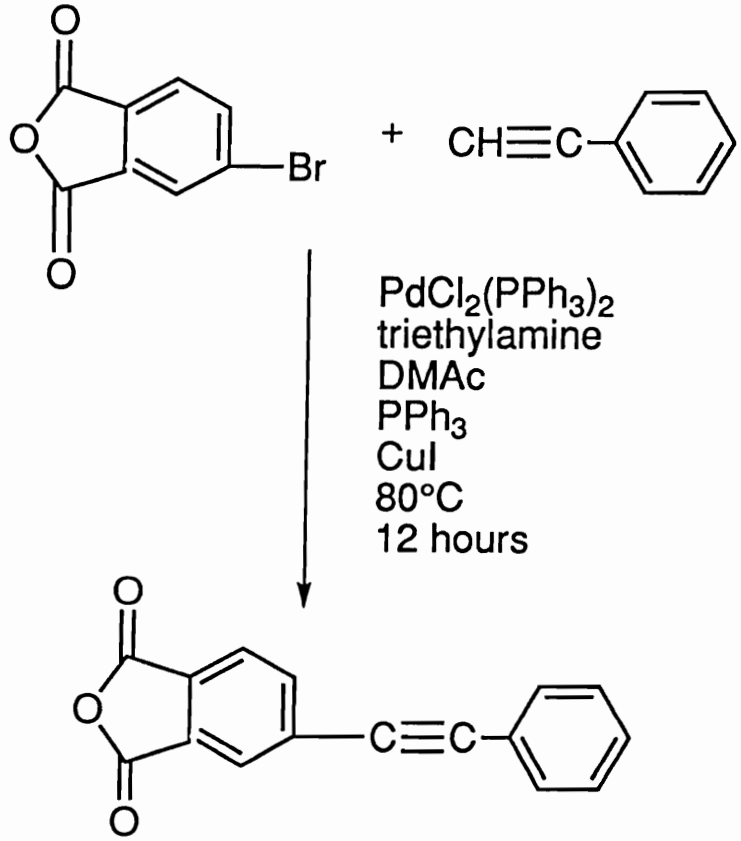
See Section 3.3 for experimental details

shown in Scheme 4.3.1. Anhydrous triethylamine and DMAc cosolvents were used in the reaction, which was completed within 12 hours at 80°C.

Crude 4-PEPA was easily obtained by pouring the reaction mixture into water and subsequently extracting with ether. The by-product di-acid from the anhydride ring opening during the work-up was removed. Therefore, the preferred purification method was to reflux the crude product in acetic anhydride for 6 hours and then recrystallize it from acetic anhydride. The final product was obtained in 84% yield and had a melting point of 151-152°C by capillary, and 151°C by DSC. This procedure resulted in a highly pure material suitable for polymerization. The ^{1}H NMR spectrum is shown in Figure 4.3.1 and the ^{13}C NMR spectrum is shown in Figure 4.3.2. In the ^{1}H NMR spectrum, the 4 different aromatic protons are clearly labeled at 7.4-7.5, 7.6 and 8.1 ppm and exhibit the proper integration. No by-product di-acid peaks were observed. The ^{13}C NMR spectra reveals that the acetylenic carbons at 88.3 and 92.4 ppm, as well as the carbonyl carbons at 168.1 ppm, are occurring in the expected regions.

4.3.2 Synthesis of 4-PEPA endcapped polyetherimide oligomers

Based on results obtained from phthalimide terminated non-reactive polyetherimide copolymers discussed previously, we focused on synthesizing reactive copolyimides based on *para*- and *meta*-PDA and 4-PEPA endcapping. As already shown, introducing 30 mole% *m*-PDA into a *p*-PDA system greatly reduced crystallinity without significantly lowering the glass transition temperature for M_n=15.0 kg/mole polymers. Therefore, BPADA/*p*-:*m*-(7:3)PDA 4-PEPA endcapped oligomers ranging from 2.0 to 10.0 kg/mole



Scheme 4.3.1 Synthesis of 4-phenylethynyl phthalic anhydride (4-PEPA)

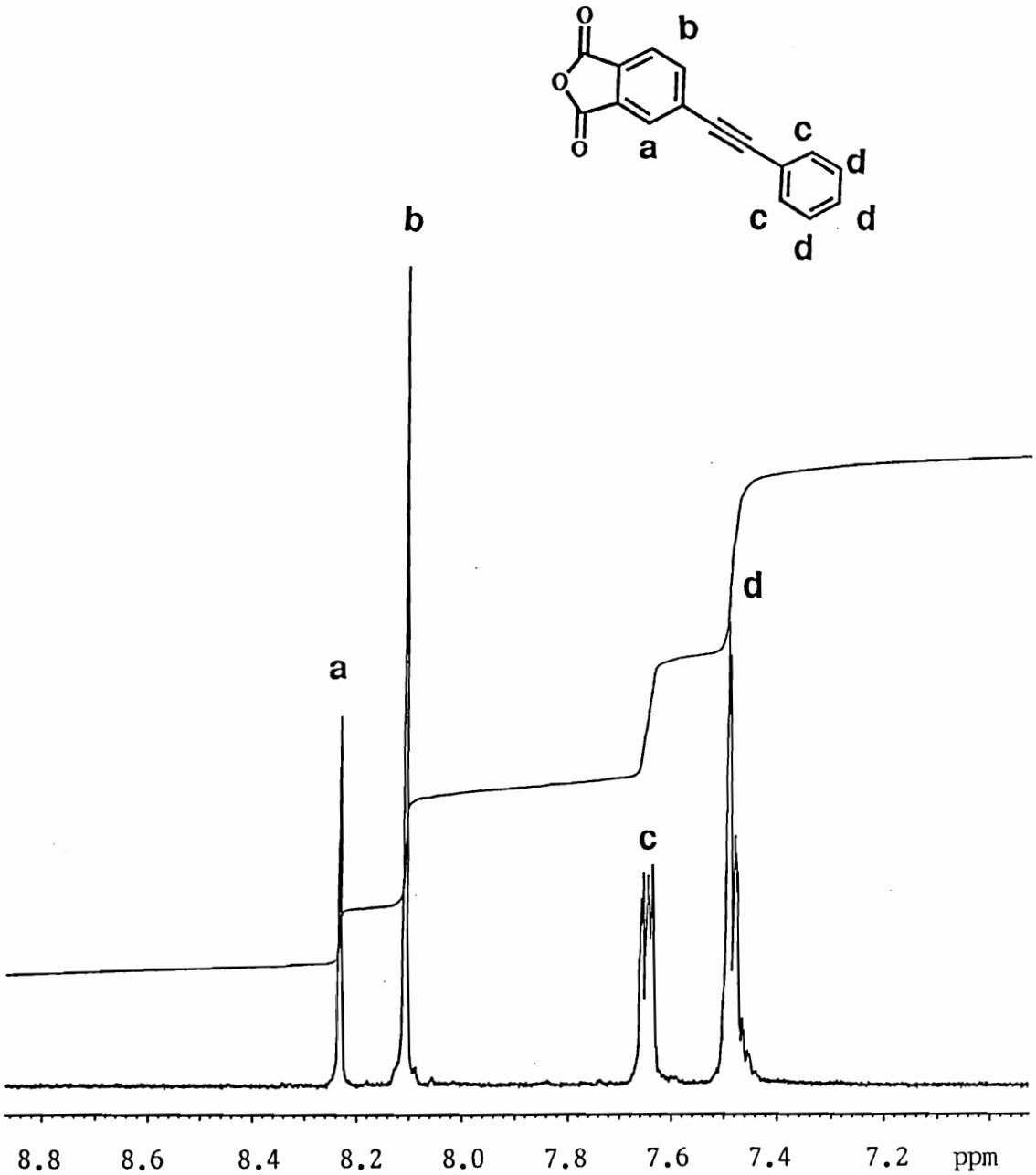


Figure 4.3.1. ^{1}H NMR (in DMSO-d6) spectrum of 4-phenylethynylphthalic anhydride.

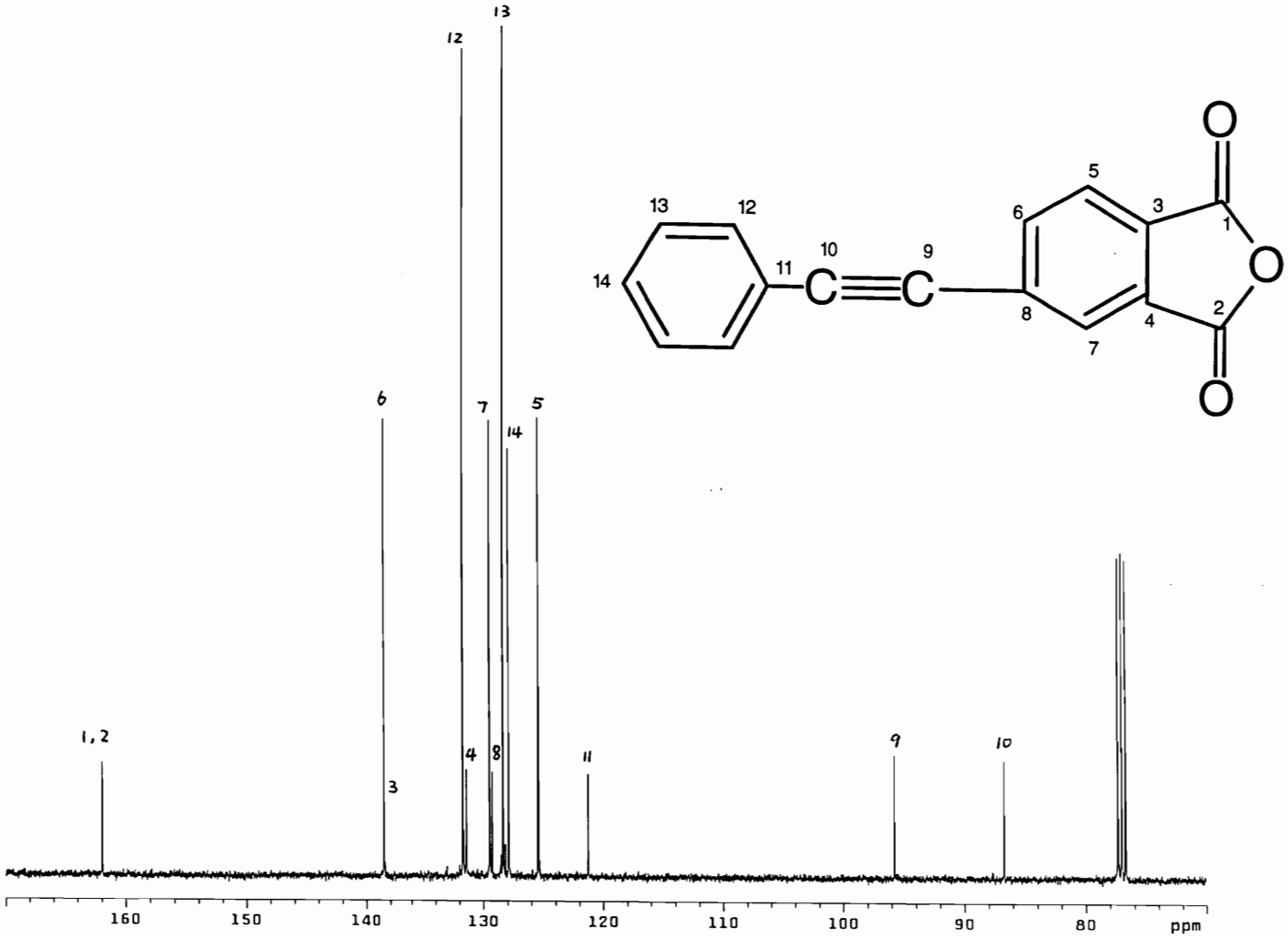
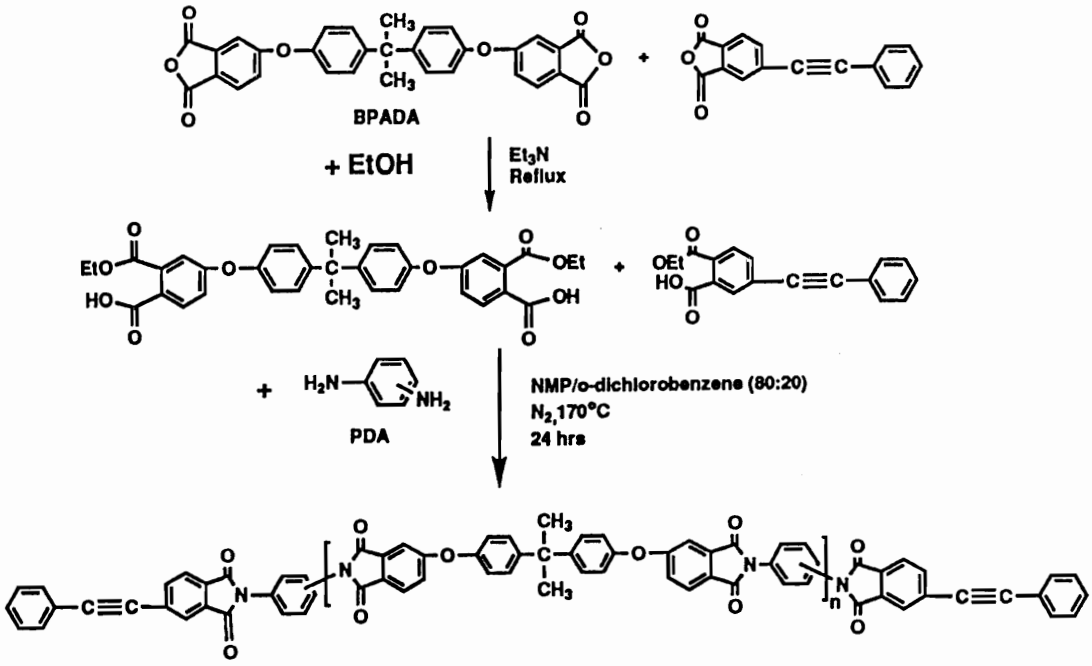


Figure 4.3.2. ^{13}C NMR (in DMSO-d6) spectrum of 4-phenylethynylphthalic anhydride.

number average molecular weight were synthesized via the acid-ester route (Scheme 4.3.2), which provided various crosslink density results after cure according to the M_n of the oligomer.

All reaction mixtures remained in solution during the entire reaction period. Having cooled the reaction mixture prior to the isolation step, only 2.0 and 3.0 kg/mole oligomers precipitated, suggesting that they are semi-crystalline in nature. The isolated 2.0 and 3.0 kg/mole oligomers were soluble in hot NMP and partially soluble in chloroform. Once dissolved in hot NMP, theoligomers remained in solution at room temperature for a few days. The 5.0 and 10.0 kg/mole oligomers, however, were soluble in both NMP and chloroform at room temperature. This solubility data are summarized in Table 4.3.1.

Molecular weight control was achieved by offsetting the stoichiometry in favor of the diamine and by utilizing 4-phenylethynylphthalic anhydride as the endcapping agent. Good molecular weight control was achieved, as demonstrated by the fact that increases in intrinsic viscosity corresponded to increases in molecular weight, as shown in Table 4.3.2. Number average molecular weight values were also estimated from end group analysis via quantitative ^{13}C NMR spectroscopy (Figure 4.3.3) by calculating the ratio of the integrals of carbons in backbone ($-CH_3$, δ=30 ppm) and in endgroup ($-C\equiv C-$, δ=88 and 94 ppm) as the degree of polymerization (DP). Experimental molecular weights obtained from ^{13}C NMR analysis corresponded well with theoretical molecular weights.



Scheme 4.3.2. Synthesis of BPADA/*p*-:*m*-(7:3)PDA 4-PEPA endcapped polyetherimide oligomers.

Table 4.3.1. Solubility of BPADA/*p*-:m-(7:3)PDA 4-PEPA endcapped polyetherimide oligomers.

Target M_n (kg/mole)	$CHCl_3$	NMP
2.0	PD	D (hot)
3.0	PD	D (hot)
5.0	D	D
10.0	D	D

D-completely dissolved

PD-partially dissolved

See Section 3.3 for experimental details

Table 4.3.2. Molecular weight characterization of BPADA/*p*-:m-(7:3)PDA 4-PEPA endcapped polyetherimide oligomers.

Target M_n (kg/mole)	η (dL/g)[a]	M_n by ^{13}C NMR (kg/mole)[b]
2.0	0.15	2.4
3.0	0.19	3.3
5.0	0.27	6.1
10.0	0.40	10.0

a: Run in NMP at 25°C

b: Run in $CDCl_3$

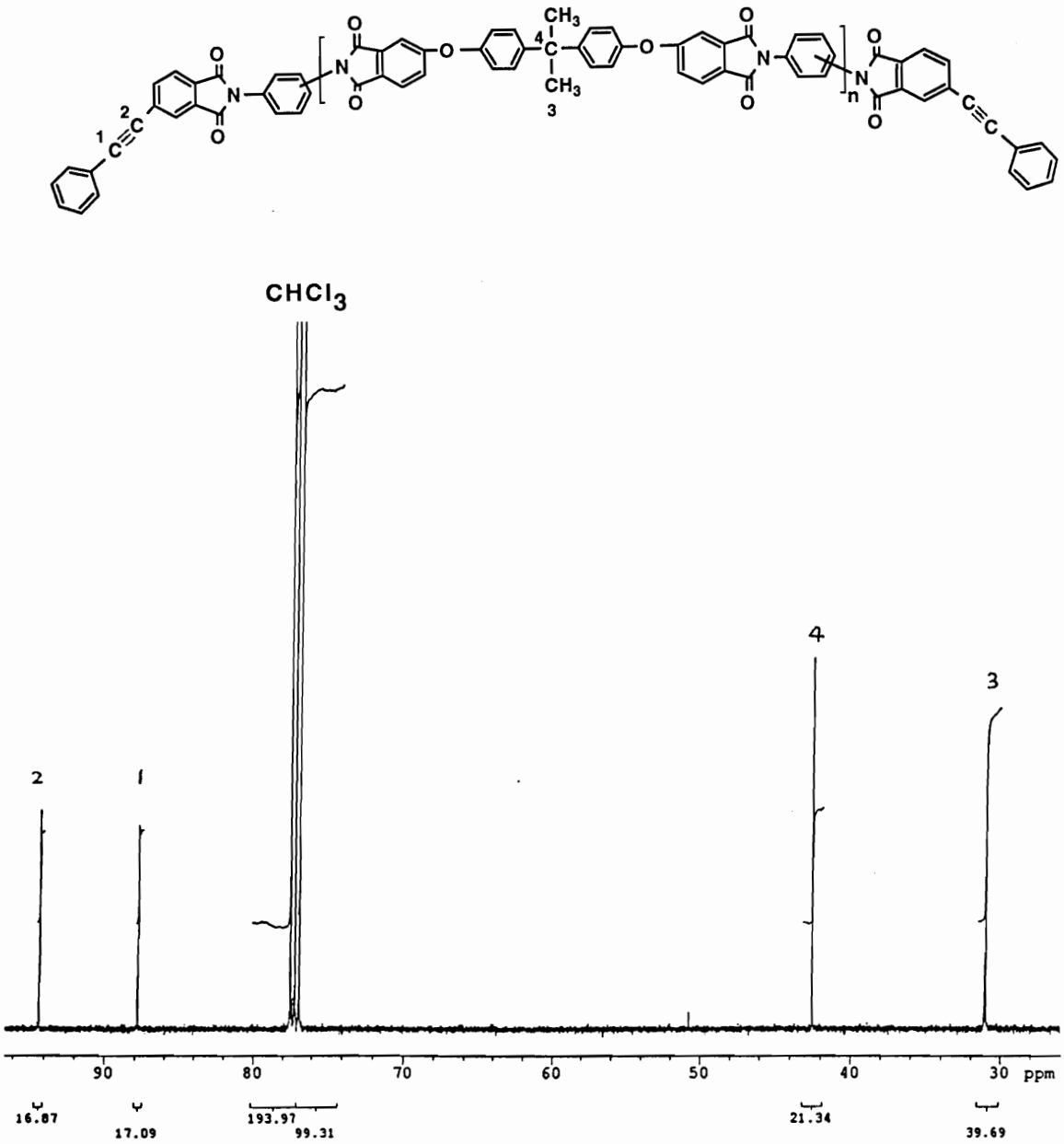


Figure 4.3.3. Quantitative ^{13}C NMR (in $CDCl_3$) spectrum of M_n=2.0 kg/mole BPADA/*p*-:*m*-(7:3)PDA 4-PEPA endcapped polyetherimide oligomers.

Glass transition temperatures prior to cure increased from 175 to 216 °C as the molecular weight increased, as shown in Table 4.3.3. Imide oligomer films were formed by melt pressing the oligomers between steel plates and curing them for 90 minutes at 380°C. After thermal curing, glass transition temperatures increased significantly to 267°C for the 3.0 kg/mole oligomers (a 74°C increase). The T_g for the cured 2.0 kg/mole oligomers could not be detected by DSC beyond 450°C. The T_g of the cured 3.0 kg/mole oligomers, however, was consistent with results obtained by DMA (265°C from DMA; Table 4.3.3). DSC curves of the 5.0 kg/mole oligomer before and after themal cure are shown in Figure 4.3.4. The onset temperature for curing endotherm as seen by DSC ranged from 344°C to 373°C, while maximum cure exotherm temperature was found to range from 396 to 415°C. This latter range is even higher than previously reported for the 3-phenylethynylaniline-terminated imide oligomers, which ranged from 360°–380°C [210-216]. This high-temperature cure exotherm may correlate to a wide processing window, which allows these polyetherimide-based polymers to be more easily fabricated via hot melt or resin infusion molding. The cured polymers also exhibited excellent thermal stability in air as shown in Table 4.3.3 (5% weight loss in air greater than 500°C). A TGA plot of a 5.0 kg/mole cured phenylethynylphthalic anhydride endcapped polyetherimide is shown in Figure 4.3.5.

The *p*-PDA containing low molecular weight oligomers tended to crystallize and precipitate out from the reaction solution upon cooling (<100°C) after cyclization was complete. Thus, the 2.0 and 3.0 kg/mole oligomers displayed melting endotherms at about 265°C and during the first

Table 4.3.3. Thermal analysis characterization of BPADA/*p*-:m-(7:3)PDA 4-PEPA endcapped polyetherimide oligomers.

Target M_n (kg/mole)	T_g (°C)[a] before cure	T_g (°C)[a] after cure	TGA[b] 5% weight loss (°C)
2.0	175	-	541
3.0	193	267	528
5.0	207	252	522
10.0	216	240	531

a: Heating rate of 10°C/minute in nitrogen; samples cured at 380°C for 90 minutes

b: Measured in air at 10°C/minute

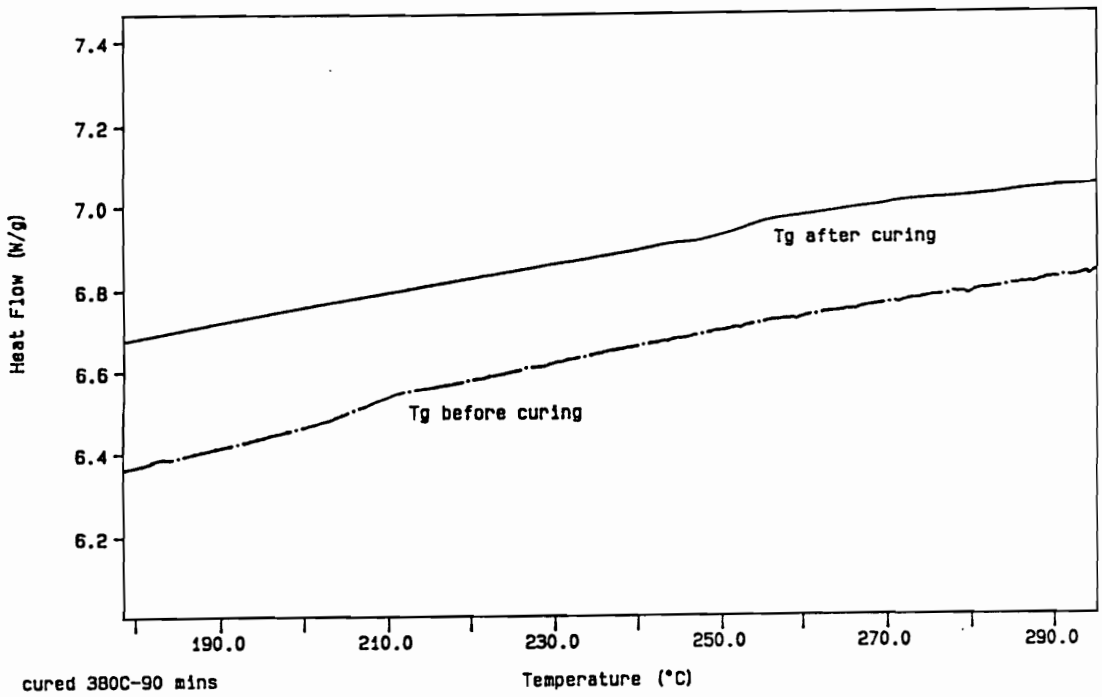


Figure 4.3.4. DSC thermogram of M_n=5.0 kg/mole BPADA/*p*-:*m*-(7:3)PDA 4-PEPA endcapped polyetherimide oligomers before and after curing.

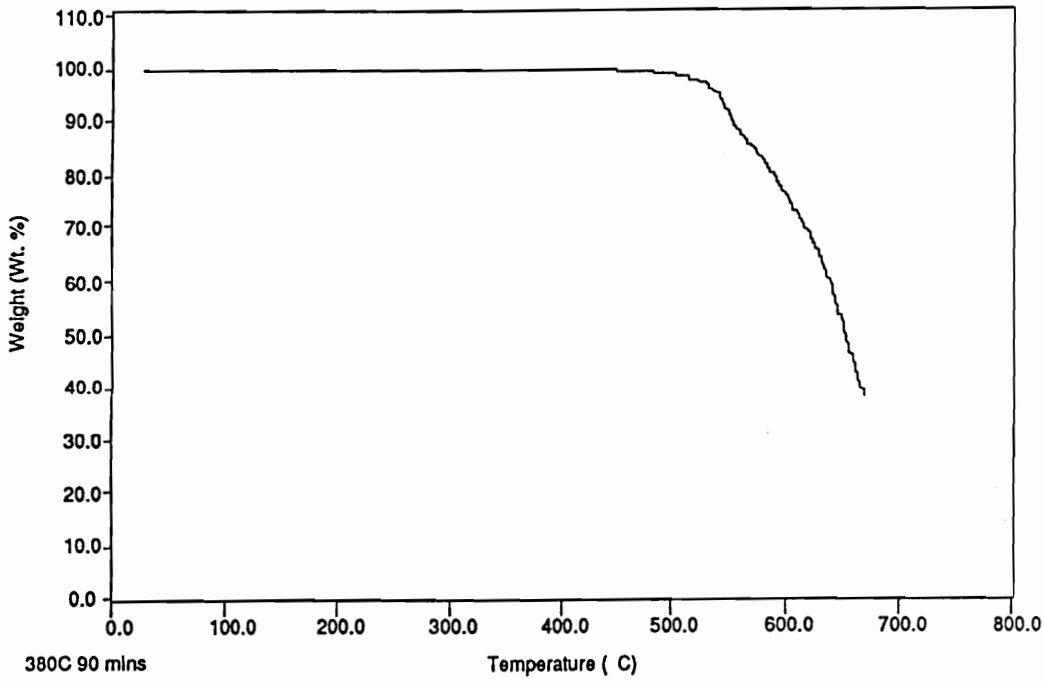


Figure 4.3.5. TGA thermogram of M_n=5.0 kg/mole BPADA/*p*-:*m*-(7:3)PDA 4-PEPA endcapped polyetherimide oligomers.

heating cycle only. This suggests that the fine particles that precipitate out may be suitable for powder prepregging. This phenomena may also simplify polymer workup procedure by allowing direct filtration of the reaction mixture. One of our reactions utilized M_n=3.0 kg/mole and 70% *p*-PDA oligomers, which resulted in a 64% yield after filtering the cooled polymer reaction mixture. Moreover, when an all *p*-PDA based oligomer was used, a quantitative yield of oligomers was obtained by the direct filtration method. However, the resulting particles were too fine to be easily filtered and they tended to aggregate to form gels. This tendency may be avoided in the future by separating the particles via centrifugation. A comparison of the different isolation methods used in the synthesis of BPADA/PDA, M_n=3.0 kg/mole oligomers is summarized in Table 4.3.4.

4.3.3 Scale up synthesis of 4-PEPA endcapped polyetherimide oligomers

With support from General Electric Corperate Research and Development (G.E. CR&D), several polyetherimide systems modified with 4-phenylethynyl phthalic anhydride endcapper were successfully scaled up using a 10-gallon reactor. Due to the high cost of operating such pilot plant reactions, it should be stressed that (1) the reaction media should be simple and relatively inexpensive, and (2) plant grade monomers (~98% pure BPADA) should be used without purification.

As suggested by G.E., the reaction method of choice was solution imidization at 170-180°C with only *o*-DCB as reaction media. The *o*-DCB was utilized as the solvent and an azeotropic agent was used during imidization. Compared to the acid-ester route most commonly used, this method does not

Table 4.3.4. Comparison of different isolation methods in the synthesis of BPADA/PDA, M_n=3.0 kg/mole imide oligomers.

System	Method	Yield %	T_g (°C)[a]
p-:m-(7:3)PDA with 4-PEPA cpped	precipitate in MeOH while hot and then filter	99	193
same as above	direct filter	64	191
p-PDA with PA endcapped	direct filter	99	-

a: Heating rate of 10°C/minute in nitrogen

require the use of an expensive NMP and is a "one step" procedure. Since *o*-DCB is also an azeotropic agent, it was not necessary to dry it before use. These reaction procedures were first developed on a small scale. Our attempt to synthesize BPADA/*p*-:*m*-(7:3)PDA 4-PEPA endcapped, M_n=3.0 kg/mole oligomers using these reaction conditions was not fully successful due to the occurrence of precipitation after about 30 minutes reaction. Thus, the semicrystalline nature of these oligomers inhibited desired molecular weight formation. Another attempt was made to synthesize BPADA/*m*-PDA 4-PEPA endcapped, M_n=3.0 kg/mole oligomers. This time, however, the reaction mixture stayed in solution due to the amorphous nature of all *meta*-linkage system, making this method suitable for BPADA/*m*-PDA systems. It was interesting to note that after all the reagents were charged and dissolved in the reaction flask, the solution turned cloudy after 20 minutes, but then clarified when heated to 180°C. This may indicate the formation of an insoluble poly(amic) acid in the early stage of the reaction. The poly(amic) acid, however, was not soluble in *o*-DCB. After immediate imidization, a soluble, fully imidized polymer was generated.

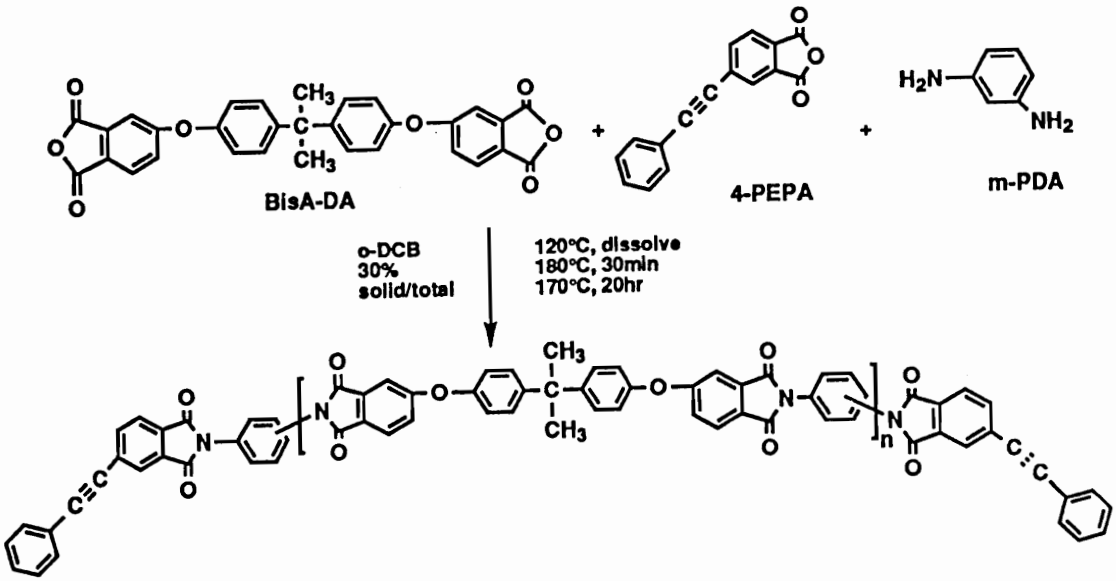
Some samples of the dianhydride, BPADA, were only about 98 mole% pure. In order to precisely control molecular weight, a detailed analysis of the BPADA was conducted by HPLC at G.E. Plastic R&D. This identified all the possible isomers and mono-functional anhydride in the BPADA that could be used to calculate the required amount of the starting materials, using the Carothers equation previously described in the Experimental Section. Molecular weight control was achieved by using an excess of diamine, while

taking account of the impurity of the mono-anhydride that essentially functioned as endcapper.

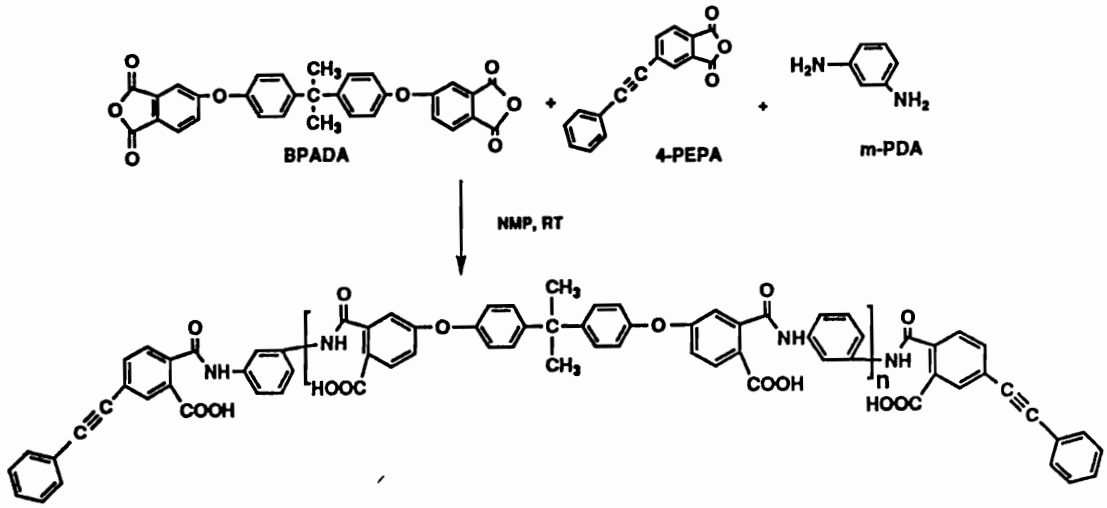
All *m*-PDA based imide oligomers were synthesized at a target M_n of 2.0 and 3.0 kg/mole under homogeneous conditions using *o*-DCB as the solvent in a 10-gallon reactor (Scheme 4.3.3). Smaller scale reactions under exactly the same reaction condition were also conducted for comparison. BPADA/*m*-PDA 4-PEPA endcapped, Mn=3.0 kg/mole poly(amic) acid was also synthesized in a 10-gallon reactor (Scheme 4.3.4). The poly(amic) acid form of the oligomer was used later for evaluating its adhesive properties to titanium substrates.

Molecular weight control was achieved by utilizing 4-phenylethynylphthalic anhydride as an endcapper, as shown in Table 4.3.5. Intrinsic viscosity measurements disclosed anticipated results, as the molecular weights obtained from ^{13}C NMR analysis correlated well with the theoretical molecular weights. The soluble all *m*-PDA based imide oligomer was analyzed by GPC (Figure 4.3.6) using a viscosity detector and universal calibration [254]. These results were also well correlated with theoretical values. Therefore, both lab-scale and pilot-plant-scale reactions afforded analgous results, proving that good molecular weight control was achieved even under scale-up reaction conditions.

A typical DSC thermogram is shown in Figure 4.3.7. For this M_n=3.0 kg/mole BPADA/*m*-PDA 4-PEPA endcapped oligomer, a glass transition temperature of 183°C was observed at a 10°C/min heating rate. No melting endothermic peaks were found, confirming that the system was amorphous. However, a curing exotherm was noted that had an onset temperature of



Scheme 4.3.3. Synthesis of BPADA/*m*-PDA 4-PEPA endcapped, M_n=2.0 and 3.0 kg/mole polyetherimide oligomers.



Scheme 4.3.4. Synthesis of BPADA/*m*-PDA 4-PEPA endcapped, M_n=3.0 kg/mole poly(amic) acids.

Table 4.3.5. Molecular weight (kg/mole) characterization of BPADA/*m*-PDA 4-PEPA endcapped systems.

System	M_n by GPC[a]; M_w/M_n (GE)	M_n by GPC[b]; M_w/M_n (VT)	η (dL/g)[c]	M_n by ^{13}C NMR[d]
M_n=2.0 imide				
Lab:	2.4; 1.8	1.5; 1.4	0.13	
Scale up:	2.5; 1.8	1.5; 1.4	0.15	2.0
M_n=3.0 imide				
Lab:	3.8; 2.0	2.4; 1.5	0.19	
Scale up:	3.7; 2.0	2.5; 1.5	0.19	2.9
Mn=3.0 amic acid				
Lab:	3.6; 2.3			
Scale up:		2.9; 1.7		

a: Based on polystyrene standard at G.E. CR&D

b: Based on universal calibration at Virginia Tech

c: Run in NMP at 25°C

d: Run in $CDCl_3$

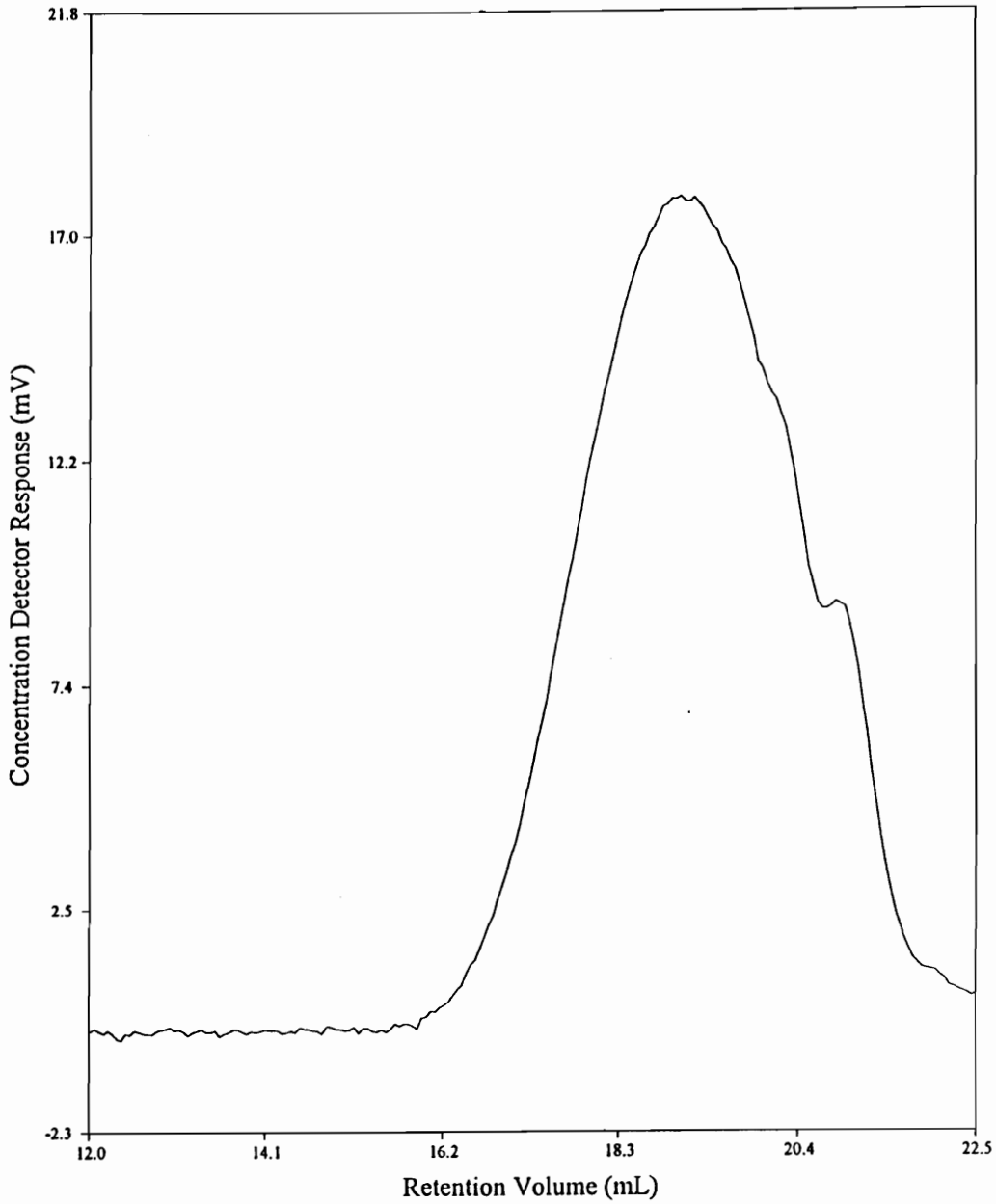


Figure 4.3.6. GPC chromatogram of M_n=3.0 kg/mole polyetherimide oligomers.

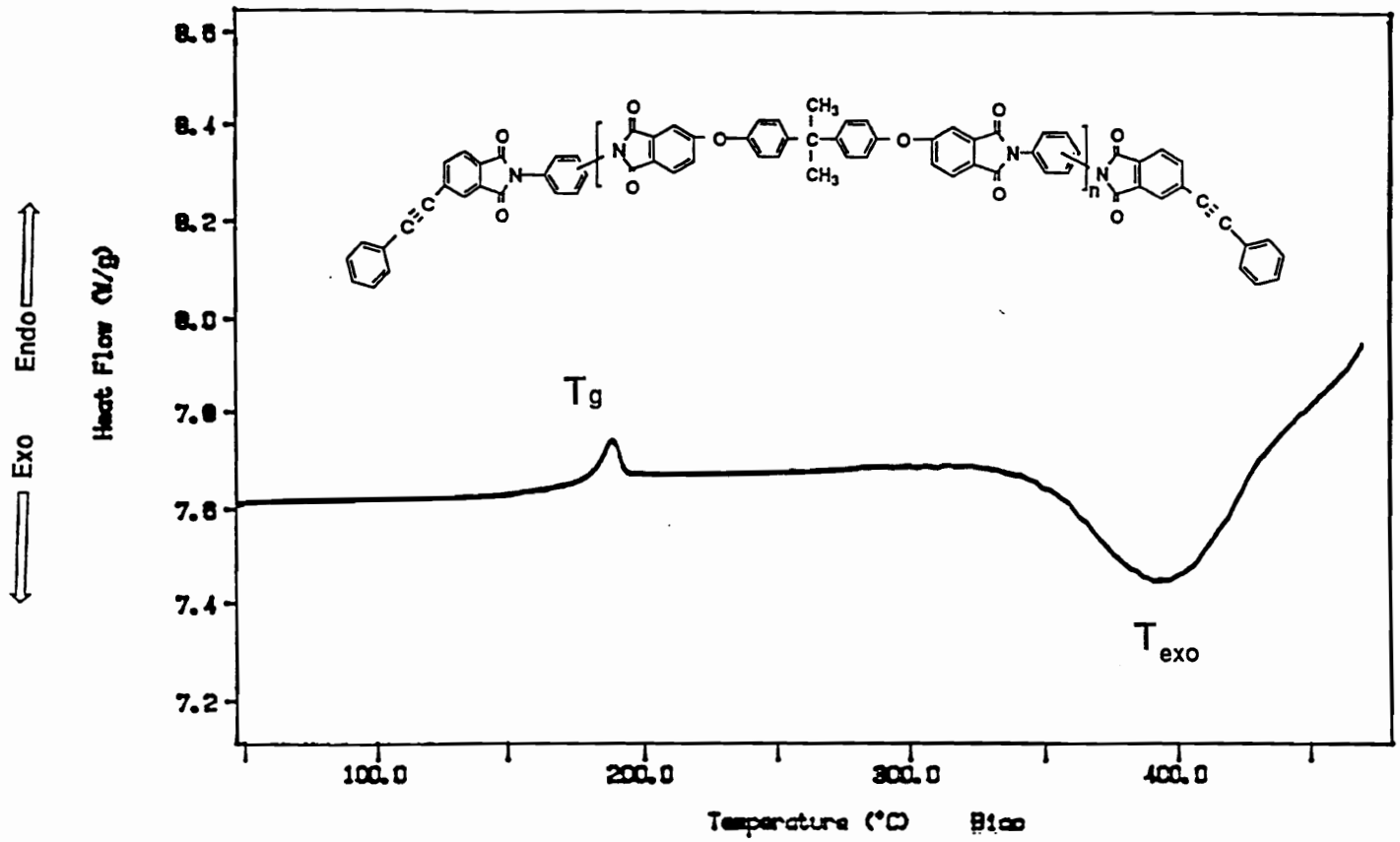


Figure 4.3.7. DSC thermogram of M_n=3.0 kg/mole BPADA/*m*-PDA 4-PEPA endcapped polyetherimide oligomers.

around 350°C and a peak temperature of 396°C (heating rate 10°C/min). This curing exothermic peak was due to the reaction of the phenylethynyl endgroups. Thus the amorphous nature of this material provides a wide processing window between T_g and the cure exotherm.

Glass transition temperature was a function of molecular weight prior to cure and ranged from 172°C to 185°C (Table 4.3.6). While the cure exotherm peak temperature at 10°C/minute was measured between 392°C and 403°C (indicating a wide processing window), if we compares these all *meta*-linkage system with previous results (Table 4.3.3), it appears that the addition of 70% *p*-PDA into the *m*-PDA based 3.0 kg/mole oligomers showed an increased T_g both before cure (193°C vs. 184°C) and after cure (267°C vs. 252°C). It should be noted that all cured network systems displayed excellent thermooxidative stability as judged by dynamic TGA at 10°C/minute (5% weight loss >500°C in air). Again, the thermal transitions seen in the scale-up reactions were analgous to those seen in the lab-scale experiments. These results confirm that such oligomers can easily be scaled up for future commercial development. About 15-18 pounds of these materials were obtained and used for this study and ongoing research.

4.3.4 Synthesis of 3-ethynyl aniline endcapped polyetherimide oligomers

Our previous results showed M_n=2.0 kg/mole, BPADA/*m*-PDA 4-PEPA endcapped oligomers had a T_g value of 172°C and a cure exotherm at 392°C. BPADA/*m*-PDA based polyetherimides can also be modified by the addition of an unsubstituted acetylene endgroup, which has a lower cure exotherm of around 200°C. For the 2.0 kg/mole oligomers, with a T_g of about 172°C, only

Table 4.3.6. Thermal analysis characterization of BPADA/*m*-PDA 4-PEPA endcapped systems.

System	T_g (°C)[a] before cure	T_g (°C)[a] after cure	Cure exotherm (°C)	TGA[b] 5% weight loss (°C)
M_n=2.0k imide				
Lab:	170	264	393	525
Scale up:	172	265	392	516
M_n=3.0k imide				
Lab:	185	248	402	520
Scale up:	185	250	403	526
M_n=3.0k amic acid				
Lab:	186	250		
Scale up:		246	396	

a: Heating rate of 10°C/minute in nitrogen; samples cured at 380°C for 90 minutes

b: Measured in air at 10°C/minute

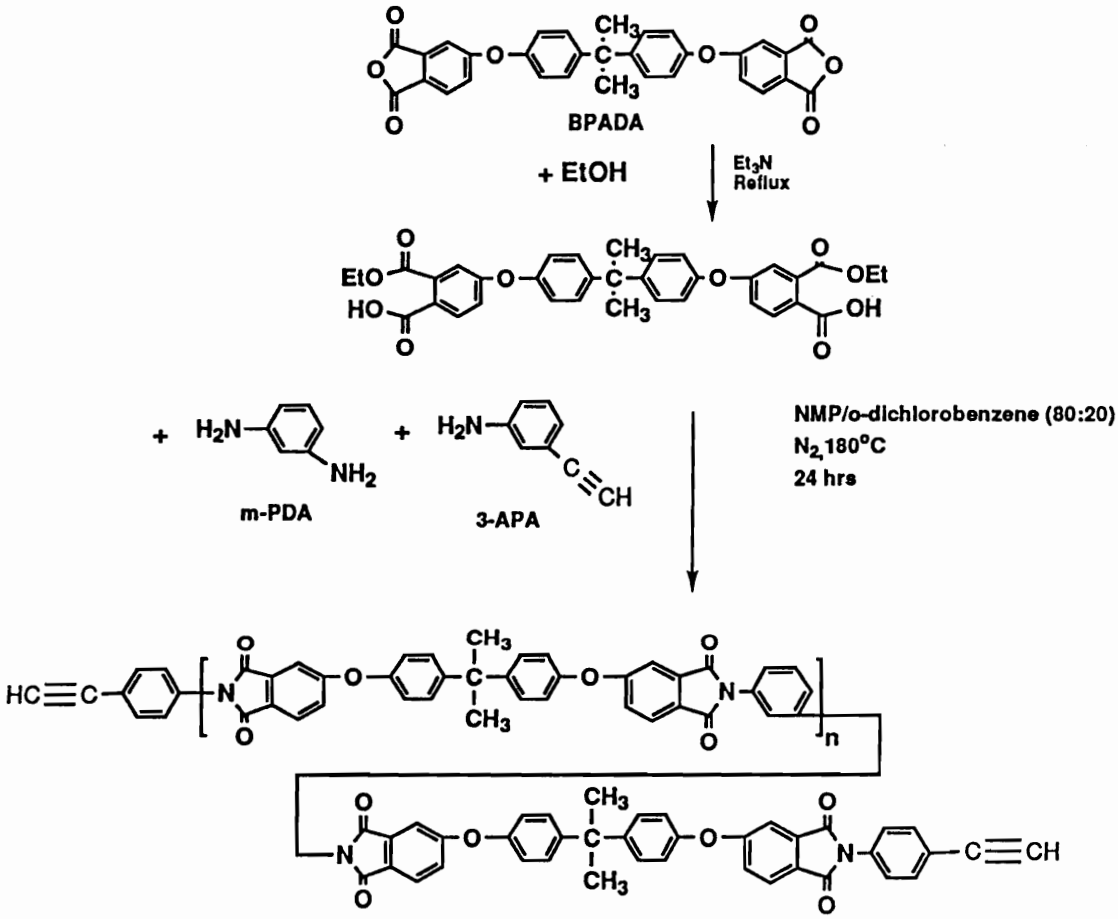
a relatively narrow processing window is possible. Such acetylene terminated oligomers, however, may be used as "repair" agents for structural adhesive applications.

With an M_n of 2.0 kg/mole, BPADA/*m*-PDA endcapped with 3-ethynyl aniline (3-APA) endgroup oligomers were successfully synthesized by the acid-ester route (Scheme 4.3.5). Molecular weight control was achieved by using an excess of dianhydride and a 3-APA endcapper. Subsequent GPC testing of these oligomers indicated that the M_n was 2.3 kg/mole and the cure exotherm reached 240°C (Figure 4.3.8). However, an immediate cure exotherm onset was observed just after Tg was achieved. It was therefore concluded that this material was not suitable for further investigation due to its narrow processing window.

4.3.5 Synthesis of poly(amic) acids

Several poly(amic) acid systems have been successfully synthesized at room temperature using NMP as a solvent, which makes them suitable for aqueous suspension prepregging of carbon fibers.

A BTDA/BisP PA endcapped poly(amic) acid with number average molecular weight of 20.0 kg/mole was synthesized as shown in Scheme 4.3.6. Prior to the reaction, NMP was thoroughly purified and the necessary apparatus was flame dried. Once initiated, the viscosity built up quickly and after 24 hours the poly(amic) acid solution had to be diluted from 20 wt.% to 13 wt.% for easier workup. The poly(amic) acid was precipitated in water and then dried under reduced pressure at room temperature for 5 days. GPC results verified that a M_n=14.0 kg/mole polymer was obtained. It should be



Scheme 4.3.5. Synthesis of BPADA/m-PDA 3-APA endcapped, M_n=2.0 kg/mole polyetherimide oligomers.

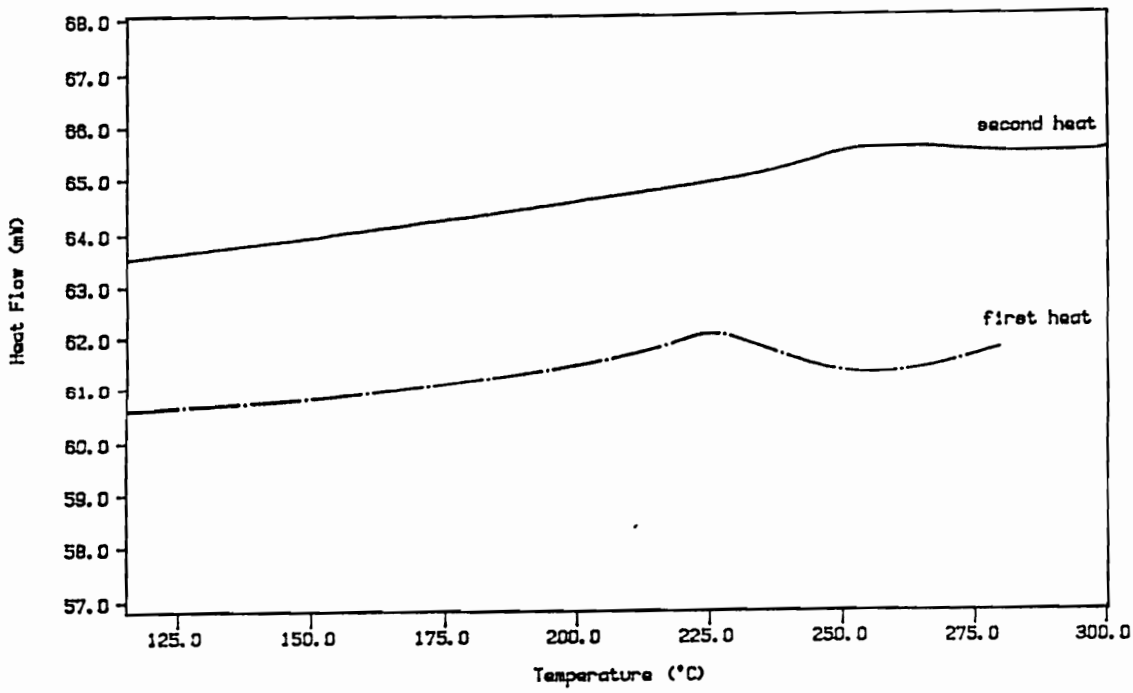
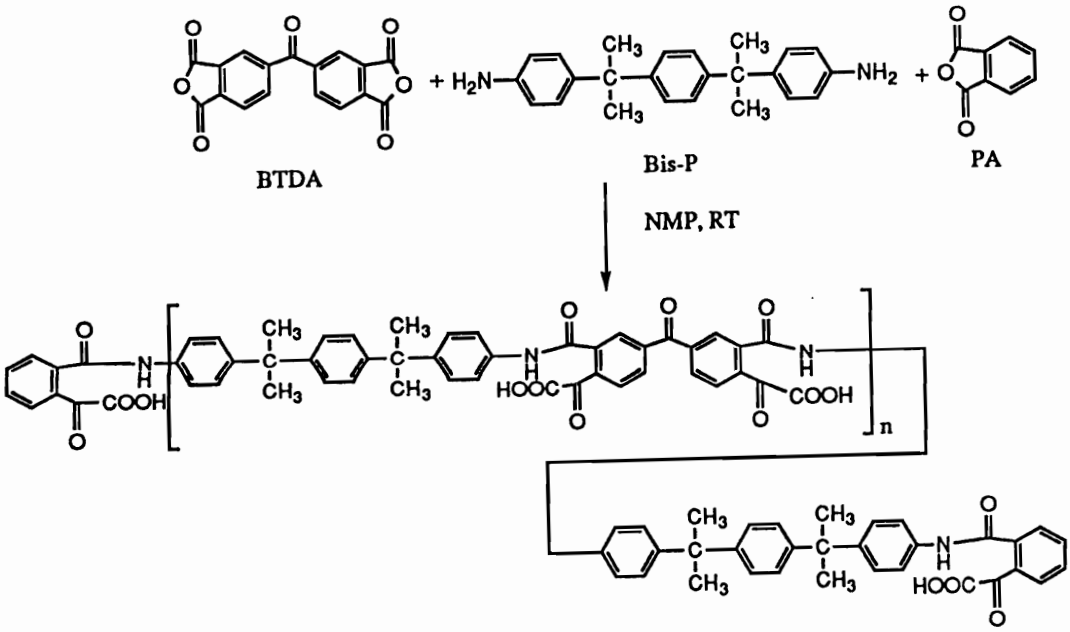


Figure 4.3.8. DSC thermogram of M_n=2.0 kg/mole BPADA/*m*-PDA 3-APA endcapped polyetherimide oligomers.



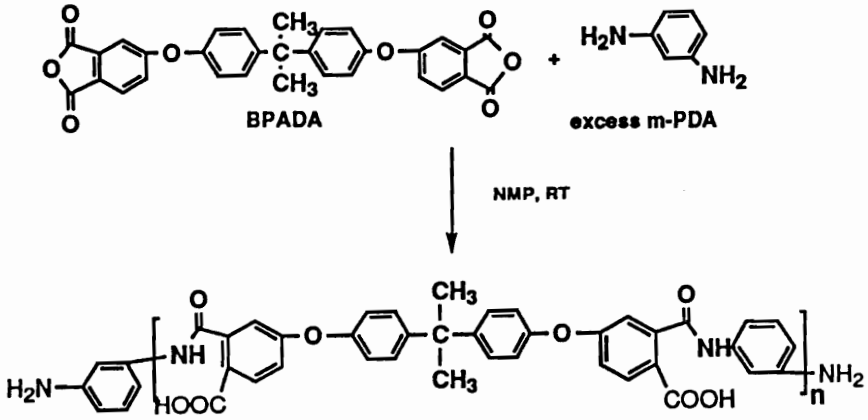
Scheme 4.3.6. Synthesis of BTDA/BisP PA endcapped, M_n=20.0 kg/mole poly(amic) acid.

noted that lower reported molecular weights may have been due to hydrolysis during the workup. Water was the precipitation medium of choice since resulting the poly(amic) acid did not easily precipitate to a powder in other non-solvents The product was stored in a freezer for possible future use as an aqueous binder.

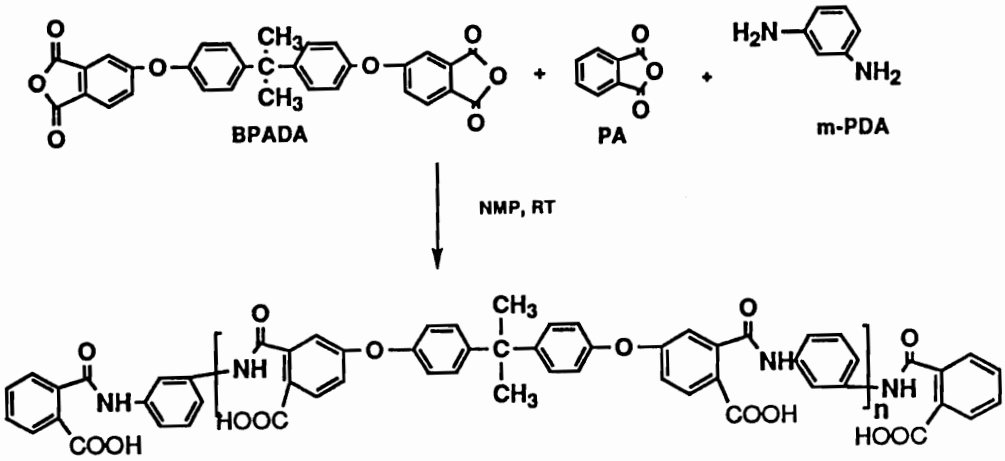
Two other poly(amic) acid systems based on polyetherimides were also synthesized in a 10-gallon reaction at the G.E. pilot plant. The first system was a BPADA/*m*-PDA with excess diamine to achieve an amine terminated, M_n=10.0 kg/mole poly(amic) acid. The second was BPADA/*m*-PDA PA endcapped, M_n=20.0 kg/mole poly(amic) acid (Scheme 4.3.7, 4.3.8). An unpurified NMP solvent was used in this reaction and GPC measurements of the resulting materials showed an M_n of 11,400 g/mole for the first system and an M_n of 15.2 kg/mole for the second system. The relatively low molecular weight of the latter system may be due to moisture content in the NMP used for synthesis. The products were stored in a freezer and, surprisingly, molecular weights as mesured by GPC did not drop – even after one year of storage

Davis et al. [256] used BTDA/BisP poly(amic) acid salts as binders in designing a fiber-matrix interphase. They discovered that a PEEK matrix is miscible with BTDA/BisP or polyetherimide binders. These polyimides, it is believed, interdiffuse into the PEEK matrix to form a thin interphase region near the carbon fiber surface. The precise structure of the resulting interphase is still under examination, but its effects on mechanical properties are clear. Figure 4.3.9 shows that the transverse flexural strength for a PEEK composite made with a NH_4^+ salt of a BisP/BTDA polyamic acid is comparable to the

industry benchmark PEEK composite, APC-2, while a composite made with a NH_4^+ salt of a polyetherimide (Ultem™) polyamic acid has 10% lower flexural strength.



Scheme 4.3.7. Synthesis of amine terminated BPADA/*m*-PDA, M_n=10.0 kg/mole poly(amic) acids.



Scheme 4.3.8. Synthesis of BPADA/*m*-PDA PA endcapped, M_n=20.0 kg/mole poly(amic) acids.

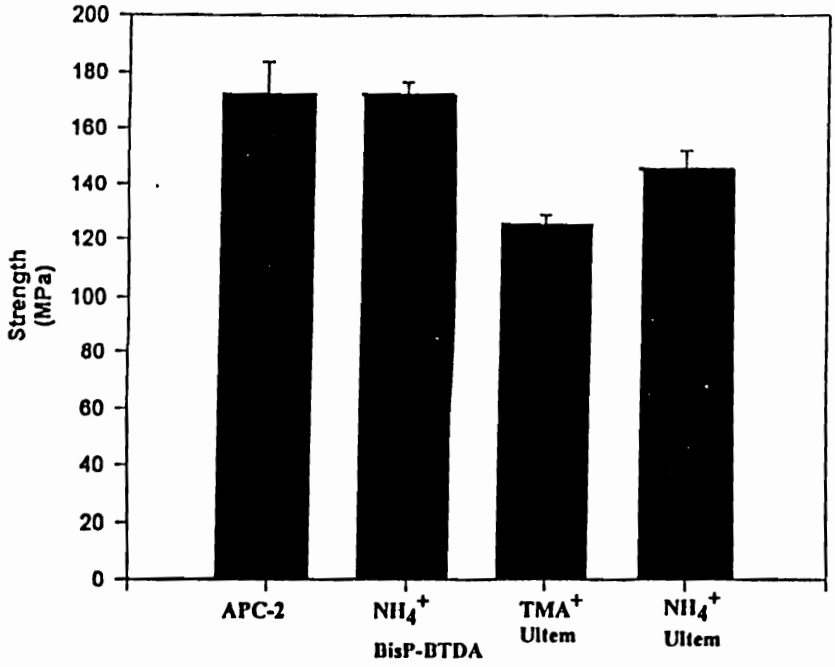


Figure 4.3.9 Transverse flexure strength for PEEK composites [256]

4.4 Properties of reactive endcapped oligomers

4.4.1. Solvent resistance of cured 4-PEPA endcapped oligomers

The gel fraction of cured samples reacted at various times and temperatures was determined via extraction with chloroform for 5 days in a Soxhlet apparatus. The samples were then dried for 5 days at 120°C under vacuum. For 70% *p*-PDA based oligomers (cured at 380°C for 90 minutes), gel fractions in chloroform were high, ranging from 97.3% to 99.8%. The solvent extraction data for M_n=3.0 kg/mole, all-*m*-PDA based oligomers are listed in Table 4.4.1. It was concluded that curing this oligomer at 350°C for 90 minutes, or at 380°C for 30 minutes, achieved high gel fractions (>95%). In addition, a longer cure at 380°C (>60 minutes) achieved almost 100% gel fraction, implying that the reactive functionality must be very high. The 2.0 kg/mole all *m*-PDA based oligomers demonstrated the same gel fraction behavior. Thus, it was concluded that all the 4-PEPA endcapped low molecular weight oligomers could generate highly solvent resistant thermoset networks after sufficient curing.

Thin films based on 2.0 and 3.0 kg/mole, 70% *p*-PDA oligomers cured at 380°C for 90 minutes were immersed in acetone, MEK, diglyme, ethylene glycol, jet fuel, hydraulic fluid and toluene at ambient temperature under stress (Table 4.4.2). Qualitatively, the film specimens exhibited excellent solvent resistance under stress. No cracking was observed for any of the specimens.

Table 4.4.1. Soxhlet extraction data in chloroform of BPADA/*m*-PDA based polyetherimides.

Curing Temperature (°C)	Curing Time (minutes)	Gel Fraction[a]
350	60	88
350	90	97
350	30	96
380	60	99
380	90	99

a: Samples were extracted for 5 days and then dried for 5 days at 120°C under vacuum

Table 4.4.2. Influence of organic liquids on stressed BPADA/*p*-:m-(7:3)PDA 4-PEPA endcapped polyimide network adhesives (Cured for 90 minutes at 380°C).

Solvent	Target M_n=2.0 kg/mole		Target M_n=3.0 kg/mole	
	Crazing	Cracking	Crazing	Cracking
Acetone	No	No	No	No
MEK	Yes	No	Yes	No
Diglyme	No	No	Yes	No
Ethylene Glycol	No	No	No	No
Jet Fuel	No	No	No	No
Hydraulic Fluid	No	No	Yes	No
Toluene	No	No	No	No

4.4.2. Film formation and tensile properties of cured 4-PEPA endcapped oligomers films

Since high boiling point solvents are utilized in reactive oligomer synthesis, the resulting materials usually contain some residual solvents. This may cause problems in subsequent processing, e.g., void formation in the compression molding of films. For instance, when completely powder oligomers were cured directly on an aluminum plate in an oven, bubbled films were usually generated. This void formation may due to residual solvents or to volatile formation during curing. The following experiments were conducted to verify that a phenylethynyl thermal curing reaction was a non-volatile process, as was anticipated.

Mass spectroscopy analysis was used to detect volatiles during the curing reaction. The BPADA/*m*-PDA 4-PEPA endcapped, 3.0 kg/mole sample from the scale-up reaction was used for this test. It was found that the *o*-DCB solvent remained in the sample in the range of 1-2 wt.%, as determined by TGA. The solid sample was then placed in a tube and put in a direct sample inlet probe of a mass spectrometer. Spectrum were scanned from mass 10 to 350 at 1 sec/scan. The probe was heated to 350°C at 5°C/sec and held at 350°C for 1 hour. The only volatile that was detected was the *o*-DCB.

The same sample was dissolved in chloroform and reprecipitated from methanol. The sample was then dried under reduced pressure at 160°C for 24 hours. This purification procedure was repeated again and the resulting oligomer was hypothesized to be solvent-free. The purified sample was analyzed by direct probe mass spectroscopy at 350°C for 60 minutes and no volatiles were detected. The mass spectrum that was measured at 200, 400 and

600 scans (this corresponds to curing at 350°C for 6, 17 and 21 minutes, respectively) showed only mass peaks from the background, as shown in Figure 4.4.1. No other detectable mass peaks were observed during the course of the analysis. Therefore, the curing reaction of phenylethynyl terminated oligomers is non-volatile, as expected.

Although the 4-PEPA reactive oligomer underwent non-volatile curing as seen by mass analysis, creating void-free films by compression molding was still a very challenging task. After several trials using a SmartPress, the following compression molding procedures were used to make void-free films of BPADA/*p*-:*m*-(7:3)PDA 4-PEPA endcapped, M_n=3.0 kg/mole thermosets for tensile property measurements:

350°: 18 minutes, no press--obtain soluble, fusible film; cut and fold, returen to mold

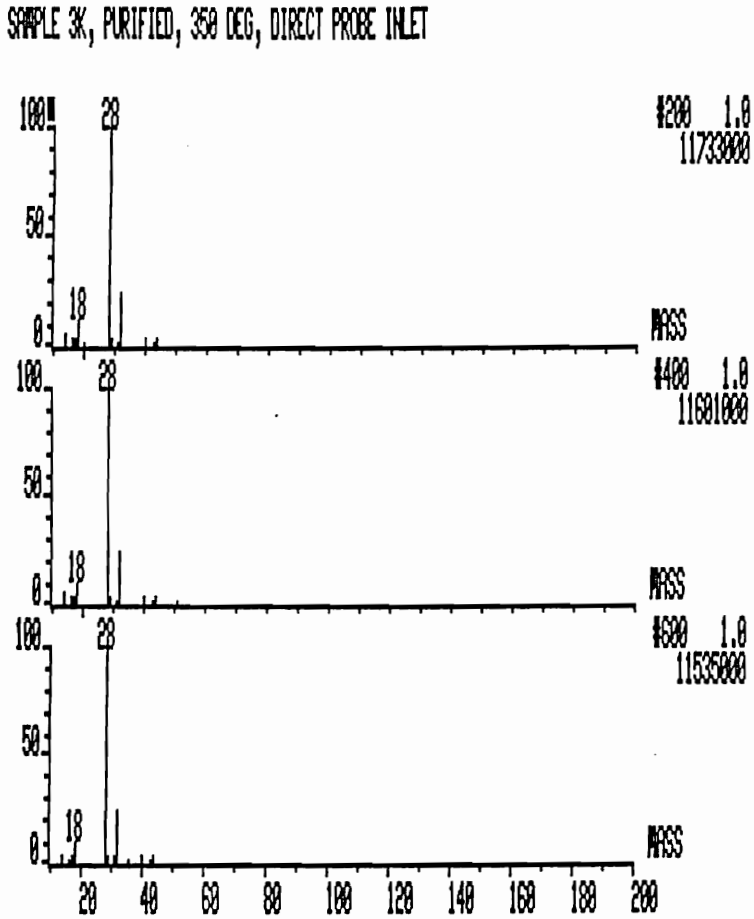
1 minute, no press,

1 minute, 1 kpsi,

5 minutes, 2-3 kpsi--void free film,

380°C: 65 minutes, contact-cured film.

Mechanical tests were performed to measure the tensile properties of the cured 3.0 kg/mole, 70% *p*-PDA based polyimide neat resin. Compression molded samples cured at various temperatures and times were prepared and are shown in Table 4.4.3. The tensile properties of this resin are much more reminiscent of a tough thermoplastic than a conventional thermoset. The material's relatively high elongation suggests that chain extension may have occurred before reaching gel point. The excellent tensile properties of these



Top: Detection of volatiles from curing reaction at 6 minutes.

Middle: Detection of volatiles from curing reaction at 17 minutes.

Bottom: Detection of volatiles from curing reaction at 21 minutes.

--All above mass spectrum showed only background peaks (He)

Figure 4.4.1. Detection of volatiles by mass spectroscopy of the curing reaction of M_n=3.0 kg/mole BPADA/*m*-PDA 4-PEPA endcapped polyetherimide oligomers at 350°C.

Table 4.4.3. Tensile properties of cured BPADA/*p*-:m-(7:3)PDA 4-PEPA endcapped, M_n=3.0 kg/mole polyetherimide thermosets.

Curing Condition	Modulus (GPa)	Yield Stress (MPa)	Yield Strain (%)	Stress at Break (MPa)	Strain at Break (%)
350°C/90min	2.8±0.3	93.9±4.1	7.8±1.5	89.1±5.4	10.7±3.3
380°C/30min	3.0±0.1	102.7±2.0	9.0±0.2	100.7±12.2	27.0±7.8
380°C/60min	3.2±0.3	100.0±2.7	8.9±0.2	95.9±1.4	22.2±3.2

materials show that they can be cured and yet still form strong, tough, ductile and solvent resistant films.

4.4.3. Single lap shear tests

Adhesive properties of phenylethynyl terminated polyimides were evaluated using titanium as a substrate. Many factors can affect lap shear test results, e.g. choice of matrix, surface treatment, test method, etc. Early work based on neat resin single lap shear tests revealed that 4-PEPA endcapped, M_n=3.0 kg/mole oligomers displayed relatively low adhesive strength. This may due to void formation in the preparation of sample bonding. Low viscosity of the precursor oligomer also made thickness control of the sample very difficult.

The following adhesive single lap shear test was recommended by the Boeing Co. (Figure 4.4.2). Titanium (6Al-4V) alloy was used as the substrate and the test coupon's form and dimensions are shown in Figure 4.4.2. The adhesive matrix (reactive oligomers) to be tested was placed in between two titanium substrate coupon with an overlap of about 1.0"×0.5" on a layer of aminopropyl tri-methoxy silane sized scrim cloth (E-glass) as support. Prior to doing so, however, the glass scrim cloth was prepared by dipping the scrim cloth in an oligomer solution and then drying it. This was repeated several times to achieve a 85 wt.% oligomer concentration. The scrim was then bonded with titanium coupons for adhesive testing as described in the experimental section.

All our tests were conducted using titanium (6Al-4V) alloy as the substrate adherent, and surface treated with Pasa-Jell according to ASTM-

D1002. Representative results are shown in Table 4.4.4. For reactive oligomers, the bonding time-temperature-pressure played an important role for adhesive test results. Even without optimizing the bonding cycle, the lap shear strengths were very strong and most of them (M_n=3.0 kg/mole) were higher than the commercial thermoplastic control; failure modes were mostly cohesive in all cases. Independently, a BPADA/*m*-PDA 4-PEPA endcapped, M_n=3.0 kg/mole poly(amic) acid oligomer was tested by the Cytec Company using a similar adhesive test method, with very high adhesive strength results reported as follows:

Substrate: 0.05" 6Al-4V Titanium

Surface treatment: Chromic acid anodized, Boeing method

Primer: BP™x5 (based on PETI-5 resin), primer cured 60 minutes at 660°F

Lap Shear Strength:	RT	6300 psi (80% cohesive)
	350°F	5250 psi (80% coh)
	400°F	4400 psi (80% coh)

by courtesy of Dr. R. T. Mayhew at Cytec Inc.

The combination of strong adhesive strength and solvent resistance suggests that this system would be a good candidate material for structural adhesive applications.

STANDARD METHOD: ASTM-D1002

FORM AND DIMENSIONS OF TEST SPECIMENS:

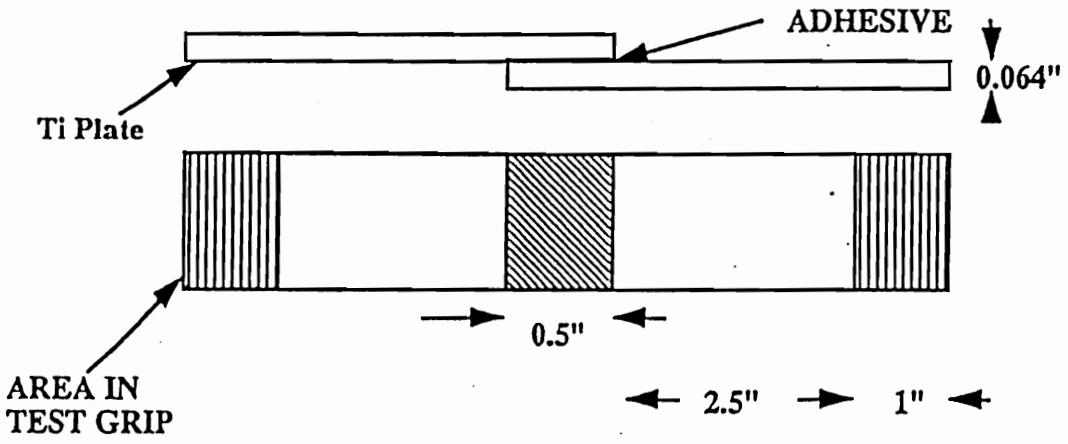


Figure 4.4.2 Adhesive single lap shear test

Table 4.4.4. Ti-Ti (6Al-4V) single lap shear tests.

System	Adhesive Strength (Psi)	Curing Conditions
BPADA/*p*-:*m*-(7:3)PDA 4-PEPA capped, 3.0 kg/mole	4,200±400	380°C, 90 min, 75 Psi
BPADA/m-PDA 4-PEPA capped, 2.0 kg/mole	3,700±300	370°C, 45 min, 25 Psi
BPADA/m-PDA 4-PEPA capped, 3.0 kg/mole (3K)	5,300±210	370°C, 45 min, 25 Psi
3K (90%)-PEI (10%)*	4,200±670	370°C, 45 min, 35 Psi
3K (75%)-PEI (25%)*	4,700±520	370°C, 45 min, 50 Psi
PEI	4,100±320	270°C, 15 min, 75 Psi

*: Samples prepard from self-supportted films

4.4.4. Improving the adhesive "green strength" by blends of the thermosets precursor with thermoplastics

The M_n=2.0 and 3.0 kg/mole oligomers are fully imidized powders, but cannot be easily melt pressed to form self-supporting films for adhesive bonding. Thus, the adhesive "green strength" is weak and a supporting layer of glass scrim cloth is needed – not only as a support for the oligomers, but also as a method of thickness control. However, introducing such scrims is known to complicate sample preparation and increase adhesive failure because it introduces another polymer-glass interface. A possible method to solve this problem is to simply blend the thermoset precursor with a thermoplastic to improve the adhesive "green strength". Such blend systems have been prepared and show some interesting results.

A BPADA/*m*-PDA 4-PEPA endcapped, M_n=3.0 kg/mole oligomer was chosen for this study of thermoset/thermoplastic blends since it demonstrates excellent adhesive strength in both fully imidized dry powder form, as well as in poly(amic) acid form. Interestingly, it was found that the poly(amic) acid form was not miscible with imidized polyetherimide thermoplastics when NMP was used as the solvent. On the other hand, the imidized dry powder form of the oligomer was miscible with several polyetherimides containing a BPADA/*m*-PDA backbone. Blends were created by dissolving the oligomer with a polyetherimide thermoplastic in chloroform to form a homogenous solution. They were then isolated by precipitation in methanol and dried under vacuum at 170°C overnight. The glass transition temperatures of several of these blends are listed in Table 4.4.5. As expected, T_g values of the blends registered between those of the oligomers and thermoplastics, i

Table 4.4.5. Glass transition temperatures of polyimide blends.

Thermoplastic system	Thermoplastic T_g (°C)	Blend T_g (°C)
BPADA/m-PDA PA endcapped, 20K	215	189
BPADA/m-PDA 4-PEPA endcapped, 20K	217	188
Ultem™-1000	216	188

Heating rate of 10°C/minute in nitrogen

Table 4.4.6. Soxhlet extraction data in chloroform of polyimide blends.

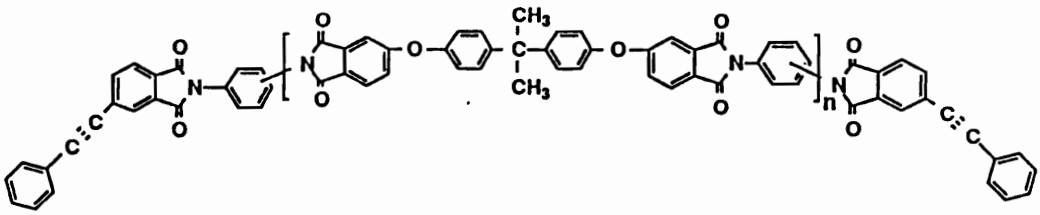
System	Gel Fraction (%)[a]
3K 4-PEPA endcapped	98.6
20K 4-PEPA endcapped	96.7
3K 4-PEPA endcapped + 20K 4-PEPA capped (10 wt.%)	98.0
3K 4-PEPA capped + 20K PA capped (10 wt.%)	96.2
3K 4-PEPA endcapped + Ultem™-1000	94.1

a: Samples were extracted for 5 days and then dried for 5 days at 120°C under vacuum

ndicating the formation of a miscible system. The gel fractions of the blends cured at 370°C for 45 minutes are shown in Table 4.4.6. It is interesting to note that blends of non-reactive, soluble thermoplastics did not noticably lower the gel fraction. Thus, for thermosetting oligomers containing a 10 wt.% commercial Ultem™ polyetherimide, a high 94.1% gel fraction was obtained.

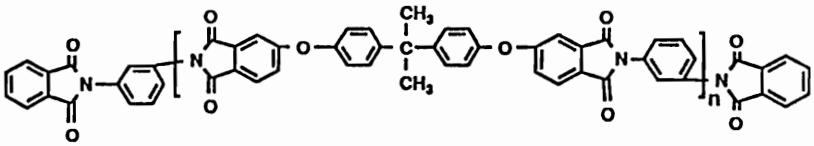
One blend system (Scheme 4.4.1) chosen for more detailed study was based on (1) an M_n=3.0 kg/mole BPADA/*m*-PDA 4-PEPA endcapped oligomer, which has a high gel fraction (>99%) after being cured at 370°C for 45 minutes, and (2) the polyetherimide (PEI) thermoplastic, which has M_n=20.0 kg/mole, good adhesive strength, but poor solvent resistance. This thermoplastic was completely soluble in chloroform after a control molding at 370°C for 45 minutes. One might have expected to observe the cured blend system to show a linear gel fraction drop as a function of the thermoplastic concentration (dotted line in Figure 4.4.4). Interestingly, the gel fraction was higher than expected and for the 25 wt.% PEI blend, the gel fraction was as high as 94%. Samples with longer extraction time (up to 10 days) remained 94% insoluble, indicating good solvent resistance (Figure 4.4.4). This may be due to tight semi-IPN formation, which makes it difficult for the solvent to extract out the linear miscible PEI. The glass transition temperatures of the cured samples were a function of the PEI wt.% as shown in Figure 4.4.5. Every samples exhibited a single T_g, indicating that they are miscible. A thermoplastic content in the 10-25 wt.% range could be important since the T_g and gel fraction are reasonably high and the material can be melt-pressed to form self-supporting films for adhesive tests. Such films have been made for adhesive lap shear tests and the results are also listed in Table 4.4.4. The

Thermosets:



M_n=3.0 kg/mole

Thermoplastics:



PEI

M_n=20.0 kg/mole, good adhesive strength, poor solvent resistance

Scheme 4.4.1 An approach for improving adhesive "green strength" by blending

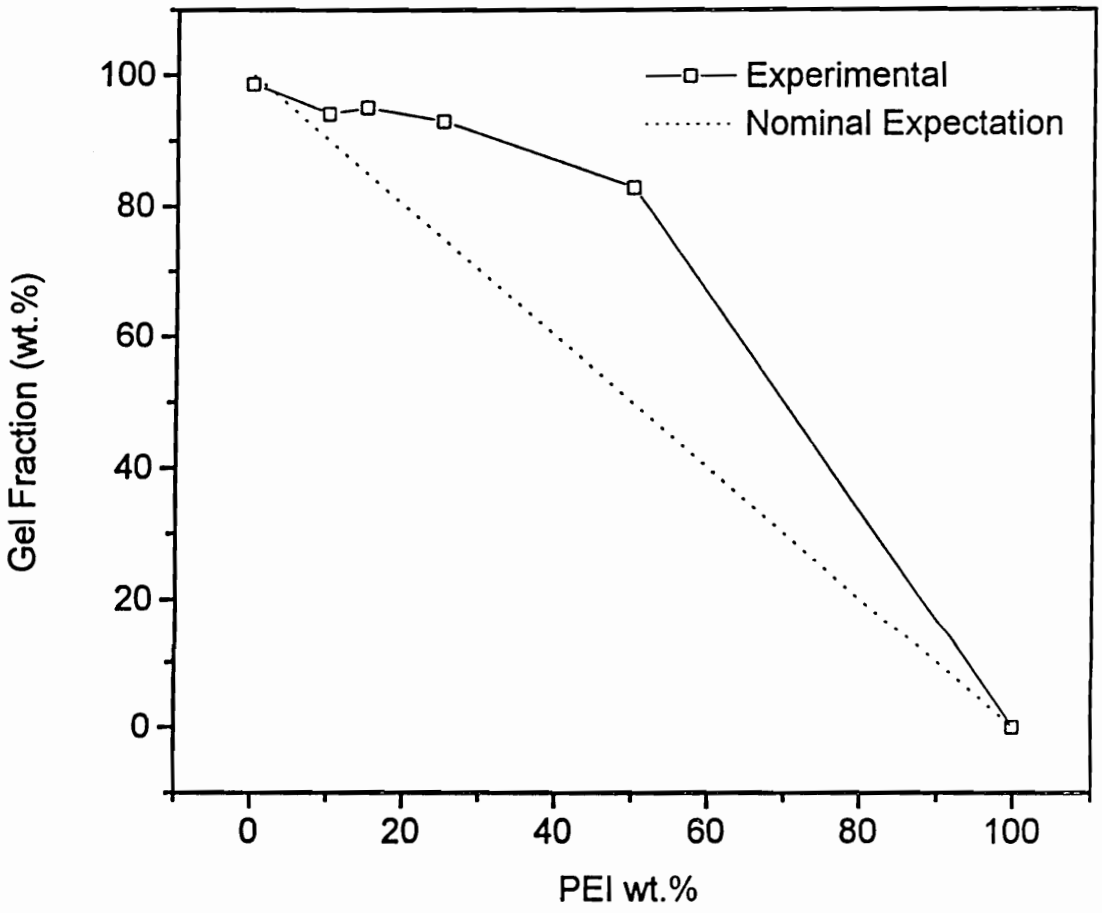


Figure 4.4.3. Gel fraction of cured blends of 3K oligomer with polyetherimide thermoplastics (cured at 370°C-45 minutes and Soxhlet extracted with chloroform for 4 days).

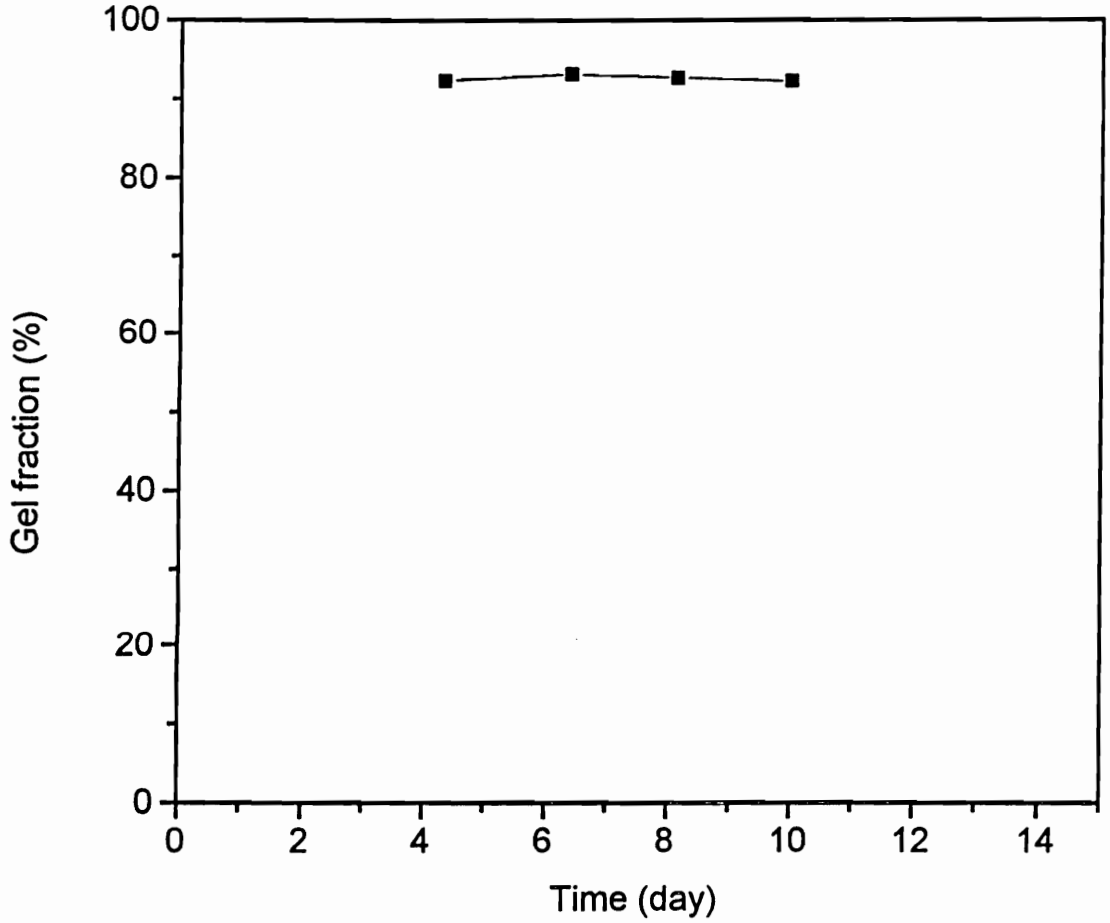


Figure 4.4.4 Long term solvent extraction of 3K oligomer-PEI (25 wt.%) blend (cured at 370°C/45 minutes and extracted from chloroform)

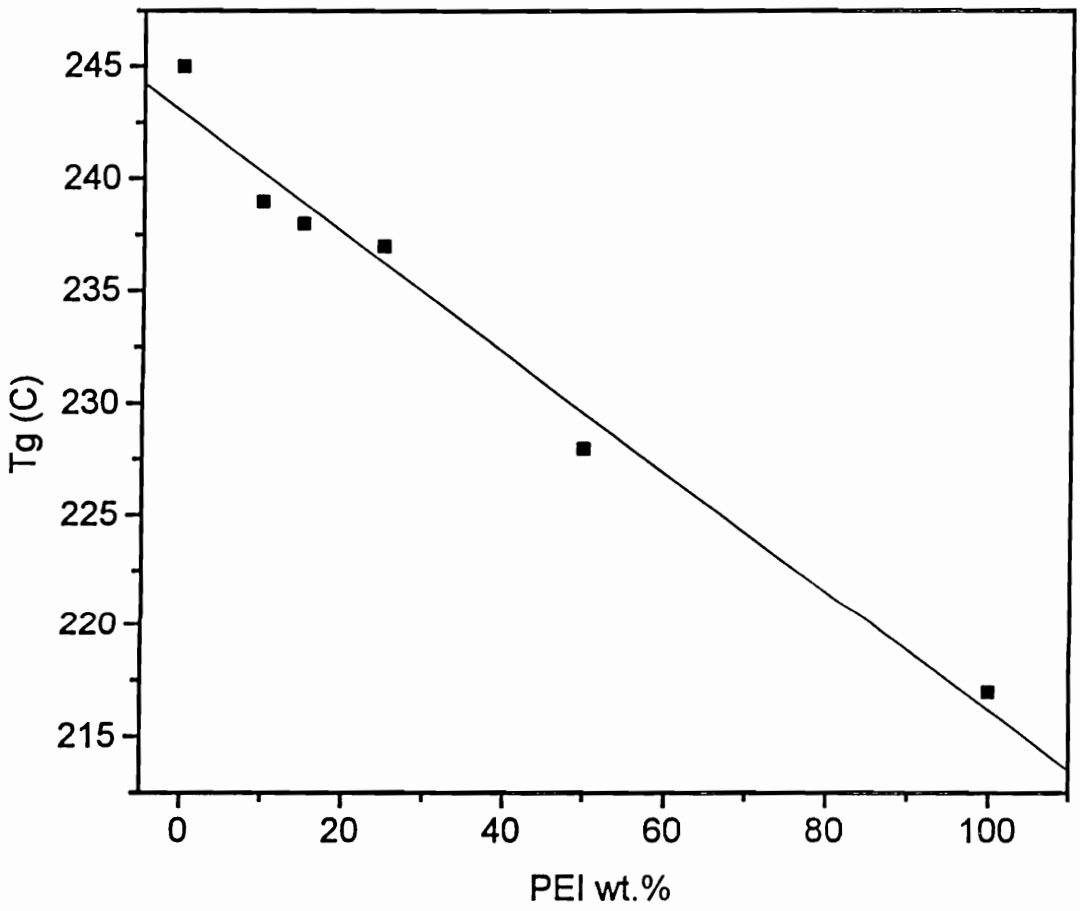


Figure 4.4.5 Influence of PEI weight fraction on the T_g of cured 3K-PEI blends (cured at 370°C for 45 minutes)

adhesive strength of the blends offers an improved way to prepare adhesives at lower cost, since the commercial thermoplastic is relative inexpensive.

4.4.5. Curing reaction studies by FTIR and DSC

Since the 4-phenylethynyl phthalic anhydride terminated oligomers were developed just a few years ago, very little basic structural information is known about the curing chemistry of the phenylethynyl endgroups and their resulting molecular structure. Several model compounds studies have provided some kinetic information [223], but only one kinetic study on the oligomer itself has been reported recently [255]. By examining the curing reaction of our reactive oligomers, we generated useful information about its processing capabilities. This work may also shed some light on the curing chemistry of the phenylethynyl groups.

The ethynyl carbon-carbon bond at both ends of the oligomer was detected by FTIR spectroscopy at a characteristic absorption of 2211cm^{-1} (Figure 4.4.6). As the reaction proceeded, the peak gradually disappeared over time at high temperatures (300-345°C), which confirmed that the curing reaction involved triple bonds. However, it wasn't possible to precisely define the nature of the new bond formation. To do this, studies are continuing in our laboratories utilizing model compounds.

When using -CH_3 bond stretch (2967 cm^{-1}) in the backbone as an internal standard (Figure 4.4.6), the normalized intensity of triple bonds vs. time at different curing temperatures is shown in Figure 4.4.7. As we expected, the reactive triple bond sites are consumed more quickly at higher temperatures. The disappearance of triple bond appeared to follow first-order

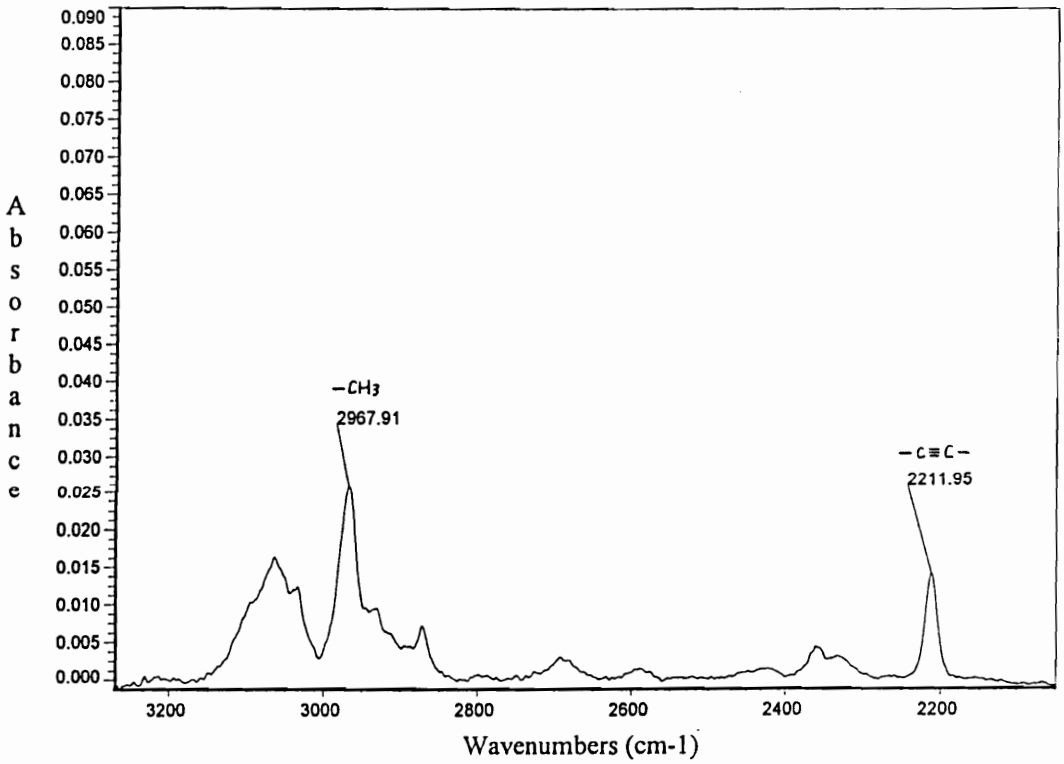


Figure 4.4.6. FTIR spectrum of M_n=2.0 kg/mole, phenylethynyl phthalimide-terminated imide oligomer.

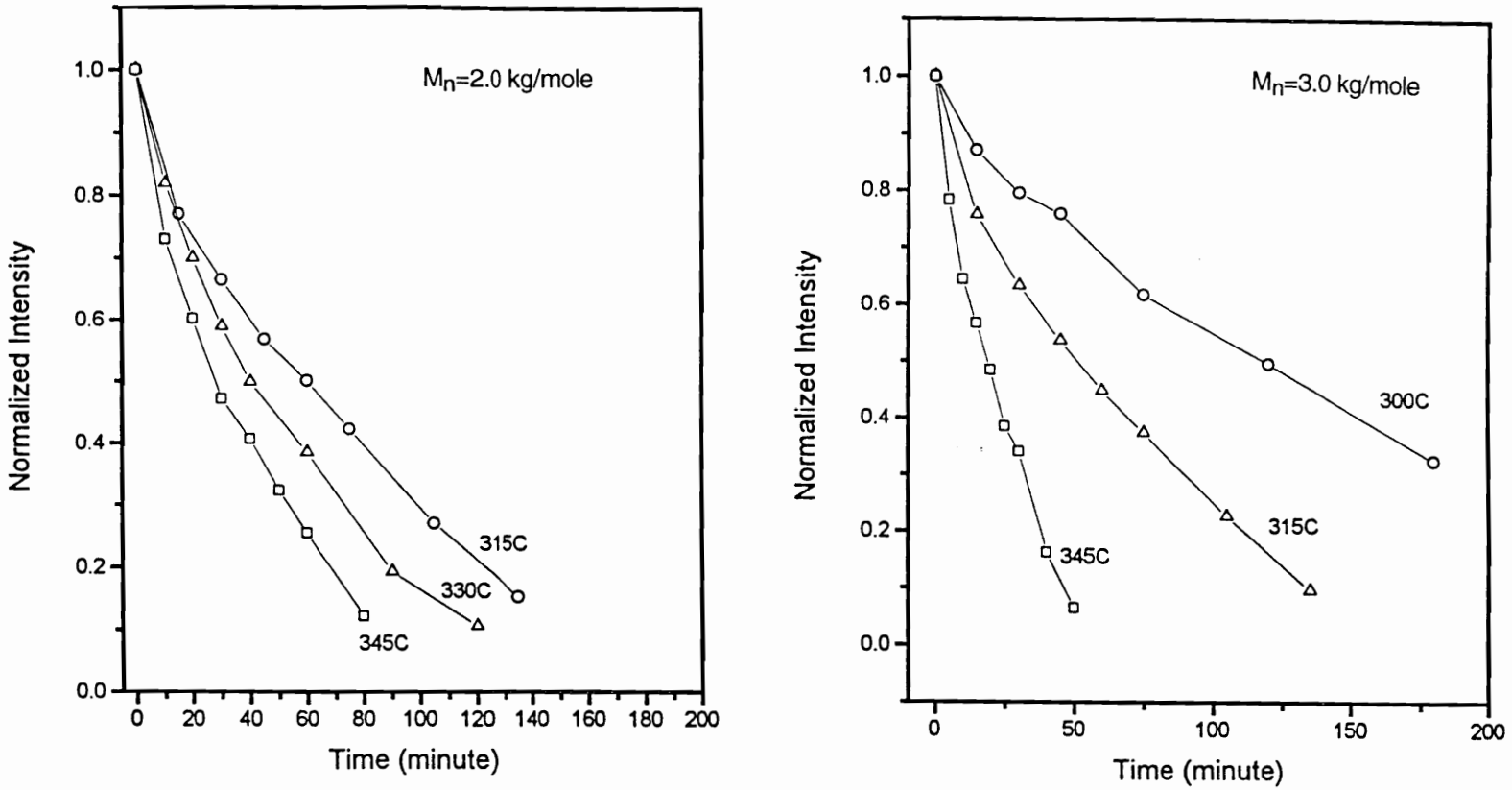


Figure 4.4.7 FTIR absorbance at 2212 cm^{-1} of BPADA/*m*-PDA 4-PEPA capped polyetherimide oligomers cured at different temperatures

reaction kinetics for a initial 80 minute curing reaction, as shown in Figure 4.4.8. Later deviation from the first-order reaction was difficult to fit in any kinetic model due to very low peak intensity. After 80 minutes, the triple bonds are consumed faster than expected for first-order reaction kinetics. First-order reaction kinetics were also reported by Takekoshi, et al. in their model compound study by f.d.-m.s. [223]. Very recently, Hinkley reported that new reaction mechanisms may come into play after the initial chain ends of the phenylethynyl groups are exhausted, as described in a DSC study of PETI-5 phenylethynyl endcapped imide oligomers [255]. This is consistent with our finding of deviations from first-order reactions. The Arrhenius plot and kinetic results of the initial curing stage are shown in Figure 4.4.8 and Table 4.4.7, respectively. Therefore, FTIR provides us a useful way to follow curing reactions.

Another widely used method to detect thermoset curing activation energy (E_a) is by dynamic DSC measurements. A simple relationship between activation energy (E_a), heating rate (ϕ, °C/min) and peak exotherm temperature (T_p), based on the work of Ozawa [257,258] and Doyle [259,260] is presented as:

$$E_a = \frac{-R\Delta \log \phi}{0.4567\Delta(1/T_p)} \qquad \text{Ozawa equation}$$

Several 4-phenylethynyl phthalic endcapped oligomers were studied by dynamic DSC at different heating rates. A typical dynamic DSC trace at 10°C/min. is shown in Figure 4.3.7. The heating rate vs. cure exotherm peak temperature is listed in Table 4.4.8. One example of an Ozawa plot is shown

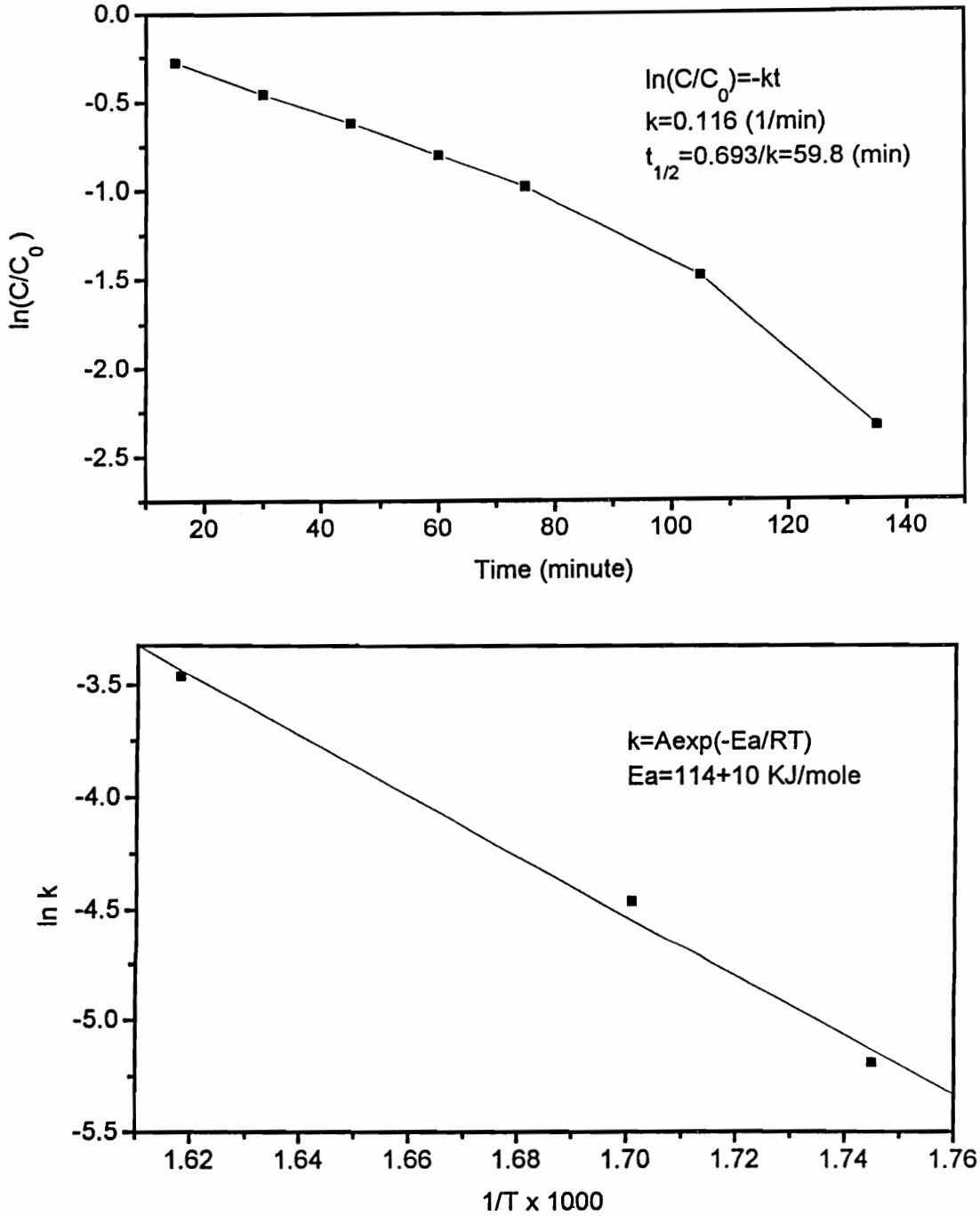


Figure 4.4.8. Apparent first order reaction of BPADA/*m*-PDA 4-PEPA endcapped polyetherimide oligomers cured at 315°C and Arrhenius plot.

Table 4.4.7. Kinetic results from following the apparent first order reaction of triple bonds in the curing of BPADA/*m*-PDA 4-PEPA endcapped oligomers by FTIR.

M_n=3.0 kg/mole

Temperature (°C)	k (1/min)	$t_{1/2}$ (min)
300	0.00558	124.2
315	0.01158	59.8
345	0.03140	22.1
Activation Energy:	114±10 KJ/mole	

M_n=2.0 kg/mole

Temperature (°C)	k (1/min)	$t_{1/2}$ (min)
315	0.00985	70.4
330	0.01587	43.7
345	0.02080	33.3
Activation Energy:	75±10 KJ/mole	

Table 4.4.8. Curing exothermic peak temperatures.

System	Heating rate (°C/min)	exotherm peak (°C)	System	Heating rate (°C/min)	exotherm peak (°C)
1	5	424.2	6	10	403.1
	10	412.0		20	421.8
	20	391.4		30	433.6
	30	372.2		40	441.7
2	5	385.0	7	10	409.8
	10	401.3		20	425.8
	20	422.1		30	433.1
	30	430.9		40	440.0
3	5	416.7	8	5	376.7
	10	409.6		10	391.9
	20	387.9		20	406.5
	30	374.6		30	422.8
4	5	380.3	9	10	396.0
	10	402.4		20	411.4
	20	414.2		30	420.0
	30	426.7		40	434.7
5	5	374.1			
	10	392.2			
	20	409.5			
	30	426.2			

System 1: BPADA/m-PDA 4-PEPA endcapped, M_n=2.0 kg/mole
System 2: BPADA/m-PDA 4-PEPA endcapped, M_n=3.0 kg/mole
System 3: 50 wt.% system 1 + 50 wt.% system2
System 4: 90 wt.% system 1 + 10 wt.% Ultem™-1000
System 5: BPADA/p-:m-(7:3)PDA 4-PEPA endcapped, M_n=2.0 kg/mole
System 6: BPADA/p-:m-(7:3)PDA 4-PEPA endcapped, M_n=3.0 kg/mole
System 7: BPADA/p-:m-(7:3)PDA 4-PEPA endcapped, M_n=5.0 kg/mole
System 8: BPADA/DAMPO 4-PEPA endcapped, M_n=2.0 kg/mole
System 9: BPADA/DAMPO 4-PEPA endcapped, M_n=3.0 kg/mole

in Figure 4.4.9. The activation energy (E_a) values obtained by this method are listed in Table 4.4.9. In the literature, only Hinkley [255] reported a M_n=5.0 kg/mole PETI-5 phenylethynyl endcapped oligomer with a E_a value of 138 KJ/mole by DSC. Our results indicated two trends from these activation energy results: (1) E_a increases as the oligomer's molecular weight increases, and (2) incorporation of very polar phosphine oxide group in the backbone results in an increase in E_a values. These trends may be related to the diffusion control curing process of the phenylethynyl endgroups. Therefore, the higher activation energy barrier is attributed to a higher molecular weight oligomer or stronger inter-molecular interactions from polar backbone. Fully cured products are seldom obtained using diffusion control curing. This may explain the T_g increase seen in longer curing reactions, as reported by others [218, 219].

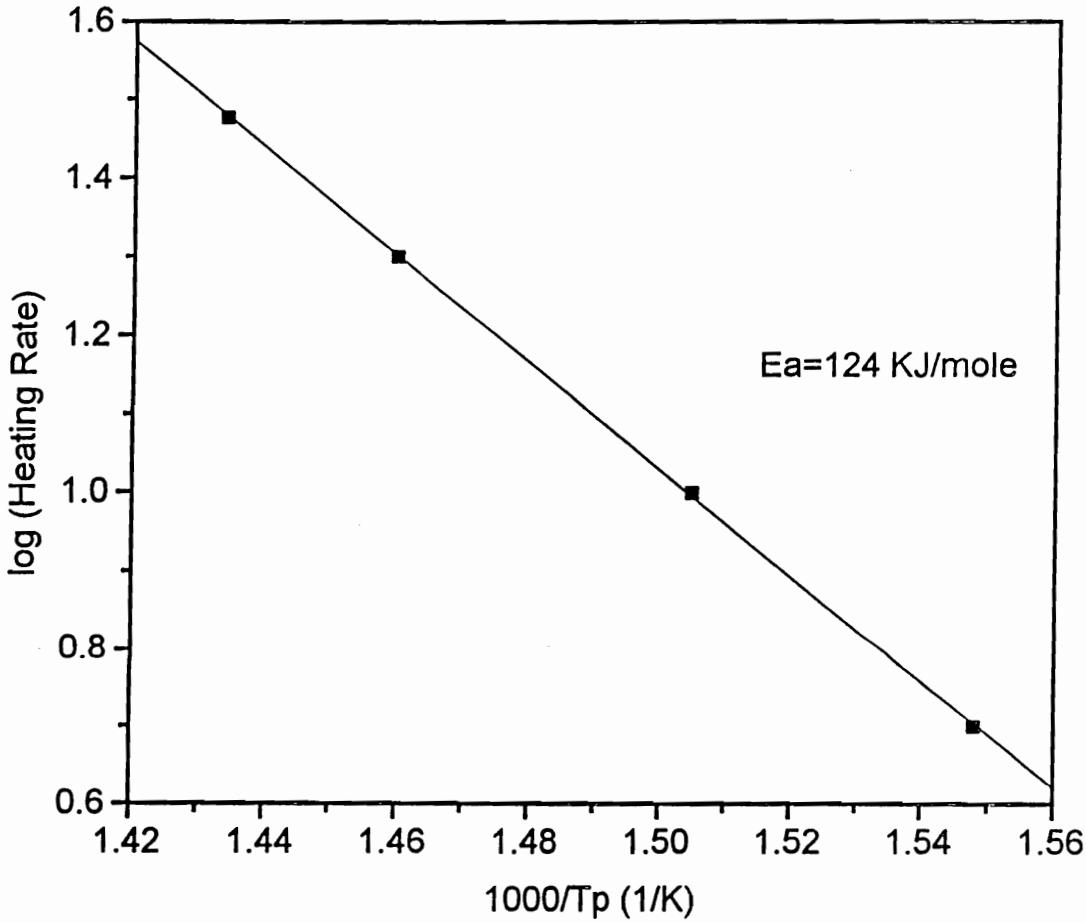
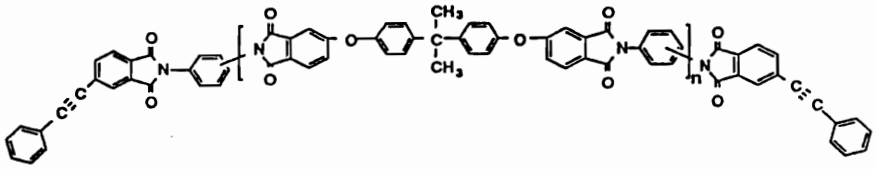
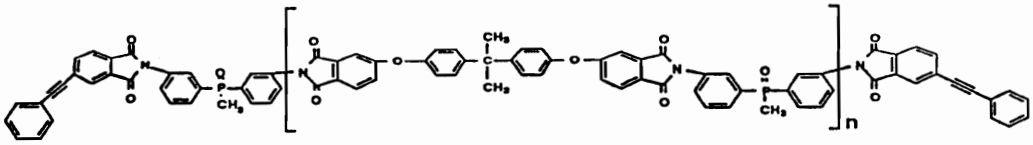


Figure 4.4.9. Ozawa plot of M_n=2.0 kg/mole BPADA/*m*-PDA 4-PEPA endcapped polyetherimide oligomers by DSC.

Table 4.4.9. Activation energy (E_a) of curing reaction of 4-PEPA endcapped oligomers by DSC.



System	M_n (kg/mole)	E_a (kJ/mole)
BPADA/*m*-PDA	2.0	124
	3.0	139
	2.0 (50%) + 3.0 (50%)	143
	3.0 (90%) + PEI (10%)	144
BPADA/*p*-:*m*-(7:3)PDA	2.0	126
	3.0	149
	5.0	189



System	M_n (kg/mole)	E_a (kJ/mole)
BPADA/*m*-DAMPO	2.0	142
	3.0	189

4.4.6. Rheological behavior of reactive oligomers and carbon fiber composite applications

The oligomers synthesized herein produce fine particle products suitable for powder prepregging in carbon fiber composite processing. Evaluation of composite materials based on a M_n=3.0 kg/mole, BPADA/*p*-:*m*-(7:3)PDA 4-PEPA endcapped polyimide matrix system has been initiated in Dr. Alfred C. Loos' processing lab and preliminary results are encouraging. Iosipescu tests of a G30 fiber composite cured at 380°C for 60 minutes had a shear modulus of 4.20±0.28 GPa and a shear strength of 60±2 MPa.

Flow behavior was examined by rheological parallel plate studies. The viscosity vs. time results for a 70% *p*-PDA based, 3.0 kg/mole oligomer indicated very low viscosity levels for the initial 11 minutes at 350°C. Then the viscosity quickly increased as the gel point was achieved. Similar behavior was observed under either air or nitrogen. As previously discussed, this material had a large processing window (the temperature difference between T_g and cure exotherm). Further investigations revealed that the 3.0 kg/mole oligomers flowed well (indicating low viscosity) at 300°C for more than 60 minutes before curing, which provides sufficient time for processing. The 2.0 kg/mole oligomers demonstrate very low melt viscosity (<5 Pa s) at 350° (Table 4.4.10), which makes them suitable candidates for resin infusion molding (RIM).

The typical melt viscosity temperature ramp of all *m*-PDA-based oligomers is shown in Figure 4.4.10. These oligomers flow well within specific temperature-time ranges and the RIM method (Figure 4.4.11) was successfully applied to make M_n=2.0 kg/mole matrix composites. Warp

flexural test results based on AS 4, 3K, plain-weave, G-sized fabric showed flexural strength of 790±66 MPa and flexural modulus of 73.8±1.7 GPa. These results suggest the potential for these materials to be used in carbon fiber matrix systems.

Table 4.4.10. Melt viscosity of BPADA/*p*-:m-(7:3)PDA 4-PEPA endcapped polyetherimide oligomers.

M_n (kg/mole)	Temperature (°C)	Time begin to cure (min)	Melt viscosity before cure (Pa·s)
2.0 (in air)	350	7	<5
3.0	300	>60	-
3.0	350	11	<100
3.0	380	8	<5
10.0	350	20	<20.0

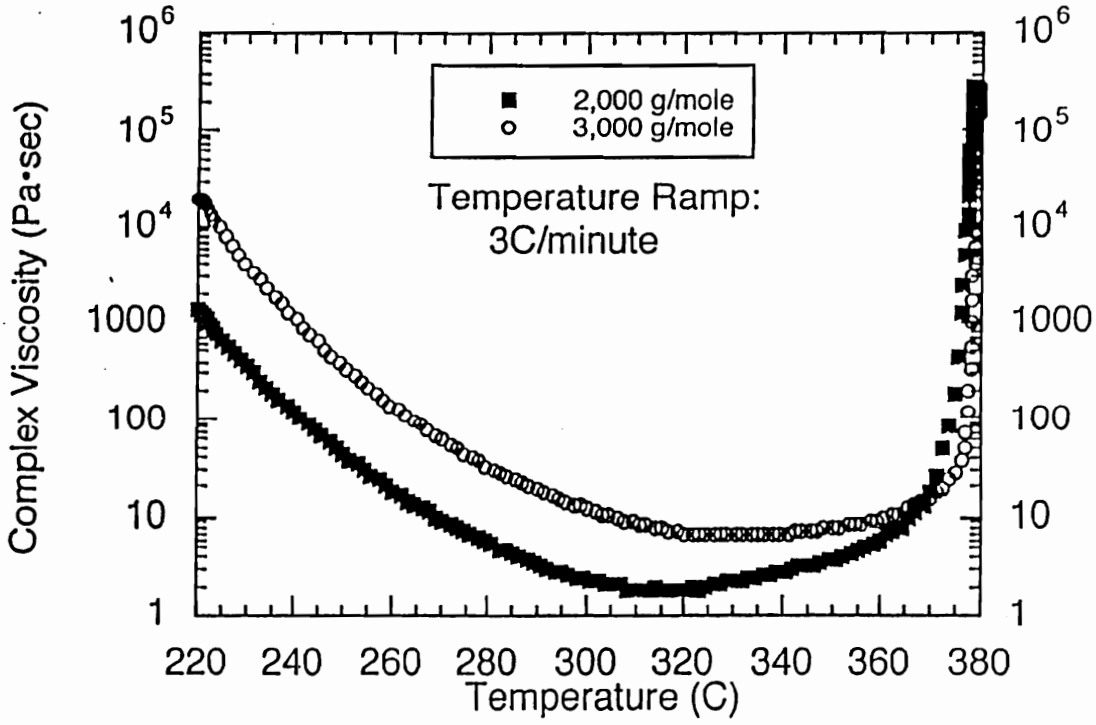


Figure 4.4.10. Rheological characterization of BPADA/*m*-PDA 4-PEPA endcapped polyetherimide oligomers (courtesy of Mr. T. Bullions).

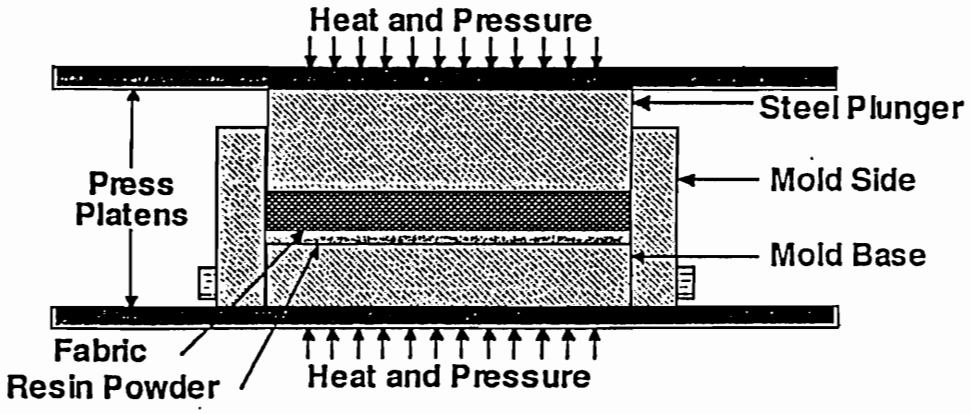


Figure 4.4.11 Resin powder infusion technique (RIM)

4.5 Phosphine oxide containing polyetherimides

4.5.1 Synthesis of bis(*m*-aminophenyl)methyl phosphine oxide (DAMPO)

In order to improve the fire-resistant properties of polyimides and explore new phosphine oxide containing polymers, we focused our research on the phosphine oxide containing monomer, bis(*m*-aminophenyl)methyl phosphine oxide. This monomer contains high phosphorus content compared to a triaryl phosphine oxide system and is easily prepared and purified.

Polymers based on this phosphine oxide structure may not only offer increased fire resistance and improved adhesive properties, but also show improved solubility in organic solvents and thus be used for carbon fiber composite sizing agents.

The phosphine oxide diamine monomer (DAMPO) was prepared via the following three-step reaction (Scheme 3.1.1) beginning with commercially available methyl triphenyl phosphonium bromide **1**.

1. Selective decomposition of **1** with a base yielded diphenyl methyl phosphine oxide **2**.
2. Nitration of **2** with a mixture of fuming nitric acid and concentrated H_2SO_4 yielded bis(*m*-nitrophenyl)methyl phosphine oxide **3**
3. This was then reduced by H_2 in the presence of the catalyst, Pd/C, to yield bis(*m*-aminophenyl)methyl phosphine oxide (**4**, DAMPO).

The melting point of DAMPO after purification was sharp (152-153°C) and was higher (145-147°C) than previously reported [237]. Monomer grade DAMPO was obtained by above mentioned route. The molecular structure

was verified by elemental analysis, NMR, TLC, HPLC and GC analysis. The ^{1}H NMR is shown in Figure 4.5.1 with methyl peaks at 1.79 ppm and amino peak at 5.38 ppm, as expected. ^{31}P NMR exhibited a single peak at 29.11 ppm, as shown in Figure 4.5.2. The starting material, triphenyl methyl phosphonium bromide **1**, can be obtained easily by using commercially available triphenyl phosphine and thus could be used for scale up of this monomer. The diamine DAMPO was used as a monomer or copolymer during polyimide synthesis and will be discussed in a later section. It has also been utilized as a curing agent for epoxy resins [261] and as a chain extender for polyurethane synthesis [262] in the development of potentially fire-resistant materials.

4.5.2 Synthesis of DAMPO based homo-polyimide thermoplastics

The BPADA/DAMPO amorphous polyimides were successfully synthesized via an ester-acid route (Scheme 4.5.1) in high yields and purity. When equal molar amounts of BPADA and DAMPO were used in the polymerization without an endcapper (uncontrolled MW), a very high MW homopolyimide was obtained, e.g. $[\eta]$=2.95 (dL/g) and M_n=98.0 (kg/mole) by GPC (Table 4.5.1). Previous research [249] indicated that only low MW homopolyimides could be obtained from the polymerization of 6FDA/DAMPO, which was attributed to the low reactivity of the DAMPO. In contract, our results indicated that this was not the case if the DAMPO was pure and optimal reaction conditions were appropriate (e.g. concentration and temperature, etc.). Thus, our results [247] appears to be the first to describe a DAMPO-based high MW homopolyimide.

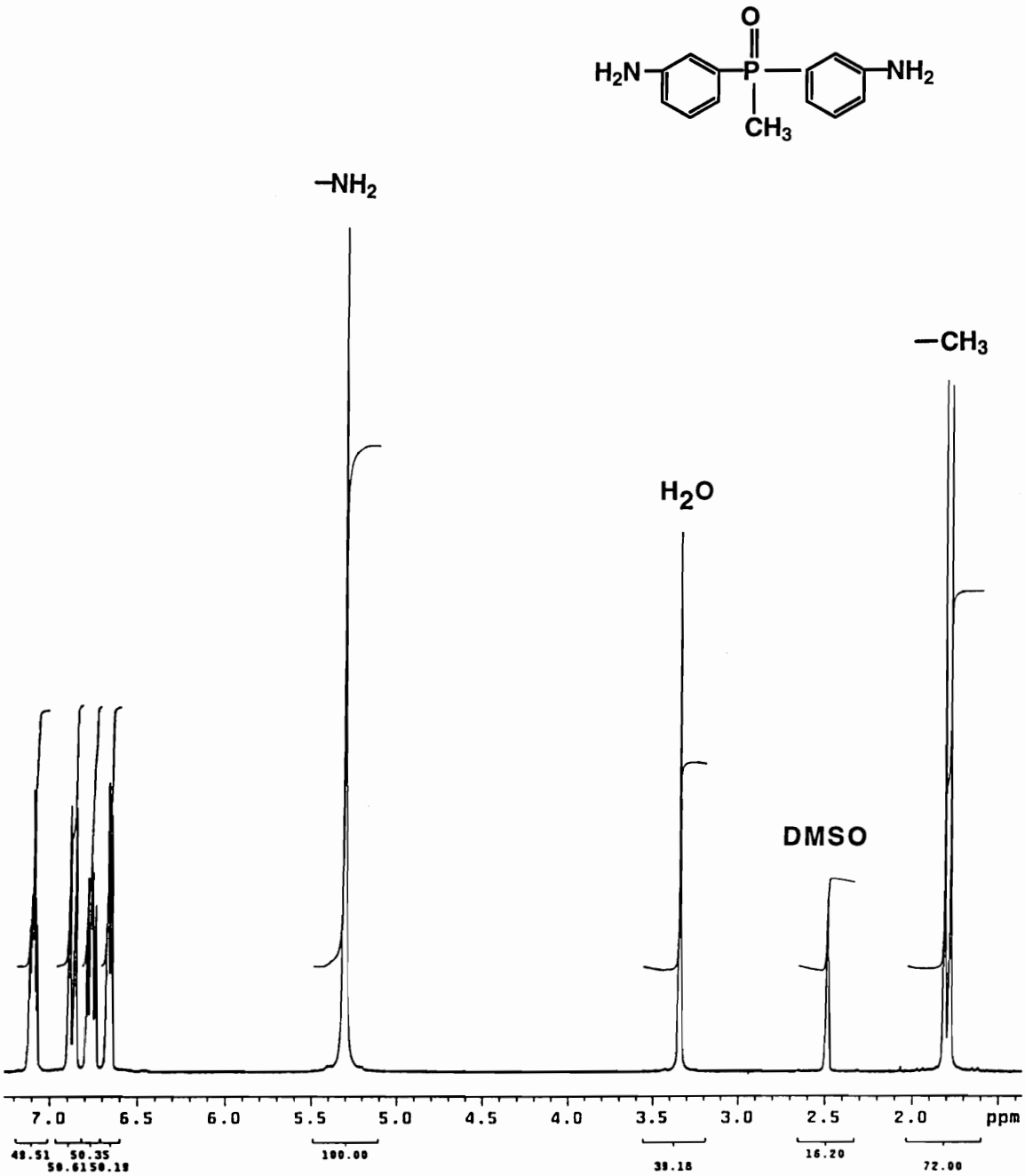


Figure 4.5.1. ^{1}H NMR spectrum (in $CDCl_3$) of bis(*m*-aminophenyl) methyl phosphine oxide.

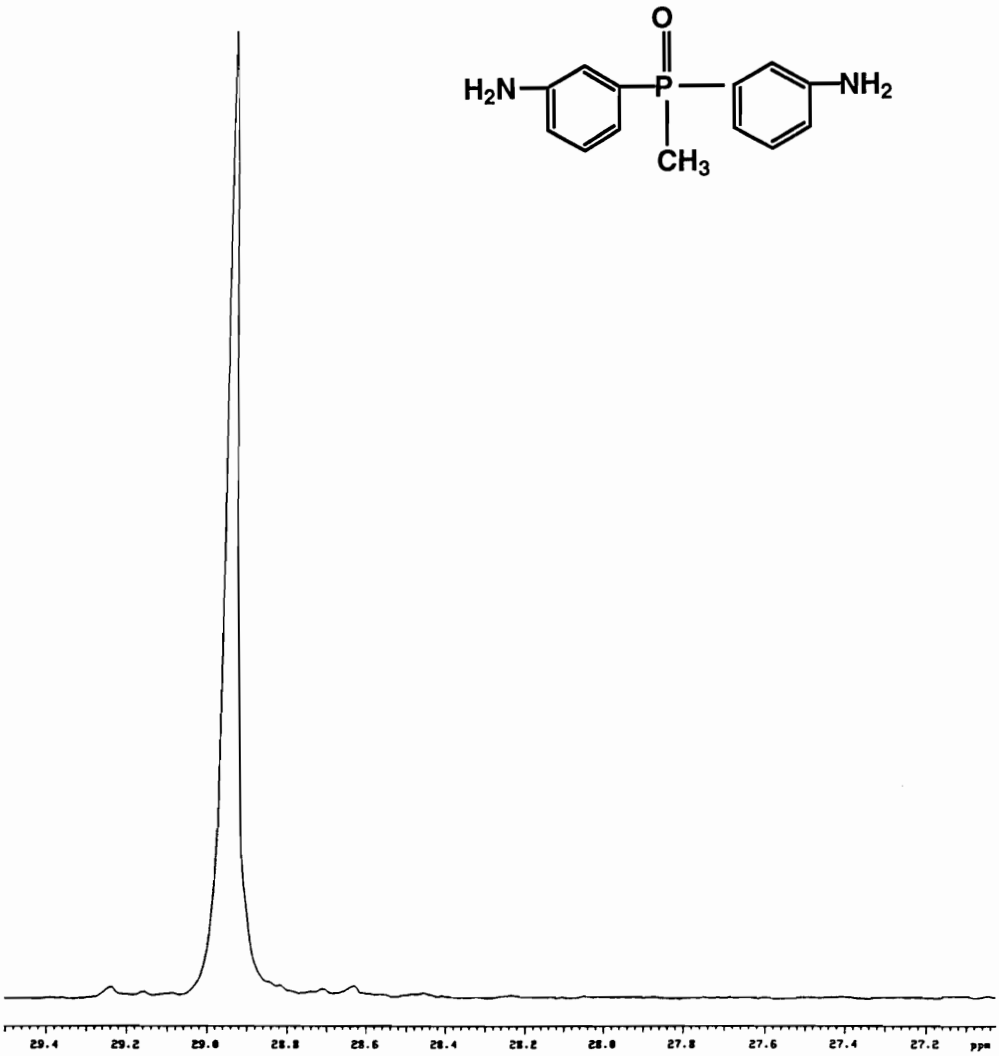
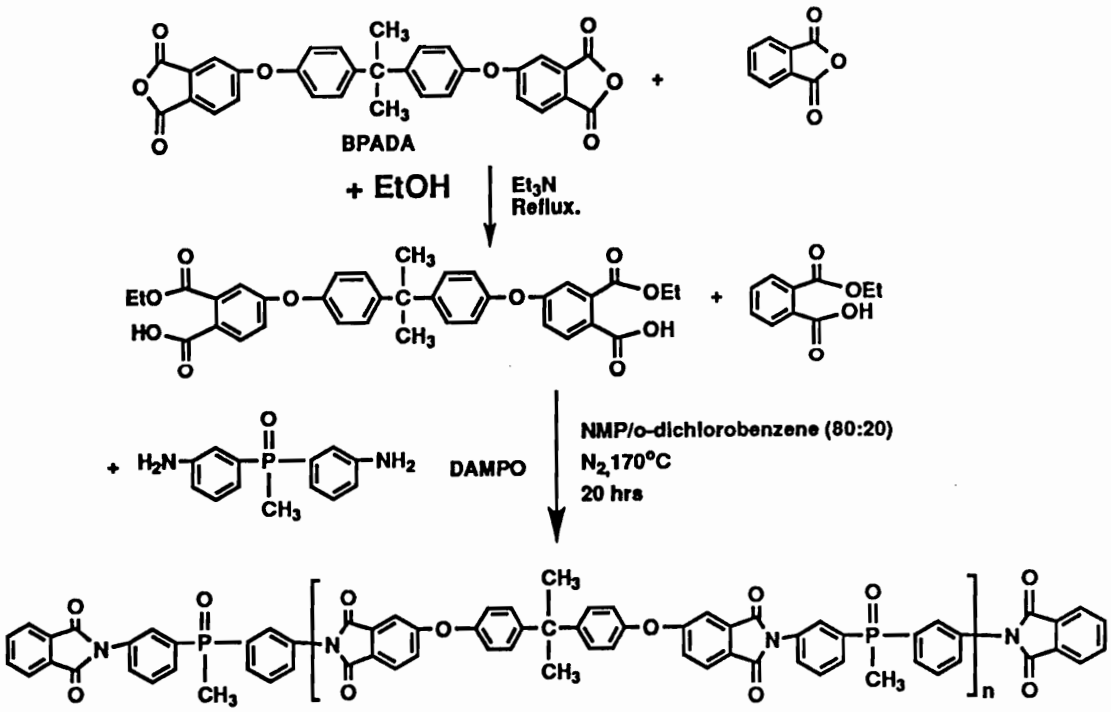


Figure 4.5.2. ^{31}P NMR spectrum of bis(*m*-aminophenyl) methyl phosphine oxide.



Scheme 4.5.1. Synthesis of BPADA/DAMPO PA endcapped polyimides.

Table 4.5.1. Characterization of BPADA/DAMPO thermoplastic polyimides.

Target M_n (kg/mole)	[η] (dlg^{-1}, NMP 25°C)	T_g (°C)[a]	5% wt. loss (°C)[b]	750°C char yield in air (%)[b]
5.0, PA endcap	0.15	197	493	42
30.0, PA endcap	0.47	215	519	58
1:1 Stoichiometry	2.95	221	509	62

[a]Heating rate of 10°C/minute in nitrogen

[b]Measured in air at 10°C/minute

Controlled MW polyimide thermoplastics were prepared by the reaction of a dianhydride with a stoichiometric excess of diamine and phthalic anhydride (PA) endcapper. The BPADA/DAMPO PA endcapped (M_n=30.0 kg/mole) polyimide compression moldable thermoplastics displayed a T_g value of 215°C (Table 4.5.1). All these polyimides were soluble in NMP, DMAc and $CHCl_3$ and no melting endothermic peak were detected by DSC, indicating that the systems are amorphous. The BPADA/DAMPO based thermoplastics had a high (54%) char yield at 750°C in air (Figure 4.5.3) as seen by dynamic thermogravimetric analysis. The control BPADA/*m*-PDA-based polyetherimide thermoplastics, however, did not show any char in air at that temperature. Careful examination of the TGA pan after having heated the phosphorus containing imide film in air to 800°C suggests that the film expanded, possibly indicating intumescence during char formation. The residue char was collected for solid state ^{31}P NMR analysis and revealed that the char contained some inorganic phosphorus compounds (Figure 4.5.4). These char-forming characteristics are considered to be very important for fire-resistance, since the char insulates the underlying polymer and restricts flammable volatiles from diffusing through and feeding the flame. This may explain the apparent excellent self-extinguishing features of these phosphine oxide containing polyimides relative to other engineering thermoplastics.

Attempts were also made to synthesize PMDA/DAMPO (Scheme 4.5.2) based polyimides via the ester-acid route in order to achieve higher T_g materials. However, the polymer precipitated out of the solution after about 30 minutes. The DSC thermogram on the resulting powder displayed melting endothermic peaks around 402°C and 431°C. High molecular weight

PMDA/DAMPO was prepared using the established two-step route by first forming a very viscous polyamic acid solution in DMAc, followed by thermal consolidation in an oven to produce an imidized film. However, the chracterization of this film has been limited because of the insolubility of the film, which was soluble only in hot NMP.

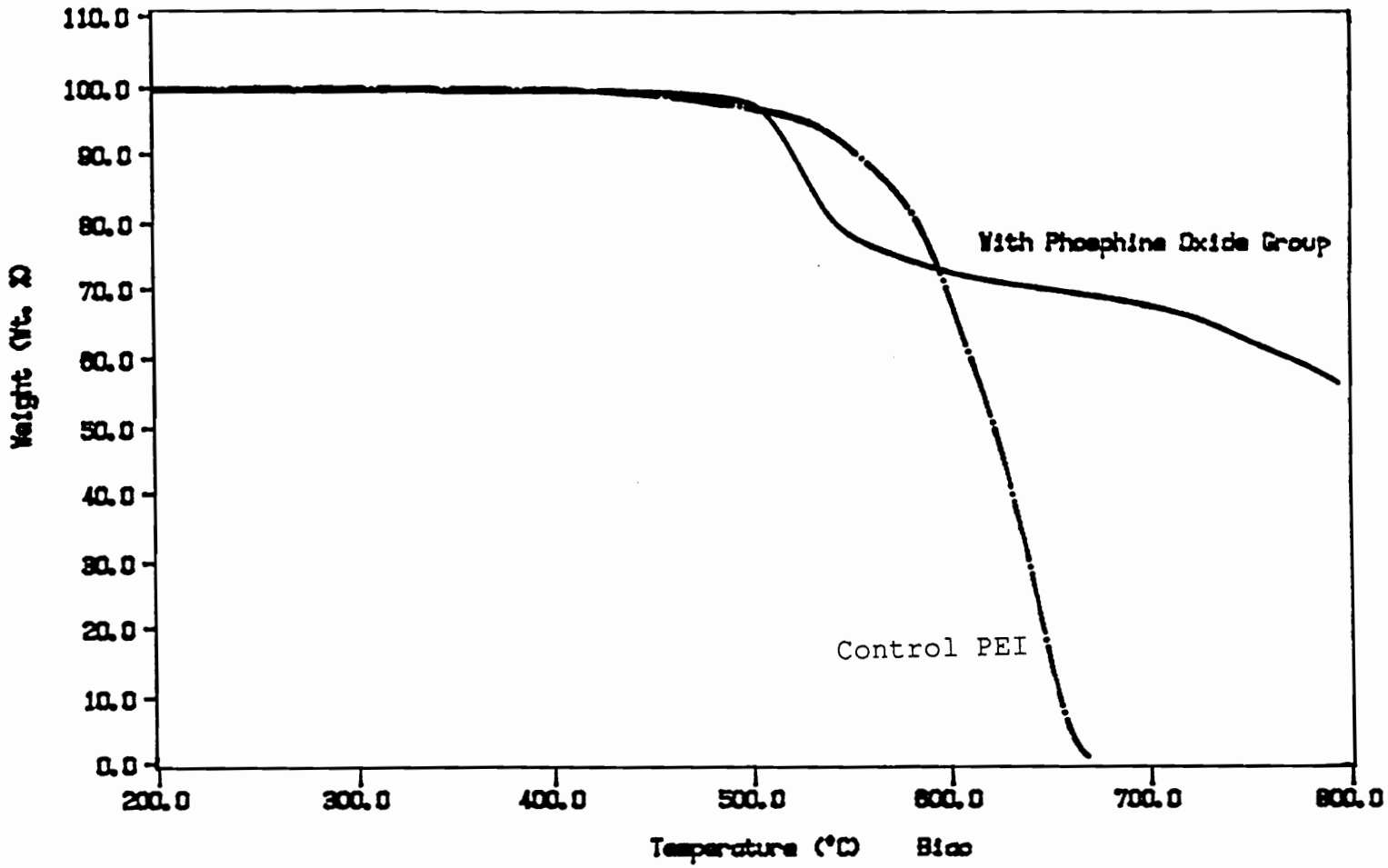


Figure 4.5.3. TGA thermogram showing the influence of phosphine oxide group on the char yield at 10°C/min in air.

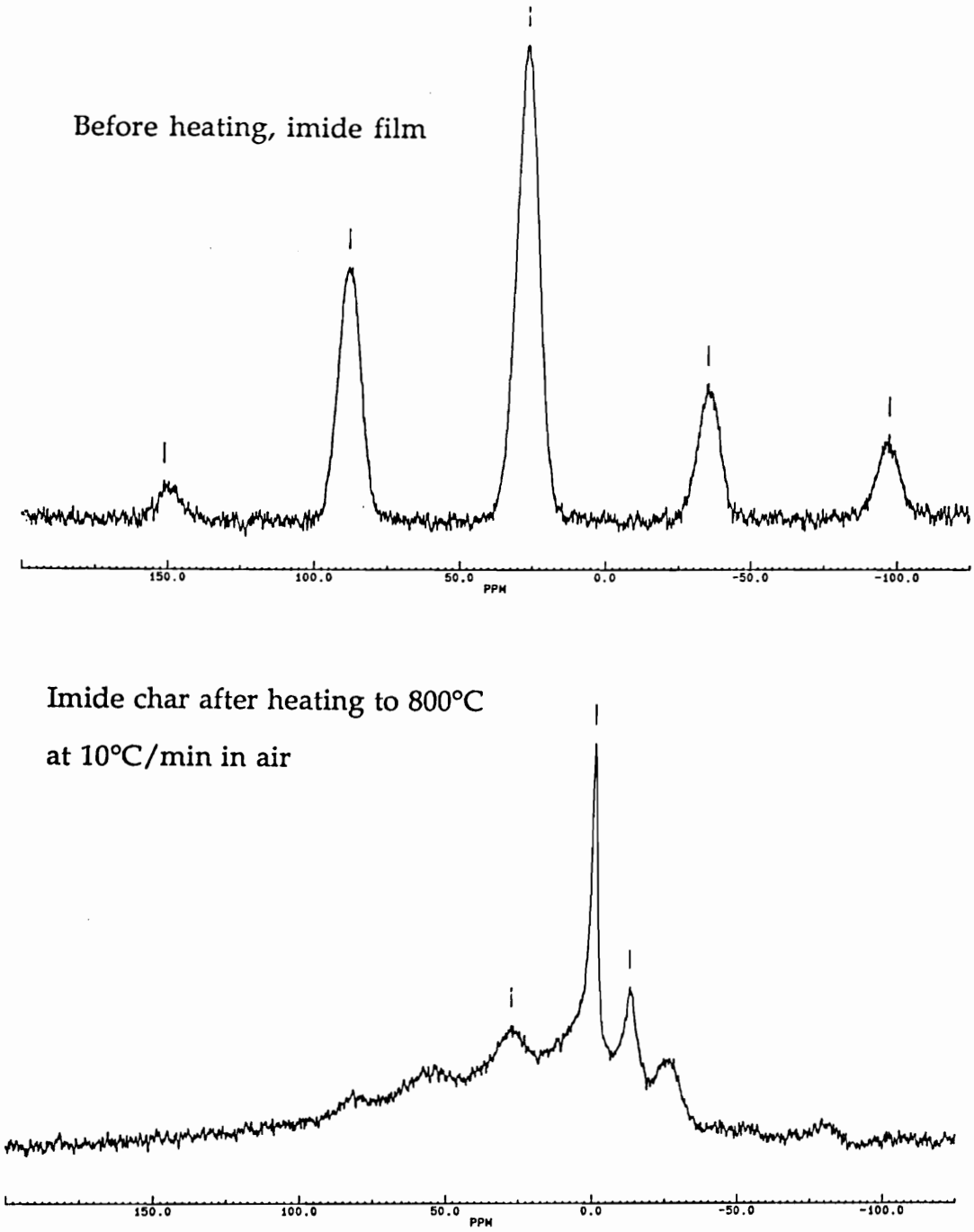
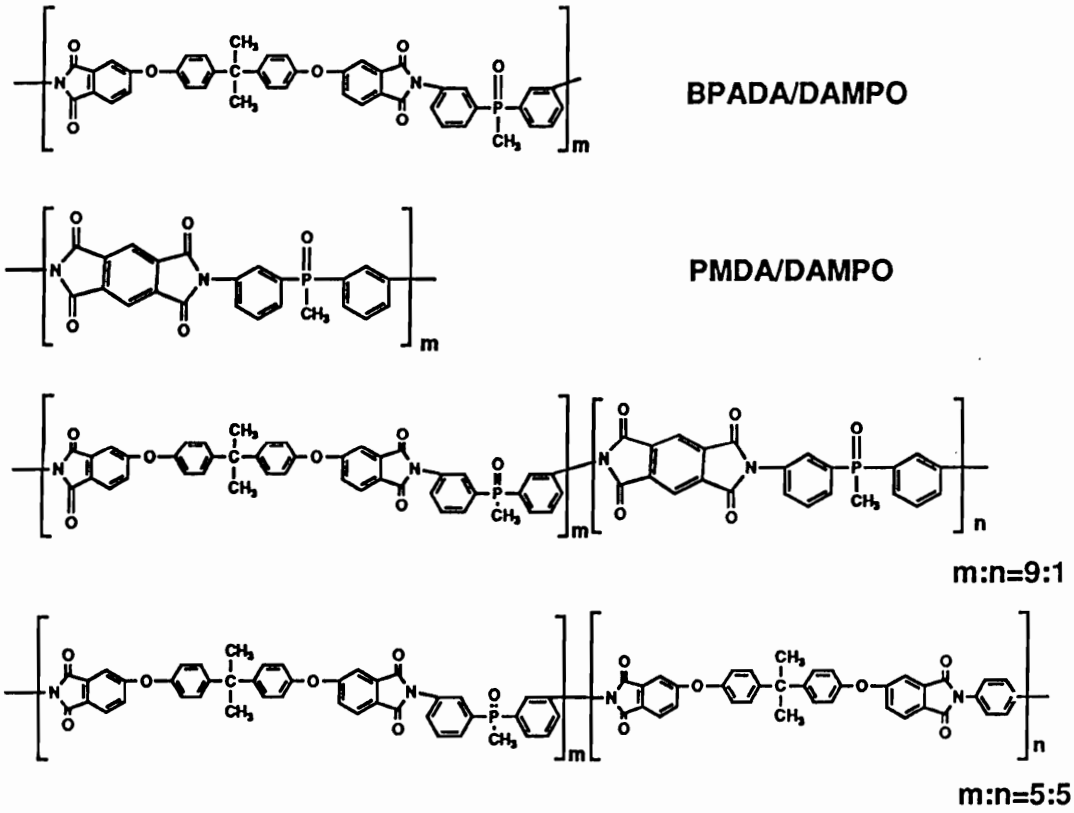


Figure 4.5.4 ^{31}P NMR of BPADA/DAMPO polyimide before and after heating to 800°C in air



Scheme 4.5.2 Phosphorus containing polyimide homo- and co-polymers

4.5.3 Synthesis of DAMPO based copolyimide thermoplastics

Several other thermoplastics copolyimides were synthesized, as listed in Scheme 4.5.2. Interestingly, both homo- and copolyimide thermoplastic materials showed better tensile properties than the polyetherimide (Ultem™) control (Table 4.5.2). The modulus and yield stress of BPADA/DAMPO PA endcapped M_n=30.0 kg/mole polymer increased and the yield strain was almost the same as the Ultem™. When 10 mole% of PMDA was incorporated into the BPADA/DAMPO system, the tensile modulus increased to more than 670±50 ksi. Thus may be due to enhanced intermolecular forces as a result of the presence of a polar phosphine oxide group in the imide backbone.

The glass transition temperature (T_g) increased to 223°C when 10 mole% PMDA was incorporated into the BPADA/DAMPO system (Table 4.5.3) T_g value also slightly increased by incorporating 50% *p*-PDA into the BPADA/DAMPO system. The resulting copolyimides had good thermo-oxidative stability as judged by 5% weight loss > 505°C. However, incorporation of *p*-PDA decreased the char yield as expected, since fewer phosphine oxide groups were present in the copolyimide backbone. All these copolymers were soluble in NMP, DMAc and $CHCl_3$ and no melting endothermic peaks were determined by DSC. In other words, incorporating DAMPO into BPADA/*p*-PDA systems greatly depressed the crystallinity of this material, as reported in Section 4.2.2.

The *p*-PDA modified BPADA/DAMPO copolymer system allows for greater char to form at high temperatures. It may also improve the cost effectiveness of the material. Another practical way to achieve the same

Table 4.5.2. Tensile properties of BPADA/DAMPO based polyimides.

System	Modulus (kpsi)	Yield stress (kpsi)	Yield strain (%)
M_n=30.0 kg/mole PA endcapped	610±60	20±2	7.1±0.3
M_n=30.0 kg/mole, 10 % PMDA PA endcapped	670±50	20±1	6.6±0.5
Ultem™	530±40	17±1	6.9±0.1

Table 4.5.3. Thermal analysis characterization of BPADA/DAMPO-based copolyimides.

System	η (dL/g)[a]	Tg (°C)[b]	TGA 5% wt. loss (°C)[c]	TGA 750°C char yield in air (%)
control	0.47	215	519	58
10 mole% PMDA	0.52	223	507	58
50 mole% *p*-PDA	0.67	220	505	45

a: Run in NMP at 25°C

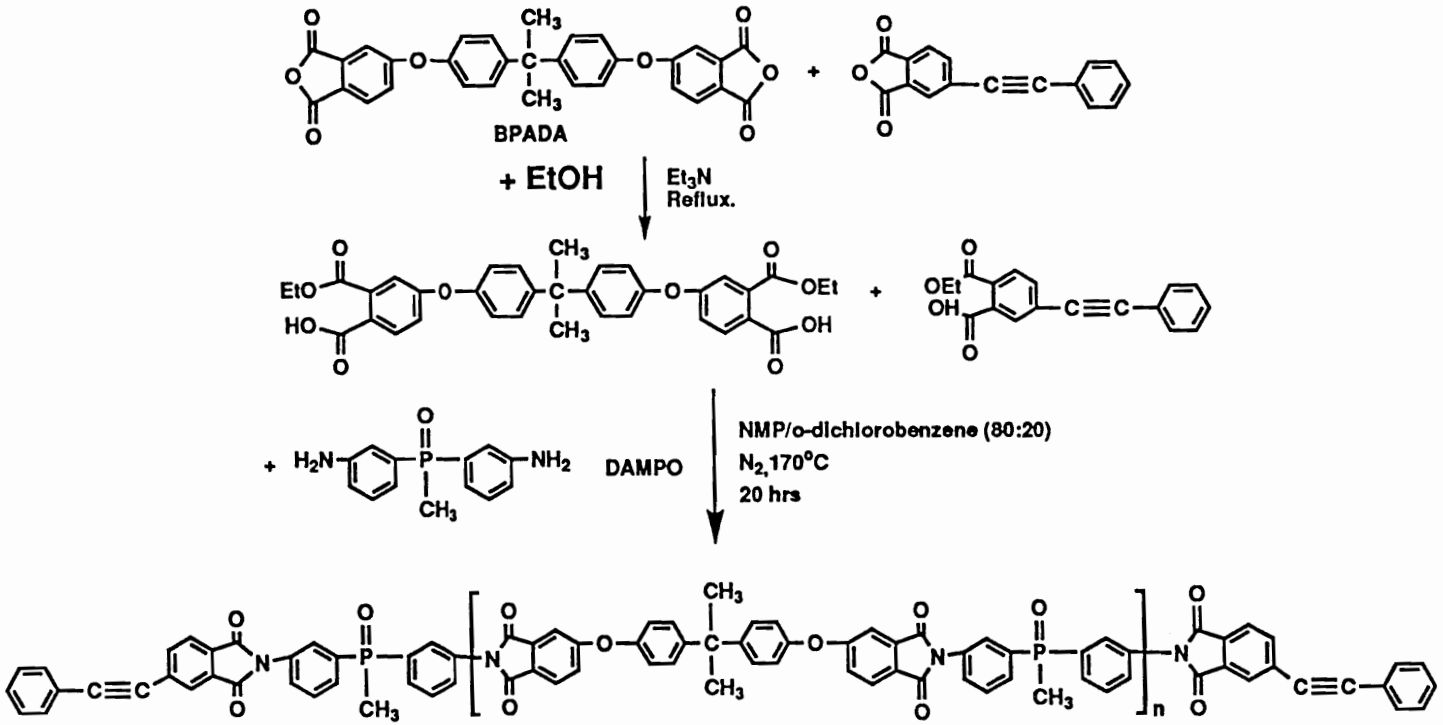
b: Heating rate of 10°C/minute in nitrogen

c: Measured in air at 10°C/minute

results would be to blend polyetherimides (PEI) with BPADA/DAMPO polyimides (M_n=30.0 kg/mole). To do so, transparent films were cast from chloroform solution at 1:1 wt. ratio of these two polyimides. Since both imides have essentially the same T_g values, it is impossible to define miscibility of these two imide by DSC. However, the refractive index value of the blend (1.655) is the average of the two imides homopolymers (polyetherimide: 1.658, BPADA/DAMPO: 1.652). This suggests that the two imides are miscible, even though the differences are rather small. We anticipate that char yields at high temperature can be controlled by optimizing the composition of the blends, which may provide ways to improve the char yield/fire resistance relationship, as well as reduce costs.

4.5.4 Synthesis of DAMPO-based imide oligomer thermoset precursors

Reactive imide oligomers were prepared utilizing 4-phenylethynyl phthalic anhydride (4-PEPA) as an endcapper (Scheme 4.5.3). The BPADA/DAMPO 4-PEPA endcapped imide oligomers with M_n values of 2.0 to 10.0 kg/mole were synthesized and MW control was achieved, as shown in Table 4.5.4. Intrinsic viscosity measurements indicated anticipated results and M_n values were also estimated from endgroup analysis via quantitative ^{13}C NMR spectroscopy (Figure 4.5.5) by ratioing the integrals of the carbons in the backbone ($-CH_3$, δ=30 ppm) to the endgroup -C≡C- (δ=88 and 94 ppm). The experimental molecular weights obtained from ^{13}C NMR analysis correlated appropriately with the theoretical molecular weights. A soluble all-DAMPO based imide oligomer was also analyzed by universal calibration GPC (an



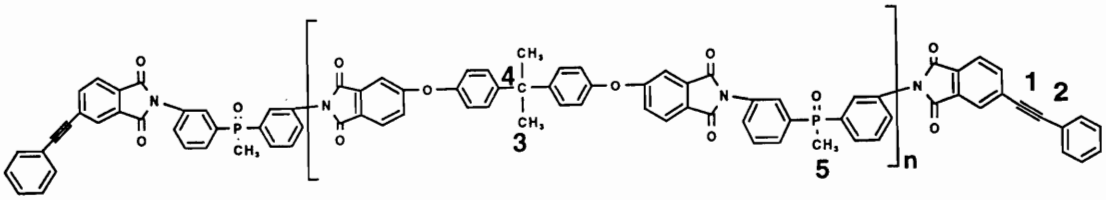
Scheme 4.5.3 Synthesis of BPADA/DAMPO 4-PEPA capped imide oligomers

Table 4.5.4. Molecular weight characterizations of BPADA/DAMPO 4-PEPA endcapped imide oligomers.

Target M_n (kg/mole)	[η] (dlg^{-1}, NMP 25°C)	Mn by ^{13}C NMR (kg/mole)[a]	Mn by GPC[b] (kg/mole); M_w/M_n
2.0	0.08	2.1	1.8; 1.4
3.0	0.14	3.4	3.3; 1.5
5.0	0.19	5.7	4.9; 1.8
10.0	0.28	12.0	10.0; 1.9

a: Run in $CDCl_3$

b: Based on universal calibration



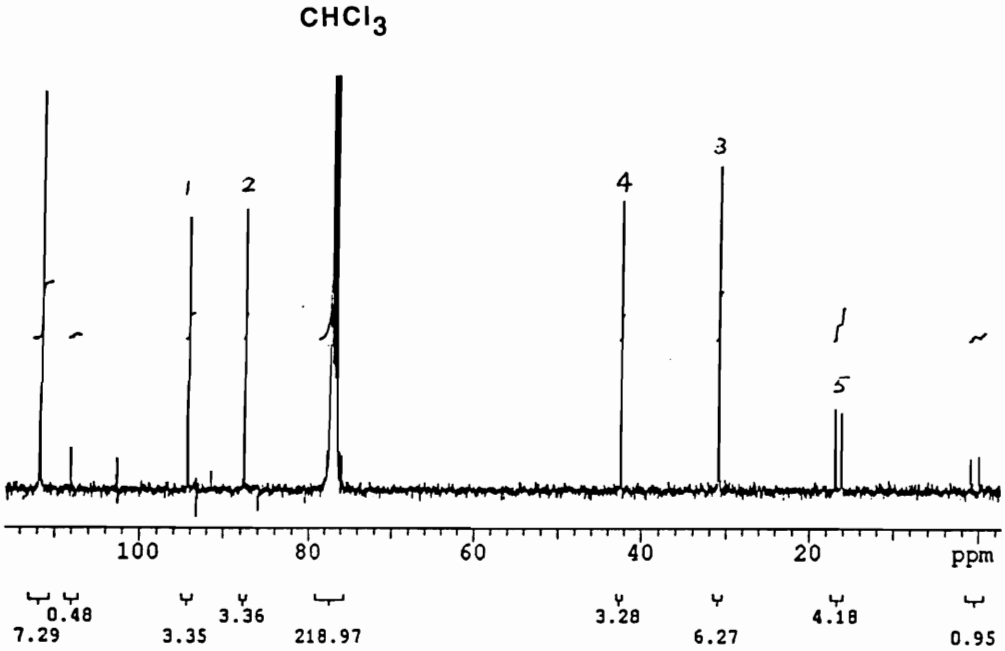


Figure 4.5.5. Quantitative ^{13}C NMR (in $CDCl_3$) spectrum of M_n=2.0 kg/mole BPADA/DAMPO 4-PEPA endcapped imide oligomers.

example of which is shown in Figure 4.5.6), using a viscosity detector [254], and the results also satisfactorily matched theoretical values.

A typical DSC thermogram of a reactive endcapped oligomer is shown in Figure 4.5.7. The glass transition temperature at 10°C/minute was determined to be 196°C and no melting endothermic peaks were observed. The cure exotherm temperature was noted at around 400°C. This relatively high cure exotherm temperature indicates a wide curing window for these DAMPO-based polyimides, and therefore may allow them to be fabricated by resin infusion or resin transfer molding.

Glass transition temperatures of these materials were a function of oligomer molecular weight before curing, and ranged from 175 to 206°C (Figure 4.5.8). All imide oligomers were cured at 380°C for 60 minutes and yielded tough, but somewhat, dark films. The cured materials displayed T_g values from 227°C to 262°C and depended on the M_n of the oligomer precursor. Thus the 2K oligomers experienced an 85°C increase in T_g after curing. All cured oligomers displayed excellent thermooxidative stability as judged by dynamic TGA at 10°C/minute (5% weight loss ~500°C in air). In addition, the cured samples displayed high char yield (45-66%) at 750°C in air, suggesting that they are candidates for fire resistant matrix materials (Table 4.5.5).

A BPADA/DAMPO:*p*-PDA(1:1) 4-PEPA endcapped, M_n=3.0 kg/mole copolyimide oligomer was synthesized by the same polymerization route. The characterization of this oligomer is also listed in Table 4.5.5. The glass transition temperatures of this copolyimide oligomer before and after cure are

higher than those of the same molecular weight homopolymer oligomer. However, the char yield at 750°C was lower.

The gel fraction of the cured samples was measured for films cured at 380°C for 60 minutes by continuous extraction with chloroform for 4 days. After drying for 3 days at 120°C and for 1 day at 180°C under vacuum, high gel fractions in chloroform were determined (84 to 99%, Table 4.5.5).

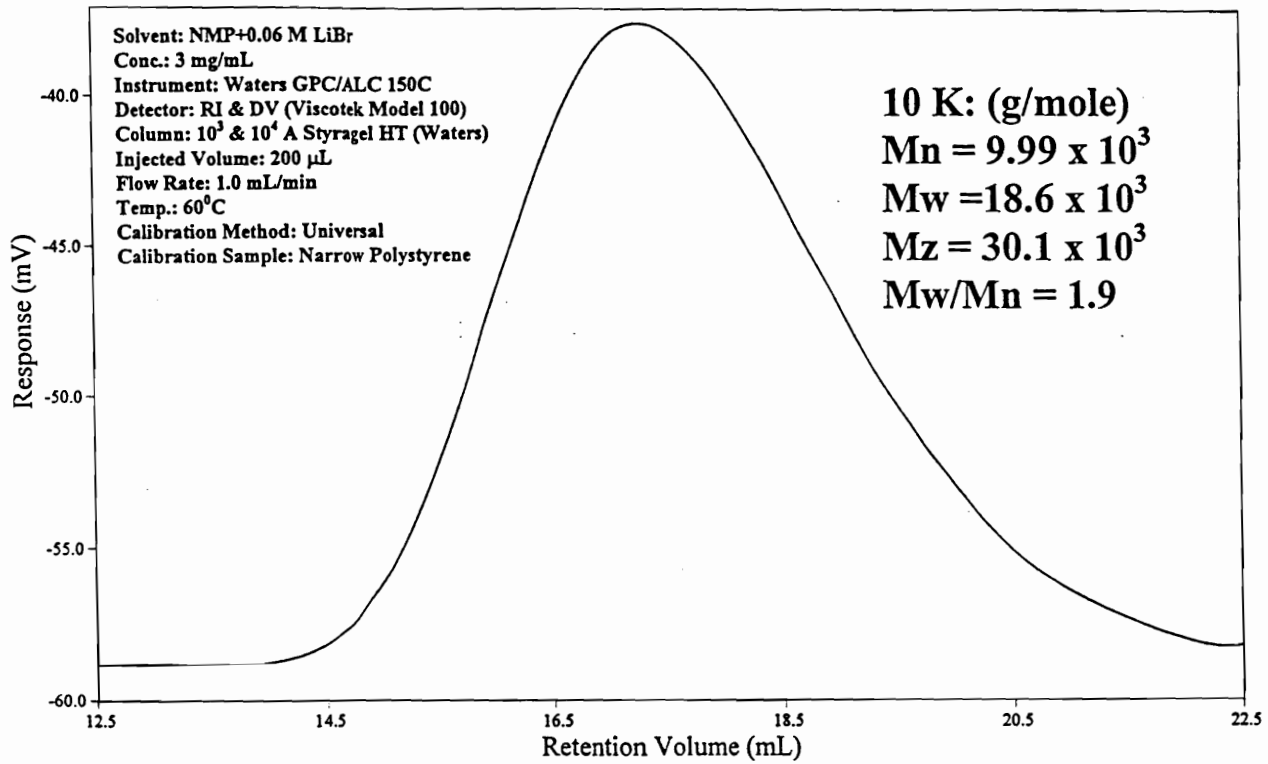


Figure 4.5.6. GPC chromatogram of M_n=3.0 kg/mole BPADA/DAMPO 4-PEPA endcapped imide oligomers.

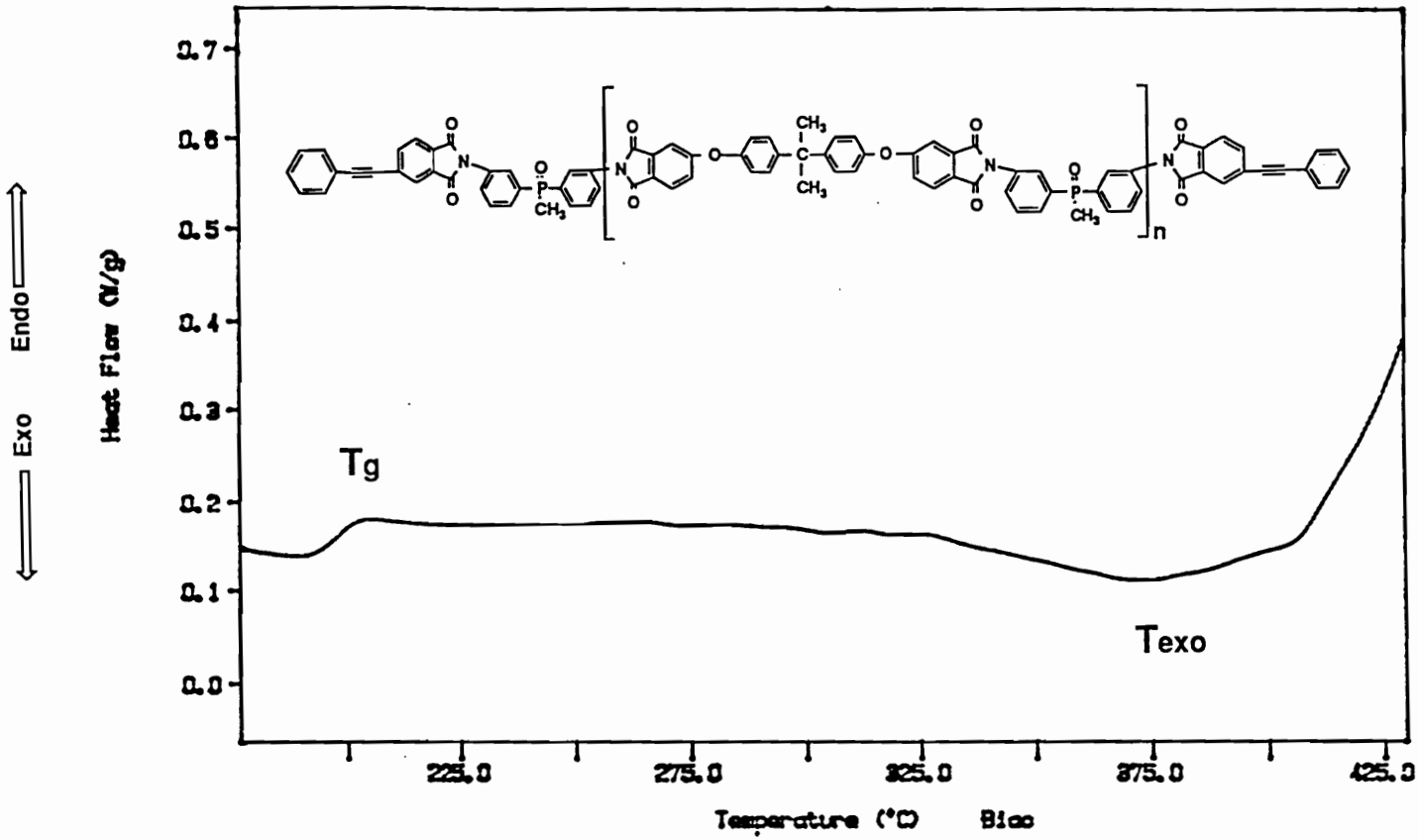


Figure 4.5.7 DSC thermogram of 5K BPADA/DAMPO 4-PEPA capped imide oligomers

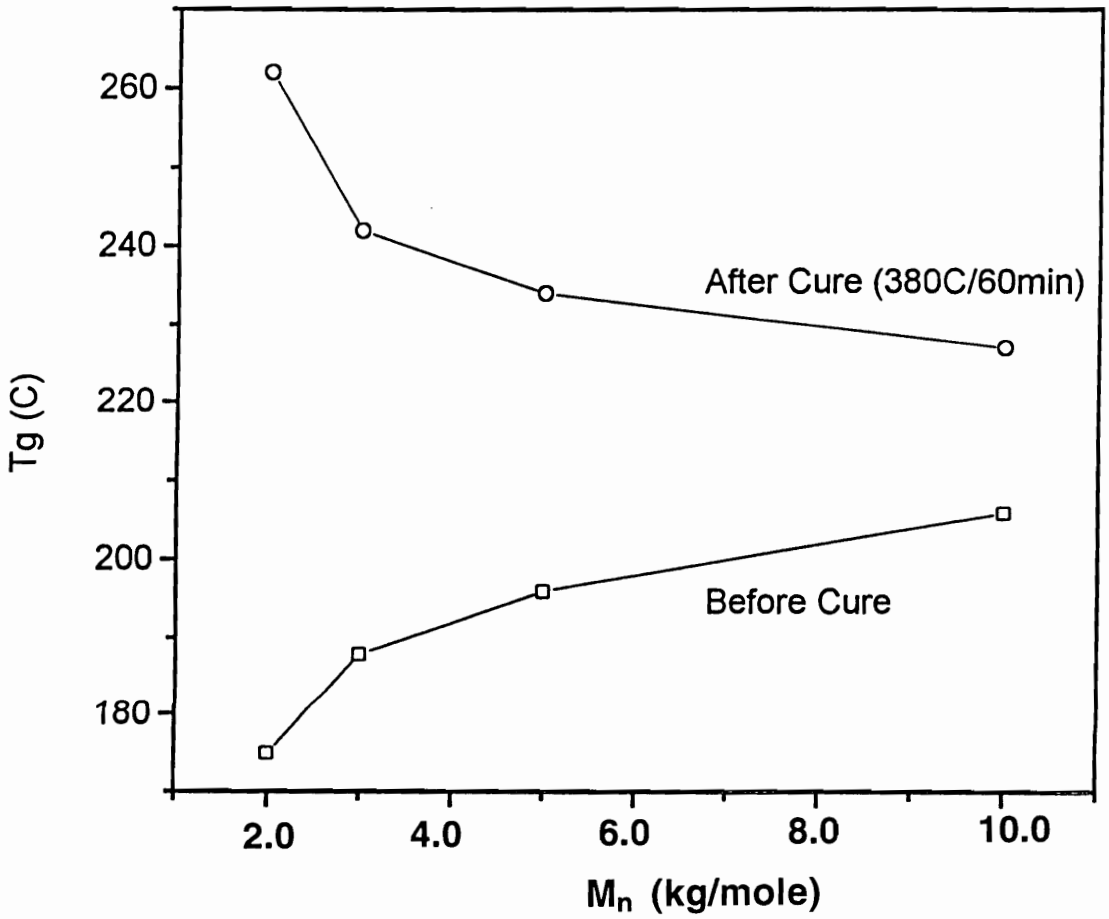


Figure 4.5.8 Influence of molecular weight on the glass transition temperatures of BPADA/DAMPO 4-PEPA endcapped imide oligomers

Table 4.5.5. Characterization of BPADA/DAMPO 4-PEPA endcapped imide oligomers.

Target M_n (kg/mole)	Tg before cure (°C)[a]	Tg after cure (°C)[a]	5% wt. loss (°C)[b]	750°C char yield (%)[b]	Gel fraction (%)[c]
2.0	175	262	510	57	99
3.0	188	242	513	66	96
5.0	196	234	516	53	94
10.0	206	227	478	45	84
3.0 with 50 mole% p-PDA	203	252	508	27	97

a: Heating rate of 10°C/minute in nitrogen

b: Cured samples measured in air at 10°C/minute

c: Samples were extracted for 5 days and then dried for 5 days at 120°C under vacuum

Chapter 5. CONCLUSIONS

The major goal of this dissertation research was to synthesize and characterize phenylethynyl endcapped polyetherimide oligomers. Detailed synthetic procedures were developed and structure-property relationships of 4-phenylethynyl phthalimide terminated oligomers were investigated. The synthesis of new diaryl methyl phosphine oxide containing polyetherimides was also explored and basic physical behavior characteristics were established.

Non-reactive thermoplastic phthalimide-terminated controlled molecular weight polyetherimides were successfully synthesized by an ester-acid route. This solution synthetic method was suitable for the amorphous systems, and high molecular weight polyetherimides were obtained with similar thermal characterization results as the control systems. Substitution of *meta*-phenylene diamine with the *para* isomer increased the glass transition temperature value to 231°C and produced a system that was semi-crystalline. Incorporation of rigid PMDA moieties into the polyetherimide system further increased glass transition temperature and also resulted in a high melting (~300°C), semi-crystalline material. They did not, however, recrystallize on the second heating in DSC. A statistical copolyimide based on *p*-:*m*-(7:3)PDA, M_n=15.0 kg/mole polyetherimide was found to have a T_g of 225°C and was essentially amorphous. This system was suitable for further modification by the introduction of a reactive 4-phenylethynyl endcapper.

4-phenylethynyl phthalic anhydride endcapped, fully imidized polyetherimide oligomers with M_n=2.0 to 10.0 kg/mole were successfully synthesized. Good molecular weight control was obtained by using a

calculated excess of the diamine together with a reactive endcapper. This was verified by intrinsic viscosity, quantitative ^{13}C NMR and GPC equipped with a viscosity detector and hydrodynamic volume calibration. Thermal curing of the oligomers produced insoluble, solvent resistant and ductile films with relatively high T_g values, which were related to network density. The cured films exhibited excellent thermooxidative stability as judged by TGA measurements. The wide processing window (~150°C between oligomer T_g and cure temperature) afforded by the phenylethynyl endcaps was very important. For example, a Mn=3.0 g/mole, BPADA/*p*-:*m*-(7:3)PDA 4-PEPA endcapped oligomer displayed a cured T_g as high as 267°C (an increase of 74°C). Such materials are potentially suitable for many high performance applications.

Several oligomers were successfully scaled up in a 10-gallon reactor at the G.E. CR&D Center, utilizing a simplified, single-solvent synthetic route. The resulting products, however, displayed characteristics quite similar to those obtained via laboratory reactions. Thus, the materials were prepared in quantities which allowed engineering colleagues, as well as government and industrial scientists, to evaluate potential adhesive and composite matrix applications.

Poly(amic) acid systems were also successfully synthesized in both lab-scale quantities and in 10-gallon reactor amounts. Molecular weight control was achieved by controlling stoichiometry in favor of the diamine and using phthalic anhydride as an endcapper. Utilizing the salt form of these poly(amic) acids as binders for carbon fiber/PEEK composites showed that improvements in transverse flexural strength could be achieved.

Thermally curing the phenylethynyl endcapped oligomers afforded flexible, yet ductile films. The excellent solvent resistance exhibited by these cured oligomers was a result of very high gel fractions, which was determined via Soxhlet extraction experiments with chloroform. The cured oligomers possessed tensile properties similar to those of the commercial thermoplastic polyetherimide control, which may be due to a large amount of linear chain extensions before reaching the gel point.

Single lap shear adhesive tests of these reactive oligomers to titanium alloys were conducted and good adhesive strength values were achieved. The "green" or uncured strength of the adhesive matrix was improved by blending the thermoset precursor with a PEI thermoplastic. Importantly, this was achieved without significantly diminishing solvent resistance. Single T_g behavior was also observed.

The phenylethynyl curing reaction was monitored by FTIR and dynamic DSC, both of which provided activation energies of cure (E_a) for a series of oligomers with different backbones and molecular weights. The curing process appears to be diffusion controlled, based on these E_a values. This research further verified that large processing window and easy thermal curing of the oligomers were possible, which makes them good candidates for composite matrix systems.

Diphenyl methyl phosphine oxide diamine based polyimide thermoplastics and thermosets were also synthesized via an ester-acid route, which permitted good molecular weight and endgroup control. Both thermoplastic and thermoset systems displayed high char yield and good thermooxidative stability. The high molecular weight thermoplastic

homopolyimides and copolyimides both had good tensile strength. The cured thermoset oligomers displayed excellent solvent resistance, which suggest that these networks could be utilized in fire resistant matrix material systems.

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VITA

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After two years of research on epoxy molding composites at the Institute of Material Science at Fudan University, he continued his studies by joining the Chemistry graduate program at East Tennessee State University in September of 1991. His M. S. research focused on the synthesis and characterization of model compounds for nuclease enzymes, under the guidance of Dr. I. O. Kady. After receiving his Master of Science degree in August of 1993, he was accepted at Virginia Polytechnic Institute and State University in order to work towards his goal of obtaining a Ph.D. In the summer of 1995, he worked at the General Electric Corporate Research and Development Center, Schenectady, NY. His graduate research efforts at Virginia Tech under the guidance of Dr. James E. McGrath focused on developing phenyl ethynyl based matrix resins and on phosphorus containing polyimides.

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