

Synthesis and Characterization of Soluble, High Temperature  
Aromatic Polyimides

by

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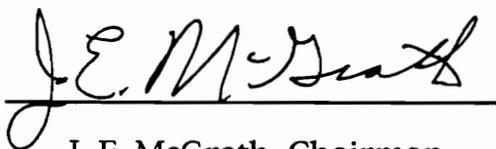
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in

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APPROVED:



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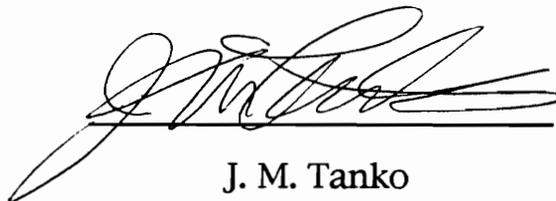
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Aromatic Polyimides

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(ABSTRACT)

High molecular weight, soluble polyimides were synthesized by a non-traditional synthetic route utilizing solution imidization techniques and diester-diacid derivatives of various commercially available dianhydrides. "One pot" syntheses were conducted using a solvent system of N-methylpyrrolidinone and *o*-dichlorobenzene at temperatures of 170°C to 180°C and times of 24 hours or less. The resulting polyimides were soluble in amide solvents at concentrations of 15 to 20 percent (w/v) at 25°C, were fully cyclodehydrated as determined by non-aqueous potentiometric titrations, possessed molecular weight distributions very close to the theoretical value of 2.0 and displayed glass transition temperatures consistent with accepted values for the same materials synthesized via conventional methods. Model studies indicated that polymerization proceeds via intermediate conversion of the ester-acid functional groups to anhydride groups.

This method was also successfully employed in the synthesis of controlled molecular weight ethynyl-functionalized thermosetting

imides. High  $T_g$ 's, low end group concentrations and the relatively low cure temperature of the ethynyl end group restricted sample fabrication to thin, solution-cast films; nevertheless, several of these systems were evaluated for high temperature stability and were identified as potential candidates for 700°F (371°C) applications.

Several novel thermosetting polyimides based on 1,4-bis-(phenylmaleic anhydride)benzene were also prepared. The uncured materials were soluble in methylene chloride, chloroform and THF, as well as amide solvents. Crosslinking occurred at temperatures of 350°C and above, and the cured polyimides displayed  $T_g$ 's 20°C to 25°C greater than their linear precursors.

In addition, a novel polyimide synthesis utilizing diamine dihydrochlorides as substitutes for unstable diamines was also investigated, and a series of novel polyimides based on diaminoresorcinol and commercial dianhydrides was synthesized. Diaminoresorcinol dihydrochloride and dianhydride were heated in an NMP/dichlorobenzene mixture; at sufficiently high temperatures the insoluble dihydrochloride dissociates, liberating hydrogen chloride gas and the soluble free diamine, which rapidly dissolves and reacts with dianhydride before decomposition occurs. The poly(hydroxy-imide)s possess  $T_g$ 's in excess of 250°C, are soluble in amide solvents and, as might be expected, are extremely hygroscopic.

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## I. INTRODUCTION

Aromatic polyimides have been firmly established as technologically significant high temperature, high performance thermoplastic and thermosetting polymers. Applications include films and protective coatings, high temperature adhesives, interlayer dielectrics in computer chips, and wire insulation and composite structures in advanced combat aircraft.

The first successful polyimide synthesis was reported in the mid 1950's and involved the melt polymerization of aromatic diester-diacid monomers and aliphatic diamines. However, these were not true "high temperature" materials due to the high content of aliphatic segments in the polymer backbone, and the desire for polymers possessing both higher glass transition temperatures and improved thermooxidative stability led to the development of wholly aromatic polyimides.

The early aromatic polyimides indeed displayed both increased glass transition temperatures and thermooxidative stability, but were insoluble and infusible, precluding synthesis via conventional melt or solution polymerizations. Two major obstacles to the successful synthesis of high molecular weight, processable aromatic polyimides were a lack of knowledge of structure-property relationships in polyimides and the limited number of commercially available dianhydrides and diamines. As a result, most early

aromatic polyimides were correctly described as amorphous, insoluble, infusible and intractable.

Initially the desirable properties of aromatic polyimides could not be exploited due to the inability to synthesize these materials, but this problem was soon eliminated with development of the now well-known "two-step" synthesis. In this procedure, dianhydrides and diamines polymerize in solution to yield a soluble intermediate poly(amic acid), which is subsequently converted to polyimide with loss of water and solvent via a bulk thermal cyclodehydration process. High molecular weight aromatic polyimides were prepared, but insolubility and infusibility limited applications to films and coatings.

In addition, the success of this process depends upon a variety of factors, including monomer purity, rigorous exclusion of moisture from the reaction system, choice of solvents, order of monomer addition, reaction temperature and monomer concentration.

Particularly over the past two decades, a variety of processable aromatic polyimides with a wide range of properties and potential applications has become available. In addition to soluble polyimides, liquid crystalline polyimides and semicrystalline polyimides are now known. This is largely due to the development of new monomers, which has contributed to the knowledge of polyimide structure-property relationships; this knowledge, in turn, aids in the design of additional monomers for polyimides with specific, desired properties.

Equally important are such advances as molecular weight and end group control which facilitate synthesis and processing, "PMR" bulk polymerizations for the synthesis of high  $T_g$  end-functionalized thermosetting polyimides for structural applications, and the development of solution imidization techniques for soluble polyimides.

Despite these advances, the traditional view of polyimides persists, and perusal of the literature reveals that the "conventional" two-step bulk thermal imidization process, now nearly thirty years old, remains the preferred synthetic route for high molecular weight aromatic polyimides regardless of solubility. Currently, hydrolytically stable diester-diacid dianhydride derivatives are routinely utilized only in PMR polymerizations, and commercial use of diamine derivatives in polyimide synthesis is limited to LEPSIG's use of unstable diisocyanates.

The research presented in this dissertation is focused on the synthesis and characterization of soluble, high  $T_g$ , high molecular weight aromatic polyimides and controlled molecular weight, ethynyl-functionalized thermosetting polyimides utilizing diester-diacid monomers and solution imidization techniques. This polymerization is tolerant of "wet" solvents and glassware and was shown to proceed via intermediate anhydride formation. Reaction conditions for reproducible polyimide synthesis were established, and successful molecular weight control and molecular weight distributions very closely approaching the theoretical value of 2.0

were demonstrated. A number of soluble polyimides were prepared utilizing a variety of monomer combinations containing various flexibilizing groups, and two systems were identified as potential candidates for 700°F (371°C) applications.

In addition, a novel polyimide synthesis based on the direct use of diamine dihydrochlorides as monomers and a series of novel polyimides based on diaminoresorcinol dihydrochloride are reported. Finally, the synthesis and properties of a series of novel, high  $T_g$  thermosetting polyimides containing backbone phenyl maleimide structures are reported.

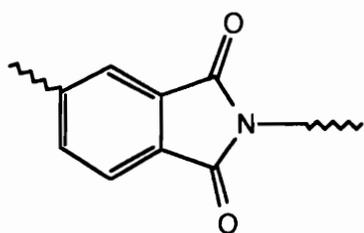
The literature review that follows, Chapter Two, contains discussions of polyimide applications, properties, structural features which promote solubility in organic solvents, various synthetic routes and commonly employed reactive end groups employed in thermosetting polyimides. Synthetic and analytical experimental methods employed in this research are discussed in Chapter Three. Experimental results are discussed in Chapter Four, followed by conclusions (Chapter Five), suggested future studies (Chapter Six) and references.

## II. LITERATURE REVIEW

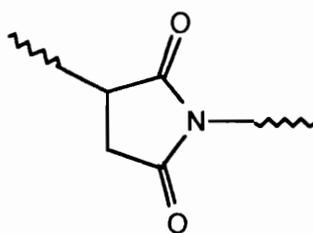
### 2.1 Introduction

Polyimides are polymers containing in-chain heterocyclic imide functionalities; these are most commonly five membered isoindole-1,3-dione (phthalimide) structures but polymers containing succinimide, glutarimide and maleimide structures are also classified as polyimides. Various imide heterocycles are illustrated in Figure 2.1.1 Polyimides may have been synthesized as early as 1908 from aminophthalic acid derivatives [1]. However, the first successful synthesis is generally recognized as that reported by Edwards and Robinson in the mid 1950's, in which polyimides were synthesized via melt reactions involving tetracarboxylic acids or their diester derivatives and various aliphatic diamines [2,3]. These were not true "high temperature" materials, but it was recognized that fully aromatic polyimides were potential candidates for high temperature applications [4].

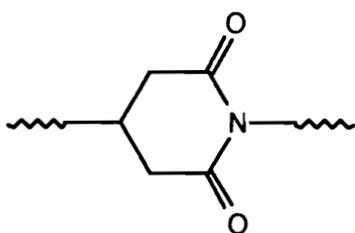
The insolubility and infusibility of early aromatic polyimides precluded their successful synthesis via conventional solution or melt polymerization techniques, however, continued interest in polyimides and attempts to refine synthetic techniques led to the development of the "two-step" synthesis in the mid 1960's [5-13]. This procedure was a major advance, permitting for the first time the successful synthesis of high molecular weight, fully cyclodehydrated aromatic polyimides; three decades later, this technique remains the



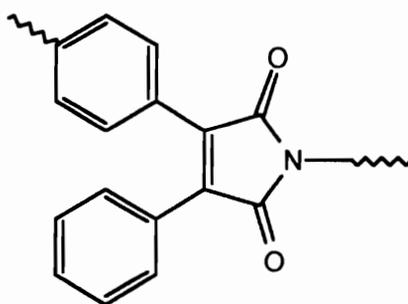
Phthalimide



Succinimide



Glutarimide



Phenyl maleimide

Figure 2.1.1. Imide Heterocycles

method of choice for synthesizing high molecular weight aromatic polyimides.

Although the "two-step" route allowed the successful synthesis of aromatic polyimides, the insolubility and infusibility of these materials still posed problems in their fabrication into useful articles; consequently, early applications were largely confined to films and coatings.

Many attempts to improve flow characteristics and/or solubility to facilitate processing were met with limited success; improvements in these properties were realized at the expense of high glass transition temperatures and thermal stability [14,19]. Even so, these efforts were significant in that they were the beginning of a continuously evolving understanding of structure-property relationships in aromatic polyimides. This knowledge has led to the design of new monomers [20-25], copolymers [26-30] and blends [31,32] which have served to offset the trade-off between processability and high temperature, high performance characteristics.

Other advances in this regard include the identification of side reactions during the imidization process, such as chain extension involving reactive end groups and high temperature crosslinking of substituents or linking groups [33-35] in the polymer backbone; these problems can be minimized by molecular weight and end group control and/or cyclodehydration under an inert atmosphere or in vacuo. In addition, the development of soluble polyimides has led

to the development of solution imidization techniques which permit the synthesis of high or controlled molecular weight, fully cyclodehydrated polyimides under relatively mild conditions [36-40].

The problems of fabricating polyimides into thick components for structural applications has been circumvented by the use of controlled molecular weight, functionalized thermosetting imide oligomers [41-43]; prior to crosslinking, the low molecular weight oligomers possess better flow properties than their high molecular weight analogs, and after crosslinking, higher glass transition temperatures and superior solvent resistance.

Furthermore, a number of "melt processable" semicrystalline polyimides have been reported [44-46].

As a result of improvements in polyimide synthesis and design, these materials are now employed as adhesives, foams, laminates, molded components, and composite matrices, in addition to films and coatings. Polyimides are important materials in the chemical, electrical, electronic, automotive, and aerospace industries, and are found in such applications as gas separation membranes, wire insulation, interlayer dielectrics in computer chips, structural components and wingskins on advanced combat aircraft.

Early aromatic polyimides were described as amorphous, insoluble, infusible and intractable materials, with high glass transition temperatures and excellent thermal stability [47]. This traditional view persists and is still applicable to a large number of aromatic polyimides, but it is no longer all-encompassing.

Refinements in synthetic techniques and the design of new monomers, copolymers and blends have made possible a nearly infinite variety of polyimides or polyimide-based materials which do not conform to the traditional description.

## 2.2 Polyimide Properties

Aromatic polyimides are renowned for their high glass transition temperatures, excellent thermooxidative stability and mechanical properties. These desirable properties are attributed to the strength of the primary (aromatic) "backbone" bonds and the rigidity which the imide heterocycle imparts to the polymer. A relatively small number of organic polymers approaches their level of performance, and these are mostly other aromatic poly(heterocycle)s: polybenzimidazoles, polybenzothiazoles, polybenzoxazoles and poly(phenylquinoxaline)s.

If not carefully designed, aromatic polyimides are inherently insoluble and infusible. Although these properties may be desirable, indeed critical in many applications, they present problems in the synthesis of polyimides and render them, for practical purposes, impossible to process into useful forms.

Attempts to mold the soluble, fusible poly(amic acid) precursor, followed by cyclodehydration, have been unsuccessful due to the hydrolytic instability of poly(amic acid)s and the creation of voids in the finished product arising from the release of residual solvent and condensation volatiles at high temperatures.

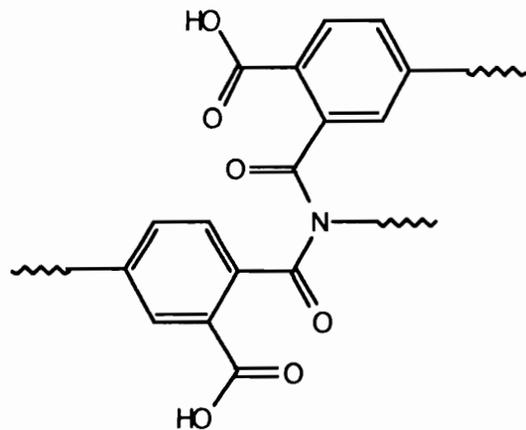
Therefore, a major goal of much of the current polyimide research is the synthesis of soluble, processable, fully-cyclized polyimides with minimal sacrifice in glass transition temperatures, thermooxidative stability and mechanical properties.

## 2.2.1 Insolubility/Infusibility

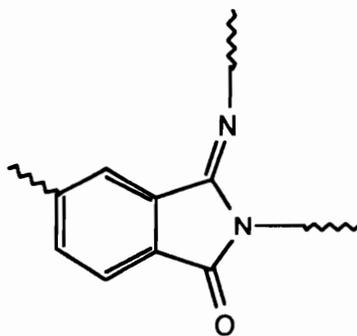
### 2.2.1.1 Crosslinking

Crosslinking or network formation has been proposed as a possible explanation for the insolubility typical of many polyimides [48-50]. In theory, the crosslinks are formed via intermolecular as opposed to intramolecular imide formation, or from intermolecular imine formation arising from the condensation of amine end groups with imide carbonyl groups. These structures are shown in Figure 2.2.1.1.1. Although these reactions could occur in principle, little evidence exists to support this view.

Linear polyimides exist which are known to undergo crosslinking reactions; however, these contain substituents or connecting groups which readily form free radicals at high temperatures. In particular, methyl substituents and methylene links have been implicated in crosslink formation during bulk thermal imidization, but these reactions do not involve the amic acid functionalities or imide heterocycle [34, 35, 51]. Moreover, the existence of soluble polyimides tends to refute crosslinking as a general explanation of polyimide insolubility. Crosslinking as a



Intermolecular Imide Crosslink



Intermolecular Imine Crosslink

Figure 2.2.1.1.1 [48-50]. Proposed Crosslink Structures in Polyimides

potential side reaction during cyclodehydration will be discussed further in Section 2.3.4.

#### 2.2.1.2 Chain rigidity/Orientation

Chain rigidity and orientation have also been used to explain the insolubility of many polyimides. One of the arguments against crosslinking is based on the sulfuric acid solubility of Kapton, or pyromellitic dianhydride-4,4'-oxydianiline polyimide (which is insoluble in organic solvents); the repeat unit is shown in Figure 2.2.1.2.1. It is argued that if the material is soluble, it cannot be crosslinked. Comparison of the weight average molecular weights of the soluble poly(amic acid)s and fully cyclized polyimides dissolved in concentrated sulfuric acid indicated little or no change in molecular weight or dimensions occurred during cyclization, i.e., no branching or crosslinking took place [52, 53, 54]. These results suggest that insolubility is a result of polymer chain rigidity.

In addition, structural anisotropy resulting from orientation has been reported in a number of polyimides, including Kapton [55-58]. Orientation is especially apparent in polyimides derived from combinations of rigid monomers such as pyromellitic dianhydride, biphenyltetracarboxylic dianhydride, benzidine and the phenylene diamines, as shown in Figure 2.2.1.2.2; Numata has reported ordered structures and even crystallinity in several of these systems, all of which are insoluble [59]. These rigid-rod polyimides possess very low coefficients of thermal expansion [60-62].

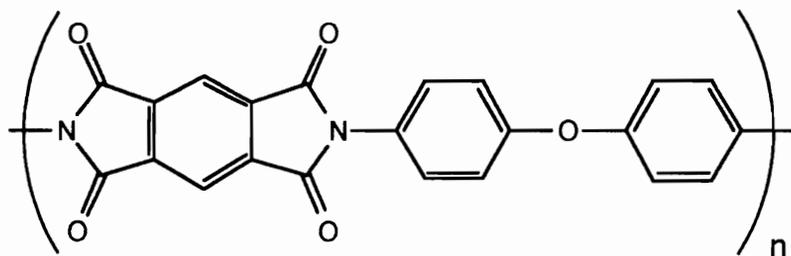
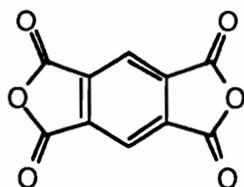
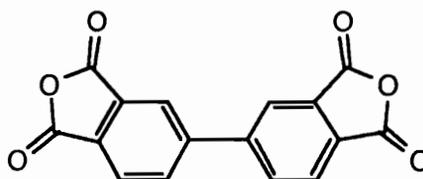


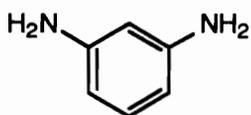
Figure 2.2.1.2.1. Repeat Unit of Kapton



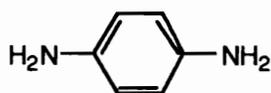
pyromellitic dianhydride



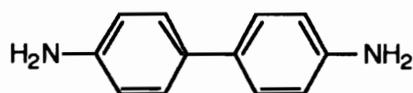
biphenyltetracarboxylic dianhydride



*m*-phenylenediamine



*p*-phenylenediamine



benzidine

Figure 2.2.1.2.2. Monomers for the Synthesis of Rigid-Rod Polyimides

### 2.2.1.3 Charge Transfer Complexes

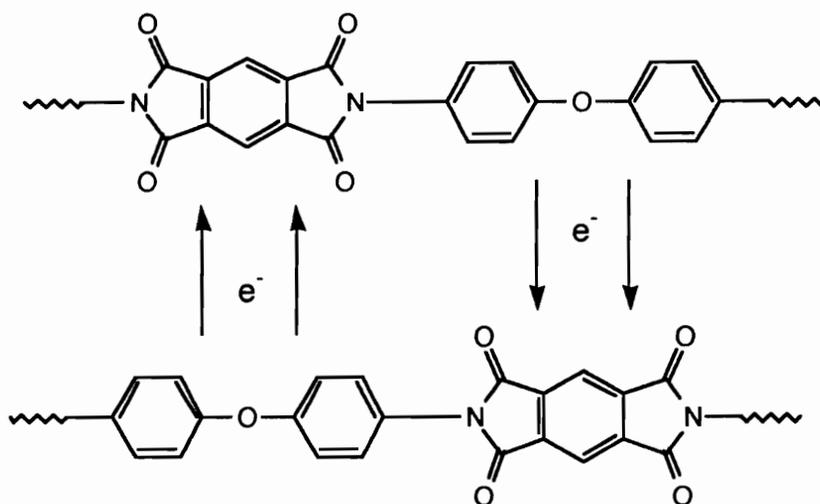
Polyimide insolubility has also been ascribed to the formation of charge transfer complexes [63-65]. Within the polymer backbone alternating regions of high and low electron density exist due to resonance and inductive effects. Alignment of these regions in adjacent polyimide chains gives rise to charge transfer complexes, as depicted in Scheme 2.2.1.3; the electronic interaction (attraction) results in the insolubility and characteristic yellow color of many insoluble polyimides.

## 2.2.2 High T<sub>g</sub> Polyimides With Improved Solubility/ Processability

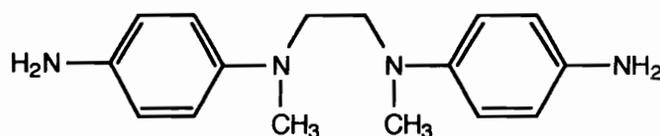
### 2.2.2.1 Flexible Segments

High glass transition temperatures and thermooxidative stability are generally associated with polyimides derived from rigid, para-substituted monomers; unfortunately these materials tend to be insoluble and infusible.

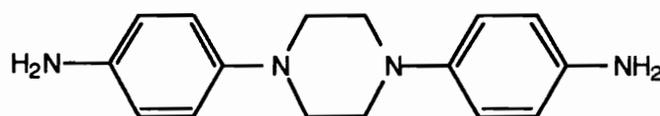
A number of strategies have been successfully employed to incorporate structures which improve polyimide solubility in organic solvents as well as modify other properties, however, these often require a substantial sacrifice in T<sub>g</sub> and thermooxidative stability. For example, one strategy involves the incorporation of flexible segments to reduce chain rigidity. Diamines based on oxyethylene can yield soluble polyimides, but at the expense of thermal properties; the introduction of low T<sub>g</sub>, aliphatic segments severely reduces T<sub>g</sub> and thermooxidative stability relative to fully aromatic



Scheme 2.2.1.3 [64]. Proposed Charge Transfer Complex Formation in Polyimides



2,5-bis-(4-aminophenyl)-2,5-diazahexane



1,4-bis-(4-aminophenyl)-1,4-diazacyclohexane

Figure 2.2.2.1.1 [67]. Diamines Containing Aliphatic Backbone Amine Connecting Groups

systems [66]. Similarly, Feld and coworkers have prepared a series of polyimides from aliphatic diamines containing in-chain amine linkages, and while reasonably high  $T_g$ 's were obtained, a significant loss in thermooxidative stability was observed as determined by TGA [67]. Several diamines containing flexible aliphatic segments are illustrated in Figure 2.2.2.1.1 Thus, introducing aliphatic groups into the polyimide backbone can improve solubility, but it may significantly lower  $T_g$  and will certainly result in substantial losses in thermooxidative stability.

#### 2.2.2.2 Isomeric Substitution/Assymetry

Many of the early aromatic polyimides were synthesized from pyromellitic dianhydride or benzophenonetetracarboxylic dianhydride in combination with *para*-substituted diamines such as 4,4'-diaminodiphenyl ether (4,4'-oxydianiline, ODA), 4,4'-diaminodiphenyl methane (4,4'-methylene dianiline, MDA) or *p*-phenylene diamine (*p*-PDA); these were the most common commercially available monomers for polyimide synthesis. Therefore, the effect of isomeric substitution on polyimide properties was investigated. Bell, Stump and Gagin synthesized diamine derivatives with *o,o'*; *o,m'*; *o,p'*; *m,m'*; and *m,p'* substitution, and compared the properties of the resulting polyimides with those of the polymers derived from *para*-substituted diamines.

Generally, *meta* catenation led to improved solubility, but diamines with *m,p'* or *m,m'* substitution were found to lower  $T_g$ 's

substantially relative to the *para*-substituted diamines; curiously, *o,p'*-diamines afforded the same  $T_g$ 's as *p,p'*-diamines [35]. The *o,o'*-diamines did not afford high molecular weights, however, probably due to steric restrictions. Glass transition temperatures of polyimides from isomerically substituted diamines are listed in Table 2.2.2.2.1. Thus, *meta* catenation and assymerty are structural modifications which can enhance polyimide solubility. The effect of these structural features is the introduction of bends or "kinks" in the polymer backbone which disrupt structural regularity, thereby reducing its rigidity.

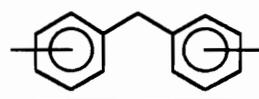
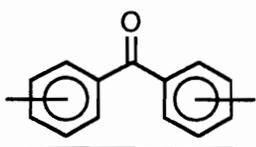
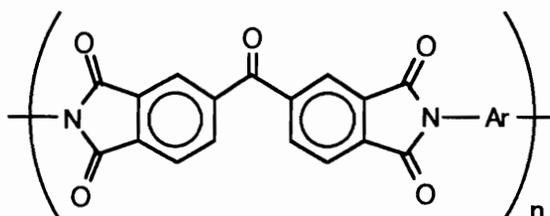
Diaminoindane derivatives, shown in Figure 2.2.2.2.1 represent another example of assymetry; incorporation of the indane structure yields polyimides with  $T_g$ 's in excess of 300°C [68]. The cycloaliphatic link would be expected to result in reduced thermooxidative stability, however.

### 2.2.2.3 Flexible Linkages

Other variations in monomer structure involve the incorporation of flexible connecting groups between aromatic rings, and include such structures as ether, sulfone, carbonyl, alkyl, perfluoro alkyl and phenylphosphine oxide. Again, the purpose of these structures is to provide a kink or bend to lower rigidity in the polymer chain.

Several flexible connecting groups are illustrated in Figure 2.2.2.3.1. Various combinations of monomers containing these

Table 2.2.2.2.1 [35]. Glass Transitions of Polyimides from Isomeric Diamines of Diaminobenzophenone and Methylenedianiline



<u>Ar</u>	<u>T<sub>g</sub> (°C)</u>	<u>Ar</u>	<u>T<sub>g</sub> (°C)</u>
<i>p,p'</i>	295	<i>p,p'</i>	290
<i>o,o'</i>	289	<i>o,p'</i>	289
<i>o,p'</i>	289	<i>o,o'</i>	285
<i>m,p'</i>	283	<i>m,p'</i>	259
<i>m,m'</i>	264	<i>o,m'</i>	258
<i>o,m'</i>	259	<i>m,m'</i>	234

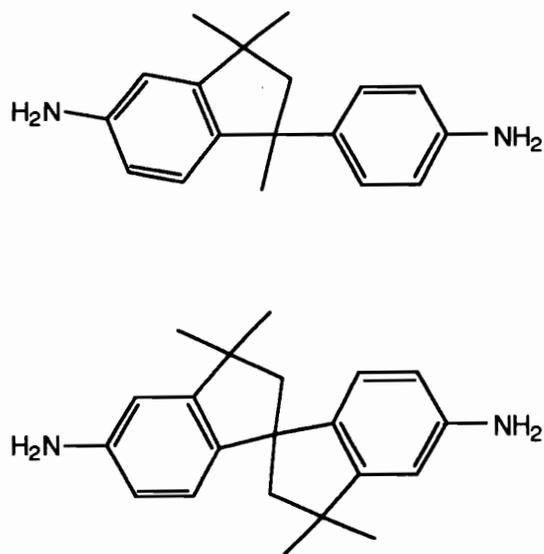


Figure 2.2.2.2.1. Diaminoindane Derivatives

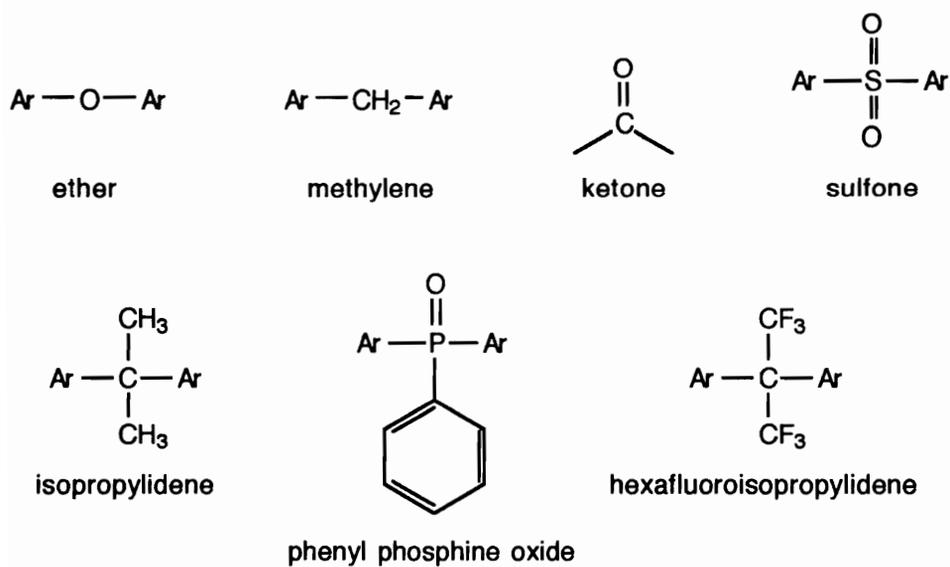


Figure 2.2.2.3.1. Flexible Connecting Groups

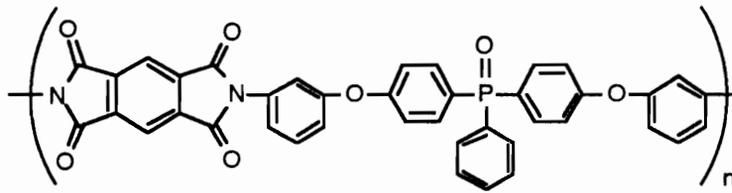
connecting groups readily afford soluble polyimides with  $T_g$ 's in excess of 250°C; repeat units and the respective  $T_g$ 's of several are shown in Figure 2.2.2.3.2.

It should be emphasized here, however, that the incorporation of these structures by no means insures that a soluble, amorphous polyimide will be obtained.

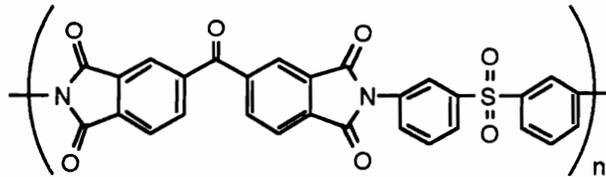
Indeed, LARC-TPI, a well-known semicrystalline polyimide, contains both ether and carbonyl connecting groups [44, 69-71]; BTDA-1,3-bis-(4-aminophenoxy)-2,2-dimethylpropane polyimide, also semicrystalline, contains ether, ketone and isopropylidene linkages [46]. Recently, the polyimide synthesized from BTDA and 3,3'-diaminodiphenyl sulfone has been shown to crystallize from dilute solution over a period of several weeks [73]. Repeat units are illustrated in Figure 2.2.2.3.3. In these examples the flexible links fail to reduce rigidity to the extent that an amorphous material is obtained; rather, they permit sufficient structural regularity and segmental mobility such that crystallization is possible.

#### 2.2.2.4 Non-Coplanarity

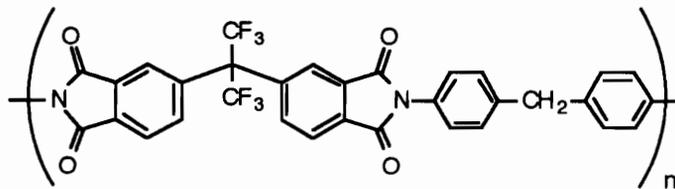
Just as the presence of flexible linkages does not insure an amorphous, soluble polyimide, the absence of flexible links in the polyimide backbone does not guarantee insolubility; the polyimide based on 3,3',4,4'-biphenyltetracarboxylic dianhydride and 2,2'-trifluoromethylbenzidine (Figure 2.2.2.4.1) contains no flexible backbone bonds yet displays good solubility in *m*-cresol [74-77].



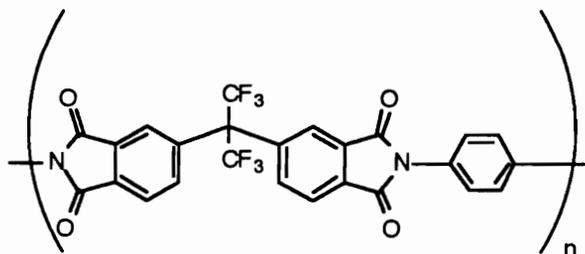
PMDA-*m*-BAPPO  $T_g = 250^\circ\text{C}$



BTDA-3,3'-DDS  $T_g = 265^\circ\text{C}$

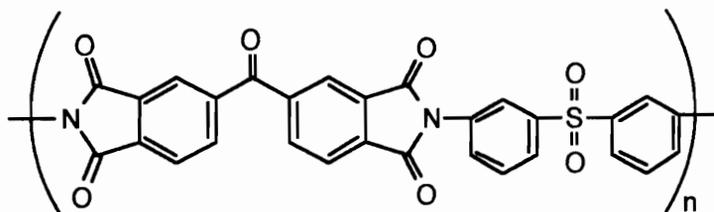


6F-4,4'-methylenedianiline  $T_g = 290^\circ\text{C}$

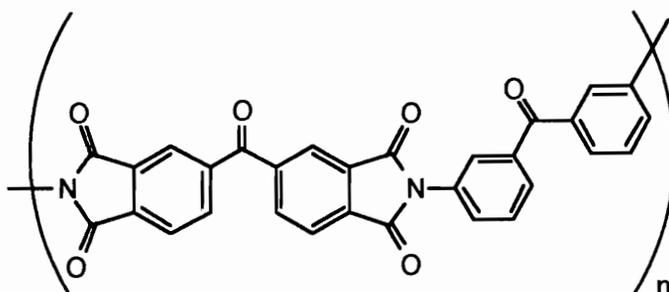


6F-*p*-phenylenediamine  $T_g = 350^\circ\text{C}$

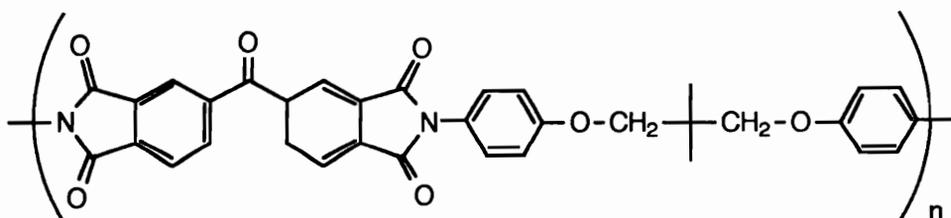
Figure 2.2.2.3.2. Soluble High  $T_g$  Polyimides



BTDA-3,3'-DDS  $T_g = 265^\circ\text{C}$



LARC-TPI  $T_g = 260^\circ\text{C}$



BTDA-1,3-bis(4-aminophenoxy)-2,2-dimethylpropane  $T_g = 230^\circ\text{C}$

Figure 2.2.2.3.3. Semicrystalline Polyimides

This polyimide will undergo strain induced crystallization, however. The solubility of the unstrained polymer could be a consequence of the non-coplanar conformation of the aromatic backbone units, which may prevent efficient "packing" of adjacent chain segments and thus reduce intermolecular attractions.

Similarly, 2,2'-dichloro BTDA (Figure 2.2.2.4.2) has been found to produce polyimides with improved solubility relative to unsubstituted BTDA; the proposed explanation for this behavior is non-coplanarity in the benzophenone unit due to the chloro substituents [78].

#### 2.2.2.5 Pendant Substituents

Monomers bearing pendant substituents have also been employed in attempts to improve polyimide solubility; substituents may be alkyl or alkoxy [79-81], perfluoroalkyl [81], hydroxyl [82, 83] or phenyl groups [20, 21]. Solubility can be explained in terms of reduced intermolecular interactions due to the steric bulk of the pendent groups. As discussed above, non-coplanar conformations may also contribute to solubility in some instances.

Methyl substitution has been demonstrated to be particularly effective in the synthesis of high  $T_g$  soluble polyimides; a number of methyl substituted phenylenediamines and methylenedianilines can be polymerized with BTDA to produce soluble polyimides with  $T_g$ 's ranging from 280-440°C; repeat units and  $T_g$ 's are listed in Table 2.2.2.5.1. The high aliphatic content is detrimental to

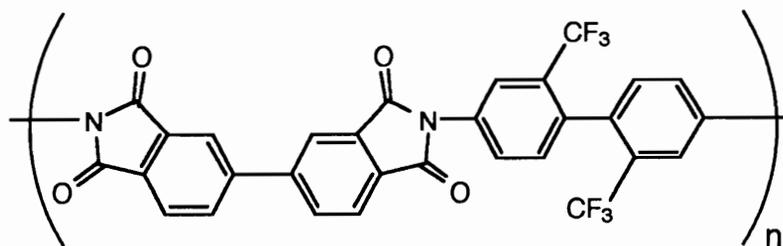


Figure 2.2.2.4.1. Repeat Unit of Biphenyl Dianhydride-2,2'-bis-(Trifluoromethyl)benzidine Polyimide

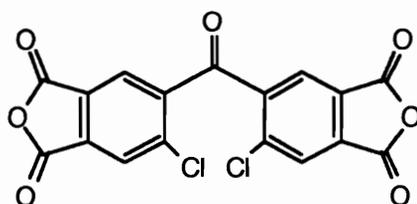
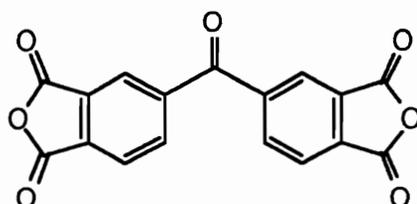
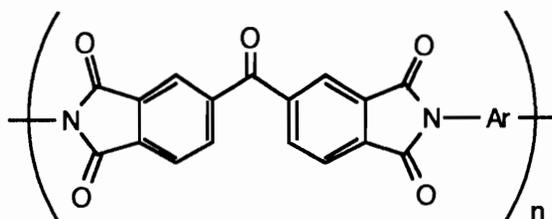


Figure 2.2.2.4.2. Benzophenone Dianhydrides: Benzophenone-tetracarboxylic Dianhydride (top) and 2,2'-Dichlorobenzophenone-tetracarboxylic Dianhydride (bottom)

Table 2.2.2.5.1 [51]. High  $T_g$  Methyl-Substituted Polyimides



<u>Ar</u>	$T_g$ (°C)	<u>Ar</u>	$T_g$ (°C)
	384		285
	398		309
	429		373
	439		

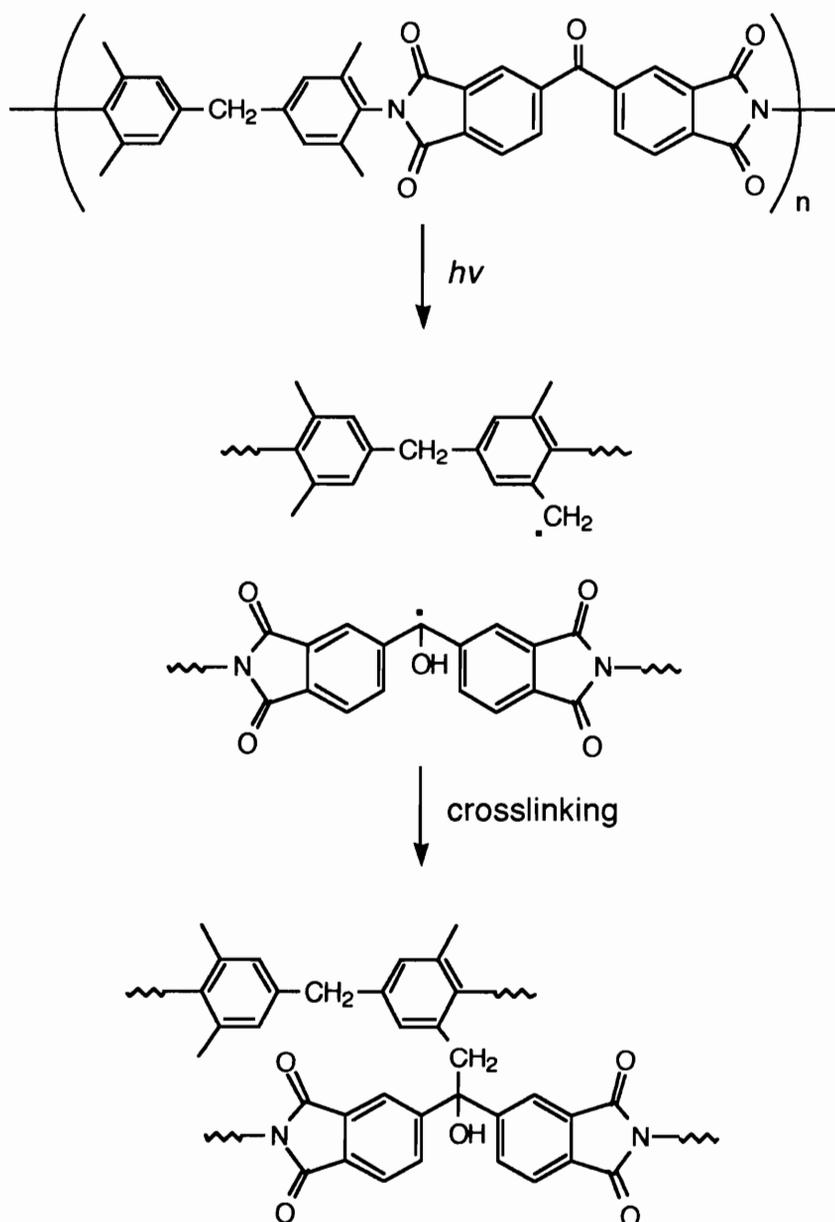
thermooxidative stability, however.

In addition, these systems have been found to undergo a facile crosslinking reaction involving the ketone carbonyl groups and benzylic radicals generated by UV radiation or exposure to temperatures in excess of 350°C [51], as shown in Scheme 2.2.2.5.1. This may be useful for some electronic applications, i.e., photoresist materials, but is a serious obstacle if thermoplastic behavior is desired. Alkyl substituents or linking groups are also known to co-crosslink at high temperatures [34, 35].

Perfluoroalkyl substituents tend to improve solubility as well but impart better thermal stability than alkyl substituents. In addition, fluoro substitution tends to decrease water uptake, dielectric constants and refractive indices in aromatic polyimides [84]. The major drawback of fluorinated polyimides is the expense of fluorinated monomers.

Phenyl substituted monomers have also been successfully employed in the synthesis of soluble high  $T_g$  polyimides. Harris and coworkers have reported a number of *m*-cresol soluble polyimides based on 3,6-diphenyl pyromellitic dianhydride and various phenyl-substituted diamines [20].

In addition, the synthesis and properties of polyimides derived from 4,4'-diamino triphenylamine have been reported [21]. These systems also possess high  $T_g$ 's but thermal stability is not exceptional, no doubt due to the in-chain amine linkage.



Scheme 2.2.2.5.1 [51]. Photocrosslinking of Polyimide Containing Ketone Carbonyl Groups and Pendant Methyl Groups

A more successful approach utilizes both fluoroalkyl substitution and a pendant phenyl group in the same monomer; the "3F" diamine has recently been shown to yield a soluble polyimide with PMDA, with a  $T_g$  in excess of  $420^\circ\text{C}$  [85].

The fluorene group is another pendant substituent which has recently generated some interest due to the solubility and high  $T_g$ 's it may potentially impart to polyimides. The diamine 9,9-bis-(4-aminophenyl)-fluorene ("FDA") is currently available from commercial sources; it may be synthesized from 9-fluorenone and aniline hydrochloride [23, 86]. Sillion and coworkers have reported  $T_g$ 's in excess of  $360^\circ\text{C}$  and solubility in amide solvents for oligomers synthesized from BTDA and FDA [86]. 4,4'-diaminotriphenylamine, "3F" diamine and fluorenediamine are shown in Figure 2.2.2.5.1.

#### 2.2.2.6 Modifications In Dianhydride Structure

Several recent attempts to design dianhydrides for improved polyimide solubility have led to a departure from the more conventional pyromellitic dianhydride or bis(phthalic anhydride) derivatives.

Polyimides based on bis(succinic anhydride) [24], bis(glutaric anhydride) [87] and bis(phenylmaleic anhydride) [25] monomers have been successfully synthesized; although  $T_g$ 's are not exceptional these materials are indeed soluble in organic solvents, such as NMP or DMAc. These structures probably afford much greater flexibility than do the bis(phthalic anhydride) monomers, as the resulting imide

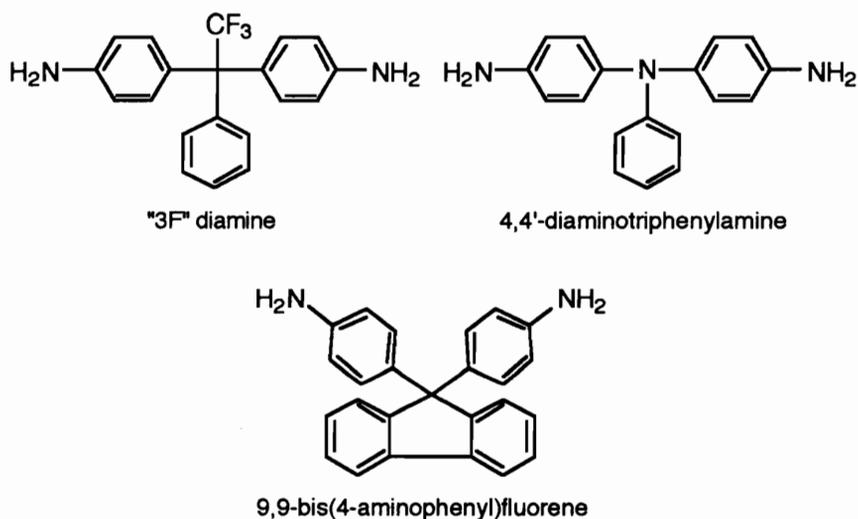


Figure 2.2.2.5.1. High Temperature Diamines

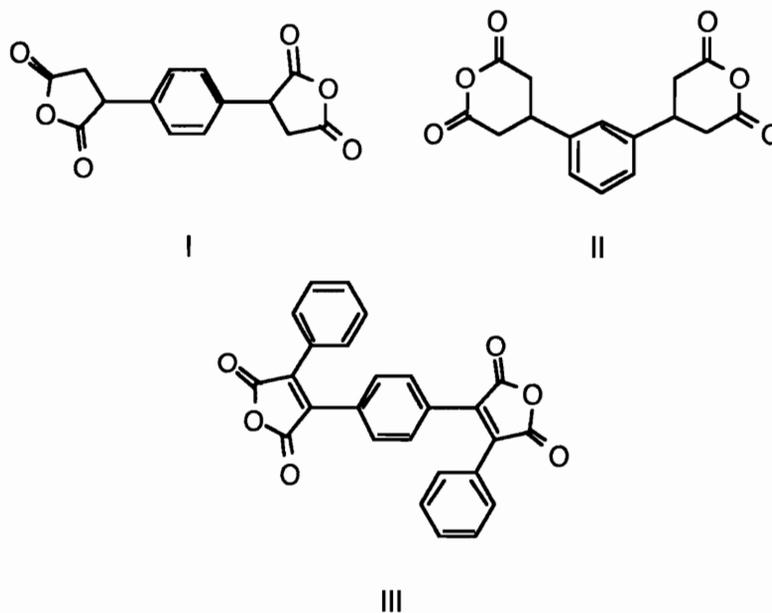


Figure 2.2.2.6.1. Non Fused-Ring Dianhydrides: (I) 1,4-phenylene bis(succinic anhydride), (II) 1,3-phenylene bis(glutaric anhydride) and (III) 1,4-phenylene bis(phenylmaleic anhydride)

heterocycle is not integrated into a fused aromatic system.

Additionally, the pendant phenyl groups of 1,4-bis-(phenylmaleic anhydride)benzene probably contribute to solubility in polyimides prepared from this monomer. Dianhydrides are shown in Figure 2.2.2.6.1.

### 2.2.3 Morphology of Polyimides

Polyimides have generally been described as amorphous materials, and while this may have been true of early aromatic polyimides there exist today a number of important exceptions. Polyimides exhibiting semicrystalline or liquid crystalline behavior are no longer a rarity-some have been developed "by accident", others by design. For example, early attempts to prepare soluble polyimides from oxyalkylene diamines instead yielded insoluble semicrystalline polyimides [88].

Recently, Kricheldorf has intentionally synthesized liquid crystalline aromatic poly(ester-imide)s [45, 89, 90]; this was accomplished by incorporating an imide-containing bisphenol synthesized from *p*-aminophenol and 4-hydroxyphthalic anhydride or a dicarboxylic acid monomer synthesized from trimellitic anhydride and *p*-aminobenzoic acid into linear aromatic polyesters.

Polyimides which are capable of crystallization may be difficult to crystallize by annealing, but may readily undergo solvent-induced crystallization; examples include LARC-TPI, Ultem 5001 [72] (structure undisclosed) and BTDA-DDS. Sufficient mobility does not

exist to permit crystallization in the bulk state for these systems. The uptake of a suitable solvent, however, plasticizes the material and sufficiently lowers  $T_g$  such that crystallization may occur.

BTDA-1,3-bis(4-aminophenoxy)-2,2-dimethylpropane polyimide is an example of a polyimide which can be crystallized by annealing [46], and biphenyl dianhydride-2,2'-trifluoromethylbenzidine polyimide can undergo strain-induced crystallization [75-77]. As mentioned in Section 2.2.2.3, some of the structural features which are known to promote solubility are found in semicrystalline polyimides, e.g. ether, carbonyl, isopropylidene or sulfone linkages or combinations thereof.

In addition to processing advantages (low melt viscosity) semicrystalline polyimides can offer several advantages over amorphous polyimides, such as increased upper use temperatures, reduced oxygen permeability which may result in greater thermooxidative stability, and reduced water uptake.

#### 2.2.4 Water Uptake/Hydrolytic Stability

Polyimides are generally stable toward acid hydrolysis; Kapton can be dissolved in concentrated sulfuric acid for three to five days with no apparent degradation in molecular weight [52-54]. In contrast, the imide heterocycle is readily hydrolyzed by strong aqueous bases and is rapidly attacked by strong nucleophiles such as hydrazine or aliphatic diamines [91].

In general, polyimides are hygroscopic materials; it has been reported that two imide functionalities can hydrogen bond up to seven water molecules [92-94], and polyimides may absorb several per cent of their weight in water; values for Kapton are on the order of 3 to 4 per cent [95,96]. Water uptake has been shown to have a detrimental effect on polyimide mechanical properties [97].

Intuitively one might expect the presence of nonpolar, hydrophobic substituents to decrease water uptake. Although this has been demonstrated, particularly with fluoro-substituted monomers, recent investigations reveal that morphology is also an important consideration.

PMDA-ODA polyimide was found to absorb less water than PMDA-*m*-phenylene diamine polyimide, despite the presence of the polar ether link in the former. The rationale for this observation was that PMDA-ODA was able to achieve a greater degree of packing and hence less free volume than PMDA-*m*-PDA due to additional mobility afforded by the ether bond; the lower water uptake of PMDA-ODA was attributed to its low free volume [98].

#### 2.2.5 Gas Transport Properties

Investigations of polyimide gas transport properties have recently intensified; it has been recognized that polyimides possess potentially useful or desirable properties as gas separation membranes. Impact on the industrial gas and energy industries could be significant if effective gas separations could be performed

via membrane technology as opposed to energy-intensive cryogenic processes; potential applications include nitrogen purification, separation of carbon dioxide from methane, and recovery of hydrogen from industrial waste gases [99-102].

Researchers are beginning to establish structure-gas transport property correlations. Yamamoto has proposed four criteria which determine gas transport properties in polyimides: (1) polymer backbone stiffness, (2) interchain distance or free volume and its distribution, (3) strength of charge-transfer complexes, and (4) penetrant gas-polymer interactions, reflected by the solubility of a gas in the polymer [99].

Generally it has been found that increasing interchain spacing results in higher gas solubility, but lower selectivity among penetrant gases, i.e., poorer separation. Increased interchain distance or free volume has been correlated with the presence of flexible linkages such as hexafluoro isopropylidene [102] and pendant groups including methyl and trifluoromethyl [99]. The contribution of intermolecular attractions between polyimide and penetrant gases is as yet undetermined.

As might be expected, thermal history also has a significant influence on gas transport properties; polyimides quenched from above  $T_g$  show increased gas absorption and permeation relative to identical slow-cooled polyimides due to greater free volume [100].

## 2.3 Polymerization of Aromatic Dianhydrides and Aromatic Diamines

### 2.3.1 Two-Step or "Classical" Synthesis

Aromatic polyimides are commonly synthesized via the well-known "two-step" route, wherein an aromatic diamine and dianhydride are polymerized in a suitable solvent at low or ambient temperatures to yield a soluble, high molecular weight poly(amic acid) which is subsequently converted to polyimide via thermal or chemical processes [103-105]. The two-step synthesis is shown in Scheme 2.3.1.1. A particular advantage of this synthesis is its applicability to both soluble and insoluble polyimides.

The "two-step" synthesis, initially reported in the 1960's, is so widely utilized and familiar that it is often considered the "classical" or "conventional" polyimide synthesis; consequently this has been the most thoroughly investigated route to polyimides, and continues to generate considerable interest.

However, despite the interest in and widespread use of this reaction, the processes leading to poly(amic acid) formation and subsequent conversion to polyimide are not fully understood. A variety of factors have been found to be variables in determining the successful application of this method, including monomer purity, exclusion of moisture from the reaction system, choice of solvents, order of monomer addition, reaction temperature, monomer concentration and molecular weight and end group control.

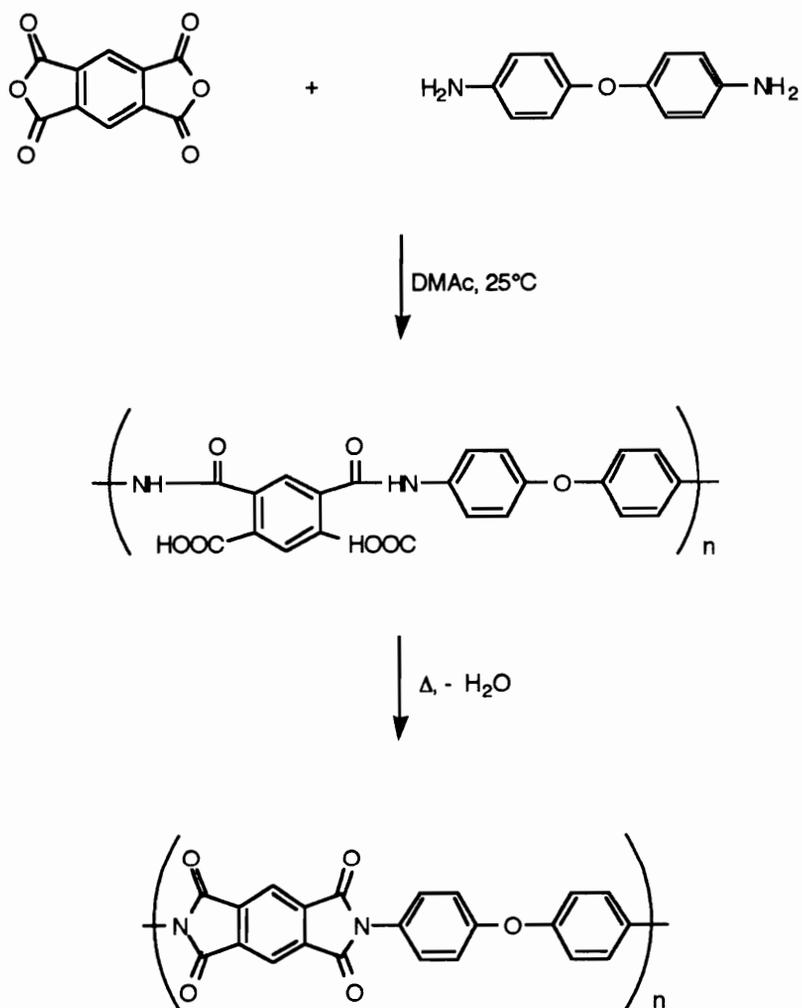
As with nearly all polymerizations (interfacial polymerizations are an exception) monomer purity is of the utmost importance;

monomers must be exactly difunctional and of greater than 99 per cent purity in order to achieve high molecular weights.

Carboxylic acid groups resulting from the hydrolysis of the dianhydride will fail to react with the diamine at low temperatures; therefore, in addition to extremely pure dianhydrides, carefully dried solvents and reactors are essential. In addition, the intermediate poly(amic acid) is hydrolytically unstable and must be protected from moisture as well.

This moisture sensitivity is a major drawback of the two-step synthesis. Although rigorous exclusion of moisture is a relatively simple exercise (flaming glassware and distilling solvents over dehydrating agents) for small-scale laboratory syntheses, it is difficult and inconvenient for industrial scale polymerizations. This problem is further aggravated by the fact that suitable solvents for monomers and poly(amic acid)s are almost without exception hygroscopic amide solvents, dimethyl sulfoxide, or various ether solvents such as diglyme [109, 106].

The particular choice of polymerization solvent may be critical in the formation of high molecular weight poly(amic acid), particularly if unreactive diamines are utilized. It has been reported that in such circumstances ether solvents promote the formation of high molecular weight poly(amic acid); this has been rationalized by complexation or hydrogen bonding of the ether oxygens with amino protons, resulting in increased nucleophilicity of the diamine [106].



Scheme 2.3.1.1 [103]. Conventional or "Two-Step" Polyimide Synthesis

The order of monomer addition has also been cited as an important parameter. Usually, powdered dianhydride is introduced to a rapidly stirring diamine solution; this sequence has been shown to yield higher molecular weight poly(amic acid) than the reverse procedure [4]. Two explanations have been offered: (1) traces of moisture in the solvent may rapidly hydrolyze the dianhydride, yielding unreactive carboxylic acids, and (2) complex formation between dianhydride and solvent [107, 108, 110].

Additionally, the form in which the dianhydride is introduced may have a profound effect on molecular weight. Cotts and Volksen demonstrated by light scattering that for a series of controlled molecular weight PMDA-ODA poly(amic acid)s, addition of a dianhydride solution to a diamine solution yielded molecular weights in good agreement with the calculated values [107]. In contrast, extremely high molecular weights were initially obtained when the dianhydride was introduced as a solid; molecular weights were found to equilibrate slowly, over a period of four weeks, to the calculated values.

Monomer concentration is yet another consideration; dilute poly(amic acid) solutions are generally less stable and have shorter shelf lives than concentrated solutions [109, 111]. Therefore, one might conclude that it is desirable to employ the maximum monomer concentration possible. However, Cotts and Volksen also reported significant effects of monomer concentration on initial molecular weights. At total solids contents of less than 10 weight percent good

agreement was found between calculated and actual molecular weights, regardless of the mode of monomer addition. For monomer concentrations of 20 weight percent, however, calculated and actual molecular weights were in good agreement only when the dianhydride was introduced in solution; adding solid dianhydride to a diamine solution initially yielded significantly greater molecular weights than calculated, and molecular weights were found to equilibrate slowly to the desired values [107].

Reaction temperature is another crucial factor; the initial stage of the reaction is typically conducted at temperatures below 50°C to prevent cyclization to imide. The purpose in preventing premature imidization is twofold: first, imidization releases water, which may rapidly hydrolyze poly(amic acid) [11], resulting in reduced molecular weights. Model studies indicate that the rate of ortho acid-amide hydrolysis exceeds that of unsubstituted amides by five orders of magnitude [112]. Second, if the fully cyclized polyimide is insoluble, premature imidization at initial stages of the polymerization results in precipitation of low molecular weight imide oligomers [113].

### 2.3.2 Bulk Thermal Imidization (Cyclodehydration)

Conversion of poly(amic acid)s to polyimides is most commonly effected by thermal treatment of solution cast films; this procedure is suitable for both soluble and insoluble polyimide systems. Heating is usually conducted in stages in order to remove the casting solvent,

induce cyclization and remove the water liberated by the imidization process. A typical heating cycle may proceed as follows:

1. One hour @ 70°C
2. One hour @ 100°C
3. One hour @ 200°C
4. One hour @ 300°C
5. Slow cool to room temperature.

Variations of this cycle may be employed; for example, if a vacuum oven is utilized, most of the casting solvent may be removed at room temperature over a period of several hours before heating begins, or if the  $T_g$  of the polyimide is in excess of 300°C, the final  $T_g$  must be exceeded in order to insure complete imidization and solvent removal.

Investigation of the imidization process by DSC and TGA of PMDA-ODA poly(amic acid)s has revealed that the majority of imidization occurs in the range of 100-250°C [114]. Isothermal imidization studies, monitoring the appearance of imide by IR in the temperature range of 160-188°C, demonstrated that the rate of imidization is initially rapid but decreases over time, and comes to a halt before complete conversion is attained (66 per cent) [115]. This is illustrated in Figure 2.3.2.1.

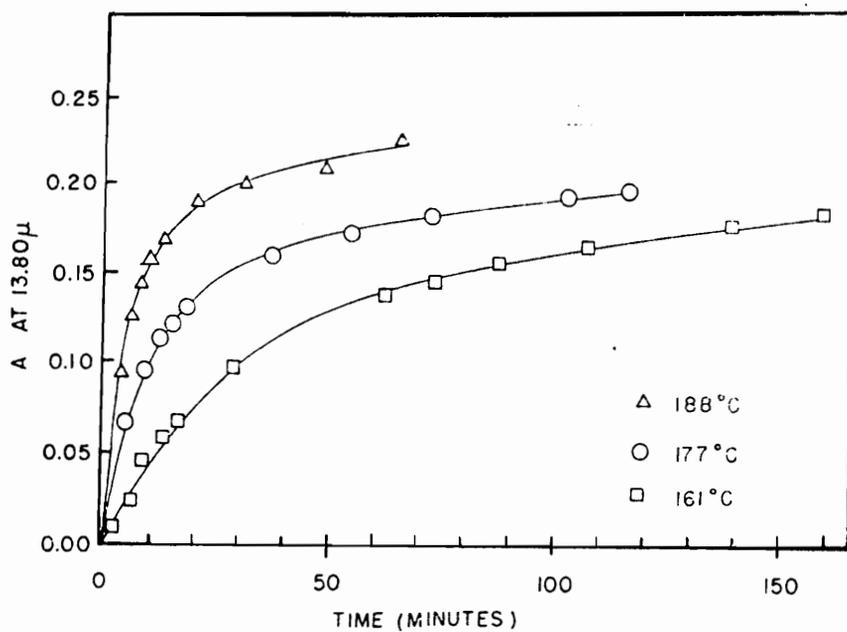


Figure 2.3.2.1. Conversion Rates of Poly(amic acid) at Various Temperatures [115]

Additional investigations of isothermal imidization by TGA yielded similar results, i.e., initially a rapid rate of imidization, followed by a marked decrease with a less than quantitative final extent of conversion (80 per cent), as shown in Figure 2.3.2.2 [115]. However, rapid heating to the  $T_g$  of the fully cyclized polyimide effected complete imidization; it was concluded that the  $T_g$  of the polymer increases as cyclization proceeds. When  $T_g$  reaches the imidization temperature there is no longer sufficient molecular mobility for further cyclization; only when this temperature is exceeded may the imidization process resume, and only if the  $T_g$  of the fully cyclized polyimide is exceeded can quantitative conversion be attained.

### 2.3.3 Molecular Weights

Various studies have compared the solution properties of poly(amic acid)s and their corresponding fully cyclized polyimides and found little or no difference in molecular weights [54, 117-119]. At a glance, this might suggest that imidization is a relatively simple cyclization process, with molecular weight remaining constant.

Bulk thermal imidization has in fact been shown to be a complex, dynamic process by various investigators and has been described as "a competition between cyclization and depolymerization" [35]. Bell and coworkers and Dine-Hart and Wright [4] observed that flexible poly(amic acid) films became brittle at intermediate stages of imidization (175-225°C) but formed strong

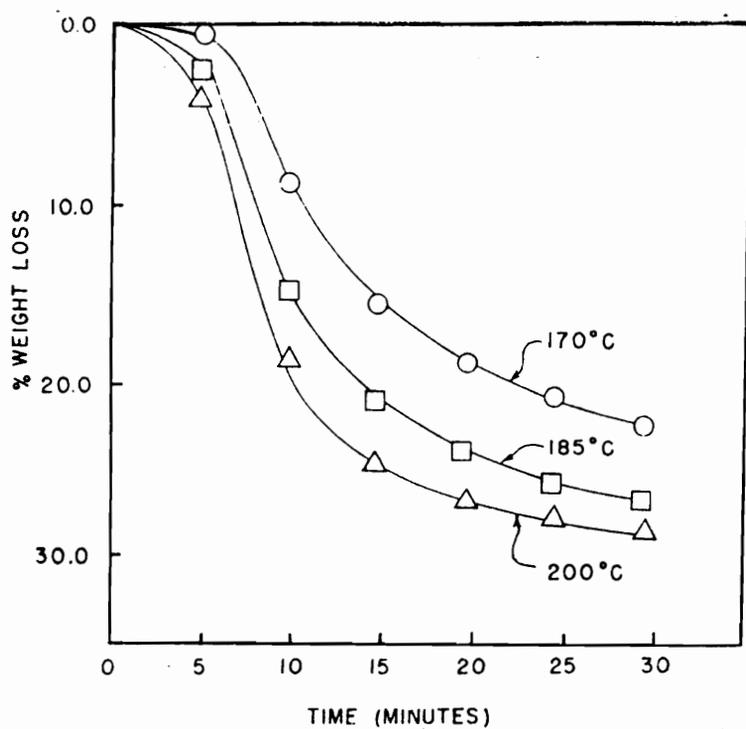


Figure 2.3.2.2. Weight Losses of Poly(amic acid) Films [115]

flexible films upon heating to 250-300°C. It was surmised that water liberated early in the imidization process hydrolyzed a portion of the uncyclized amic acid functions, leading to chain scission and hence decreased molecular weights and mechanical properties.

Furthermore, at high temperatures the reactive end groups reacted again, regenerating high molecular weight polymer. This explanation has been supported by infrared analysis of the imidization process. Infrared spectroscopy has been used to monitor the imidization process and estimate the degree of imidization; characteristic imide and amic acid bands are listed below [120-124].

Imide I	1780-1770 $\text{cm}^{-1}$ and 1730-1720 $\text{cm}^{-1}$
Imide II	1400-1340 $\text{cm}^{-1}$
Imide III	1140-1100 $\text{cm}^{-1}$
Imide IV	740-710 $\text{cm}^{-1}$
Amide (carbonyl)	1550-1540 $\text{cm}^{-1}$ ; (NH) 3250 $\text{cm}^{-1}$
Anhydride	1860-1850 $\text{cm}^{-1}$ and 1780-1770 $\text{cm}^{-1}$

The signal at 1370  $\text{cm}^{-1}$  has been recommended as a suitable absorbance to monitor imidization, as anhydride formation could interfere with bands at 1780 and 720  $\text{cm}^{-1}$  [125].

The appearance of an anhydride band has been reported during the imidization of PMDA-ODA poly(amic acid); maximum intensity for this signal was observed in the temperature range of 150-200°C, and it disappeared at higher temperatures [126]. This

result in and of itself does not confirm an initial chain scission (hydrolysis) and subsequent chain extension, but it does indicate that reactive anhydride end groups can be generated under the imidization conditions.

In a recent investigation intrinsic viscosity, number average and weight average molecular weights and IR absorbances were monitored during the bulk thermal imidization of a soluble polyimide [127]. Anhydride was present at temperatures of 150-300°C, and intrinsic viscosity was found to decrease from 150-200°C, followed by an increase above 200°C. Weight average molecular weights as determined by light scattering and number average molecular weights as determined by gel permeation chromatography were found to follow the same trend as intrinsic viscosity. These results clearly support the contention that molecular weights decrease during the initial stages of imidization due to hydrolysis, and at later stages (higher temperatures) reactive anhydride end groups are regenerated and chain extension occurs.

In addition, Young and Chang reported that uncontrolled molecular weight poly(amic acid) significantly increased in molecular weight above 225°C [33], indicating that reactive end groups are an important factor in determining final polyimide molecular weights.

#### 2.3.4 Potential Side Reactions

In addition to the desired imide formation, bulk thermal imidization can in principle lead to other undesirable chemical

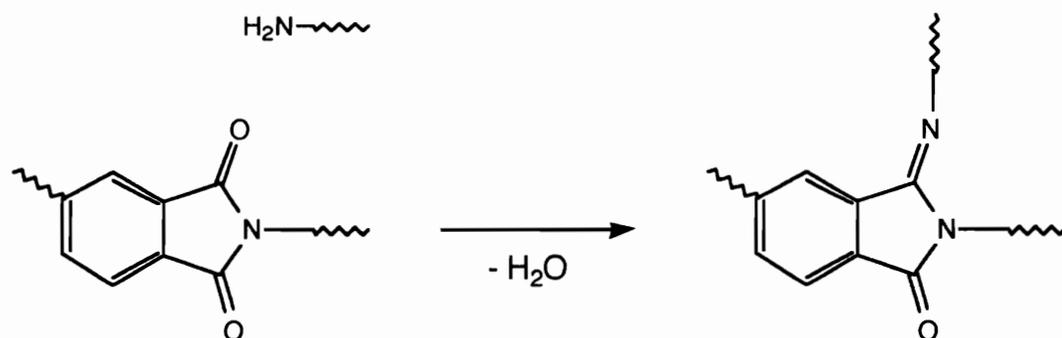
structures. As previously mentioned, chain extension can lead to extremely high molecular weights, which is not always advantageous.

Other proposed side reactions include intermolecular imide formation and end group reactions leading to branched and/or crosslinked structures [48-50, 128, 129] as shown in Scheme 2.3.4.1. Soviet researchers have proposed that at temperatures in excess of 300°C, transimidization or intermolecular imide formation occurs, yielding a crosslinked structure [49]. Similarly, using steric and kinetic arguments, Sacher also proposed the formation of linear, intermolecular imide groups to form a network structure as the basis for the insolubility of PMDA-ODA polyimide; according to this explanation, at sufficiently high temperature a number of these intermolecular imide links would revert to cyclic imide structures, but enough crosslinks would remain to preserve a network structure [50]. These potential crosslinking reactions have been proposed as a partial explanation for the insolubility typical of many aromatic polyimides.

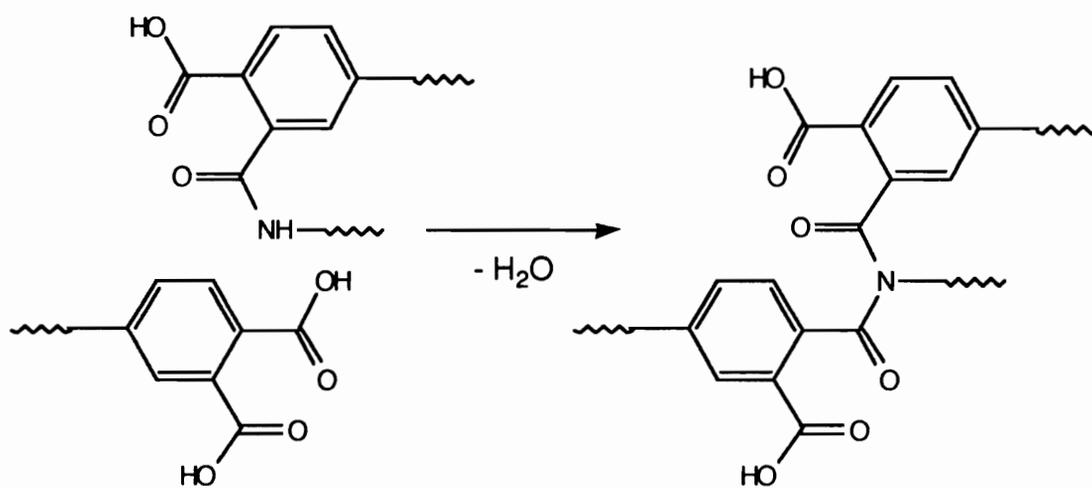
One argument against the crosslinking explanation is the fact that PMDA-ODA polyimide, otherwise insoluble, will dissolve in concentrated sulfuric acid and therefore cannot be a crosslinked material; the dilute solution properties of this polyimide have been measured in sulfuric acid [52-54]. However, the solubility of PMDA-ODA in sulfuric acid cannot completely dismiss the possibility of intermolecular crosslinking.

Another proposed structure is an intermolecular imine linkage

### Imine Crosslink Formation



### Imide Crosslink Formation



Scheme 2.3.4.1 [48-50]. Proposed Crosslink-Forming Side Reactions

formed by the condensation of a free amine end group and an imide carbonyl group [130]; model studies confirm that this reaction can indeed occur at high temperatures [131, 132]. This reaction is also shown in Scheme 2.3.4.1. Furthermore, the imine or Schiff Base is known to be hydrolytically unstable in acidic media [133]; one could conceivably design an imine-crosslinked thermoset, which would hydrolyze to linear polymer upon exposure to strong acids.

Shalaby and McCaffrey attempted to detect intermolecular crosslinks, such as iminolactone (isoimide) and interchain imides, in bulk imidized polyimides utilizing infrared spectroscopy [134]. Although their efforts were unsuccessful, these structures could be present in concentrations too low for detection; only a few percent would be sufficient to generate an insoluble network.

Several general classes of linear polyimides are known to crosslink under the conditions of bulk thermal imidization: (1) polyimides with aliphatic substituents, (2) polyimides containing both ketone carbonyl groups and either benzylic linkages or aliphatic substituents, and (3) polyimides with amine end groups, which are comprised of at least one ketone-containing monomer. Aliphatic substituents can form free radicals at the high temperatures required for complete imidization; recombination of the radicals generates a network system [34, 35]. In addition, polyimides containing both ketone and aliphatic groups undergo a facile crosslinking reaction involving the ketone carbonyl groups and benzylic radicals generated at temperatures in excess of 350°C [51].

Crosslinking via intermolecular imine formation is possible in ketone-containing polyimides with reactive (amine) end groups [135]; the dehydrating conditions which favor imide formation favor this reaction as well. None of these crosslinking reactions involve amic acid or imide groups.

Overall, little evidence exists to support crosslink formation involving amic acid or imide groups as a significant contribution to polyimide insolubility; perhaps the most convincing argument against such crosslink formation is the existence of soluble polyimides.

### 2.3.5 Chemical Imidization

Cyclodehydration of poly(amic acid)s to polyimides may also be effected at room temperature by using various combinations of chemical agents. Chemical cyclodehydration can result in two possible heterocyclic structures, imide and iminolactone (isoimide). The efficiency of the reaction varies according to the specific combination of chemical agents employed.

Typically, common anhydrides such as acetic anhydride, propionic anhydride or n-butyric anhydride are used in conjunction with organic bases, usually pyridine or triethylamine [136]. The overall process is poorly understood.

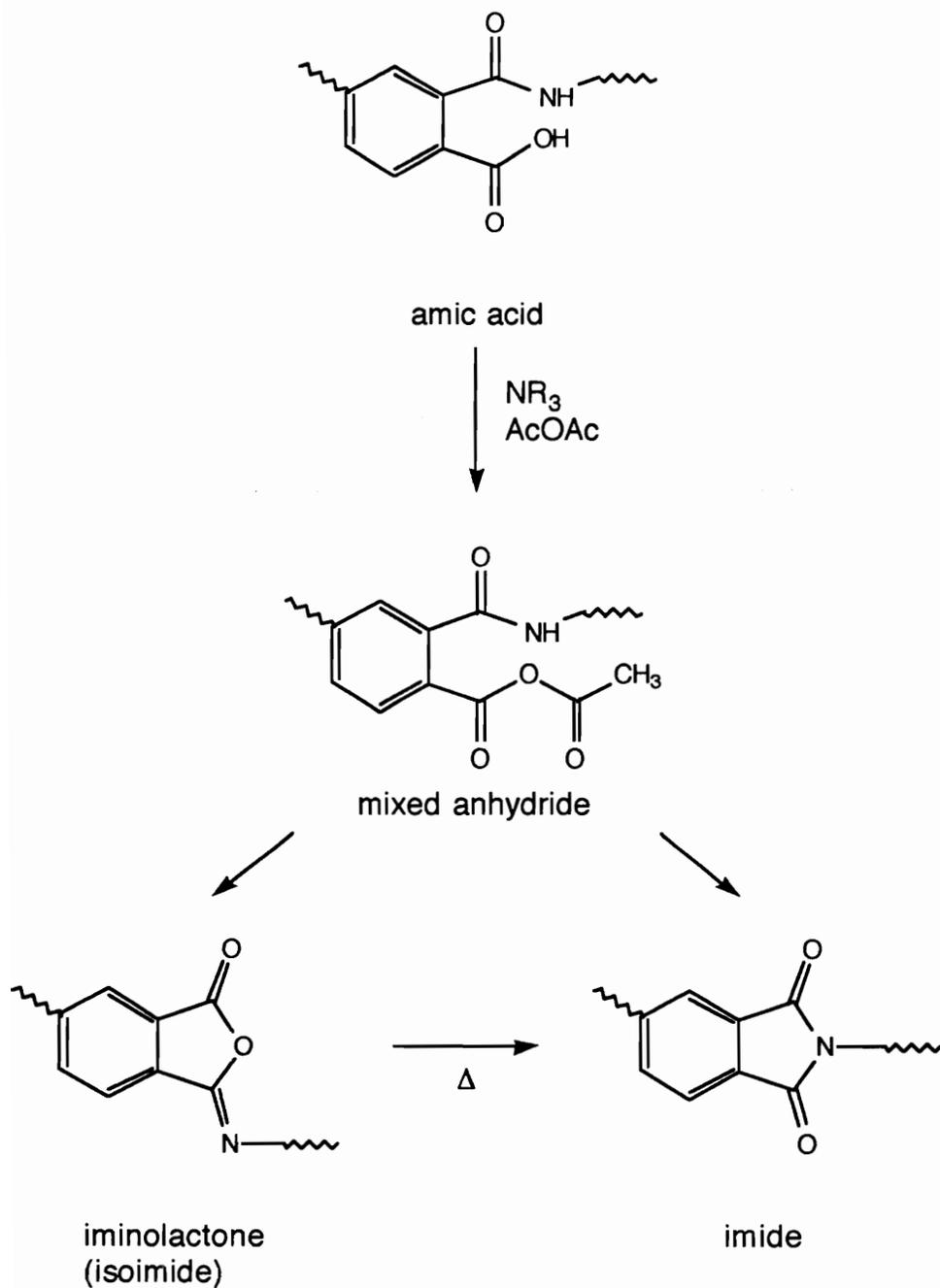
The first step in the process is believed to be formation of a mixed anhydride; subsequent *N*-acylation yields the imide

heterocycle, while O-acylation yields the iminolactone or isoimide heterocycle.

Cyclodehydration utilizing anhydrides and triethylamine reportedly affords the imide structure exclusively; a mixture of predominantly imide and iminolactone is obtained if pyridine is substituted for triethylamine [136]. Cyclodehydration of poly(amic acid)s with trifluoroacetic anhydride or dicyclohexyl carbodiimide reportedly affords the iminolactone structure exclusively [137-139]. Chemical imidization reactions are summarized in Scheme 2.3.5.1.

Iminolactone formation has been considered a disadvantage of chemical imidization; the iminolactone structure has historically been regarded as an undesired structure in polyimides, a "weak link" with regard to thermal and hydrolytic stability [140-142]..

However, poly(iminolactone)s are known to isomerize to polyimides upon heating; the process is not diffusion controlled but is sensitive to the onset of  $T_g$ . In addition, poly(iminolactone)s display lower  $T_g$ 's and greater solubility than their polyimide analogs [143, 144] , characteristics which are advantageous in synthesis and processing. Because of these attractive properties, poly(iminolactone)s have found commercial application, notably the acetylene terminated Thermid resins, originally developed by Hughes Aircraft and currently marketed by National Starch [145, 146].



Scheme 2.3.5.1 [136]. Chemical Imidization Process

### 2.3.6 Solution Imidization

The insolubility of the early aromatic polyimides made solution polymerizations impossible; the two-step synthesis and chemical imidization techniques evolved from attempts to synthesize high molecular weight, high  $T_g$ , fully cyclized polyimides. Continued attempts to improve polyimide processability through structural modifications led to the development of high  $T_g$  polyimides which are soluble in organic solvents at concentrations typically employed for poly(amic acid) synthesis. This in turn has led to the development and refinement of solution imidization techniques, which represent a significant advance in polyimide technology; "one pot" syntheses are possible, cyclodehydration can be effected at relatively low temperatures without dehydrating agents, avoiding degradation and side reactions, and polyimides may be stored in solution rather than their hydrolytically unstable poly(amic acid) precursors.

Attempts to synthesize soluble polyimides via thermal imidization of poly(amic acid)s in solution were reported as early as 1970. Reactions were conducted in N-methylpyrrolidinone at 200°C but failed to yield high molecular weight polyimides [147]. This could have been due to the fact that no provision was made to remove the water of imidization, resulting in hydrolysis and consequent molecular weight reduction. Alternatively, the high temperature may have generated NMP decomposition products capable of cleaving the polyimide chains.

The use of phenol or cresols as primary solvents in combination with cosolvents such as toluene or chlorobenzene in poly(etherimide) synthesis was reported in the mid 1980's [148]. The purpose of the cosolvent was to remove water azeotropically from the reaction; syntheses were reported for these solvent systems at temperatures of 160-180°C.

The use of NMP as the primary polymerization solvent with N-cyclohexylpyrrolidinone (CHP) as a cosolvent to remove the water of imidization was reported during the same period, and was successfully employed in the synthesis of soluble polyimide homopolymers and poly(imide-siloxane) copolymers [36, 37]. CHP does not form an azeotrope with water; the immiscibility of CHP and water is the basis of water removal at high temperatures. Waldbauer has successfully employed a solvent system of NMP and *o*-dichlorobenzene to solution imidize poly(amic acid)s to high and controlled molecular weight polyimides at 180°C [38].

### 2.3.7 The Solution Imidization Process

The process of thermal solution imidization has not been as extensively investigated as the bulk thermal imidization process; consequently, little was known about the processes occurring in solution until quite recently. Recent work by Kim et al. has revealed several interesting features.

Intrinsic viscosity measurements of polymer solutions during various stages of the imidization process revealed an initial decrease, followed by an increase during the latter stages of imidization. This was correlated with  $^1\text{HNMR}$  studies, which initially showed an increase in amine concentration during the early stages of imidization, and then gradual disappearance of amine with time.

These results clearly demonstrate initial hydrolysis of the partially imidized poly(amic acid) by water liberated from the imidization process, resulting in molecular weight degradation and therefore increased end group concentration. At later stages of the reaction, as water concentration diminishes, subsequent reaction of end groups results in an increase in molecular weight and consequent decrease in end group concentration [149]. This same behavior is believed to occur during bulk thermal imidization.

In addition, this process was shown to be temperature dependent. Polymerizations conducted at  $150^\circ\text{C}$  were incomplete after 20 hours; intrinsic viscosities did not attain their limiting values and amine resonances were still apparent in the  $^1\text{HNMR}$  spectra. In contrast, complete imidization, in terms of "relinking" of partly hydrolyzed polymer and cyclodehydration, was possible at  $180^\circ\text{C}$ ; intrinsic viscosities reached a limiting value, and amine end groups and amic acid groups disappeared within 12 hours.

Furthermore, Kim has demonstrated that cyclodehydration is an acid-catalyzed process [40]; acid catalysis may possibly permit lower reaction temperatures and shorter reaction times.

In addition to elucidating some of the mechanistic aspects and kinetics of solution imidization, Kim demonstrated the occurrence of crosslinking in ketone-containing polyimides with amine end groups [135]; the amine end groups attack in-chain ketone carbonyl groups to form an imine-linked, insoluble polyimide network. The polyimide gels are readily hydrolyzed, however, upon addition of a trace amount of aqueous hydrochloric acid. This is a possible side reaction which has not been generally recognized in polyimide synthesis, and as a result, has not been investigated in detail.

## 2.4 Additional Routes to Polyimides

### 2.4.1 "One-Step" Synthesis

Soluble polyimides need not be prepared from poly(amic acid) precursors via the "two-step" synthesis. Harris and coworkers have reported the synthesis of high molecular weight soluble polyimides via a "one step" synthesis in refluxing *m*-cresol without azeotroping cosolvents; dianhydride and diamine are directly polymerized at high temperature without the formation of an intermediate high molecular weight poly(amic acid) [74, 75]. In light of Kim's findings regarding the solution imidization process, the high temperature and the acidity of *m*-cresol may account for the success of this reaction.

### 2.4.2 Vapor Deposition Polymerization

Polyimide films may be prepared from aromatic dianhydrides and diamines without solvents, eliminating contaminants such as

residual solvent or solvent decomposition products. In vapor deposition polymerization, monomers are coevaporated under vacuum at 200°C and deposited on the desired substrate. The deposited film consists of 30-50% unreacted monomers; poly(amic acid) oligomers comprise the remaining material. Additional heating is required to continue polymerization and imidization [150, 131, 132]. In this manner, films of controlled thickness with excellent dielectric properties can be produced; however, molecular weights are generally low, on the order of  $1.3 \times 10^4$  Daltons [150].

#### 2.4.3 Nucleophilic Aromatic Substitution: Poly(ether-imide)s

Nucleophilic aromatic substitution is a well-known route for the reproducible synthesis of soluble high molecular weight poly(arylene ether-ketone)s and poly(arylene ether-sulfone)s [151-156]. The synthesis typically employs an activated dihalide monomer, bisphenol, and potassium carbonate to generate phenolate, the active nucleophile. N,N-dimethylacetamide is commonly employed as the primary solvent with toluene as the azeotroping cosolvent.

The purpose of water removal is twofold: (1) to remove a reaction byproduct, thereby shifting the reaction equilibrium toward products, and (2) to prevent hydrolysis of the activated halide, thereby preserving functional group stoichiometry.

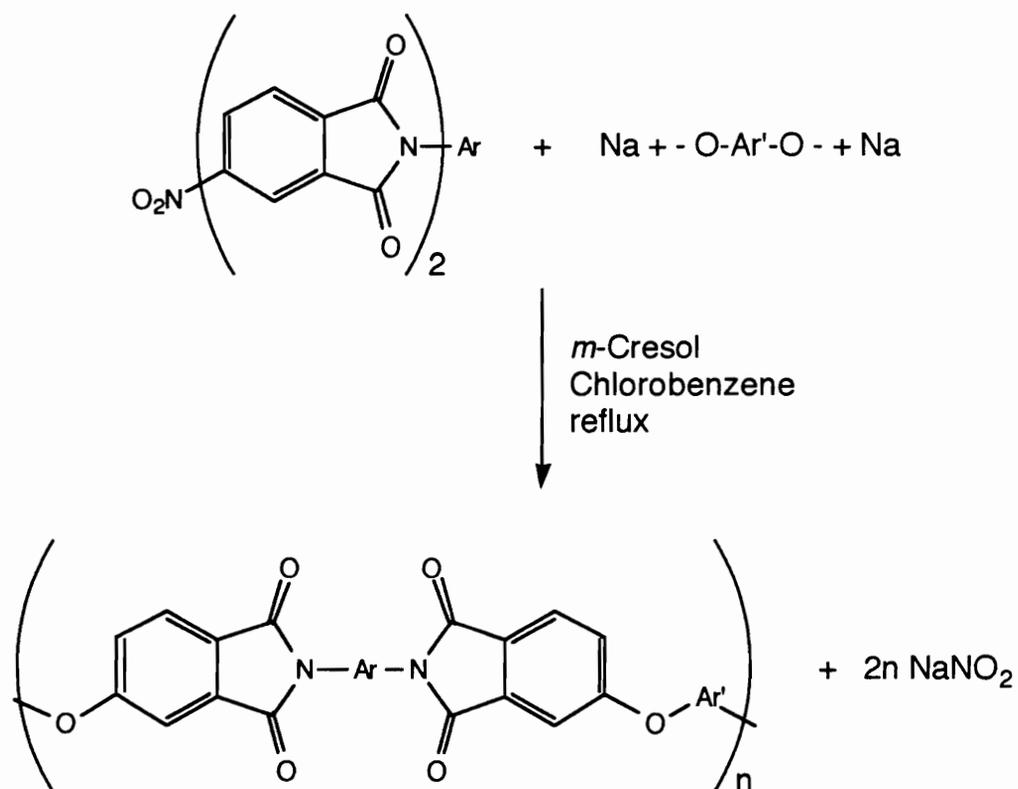
A similar synthesis has been reported for the preparation of poly(ether-imide)s using dinitro substituted bisimide monomers and

pre-formed bisphenolates [148, 157-160]. This synthesis also employs primary solvent-azeotroping cosolvent combinations and is shown in Scheme 2.4.3.1. In this reaction, effective water removal is vital, in order to (1) drive reaction equilibrium toward products, (2) prevent nitro group hydrolysis, and (3) prevent imide hydrolysis. Imide hydrolysis may result in deactivation of the nitro group and chain scission, both of which result in low molecular weights.

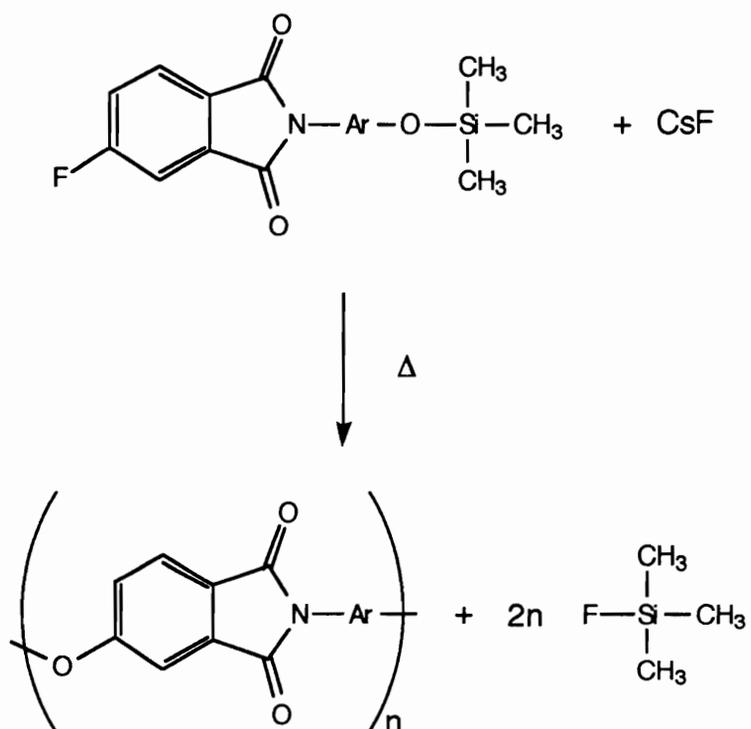
Indeed, under optimal conditions, only low molecular weight polyimides are usually obtained [158]. General Electric's Ultem, believed to be produced by this method, is likely synthesized by an indirect multistep route involving nitro displacement [160]. Nitro displacement is utilized in the synthesis of an ether-linked bis(phthalic anhydride) monomer, which is subsequently polymerized with a diamine in the normal fashion.

Another poly(ether-ketone) synthesis based on nucleophilic aromatic substitution is the method reported by Kricheldorf, which utilizes aromatic activated dihalide and aromatic bis(trimethylsilyl ether) monomers [161]. This polymerization is conducted in the melt and employs a catalytic amount of cesium fluoride to generate phenolate at high temperature; the reaction proceeds with the evolution of fluorotrimethylsilane.

This strategy has recently been exploited in the synthesis of polyimides from A-B monomers bearing both activated fluoride and trimethylsilyl ether functional groups, as shown in Scheme 2.4.3.2 [162]. Monomers are prepared by reacting 4-fluorophthalic



Scheme 2.4.3.1 [148]. Poly(ether-imide) Synthesis Via the Nucleophilic Aromatic Substitution (Nitro Displacement) Route



Scheme 2.4.3.2 [162]. Synthesis of a Poly(ether-imide) Via Kricheldorf's Nucleophilic Aromatic Substitution Route

anhydride with an aminophenol and converting the resulting imide-phenol to its trimethylsilyl ether derivative.

Alternatively, a number of commercially available ether-linked monomers may be employed to synthesize poly(ether-imide)s; these are shown in Figure 2.4.3.1.

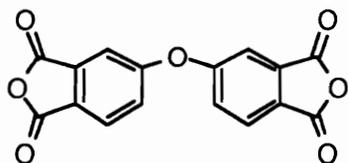
#### 2.4.4 Diels-Alder Polymerizations

The Diels-Alder reaction has been utilized in the synthesis of polyimides from bismaleimides and bis(cyclopentadienone) derivatives [20, 163-165]. Initial polymerization results in an unstable intermediate which spontaneously liberates carbon monoxide, forming a linear polyimide comprised of dihydrophthalimide units. Aromatization (dehydrogenation) is effected by heating the polyimide in nitrobenzene. This polymerization is shown in Scheme 2.4.4.1. Disadvantages of the Diels-Alder polymerization include low molecular weights and incomplete aromatization.

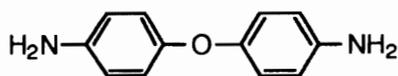
A more successful approach employs the Diels-Alder Reaction reaction in dianhydride synthesis; completely aromatized phenyl-substituted dianhydrides can be isolated, which can then be polymerized with diamines in the conventional manner [20].

#### 2.4.5 Poly(aspartimide) Synthesis

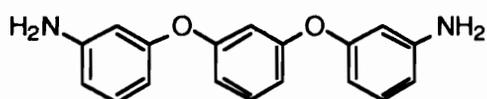
The carbon-carbon double bond of the maleimide heterocycle is sufficiently electrophilic such that polymerization of bismaleimides



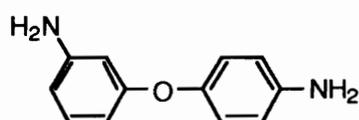
4,4'-oxydiphthalic anhydride



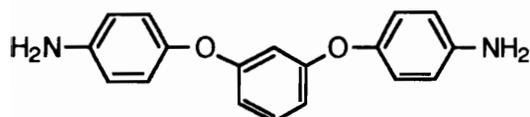
4,4'-oxydianiline



1,3-bis(3-aminophenoxy)benzene



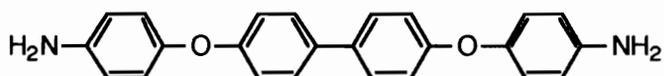
3,4'-oxydianiline



1,3-bis(4-aminophenoxy)benzene

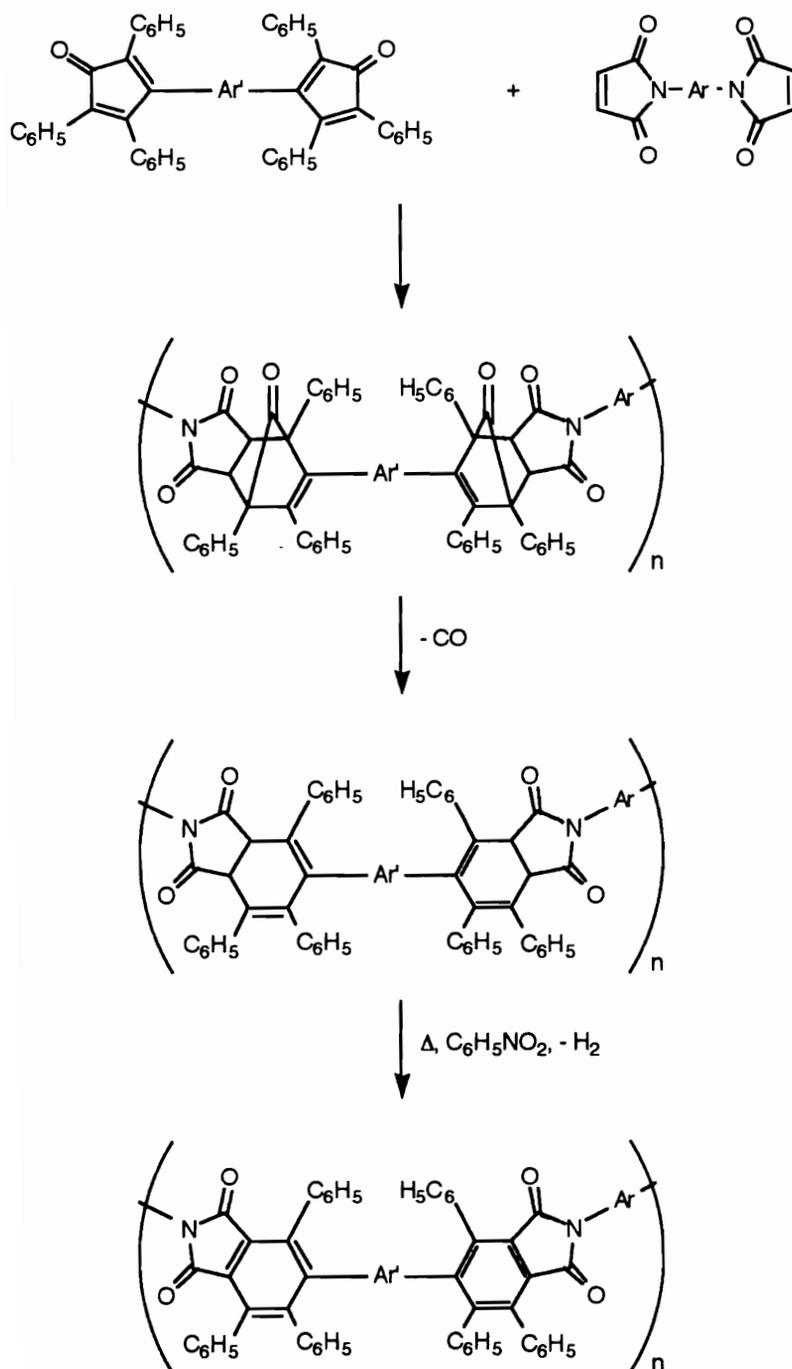


1,4-bis(4-aminophenoxy)benzene



4,4'-bis(4-aminophenoxy)biphenyl

Figure 2.4.3.1. Commercially Available Monomers  
Containing Ether Connecting Groups



Scheme 2.4.4.1 [20]. Polyimide Synthesis Via  
The Diels-Alder Reaction

occurs readily with such nucleophiles as aromatic diamines or aromatic dithiols via Michael Addition [166], as shown in Scheme 2.4.5.1. Polymerization at high temperatures in protic solvents, i.e., cresols, generally affords high molecular weight poly(aspartimide)s. Protic solvents are necessary in order to prevent crosslinking of anionic intermediates.

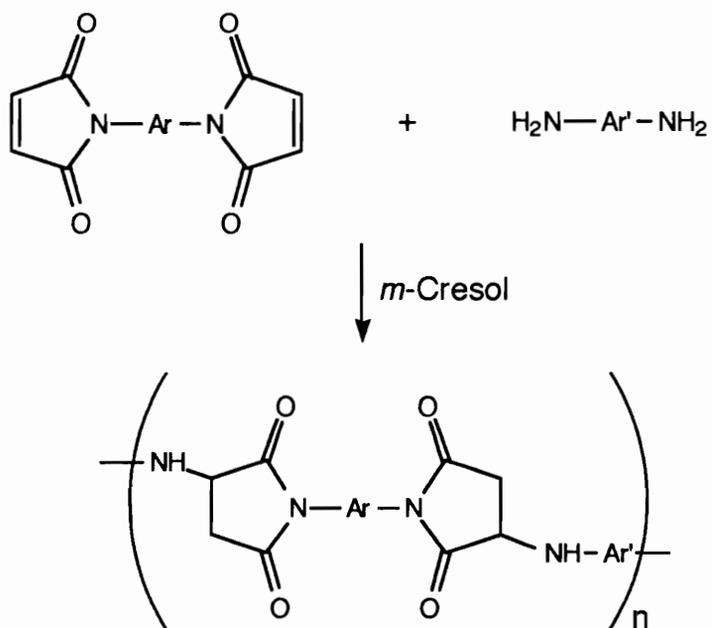
Poly(aspartimide)s are not obtained if aliphatic diamines are utilized. For example, 1,2-ethanediamine or 1,3-propanediamine open the maleimide heterocycle, yielding linear poly(maleamide)s [91], as shown in Scheme 2.4.5.2.

## 2.4.6 Syntheses Utilizing Diamine Derivatives

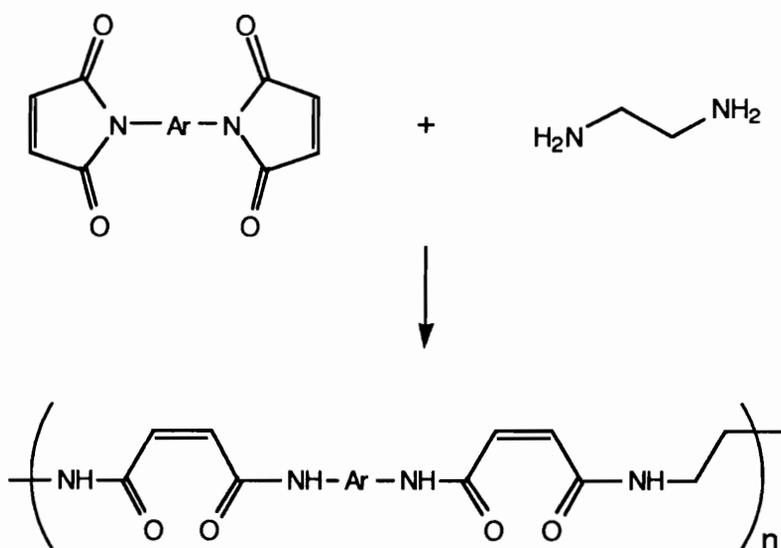
### 2.4.6.1 Diisocyanates

Polyimides have been synthesized from the polymerization of diisocyanates with dianhydrides or mixtures of dianhydrides with their tetraacid or diester-diacid derivatives [167-175]. The polymerization reportedly proceeds, at least in part, via formation of an intermediate 7-membered heterocycle which decomposes to the five-membered imide heterocycle with the evolution of carbon dioxide and water [174]. Scheme 2.4.6.1.1 illustrates polyimide synthesis from diisocyanates. Meyers claimed spectroscopic evidence for the 7-membered heterocycle, and reported that the yield of this structure increased if the polymerization was performed under a carbon dioxide atmosphere [170].

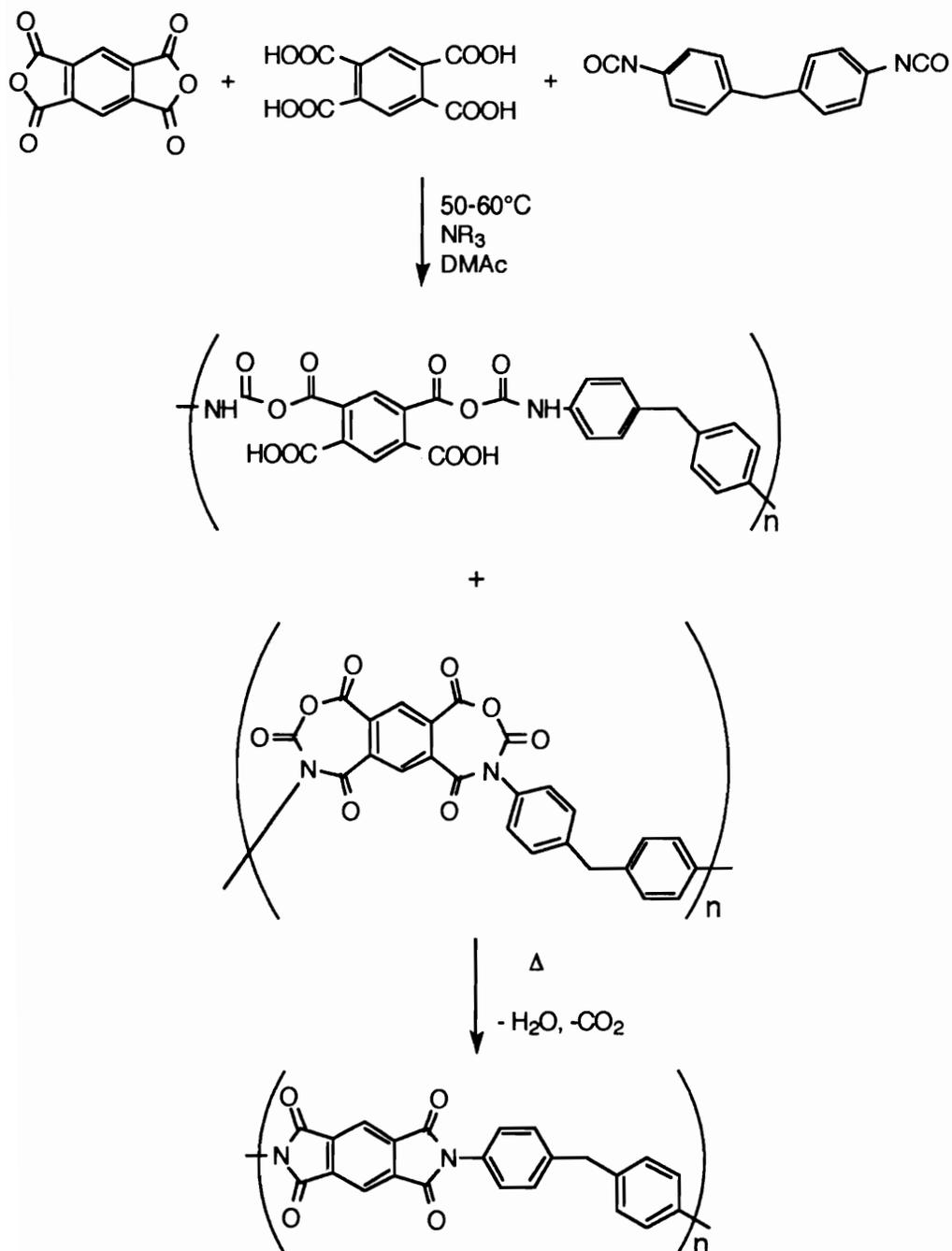
Upjohn's original Polyimide 2080, which is now produced by



Scheme 2.4.5.1 [91]. Poly(aspartimide) Synthesis



Scheme 2.4.5.2 [91]. Formation of a Polymaleamide from a Bismaleimide and Aliphatic Diamine



Scheme 2.4.6.1.1 [167-175]. Polyimide Synthesis Utilizing Diisocyanates

LEPSIG in Austria, is reportedly produced by this method [171-173]. Requirements for the success of this reaction include the addition of trace amounts of water, tetracarboxylic acid : dianhydride ratios of 1:1-1:4, and the addition of tertiary amine catalysts. In addition, best results were obtained when solid diisocyanate was introduced to a dianhydride solution and reaction temperatures of 10-100°C were employed. The reaction is catalyzed by water [169], metal alkoxides [172], and alkali metal lactamates [173]. The catalytic effect of water has been explained as being due to hydrolysis of the moisture sensitive diisocyanate to carbon dioxide and diamine, followed by reaction of the diamine and dianhydride [175].

#### 2.4.6.2 Trimethylsilylated Diamines

*N,N'*-bis(trimethylsilyl) substituted diamines have been successfully utilized in the synthesis of a number of high temperature, high performance polymers including poly(aramide)s and poly(amide-imide)s [176-178] and polyimides [179-184 ]. Trimethylsilyl-substituted diamines react with dianhydrides at low or ambient temperatures to form soluble, high molecular weight poly(amic trimethylsilylester)s; subsequent heating effects cyclodehydration with the evolution of trimethylsilanol. A major advantage of using these diamine derivatives is increased stability relative to the free base form of the diamine.

A recent application of this method involves the successful synthesis of hydroxyl-containing polyimides from *N,N',O*-tris-

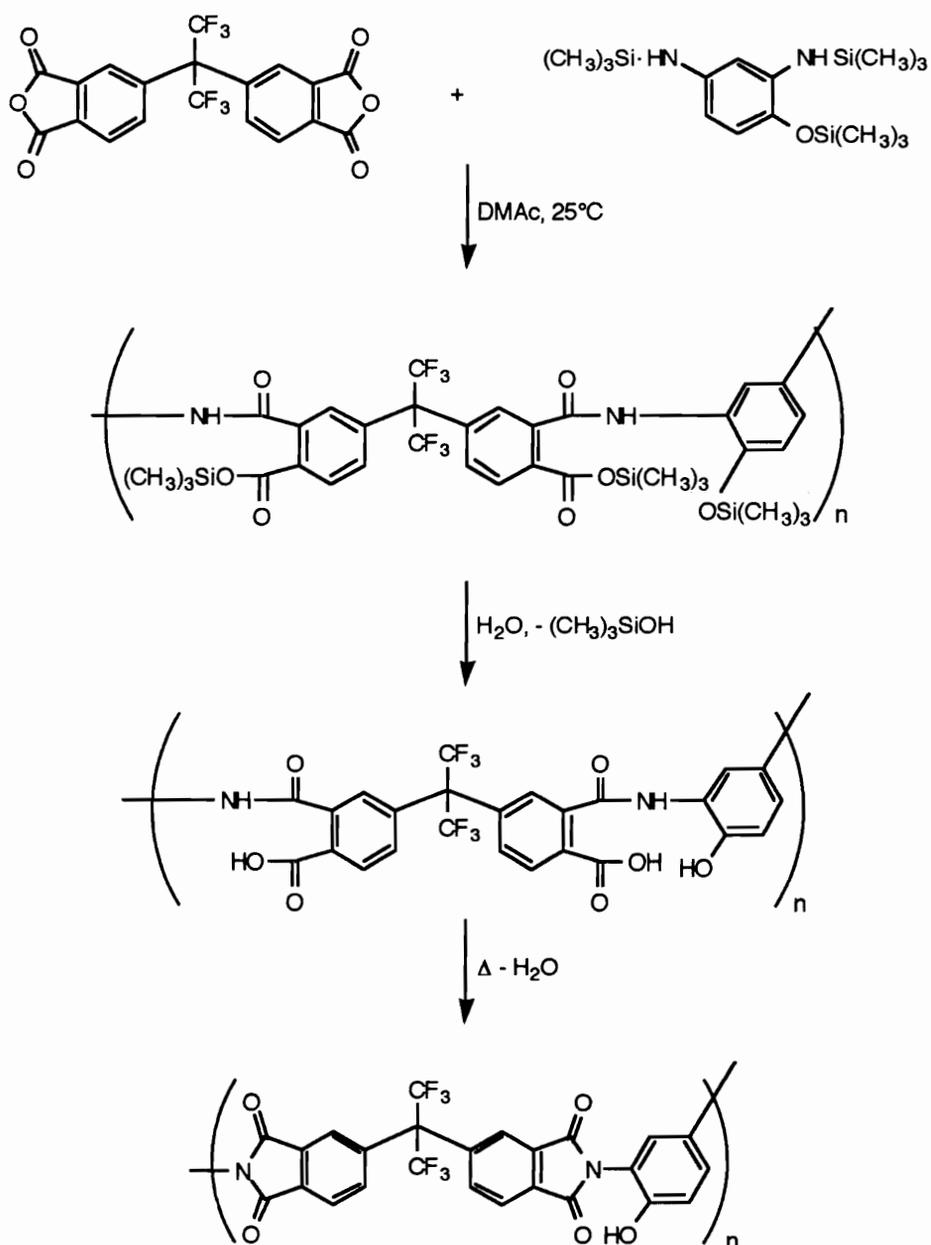
trimethylsilyl-2,4-diaminophenol [183], as shown in Scheme 2.4.6.2.1. Polyimide synthesis using 2,4-diaminophenol was not possible due to the rapid oxidation of this monomer. It has also been claimed that fully substituted diamines polymerize with dianhydrides, evolving disiloxane as a byproduct [184].

### 2.4.6.3 Diamine Dihydrochlorides

The direct use of diamine dihydrochlorides has been reported in the synthesis of polybenzothiazoles [185] and polybenzoxazoles [186] in polyphosphoric acid; upon heating the dihydrochloride salt dissociates, yielding hydrogen chloride gas and diamine which can react with an aromatic dicarboxylic acid to form the desired heterocyclic polymer as shown in Scheme 2.4.6.3.1. Interestingly, there are no reports of the direct use of diamine dihydrochlorides in polyimide synthesis. This is an alternate synthetic route which, if feasible, could offer several potential benefits over the use of diamines or other diamine derivatives. Amine hydrochlorides are generally easier to purify than their analogous free bases, have longer shelf lives and greater stability than their free base or isocyanate forms, and are less costly than trimethylsilyl derivatives.

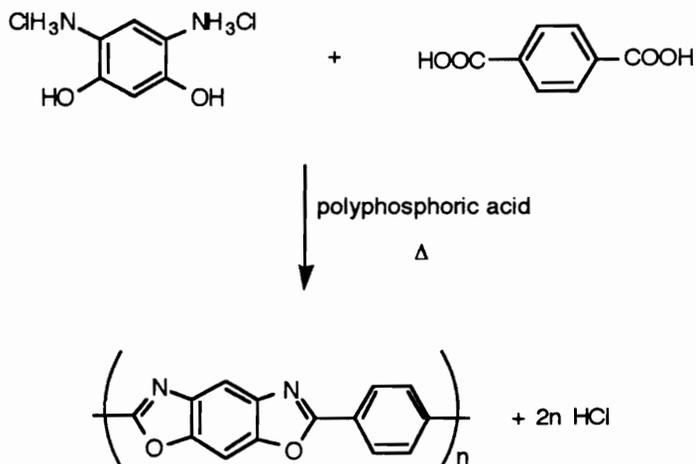
### 2.4.7 Syntheses Utilizing Dianhydride Derivatives

Polyimides may also be synthesized from dianhydride derivatives, e.g., tetracarboxylic acids or bis(*ortho*-ester-acids). The

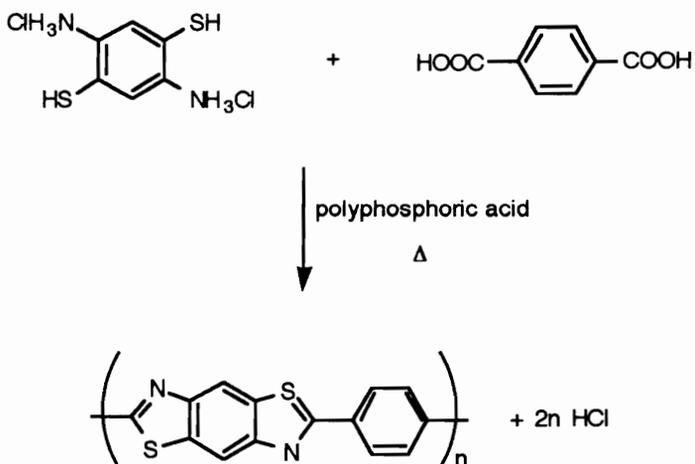


Scheme 2.4.6.2.1 [183]. Synthesis of a Soluble Polyimide from 6F Dianhydride and *N,N',O*-tris(trimethylsilyl)-2,4-diaminophenol

### Polybenzoxazole Synthesis



### Polybenzothiazole Synthesis



Scheme 2.4.6.3.1 [185, 186]. Polymer Syntheses Utilizing Diamine Dihydrochlorides

first successful polyimide synthesis utilized diester-diacid dianhydride derivatives and aliphatic diamines in a bulk polymerization [2, 3].

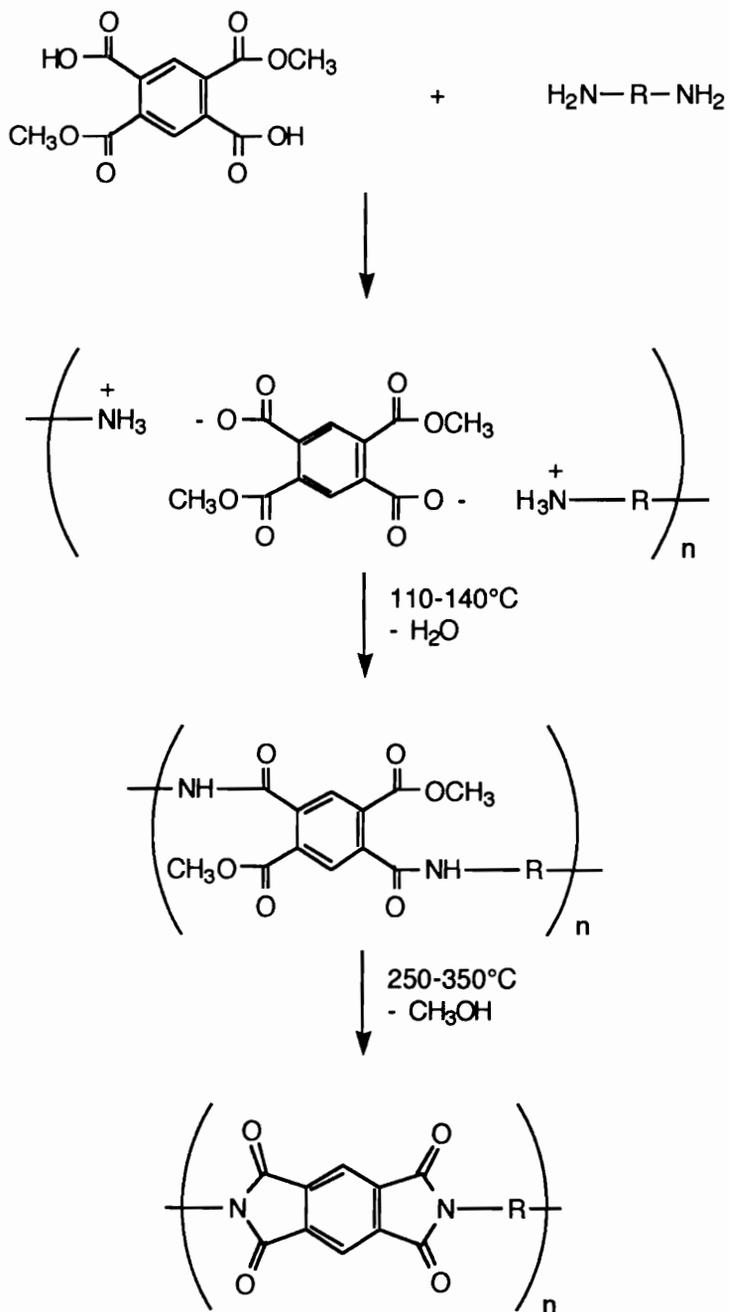
Under these conditions, the polymerization proceeds via initial formation of a salt, as in nylon synthesis; heating results in amidation and water evolution during intermediate stages followed by cyclization to polyimide at high temperatures. Scheme 2.4.7.1 illustrates this process.

Attempts to synthesize polyimides based on aromatic diamines by this route failed to afford high molecular weight polymer due to the high  $T_g$ 's and poor flow properties of fully aromatic systems and led to the development of the two-step synthesis. The bulk polymerization of diester-diacids and aromatic diamines reportedly proceeds in the same manner as when aliphatic diamines were employed; there have been claims of salt formation as the first step [187, 188] and poly(amic ester) intermediates [189].

Nevertheless, the fact that the bulk polymerization affords only low molecular weight aromatic imide oligomers has been used to great advantage in the manufacture of high temperature composites.

The process has been dubbed "PMR" for *polymerization of monomeric reactants* and utilizes calculated amounts of aromatic diester-diacid, aromatic diamine, and a suitable addition-curing endcap to afford controlled molecular weight, end-functionalized thermosetting imide oligomers [42, 190-197].

Typically, methanolic solutions containing 40-60 weight

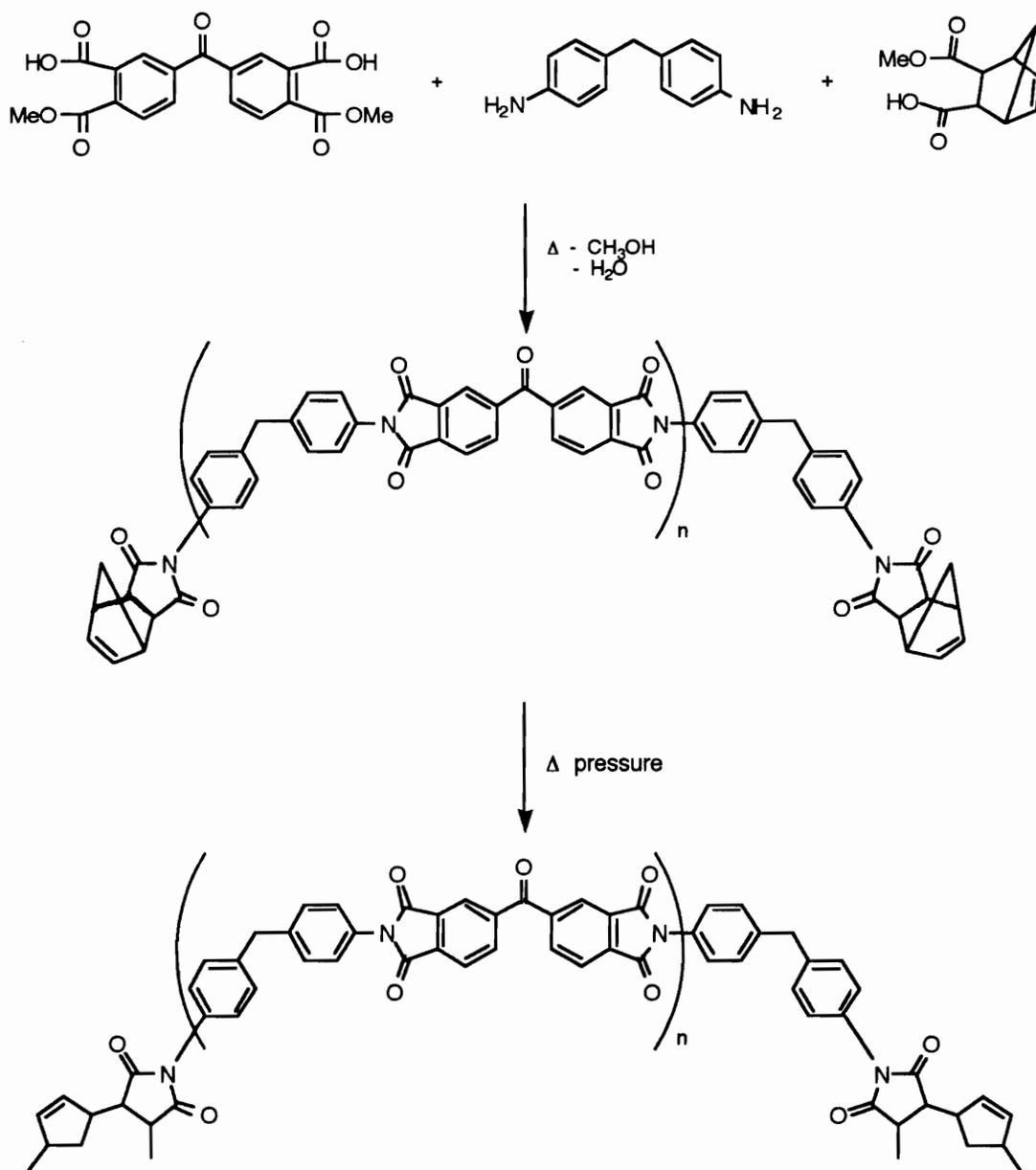


Scheme 2.4.7.1 [2, 3]. Polyimide Synthesis Via Melt Polymerization

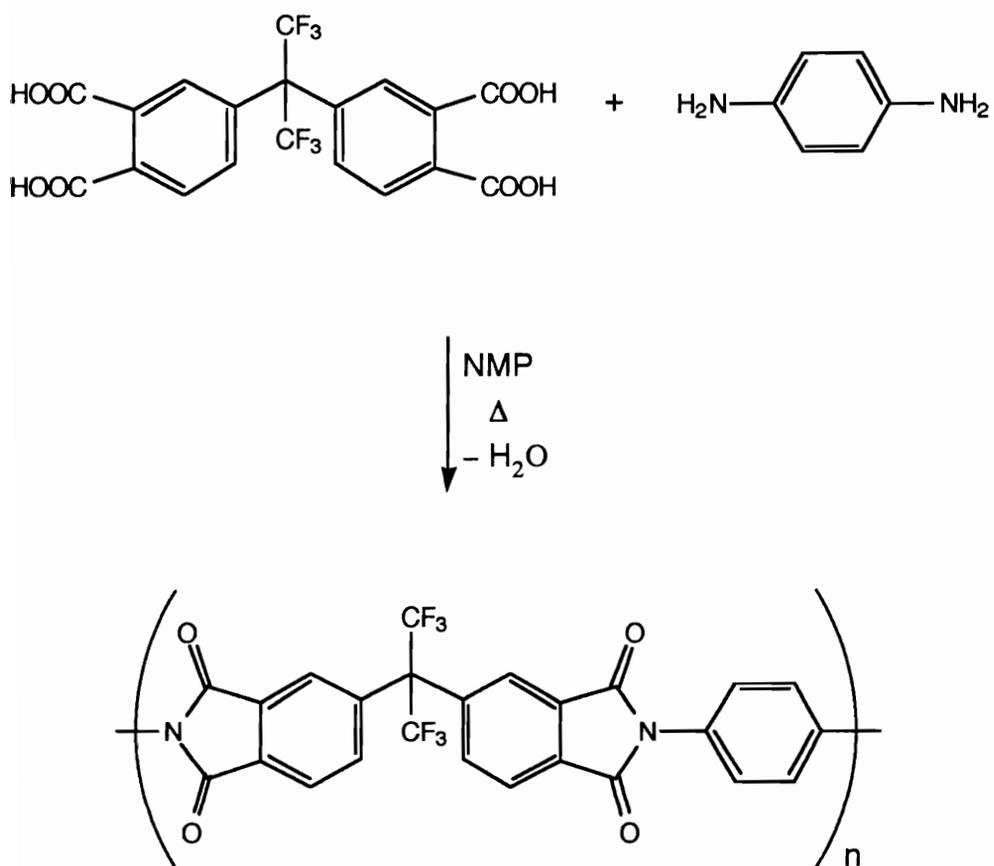
percent of monomers and endcap are used to impregnate carbon fibers; staged heating removes excess solvent and promotes polymerization, yielding functionalized amic acid-imide oligomers. At sufficiently high temperatures cyclodehydration and finally crosslinking occur to form an imide network. The processes involved in PMR chemistry are not fully understood, and the process is generally represented without intermediates as in Scheme 2.4.7.2. Soluble, high molecular weight polyimides may also be synthesized in solution from dianhydride derivatives.

This approach offers several potential advantages over the conventional "two-step" synthesis: because moisture-sensitive monomers are not employed, the "ester-acid" route should be more tolerant of water in solvents and reactors, ester-acids are more soluble in organic solvents and possibly less toxic than anhydrides, and "one pot" solution imidizations should be possible. In addition, the preparation of stable monomer solutions with good shelf lives should be possible.

DuPont produces its Avimid polyimides from 6F tetraacid, *p*-phenylenediamine and *m*-phenylenediamine in *N*-methylpyrrolidinone [198] (Scheme 2.4.7.3). Despite the successful commercial application of solution polymerizations involving dianhydride derivatives, little attention has been devoted to determination of the factors necessary for the consistent synthesis of soluble polyimides by this method. Some of the factors which should be addressed include the polymerization mechanism or identification



Scheme 2.4.7.2 [42]. PMR-15 Synthesis



Scheme 2.4.7.3 [198]. Synthesis of 6F Dianhydride-*p*-phenylenediamine Polyimide (Avimid-N)

of the reactive species, suitable solvent-cosolvent combinations and reaction temperatures, molecular weight control techniques, molecular weight distributions, extent of imidization and identification of potential side reactions.

Of these, only the reaction mechanism has been addressed, and studies of imide formation from ester-acids and amines have primarily been conducted to elucidate the processes occurring in bulk PMR systems. Among the proposed polymerization mechanisms are (1) initial salt formation as in nylon synthesis, followed by amidation and imidization, (2) attack of the amine on esters, yielding an intermediate amic acid prior to imidization, and (3) in situ regeneration of dianhydride from diester-diacid, followed by polymerization of dianhydride and diamine.

Salt formation occurs when aliphatic diamines are utilized, but despite several claims in the patent literature, it is questionable as to whether this actually occurs with aromatic diamines, considering the relatively low basicity of aromatic diamines relative to aliphatics. Sillion and coworkers observed amic acid at temperatures up to 160°C during the synthesis of polyimides from ester-acids in NMP [199]; this no doubt has contributed to the view that polymerization proceeds via initial amine-ester reaction and subsequent imidization of the amic acid intermediate. However, evidence exists which contradicts this proposed mechanism.

Diester-diacids are conveniently prepared by dissolving pure dianhydride in refluxing alcohol, but tri- and tetra-esters may be

produced as well if the ester-acid remains in alcoholic solution for extended periods of time [200, 201]. The presence of tri- and tetraesters has been associated with substandard performance in PMR composites; it has been concluded that these species in fact do not react with diamines in the desired fashion.

Through model studies, Takekoshi has recently demonstrated that this conclusion is correct [202]. Dimethyl phthalate and *p*-toluidine were co-reacted in order to determine whether *ortho*-diesters react to form the imide heterocycle and to identify possible side reactions. At temperatures below 200°C, no detectable reaction occurred; heating at 200°C for 24 hours afforded a 68 percent yield of the desired phthalimide derivative. In addition to the desired product, the reaction mixture contained unreacted dimethyl phthalate (30%) and a small amount of phthalic anhydride; *N,N*-dimethyltoluidine accounted for 32 percent of the *p*-toluidine consumed in the reaction.

The results were explained as follows: an  $S_N2$  reaction involving *p*-toluidine and dimethyl phthalate results in *O*-alkyl cleavage, yielding *N*-methyltoluidine and monomethyl phthalate; monomethyl phthalate cyclizes to phthalic anhydride with the loss of methanol. Phthalic anhydride then reacts with *p*-toluidine to form the desired imide; meanwhile, *N*-methyltoluidine undergoes an additional  $S_N2$  reaction with the diester, generating *N,N*-dimethyltoluidine and additional phthalic anhydride. The overall reaction is summarized in Scheme 2.4.7.4.

These results clearly indicate that *ortho*-dialkylesters are unreactive toward aromatic diamines at temperatures typically employed for solution imidization (below 200°C). At higher temperatures imide formation is possible, but the reaction is not quantitative and is accompanied by side reactions which yield mutually unreactive *N*-aryl-*N',N''*-dialkyl amine and anhydride end groups.

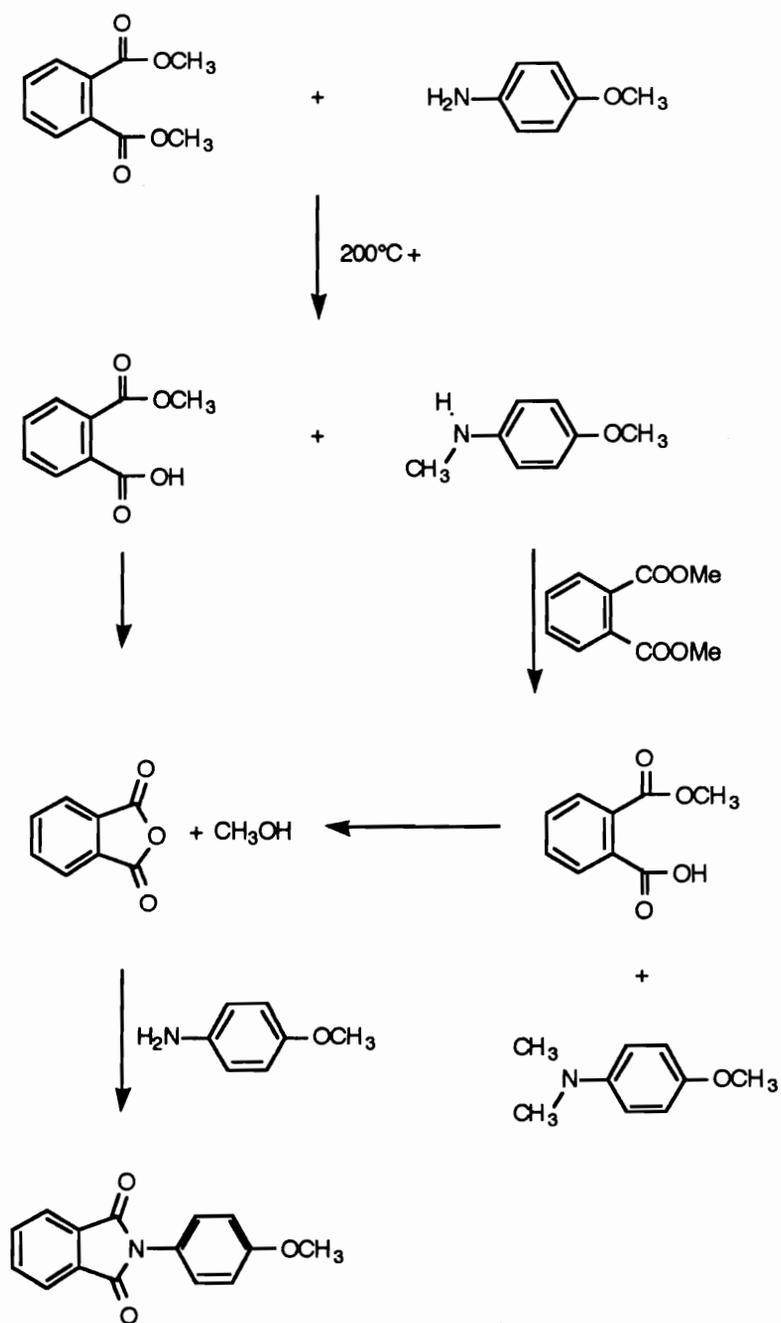
The potential formation of anhydride intermediates is significant, and most likely explains the synthesis of polyimides from dianhydride derivatives. Alston and coworkers observed the formation of phthalic anhydride at temperatures as low as 80°C in DMSO solutions of monomethyl phthalate and triethylamine [203]. Based on these results, it was concluded that the ester-acids are not the reactive species; rather, no reaction occurs until ester-acid is converted to anhydride.

The proposed mechanism is as follows: first, the ester-acid is deprotonated by the amine; next, the ester-carboxylate cyclizes, forming anhydride and alcohol. Finally, anhydride and amine react to first form amic acid and ultimately, imide and water. Scheme 2.4.7.5 illustrates the process of anhydride formation.

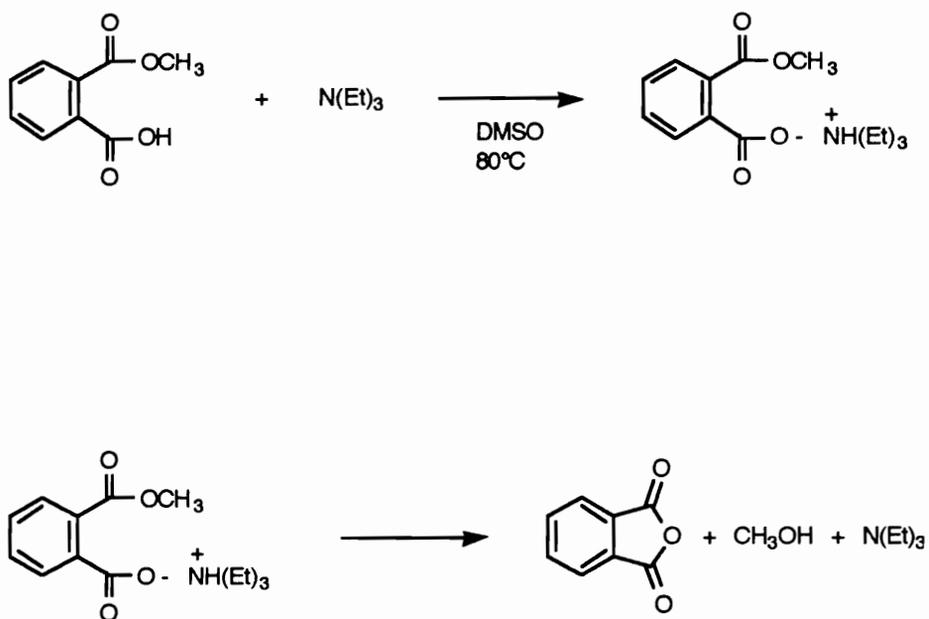
## 2.5 Thermosetting Imides

### 2.5.1 Introduction

The desirable properties of aromatic polyimides, such as low density and high mechanical strength,  $T_g$ 's and thermooxidative



Scheme 2.4.7.4 [202]. Imide Synthesis Utilizing Dimethylphthalate



Scheme 2.4.7.5 [203]. Conversion of Monomethylphthalate to Phthalic Anhydride in Solution

stability make these materials natural candidates for metal substitutes in high temperature, high performance applications, particularly aerospace applications. Substitution of organic polymers for metals in combat aircraft, for example, offers such advantages as decreased weight, which in turn may allow for greater speed and maneuverability or increased weapons and electronics payloads, or a reduced radar signature relative to metal structures.

The AV-8 Harrier, a combat jet which distinguished itself in the 1982 Falklands War and more recently in Operation Desert Storm, contains 26-27 weight percent of graphite-epoxy composite. The weight reduction afforded by the use of composite structures permits unique performance characteristics impossible in other aircraft; the Harrier can take off or land vertically or hover like a helicopter, yet is powered by but a single jet engine.

Unfortunately, the poor processability, in particular poor flow characteristics, of many high molecular weight aromatic polyimides renders them unsuitable for the fabrication of large structural components. Although low molecular weight imide oligomers possess better flow properties, they lack sufficient mechanical strength and  $T_g$ 's for high temperature structural applications. Therefore, a great deal of effort has been expended in the development of new materials and processes which combine the processability of low molecular weight imides and the performance characteristics of high molecular weight polyimides. This has been accomplished through the synthesis of controlled molecular weight, functionalized imide

oligomers which crosslink at elevated temperatures to generate imide networks.

This approach thus allows good flow and wetting properties due to low molecular weights prior to cure; subsequent generation of an infinite network results in good mechanical properties, high  $T_g$ 's due to restricted segmental motions and excellent solvent resistance (insolubility). This strategy is exemplified by the commercially successful PMR-15 system, a nadic-encapped oligomer based on benzophenonetetracarboxylic dianhydride and 4,4'-diaminodiphenylmethane [42, 190-197].

Currently, efforts are under way to identify polymeric materials which are suitable for use as composite matrix resins in the proposed High Speed Civil Transport (HCST) aircraft, which will be designed for flight speeds of Mach 2.0-2.4 [204]. Materials utilized in this aircraft will be required to retain acceptable mechanical properties through temperature extremes of -54 to 177°C (-65-350°F) for 72,000 hours. In addition, good resistance to moisture, fuels and solvents is necessary.

Projected estimates are for 75,000 pounds of composite per aircraft, with an anticipated fleet of 500 HCST's. Thus, cost effectiveness in terms of materials and processing costs will undoubtedly be a major consideration, as well as performance characteristics, in selecting suitable matrix resins.

The attractiveness of polyimides is reflected by the fact that more than two-thirds of the materials under consideration are

thermoplastic polyimides and poly(amide-imide)s or thermosetting imides; of these approximately half are thermosetting imides (bismaleimides).

In addition, there is a need to identify processable, cost effective polyimide resins capable of withstanding thousands of hours at 371°C [205]; such materials are desired for use in engine components for the next generation of fighter aircraft.

The demands of the military and the aerospace industry present unique challenges to polymer chemistry and engineering; existing materials and processes can satisfy some of the current demands, but the continued success of thermosetting imides will undoubtedly rely on the continued development of cost effective, well-designed materials with well-defined properties and improved processability.

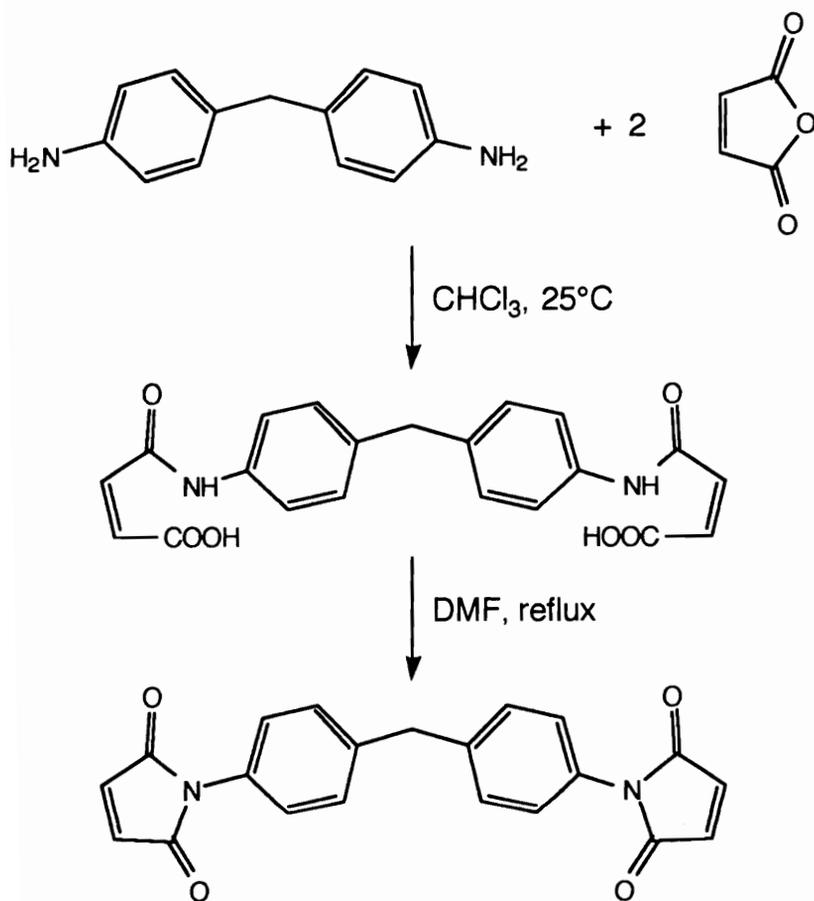
Attempts to design imide thermosets with improved properties, such as higher  $T_g$ 's, thermooxidative stability or wider processing windows, has led to the investigation of a variety of backbone structures and reactive end groups. These include bismaleimides (BMI's), nadimides, and functionalized oligomers terminated with styrene, substituted and unsubstituted acetylene end groups, paracyclophane, and biphenylene end groups. These will be discussed in the following sections.

### 2.5.2 Bismaleimides

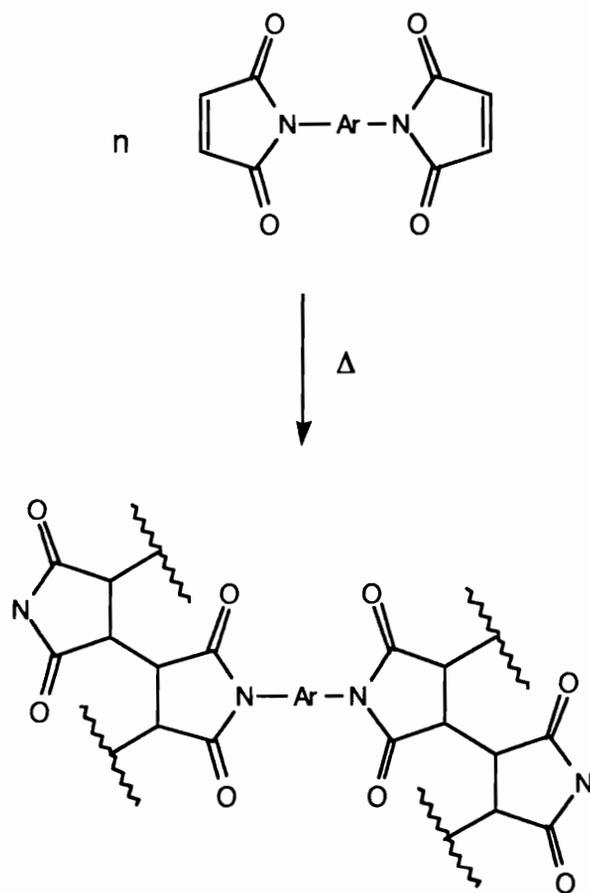
Bismaleimides (BMI's) are commonly synthesized by the reaction of an aromatic diamine with excess maleic anhydride in low boiling organic solvents such as chloroform or acetone or aromatic solvents such as toluene. The intermediate bis(amic acid) may be cyclodehydrated to the final bismaleimide by heating in N,N-dimethylformamide (DMF) or acetic acid [206-208]. Alternatively, cyclodehydration may be effected by a low temperature imidization utilizing sodium acetate in acetic anhydride [209-212]. Crosslinking occurs through the unsaturated maleimide group.

BMI's are attractive for several reasons, including ease of synthesis, relatively low cost and well-defined molecular weight. Major drawbacks include inherent brittleness due to the high crosslink density and the relatively low curing temperatures; onset of cure generally occurs at 200-210°C [41].

Significant improvements in the mechanical properties of BMI's may be realized by blending with reactive thermoplastic tougheners (poly(arylene ether sulfone)s, poly(arylene ether phosphineoxide)s and polyimides) [213]. Additionally, BMI's may be blended with non reactive thermoplastic polyimides to form semi interpenetrating networks. Prior to crosslinking, the BMI behaves as a plasticizer, depressing the  $T_g$  of the thermoplastic component and thus facilitating processing [214, 215]. Curing affords a semi-interpenetrating network with properties intermediate between those of the individual components. Other attempts to improve BMI



Scheme 2.5.2.1 [206]. Bismaleimide Synthesis



Scheme 2.5.2.2 [41]. Crosslinking of a Bismaleimide

properties have focused on lowering the melting temperatures of uncured BMI's [216] or increasing the molecular weight between crosslinks (reduction of crosslink density) [217-219]. Goldfarb and coworkers reported melting temperatures in the range of 20-215°C for BMI's based on oxyalkyl-linked diamines with aliphatic pendant substituents; final  $T_g$ 's ranged from 340-395°C [216].

Several recent reports claim the synthesis of maleimide functional oligomers via the acid-catalyzed reaction of formaldehyde with either *N*-phenylmaleimide or *N*-(4-phenoxy)-phenylmaleimide and various activated aromatic compounds including diphenylether, diphenylmethane or dibenzofuran. The polymerization yields methylene-linked maleimide functional oligomers, some of which possess  $T_g$ 's in excess of 400°C after curing [217-219].

### 2.5.3 Polyimides With In-Chain Maleimide Structures

The monomer 1,4-bis(phenylmaleic anhydride)benzene affords linear polyimides with in-chain maleimide groups [25]. In principle, thermal crosslinking of these unsaturated sites should be possible, but there are no reports of this to date. The pendant phenyl substituents, by providing a steric barrier to crosslinking, may increase the cure temperature sufficiently such that imide networks could be easily generated from linear, non-reactive endcapped polyimides without the evolution of volatiles.

## 2.5.4 PMR Resins

### 2.5.4.1 Nadimides

Perhaps the most widely utilized reactive endcap for the synthesis of functionalized polyimides is the nadimide end group. Nadimides are generated by the reaction of an amine end group with norbornene anhydride or its methyl ester-acid. The well-known, commercially and technologically important PMR-15 is an example of a nadic-endcapped thermosetting imide. The preparation of PMR systems was discussed in Section 2.4.7. Crosslinking occurs via an initial retro Diels-Alder Reaction, followed by reaction of cyclopentadiene with maleimide end groups [190, 191].

The desirable attributes of PMR-15 include good processability, physical and mechanical properties, acceptable thermal stability (for 316°C or 600°F applications), an established data base, cost competitiveness, and availability from multiple sources [42].

However, there are disadvantages associated with the nadic end group. Blisters and voids may be present in finished composites due to the evolution of cyclopentadiene during cure [192]. In addition, the nadic endcap has been associated with the high temperature decomposition of PMR-15. Several studies conducted at the NASA Lewis Research Center have confirmed that long-term isothermal stability improves with decreasing nadic end group concentration (increasing molecular weight between crosslinks) [194-197]. Decomposition reportedly begins with cleavage of the methylene bridge of the nadic end group [192, 197].

#### 2.5.4.2 Additional PMR Resins

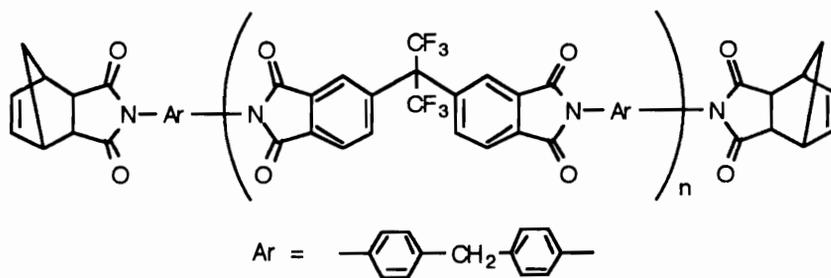
In addition to decreasing end group concentration, efforts to improve the processability and final properties of PMR resins have focused on replacement of either or both monomers and/or end group with more stable substitutes. For example, Sillion and coworkers have reported on the synthesis of a PMR-15 analog in which 6F dianhydride was substituted for the usual benzophenone tetracarboxylic dianhydride. Prior to crosslinking the oligomers are soluble in organic solvents, and the synthesis was in fact performed in refluxing diglyme [220].

Similarly, researchers at NASA Lewis have investigated the properties of PMR nadic-capped resins based on the soluble Avimid systems (6F dianhydride and *p*-phenylene diamine); these systems, designated PMR-II's, reportedly display thermooxidative stability equivalent to that of PMR-15 as determined by isothermal weight loss. However, they possess sufficiently high  $T_g$ 's such that 371°C (700°F) applications should be possible [195]. VCAP-75 is similarly based on 6F dianhydride and *p*-phenylene diamine but employs *p*-aminostyrene as an end cap instead of the usual norbornene ester-acid, thus affording styrene- functionalized imide oligomers. VCAP resins reportedly display better thermal stability than the corresponding PMR-II resins, suggesting that the styrene end groups afford more thermally stable crosslinks [221, 222]. Styrene end groups offer an additional advantage in that cure proceeds without evolution of volatiles.

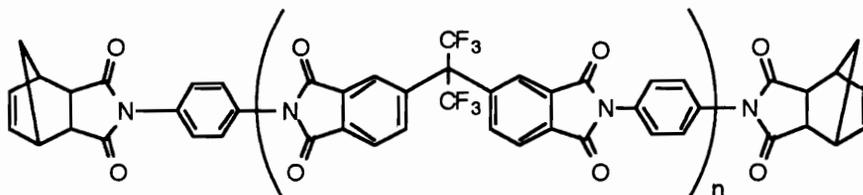
Recently, the substitution of benzonorbornadienyl for norbornenyl end groups in PMR systems has been reported [223]. PMR-15 analogs utilizing this end cap were found to soften and crosslink at temperatures approximately 50°C higher than the corresponding values for commercial PMR-15 (225°C and 300°C, respectively). In addition, isothermal weight loss after 1000 hours at 316°C was comparable to PMR-15. Although the mechanism of the crosslinking reaction has not yet been determined, no evidence of a Retro Diels-Alder Reaction was observed, i.e., no cyclopentadiene evolved during cure. The benzonorbornadienyl end group may in principle offer several advantages over the more conventional nadic or norbornenyl end group; the higher cure temperature affords a wider processing window for the conventional BTDA-MDA based resins or may permit the successful preparation of higher  $T_g$  systems, and the absence of volatiles evolution during cure should greatly reduce the problem of bubbling and void formation relative to nadic-functionalized imides. Miscellaneous PMR systems are illustrated in Figure 2.5.4.2.1.

### 2.5.5 Acetylene-Functionalized Imides

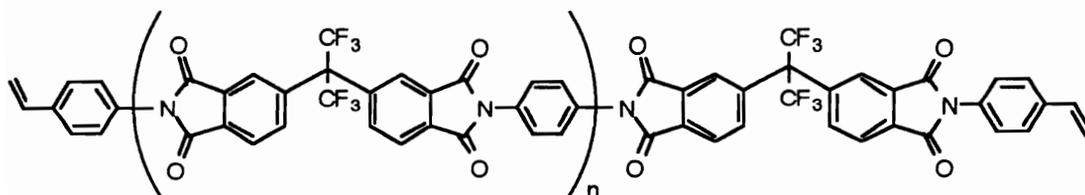
Acetylene (ethynyl) groups are also known to undergo thermal crosslinking reactions and have been incorporated as pendant or terminal reactive functionalities into a number of polymers, including poly(arylene ether-ketone)s [224], poly(arylene ether-sulfone)s [225, 226], polyquinoxalines and polyphenylquinoxalines



Nadic-functionalized 6F-4,4'-methylene dianiline polyimide [220]



PMR-II [195]



VCAP [221]

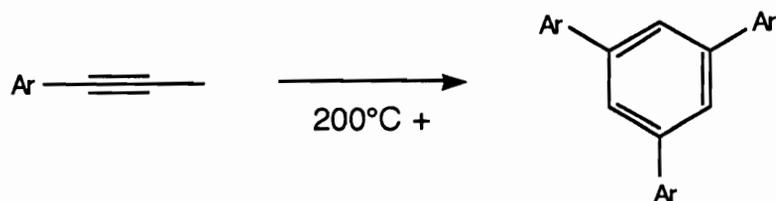
Figure 2.5.4.2.1. Miscellaneous PMR Resins

[227, 228], poly(iminolactone)s [145, 146], polyaspartimides [229] and aromatic polyimides [230-245].

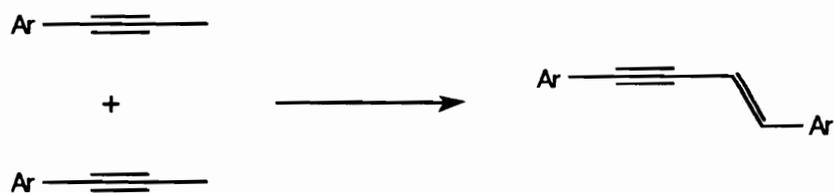
Although ethynyl-functionalized imides were first reported nearly twenty years ago, the crosslinking of terminal ethynyl groups still is not fully understood. Early investigators believed that crosslinking occurred by simple cyclotrimerization to form an aromatic crosslink, as shown in Scheme 2.5.5.1 [243]. Subsequent studies suggested that crosslinking does not occur in such a simple, straightforward manner. Additional investigations indeed indicated increased aromatic content after cure; however, it was estimated that no more than 30% of the end groups underwent cyclotrimerization, while the remainder underwent other addition reactions [237, 238, 240]. Alkene end group intermediates have been claimed [239], and end group coupling to form ene-yne and yne-yne structures, followed by rearrangement and aromatization, have been proposed as curing reactions [240, 242, 245]. These structures are shown in Figure 2.5.5.1.

Recent studies reveal the complexity of the curing process in ethynyl functionalized imides; in a recent  $^{13}\text{C}$  NMR study of acetylene cure several cure products were detected, including aromatic groups, polycyclic aromatic structures (naphthalene and phenanthrene), and bridged structures presumably resulting from electrophilic addition of ethynyl groups to backbone aromatic rings [234]. A recent FTIR cure study of ethynyl-functionalized imide

### Cyclotrimerization [243]



### Formation of Ene-yne Intermediates [240]

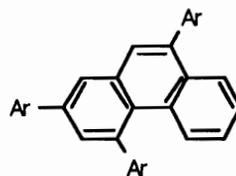
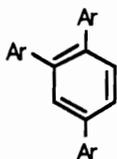
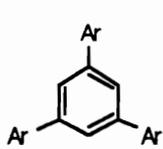


Scheme 2.5.5.1. Proposed Crosslinking Reactions of Ethynyl End Groups

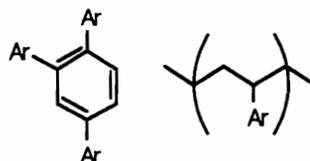
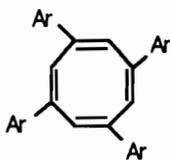
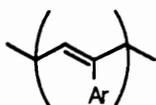
### Reaction mechanism and products

### Further reaction or degradation products

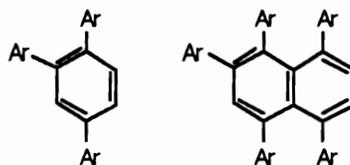
#### Cyclotrimerization



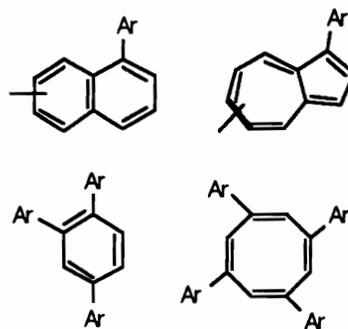
#### Biradical Mechanisms



#### Glaser Coupling



#### Strauss Coupling



#### Electrophilic Addition

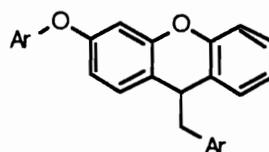
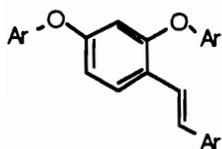


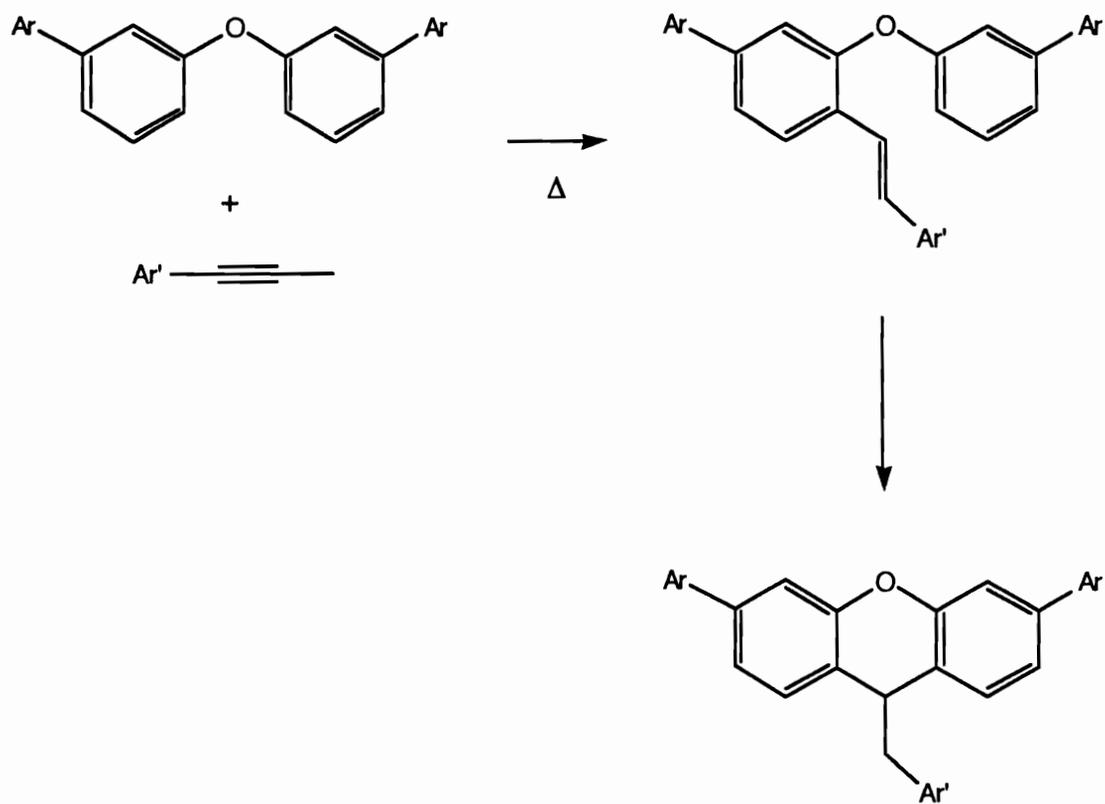
Figure 2.5.5.1 [234]. Acetylene Cure Reactions and Products

oligomers indicated no apparent cyclotrimerization or aromatization; rather, crosslinking occurred exclusively by electrophilic addition of ethynyl end groups to backbone aromatic rings, as depicted in Scheme 2.5.5.2 [233].

Crosslinking begins at temperatures in excess of 200°C and occurs rapidly without the evolution of volatiles; depletion of ethynyl functions reportedly occurs within 30 minutes at 240°C [233], and a gel time of less than 3 minutes at 250°C has been reported for Thermid MC-600, an ethynyl-terminated imide oligomer based on benzophenone tetracarboxylic dianhydride and 1,3-bis-(3-aminophenoxy)benzene [236].

The fact that cure proceeds without generation of volatiles is of course advantageous in composite applications, however, the relatively low cure temperature and high end group concentration of early ethynyl functionalized imide oligomers caused processing problems; good flow and wetting behavior of the resin was hampered by preliminary reactions of the end groups during cure, preventing adequate contact with substrates [231].

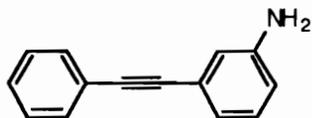
Two approaches have been devised to circumvent this problem; one approach involves the use of acetylene-functionalized iminolactone (isoimide) oligomers, which display lower  $T_g$ 's than their imide analogs and undergo both crosslinking and isomerization to imide at elevated temperatures [145, 146]. National Starch and Chemical Company produces such resins commercially.



Scheme 2.5.5.2 [233]. Electrophilic Addition of an Ethynyl End Group to an Aromatic Polymer Backbone

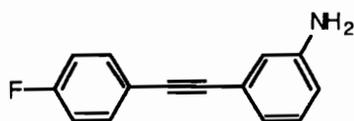
3-ethynylaniline derivative

Cure Temperature, °C



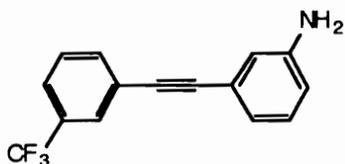
332

3-phenylethynylaniline



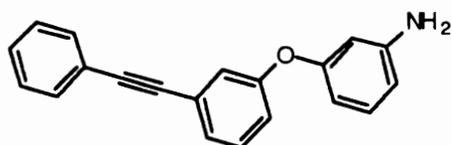
343

3-(4-fluorophenylethynyl)aniline



343

3-(3-(trifluoromethyl)phenylethynyl)aniline



303

3-(3-(phenylethynyl)phenoxy)aniline

Figure 2.5.5.2 [246]. Derivatives of 3-ethynylaniline

Another approach employs substituted derivatives of 3-ethynylaniline (*m*-aminophenylacetylene); several of these are depicted in Figure 2.5.5.2 [246]. Replacement of the ethynyl proton with phenyl or substituted phenyl substituents dramatically raises the cure temperature, thus insuring solvent removal prior to crosslinking, affording a wider processing window and permitting the use of higher T<sub>g</sub> imide backbones. Phenylethynylaniline may be a promising high temperature curing end group for 700°F (371°C) imide thermosets, particularly if it can be produced inexpensively.

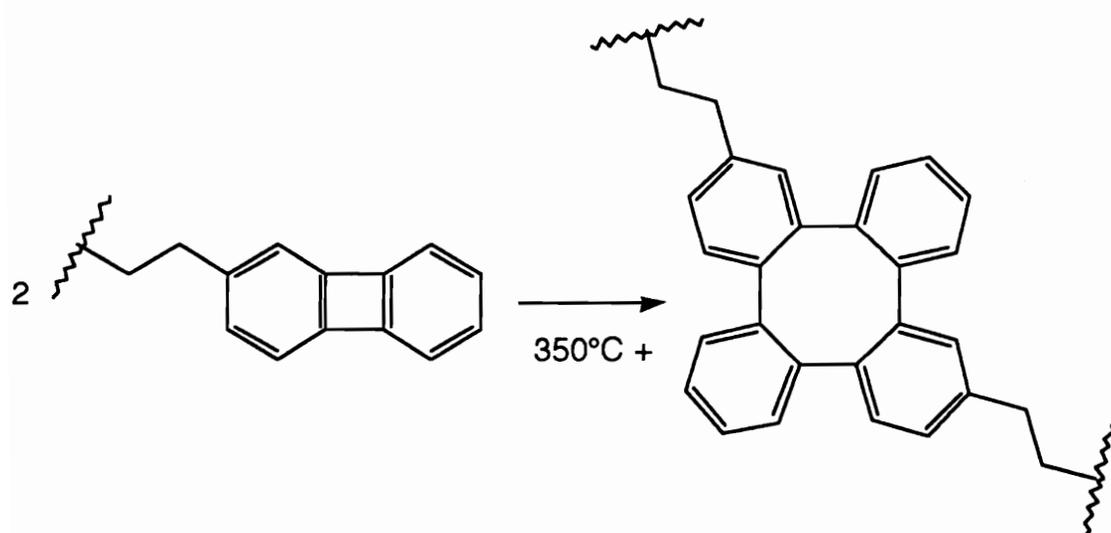
Although a detailed study of end group structure versus cure temperature was not conducted for these compounds, several trends are apparent. First, phenyl substitution increases cure temperature by well over 100°C; the bulk of the terminal phenyl substituent undoubtedly hinders mutual end group reaction. Second, incorporation of a "flexible link" into the end group, as in 3-(3-(phenylethynyl)phenoxy)aniline, serves to again lower cure temperature. Such a structure provides additional mobility to the end groups, thus promoting a favorable orientation of end groups for crosslinking. Third and last, it appears that phenyl substituents bearing electron withdrawing groups further raise cure temperature relative to the unsubstituted phenyl substituent. However, the temperature increase is small, on the order of 10°C, and it cannot be claimed with certainty that electron donating groups would lower cure temperature as no such compounds were reported.

### 2.5.6 Additional High Temperature Curing End Groups: Biphenylene and Paracyclophane

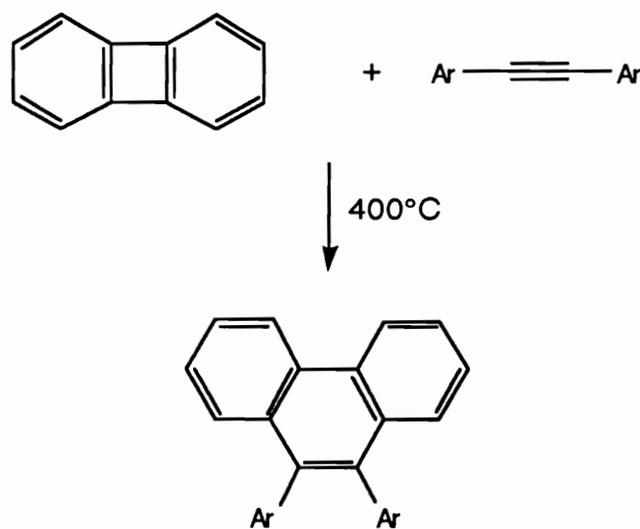
Biphenylene has been employed as a reactive end group in poly(phenylquinoxaline)s [247] and polyimides [248-251]. Biphenylene undergoes ring opening at temperatures above 350°C and further reaction ensues without volatiles evolution; however, crosslinking efficiency is low. The majority of endgroups dimerize, resulting in a chain extended, lightly crosslinked network system as shown in Scheme 2.5.6.1 [247-250]. Better results have been achieved by the co-curing of blends of biphenylene-functionalized polyimides with polyimides containing in-chain (internal) acetylene linkages; the terminal biphenylene groups and internal acetylenes coreact at temperatures of 350-400°C to form phenanthrene crosslinks, as illustrated in Scheme 2.5.6.2 [250, 251].

Paracyclophane has also been investigated as a potential high temperature curing end group; paracyclophane-functionalized polyquinolines [252, 253] and polyimides have been reported [254, 255]. Paracyclophane reportedly polymerizes at temperatures in excess of 250°C [255] without the evolution of volatiles [256-259].

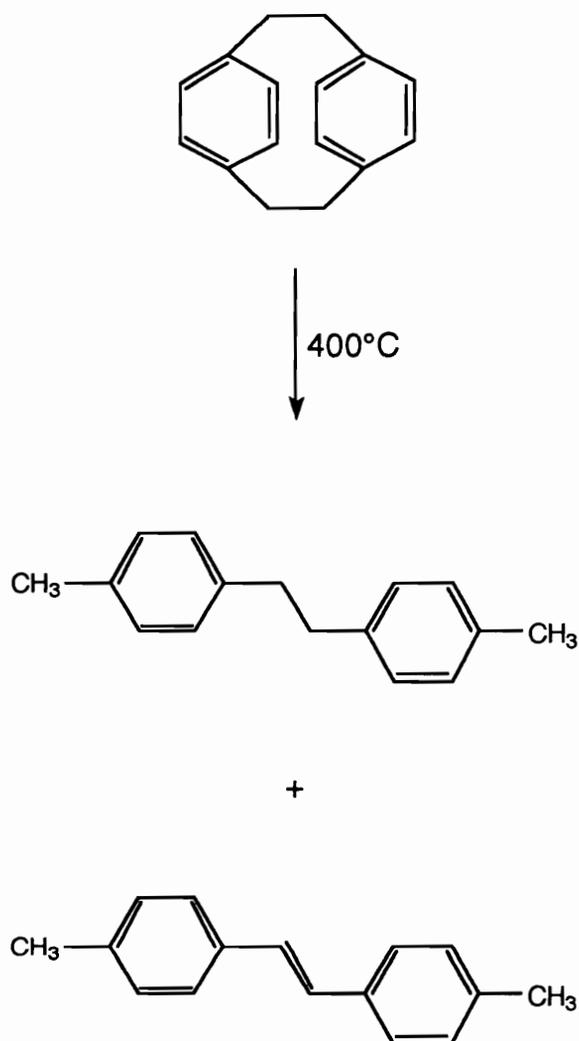
The exact crosslinking mechanism of paracyclophane-functionalized imides is not known, but thermolysis studies of [2.2]-paracyclophane provide insight into the possible identities of reactive intermediates. Cram found that heating [2.2]-paracyclophane at 400°C yielded both 4,4'-dimethylbibenzyl and 4,4'-dimethylstilbene (Scheme 2.5.6.3) [260]; homolytic cleavage of



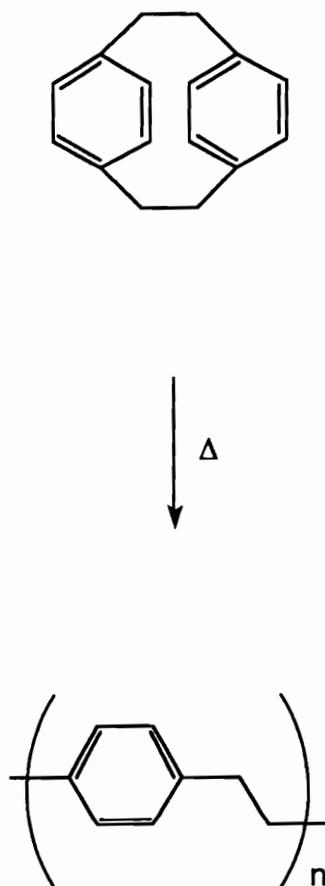
Scheme 2.5.6.1 [247]. Biphenylene Dimerization



Scheme 2.5.6.2 [250]. Crosslinking of Terminal Biphenylene and Internal Acetylene



Scheme 2.5.6.3 [260]. Thermal Decomposition of [2.2]-Paracyclophane



Scheme 2.5.6.4 [259, 261]. Polymerization of [2.2]-Paracyclophane

an ethylene bridge followed by hydrogen abstraction by methylene radicals would account for these products. Crosslinking via coupling of radical end groups has been proposed regarding the cyclophane-functionalized imides [260], however, reaction of unsaturated end groups generated at high temperatures is also a possibility. In addition to high temperature thermolysis which yields 4,4'-dimethylbibenzyl and 4,4'-dimethylstilbene, [2.2]-paracyclophane can polymerize as shown in Scheme 2.5.6.4 [259, 261]. Currently, biphenylene and paracyclophane functionalized imide resins are not commercially significant and are primarily of academic interest.

### III. EXPERIMENTAL

#### 3.1 Reagents and Purification

In order to synthesize polyimides of high molecular weight and controlled molecular weight functionalized oligomers, it was necessary to obtain extremely pure starting materials and solvents. For this reason, reagents and monomers were carefully purified by various techniques, including recrystallization, distillation or sublimation as necessary. Polymerization solvents were distilled from dehydrating agents under reduced pressure. In all distillations the constant boiling middle fraction was collected and stored in a round bottom boiling flask sealed with a rubber septum. Dried solvents were subsequently handled using syringe techniques.

##### 3.1.1 Solvents

3.1.1.1 Acetone (Fisher) was received as an HPLC grade solvent and was not further purified (bp = 56.5°C).

3.1.1.2 Ethanol (absolute) (AAPER Alcohol and Chemical) was used as received (bp = 78.5°C).

3.1.1.3 Methanol (Fisher) was received as an HPLC grade solvent and was not further purified (bp = 64.7°C).

3.1.1.4 2-Propanol (Fisher) was used as received (bp = 82.5°C).

3.1.1.5 Chloroform (Fisher) was used as received (bp = 61-62°C).

3.1.1.6 Chlorobenzene (Fisher) was distilled prior to use using a simple distillation apparatus (bp = 131-132°C).

3.1.1.7 *o*-Dichlorobenzene (Fisher) was distilled prior to use using a simple distillation apparatus (bp = 180.5°C).

3.1.1.8 Dichloromethane (Fisher) was used as received (bp = 39.8°C).

3.1.1.9 Diethyl ether (Fisher) was used as received (bp = 34.6°C).

3.1.1.10 *m*-Cresol (Fisher) was dried by stirring over crushed calcium hydride for 12 hours. The dried solvent was then distilled under nitrogen (bp = 200-202°C).

3.1.1.11 *N,N*-dimethylacetamide (DMAc: Fisher) was dried by stirring over crushed calcium hydride for 12 hours. The dried solvent was then distilled under reduced pressure generated by a mechanical vacuum pump (bp = 163-165°C; bp = 96°C at 80 Torr).

3.1.1.12 *N*-methylpyrrolidinone (NMP: Fisher) was dried by stirring over crushed calcium hydride for 12 hours. The dried solvent was then distilled under reduced pressure generated by a mechanical

vacuum pump to avoid solvent decomposition (bp = 200-202°C; bp = 154-156 at 80 Torr).

3.1.1.13 Tetrahydrofuran (THF: Fisher) was used as received (bp = 66°C).

3.1.1.14 Toluene (Fisher) was distilled prior to use (bp = 110.6°C).

### 3.1.2 Monofunctional Amines

3.1.2.1 Aniline (Fisher) was received as an impure yellow liquid, which was purified by distillation under nitrogen (bp = 184-186°C).

3.1.2.2 3-Ethynylaniline (*m*-aminophenylacetylene: Eastman Kodak) was received as an impure yellow liquid, which was readily purified by vacuum distillation (bp = 126-128°C at 50 Torr).

3.1.2.3 Triethylamine (Aldrich) was received as an HPLC grade solvent and was used without further purification (bp = 89-90°C).

3.1.2.4 Pyridine (Aldrich) was received as an HPLC grade solvent and was used without further purification (bp = 114-115°C).

### 3.1.3 Carboxylic Acids and Derivatives

3.1.3.1 Benzoic acid (Eastman Kodak) was recrystallized from ethanol prior to use (mp = 121-122°C)

3.1.3.2 p-Chlorobenzoic acid (Aldrich) was recrystallized from ethanol prior to use (mp = 241-243°C).

3.1.3.3 Phenyl benzoate (Aldrich) was recrystallized from ethanol prior to use (mp = 68-70°C).

3.1.3.4 Phthalic anhydride (PA: Aldrich) was received in 99 percent purity. Pure material was obtained via vacuum sublimation, using a pressure of approximately 50 Torr. Thus, crude PA was placed in the bottom of a sublimator and the cold finger was filled with a dry ice/isopropanol mixture. The temperature was then raised to 110°C, at which time white crystals of PA began to collect on the cold finger. After approximately three hours the accumulated crystals were scraped from the cold finger, vacuum dried at room temperature for 8 hours, placed in a glass bottle and stored in a dessicator (mp = 130-131°C).

3.1.3.5 Diethyl phthalate (Aldrich) was distilled prior to use (bp = 293-295°C)

3.1.3.6 Monoethyl phthalate was prepared by dissolving pure phthalic anhydride in excess refluxing ethanol (10 ml per gram). Esterification was monitored via FTIR by the disappearance of anhydride absorbances. Complete dissolution of PA coincided with formation of its' half-ethyl ester; heating was continued to remove excess ethanol (mp = 2°C)

### 3.1.4 Monomers

#### Diamines

3.1.4.1 1,4-bis(2-(4-aminophenyl)isopropyl)benzene (Bisaniline P, Bis P: Shell) was obtained in high purity, but recrystallization from toluene was required to obtain monomer grade material. Thus, 100 g of Bis P was added to a 2000 ml Erlenmeyer flask and rinsed in with 800 ml of toluene. With stirring, the mixture was heated to boiling on a hot plate/stirrer. Upon solvation of Bis P, 4 g decolorizing carbon was added in approximately 0.5 g increments; the mixture was allowed to continue stirring for 10 minutes. The mixture was vacuum filtered while hot through Celite. The resulting orange-yellow solution was immediately transferred to a 2000 ml Erlenmeyer flask and again heated with stirring. Charcoal treatment and vacuum filtration through Celite was repeated, affording a pale yellow solution which was allowed to cool to room temperature without agitation. The recrystallizing Bis P was left undisturbed for 8 hours; recrystallized Bis P was isolated as a white powder via vacuum filtration, air dried 3 hours and finally vacuum dried for 12

hours at 100°C. The monomer was then placed in a brown glass bottle and stored in a dessicator (mp = 163-165°C)

3.1.4.2 Bis(3-aminophenoxy-4'-phenyl)phenylphosphine oxide (*m*-BAPPO) was synthesized and purified according to reported procedures (mp = 72-74°C; literature mp = 72-74°C) [262].

3.1.4.3 1,4-bis(4-aminophenoxy)benzene (TPE-Q; Kennedy & Klim) was obtained as a polymerization grade monomer and was used without further purification (mp = 170-172°C).

3.1.4.4 4,4'-bis(4-aminophenoxy)biphenyl (BAP-B; Kennedy & Klim) was obtained as a polymerization grade monomer and was used without further purification (mp = 198-200°C).

3.1.4.5 4,4'-bis(3-aminophenoxy)diphenylsulfone (*m*-BAPS; Kennedy & Klim) was obtained as a fine white powder in high purity, however, recrystallization from deoxygenated ethanol was required to obtain monomer grade material. Thus, 200 ml absolute ethanol was poured into a 500 ml Erlenmeyer flask and purged with nitrogen for 5-6 hours. With stirring, the methanol was heated to boiling and 20 g of *m*-BAPS was added in portions. Upon dissolution of *m*-BAPS the solution was vacuum filtered hot, and the solution was allowed to cool to room temperature, then placed in a freezer for 8 hours. *m*-

BAPS crystallized as a fine white powder, which was air dried and then vacuum dried at 70°C for 12 hours (mp = 134-135°C).

3.1.4.6 4,4'-bis(4-aminophenoxy)diphenylsulfone (*p*-BAPS: Kennedy & Klim) was obtained as a fine white powder in high purity; however, recrystallization from deoxygenated acetone was required to obtain monomer grade material. Thus, 400 ml acetone was poured into a 1000 ml Erlenmeyer flask and purged with nitrogen for 5-6 hours. With stirring, the acetone was heated to boiling and 20 g of *p*-BAPS was added in portions. Upon dissolution of *p*-BAPS the solution was vacuum filtered hot, and the solution was allowed to cool to room temperature, then placed in a freezer for 8 hours. *p*-BAPS crystallized as a fine white powder, which was air dried and then vacuum dried at 70°C for 12 hours (mp = 186-188°C).

3.1.4.7 9,9-bis(4-aminophenyl)fluorene (FDA: Kennedy & Klim) was obtained as a polymerization grade monomer and was used without further purification (mp = 235-237°C).

3.1.4.8 1,4-cyclohexanediamine (Aldrich) was received as a 98% pure mixture of cis/trans isomers in a ratio of 80:20 and was used as received (bp = 179-181°C).

3.1.4.9 3,3'-dimethylbenzidine (3,3'-DMB, *o*-tolidine: TCI America) was obtained as a fine off-white powder and was purified in the same manner as Bis P (mp = 127-129°C).

3.1.4.10 3,3',5,5'-tetramethylbenzidine (3,3',5,5'-TMB: TCI America) was obtained as a fine off-white powder and was purified in the same manner as Bis P (mp = 167-169°C).

3.1.4.11 4,4'-diaminodiphenylether (4,4'-oxydianiline, 4,4'-ODA: Kennedy & Klim) was received as a light brown powder, 99% pure. Monomer grade material was obtained via vacuum sublimation. Thus, crude ODA was placed in the bottom of a sublimator and the cold finger was filled with a dry ice/isopropanol mixture. The temperature was then raised to 180-190°C, at which time white crystals of ODA began to collect on the cold finger. After approximately three hours the accumulated crystals were scraped from the cold finger, vacuum dried and stored under nitrogen in a brown glass bottle (mp = 190-192°C).

3.1.4.12 4,4'-diaminodiphenylmethane (4,4'-methylenedianiline, 4,4'-MDA: Aldrich) was received as impure dark yellow pellets. Purification was identical to the procedure used for Bis P, except benzene was substituted for toluene and MDA was vacuum dried at 50°C (mp = 89-91°C).

3.1.4.13 3,3'-diaminodiphenylsulfone (3,3'-DDS: Aldrich) was received as a fine white powder of 99% purity. Recrystallization from deoxygenated absolute ethanol yielded monomer grade material. Thus, 500 ml ethanol was poured into a 1000 ml Erlenmeyer flask and purged with nitrogen for 5-6 hours. With stirring, the ethanol was heated to boiling and 50 g of 3,3'-DDS was added in portions. Upon dissolution of DDS 3-4 g decolorizing carbon was added, and the mixture was allowed to continue stirring for 15 minutes, after which it was vacuum filtered hot through a Celite bed. Charcoal treatment and filtration through Celite was repeated; the resulting pale yellow solution was allowed to cool slowly to room temperature and was then placed in a freezer for 8 hours to induce crystallization. Recrystallized DDS was isolated as a fine pale yellow powder via vacuum filtration; after air drying the monomer was vacuum dried at 70°C for 12 hours (mp = 171-172°C).

3.1.4.14 4,4'-diaminodiphenylsulfone (4,4'-DDS: Chriskev) was received as a fine white powder in high purity, however, recrystallization from deoxygenated methanol was required to obtain monomer grade material. Thus, 500 ml methanol was poured into a 1000 ml Erlenmeyer flask and purged with nitrogen for 5-6 hours. With stirring, the methanol was heated to boiling and 40 g of 4,4'-DDS was added in portions. Upon dissolution of 4,4'-DDS the solution was vacuum filtered hot, and the solution was allowed to cool to room temperature. 4,4'-DDS crystallized as a white powder, which

was air dried and then vacuum dried at 70°C for 12 hours (mp = 176-177°C).

3.1.4.15 Diaminoresorcinol dihydrochloride (Dow Chemical) was obtained as a polymerization grade monomer and was used without further purification.

3.1.4.16 p-Phenylenediamine (*p*-PDA: Aldrich) was received as dark colored flakes. Monomer grade material was obtained via vacuum sublimation at approximately 50 Torr. Thus, crude PDA was placed in the bottom of a sublimator and the cold finger was filled with a dry ice/isopropanol mixture. The temperature was then raised to 110-120°C, at which time white crystals of PDA began to collect on the cold finger. After approximately three hours the accumulated crystals were scraped from the cold finger, and resublimed twice for a total of three sublimations. PDA was then vacuum dried at 25°C for 8 hours and stored under nitrogen in a brown glass bottle covered with aluminum foil. PDA was used within 3-4 days after purification (mp = 145-147°C).

3.1.4.17 p-Phenylenediamine dihydrochloride was prepared by treating PDA with concentrated hydrochloric acid. Thus, 11 g pure PDA were placed in a 250 ml Erlenmeyer flask, followed by 125 ml deionized water; with stirring, 17 ml concentrated hydrochloric acid was slowly added and the mixture was heated to 75-80°C. Upon

solvation of the salt 1 g decolorizing carbon was added and the solution was allowed to continue stirring for 15 minutes; while still hot, the solution was vacuum filtered through a Celite bed. The resulting pale yellow solution was immediately transferred to a 250 ml separatory funnel and dripped slowly with stirring into a 1000 ml Erlenmeyer flask containing 800 ml acetone. Via vacuum filtration PDA dihydrochloride was isolated as a white powder, which was washed with acetone, air dried and vacuum dried at 80°C for 12 hours. After drying, PDA dihydrochloride was stored under nitrogen in a foil-covered brown glass bottle and placed in a dessicator.

3.1.4.18 p-Xylylenediamine (Aldrich) was received as a 99% pure pale yellow crystalline solid which was used as received (mp = 62-64°C).

#### Dianhydrides

3.1.4.19 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA: Allco Chemical) was obtained as a fine white powder of monomer grade purity. BTDA was placed in a vacuum oven at 150°C for 12 hours prior to use to insure cyclodehydration to anhydride of any existing ortho dicarboxylic functionalities. No further purification was deemed necessary (mp = 224-226°C).

3.1.4.20 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA: Chriskev) was obtained as a fine white powder of monomer grade

purity. BPDA was placed in a vacuum oven at 150°C for 12 hours prior to use. No further purification was deemed necessary (mp = 298-300°C).

3.1.4.21 3,3',4,4'-Oxydiphthalic anhydride (ODPA: Oxychem) was obtained as a fine white powder of monomer grade purity. ODPA was placed in a vacuum oven at 150°C for 12 hours prior to use. No further purification was deemed necessary (mp = 225-227°C).

3.1.4.22 Pyromellitic dianhydride (PMDA: Allco Chemical) was obtained as fine white granular crystals of monomer grade purity. PMDA was placed in a vacuum oven at 150°C for 12 hours prior to use. No further purification was deemed necessary (mp = 284 - 286°C )

3.1.4.23 2,2-bis-(3,4-dicarboxyphenyl)hexafluoropropane Dianhydride (6F: Hoechst Celanese) was obtained as fine white granular crystals of ultra pure, electronic grade purity. 6FDA was placed in a vacuum oven at 150°C for 12 hours prior to use. No further purification was deemed necessary (mp = 245-247°C)

3.1.4.24 3,3',4,4'-diphenylsulfonedianhydride (DSDA: Chriskev) was obtained as a fine white powder of monomer grade purity. DSDA was placed in a vacuum oven at 150°C for 12 hours prior to use. No further purification was deemed necessary.

3.1.4.25 1,4-bis(phenylmaleic anhydride)benzene (BPMB: Amoco Research), kindly donated by Dr. Ellis K. Field, was obtained as bright yellow-green platelets of monomer grade purity. BPMB was placed in a vacuum oven at 150°C for 12 hours prior to use. No further purification was deemed necessary (mp = 258-260°C; literature mp = 260-262°C).

3.1.4.26 Half-ester dianhydride derivatives were prepared in situ in the same manner as monoethyl phthalate, i.e., by dissolving monomer grade dianhydride in refluxing alcohol. Esterified bis(phthalic anhydride) derivatives were obtained as viscous oils or syrups, whereas PMDA derivatives could be isolated as granular white crystalline solids. Alternatively, esterification times were significantly reduced by adding a stoichiometric amount of triethylamine; the resulting bis(ester-triethylammonium carboxylate) could be used as a monomer directly without conversion to the parent ester-acid.

## 3.2 Model Reactions

Various model reactions were conducted in order to determine the mechanism of polymerization of ester-acids and diamines and to establish suitable reaction conditions for the reproducible synthesis of high and controlled molecular weight, high  $T_g$ , fully cyclized soluble polyimides. These are listed below.

### 3.2.1 Salt Formation

Benzoic acid and several bis(ester-acids) were dissolved in ethanol and mixed with ethanolic solutions of various diamines at room temperature to determine if salt formation is the initial reaction in the polymerization of ester-acids and diamines. For example, 2.4424 g ( $2.000 \times 10^{-2}$  mole) benzoic acid was placed in a 100 ml Erlenmeyer flask and dissolved in 50 ml ethanol with stirring. 1.3620 g ( $1.000 \times 10^{-1}$  mole) *p*-xylylenediamine was placed in a second 100 ml Erlenmeyer flask and dissolved in 25 ml ethanol; upon solvation of the diamine, the diamine solution was poured into the benzoic acid solution with stirring. Within 10 minutes, a granular white solid precipitated, which was isolated by vacuum filtration, air dried, washed with diethyl ether and vacuum dried at 25°C for 8 hours. After this time the solubility of this material in deionized water was determined and its FT-IR spectrum was obtained. Bis(ester-acids) were combined with a stoichiometric amount of diamine.

### 3.2.2 Anhydride Formation

The half-ethyl ester of BTDA was heated in dichlorobenzene and an NMP/dichlorobenzene mixture to determine whether conversion of ester-acid to anhydride readily occurs under solution imidization conditions. Thus, to a 100 ml three neck flask fitted with an egg-shaped magnetic stir bar, nitrogen inlet, thermometer,

condenser and reverse Dean-Stark trap was introduced 3.2223 g BTDA ( $1.000 \times 10^{-2}$  mole) followed by 35 ml absolute ethanol. The reverse Dean-Stark trap was filled with ethanol, and with stirring under nitrogen the mixture was rapidly heated to reflux. When a clear solution was obtained, the trap was drained in order to collect excess ethanol from the esterification reaction; when ethanol distillation ceased the trap was again drained and filled with dichlorobenzene. 40 ml dichlorobenzene was then introduced to the flask, and the resulting solution was heated to 70°C; this temperature was maintained for two hours, after which an aliquot was removed and placed on a sodium chloride plate for IR analysis. Temperature was raised in 20°C increments and held constant for two hours until anhydride bands were detected.

### 3.2.3 Benzanilide and N-phenylphthalimide Syntheses

Benzoic acid, phenyl benzoate, monoethyl phthalate and diethyl phthalate were reacted with stoichiometric amounts of aniline in dichlorobenzene or mixtures of NMP/dichlorobenzene to determine whether polymerization occurs via amine-acid, amine-ester or amine-anhydride reactions. A typical reaction is as follows: to a 100 ml three neck flask fitted with an egg-shaped magnetic stir bar, nitrogen inlet, thermometer, condenser and reverse Dean-Stark trap 1.9418 g aniline ( $2.085 \times 10^{-2}$  mole) followed by 2.5257 ( $1.000 \times 10^{-2}$  mole) benzoic acid, and 30 ml dichlorobenzene were introduced. The reverse Dean-Stark trap was filled with dichlorobenzene, and with

stirring under nitrogen the mixture was heated to 170°C for 24 hours. After this time, the reaction was allowed to cool to room temperature; products were collected by vacuum filtration, washed with cold ethanol to remove unreacted starting materials and residual solvent, and vacuum dried at 80°C for 10 hours. Products were identified by FT-IR spectroscopy, melting points, and solubility.

### 3.2.5 Model Polymerizations

#### 3.2.5.1 BTDA-3,3'-DDS System

The polyimide based on BTDA and 3,3'-DDS was selected as a model system to determine optimum conditions for the ester-acid route for several reasons: previous reports of this polyimide indicated that it possessed a reasonably high  $T_g$  (in excess of 260°C) and was readily synthesized by solution techniques to afford reasonably high molecular weights ( $>2.0 \times 10^4$  Daltons) [40]; in addition, the required monomers were relatively inexpensive and readily available in high purity. Polymerizations were conducted as follows: Using the reaction apparatus and esterification procedures described above, BTDA ethyl ester-acid ( $2.000 \times 10^{-2}$  mole) was prepared in situ. After removal of alcohol from the system, the reverse Dean-Stark trap was filled with dichlorobenzene and 4.9660 g ( $2.000 \times 10^{-2}$  mole) 3,3'-DDS was introduced to the flask, followed by 75 ml of an NMP/dichlorobenzene mixture (85/15 v/v). With stirring under nitrogen, the solution was heated to 170-180°C for times ranging from 12 to 96 hours. After this time the polymer

solution was allowed to cool to 50°C and precipitated by slowly dripping the polyimide solution into 700 ml methanol or isopropanol in a high speed blender. The polymer was isolated by filtration, air-dried 6-8 hours and vacuum dried at 160-170°C for 24 hours.

### 3.2.5.2 6FDA-1,4-bis(4-aminophenoxy)benzene System

The polyimide based on 6FDA and 1,4-bis(4-aminophenoxy)benzene was chosen to determine the qualitative effect of polymerization solvents on polyimide molecular weight as reflected by intrinsic viscosity measurements. This system was selected for its solubility and absence of undesirable side reactions during polymerization. Solvent systems included DMAc, DMAc/chlorobenzene (85/15 v/v), NMP, NMP/dichlorobenzene (85/15 v/v) and *m*-cresol, at solids concentrations of 15 percent (w/v). Using the reaction apparatus and esterification procedures described above, 6FDA ethyl ester-acid ( $5.018 \times 10^{-3}$  mole) was prepared in situ. After removal of alcohol from the system, the reverse Dean-Stark trap was filled with dichlorobenzene and 1.4671 g ( $5.018 \times 10^{-3}$  mole) 1,4-bis(4-aminophenoxy)benzene was introduced to the flask, followed by 25 ml of an NMP/dichlorobenzene mixture (85/15 v/v). With stirring under nitrogen, the solution was heated to reflux for 10 hours. After this time the polymer solution was allowed to cool to 50°C and precipitated by slowly dripping the polyimide solution into 700 ml methanol or isopropanol in a high

speed blender. The polymer was isolated by filtration, air-dried 6-8 hours and vacuum dried at 160-170°C for 24 hours.

### 3.2.5.3 ODPA-3,3'-DDS System

The polyimide based on ODPA and 3,3'-DDS was selected to determine the effect of polymerization solvent on the color of the final polyimide. This system was chosen for its low reactivity so that results could be generalized for more reactive monomer combinations. Solvent systems included NMP/dichlorobenzene (85/15 v/v), DMAc/chlorobenzene (85/15 v/v) and DMAc/chlorobenzene (85/15 v/v) containing *p*-toluenesulfonic acid as an imidization catalyst. Higher solids concentrations (35 percent w/v) were employed to promote polymerization. Thus, using the reaction apparatus and esterification procedures described above, ODPA ethyl ester-acid ( $2.026 \times 10^{-2}$  mole) was prepared in situ. After removal of alcohol from the system, the reverse Dean-Stark trap was filled with dichlorobenzene and 5.0296 g ( $2.026 \times 10^{-2}$  mole) 3,3'-DDS was introduced to the flask, followed by 30 ml of a DMAc/chlorobenzene mixture (85/15 v/v) and 0.0100 g ( $5.3 \times 10^{-5}$  mole or 0.26 mole per cent relative to ODPA) *p*-toluenesulfonic acid. With stirring under nitrogen, the solution was heated to reflux until it became difficult to stir; the solution was then diluted to a solids concentration of 25 percent with 15 ml of DMAc/chloro benzene mixture to facilitate stirring, and the reaction was continued at reflux for a total time of 24 hours. After this time the polymer solution was

allowed to cool to 50°C and precipitated by slowly dripping the polyimide solution into 700 ml methanol or isopropanol in a high speed blender. The polymer was isolated by filtration, air-dried 6-8 hours and vacuum dried at 160-170°C for 24 hours.

### 3.2.6 Polymerizations

#### 3.2.6.1 Linear Polyimides

##### 3.2.6.1.1 High (Uncontrolled) Molecular Weight Polyimides

Various high molecular weight soluble polyimides were synthesized via the ester-acid route using the general synthetic method reported for the BTDA/3,3'-DDS model system, however, reaction times were limited to 8 to 24 hours.

##### 3.2.6.1.2 Controlled Molecular Weight Polyimides

Controlled molecular weight polyimides were synthesized under the conditions reported above, but a calculated excess of diamine or dianhydride or a calculated amount of a monofunctional molecular weight limiting reagent was employed to limit molecular weights according to the Carrothers Equation. Sample calculations for each scenario are shown in Scheme 3.2.6.1.2.

Thus, to synthesize a 15k g/mole phthalic anhydride-capped 6F-1,4-bis(4-aminophenoxy)benzene polyimide, 5.3638 g ( $1.000 \times 10^{-2}$  mole) 6F ethyl ester-acid and 0.1942 g monoethyl phthalate ( $1.000 \times 10^{-3}$  mole) were prepared using the apparatus and procedures described previously. 3.0771 g 1,4-bis(4-amino-phenoxy)benzene ( $1.053 \times 10^{-2}$

### Scheme 3.2.6.1.2.a

#### Calculation for the Synthesis of Controlled Molecular Weight Anhydride-Terminated Polyimide

Desired polymer molecular weight	= 15k g/mole
Molecular weight of 6F-TPE-Q repeat unit	= 700.55 g/mole

$D_p$  = degree of polymerization

$r$  = stoichiometric imbalance ratio

$N_a$  = moles of diamine

$N_b$  = moles of dianhydride

$$D_p = (2 \times \langle M_n \rangle \text{ polymer}) / \text{MW repeat unit}$$

$$r = (D_p - 1) / (D_p + 1)$$

For 15k g/mole target:  $D_p = 42.82$      $r = 0.95$

$$r = N_a / N_b$$

Reactant quantities:

Monomer	MW	Moles	grams/100
6FDA	444.24	1.00	4.4424
TPE-Q	292.34	0.95	2.7773

### Scheme 3.2.6.1.2.b

#### Calculation for the Synthesis of Controlled Molecular Weight Amine-Terminated Polyimide

Desired polymer molecular weight	= 15k g/mole
Molecular weight of 6F-TPE-Q repeat unit	= 700.55 g/mole

Dp = degree of polymerization

r = stoichiometric imbalance ratio

N<sub>a</sub> = moles of dianhydride

N<sub>b</sub> = moles of diamine

$$Dp = (2 \times \langle M_n \rangle \text{ polymer}) / MW \text{ repeat unit}$$

$$r = (Dp - 1) / (Dp + 1)$$

For 15k g/mole target: Dp = 42.82    r = 0.95

$$r = N_a / N_b$$

Reactant quantities:

Monomer	MW	Moles	grams/100
TPE-Q	292.34	1.00	2.9234
6FDA	444.24	0.95	4.2203

Scheme 3.2.6.1.2.c. Calculation for the Synthesis of Controlled  
Molecular Weight Nonfunctionally-Terminated Polyimide

Desired polymer molecular weight = 15k g/mole  
Molecular weight of 6F-TPE-Q repeat unit = 700.55 g/mole

$D_p$  = degree of polymerization

$r$  = stoichiometric imbalance ratio

$N_a$  = moles of diamine

$N_b$  = moles of dianhydride

$N_{b'}$  = moles monofunctional reagent (phthalic anhydride)

$D_p = (2 \times \langle M_n \rangle_{\text{polymer}}) / \text{MW repeat unit}$

$r = (D_p - 1) / (D_p + 1)$

For 15k g/mole target:  $D_p = 42.82$      $r = 0.95$

and  $r = N_a / (N_b + 2N_{b'})$  where  $N_{b'} = 0.10$  moles phthalic anhydride

Reactant quantities:

Monomer	MW	Moles	grams/100
TPE-Q	292.34	1.00	2.9234
6FDA	444.24	0.95	4.2203
PA	148.12	0.10	0.1481

mole) was then introduced to the reaction flask, followed by 50 ml NMP and 10 ml dichlorobenzene. With stirring under nitrogen, the solution was heated to 170-180°C for 8 hours. After this time the polymer solution was allowed to cool to 50°C and precipitated by slowly dripping the polyimide solution into 700 ml methanol or isopropanol in a high speed blender. The polymer was isolated by filtration, air-dried 6-8 hours and vacuum dried at 160-170°C for 24 hours.

### 3.2.6.2 Polyimides Synthesized from Diamine Dihydrochlorides

#### 3.2.6.2.1 Polyimides from *p*-Phenylenediamine Dihydrochloride

Polyimides based on 6FDA and *p*-PDA were prepared using the dihydrochloride salt of *p*-PDA to determine the feasibility of utilizing diamine dihydrochlorides as monomers in polyimide synthesis for a commercial system.

Thus, using the same apparatus and procedures as before, 5.4336 g ( $1.013 \times 10^{-2}$  mole) 6F ethyl ester-acid was prepared; 3.0 ml triethylamine was then introduced as a hydrogen chloride acceptor, followed by 1.8341 g ( $1.013 \times 10^{-2}$  mole) *p*-phenylene diamine dihydrochloride, 35 ml NMP and 10 ml dichlorobenzene. With stirring under nitrogen, the solution was heated to 170-180°C for 8 hours. After this time, the reaction was cooled to room temperature to permit the crystallization of triethylamine hydrochloride; the polymer solution was then poured through a coarse glass funnel to

remove the salt and the polymer was isolated and dried as described before.

#### 3.2.6.2.2 Polyimides from Diaminoresorcinol Dihydrochloride

Polyimides were synthesized via solution techniques from diaminoresorcinol dihydrochloride to further demonstrate the utility of diamine dihydrochlorides as monomers in polyimide synthesis. Reaction apparatus was as before, however, ester-acids and hydrogen chloride acceptors were not employed. Thus, 6.5529 g ( $2.112 \times 10^{-2}$  mole) ODPA and 4.5005 ( $2.112 \times 10^{-2}$  mole) diaminoresorcinol dihydrochloride were introduced to the reaction vessel; residues were rinsed in with 10 ml dichlorobenzene and 40 ml NMP and the reverse Dean-Stark trap was filled with dichlorobenzene. With stirring under nitrogen, the mixture was heated to 170-180°C for 4 hours, after which time the solution was diluted with NMP to approximately 10 percent solids (w/v) and slowly dripped into 1000 ml methanol in a high speed blender. The polymer was isolated and dried as before.

#### 3.2.6.3 Thermosetting Imides

##### 3.2.6.3.1 Acetylene-Functionalized Imide Oligomers

Controlled molecular weight acetylene functionalized imides were prepared in a similar manner as controlled molecular weight linear polyimides, except triethylamine was utilized to decrease esterification times in ester-acid synthesis and *m*-aminophenyl

acetylene was used as a molecular weight limiting reactive end group.

The synthesis of a 10k g/mole 6F-*p*-phenylene diamine ethynyl-functionalized imide oligomer follows. 6F ethyl ester-triethylammonium carboxylate was prepared from 6.8159 g 6FDA ( $1.534 \times 10^{-2}$  mole) and 5.00 ml triethylamine ( $3.6 \times 10^{-2}$  mole); after removal of excess ethanol and triethylamine from the reaction flask, 1.5718 g *p*-PDA ( $1.454 \times 10^{-2}$  mole) and 0.1892 g *m*-aminophenyl-acetylene ( $1.62 \times 10^{-3}$  mole) were introduced to the flask, followed by 40 ml NMP and 10 ml dichlorobenzene. The reverse Dean-Stark trap was filled with dichlorobenzene and with stirring under nitrogen the solution was heated to 175°C for 8 hours. After this time, the solution was allowed to cool to 50°C, transferred to a 125 ml separatory funnel and dripped slowly into 500 ml methanol in a high speed blender. The oligomer was isolated as a pale yellow powder by vacuum filtration and air dried 5 hours.

The powder was then placed in a 500 ml Erlenmeyer flask with 200 ml diethyl ether and stirred 8 hours to remove residual solvents; after this time the oligomer was again collected by vacuum filtration, air dried and finally vacuum dried at 150°C for 24 hours.

#### 3.2.6.3.2 Polyimides Containing Backbone Maleimide Units

Polyimides derived from BPMB were prepared via a one-step high temperature solution imidization procedure. High and controlled molecular weight experiments were conducted utilizing

phthalic anhydride as a molecular weight and end group controlling structure. Thus, 6.4375 g ( $1.524 \times 10^{-2}$  mole) BPMB and 3.0518 g ( $1.524 \times 10^{-2}$  mole) 4,4'-ODA were introduced to the reaction vessel; residues were rinsed in with 15 ml dichlorobenzene and 35 ml NMP and the reverse Dean-Stark trap was filled with dichlorobenzene. With stirring under nitrogen, the mixture was heated to 170-180°C for 24 hours, after which time the solution was diluted with NMP to approximately 10 percent solids (wt/vol) and slowly dripped into 1000 ml methanol in a high speed blender. The polymer was isolated and dried as before.

#### 3.2.6.4 Curing of Functionalized Polyimides

##### 3.2.6.4.1 Acetylene-Functionalized Polyimides

Solvent cast films of acetylene-functionalized polyimides were thermally cured in a Thermolyne Type 47900 Furnace under nitrogen. The oven was purged with nitrogen for 15 minutes at room temperature. Films cast in 10 cm aluminum pans were then placed in the oven and the temperature was raised to 20°C above  $T_g$ ; upon reaching this temperature the films remained in the oven for an additional 20 minutes, after which time they were removed.

##### 3.2.6.4.2 Polyimides Containing Backbone Maleimide Units

Solvent cast films of backbone maleimide-functionalized polyimides were thermally cured in a Thermolyne Type 47900 Furnace under nitrogen. The oven was purged with nitrogen for 15

minutes at room temperature. Films cast in 10 cm aluminum pans were then placed in the oven and the temperature was raised to 350°C; upon reaching this temperature the films remained in the oven for an additional 30-60 minutes, after which time they were removed.

### 3.3 Characterization

#### 3.3.1 Intrinsic Viscosities

Intrinsic viscosities provided a qualitative measure of the molecular weights of the various polymers and oligomers synthesized. Measurements were obtained using a Cannon-Ubbelohde viscometers; samples were dissolved in NMP and measurements were performed at 25°C. Intrinsic viscosity values were obtained using four different concentrations and the data were analyzed by a linear extrapolation to zero concentration.

#### 3.3.2 Gel Permeation Chromatography

Gel permeation chromatography was employed to obtain a more accurate measure of polymer and oligomer molecular weights and to determine the molecular weight distributions of the various polymer and oligomer samples. GPC measurements were performed in NMP/LiBr at 60°C using a Waters 150-C ALC/GPC with a refractive index detector and Viscotek Model 100 viscosity detector. Molecular weights were determined using universal calibration with polystyrene standards [263, 264].

### 3.3.3 Polyimide Titration

Non-aqueous potentiometric titrations were employed to determine the amount of residual amic-acid groups using an MCI GT05 Automatic Titrator . A standard calomel electrode and reference electrode were employed and stored in a buffer solution when not in use. Tetramethylammonium hydroxide (approximately 0.025 N in methanol) was employed to titrate the residual carboxylic acid. The titrant was standardized by titrating a known quantity of potassium hydrogen phthalate (KHP).

The polymer to be titrated was weighed out in a 250 ml beaker, NMP was added and the solution was stirred until complete solvation of the polyimide was achieved; typical sample size was approximately 1 g of polymer in 100 ml NMP. The electrodes were then inserted and the titration was begun. Upon reaching the endpoint, the final potential in millivolts was recorded and the endpoint volume was recorded by the computer. A blank titration was then performed under similar conditions using the same titrant and an identical volume of NMP. After subtracting the blank volume from the endpoint volume the per cent of residual amic-acid was calculated as follows:

$$\% \text{ amic acid} = (100 (C) (V)) / ( 2 (\text{wt}) / (\text{MW}_r))$$

where "C" is the concentration of titrant, "V" is the volume of titrant, "wt" is sample mass in grams and "MW<sub>r</sub>" is the polyimide repeat unit molecular weight in grams per mole.

#### 3.3.4 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectra were obtained using a Nicolet MX-1 FT-IR Spectrometer with 4  $\text{cm}^{-1}$  resolution. FT-IR was used to monitor the progress of model reactions and to confirm the identities of model compounds. Samples removed during the course of a reaction were analyzed as solutions on sodium chloride plates; products obtained at the end of a reaction were analyzed as potassium bromide (KBr) pellets.

In addition, polymers were analyzed as thin films, whereas functionalized oligomers were analyzed as KBr pellets. FT-IR bands occurring at 1780, 1730, 1375 and 720  $\text{cm}^{-1}$  confirmed the presence of imide heterocycles in polymers and oligomers.

#### 3.3.5 Proton Nuclear Magnetic Resonance

Proton NMR spectra were obtained using a Varian Unity 400 MHz instrument. Samples were dissolved in deuterated DMSO at concentrations of 3 to 5 per cent and were analyzed at room temperature, with tetramethylsilane (TMS) as the lock reference. Proton NMR was used primarily to detect residual amic-acid and alkyl esters in polyimides and to detect terminal ethynyl groups in acetylene-functionalized imide oligomers.

#### 3.3.6 Differential Scanning Calorimetry

Glass transition temperatures of polymers and oligomers were determined using a Perkin-Elmer Model DSC 7. Scans were

conducted under a nitrogen atmosphere in the range of +100°C to +450°C at a heating rate of 10°C per minute. Samples were scanned at least two times to accurately determine  $T_g$  values. Glass transition temperatures were taken as the midpoint of the change in slope of the baseline.

### 3.3.7. Thermogravimetric Analysis

#### 3.3.7.1 Dynamic Thermogravimetric Analysis

Dynamic TGA was employed to assess the thermal stability of polyimide and imide oligomer samples using a Perkin-Elmer TGA 7 thermogravimetric analyzer. Thin film or powder samples were placed in a platinum pan connected to an electronic microbalance. The sample was then heated at a rate of 10°C per minute in flowing air and weight loss was measured versus temperature. The temperature range range examined was 30°C to 650°C.

#### 3.3.7.2 Isothermal Thermogravimetric Analysis

Isothermal TGA was employed to assess the long term thermal stability of several samples at 371°C (700°F) in a flowing air atmosphere. Solution-cast films were placed in a Blue M Electric oven at 371°C at one atmosphere and were removed and weighed periodically over a period of at least 100 hours.

### 3.3.8 Solvent Extraction of Imide Thermosets

Cured thermosetting imides were extracted with chloroform to determine the gel fraction in crosslinked polyimide films. Films cast from chloroform were cured according to the methods described in Section 3.2.6.4. Films were removed from the oven after curing and immediately inserted into dried, pre-weighed cellulose thimbles; the combined weight of the sample and thimble was recorded and the assembly was placed in a Soxhlet extractor under refluxing chloroform for 120 hours. Sample weight was determined by subtracting the thimble weight from their combined weight. After this time, thimble and sample were removed from the extractor, air dried and then vacuum dried at room temperature for 24 hours. Thimble and sample were then dried under vacuum at 120°C and weighed periodically until a constant weight was attained; gel fraction weight was determined by subtracting the thimble weight from their combined weight, and the per cent gel fraction was calculated as shown below:

$$\% \text{ gel fraction} = (\text{wt}_i/\text{wt}_f) \times 100,$$

where "wt<sub>i</sub>" is the sample weight prior to solvent extraction and "wt<sub>f</sub>" is the sample weight after extraction.

### 3.3.9 Polymer Solubility

The solubilities of various polyimides and imide oligomers were determined in a number of solvents including methylene chloride, chloroform, THF, NMP and DMAc. Polyimides were

designated "soluble" if they formed clear solutions at concentrations of 10 percent (w/v) or greater within the medium at room temperature. Polyimides which precipitated from solution during synthesis were designated "insoluble."

#### 3.3.10 Water Uptake

Water uptake in poly(hydroxy-imide)s (polyimides derived from diaminoresorcinol dihydrochloride) was determined as follows: thin films dried to constant weight at 250°C were weighed immediately after drying and immersed in deionized water at 30°C for ten days, periodically removed from water, blotted dry and weighed until a constant weight was attained, in order to determine water uptake.

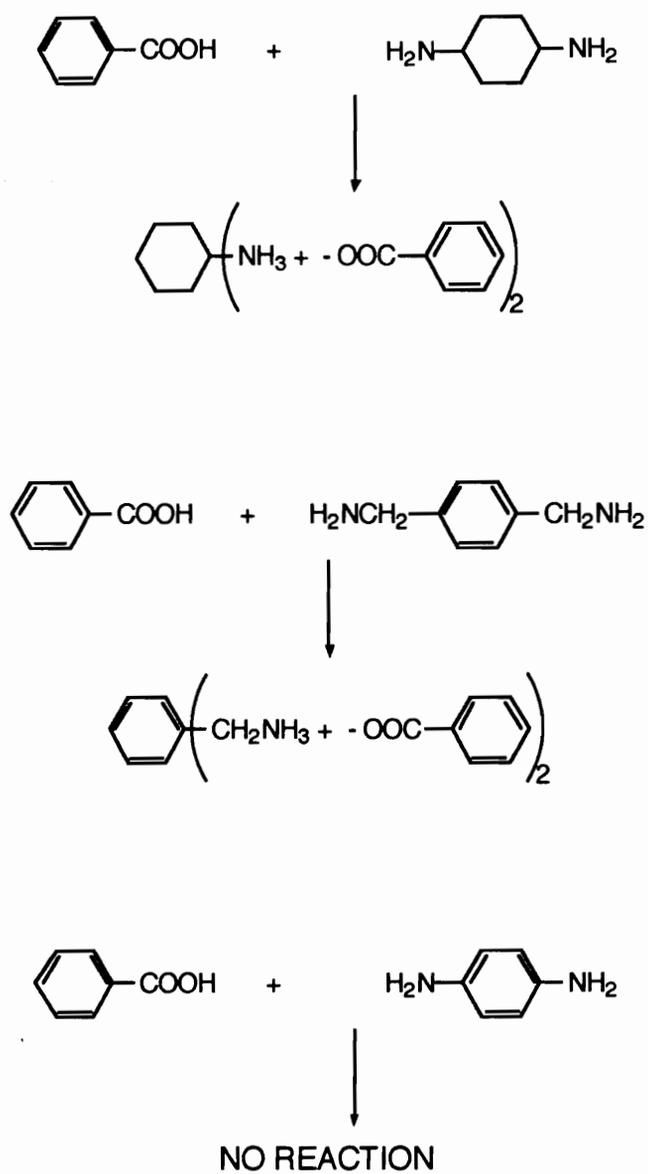
## IV. RESULTS AND DISCUSSION

### 4.1 Model Reactions

#### 4.1.1 Salt formation

Protonation of the diamine by the bis(ester-acid) to form a polymeric salt has been claimed as the initial reaction in the polymerization of bis(ester-acids) and diamines to form polyimides. This seemed unlikely when aromatic diamines were employed, owing to their low basicity, but the possibility could not be dismissed. Therefore, dilute ethanolic solutions of benzoic acid and the half-ethyl ester of PMDA were mixed with ethanolic solutions of the following diamines: 1,4-cyclohexanediamine, *p*-xylylenediamine and *p*-phenylenediamine, as shown in Scheme 4.1.1.1.

Results were as follows. Combining benzoic acid with either 1,4-cyclohexanediamine or *p*-xylylenediamine resulted in the precipitation of a white granular solid, which was soluble in water at a concentration of 10 per cent (w/v) at 25°C. The precipitation from ethanol and solubility in water suggested the formation of ionic species. In addition, the wavenumber shift of the carbonyl group observed in the IR spectra of these mixtures relative to benzoic acid indicates salt formation; see Figure 4.1.1.1. In contrast, no apparent salt formation occurred upon mixing benzoic acid and *p*-phenylenediamine; no solid precipitated, and the IR spectrum of the dried residues obtained from solvent evaporation did not indicate salt



Scheme 4.1.1.1. Formation of bis(ammonium) benzoates

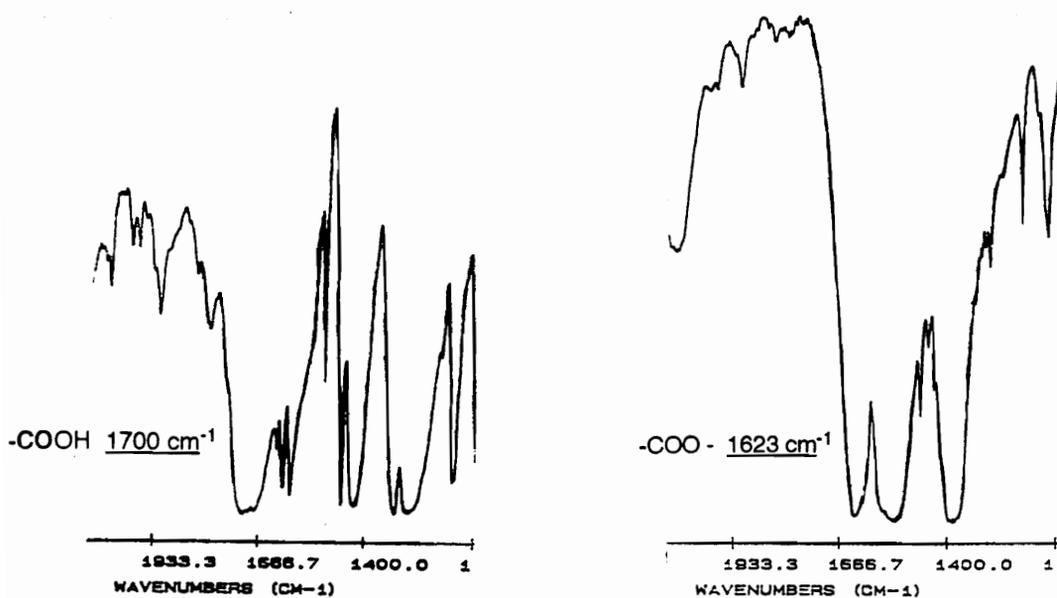


Figure 4.1.1.1. Partial FT-IR Spectra of Benzoic Acid (left) and *p*-Xylylenediammonium Benzoate (right)

formation. The same results were obtained when PMDA half-ethyl ester or BTDA half-ethyl ester was substituted for benzoic acid.

Triethylamine also deprotonates ester-acids, for example, the addition of a stoichiometric amount of triethylamine to 6F ethyl ester-acid yields a product which is both ethanol and water soluble (10 percent wt/vol); the ester-acid is insoluble in water.

In summary, salt formation is indeed the initial reaction in the polymerization of ester-acids and either aliphatic or benzylic diamines, but does not appear to be significant when aromatic diamines (with N bonded directly to aromatic carbon) are employed.

#### 4.1.2 Anhydride Formation

Conversion of ester-acid to anhydride with loss of alcohol has also been proposed as the initial reaction in the polymerization of bis(ester-acids) and diamines to form polyimides [203]. However, this explanation was based on model reactions involving monomethyl phthalate and triethylamine, which is sufficiently basic to deprotonate the carboxylic acid, thereby generating a more nucleophilic carboxylate anion and possibly facilitating cyclization to anhydride. In contrast, deprotonation by aromatic amines does not appear to occur to a significant extent.

In order to determine whether anhydride groups are generated from ester-acids under solution imidization conditions, BTDA ethyl ester-acid was first heated in dichlorobenzene in the absence of amines. The boiling point of dichlorobenzene is in the temperature

range intended for polymerizations (175-185°C) and the absence of IR absorbances in the carbonyl region facilitated detection of anhydride bands. The first appearance of IR bands indicative of cyclic anhydride structures was observed at a temperature of 110°C.

In another experiment, BTDA ester-acid was dissolved in refluxing dichlorobenzene for eight hours. Upon cooling, a white crystalline solid precipitated from solution; after vacuum filtration and air drying, this material was identified as BTDA by its infrared spectrum and melting temperature. IR analysis of dichlorobenzene used in the reaction revealed an absence of carbonyl-containing compounds; these results indicate that anhydride formation from ester-acids is possible in solution at moderate temperatures, and at typical solution imidization temperatures (180°C) quantitative conversion can be achieved in a reasonable period of time. Moreover, this reaction occurs in the absence of amines; thus salt formation is not a necessary precondition for anhydride formation.

While dichlorobenzene was an ideal solvent for these model studies, the solvent system proposed for polymerizations was a mixture of NMP and dichlorobenzene in a volume ratio of 80/20-85/15. Thus BTDA ester-acid was heated in this solvent mixture as well, beginning at 80°C. In NMP/dichlorobenzene the ester-acid also cyclizes to form anhydride; anhydride was first detected by FT-IR at a temperature of 120°C. The continued increase of reaction temperature in 20°C increments resulted in an increase in the intensity of anhydride absorbances up to 160°C (see Figure 4.1.2.1.).

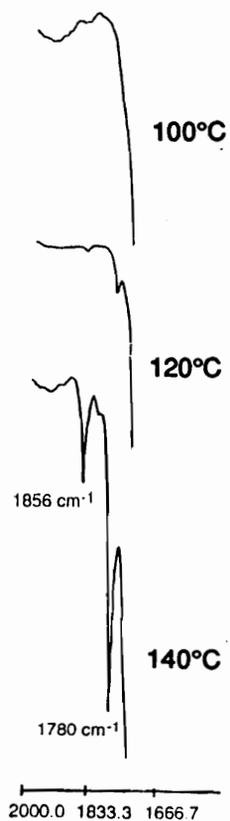


Figure 4.1.2.1. FT-IR Spectra Showing Appearance of Anhydride Bands for BTDA-Ethyl Ester-Acid in NMP/Dichlorobenzene

Thus, under the desired conditions of both temperature and solvent, ester-acids were found to cyclize to the parent anhydride. The slightly higher temperature required in the NMP/dichloro benzene mixture may be due to the more hygroscopic nature and lower vapor pressure of this mixture relative to pure dichloro benzene.

The triethylammonium carboxylate salt of BTDA ethyl ester-acid was also heated in NMP/dichlorobenzene. This material was prepared by adding a stoichiometric amount of triethylamine to BTDA in ethanol prior to reflux. The addition of the tertiary amine greatly reduced esterification time: in the absence of triethylamine complete esterification (as evidenced by a clear solution) was attained after 30 to 40 minutes at reflux, whereas esterification in the presence of triethylamine was complete within 5 to 10 minutes. BTDA ethyl ester-triethylammonium carboxylate began cyclizing to BTDA in the temperature range of 80°C to 90°C.

Although not necessary, the use of triethylamine in esterification reactions provides several potential advantages: esterification times are greatly reduced, initial carboxylate formation appears to facilitate cyclization to anhydride and ester-triethylammonium carboxylates may thus be directly employed as monomers in polyimide synthesis.

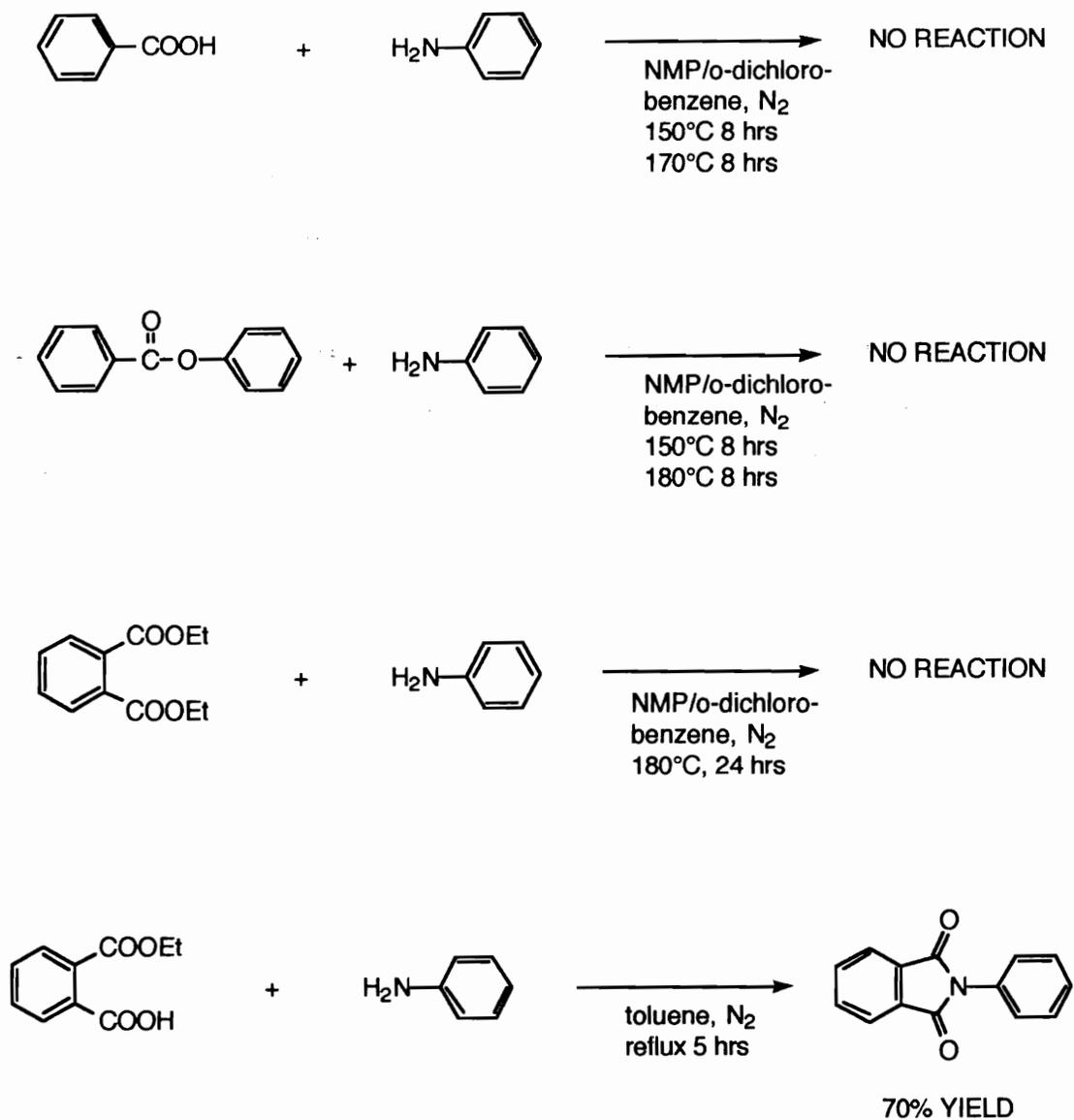
#### 4.1.3 Benzanilide and N-phenylphthalimide Syntheses

Although the preceding reactions confirm that anhydride formation can occur under the conditions of solvent and temperature employed for solution imidizations, the identity of the reactive carboxylic acid derivative could not be verified due to the absence of amines. The possibility remained that polymerization could occur via amine-carboxylic acid or amine-ester reactions as well as an amine-anhydride reaction.

Thus, in an attempt to distinguish between these possible polymerization mechanisms, benzoic acid, phenyl benzoate and diethyl phthalate were heated with stoichiometric amounts of aniline under polymerization conditions (NMP/dichlorobenzene (85/15 vol/vol), reactant concentration of 15 percent (wt/vol), 150-180°C). Model reactions are summarized in Scheme 4.1.3.1.

None of these reactions yielded the desired products; FT-IR analysis revealed no amine consumption and no amide or imide products were isolated. In contrast, monoethyl phthalate, which can cyclize to form phthalic anhydride, reacts with aniline in refluxing toluene to form N-phenylphthalimide within 5 minutes; a 70 percent yield of N-phenylphthalimide is obtained within 5 hours, suggesting that polymerization occurs via initial anhydride formation, followed by the reaction of amine and anhydride in the normal fashion.

The failure of phenyl benzoate and aniline to yield benzanilide was quite unexpected, as phenyl benzoate bears a good leaving group. To facilitate IR analysis and product isolation, this reaction



Scheme 4.1.3.1. Model Investigations of The Ester-Acid Route

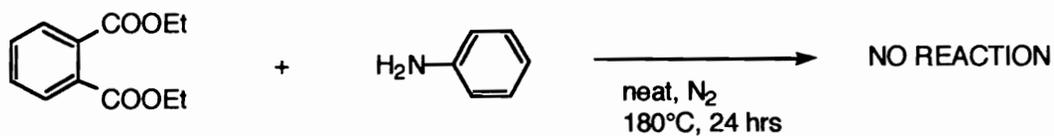
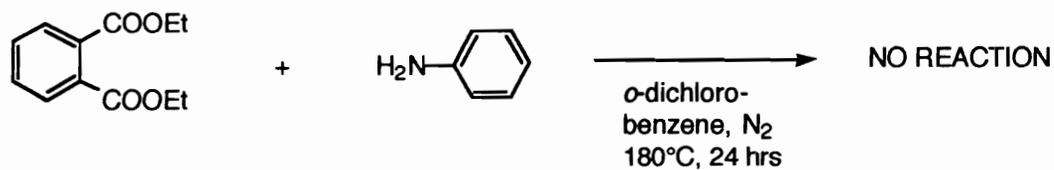
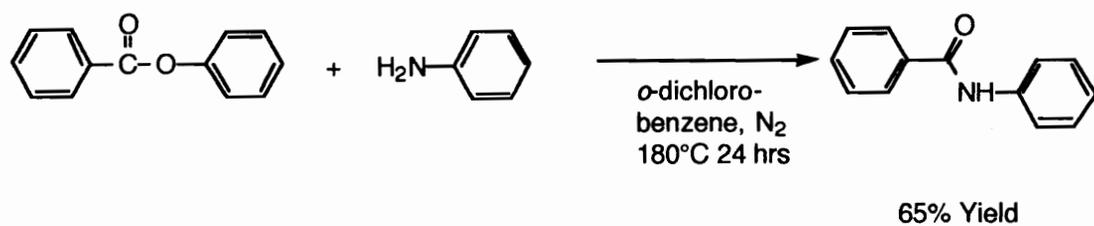
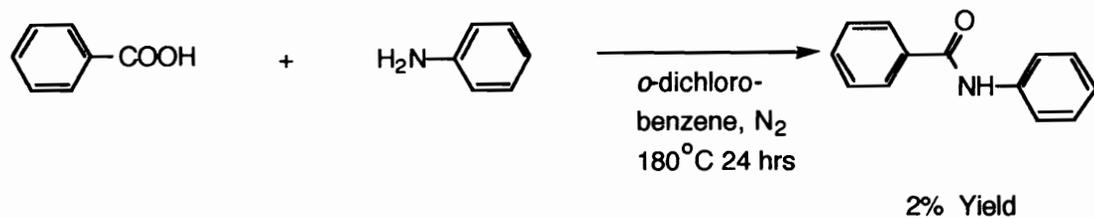
was repeated in refluxing dichlorobenzene; likewise, the reactions involving benzoic acid and diethyl phthalate were repeated. In addition, diethyl phthalate and aniline were heated at 180°C (no solvent). The second series of model reactions is summarized in Scheme 4.1.3.2.

Benzanilide crystallized readily from dichlorobenzene; in dichlorobenzene, a 65 percent yield of benzanilide was obtained from the reaction of phenylbenzoate and aniline, whereas benzoic acid and aniline afforded only a 2 percent yield of benzanilide.

Diethyl phthalate, which cannot cyclize to phthalic anhydride, failed to yield any amide or imide products with aniline whether in dichlorobenzene or neat; these results are consistent with Takekoshi's findings [202].

These results clearly indicate that under the specified polymerization conditions, nucleophilic attack of an aromatic amine on carboxylic acids and alkyl esters does not occur to a significant extent; rather, the polymerization proceeds via initial anhydride formation, followed by the reaction of amine and anhydride in the normal fashion.

However, the results of the model reactions involving phenyl benzoate do show that phenyl esters are sufficiently reactive to generate aromatic amide bonds under moderate conditions; unfortunately, this was only possible in nonpolar dichlorobenzene, which is generally a non-solvent for poly(amic acid)s, soluble poly(aramide)s and soluble polyimides. A possible explanation for



Scheme 4.1.3.2. Additional Investigations of The Ester-Acid Route

these results may be complexation between phenyl benzoate and NMP which lowers the reactivity of phenyl benzoate toward aromatic amines.

#### 4.1.4 Model Polymerizations

##### 4.1.4.1 BTDA-3,3'-DDS System

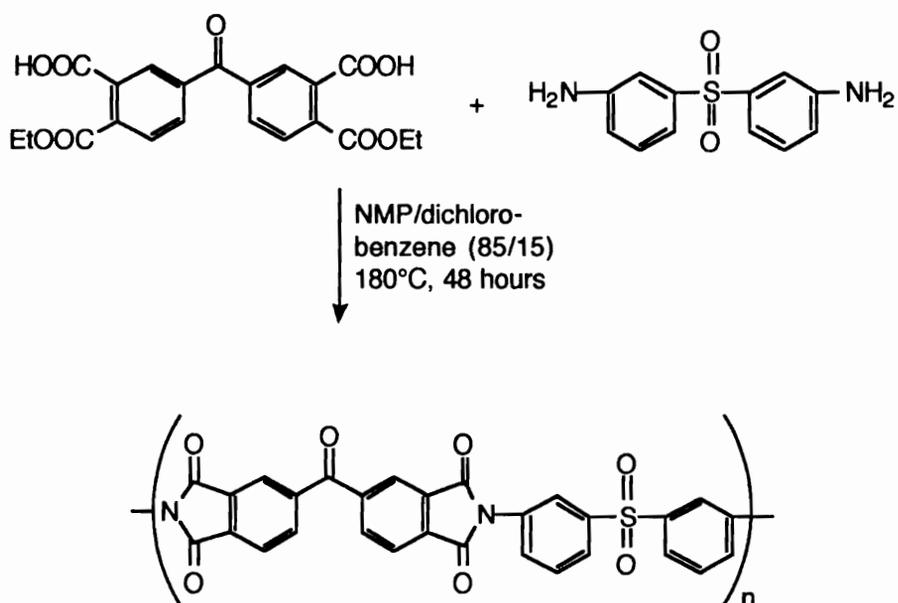
Model polymerizations were conducted to determine suitable polymerization conditions for the consistent synthesis of high molecular weight, soluble, fully cyclized high  $T_g$  polyimides from bis(ester-acids). The polyimide based on BTDA and 3,3'-DDS was selected as a model polymerization system due to its reasonably high  $T_g$  ( $>260^\circ\text{C}$ ), molecular weights ( $>2.0 \times 10^4$  Daltons) and solubility in NMP [40]; in addition, the required monomers were readily available in large quantities and in high purity.

The ideal solution reaction conditions were unknown, as most reported syntheses of polyimides from ester-acids involved bulk (PMR-type) polymerizations. Most of the reaction parameters were therefore based on conditions successfully employed in the two-step solution polymerization of soluble polyimides: an NMP/dichlorobenzene solvent mixture (85/15 v/v), 15 percent solids concentration (w/v) and temperature of approximately  $180^\circ\text{C}$  [38]. Reaction time was the main variable; it was unknown whether polymerizations utilizing ester-acids would require more or less time than the conventional solution imidization method (typically 8-24

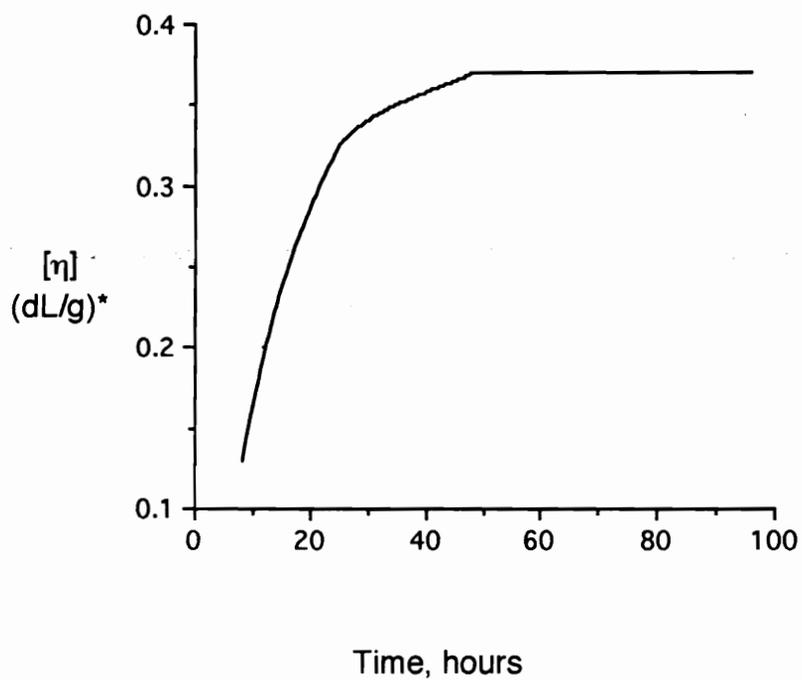
hours for poly(amic-acid) synthesis and 8-24 hours for cyclodehydration). A typical synthesis is depicted in Scheme 4.1.4.1.1.

Monomer stoichiometry of 1:1 and reaction times ranging from 12 to 96 hours were employed; intrinsic viscosities of the resulting polyimides were measured to qualitatively determine the influence of reaction time on molecular weight. Results of the initial experiments are shown in Figure 4.1.4.1.1, a curve representing intrinsic viscosity versus reaction time.

As the data indicate, molecular weight increases for this system up to 24 hours and then reaches a plateau value; however, high molecular weights were not attained. Despite the use of pure solvents and polymerization grade monomers, low molecular weight polymers were obtained, with intrinsic viscosities of less than 0.40 dL/g; an intrinsic viscosity value on the order of 0.50 dL/g would be expected for a number average molecular weight of  $2.0 \times 10^4$  to  $2.5 \times 10^4$  Daltons. However, the FT-IR spectra of these materials, shown in Figure 4.1.4.1.2, displayed characteristic imide absorbances at 1783, 1722, 1367 and  $722 \text{ cm}^{-1}$ , aromatic ketone at  $1672 \text{ cm}^{-1}$ , and an absence of the amic-acid absorbance at  $1548 \text{ cm}^{-1}$ , indicating that a high degree of cyclodehydration was achieved. The failure of this system to achieve high molecular weights at extended periods of time indicated the possibility of undesired, molecular weight-limiting end group reactions. In addition, side reactions involving the products of solvent (NMP) decomposition were another potential explanation. Solvent decomposition at extended times was revealed



Scheme 4.1.4.1.1. Synthesis of BTDA-3,3'-DDS Polyimide Using the Half-Ethyl Ester of BTDA



\* intrinsic viscosities determined in NMP at 25°C

Figure 4.1.4.1.1. Intrinsic Viscosity versus Reaction Time for the BTDA-3,3'-DDS System

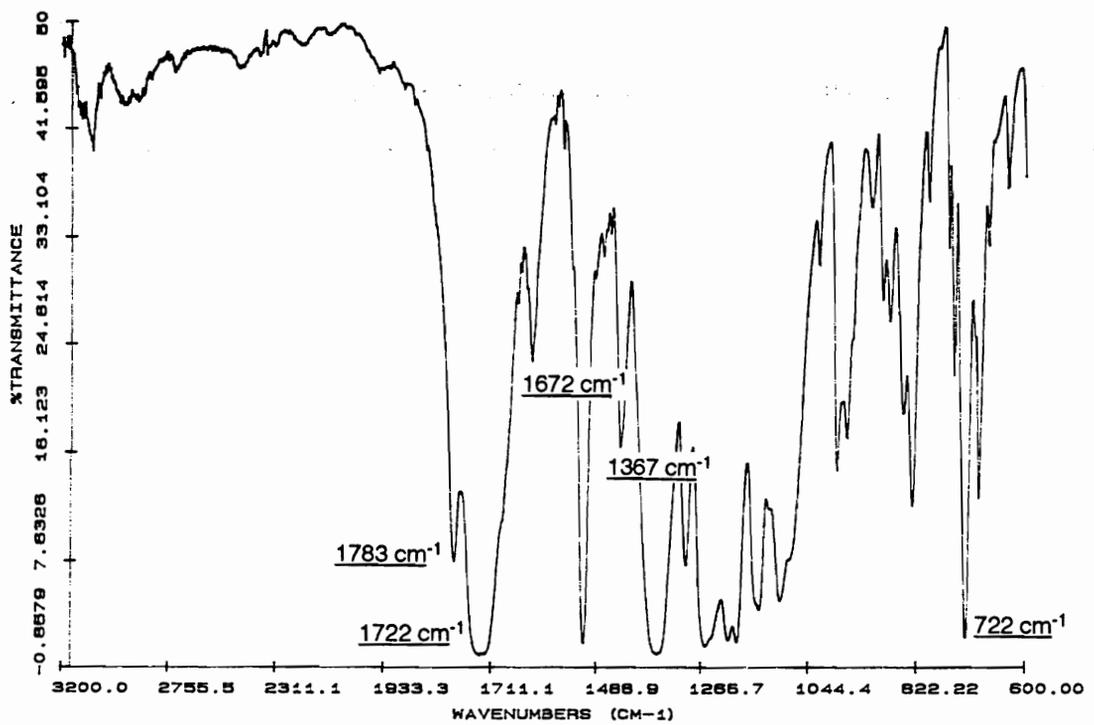


Figure 4.1.4.1.2. FT-IR Spectrum of BTDA-3,3'-DDS Polyimide

by the color of the isolated polyimides; reaction times of 24 hours or less yielded pale yellow polymer, whereas longer reaction times produced polymers ranging in color from light grey to brown.

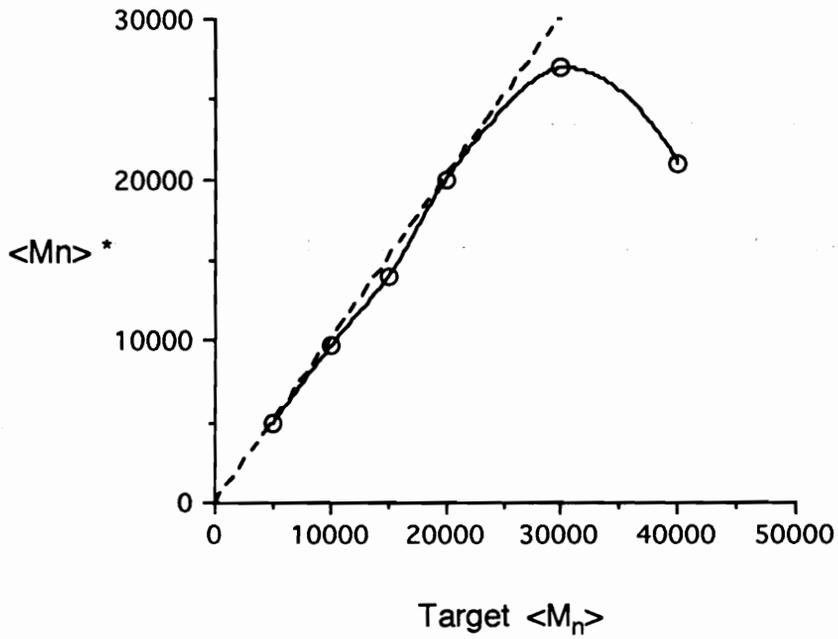
Subsequent investigations were thus conducted, in which reaction times were limited to 24 hours in order to avoid solvent decomposition, and 2 (mole) percent phthalic anhydride was added to consume reactive amine end groups in an attempt to suppress end group reactions which might occur. This approach was somewhat more successful; fibrous pale yellow to light grey polyimides were isolated with intrinsic viscosities of 0.52 to 0.54 dL/g, suggesting number average molecular weights on the order of  $2.0 \times 10^4$  Daltons had been attained. These polymers also displayed characteristic imide IR absorbances at 1783, 1722, 1367 and 722  $\text{cm}^{-1}$ , and an absence of the amic-acid absorbance at 1548  $\text{cm}^{-1}$ . Measured  $T_g$ 's (263°C) were in good agreement with the reported value of 265°C for this system. It was thus concluded that the conditions of solvent, concentration and temperature generally used in conventional solution imidizations were suitable for the "ester-acid route," with reaction times of 24 hours or less.

However, the molecular weight-limiting side reaction was as yet unknown; imine or Schiff Base formation from amino groups and the ketone carbonyl group of BTDA was the most likely explanation, although this structure was not observed spectroscopically. Therefore, the occurrence of this side reaction was demonstrated indirectly.

In one polymerization, a 2 percent excess of 3,3'-DDS relative to BTDA was employed in an attempt to generate an imine-crosslinked imide network; in another experiment, 1/1 monomer stoichiometry was employed with 2 (mole) percent *p*-chlorobenzoic acid added to promote imine formation. Both reactions yielded highly swollen, insoluble gels which dissolved upon addition of hydrochloric acid, indicating the presence of hydrolytically unstable crosslinks. Kim has since confirmed this reaction in BTDA-based polyimides [40]. Molecular weights may be successfully controlled in this system up to a value of approximately  $2.0 \times 10^4$  Daltons (number average) by utilizing a calculated excess of BTDA ethyl ester-acid. As shown in Figure 4.1.4.1.3, good agreement was obtained between calculated number average molecular weights and actual molecular weights determined by GPC up to  $2.0 \times 10^4$  Daltons. Up to this limit the side reaction is apparently suppressed by the excess BTDA; beyond this limit, as monomer stoichiometry closely approaches unity, the side reaction can no longer be suppressed and reliable molecular weight control becomes impossible.

#### 4.1.4.2 6FDA-1,4-bis(4-aminophenoxy)benzene System

The 6FDA-1,4-bis(4-aminophenoxy)benzene system was used to determine the suitability of various solvent systems for utilization in the ester-acid route. Solvent systems included DMAc, DMAc/chlorobenzene (85/15 v/v), NMP, NMP/dichlorobenzene (85/15 v/v) and *m*-cresol, at solids concentrations of 15 percent



$\langle M_n \rangle = \text{Target } \langle M_n \rangle$  is represented by dashed line

\* Determined by absolute GPC

Figure 4.1.4.1.3. Number Average Molecular Weight versus Target Molecular Weight for the BTDA-3,3'-DDS system

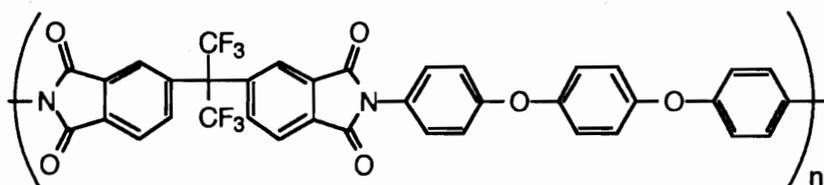
(w/v). Although *m*-cresol is corrosive, toxic and noxious, Harris and coworkers have successfully polymerized various polyimides in this solvent [74, 75]. Monomer solutions were heated for 8 to 24 hours; after isolation and drying polymer intrinsic viscosities were measured to qualitatively determine the influence of polymerization solvent on molecular weight.

As shown in Table 4.1.4.2.1, low molecular weights were obtained in DMAc and DMAc/chlorobenzene. Better results were obtained with NMP and NMP/dichlorobenzene, due to the higher reaction temperatures and more effective water removal. The polymer with the highest viscosity was prepared in *m*-cresol; successful polymerization in this solvent is probably due to a combination of high temperature and its acidic nature. Kim has reported solution imidization to be an acid catalyzed process [40]. Although relatively low molecular weight polyimides were obtained in DMAc, these were the least colored polymers; polymers synthesized in DMAc were pale yellow, while the polymer synthesized in *m*-cresol was light grey and those synthesized in NMP were light brown. The use of DMAc as a polymerization solvent was therefore investigated further, in an attempt to minimize coloration in solution polymerized polyimides.

#### 4.1.4.3 ODPA-3,3'-DDS System

Polymerizations utilizing DMAc were continued to determine whether reaction conditions could be found to allow for the synthesis

Table 4.1.4.2.1. 6FDA-1,4-Bis(4-aminophenoxy)benzene Polyimides  
Synthesized Under Various Reaction Conditions



<u>Solvent</u>	<u>Reaction Time</u> <u>(hours)</u>	<u>Temperature</u> <u>(°C)</u>	<u>[η] (dL/g)*</u>
DMAc	24	165	0.35
DMAc/chloro- benzene	24	160	0.43
NMP	15	180	0.63
NMP/dichloro- benzene	10	180	0.78
<i>m</i> -Cresol	10	200	0.93

\* intrinsic viscosities determined in NMP at 25°C.

of moderate to high molecular weight polyimides in this solvent. DMAc was of interest for its apparent stability at reflux; polymers synthesized in DMAc are generally much lighter in color than those synthesized in NMP. Additionally, the lower boiling point of DMAc would facilitate solvent removal from isolated polyimides. The ODPA-3,3'-DDS system was chosen for its low reactivity so that results could be generalized for more reactive monomer combinations. Solvent systems included NMP/dichlorobenzene (85/15 v/v), DMAc/chlorobenzene (85/15 v/v) and DMAc/chlorobenzene (85/15 v/v) containing *p*-toluenesulfonic acid as an imidization catalyst.

The NMP solution became more viscous as the polymerization proceeded but stirred freely; because of the higher monomer concentrations, the DMAc solution without *p*-toluenesulfonic acid became difficult to stir within 20 hours and was diluted to facilitate stirring. Likewise, the DMAc solution containing *p*-toluenesulfonic became viscous and difficult to stir, but this occurred within 10 hours. The added acid apparently increases the rate of reaction but is otherwise unnecessary.

With regard to the intrinsic viscosities of the resulting polyimides, there is little difference, 0.48 dL/g for the polyimides synthesized in DMAc versus 0.52 for the polyimide synthesized in NMP/dichlorobenzene. Under proper conditions of monomer concentration and time DMAc should be a suitable polymerization solvent, particularly for the more reactive monomer combinations.

A dramatic difference was noted in the color of the polymer solution during polymerization and in the color of the isolated polyimides, however. The solutions utilizing DMAc remained clear, light yellow solutions until polymerization was terminated, and the isolated polyimides were pale yellow in color. In contrast, the polymerization utilizing NMP became dark brown, probably due to solvent degradation, and the isolated polyimide was grey in color. All produced transparent flexible films from DMAc; however, the polymers synthesized in DMAc afforded light yellow films, whereas that synthesized in NMP afforded a dark brown film.

## 4.2. Linear Polyimides

### 4.2.1 High (Uncontrolled) Molecular Weight Polyimides

Various uncontrolled molecular weight soluble polyimides were synthesized via the ester-acid route using the general synthetic method reported for the BTDA/3,3'-DDS model system.

Polyimides synthesized from ester-acids will first be discussed in general, with regard to reaction times and intrinsic viscosities, FT-IR spectra, extent of imidization (percent cyclization), molecular weights and distributions, and comparison of properties with reported values of polyimides synthesized by the conventional synthesis. In later sections, subgroups, according to dianhydride or diamine, will be discussed with regard to structure- $T_g$  and structure-solubility relationships.

#### 4.2.1.1 General

The "ester-acid" route has been demonstrated to be a practical alternative to the conventional two-step synthesis of soluble polyimides. With few exceptions, moderate to high molecular weight polyimides (intrinsic viscosities in the range of 0.40 to 1.0 dL/g in NMP at 25°C) are achieved in times of 24 hours or less. The resulting soluble polyimides are soluble in NMP and DMAc at 25°C at concentrations of 15 percent (wt/vol); some also show this level of solubility in common solvents such as methylene chloride, chloroform and THF. They display characteristic imide FT-IR absorbances at 1770, 1730, 1370 and 720  $\text{cm}^{-1}$  and symmetric GPC traces as shown for a 6FDA-*p*-phenylene diamine polyimide in Figures 4.2.1.1.1 and 4.2.1.1.2, and molecular weight distributions ( $\langle M_w \rangle / \langle M_n \rangle$ ) which closely approach the theoretical value of 2.0. The extent of imidization or percent cyclization as determined by non-aqueous potentiometric titrations is generally on the order of 98+ percent; the 2 percent of titrated carboxyl groups may be attributed to anhydride or acid end groups, as these polymers were not terminated with non-reactive end groups. Figure 4.2.1.1.3 shows a representative non-aqueous potentiometric titration curve. Titration values are listed in Table 4.2.1.1.1 for several polyimides. Also listed in Table 4.2.1.1.1 are  $T_g$ 's for the same polyimides; polyimides synthesized from ester-acids generally display  $T_g$ 's in good agreement with reported values for polymers synthesized by conventional methods. In addition, 5 percent weight loss in air as

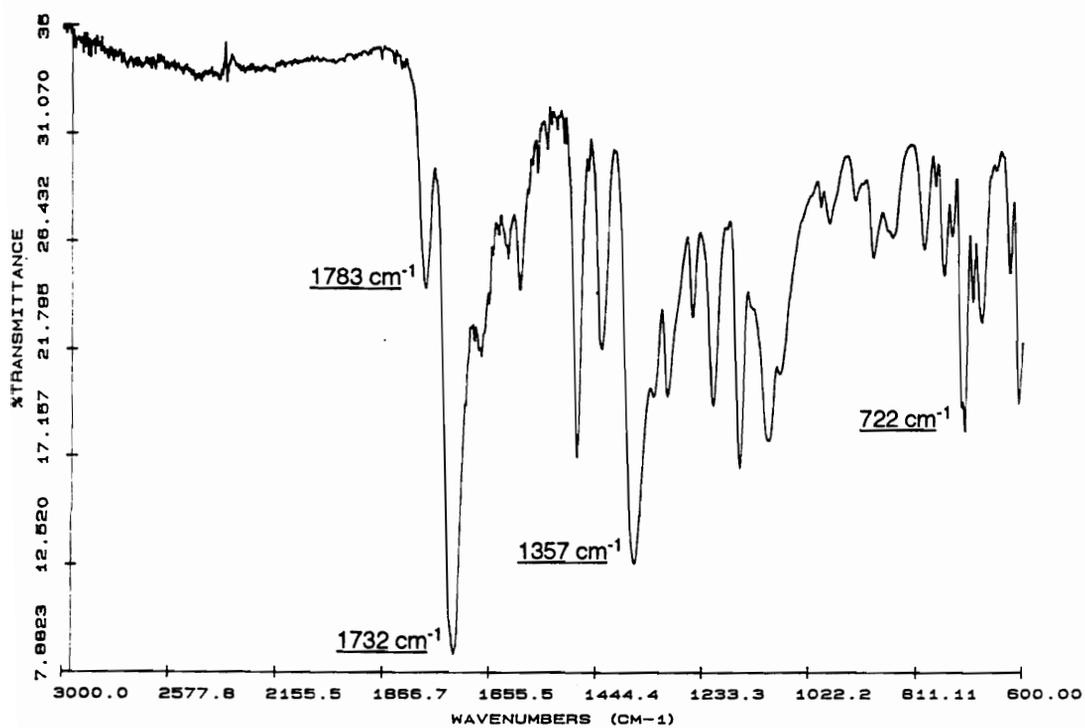


Figure 4.2.1.1.1. FT-IR Spectrum of 6FDA-*p*-Phenylene-diamine Polyimide

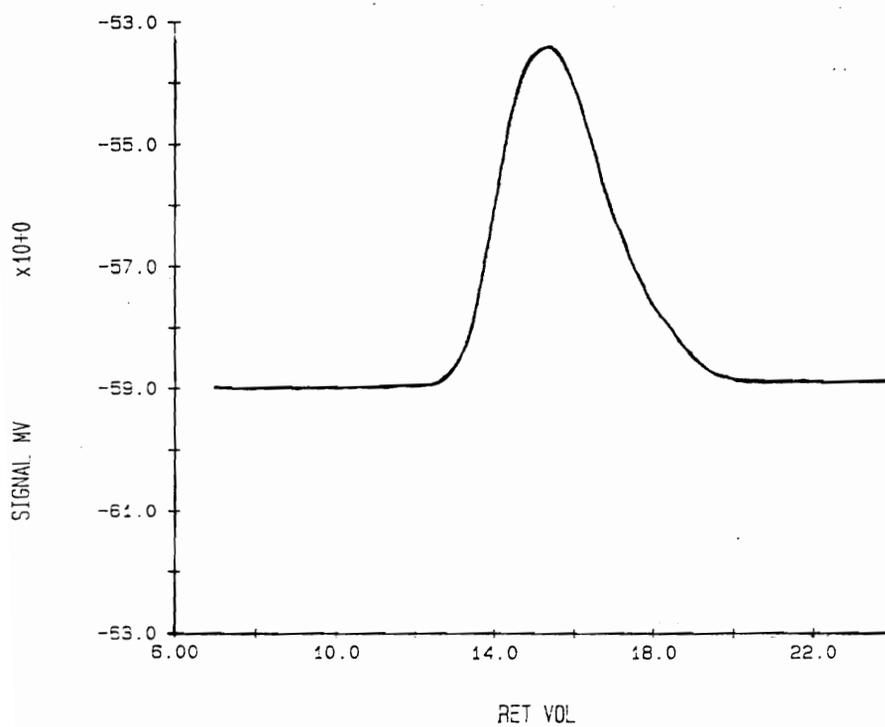
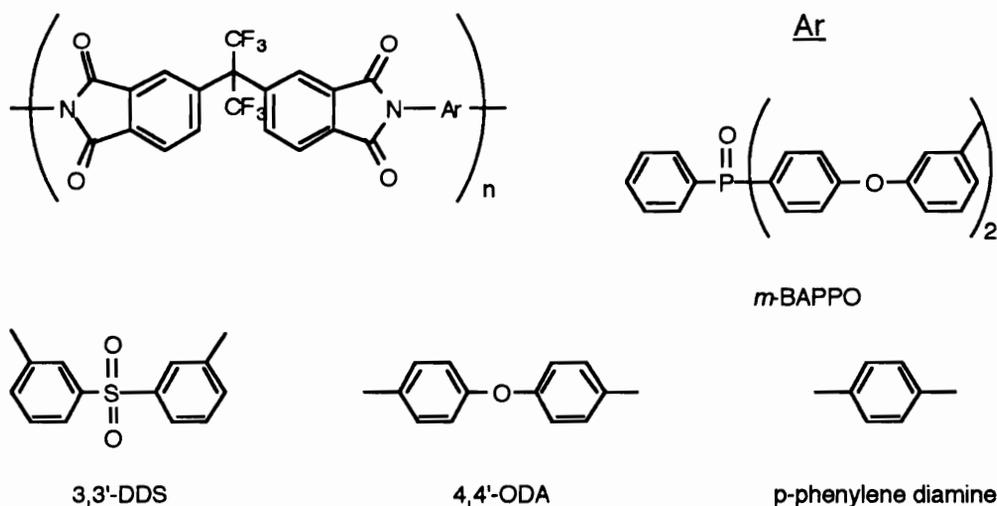


Figure 4.2.1.1.2. GPC Curve of 6FDA-*p*-Phenylene-diamine Polyimide

Table 4.2.1.1.1. Soluble 6FDA-Based Polyimides Synthesized from Ester-Acids

<u>Diamine</u>	<u>[<math>\eta</math>], dL/g</u>	<u>T<sub>g</sub> (°C)*</u>	<u>% imidization</u>
<i>m</i> -BAPPO	0.56	243 (239) [261]	98
3,3'-DDS	0.43	270 (265) [38]	99
4,4'-ODA	1.06	303 (300) [40]	98
<i>p</i> -phenylene diamine	0.80	349 (350) [197]	99

\* values in parentheses indicate accepted T<sub>g</sub> values



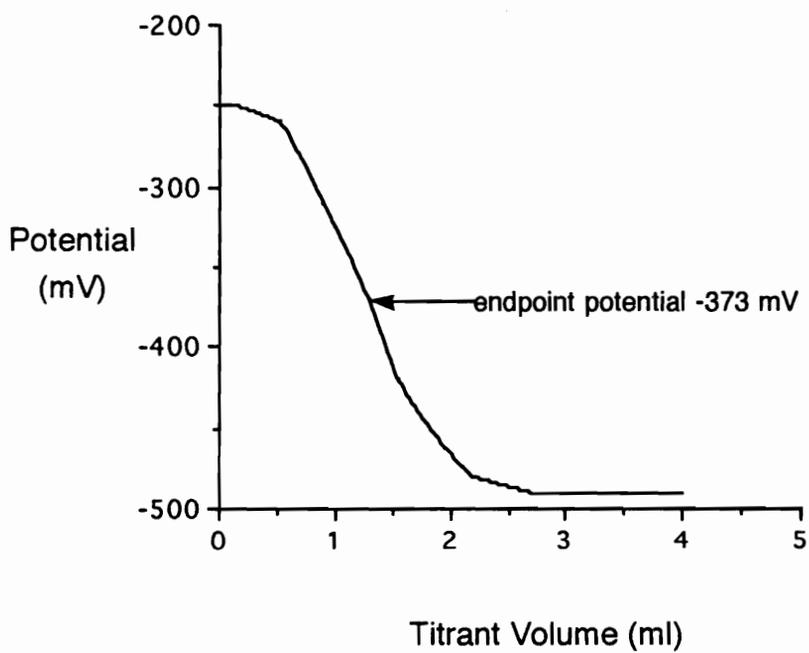
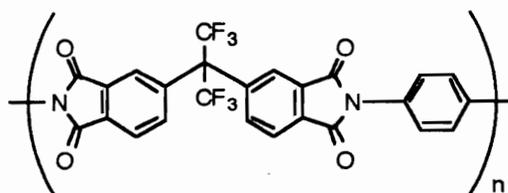


Figure 4.2.1.1.3. Non-Aqueous Potentiometric Titration Curve for a 6FDA-*p*-phenylene Diamine Polyimide

determined by dynamic TGA measurements occurs in the range of 500°C to 560°C, as is the case for aromatic polyimides in general.

#### 4.2.1.2 Polyimides Derived from Pyromellitic Dianhydride

As a monomer in polyimide synthesis, pyromellitic dianhydride (PMDA) is attractive due to its high reactivity, tendency to afford high  $T_g$  polyimides, absence of unstable connecting groups and availability in very high purity. However, PMDA-derived aromatic polyimides which are soluble in organic solvents are quite rare; of the diamines employed in these investigations, only two polymerized with PMDA to form soluble polyimides: *m*-BAPPO and *m*-BAPS. Repeat units and  $T_g$ 's are shown in Figure 4.2.1.2.1.

The unique structure of *m*-BAPPO imparts unusual solubility characteristics to PMDA-*m*-BAPPO polyimide, which is soluble in common organic solvents such as methylene chloride, chloroform and THF, as well as high boiling aprotic solvents such as DMAc and NMP. This solubility greatly facilitates molecular weight characterization of PMDA-*m*-BAPPO polyimide.

Number average ( $\langle M_n \rangle$ ) molecular weights and molecular weight distributions were determined by absolute GPC for several PMDA-*m*-BAPPO polyimides synthesized from the diethyl ester-diacid of PMDA. Reaction times ranged from 8 to 24 hours.

Reasonably high molecular weights were attained, in the range of  $3.4 \times 10^4$  Daltons to  $3.8 \times 10^4$  Daltons, and molecular weight distributions ( $\langle M_w \rangle / \langle M_n \rangle$ ) ranged from 1.9 to 2.0. All samples

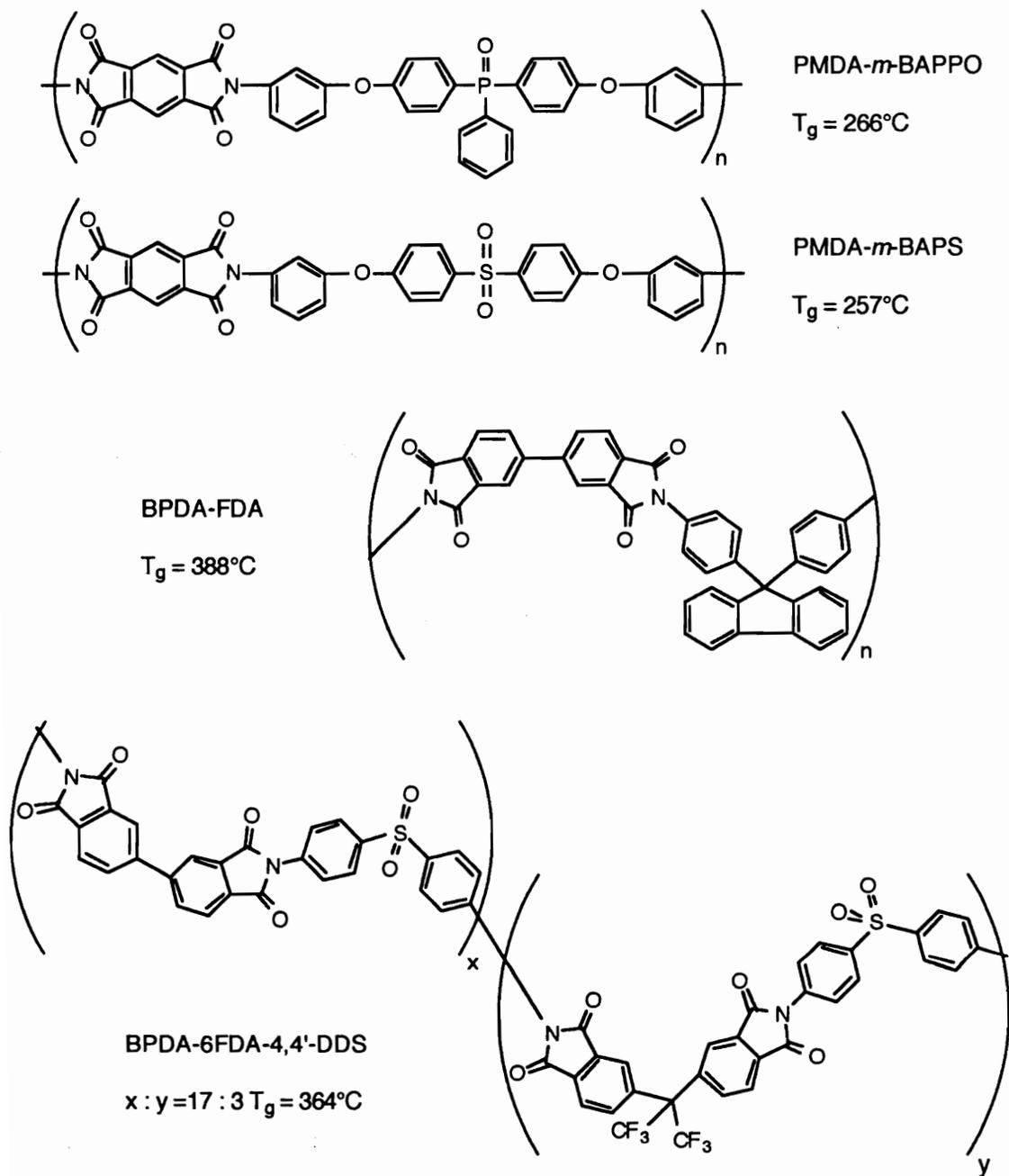


Figure 4.2.1.2.1. Soluble Polyimides Derived from Pyromellitic Dianhydride (PMDA) and Biphenyltetracarboxylic Dianhydride (BPDA)

afforded tough, transparent, flexible amber films when cast from NMP or DMAc.

As indicated previously, *m*-BAPPO contains several structural features which are known to promote solubility of polyimides and prevent structural regularity, including meta catenation, arylene ether linkages, and the flexible phosphine oxide link which also bears a pendant phenyl group.

The polyimide derived from *m*-BAPS is also soluble in DMAc and NMP; this was not entirely unexpected, owing to the structural similarities of *m*-BAPPO and *m*-BAPS. However, this polymer does not dissolve in THF and chlorinated solvents, no doubt due to the polar sulfone linkage in *m*-BAPS, and possibly in part due to the absence of a pendant phenyl group. It is not possible to ascertain which structural feature contributes most to the solubility of this polymer. It appears that both *m*-catenation and the arylene ether structures are required; the polyimides derived from PMDA and 3,3'-DDS (no arylene ether structures) and PMDA and *p*-BAPS (para substitution) are both insoluble, precipitating from solution during synthesis.

Solubility of aromatic polyimides derived from PMDA is sometimes realized at the expense of  $T_g$ , however; a  $T_g$  of 266°C was measured for PMDA-*m*-BAPPO and PMDA-*m*-BAPS displayed a  $T_g$  of 257°C. In comparison, the insoluble polyimide derived from PMDA and 4,4'-diaminodiphenyl ether (Kapton) has a  $T_g$  of 380°C.

#### 4.2.1.3 Polyimides Derived from 3,3',4,4'-Biphenyl Dianhydride

Like PMDA, 3,3',4,4'-biphenyl dianhydride (BPDA) generally yields insoluble polyimides. Only two soluble systems based on BPDA were synthesized; these are shown with their respective  $T_g$ 's in Figure 4.2.1.2.1.

The homopolymer derived from BPDA and 4,4'-diaminodiphenyl sulfone (4,4'-DDS) is an insoluble polyimide with a  $T_g$  of 365°C, while the polyimide derived from 6F dianhydride and 4,4'-DDS is soluble in amide solvents and has a  $T_g$  of 275°C.

Incorporation of 15 (mole) percent of 6F dianhydride into the BPDA-4,4'-DDS system is sufficient to produce a polyimide which is soluble in NMP and DMAc. Interestingly, the incorporation of 6F dianhydride did not result in a reduction in  $T_g$ ; the measured value for this copolymer was 364°C. This material represents a potentially useful polyimide system, due to the ease of synthesis, high  $T_g$  and minimal utilization of the costly 6F dianhydride.

Another soluble polyimide is the homopolymer derived from BPDA and 9,9-bis(4-aminophenyl)fluorene (fluorenediamine or FDA). The pendant fluorene structure in the diamine residue apparently disrupts structural regularity in the polymer backbone sufficiently to afford solubility in methylene chloride and chloroform as well as the polar amide solvents. In addition, this bulky pendant structure affords a very high  $T_g$  of 388°C.

Few soluble polyimides display  $T_g$ 's which meet or exceed this value, and these are primarily derived from the "3F" diamine.

Although the fluorenediamine may produce very high  $T_g$  soluble polyimides, their long term performance at high temperatures may not be outstanding. In terms of thermooxidative stability, the tetrahedral carbon of the diamine would be expected to be the weak link in the polymer backbone.

#### 4.2.1.4 Polyimides Derived from 3,3',4,4'-Benzophenone-tetracarboxylic Dianhydride

The ketone bridge in 3,3',4,4'-benzophenonetetracarboxylic dianhydride affords greater mobility in the polyimide backbone than PMDA or BPDA and thus allows for the synthesis of a larger variety of soluble polyimides. Repeat units and  $T_g$ 's for soluble BTDA polyimides synthesized via the "ester-acid" route are illustrated in Figure 4.2.1.4.1. None possess remarkable  $T_g$ 's, except the polyimide derived from fluorenediamine ( $T_g = 376^\circ\text{C}$ ).

Unlike PMDA and BPDA, BTDA produces a soluble polyimide with 3,3'-diaminodiphenyl sulfone. This polymer remains soluble during polymerization and can be isolated, dried and redissolved, but can reportedly crystallize from dilute solution over a period of several weeks [73]. Difficulties in the synthesis of this system were discussed in Section 4.1.5.1.

Similar difficulties were encountered in the synthesis of BTDA-*m*-BAPPO polyimide. This system would not polymerize to afford high molecular weights as evidenced by the low intrinsic viscosity

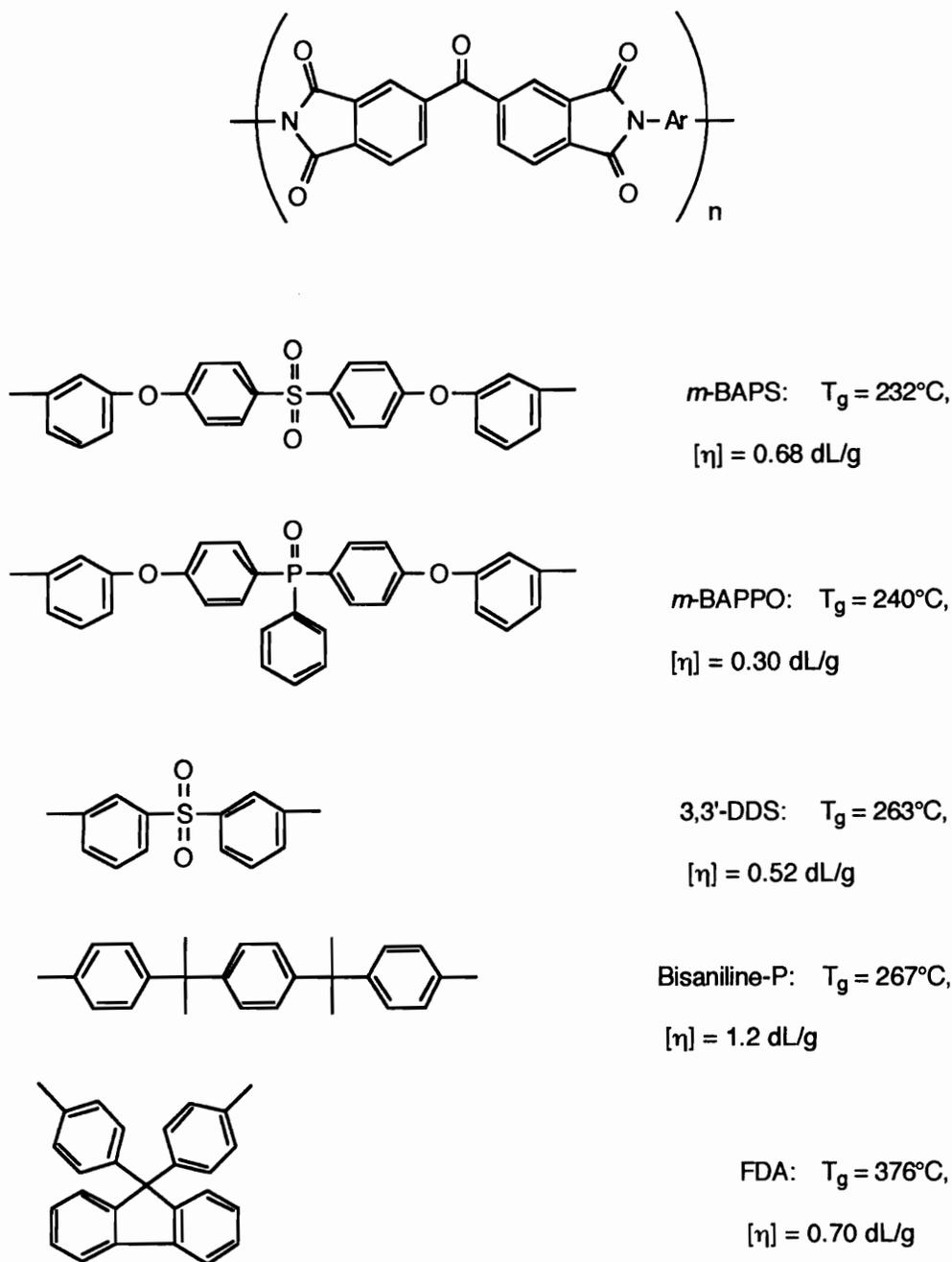


Figure 4.2.1.4.1. Soluble Polyimides Derived from Benzophenone-tetracarboxylic Dianhydride (BTDA)

obtained for this system. BTDA-*m*-BAPPO polyimide displays the same solubilities as PMDA-*m*-BAPPO. Interestingly, *m*-BAPS, FDA and Bisaniline-P polymerized with BTDA ester-acid to afford moderate to high molecular weight polyimides; the imine-forming side reaction is apparently insignificant in these systems although the reason for this is as yet unknown. Steric hindrance could perhaps explain the suppression of an imine-forming side reaction when bisaniline-P or FDA are employed, but this does not explain the unexpected result obtained with *m*-BAPS. It was expected that due to its similarity to *m*-BAPPO, *m*-BAPS would also afford only low molecular weight polyimide with BTDA ester-acid.

BTDA-Bisaniline-P polyimide is soluble in methylene chloride, chloroform and THF as well as DMAc and NMP; this is no doubt a result of enhanced backbone flexibility afforded by the 2,2-isopropylidene linkages and non-polar hydrocarbon character of the diamine residue. Despite the enhanced solubility, a reasonably high  $T_g$  is maintained, roughly equivalent to the BTDA-3,3'-DDS system. BTDA-FDA polyimide displays solubility similar to that of BTDA-Bis-P, except that it swells but does not dissolve in THF. Although this polyimide was expected to possess the highest  $T_g$  of the BTDA-based polyimides, the  $T_g$  of 376°C was somewhat unexpected.

A  $T_g$  of approximately 300°C was anticipated, based on the BPDA-4,4'-DDS ( $T_g = 365^\circ\text{C}$ ), BPDA-FDA (388°C) and BTDA-4,4'-DDS systems (275°C). Overall, the BTDA polyimides show the expected  $T_g$  order: *m*-BAPS < *m*-BAPPO < 3,3'-DDS < FDA.

#### 4.2.1.5 Polyimides Derived from 3,3',4,4'-Oxydipthalic Anhydride

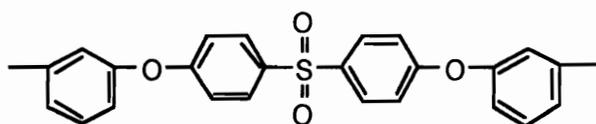
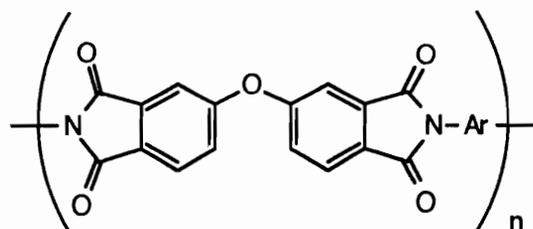
3,3',4,4'-oxydipthalic anhydride (ODPA) generally produces soluble polyimides with the same diamines as BTDA; the ether linkage does not appear to change solubility versus the ketone linkage, but  $T_g$ 's are generally on the order of 10°C to 15°C lower. An exception is ODPA-FDA polyimide ( $T_g = 373^\circ\text{C}$  versus  $376^\circ\text{C}$  for BTDA-FDA polyimide). Repeat units and  $T_g$ 's of ODPA-based polyimides are shown in Figure 4.2.1.5.1.

#### 4.2.1.6 Polyimides Derived from 2,2-bis-(3,4-dicarboxyphenyl)-hexafluoropropane Dianhydride

The hexafluoro isopropylidene linkage in 2,2-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F) affords a high degree of flexibility in the polyimide backbone and permits the synthesis of a much larger variety of soluble polyimides than is possible with PMDA, BPDA, BTDA or ODPA. Repeat units and  $T_g$ 's of 6F-based polyimides are shown in Figures 4.2.1.6.1.a and b.

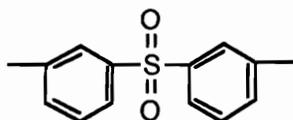
6F produces soluble polyimides with the same diamines as BTDA, and  $T_g$ 's of 6F-based polyimides are roughly equivalent to those of the corresponding BTDA-based polyimides. In addition, the 6F polyimides are soluble in the same solvents as their BTDA analogs.

However, 6F also yields soluble polyimides from diamines which yield insoluble polyimides with BTDA, including 4,4'-



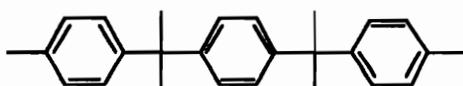
*m*-BAPS:  $T_g = 219^\circ\text{C}$ ,

$[\eta] = 0.42 \text{ dL/g}$



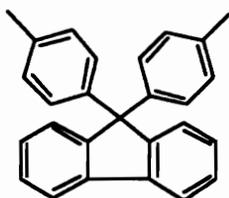
3,3'-DDS:  $T_g = 248^\circ\text{C}$ ,

$[\eta] = 0.52 \text{ dL/g}$



Bis(4-aminophenyl)propane:  $T_g = 257^\circ\text{C}$ ,

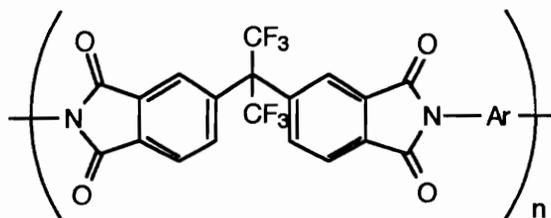
$[\eta] = 0.88 \text{ dL/g}$



FDA:  $T_g = 373^\circ\text{C}$ ,

$[\eta] = 0.55 \text{ dL/g}$

Figure 4.2.1.5.1. Soluble Polyimides Derived from Oxydiphthalic Anhydride (ODPA)



<u>Ar</u>		<u>T<sub>g</sub></u> (°C)
	<i>m</i> -BAPS	233
	<i>m</i> -BAPPO	243
	3,3'-DDS	271
	bisaniline-P	267
	1,4-bis(4-amino- phenoxy)benzene	270

Figure 4.2.1.6.1.a. Polyimides Derived from 6F Dianhydride

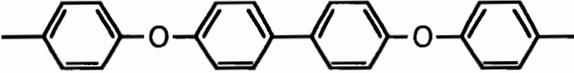
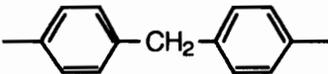
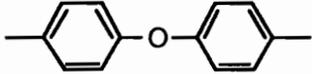
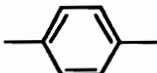
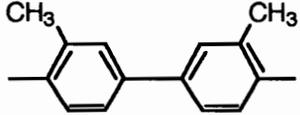
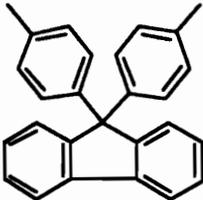
<u>Ar</u>		<u>T<sub>g</sub></u> (°C)
	4,4'-bis(4-amino- phenoxy)biphenyl	280
	4,4'-MDA	290
	4,4'-ODA	303
	<i>p</i> -phenylenediamine	349
	3,3'-dimethyl- benzidine	355
	FDA	370

Figure 4.2.1.6.1.b. Polyimides Derived from 6F Dianhydride

diaminodiphenylmethane (MDA), 1,4-bis(4-aminophenoxy)benzene (TPE-Q), 4,4'-bis(4-aminophenoxy)biphenyl (BAP-B), 4,4'-diaminodiphenylether (ODA), *p*-phenylenediamine (*p*-PDA) and 3,3'-dimethylbenzidine (3,3'-DMB). Of these six, only 6F-*p*-PDA will not dissolve in methylene chloride, chloroform or THF; the others readily dissolve in these solvents as well as NMP and DMAc. The flexible linkages in MDA, TPE-Q, BAP-B and ODA as well as increased hydrocarbon character of polyimides comprised of these monomers apparently promotes solubility in the common solvents.

It was anticipated that 6F-3,3'-dimethylbenzidine would display solubility similar to that of 6F-*p*-phenylenediamine, due to the absence of a flexible linkage in the diamine; the solubility of 6F-3,3'-DMB in common solvents probably arises from both increased hydrocarbon content relative to 6F-*p*-PDA and the pendant methyl groups of 3,3'-DMB.

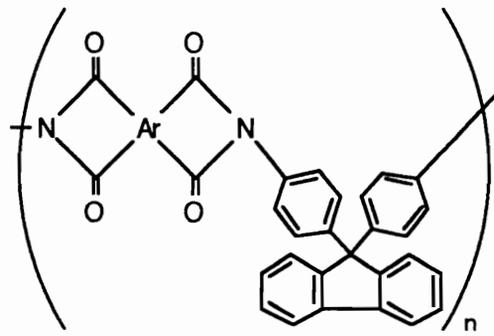
However, in addition to the solubility afforded by the hexafluoro-isopropylidene linkage in 6F and various flexible connecting groups in the diamines employed, solubility is also dependent upon some degree of rotational freedom about the N-aryl bond in the polymer backbone. The attempted synthesis of 6F-3,3',5,5'-tetramethylbenzidine (3,3',5,5'-TMB) resulted in precipitation of an insoluble powder, which could not be redissolved in NMP, DMAc, *m*-cresol, dichlorobenzene, methylene chloride, chloroform or THF. Due to the solubility of 6F-3,3'-DMB, the insolubility of 6F-3,3',5,5'-TMB was believed to result from restricted

rotation about the N-aryl bond due to additional methyl groups in the *ortho* positions.

#### 4.2.1.7 Polyimides Derived from 9,9-bis(4-aminophenyl)fluorene

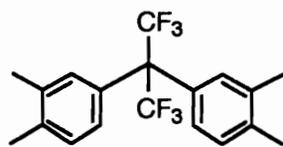
The polyimides derived from 9,9-bis(4-aminophenyl)fluorene (FDA) deserve at least brief mention as a separate category due to their solubility and high  $T_g$ 's. Polyimides based on FDA were synthesized from the following dianhydrides: pyromellitic dianhydride, 6F dianhydride (6F), oxydiphthalic anhydride (ODPA), benzophenonetetracarboxylic dianhydride (BTDA), biphenyltetracarboxylic dianhydride (BPDA) and diphenylsulfone dianhydride (DSDA). The polyimide based on PMDA precipitates from solution during synthesis. Repeat units and  $T_g$ 's of the soluble FDA-based polyimides are shown in Figure 4.2.1.7.1. In general FDA affords very high  $T_g$  polyimides which readily dissolve in a number of solvents, including NMP, DMAc, DMSO, THF, chloroform and methylene chloride.

When polymerized with bis(phthalic anhydride) derivatives, FDA affords polyimides with  $T_g$ 's of at least 370°C. The pendant fluorene group appears to dictate the properties of these polyimides, as inspection of the  $T_g$  values reveals little dependence of  $T_g$  on dianhydride structure. In addition, dianhydride structure strongly influences solubility only in the case of DSDA. The presence of the polar sulfone linkage in this polyimide renders it insoluble in THF, methylene chloride and chloroform.



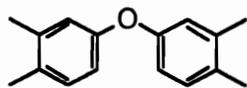
Ar

$T_g$  (°C)



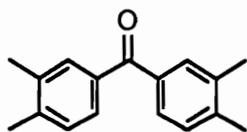
6FDA

370



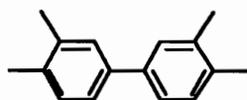
ODPA

373



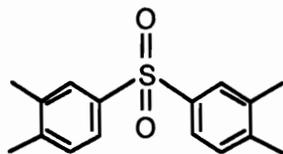
BTDA

376



BPDA

388



DSDA

392

Figure 4.2.1.7.1. Polyimides Derived from 9,9-bis(4-aminophenyl)-fluorene (FDA)

#### 4.2.2 Controlled Molecular Weight Polyimides

Controlled molecular weight polyimides were synthesized under the conditions reported above, but a calculated excess of diamine or dianhydride or a calculated amount of a monofunctional molecular weight limiting reagent was employed to limit molecular weights according to the well-known Carrothers Equation.

Demonstration of reliable molecular weight and end group control was essential in establishing the "ester-acid" route as a viable alternative to the conventional two-step synthesis of soluble polyimides. Control of polymer molecular weights and end groups may be desirable for a number of reasons.

For example, optimum properties are commonly attained at number average molecular weights on the order of  $2.0 \times 10^4$  Daltons for step-growth polymers; further increases in molecular weight may have little or no effect on  $T_g$  or mechanical properties but may result in precipitation from solution during the synthesis or dramatically increase bulk viscosity, hampering thermal processing of the material.

In such circumstances molecular weight control via the incorporation of non-reactive end groups prevents chain extension and end group degradation during subsequent thermal processing steps, i.e., oxidation of free amine end groups or decarboxylation of terminal acid/anhydride groups, affording a processable material with desired properties. In addition, effective molecular weight and

end group control utilizing crosslinking end groups is of great importance in the design of processable high  $T_g$  thermosets.

6FDA/TPE-Q was chosen for molecular weight control studies. Results are shown in Table 4.2.2.1. Number average molecular weights were limited to a value of  $1.5 \times 10^4$  g-mole<sup>-1</sup>; molecular weight control was effected by the following means: (1) a calculated excess of diester-diacid, (2) a calculated excess of diamine, (3) the reaction of a calculated amount of phthalic anhydride with diamine prior to polymerization with the diester-diacid, and (4) the addition of a calculated amount of monoethyl phthalate to a mixture of diester-diacid and diamine in order to afford non-reactive endgroups.

These materials appeared to be completely imidized, showing strong infrared imide absorptions at  $1780\text{ cm}^{-1}$ ,  $1730\text{ cm}^{-1}$ ,  $1370\text{ cm}^{-1}$ , and  $710\text{ cm}^{-1}$ , and an absence of absorptions attributable to amide-acid. The titration results for this system indicate essentially complete imidization; the somewhat lower value for sample 1 is a consequence of acidic end groups. The intrinsic viscosities qualitatively indicate that the target molecular weight was achieved regardless of the means of molecular weight control.

These techniques were then applied to a commercial system, 6F-*p*-phenylenediamine; molecular weights were limited to a value of  $2.0 \times 10^4$  Daltons, using monoethyl phthalate as the molecular weight and end group controlling structure. Properties of these

Table 4.2.2.1. 6FDA-1,4-bis-(4-aminophenoxy)-benzene  
Polyimides ( $1.5 \times 10^4$  g-mole<sup>-1</sup>)

<u>Endcap</u>	<u>[<math>\eta</math>]*, dL/g</u>	<u>% Imidization**</u>
6F Dianhydride	0.42	95
Diamine	0.45	99
Phthalic Anhydride	0.40	100
Monoethyl Phthalate	0.41	99
Monoethyl Phthalate	0.42	100

\*Determined in NMP at 25°C

\*\*Determined by non-aqueous titration

Table 4.2.2.2. 6FDA-*p*-Phenylenediamine Polyimides  
( $2.0 \times 10^4$  g-mole<sup>-1</sup>)

<u><math>\langle M_n \rangle^*</math></u>	<u><math>\langle M_w \rangle / \langle M_n \rangle</math></u>	<u><math>T_g</math> (°C)</u>	<u>5% wt loss (air) (°C)</u>	<u>% Imidization</u>
$2.1 \times 10^4$	2.0	349	535	100
$2.0 \times 10^4$	2.0	349	535	100
$1.9 \times 10^4$	2.3	348	528	99

\* Determined by absolute GPC

samples are listed in Table 4.2.2.2. These were also fully imidized as indicated by titration results. Molecular weights ranged from 1.9 to  $2.1 \times 10^4$  Daltons as determined by GPC; overall, polydispersity ratios were in close agreement with the theoretical value of 2.0. Measured  $T_g$  values also are consistent with the reported value of 350°C.

These results indicate that molecular weight control techniques can be successfully applied to the ester-acid route, yielding controlled molecular weight, fully cyclized polyimides, and monofunctional ester-acids effectively function as molecular weight and endgroup controlling structures.

#### 4.2.3. Polyimides Synthesized from Diamine Dihydrochlorides

Diamine dihydrochlorides have been successfully employed as monomers in polybenzoxazole and polybenzothiazole synthesis; the dihydrochloride salts of the required diaminobisphenols and diamino-bisthiols were necessary due to the oxidative instability of their free base forms. These polymerizations were effected in polyphosphoric acid, with dissociation of the dihydrochlorides to free amine and hydrogen chloride gas and subsequent reaction of the liberated diamine with dicarboxylic acids to afford the desired polymers [185, 186].

This synthesis has not been reported for soluble, aromatic polyimides, although in principle polyimide synthesis from diamine dihydrochlorides should also be possible. This approach offers the potential advantages of ease of purification and longer shelf lives of

diamine dihydrochlorides relative to unprotected diamines. More importantly, the use of diamine dihydrochlorides could permit the synthesis of novel and potentially useful polyimides which cannot be prepared by conventional means due to diamine instability.

#### 4.2.3.1 Polyimides from *p*-Phenylenediamine Dihydrochloride

Phenylenediamine, a component of DuPont's commercially important Avimid-N system (6F-*p*-phenylenediamine polyimide), was readily purified by vacuum sublimation but could not be purified to monomer grade by repeated recrystallizations. Moreover, the pure monomer began oxidizing after 4 to 5 days, despite storage under nitrogen in foil-covered brown glass bottles. For these reasons, the dihydrochloride salt of *p*-phenylenediamine was chosen to determine the feasibility of using diamine dihydrochlorides in polyimide synthesis.

Polymerizations were conducted using 1/1 monomer stoichiometry. A stoichiometric amount of triethylamine was added to the 6F ester-acid as an acid acceptor prior to diamine dihydrochloride addition. Triethylamine hydrochloride precipitated immediately upon addition of *p*-phenylenediamine dihydrochloride and polymerization solvents to the ester-acid. The polymerizations as conducted thus began with counterion exchange to form ester-acid, free diamine and triethylamine hydrochloride. The salt dissolved upon heating, and the resulting solutions became dark brown and increasingly viscous as polymerization proceeded.

Upon cooling to 90°C to 100°C triethylamine hydrochloride crystallized as white needles from the polymer solutions; the salt was filtered off prior to isolation of the polyimides. Fibrous tan polymers were obtained with reasonably high molecular weights, in the range of  $3.0 \times 10^4$  to  $3.5 \times 10^4$  Daltons. Although polyimide synthesis utilizing diamine dihydrochlorides works reasonably well, the use of triethylamine in the polymerization and separation of its hydrochloride salt from the resulting polyimides may not be desirable or practical on a large scale.

#### 4.2.3.2. Polyimides from Diaminoresorcinol Dihydrochloride

Polyimides derived from diaminoresorcinol have not been previously reported, and therefore represent a novel class of polyimides with potentially interesting and useful properties. The high concentration of phenolic hydroxyl groups would be expected to significantly increase water uptake and possibly afford high  $T_g$ , amide solvent-soluble polyimides due to hydrogen bonding.

Because the free base form of diaminoresorcinol is not sufficiently stable for use as a monomer and polyimides derived from this material have not been reported, polyimide synthesis from diaminoresorcinol dihydrochloride was considered a more practical and convincing demonstration of the use of diamine hydrochlorides.

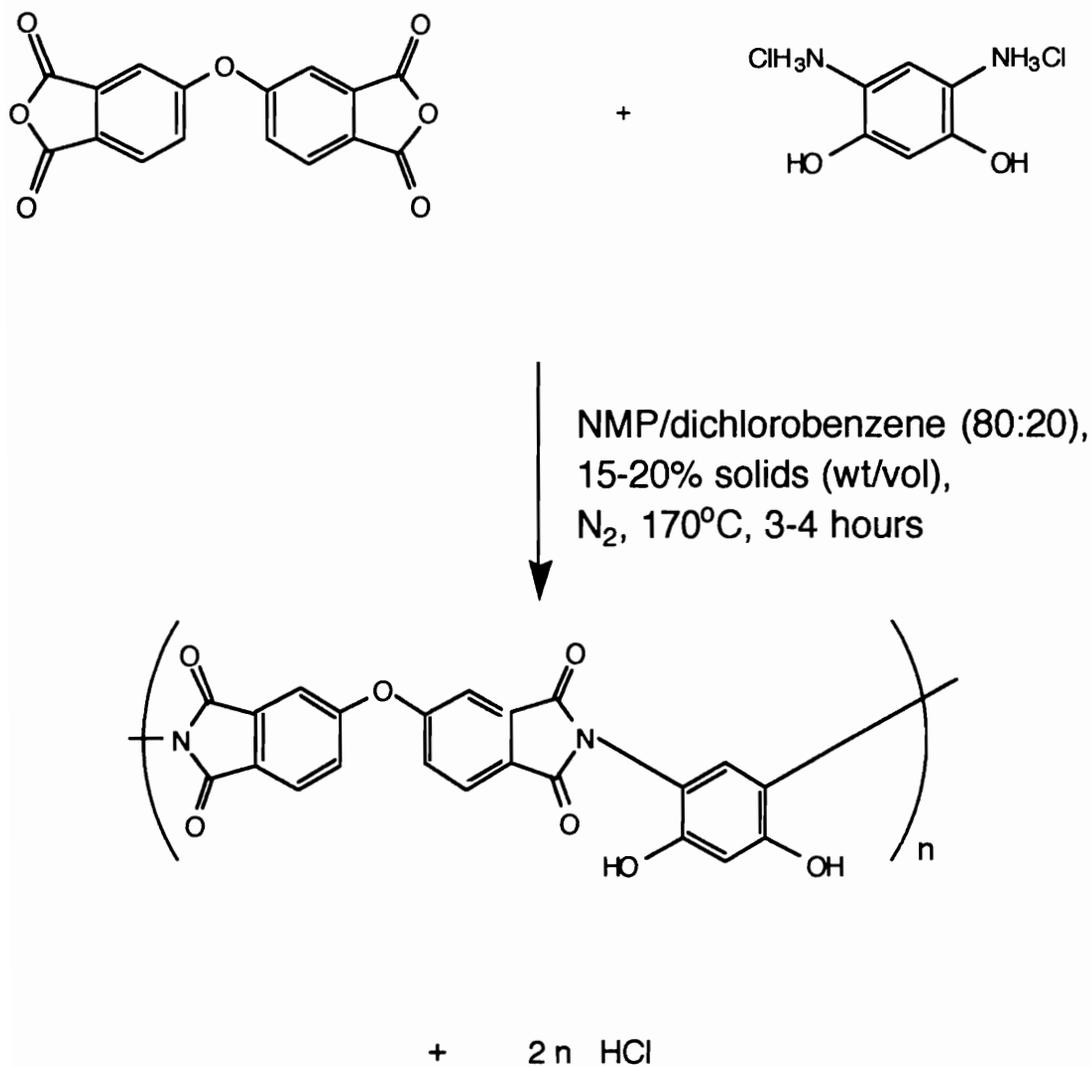
As the free base form of diaminoresorcinol is extremely susceptible to oxidation, initial deprotonation of the dihydrochloride by triethylamine (as in polyimide synthesis from *p*-phenylene-

diamine dihydrochloride) was undesired. Diaminoresorcinol dihydrochloride was heated in an NMP/dichlorobenzene mixture to determine whether dissociation to free diamine and hydrogen chloride gas occurs under solution imidization conditions. The salt was not soluble in this solvent mixture, however, in the temperature range of 85°C to 90°C a white vapor was observed evolving from the salt/solvent mixture. Moist pH indicator paper placed in the path of this vapor immediately turned bright red, indicating the evolution of hydrogen chloride at moderate temperatures.

Thus, polymerizations were performed in the absence of acid acceptors; dianhydride was introduced to the reactor first, followed by diaminoresorcinol dihydrochloride and polymerization solvents. The resulting mixture was rapidly heated to 170°C to 180°C. Scheme 4.2.3.1 illustrates poly(hydroxy-imide) synthesis. The list of dianhydrides used includes ODPA, BTDA, 6FDA, BPDA and PMDA; repeat units are indicated in Figure 4.2.3.1.

The polymerizations were heterogeneous in the initial stages: the salt dissociated to hydrogen chloride gas and diamine, which dissolved and polymerized, over a period of 2 to 3 hours. After this time no salt was visible and clear solutions were obtained.

Polymer solutions generally became too viscous to stir within 4 hours, except the 6F-based system, which became viscous within 8 hours but never ceased stirring. The dramatic increase in viscosity was no doubt a result of hydrogen bonding of the phenolic hydroxyl groups as well as increasing molecular weight, as none of these



Scheme 4.2.3.1. Synthesis of Polyimide Derived from Diaminoresorcinol Dihydrochloride

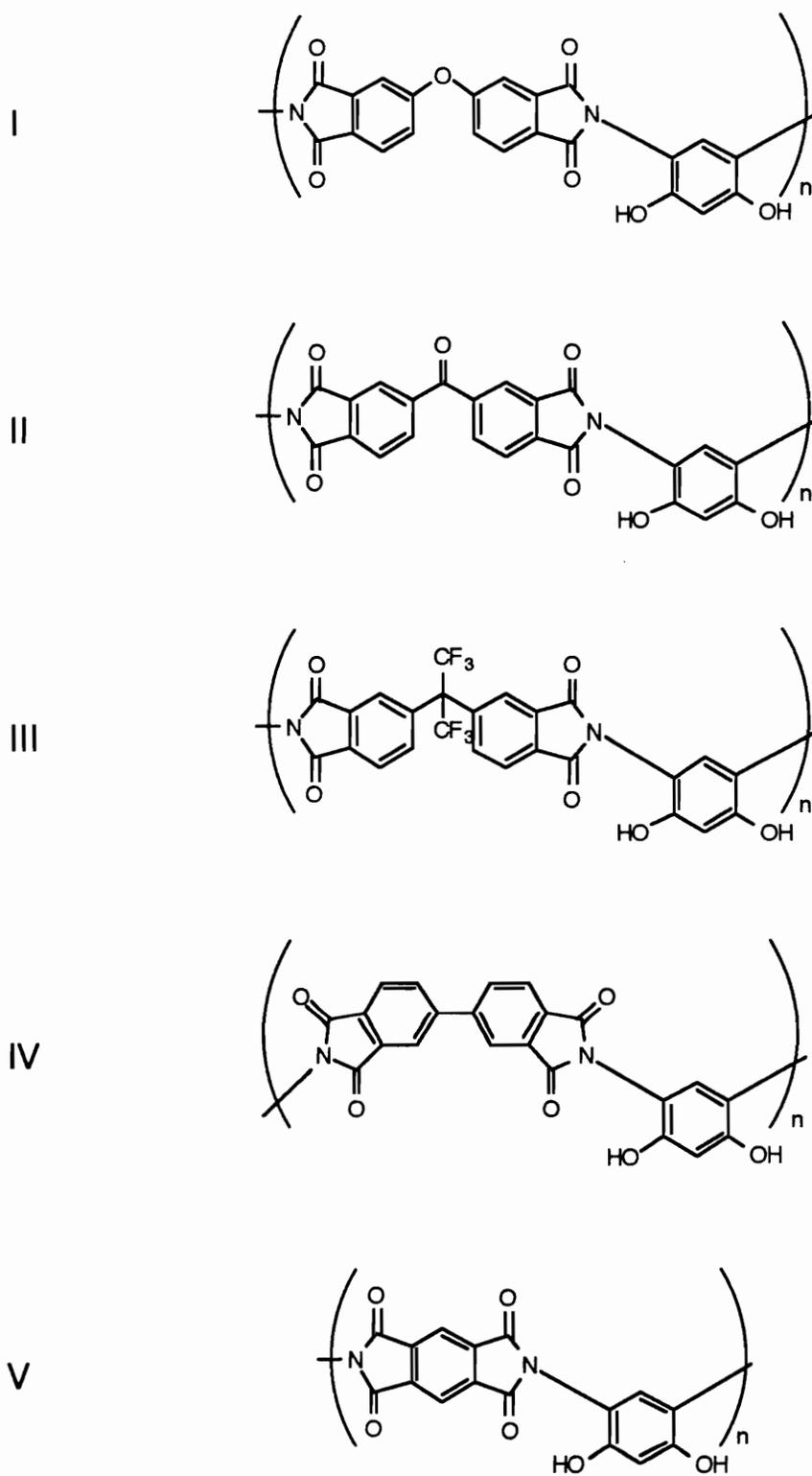


Figure 4.2.3.1. Repeat Units of Poly(hydroxy-imide)s

polymers displayed exceptionally high intrinsic viscosities. All of these polyimides remained soluble during synthesis, however.

The presence of the imide heterocycle in these polymers was confirmed by FTIR; all exhibited characteristic imide absorbances at 1780, 1730, 1370 and 720  $\text{cm}^{-1}$  as well as a strong absorbance at 3400  $\text{cm}^{-1}$  due to the phenolic hydroxyl groups. The IR spectrum of polymer III is shown in Figure 4.2.3.2.

The poly(hydroxy-imide)s were insoluble in organic solvents such as common alcohols (methanol, ethanol, isopropanol), chloroform, methylene chloride, diethyl ether, tetrahydrofuran and triethylamine; none of these solvents are sufficiently polar to dissolve these materials. Nevertheless, the high concentration of hydroxyl groups does impart interesting solubility characteristics to these polyimides.

All dissolved readily in N-methylpyrrolidinone (NMP) or N,N-dimethylacetamide (DMAc) at a concentration of 15% (wt/vol), and it was possible to cast transparent films from these solvents. In contrast, polyimides derived from 2,4-diaminophenol are reportedly insoluble, except for the polymer based on 6F dianhydride [183].

In addition, all dissolve instantly in concentrated ammonium hydroxide and also dissolve readily in strong dilute aqueous base. Polyimides based on 6FDA and ODPA readily dissolve to form dilute solutions in pyridine, and in fact, light green films of these polymers may be cast from pyridine. The remaining polymers swell but do not dissolve in pyridine. Solubilities are summarized in Table 4.2.3.1.

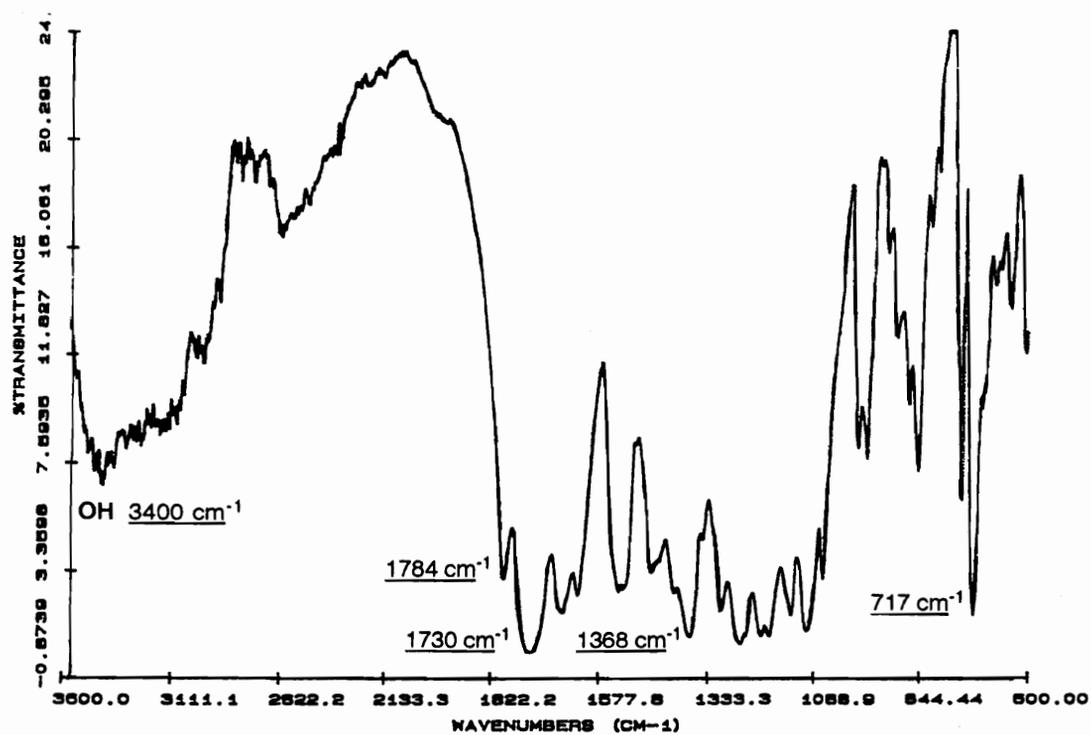


Figure 4.2.3.2. FT-IR Spectrum of Poly(hydroxy-imide) III

Table 4.2.3.1. Solubilities of Poly(hydroxy-imide)s at 25°C

Polymer	NMP 15% wt/vol	DMAc 15% wt/vol	Triethyl amine 1% wt/vol	Pyridine 1% wt/vol	NH <sub>4</sub> OH (3.7 M) 5% wt/vol	KOH (1.0 M) 1% wt/vol
I	+	+	-	+	+	+
II	+	+	-	sw	+	+
III	+	+	-	+	+	+
IV	+	+	-	sw	+	+
V	+	+	-	sw	+	+

+, soluble; -, insoluble; sw, swells

Table 4.2.3.2. Properties of Poly(hydroxy-imide)s

<u>Polymer</u>	<u>[<math>\eta</math>], dL/g*</u>	<u>T<sub>g</sub> (°C)</u>	<u>5% wt loss (°C)</u>
I	0.61	263	350
II	0.36	324	462
III	0.40	324	493
IV	0.57	343	478
V	0.32	362	418

\* Intrinsic viscosities were determined in NMP at 25°C

Glass transition temperatures were determined by DSC using a heating rate of 10°C/min. As expected, these polyimides exhibit reasonably high  $T_g$ 's, in the range of 260°C to 360°C, and the observed  $T_g$ 's follow the expected order, i.e., ODPA < BTDA = 6FDA < BPDA < PMDA.

5% weight loss temperatures were determined in air at a heating rate of 10°C/min and varied from 350°C to 490°C, considerably lower than 5% weight loss temperatures measured for aromatic polyimides without pendant hydroxyl groups. This may be due to oxidation or other decomposition reactions involving the phenolic hydroxyl groups. Thermal analysis results are listed in Table 4.2.3.2, as well as intrinsic viscosities.

Dynamic thermogravimetric analysis of samples exposed to the atmosphere for 7 days revealed that these polyimides absorb 4-9% water by weight; water loss was observed up to 250°C. Immersion of polyimides in water at 30°C for ten days resulted in substantial increases in water uptake, as shown in Figure 4.2.3.3. The polyimide based on PMDA is most remarkable, with a value of 15.6 percent. As expected, the polymer based on the relatively hydrophobic 6FDA shows the lowest water uptake, while the PMDA-based polyimide (with the highest concentration of hydroxyl groups and imide heterocycles) displays the highest water uptake.

Although water uptake is generally undesirable in electronic or structural applications, such materials could possibly be useful, for example, as membranes for the separation of water from alcohols.

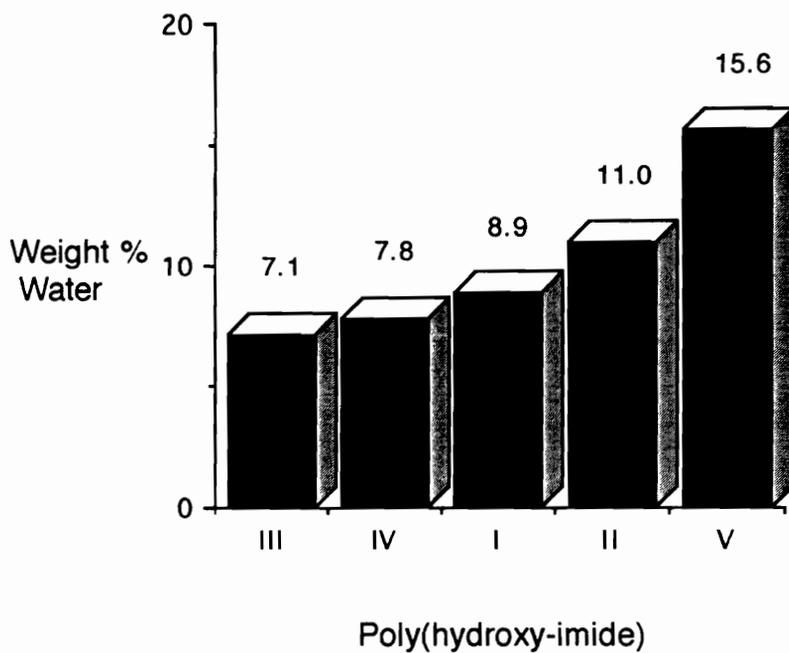


Figure 4.2.3.3. Bar Graph Showing Water Uptake of Poly(hydroxy-imide)s

Additionally, the phenolic hydroxyl groups could in principle serve as reactive sites for the attachment of pendant groups, resulting in yet more novel materials; for example, hydroxyl-substituted polyimides could be reacted with benzoyl chloride to afford pendant-ester polyimides, or with methacryloyl chloride to afford a thermosetting polyimide. Furthermore, a number of graft copolymers may be possible, such as polyimides bearing side-chain polyester, polyether, polysiloxane, poly(arylene ether-sulfone) or poly(arylene ether-ketone) segments.

Although the practical utility of the poly(hydroxy-imide)s has yet to be demonstrated, the fact that they can be synthesized is significant. The results clearly indicate that, utilizing existing solution imidization techniques and diamine dihydrochlorides, it is possible to synthesize high  $T_g$  soluble polyimides which cannot be prepared by the conventional two-step polyimide synthesis.

### 4.3 Thermosetting Imides

#### 4.3.1 Ethynyl-Functionalized Polyimides

Ethynyl-functionalized soluble imide oligomers were of interest as potentially useful materials for the generation of high  $T_g$  thermoset matrices. The use of soluble precursors offers several advantages over bulk PMR syntheses; soluble, isolable, fully cyclodehydrated imide oligomers can be prepared at relatively low temperatures without crosslinking. The solubility of these oligomers permits characterization of molecular weight and its distribution,

which should be of interest in designing high temperature thermosets. In addition, storage of stable, fully cyclodehydrated oligomers as dried powders or in solution is possible; currently available PMR resins are prepared from unstable methanolic solutions of monomers and end caps.

The ethynyl end group was of interest for several reasons; it can be incorporated as an end group using the commercially available 3-ethynylaniline (*m*-aminophenylacetylene) which is readily purified by vacuum distillation, and crosslinking occurs thermally without the evolution of volatiles.

Ethynyl-functionalized ODPA/ 3,3'DDS imide oligomers were initially evaluated as a model system . No solids precipitated and no turbidity was observed during the polymerization, indicating that no crosslinking occurred. In addition, the isolated oligomers completely redissolved in NMP. Although the ethynyl endgroups could not be detected by FT-IR spectroscopy, the <sup>1</sup>HNMR spectra of the uncured oligomers display a resonance due to the ethynyl proton, as shown in Figure 4.3.1.1. These materials became insoluble after heating to 350°C, swelling but not dissolving in NMP. Table 4.3.1.1 lists data for the ODPA/DDS oligomers; the cured ethynyl terminated materials show glass transition temperatures in the range of 239-244°C after crosslinking, slightly less than the value of 248°C measured for a high molecular weight linear ODPA/DDS polyimide.

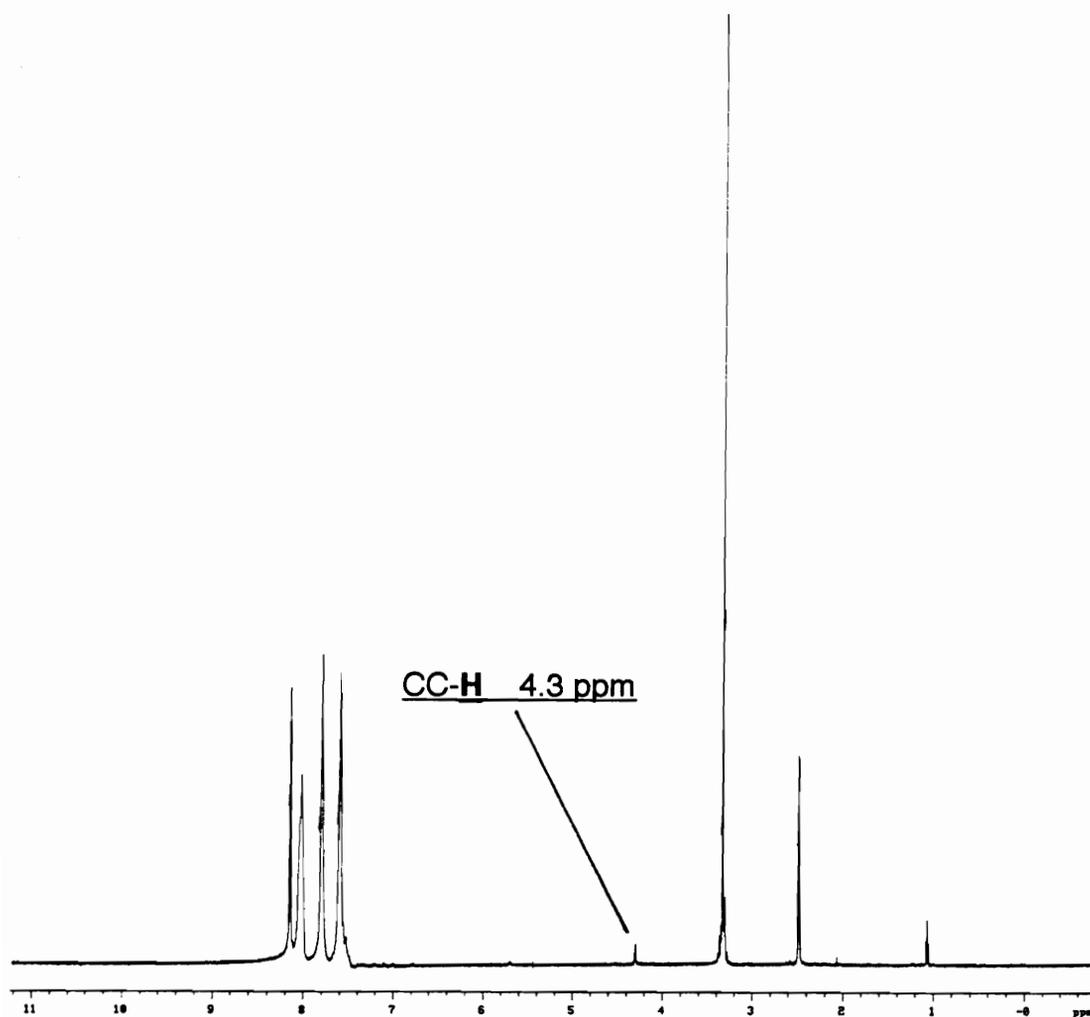


Figure 4.3.1.1. <sup>1</sup>H NMR Spectrum of Ethynyl-Functionalized ODPA - 3,3'-DDS Imide Oligomer. Ethynyl resonance occurs at 4.3 ppm.

Table 4.3.1.1. Ethynyl-Functionalized ODPA-3,3'-DDS  
Imide Oligomers

<u>Target <math>\langle M_n \rangle</math></u>	<u><math>\langle M_n \rangle^*</math></u>	<u><math>\langle M_w \rangle / \langle M_n \rangle</math></u>	<u><math>T_g</math> (°C)</u>
5.0 x 10 <sup>3</sup>	8.0 x 10 <sup>3</sup>	2.0	244
1.0 x 10 <sup>4</sup>	9.1 x 10 <sup>3</sup>	2.1	239
1.5 x 10 <sup>4</sup>	1.0 x 10 <sup>4</sup>	2.0	242

\* Determined by absolute GPC

Table 4.3.1.1. Ethynyl-Functionalized BTDA-3,3'-DDS  
Imide Oligomers

<u>Target <math>\langle M_n \rangle</math></u>	<u><math>\langle M_n \rangle^*</math></u>	<u><math>\langle M_w \rangle / \langle M_n \rangle</math></u>	<u><math>T_g</math> (°C)</u>
5.0 x 10 <sup>3</sup>	5.0 x 10 <sup>3</sup>	2.0	271
1.0 x 10 <sup>4</sup>	9.7 x 10 <sup>3</sup>	2.1	269
1.5 x 10 <sup>4</sup>	1.5 x 10 <sup>4</sup>	2.0	269

\* Determined by absolute GPC

The measured molecular weights for this series of oligomers indicate that molecular weights were indeed limited, although the desired level of molecular weight control was not achieved. The number average molecular weights as determined by GPC are not in agreement with the target molecular weights. The difficulty in achieving the target molecular weights for this system is undoubtedly a consequence of the low reactivity of ODPA, an electrophilic monomer bearing an electron donating group, and 3,3'-DDS, a nucleophilic monomer bearing a strong electron withdrawing group.

Also, because end group concentration could not be determined, it is possible that *m*-amino phenyl acetylene was not fully incorporated. In addition to the relatively high oligomer molecular weights, this might explain the low T<sub>g</sub> values of the cured oligomers.

Experiments were repeated using the BTDA-3,3'-DDS system. It was expected that more reactive monomer combinations would result in a greater degree of molecular weight control and this was indeed the case; better results were obtained for this system, as evidenced by the intrinsic viscosities and  $\langle M_n \rangle$  values of the uncured BTDA-3,3'-DDS ethynyl-functionalized oligomers (Table 4.3.3.2). In addition, polydispersity ratios were in very good agreement with the theoretical value of 2.0. The symmetric GPC traces also indicate that disproportionate amounts of high or low molecular weight species

were not obtained. Figure 4.3.3.2 shows the GPC traces for the BTDA-3,3'-DDS oligomers

$T_g$ 's of the cured oligomers were not significantly higher than the value of 265°C for the high molecular weight linear system. This is probably due to the low end group concentration in these systems; it is likely that crosslinking is accompanied by a significant degree of chain extension, resulting in a relatively high molecular weight between crosslinks.

Controlled molecular weight ethynyl-functionalized oligomers were also prepared based on the following monomer combinations to afford higher  $T_g$  thermosets: 6F-oxydianiline, 6F-methylene-dianiline, 6F-*p*-phenylenediamine and 6F-fluorenediamine. Molecular weight control was particularly effective for the 6F-*p*-phenylenediamine system, which shows excellent agreement between target and actual  $\langle M_n \rangle$  values.

The 6FDA-FDA system failed to yield all of the desired molecular weights however, and this was attributed to low mutual reactivity of the monomers, probably due in part to the steric bulk of fluorenediamine. Properties are listed in Table 4.3.1.3.

For all of these systems, the ethynyl carbon-carbon bond could not be detected by FT-IR spectroscopy but all samples displayed imide absorbances in the regions of 1780, 1730, 1370 and 710-720  $\text{cm}^{-1}$  and an absence of absorbances attributable to amide-acid. The presence of the ethynyl end group was detected by  $^1\text{H}$  NMR, although it could not be determined quantitatively.

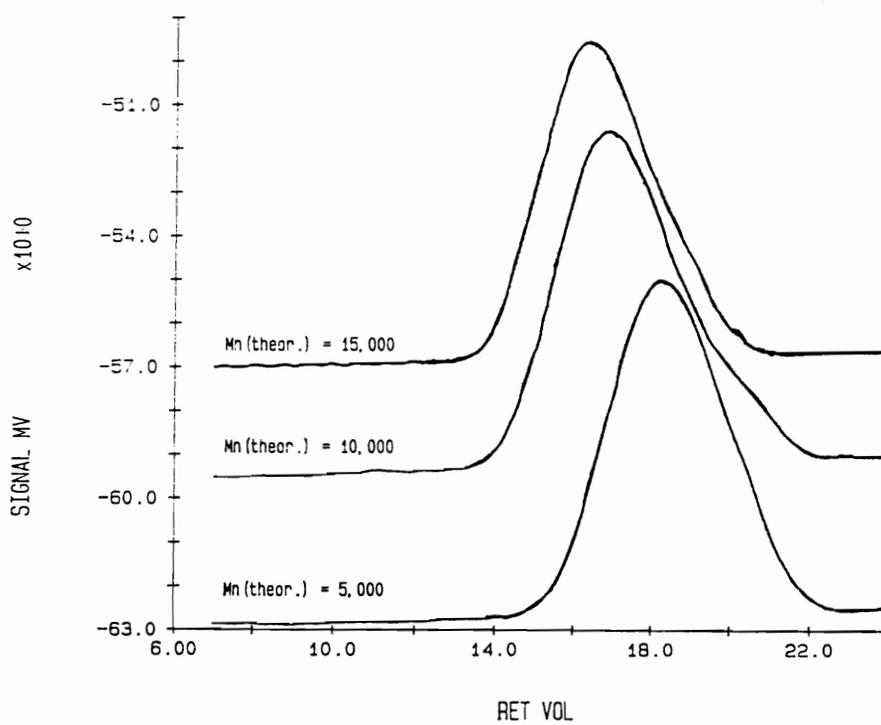


Figure 4.3.1.2. GPC Curves of BTDA-3,3'-DDS Ethynyl-Functionalized Imide Oligomers

Table 4.3.1.3. Properties of Ethynyl-Functionalized Imide Oligomers

<u>Target <math>\langle M_n \rangle</math></u>	<u><math>\langle M_n \rangle^*</math></u>	<u><math>\langle M_w \rangle / \langle M_n \rangle</math></u>	<u>T<sub>g</sub> (°C)**</u>	<u>5% weight loss (°C)***</u>
<u>6F-MDA</u>			(290)	
1.0 x 10 <sup>4</sup>	1.1 x 10 <sup>4</sup>	2.0	292	496
1.5 x 10 <sup>4</sup>	1.6 x 10 <sup>4</sup>	2.1	290	504
<u>6F-ODA</u>			(305)	
1.0 x 10 <sup>4</sup>	1.2 x 10 <sup>4</sup>	2.0	303	531
1.5 x 10 <sup>4</sup>	1.7 x 10 <sup>4</sup>	2.0	303	550
<u>6F-FDA</u>			(370)	
5.0 x 10 <sup>4</sup>	7.6 x 10 <sup>4</sup>	2.0	374	535
1.0 x 10 <sup>4</sup>	8.2 x 10 <sup>4</sup>	2.0	372	530
1.5 x 10 <sup>4</sup>	1.3 x 10 <sup>4</sup>	2.0	371	552
<u>6F-p-PDA</u>			(350)	
1.0 x 10 <sup>4</sup>	1.0 x 10 <sup>4</sup>	1.9	360	554
1.5 x 10 <sup>4</sup>	1.5 x 10 <sup>4</sup>	2.3	360	525
2.0 x 10 <sup>4</sup>	2.0 x 10 <sup>4</sup>	2.1	362	552

\* Determined by absolute GPC

\*\* T<sub>g</sub>'s are for crosslinked oligomers (2<sup>nd</sup> heat). Values in parentheses indicate T<sub>g</sub> of high molecular weight linear polyimides

\*\*\* TGA determined in air

None of these materials showed evidence of crosslinking during synthesis but heating to 400°C resulted in materials which swelled but did not completely redissolve in NMP or DMAc. Crosslinking exotherms were seldom observed during DSC scans; Figure 4.3.1.3 shows the second heat of a BTDA-3,3'-DDS ethynyl-functionalized oligomer, which displays a crosslinking exotherm immediately following the glass transition endotherm. Measured  $T_g$ 's and 5% weight losses (dynamic TGA) are consistent with the respective values for the linear high molecular weight polyimides for most of these samples; only the 6F-*p*-phenylenediamine polyimides displayed  $T_g$ 's higher than the linear high molecular weight system.

Figure 4.3.1.3 showed that when the relatively low temperature-curing ethynyl end group terminates a high  $T_g$  backbone, the crosslinking reaction can be delayed until the  $T_g$  of the imide oligomer is attained. However, despite the low end group concentration, chain extension and crosslinking apparently occur quite rapidly, as it was not possible to "melt press" any of these oligomers into crosslinked films; sufficient flow and consolidation of the material did not occur to allow the preparation of uniform, void free samples.

Solution cast films could be prepared from a number of samples, however, and several of these, based on the 6F-ODA and 6F-MDA systems, were used in extraction studies. The uncrosslinked precursors were all soluble in chloroform, facilitating solvent extraction. Results are depicted in Figure 4.3.1.4 . In all instances a

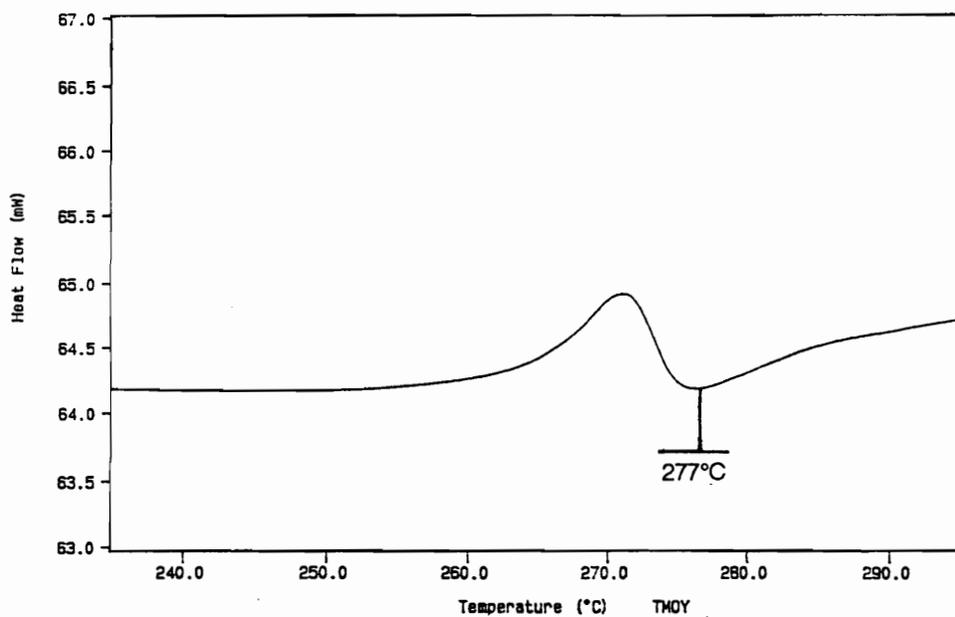


Figure 4.3.1.3. DSC Curve of 5K BTDA-3,3'-DDS Ethynyl-Functionalized Imide Oligomer. Cure exotherm occurs at 277°C.

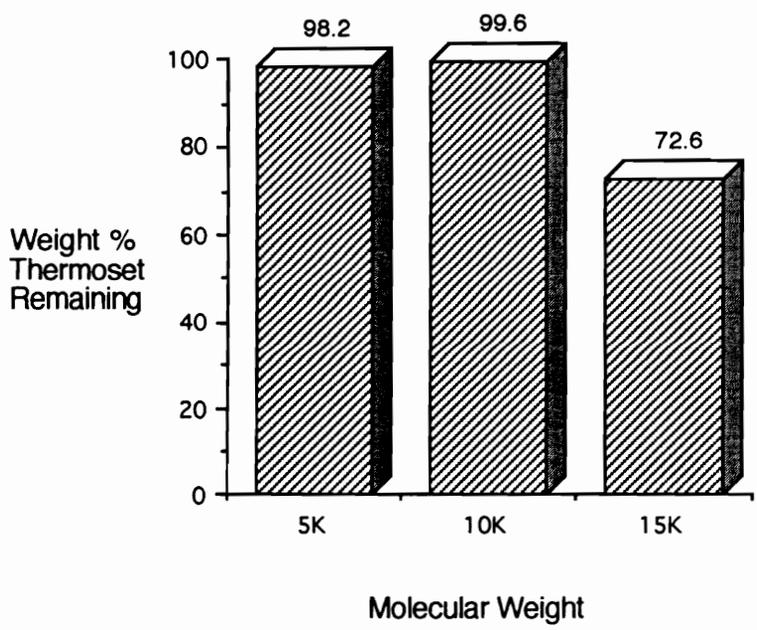
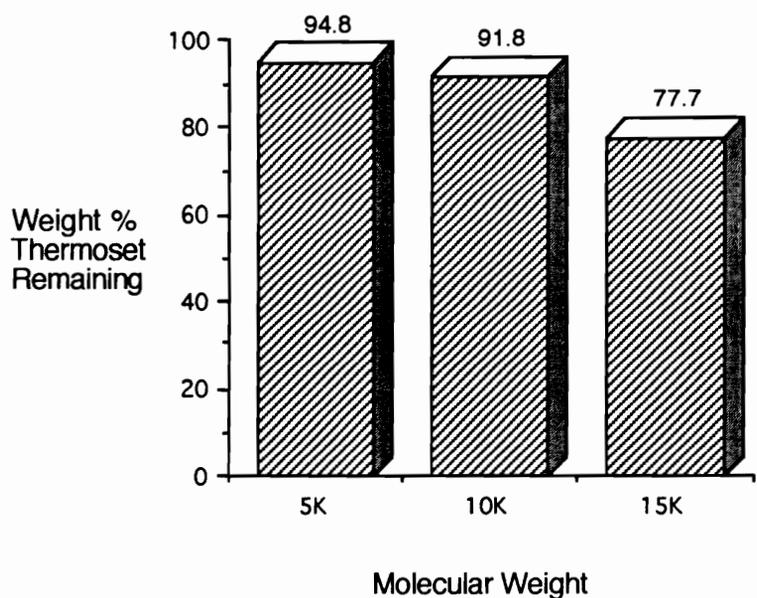


Figure 4.3.1.4. Bar Graphs Showing Gel Fraction After 120 Hour Chloroform Extraction of 6F-MDA Polyimide Thermosets (top) and 6F-ODA Polyimide Thermosets (bottom)

significant gel fraction remained, confirming that the materials were indeed crosslinked. However, there appears to be an inverse correlation between oligomer molecular weight prior to curing and gel fraction remaining after cure. This clearly indicates that for the higher molecular weight oligomers, substantial amounts of material are not incorporated into the network structure. This can be attributed to the low end group concentration; mobility becomes increasingly restricted as chain extension and crosslinking occur, with the result that some end groups become isolated and inaccessible for further reaction. Consequently, the resulting thermoset is a lightly crosslinked polyimide network which still contains a significant fraction of soluble, linear polyimide.

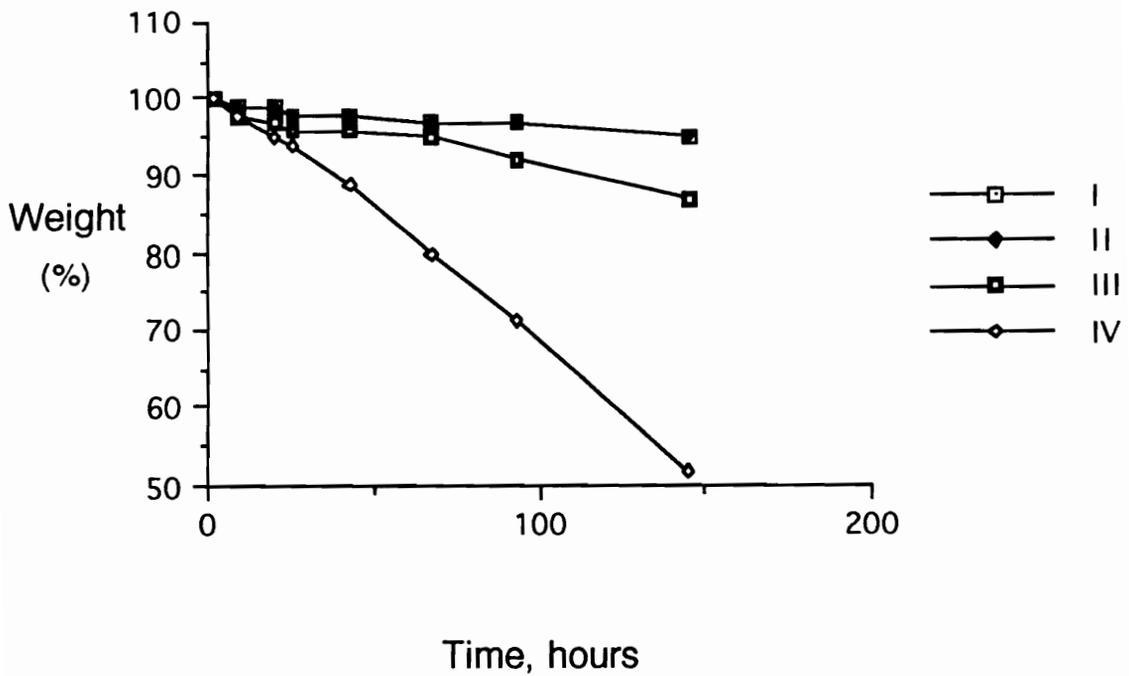
In order to identify polyimide systems for potential 700°F (371°C) applications, films of the higher  $T_g$  samples (360°C and above) were evaluated for long term isothermal stability in air at 371°C. Although it is not, strictly speaking, a realistic measure of a material's actual performance (no information is obtained regarding decomposition mechanisms and products, changes in crosslink density and mechanical properties, etc.), isothermal thermogravimetric analysis is currently an accepted and convenient means of assessing long term, high temperature thermooxidative stability of polymeric materials.

Samples included the 6F-*p*-phenylenediamine, 6F-fluorenediamine and BPDA-6F-4,4'-diaminodiphenyl sulfone polyimides. Isothermal weight loss curves are illustrated in Figure

4.3.1.5. The crosslinked 6F-*p*-phenylenediamine films displayed excellent stability as determined by isothermal TGA, retaining 95 percent of their mass after 150 hours at 371°C in air. The curves for both the 15K and 20K films are indistinguishable. In comparison, the BPDA-6F-4,4'-DDS copolymer displayed good isothermal stability under the same conditions, retaining 87 percent of its mass after 150 hours. In contrast to these systems, the 6F-FDA sample, although possessing a high  $T_g$ , exhibits relatively poor stability, losing approximately 50 percent of its mass under identical conditions.

Two features can account for the performance of 6F-phenylene diamine: first is the hexafluoroisopropylidene linkage, which is known to provide thermooxidatively stable polymers, and the second is the absence of an unstable linkage in the diamine residue of the polymer repeat unit.

The relatively good performance of the BPDA-6F-4,4'-DDS copolymer may arise from a combination of the stable "6F" and biphenyl dianhydride linkages and the sulfone linkage of 4,4'-DDS. Although the connecting sulfone group is thermooxidatively less stable than the hexafluoro isopropylidene linkage, the electron deficiency of 4,4'-diaminodiphenylsulfone may promote resistance to oxidation [34]. The sulfone linkage is most likely the "weak link" in the polymer backbone. However, without long-term isothermal TGA-mass spectrometry data, the relative contributions of each connecting group to polyimide instability (weight loss) cannot be determined.



I 6F-*p*-phenylene diamine, 20k

II 6F-*p*-phenylene diamine, 15k

III 6F/biphenyl dianhydride-4,4' diamino diphenylsulfone, 21k

IV 6F-9,9-bis(4-aminophenyl) fluorene, 15k

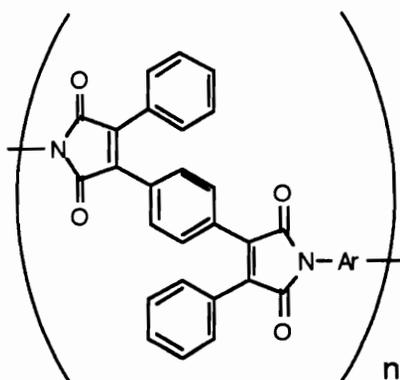
Figure 4.3.1.5. Weight Loss versus Time for Crosslinked Ethynyl-Functionalized Polyimides in Air at 371°C. Curves I and II are overlaid.

In contrast to the preceding systems, the 6F-FDA system displayed an unacceptably high weight loss and, considering the results obtained for the 6F-phenylenediamine samples, this is attributed to degradation of the fluorene segment in the polymer backbone. The tetrahedral carbon of fluorene diamine would be expected to be the most likely point of oxidation.

#### 4.3.2 Polyimides Containing Backbone Maleimide Units

As part of a continuing interest in high temperature, high performance polymeric materials, the synthesis and properties of polyimides derived from 1,4-bis(phenylmaleic anhydride)benzene (BPMB) were investigated.

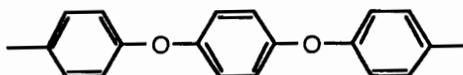
The unique structure of BPMB was expected to impart interesting and potentially useful properties to polyimides; the non-fused ring heterocyclic structure was expected to promote solubility in organic solvents and the pendent phenyl groups were also expected to contribute to solubility and high  $T_g$ 's. Moreover, it was hypothesized that the resultant backbone maleimide units could serve as reactive sites in a subsequent thermal crosslinking reaction and would cure without evolution of volatiles to form high  $T_g$ , solvent resistant polyimide thermosets. The uncured polymers derived from BPMB generally display similar solubilities but lower  $T_g$ 's than their 6F-based analogs. Repeat units are shown in Figure 4.3.2.1.



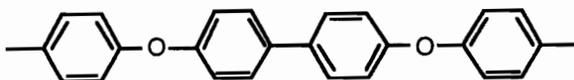
Polymer

Ar

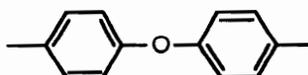
I



II



III



IV

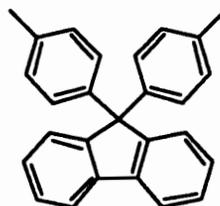


Figure 4.3.2.1. Repeat Units of BPMB-Based Polyimides

Because the anhydride carbonyl groups are not directly bonded to an aromatic structure, the reactivity of BPMB was not expected to be as great as that of conventional dianhydrides such as pyromellitic dianhydride or benzophenonetetracarboxylic dianhydride. This was indeed the case, as esterification in the presence of triethylamine required 90 minutes; PMDA and bis(phthalic anhydride) derivatives generally underwent esterification in the presence of triethylamine within 10 minutes.

Because of the apparently low reactivity of BPMB and its solubility in hot NMP and dichlorobenzene a "one-step" high temperature solution polymerization was employed, as for the synthesis of polyimides from diaminoresorcinol dihydrochloride. Monomers dissolved readily to afford yellow solutions, which gradually became dark brown and increasingly viscous as polymerization proceeded. The polymers remained in solution throughout the duration of the reaction, typically 24 hours.

Polyimides derived from BPMB have an intense, bright yellow color, whereas those based on bis(phthalic anhydride) derivatives may range in color from cream or off-white to pale yellow (in the absence of impurities). The intense coloration suggests a high degree of conjugation in these polymers. The presence of the imide heterocycle in these polymers was confirmed by FT-IR; all exhibited strong absorbances at approximately 1770, 1715, and 1377-1390  $\text{cm}^{-1}$ ; none displayed absorbances in the vicinity of 720  $\text{cm}^{-1}$  but instead showed strong signals at 750-760  $\text{cm}^{-1}$ . These absorbances

are consistent with the imide absorbances exhibited by *N*-phenylmaleimide; 1775, 1710, 1393 and 756 cm<sup>-1</sup>. Figure 4.3.2.2 shows the FT-IR spectrum of *N*-phenylmaleimide. FT-IR spectra of polyimide III are shown in Figure 4.3.3.1.

As indicated previously, the reactivity of BPMB was not expected to be as great as that of conventional dianhydrides such as pyromellitic dianhydride or bis(phthalic anhydride) derivatives. The low reactivity of BPMB is also manifested in the failure to attain the desired molecular weights in controlled molecular weight experiments, as shown in Table 4.3.2.1. However, GPC results indicate that molecular weight distributions ( $\langle M_w \rangle / \langle M_n \rangle$ ) are very close to the theoretical value of 2.0. All are soluble in NMP, DMAc, THF, methylene chloride and chloroform at room temperature at a concentration of 15% (wt/vol), as are the analogous 6FDA-based polyimides.

In uncontrolled molecular weight experiments, reasonably high molecular weights were attained for the polyimides derived from 1,4-bis(4-aminophenoxy)benzene (I), 4,4'-bis(4-aminophenoxy)biphenyl (II) and 4,4'-oxydianiline (III), as evidenced by  $\langle M_n \rangle$  values determined by GPC (Table 4.3.2.2). All three precipitated as bright yellow fibers. The polyimide derived from 9,9-bis-(4-aminophenyl)fluorene (IV) failed to yield high molecular weight polymer, and this may be due to steric factors as well as the low reactivity of BPMB; this polymer was isolated as a bright yellow powder.

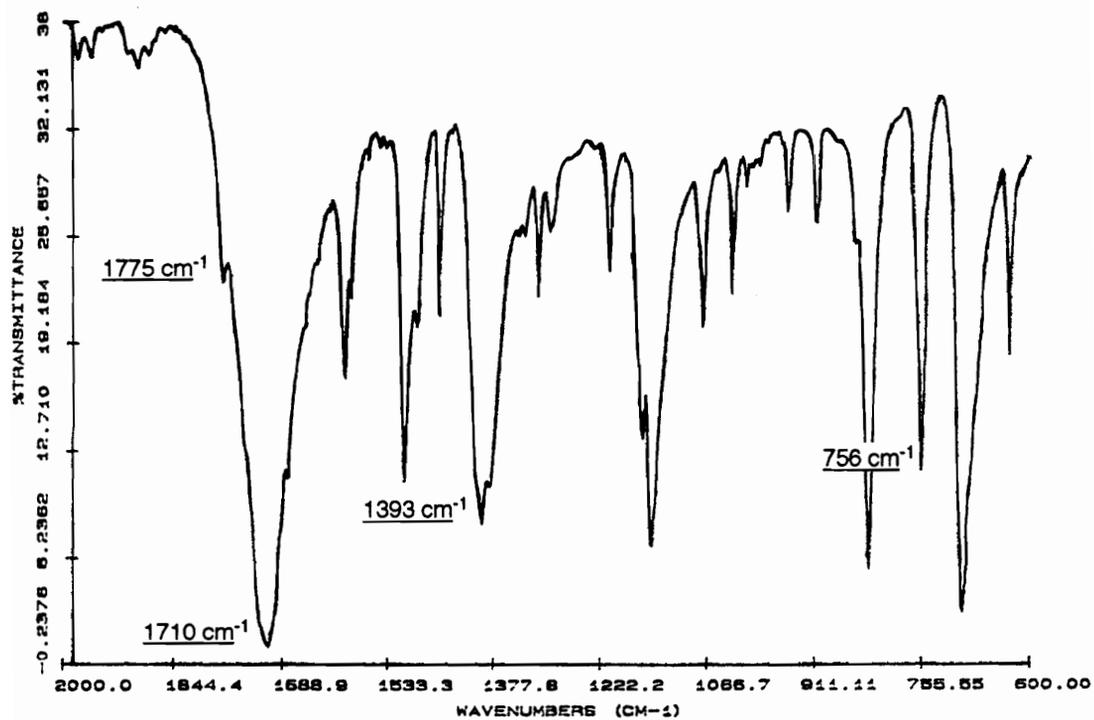


Figure 4.3.2.2. FT-IR Spectrum of N-Phenylmaleimide

Table 4.3.2.1. Properties of Controlled Molecular Weight  
BPMB-Based Polyimides

<u>Polymer</u>	$\langle M_n \rangle^*$	$\langle M_w \rangle / \langle M_n \rangle$	$T_g$ (°C)	5% weight <u>loss</u> (°C) **
I	$1.4 \times 10^4$	2.1	236	450
II	$1.0 \times 10^4$	2.2	235	494
III	$2.1 \times 10^4$	2.2	265	488
IV			302	420

\* determined by absolute GPC \*\*determined in air

Table 4.3.2.2. Properties of Uncontrolled (High) Molecular  
Weight BPMB-Based Polyimides

<u>Polymer</u>	$\langle M_n \rangle^*$	$\langle M_w \rangle / \langle M_n \rangle$	$T_g$ (°C)	5% weight <u>loss</u> (°C)**
I	$1.9 \times 10^4$	2.1	244	529
II	$3.3 \times 10^4$	2.2	256	489
III	$2.1 \times 10^4$	2.1	267	516
IV	$1.2 \times 10^4$	2.0	335	499

\* determined by absolute GPC \*\*determined in air

Uncontrolled molecular weight polyimides also displayed molecular weight distributions very closely approaching the theoretical value of 2.0 and showed the same solubility behavior as the low (controlled) molecular weight polyimides. As indicated in Table 4.3.2.2 the high molecular weight polyimides derived from BPMB possess reasonably high glass transition temperatures, in excess of 240°C. The molecular weights of I-III are sufficiently high that the corresponding  $T_g$ 's are believed to be the true values for these polymers; the value of 268°C for I is in excellent agreement with the literature value of 270°C. Polyimides I-III display  $T_g$ 's approximately 30°C lower than their 6F-based analogs.

These results and the low molecular weight of IV suggest that a higher  $T_g$  would be obtained for a high molecular weight (20k Daltons or greater) polyimide IV. If the trend observed for I-III is applicable to BPMB-based polyimides in general, the  $T_g$  of a high molecular weight BPMB-FDA polyimide may be on the order of 340°C to 350°C.

#### 4.3.3 Polymer Cure

Cure exotherms were not observed during DSC scans of these polymers. Indeed, films of both "controlled" and uncontrolled molecular weight samples heated at 320-330°C in nitrogen or air for 15 to 30 minutes dissolved completely when immersed in chloroform or methylene chloride. However, crosslinked samples were obtained at higher temperatures; after heating at 350-360°C

for 15 minutes in nitrogen, films would swell but not completely redissolve in chloroform or methylene chloride. The high curing temperature represents a potential processing window of approximately 100°C for several of these polymers, which offers the possibility of generating void-free thermosets via compression molding of solvent-free, fully-cyclized polyimides. Films of uncontrolled (high) molecular weight samples I-IV were cured at 30 and 60 minutes in nitrogen. All films darkened from yellow to brown and became less flexible with curing.

FT-IR spectra of cured and uncured films displayed the same absorbances and were virtually identical, as shown in Figure 4.3.3.1. The crosslinking efficiency may not be sufficiently high to cause significant spectroscopic changes upon curing. Therefore, additional methods were employed to demonstrate that crosslinking occurs in these systems.

$T_g$ 's would be expected to increase with the development of a three dimensional network structure as segmental motions become increasingly restricted; DSC results (see Figure 4.3.3.2) showed a significant increase in  $T_g$  upon curing, on the order of 25°C for polymer III, and increases of 20°C to 25°C, for polymers II-IV, as indicated in Figure 4.3.3.3. In addition, extraction studies were conducted to confirm that a significant gel fraction was obtained upon curing. Films of polymers I-III cured at 360°C for 30 minutes and a film of IV cured at 360°C for 60 minutes were exposed to

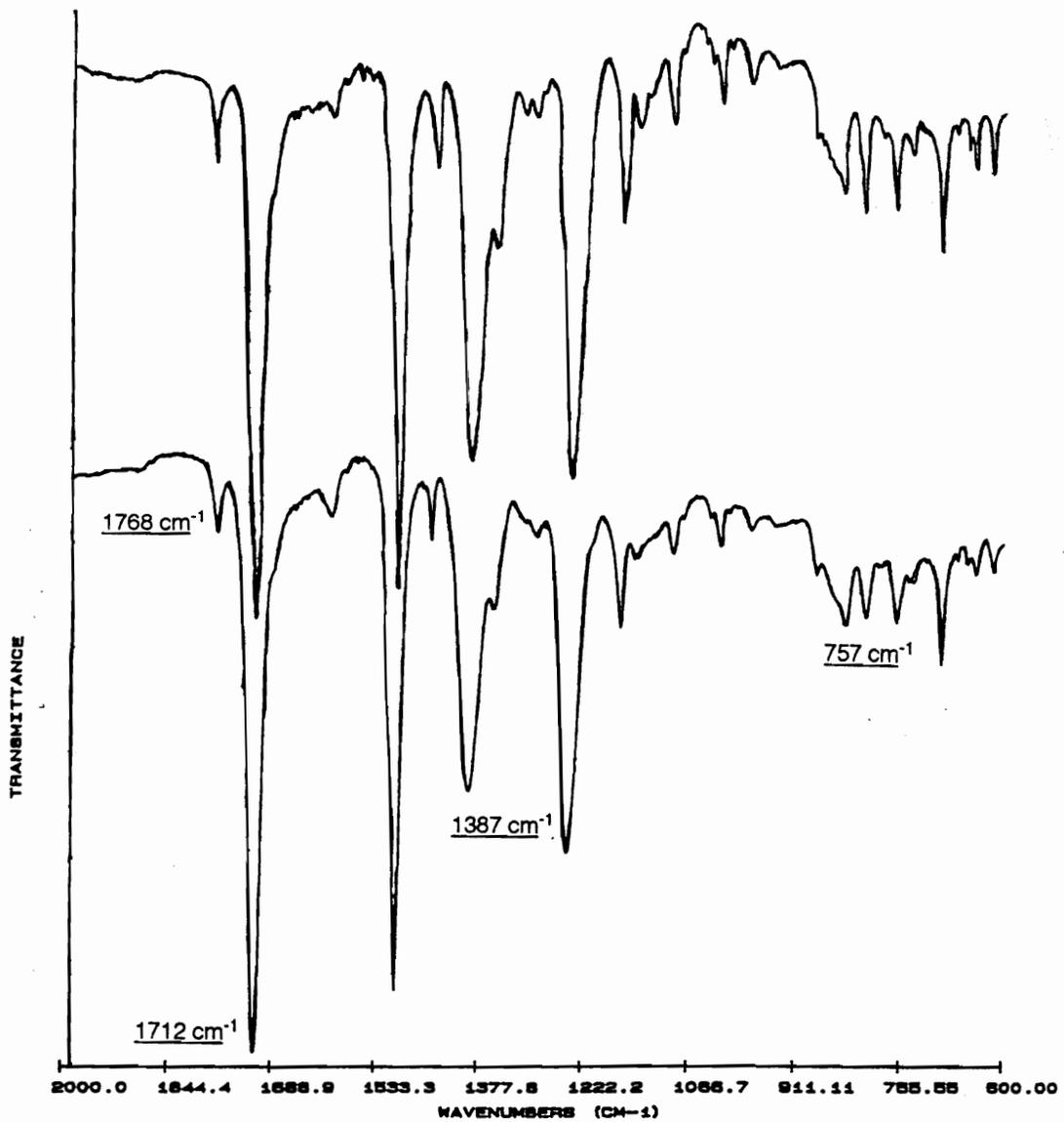


Figure 4.3.3.1. FT-IR Spectra of Polymer III Before (top) and After 30 Minute Cure at 350°C (bottom)

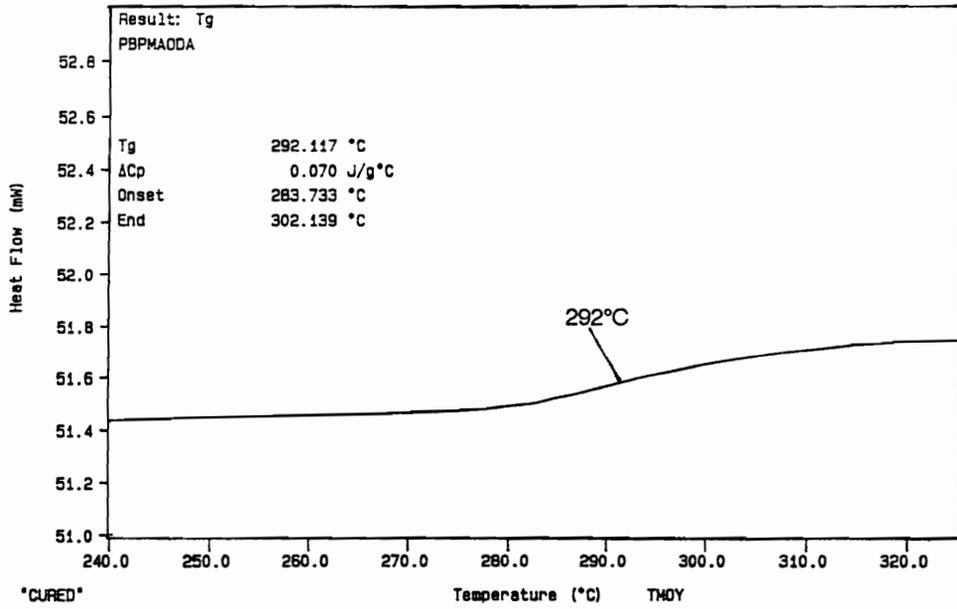
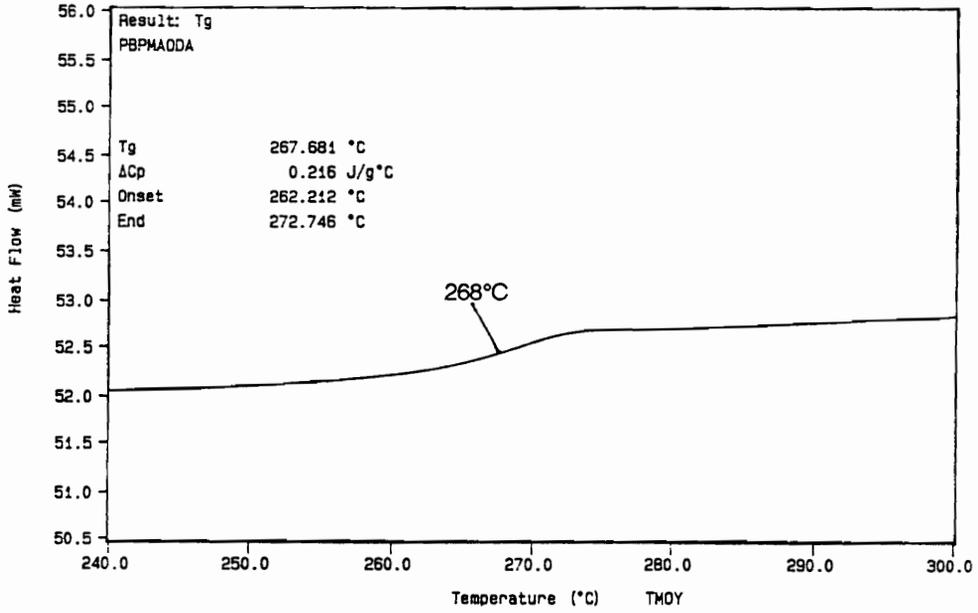


Figure 4.3.3.2. DSC Curves Showing Increase in Glass Transition Temperature With Cure for Polymer III: Uncured polyimide (top); Polyimide Cured at 350°C for 30 minutes (bottom)

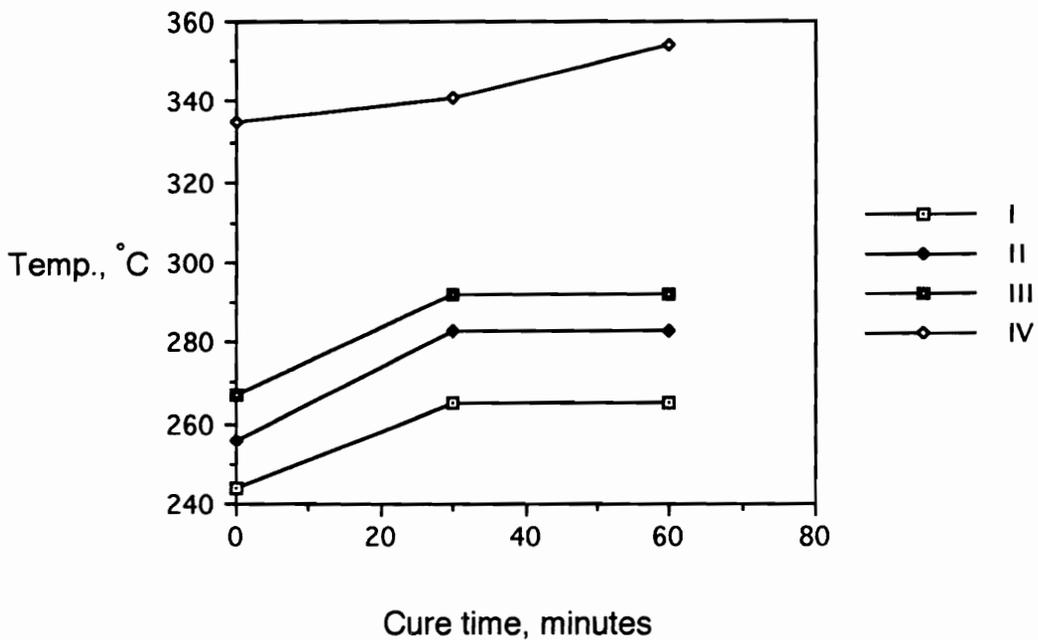


Figure 4.3.3.3. Line Graph Showing Glass Transition Temperature versus Cure Time (at 350°C) for BPMB-Based Polyimides

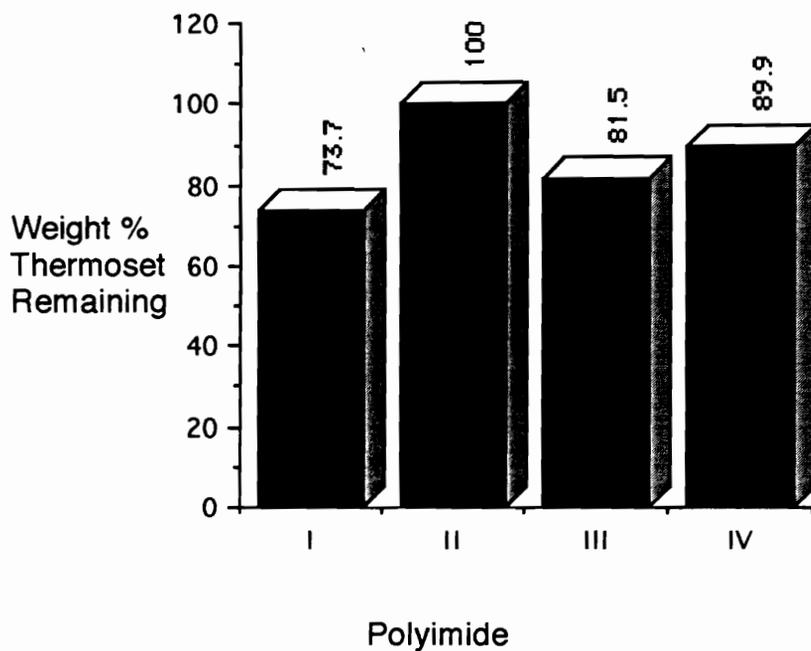


Figure 4.3.3.4. Bar Graph Showing Insoluble Fractions of Cured BPMB-Based Polyimides After 120 Hour Chloroform Extraction

refluxing chloroform for 120 hours; insoluble fractions ranged from 73-100 percent (weight), as shown graphically in Figure 4.3.3.4 .

## V. CONCLUSIONS

The major objectives of the research presented in this dissertation were the synthesis and characterization of soluble, processable linear and thermosetting polyimides for potential use as structural matrix resins, adhesives, coatings or gas separation membranes. Non-traditional synthetic methods were employed and several novel polyimides were successfully synthesized.

Suitable reaction conditions were established for the reproducible synthesis of polyimides utilizing diester-diacid monomers and aromatic diamines in an N-methylpyrrolidone/*o*-dichlorobenzene solvent mixture. Reaction conditions included solids contents of 15 to 20 percent (wt/vol), temperatures of 170°C to 180°C, and reaction times of 24 hours or less; "wet" glassware could be employed, i.e., flaming was unnecessary. The resulting polyimides were soluble in N-methylpyrrolidinone or N,N-dimethylacetamide at 25°C at concentrations of 15 to 20 percent (wt/vol), and many also displayed similar solubility in common solvents such as tetrahydrofuran, chloroform and methylene chloride. Moderate to high molecular weights were achieved, and the polyimides were completely cyclodehydrated and displayed T<sub>g</sub>'s by DSC which were consistent with the values obtained for identical materials synthesized by conventional methods. Model studies indicated that the polymerization is preceded by in situ formation of anhydride functional groups from the ortho ester-acids.

Controlled molecular weight ethynyl-functionalized polyimides were also successfully prepared from ester-acids using solution imidization techniques. This was accomplished without premature reaction of the terminal ethynyl groups, as evidenced by the solubility of the uncured materials, agreement between target number average molecular weights and values determined by GPC and molecular weight distributions as determined by GPC, which were generally in good agreement with the theoretical value of 2.0.

$T_g$ 's of the cured systems were not appreciably greater than those of the corresponding high molecular weight linear systems and displayed essentially no dependence on the molecular weight of the uncured oligomers. This was likely a consequence of the low end group concentration, resulting in substantial chain extension and a low crosslink density.

Despite the low end group concentration, the ethynyl-functionalized polyimides gelled rapidly; "melt pressing" failed to afford uniform, void free samples. Insoluble films could be obtained, however, by curing solvent-cast films for 15 to 20 minutes at 20°C above  $T_g$ ; solvent extraction of some of these samples revealed gel fractions ranging from 72 to 99 percent.

Although the ethynyl functionalized imides were of limited utility in terms of processability, at least two polyimide systems were identified for potential use at or near 700°F (371°C); one is a copolymer based on biphenyl dianhydride, "6F" dianhydride and 4,4'-diaminodiphenyl sulfone, which retains 87 percent of its mass

after 150 hours in air at 700°F. More promising is the thermoset based on "6F" dianhydride and *p*-phenylenediamine, which retains at least 95 per cent of its mass under identical conditions.

A previously unreported synthetic route to soluble polyimides was developed which makes use of diamine dihydrochlorides; this synthesis was also performed in an NMP-dichlorobenzene solvent mixture at 170°C to 180°C. Polymerization proceeds via initial dissociation of the hydrochloride salt to free amine and hydrogen chloride gas upon heating; the diamine rapidly dissolves and reacts with the dissolved dianhydride.

Although this synthetic route may not be attractive on an industrial scale due to the large volumes of hydrogen chloride gas which would be generated, it does permit the synthesis of soluble polyimides which cannot be prepared by conventional methods due to diamine instability.

A series of polyimides based on diaminoresorcinol was prepared in this manner, representing both a novel synthetic route to polyimides and a series of novel polyimides which contain two phenolic hydroxyl groups per repeat unit. The poly(hydroxy-imide)s display high  $T_g$ 's, in excess of 250°C.

The high concentration of pendant hydroxyl groups in these materials renders them soluble in dilute aqueous bases as well as high boiling aprotic amide solvents. Not surprisingly, these materials are also extremely hygroscopic, with weight increases in the range of 7 to 15 percent due to water uptake. Although water uptake is

generally undesirable in polyimides, this characteristic could possibly be of benefit, for example, in membranes for the removal of water from alcohol.

Finally, several novel thermosetting polyimides were derived from 1,4-bis(phenylmaleic anhydride)benzene (BPMB), a potentially inexpensive dianhydride monomer. These were synthesized via solution imidization techniques; however, due to the low reactivity of the bis(maleic anhydride) monomer, a "one-step" synthesis was employed, i.e., ester-acid intermediates were not employed, nor were intermediate poly(amic acid)s synthesized.

The resulting polyimides were soluble in NMP, DMAc, THF, chloroform and methylene chloride at 25°C at concentrations of 15 to 20 percent (wt/vol). Structural features contributing to the solubility of these materials are the flexible maleimide linkages and pendant phenyl groups which disrupt structural regularity.

The polyimides based on BPMB were expected to undergo a thermal crosslinking reaction due to the high concentration of maleimide units; crosslinking was found to occur at 350°C, substantially higher than the value of 200°C to 210°C reported for common bismaleimides. The high cure temperature required can be attributed to restricted motion of the backbone maleimide units and to the pendant phenyl groups, which present a steric barrier to crosslinking.

Spectroscopically, cured and uncured materials showed no difference, suggesting low crosslink density, but solvent extractions

confirmed that these were indeed thermosetting materials; gel fractions after cure ranged from 73 to 100 percent. In addition, curing was accompanied by a 20°C to 25°C increase in  $T_g$ . The cure temperature of 350°C potentially affords a reasonable processing window for several of these materials with  $T_g$ 's in the range of 240°C to 270°C prior to crosslinking.

## VI. SUGGESTED FUTURE STUDIES

In the course of many scientific investigations, the research conducted may provide solutions to current problems or resolve previously unresolved issues while presenting new questions and possibilities. Discussions will be devoted to recommended additional investigations which may prove beneficial as research in high temperature polyimides continues.

Ethynyl-functionalized imides discussed in this dissertation were synthesized utilizing 3-ethynylaniline as a reactive end group. The low cure temperature of this end group and low end group concentrations employed thwarted attempts to fabricate crosslinked samples other than solvent-cast films.

Currently, efforts are underway to functionalize low molecular weight, soluble imide oligomers using phenylethynylaniline, a reactive end group which cures slowly at temperatures in excess of 350°C. Due to the extremely high cure temperature, investigation of the feasibility of PMR (bulk) reactions for these systems may be in order. Successful polymerization without solvents would be of benefit in the fabrication of void and defect free composites and would also be advantageous with regard to increasingly stringent environmental regulations imposed upon the chemical industry.

In addition, the high cure temperature may permit the synthesis of fully cyclized, acetylene-functionalized oligomers prior to crosslinking; the soluble oligomers could be analyzed by GPC to

determine if the PMR approach affords the desired molecular weights and molecular weight distributions close to the theoretical value of 2.0.

Very little is known about polyimides based on 1,4-bis(phenyl maleic anhydride)benzene and continued investigation of these systems should prove interesting. Studies which may be beneficial include molecular weight control and synthesis of controlled molecular weight oligomers utilizing PMR technology. Because the crosslinking functional groups are contained within the polymer backbone, it should be possible to generate thermosets from low molecular weight oligomers terminated with either phthalic anhydride or aniline, thereby minimizing chain extension and decomposition due to high temperature end group reactions. Additionally, the high cure temperature may permit synthesis of these oligomers via bulk polymerizations. The use of low molecular weight oligomers might also result in higher crosslink densities and therefore substantially higher  $T_g$  values than previously reported.

The unsaturated maleimide backbone units are expected to be thermooxidatively unstable sites; investigation of polymer decomposition via TGA-mass spectrometry could help answer this question. In addition, isothermal weight loss studies would provide information regarding the long term stability of these materials.

Additional studies of a practical nature include investigation of the adhesive properties and gas transport properties of these materials, properties which are currently of interest for polyimides

in general but are completely unknown for this particular class of polyimides.

The polyimides derived from diaminoresorcinol dihydrochloride represent another class of polyimides with a number of undetermined properties and potential uses and, as emphasized previously, the direct use of diamine dihydrochlorides as monomers in polyimide synthesis presents many possibilities for the synthesis of novel, potentially useful materials. Additional monomers which could be used to incorporate phenolic groups into polyimides include the dihydrochloride salts of 2,4-diaminophenol, 2,2-bis(3-amino-4-hydroxyphenyl)propane, and 3,3'-diamino-4,4'-dihydroxybiphenyl.

Phenolic end-functionalized polyimides have been suggested as potential thermoplastic tougheners for cyanate thermosets, and this is an area to be considered; in principle, it should be possible to synthesize polyimide copolymers with a wide range of pendant hydroxyl group concentrations in order to achieve the desired properties.

In addition, such novel materials may serve as intermediates for a wider array of new polymers. Novel, potentially useful materials could be produced via azo coupling reactions or established phenol-formaldehyde chemistry. Derivatization of the pendant hydroxyl groups offers a number of possibilities, including polyimides with pendant ester, ether, arylene ether-ketone, arylene ether-sulfone, arylene ether-phosphine-oxide or siloxane segments. A particularly interesting prospect would involve the grafting of a

thermally labile branch or chain to the high  $T_g$  polyimide backbone. Heating a solution cast film or coating to decompose the unstable segments could in principle generate a polyimide "nano-foam," an insulating film which would possess a dielectric constant approaching that of air.

Investigation of the chelating properties of poly(hydroxy-imide)s may prove interesting and, as liquid-liquid separation membranes (i.e., removal of water from alcohols) were a suggested application for the polyimides derived from diaminoresorcinol, this is also an appropriate area for investigation.

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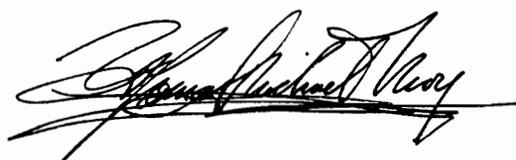
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## VIII. VITA

Thomas M. Moy was born the son of Alan G. K. Moy and Inge R. Moy on October 14, 1962 in New Britain, Connecticut. His family moved to Petersburg, Virginia in 1968 where he eventually attended and graduated from Petersburg High School in 1981. In June 1985 he received an A.S. in Science from John Tyler Community College in Chester, Virginia, and continued his studies at Virginia Commonwealth University in Richmond, majoring in Chemistry. While at V.C.U. he had the opportunity to work in the laboratories of Professor R. Gerald Bass, where he first developed an interest in polymer synthesis. He received a B.S. in Chemistry from V.C.U. in May 1988, and married Phyllis Ann Buckland on June 11, 1988.

In the fall of 1988 Thomas began graduate studies in the Department of Chemistry at Virginia Polytechnic Institute & State University under the guidance of Professor James E. McGrath. His graduate research focused on the synthesis and characterization of high temperature thermoplastic and thermosetting polyimides prepared by unconventional solution polymerization techniques. He received his Ph.D. in Chemistry in August 1993. Thomas and Phyllis Moy have one daughter, Elizabeth Claire Moy, born June 7, 1991; the Moy family currently resides in Bluefield, Virginia.

A handwritten signature in black ink, appearing to read "Thomas M. Moy". The signature is stylized with a large, sweeping initial 'T' and a horizontal line extending across the bottom of the name.