CHAPTER 4 RESULTS AND DISCUSSION

This chapter is comprised of five major sections. The first section addresses monomer syntheses involved in this research, including diaminophenylindane, triaminophenylindane and dihydroxyphenylindane. The second section details the synthesis, molecular weight and thermal characterization of several novel polyimides which were targeted for their potential advantages as permselective membranes. Following the discussion of characterization, the O_2/N_2 permselective behavior of these materials is presented.

The third section of this chapter reports the synthesis and characterization of several novel polyimides containing hydroxyl moieties in the repeat unit of the polymer. This is followed by the fourth section, which discusses the thin film O_2/N_2 permselectivity of these systems. Finally, the last section covers applicable crosslinking mechanisms for semipermeable membranes.

4.1 Monomer Synthesis

4.1.1 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane and 5,6-diamino-(4-aminophenyl)-1,3,3-trimethylindane (DAPI and TAPI) Synthesis

The synthesis and basic characterization of DAPI was presented earlier in section 3.2.2. The overall yield for this reaction, starting with α-methylstyrene, was ~35%. The low yield was largely attributed to the initial step in the synthesis, the dimerization of α-methylstyrene, which gave a relatively low yield of 50%. The product, 1-phenyl-1,3,3-trimethylindane, was thought to be a racemic mixture of both the R and S configurations. By NMR the two configurations are chemically equivalent. Although it would be worth investigating, separation of these configurations was not pursued.

1-Phenyl 1,3,3-trimethylindane (phenylindane) appears to be especially susceptible to addition of a second nitro group thereby yielding the undesired trinitro compound 5,6-dinitro-1-(4-nitrophenyl)-1,3,3-trimethylindane (TNPI) (which produced TAPI after reduction). The probability of nitrating twice on the same ring is unlikely if the nitrating species is charged in a 2:1 mole ratio (HNO_3:phenylindane).

The synthetic procedure for DAPI and TAPI are very similar and differ only in percent solids content and in the ratio of chloroform to sulfuric acid. In each case, the amount of nitric acid was held constant (2:1, HNO_3:phenylindane). The procedure to form TNPI yielded a mixture of the tri-, di- and mono- substituted products. TNPI was easily purified by recrystallization from ethanol. The synthesis of TNPI has not been reported in the literature.

Upon changing the chloroform:sulfuric acid ratio from 2:1 to 2:3, the resulting product became predominantly tri-substituted. Although details of this heterogeneous reaction need clarification, it is possible that by increasing the acid phase the likelihood of material diffusing to the chloroform/acid interface, where it can react, is also reduced.

4.1.2 6-hydroxy-1-(4-hydroxyphenyl)-1,3,3-trimethylindane (DHPI) Synthesis

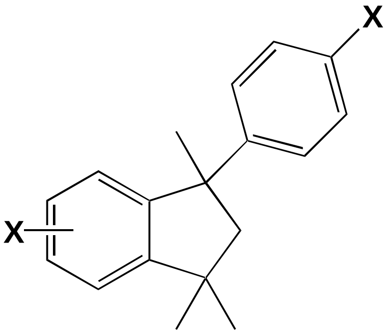
One of the objectives of this research was to prepare new monomers for tailoring the chemical structure of polyimides to impart a simultaneous increase in their oxygen permeabilities and oxygen/nitrogen selectivities. During the investigation of diaminophenylindane (DAPI), it was noticed that DAPI, in combination with the proper dianhydride, yielded films with both good permeability and good selectivity. From this starting point, effort was placed on synthesizing other related diamines which incorporated the phenylindane structure. It was thought that by incorporating the phenylindane structure into the polyimide backbone using a monomer with the modified structure of DAPI, the favorable characteristics of DAPI could be further developed. Polyimides based on these types of monomers would be expected to exhibit high T_gs, low solution and melt viscosities, and high thermal stability due to the presence of the phenylindane structure. The resulting polymers would also be expected to show good gas selectivity and, perhaps, high permeabilities due to the rigid and extremely bulky nature of phenylindane.

Synthesis of phenylindane containing monomers and/or their polymerization has been reported by a number of authors (Figure 4.1.2.1).[271-286] Polyimides have been synthesized from diaminophenylindane[285,286] or diamines resulting from the reaction of dihydroxyphenylindane[271-288] (DHPI) with either o/p-chloronitrobenzene or dinitrobenzene.[281-284] Dianhydrides from dihydroxyphenylindane (DHPI) and 4-fluorophthalic anhydride have also been reported.[274] Although polyimides utilizing DHPI based monomers have been reported in the patent literature, there is either very little or no mention of fundamental polyimide characterization, such as molecular weight or glass transition temperature. Therefore, DHPI based monomers were of interest in this thesis research.

Successful synthesis of DHPI disclosed in this thesis has opened several routes to obtaining monomers for potentially improving gas permselectivity of polyimides. Three likely monomeric candidates, all originating from DHPI, are shown in Scheme 4.1.2.2. Of the three potential candidates, the bis(o-aminohydroxy)-Containing monomer (1) has not been previously reported. Monomers (2) and (3) have been reported, but very few of their characteristics have been disclosed.

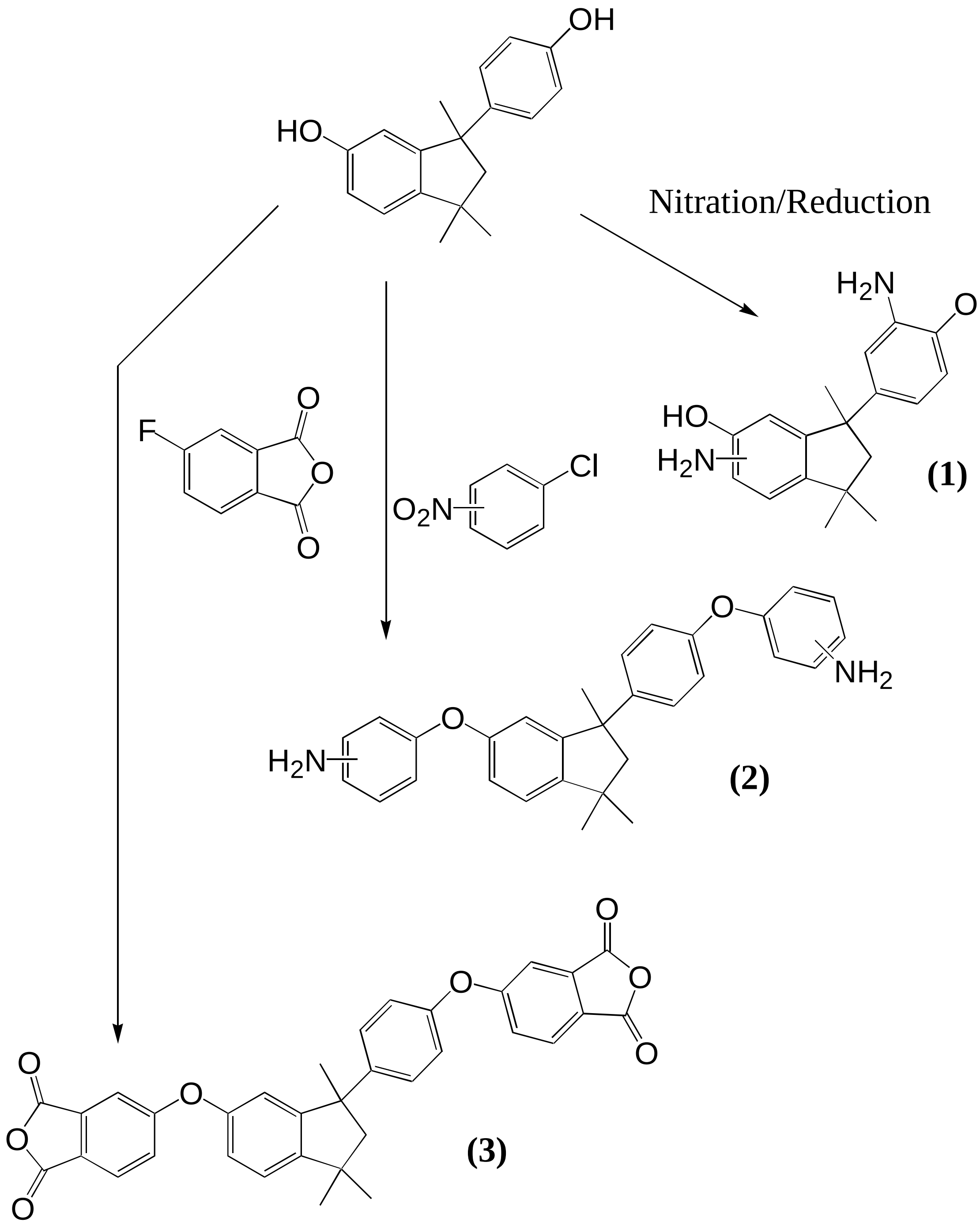
The details of the synthetic procedure used to prepare DHPI as well as basic structural characterization may be found in the experimental section. The base catalyzed cracking of bisphenol A was carried out at elevated temperatures, followed by dimerization of the resulting isopropenyl phenol, which was facilitated by an acid catalyst. This procedure gave an overall yield of ~30%. Obvious factors influencing the yield were the choice of base and acid catalysts, which may control the rate of oligomer formation. The base and acid catalysts selected were based on literature procedures. However, optimization of these reagents may improve the observed yield.

The desirable properties of polyimides containing the trimethylphenylindane structure indicate that future work should encompass synthesis and investigations of the three monomers derived from DHPI. This thesis work, however, did not develop routes to form the polyimide precursors shown in Scheme 4.1.2.2.



X = -OH[271-278]
-CO_2H[279,280]
-COCl[280]
-NH_2[285,286]

Figure 4.1.2.1 Reported Monomeric Derivatives of 1-phenyl-1,3,3-trimethylindane



Scheme 4.1.2.1 Proposed Polyimide Monomers from Reactions with 6-hydroxy-1-(4-hydroxyphenyl)-1,3,3-trimethylindane (DHPI)

4.2 Molecular Weight and Thermal Characterization of Novel Polyimides

Polyimides containing novel diamines and/or dianhydrides were investigated for their potential use as semipermeable membranes for gas permselectivity. Monomer selection for these materials was based upon previous observations reported in the literature. Through extensive experimentation, the two following criteria have emerged to guide synthetic researchers in their efforts to improve permselective membranes (Section 2.5).[233-236] This information set the stage for monomer selection. Monomers were selected to yield highly rigid polymer backbones, while simultaneously increasing interchain spacing with bulky groups. This section details the molecular weight and thermal characteristics of a number of polyimides satisfying these requirements. Following these characteristics, the permselective behavior of the polymer thin films will be presented.

4.2.1 Characterization of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) Based Polyimides via Ester-acid Solution Imidization[301]

Polyimides are well known for their excellent thermal and oxidative stability as well as excellent mechanical properties.[287-290] Due to their wide utility as matrix resins, coatings and adhesives for aerospace and microelectronic applications, a broad range of synthetic routes have been developed in an attempt to facilitate easier and more cost efficient syntheses.

The two most commonly used routes suitable for amorphous polyimide preparation are chemical and solution imidization. Both require the drying of commercially available solvents, since their water content can potentially upset the monomeric anhydride/amine stoichiometry and lead to unpredictable molecular weights.

Our research group has been interested in developing improved polyimide material systems for some time.[130,291,292] In an effort to alleviate dianhydride water sensitivity, and subsequent hydrolysis, a method has been developed based on earlier work[287-290] which involves the pre-reaction of anhydride moieties with ethanol in the presence of a tertiary amine catalyst.[291,292] The ester-acids formed can be prepared in the presence of commercially available solvents and are very tolerant of water content in both the solvents and reactor. In addition, the ester-acids are more soluble in organic solvents than their dianhydride parents. The factors necessary for the formation of high molecular weight amorphous polyimides via this route were recently reviewed.[130,291,292] It was shown that ester-acids are conveniently prepared from the monomeric dianhydrides in the presence of ethanol. At an elevated temperature, the dianhydride was reformed, followed by attack of an aryl diamine and, finally, cyclodehydration ensues to form imide.

One objective of this research was to broaden the applicability of the ester-acid solution imidization route to encompass a system which has been reportedly prepared via chemical imidization, namely, CIBA's XU218.[285,293] The latter is prepared from benzophenone tetracarboxylic dianhydride (BTDA) and a mixture of the C-5 and C-6 isomers of diaminophenylindane (DAPI), shown in Figure 4.2.1.1. For our purposes, NMR and HPLC (Figure 4.2.1.2) validated monomer grade DAPI. Both of these techniques show the DAPI to be present in a near 50:50 mixture of the C-5 and C-6 isomers, which is in good agreement with previous findings.[285,286]

Polyimides containing DAPI were one of the first truly soluble, fully cyclized systems. DAPI is of particular interest due to its inherent asymmetry and non-planarity which produces highly soluble polyimides with even the most rigid dianhydrides. At the same time, the polymers are quite rigid which is evident from the high glass transition temperatures observed for these systems. The absence of aliphatic, oxidatively susceptible benzylic hydrogens and adjacent aliphatic carbons bearing hydrogens may impede facile degradation and allow these systems to show good thermooxidative stability.

The dianhydride monomers utilized in the synthesis of DAPI containing polyimides were all commercially available and are shown in Figure 4.2.1.3. The synthesis of DAPI, which is the acid catalyzed dimerization of α-methylstyrene, and subsequent nitration and reduction, is described in the experimental section of this report.

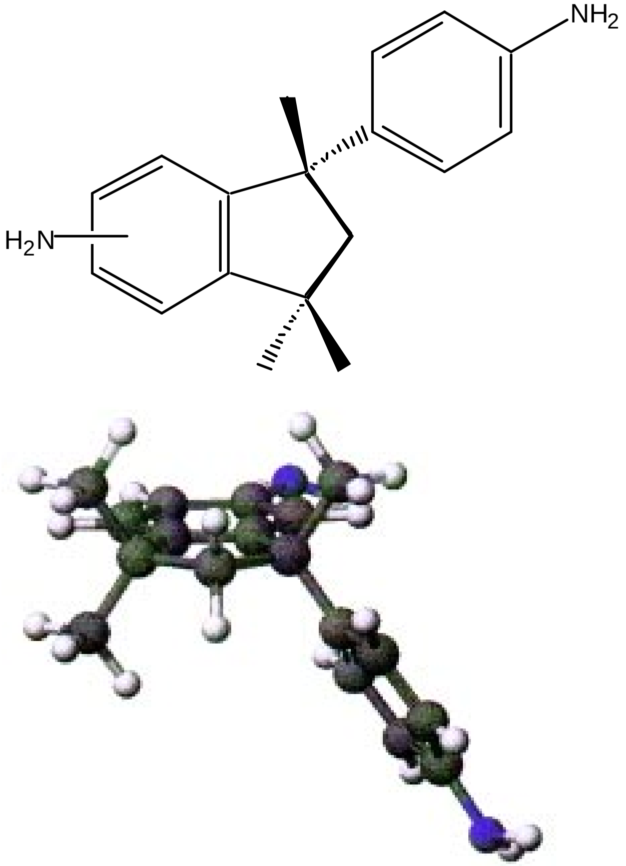
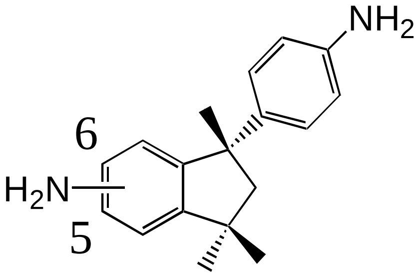
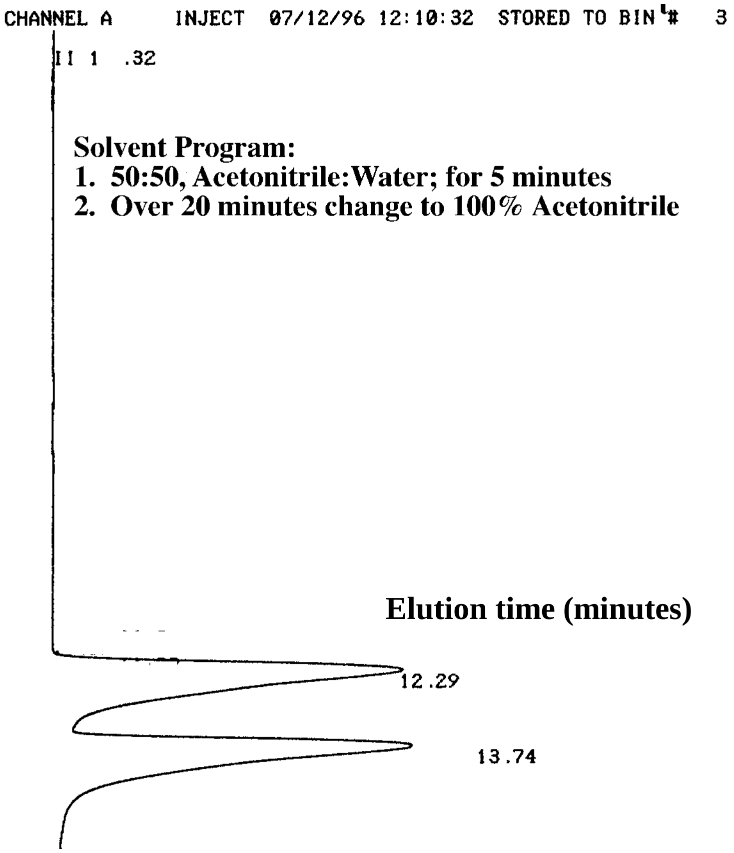


Figure 4.2.1.1 A 3-D Model of Diaminophenylindane

Isomeric Ratio via HPLC: 50% (6): 50% (5)





Solvent Program:

1. **50:50, Acetonitrile:Water; for 5 minutes**
2. **Over 20 minutes change to 100% Acetonitrile**

Figure 4.2.1.2 High Performance Liquid Chromatography of DAPI

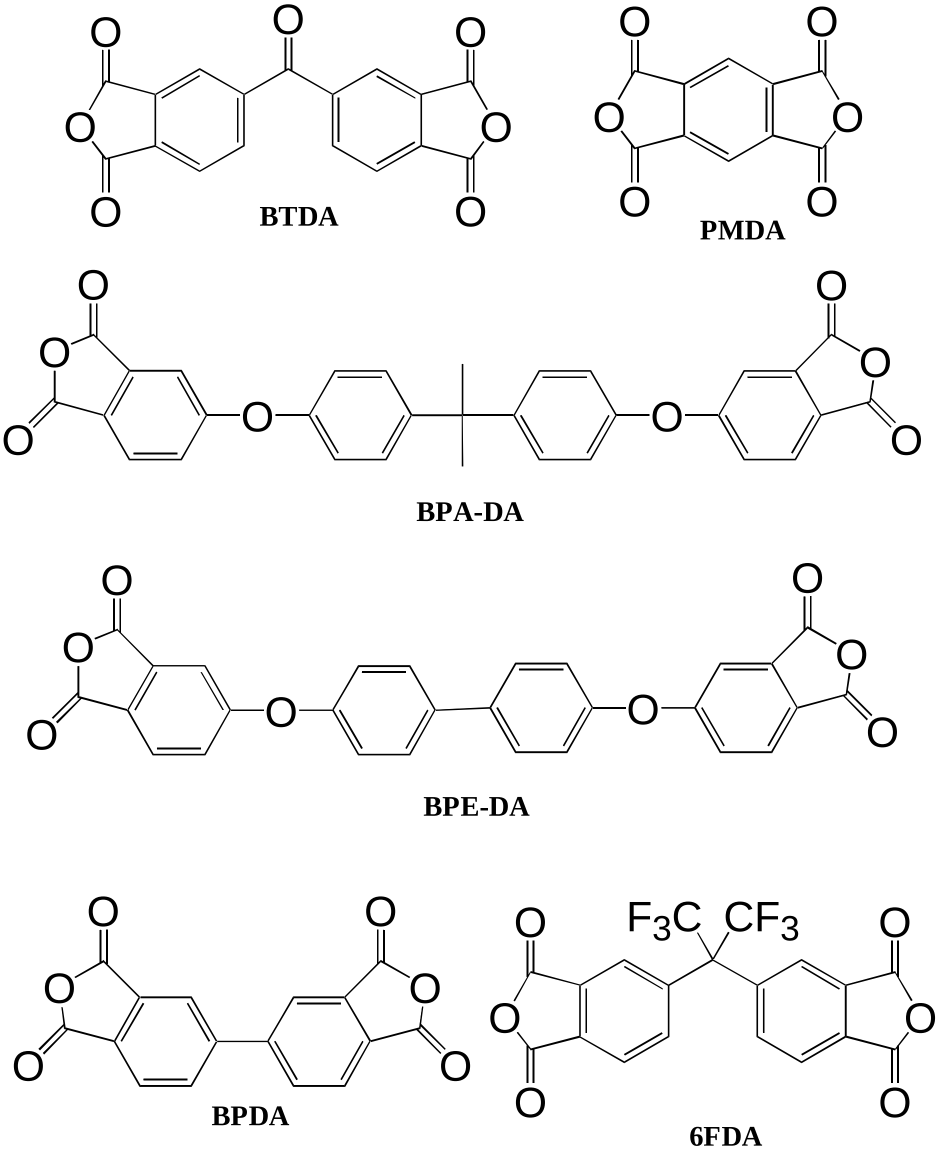


Figure 4.2.1.3 Monomers Used with DAPI for the Synthesis of Polyimides

The polyimides were prepared by forming the ester-acid precursor, followed by the addition of diamine and then solution imidization. The resulting polymers were also cast from an NMP solution to form tough creasable films. The conversion of the poly(amic acid)s to the fully cyclized polyimides was monitored by FTIR.[294-296] Cyclodehydration was confirmed by the appearance of absorption modes at approximately 1785, 1727, 1370, and 733 cm^{-1} due to symmetric C=O, asymmetric C=O and C-N stretching, and ring deformation, respectively (Figure 4.2.1.4). These wavelengths corresponded to previously reported imide ring adsorptions.[297-300] Complete cyclization was also evident by the lack of amide C=O (1640 cm^{-1}) and N-H (1550 cm^{-1}) peaks.[155,160] A representative NMR of DAPI based polyimides is given in Figure 4.2.1.5.

For each of the polymers, high molecular weights have been achieved as was confirmed by GPC (Table 4.2.1.1). Earlier reports in the literature of high molecular weights were in reference to polystyrene standards and not universal calibration. A typical raw chromatogram for DAPI/6FDA is shown in Figure 4.2.1.6. It shows a unimodal molecular weight distribution with a polydispersity index of about two, which is expected for step-growth polymerizations.

The polymer powders were thermally analyzed by DSC and TGA and the results are summarized in Table 4.2.1.1. DSC revealed the materials to have high and broad T_g values occurring over a 30°C range (Figure 4.2.1.7). The breadth of this transition is most likely due to an isomeric effect, as DAPI has four isomers. The more rigid anhydrides, such as PMDA and BPDA, would be expected to show the highest T_gs, as indeed they do. The more flexible dianhydrides show lower glass transition temperatures. The T_gs increase in the following order: BPADA<BTDA~6FDA<PMDA<BPDA.

Preliminary assessment of the thermal stability of these polymers was also determined by TGA in the presence of air. The primary factors which contribute to heat resistance are primary and secondary interactions, resonance stabilization, molecular symmetry and the mechanisms of bond cleavage. As a class, polyimides show excellent

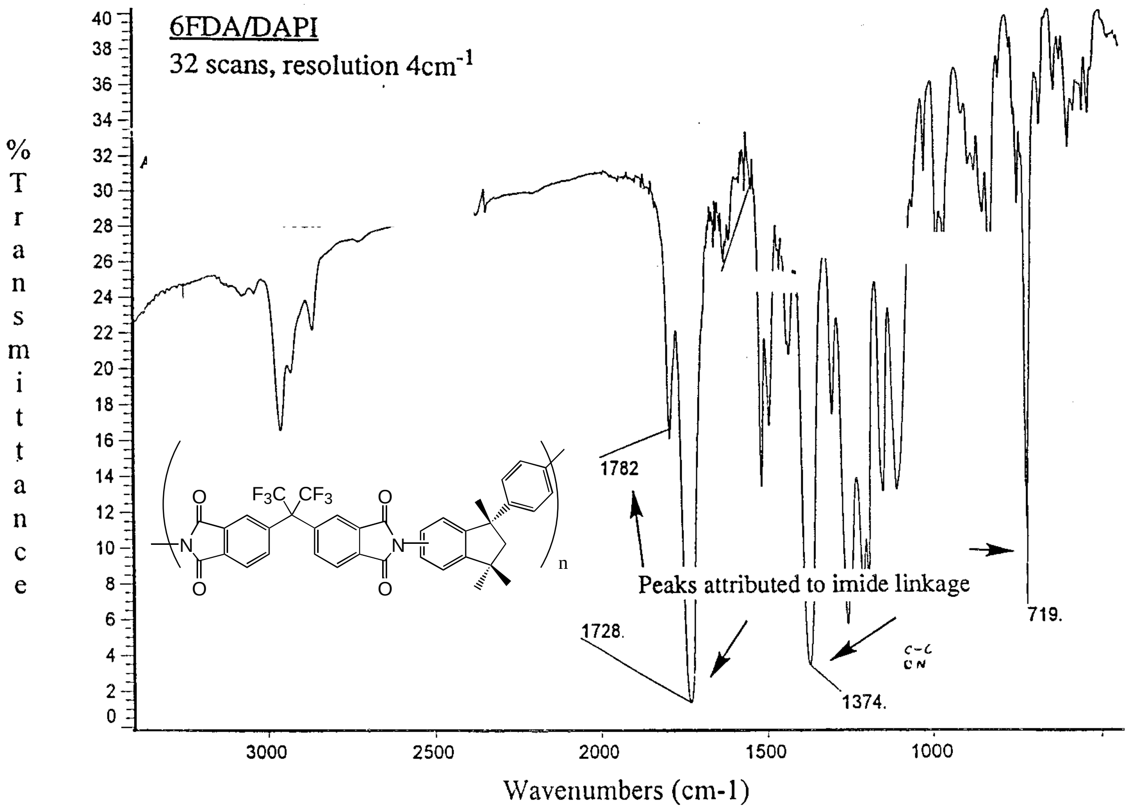


Figure 4.2.1.4 FTIR Spectrum of High Molecular Weight 6FDA/DAPI Showing Absorptions Due to Cyclic Imide Functionalities

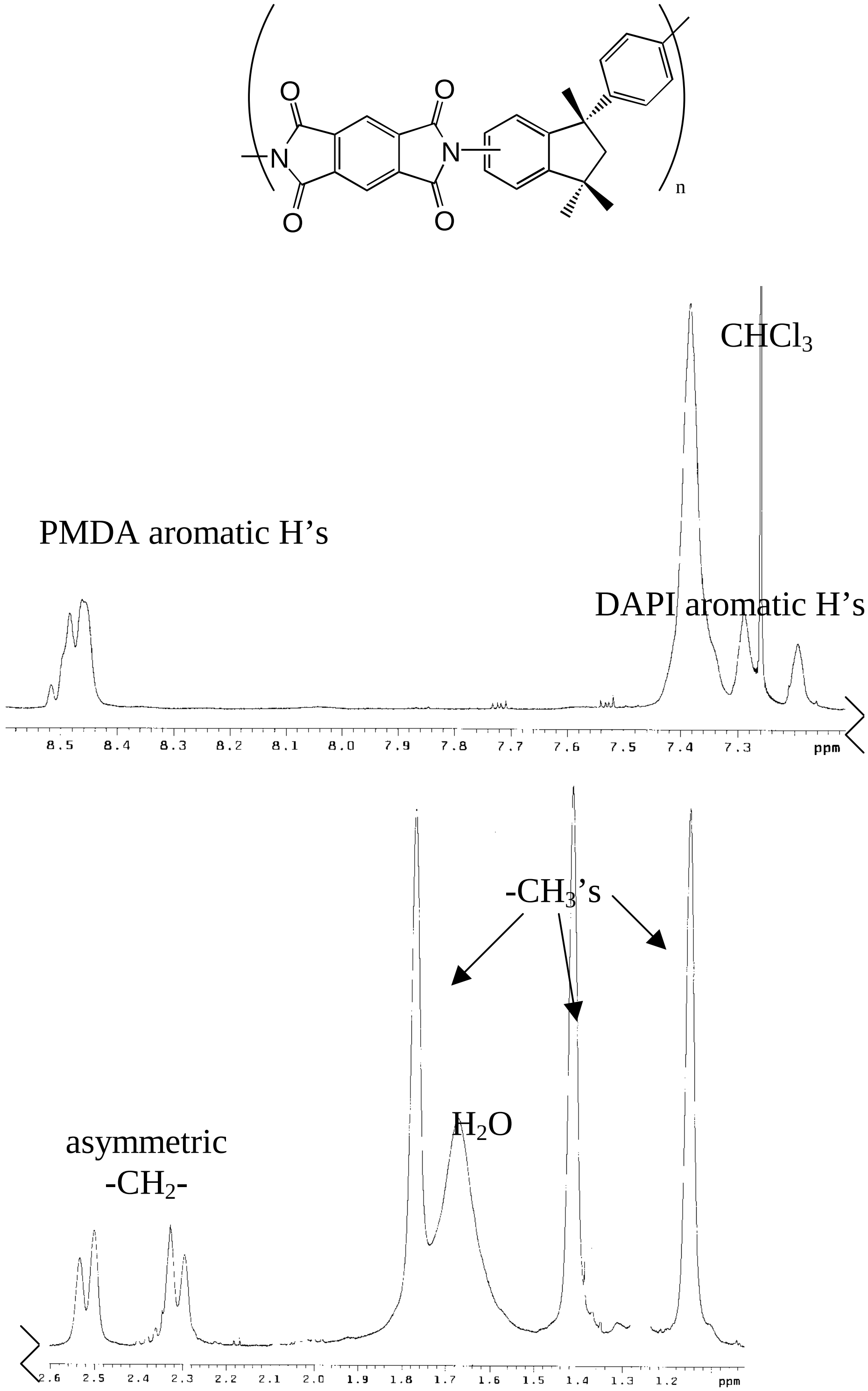
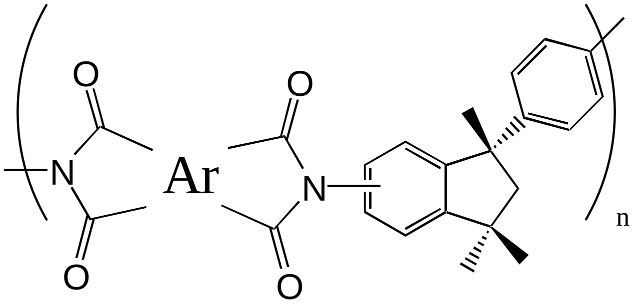


Figure 4.2.1.5 High Resolution ^1H NMR of DAPI/PMDA

Table 4.2.1.1 Molecular Weight and Thermal Analysis of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) Based Polyimides



Dianhydride	Molar Ratio	M_n (K)$^+$ (avg.)	M.W.D.	T_g (°C)*	TGA 5% Wt. Loss (°C)**
BPADA	1:1	29.9	1.7	247	536
BPEDA	1:1	27.5	2.4	288	---
BTDA	1:1	32.5	1.9	333	525
6FDA	1:1	35.1	1.9	331	493
BPDA	1:1	28.5	1.8	368	558
PMDA	1:1	26.1	1.7	354	540

+ via GPC, mobile phase was NMP + 0.02MP_2O_5, 60°C
* 2nd heating; heating rate of 20°C/min
** heating rate of 10°C/min in air

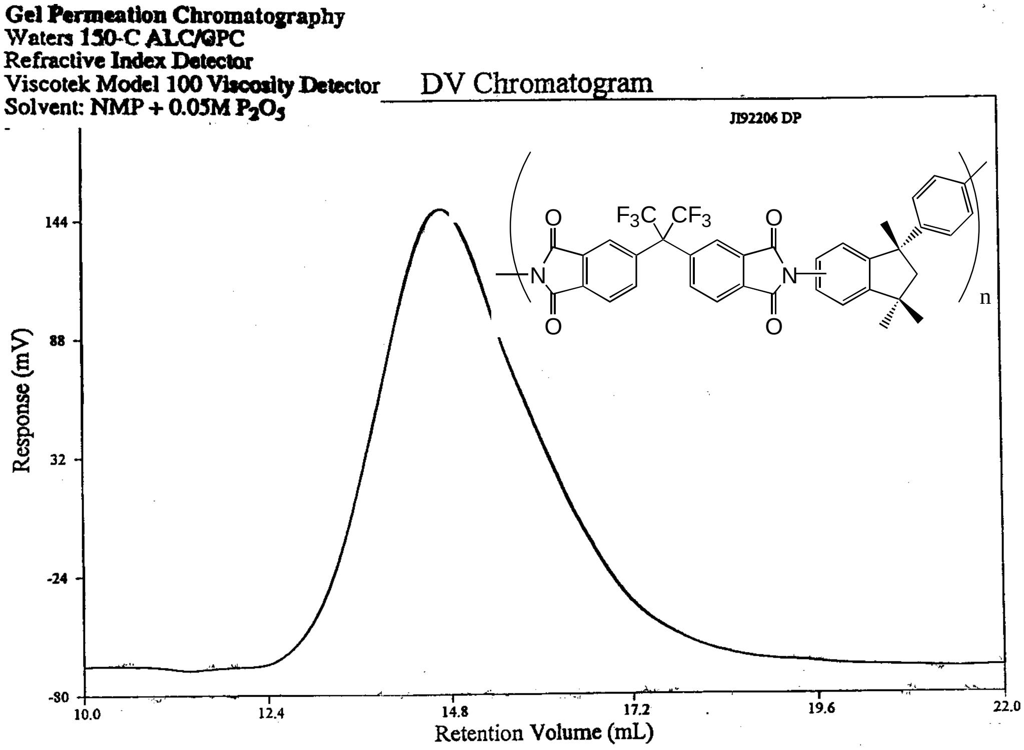


Figure 4.2.1.6 Raw GPC Chromatogram of High Molecular Weight 6FDA/DAPI Polyimide

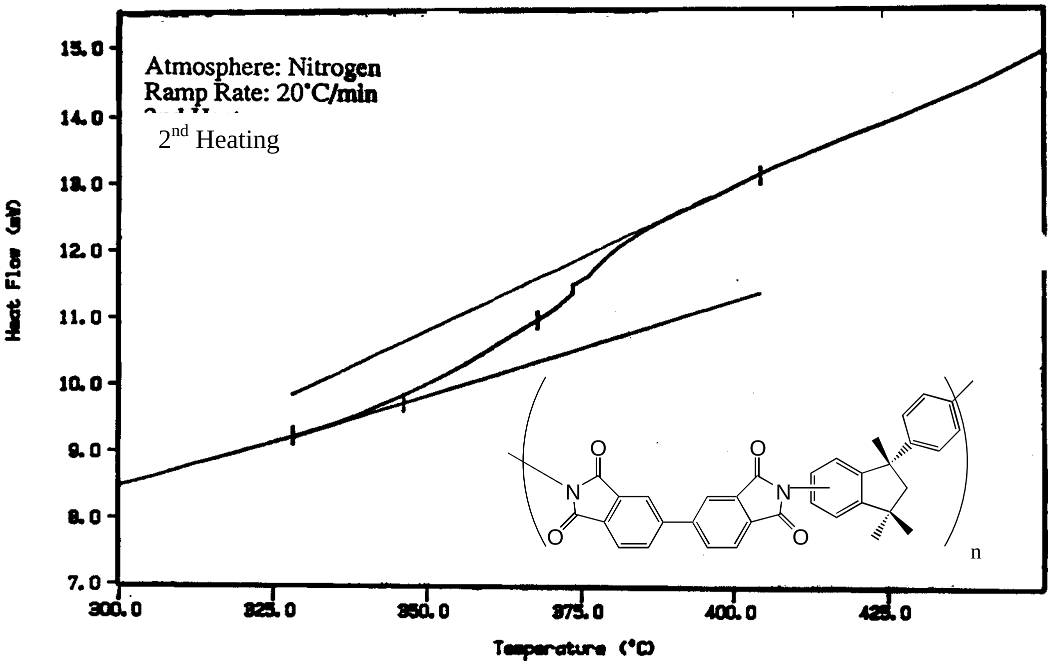


Figure 4.2.1.7 DSC Trace of High Molecular Weight BPDA/DAPI Showing a Broad Glass Transition

resistance to thermal degradation, and for these polyimides, the 5% weight loss occurred around 500°C (Figure 4.2.1.8 and Table 4.2.1.1).

The microelectronic industry screens thermally stable polymers by isothermal weight loss of the polymer at 400ºC, under nitrogen, over a two hour time interval. Surprisingly, the minimal weight loss shown by the high molecular weight 6FDA-DAPI system under these conditions was comparable to that of Kapton (PMDA/ODA) (Figure 4.2.1.9). This preliminary test suggested that this material may be able to withstand the harsh thermal environment required for certain electronic applications, despite the partially aliphatic nature of the polymer backbone. Unlike Kapton, 6FDA-DAPI has the advantage of being soluble.

Polymer solubility is presented in Table 4.2.1.2. Nearly all of these polymers were soluble in NMP, DMAc, $CHCl_3$, CH_2Cl_2 and THF, at relatively high solids content (10 wt%). Only in the more rigid systems, PMDA/DAPI and BPDA/DAPI, was dissolution not observed in THF. The good solubility in a number of solvents is attributed to the isomeric, asymmetric and non-planar structure of DAPI.

Refractive index values for the high molecular weight DAPI based polyimides are shown in Table 4.2.1.3. A polymer containing a greater percentage of polarizable groups, such as oxygen, nitrogen and aromatic rings, will display a higher refractive index value. Polymers with less polarizable functionalities, such as fluorine and aliphatic carbons, will have a lower refractive index. As expected, the lowest refractive index is observed for 6FDA/DAPI due to the six fluorine atoms per repeat unit and the aliphatic groups in DAPI. The polyimides based on DAPI were found to have increasing refractive indices in the following order: 6FDA<PMDA~BPADA<BTDA<BPDA.

To a first approximation, the dielectric constant for these presumably isotropic polymers can be estimated by the square of the refractive index[304]. The lowest dielectric constant value was found for the 6FDA/DAPI system, which had a value of 2.47. In microelectronics a low dielectric constant is desired to prevent “cross-talk” between conducting vias. A polyimide with a dielectric constant this low may be attractive for this industry.

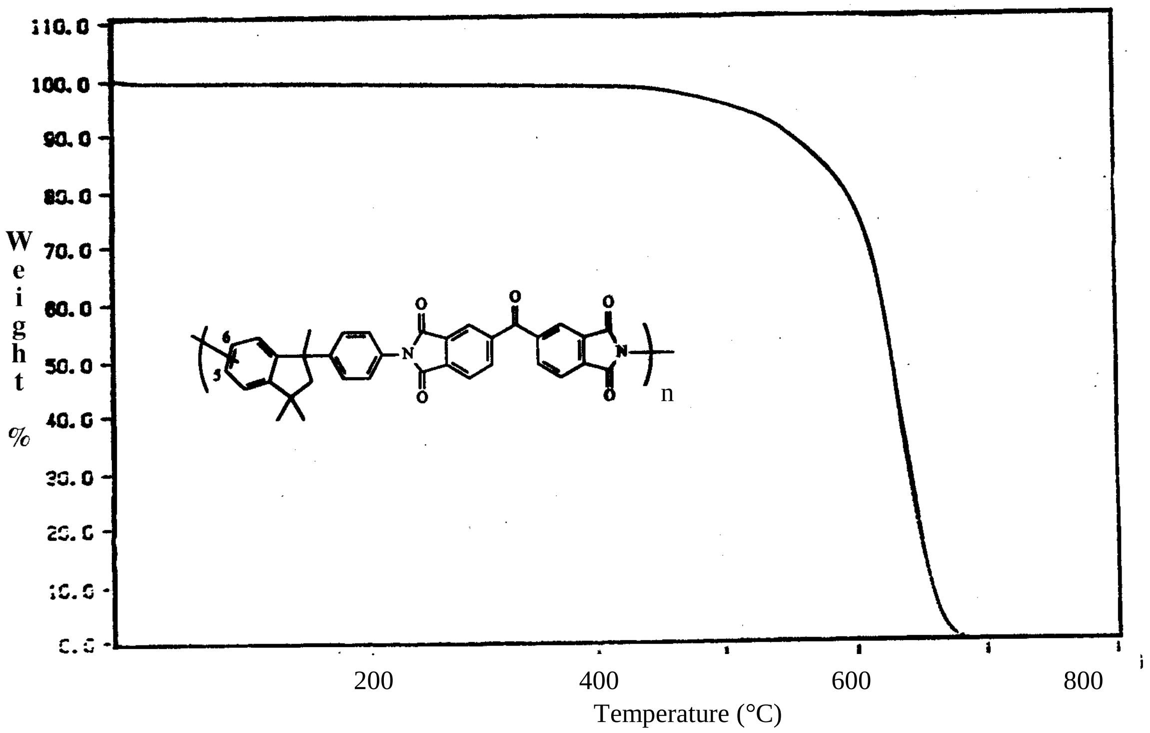


Figure 4.2.1.8 Dynamic TGA of High Molecular Weight BTDA/DAPI in Air (10°C/min)

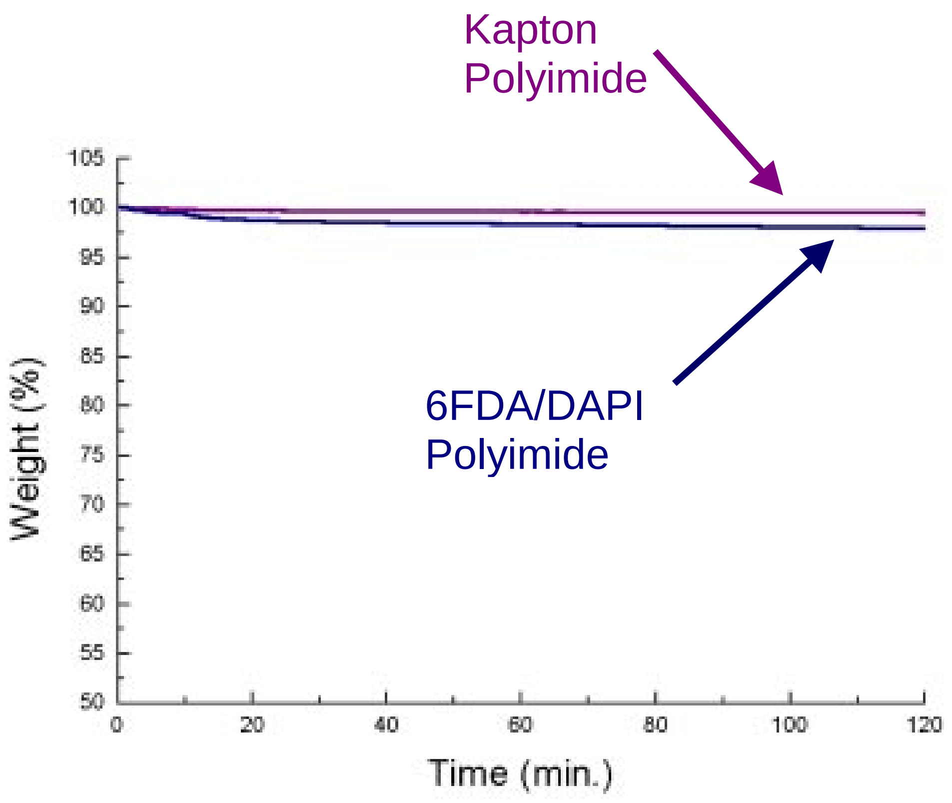
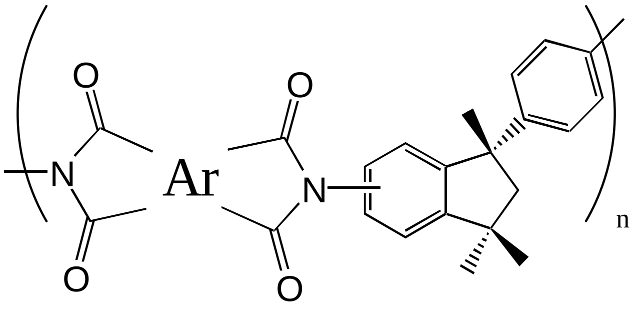


Figure 4.2.1.9 Isothermal TGA of PMDA/ODA Based Kapton and 6FDA/DAPI Based Polyimide at 400^{o}C Under Nitrogen

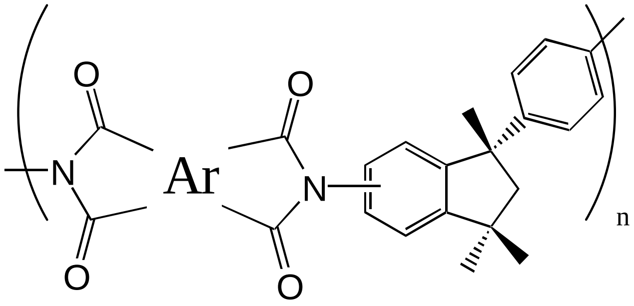
Table 4.2.1.2 Solubility of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) Based Polyimides in Common Solvents



Dianhydride	NMP	DMAc	$CHCl_3$	CH_2Cl_2	THF
ULTEM(control)	S	S	S	S	I
BPADA	S	S	SS	S	S
BTDA	S	S	S	S	S
6FDA	S	S	S	S	S
BPDA	S	SH	S	S	SW
PMDA	S	SH	S	S	SW

S - soluble at RT; SS-slightly soluble at RT;
SW - swelled; SH - soluble in hot solvent; I - insoluble
Solubility test done at 10% solids

Table 4.2.1.3 Refractive Index Values and Dielectric Constant Approximation of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) Based Polyimides



Dianhydride	Refractive Index (n)	Dielectric Constant Approx. (n^2)
6FDA	1.571	2.47
PMDA	1.623	2.63
BPADA	1.629	2.65
BTDA	1.639	2.69
BPDA	1.657	2.75

Standard Deviation for RI measurement, ±0.001

4.2.2 Effect of Imidization Method on High Molecular Weight 3,3’,4,4’-benzophenonetetracarboxylic dianhydride (BTDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)

High molecular polyimides consisting of DAPI and BTDA were synthesized using three different routes. Polyimides obtained via the ester-acid and chemical imidization methods were soluble while the thermally imidized system was insoluble in hot NMP. Insolubility may have resulted from a small amount of side reactions such as crosslinking[303]. The resulting molecular weights and thermal properties of the polyimides are presented in Table 4.2.2.1. The soluble polyimides, prepared via the ester-acid and chemically imidization methods, were found to have high molecular weight by GPC.

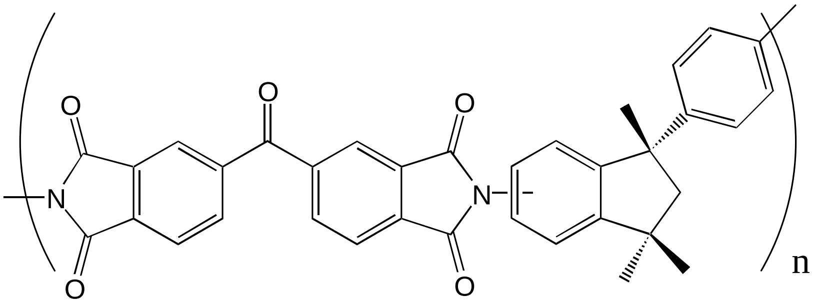
A noticeable difference in thermal behavior was observed for the chemically imidized polyimide with respect to the T_g and 5% weight loss values. Although there was no noticeable difference in the FTIR spectra of the polymers synthesized by the different methods, it is possible that the lower T_g and lower 5% weight loss values resulted from residual amide acid groups present in low concentration and, therefore, below the detection limit of the infrared instrument (i.e. <1%).

The polyimides synthesized using the ester-acid and thermal imidization routes have similar T_g and 5% weight loss values. It is possible that the slight differences observed may have resulted from small structural changes in the thermally imidized sample, since it is known that carbonyl functionalities may abstract labile protons such as those present in the DAPI when exposed to UV light or high temperatures[1,303].

4.2.3 Effect of the DAPI Isomeric Ratio on Thermal Properties

It was of interest to investigate the effect of altering the 5- and 6-amino isomeric ratio of DAPI from the normal equimolar mixture. To increase the ratio of one of the isomers relative to the other, the diamine was recrystallized multiple times from toluene.[286] Three different isomeric mixtures were studied in polycondensations with

Table 4.2.2.1 Molecular Weight and Thermal Characterization of 3,3',4,4'-Benzophenonetetracarboxylic Dianhydride (BTDA)/5(6)-Amino-(4'-aminophenyl)-1,3,3-trimethylphenylindane (DAPI) Based Polyimides



Imidization Method	Molar Ratio	M_n (K)$^+$ (avg.)	M.W.D.	T_g (C°)*	TGA 5% Wt. Loss (C°)**
Chemically	1:1	21.1	1.9	311	457
Thermally	1:1	insoluble	---	324	510
Ester-Acid	1:1	32.5	1.9	333	525

+ via GPC, mobile phase was NMP + 0.02MP_2O_5, 60ºC

* 2nd heating; heating rate of 20ºC/min

** heating rate of 10ºC/min in air

BTDA. The following are the ratios used with regard to 6-amino:5-amino DAPI isomers: 60:40, 50:50 and 30:70 (ratios determined by HPLC). In order to obtain completely soluble polyimides required for gas membrane production, it was found that the isomeric ratio could not be below 30:70 (6:5) due to reduced solubility observed with regard to the BTDA/DAPI polyimide.

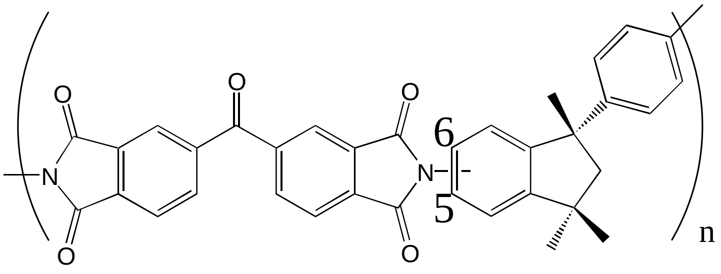
Polycondensation and chemical imidization of the DAPI/BTDA systems produced polyimides with high molecular weight as shown in Table 4.2.3.1. There were no noticeable differences in either the thermal behavior or molecular weight values for the series. Hence, the results suggested that a slight change in the isomeric ratio had negligible effect in altering the polymer properties such as T_g, 5% weight loss in air, M_n and molecular weight distribution.

4.2.4 Biphenylether Dianhydride (BPEDA) and Bisphenol A Dianhydride (BPADA) Based Polyimides

Anhydride functional groups in BPADA are connected through an isopropylidene bridge, whereas the anhydride functional groups in BPEDA are linked via a biphenyl unit. The two flexible ether linkages in BPADA and BPEDA afforded sufficient backbone mobility to yield soluble polyimide systems. Monomer composition, thermal characteristics and molecular weight values are reported in Table 4.2.4.1. The BPEDA based polymers were synthesized via the high temperature solution imidization method, while the BPADA based polyimides were synthesized by the ester-acid solution imidization method. Each of the polyimides was high molecular weight and had polydispersities near two.

Earlier, the polyimide derived from BPADA/DAPI was shown to have a T_g of 288°C. Substitution of *m*-PDA for DAPI reduced the T_g from 288°C to 254°C. Even though *m*-PDA is also very rigid (i.e., like DAPI), the observed decrease in T_g resulted from the smaller diamine, *m*-PDA, contributing a smaller weight percent to the polyimide repeat unit, and thus a smaller portion of its own character to the polymer chain. For the

Table 4.2.3.1 Molecular Weight and Thermal Characterization of 3,3’,4,4’-benzophenonetetracarboxylic dianhydride (BTDA)/5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylphenylindane (DAPI) Based Polyimides Upon Altering the DAPI Isomeric Ratio



Chemically Imidized

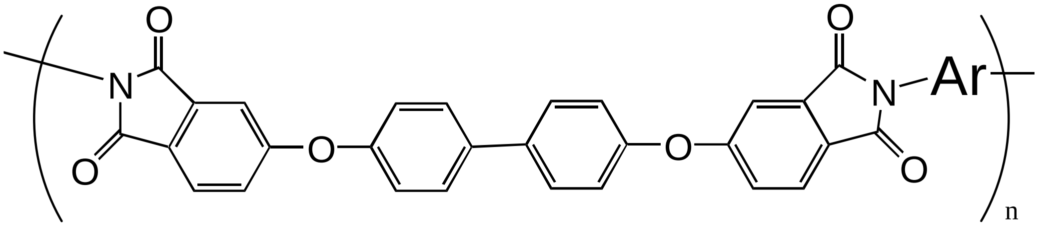
Isomeric Ratio (6:5)	**Molar Ratio**	**M_n (K)$^+$ (avg.)**	**M.W.D.**	**T_g (°C)***	**TGA 5% Wt. Loss (°C)****
60:40	1:1	26.3	2.2	311	456
50:50	1:1	21.1	1.9	311	457
30:70	1:1	26.5	2.0	312	449

+ via GPC, mobile phase was NMP + 0.02MP_2O_5, 60°C

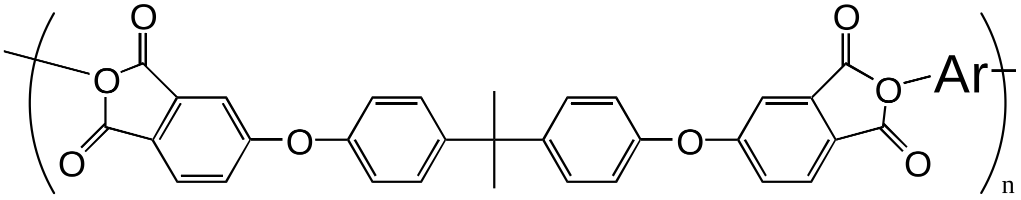
* 2nd heating; heating rate of 20°C/min

** heating rate of 10°C/min in air

Table 4.2.4.1 Molecular Weight and Thermal Characterization of High Molecular Weight 4,4'-bis [4-(3,4-dicarboxyphenoxy)]biphenyl dianhydride (BPE-DA) and 2,2'-bis [4-(3,4-dicarboxyphenoxy)phenyl] propane dianhydride (BPA-DA) Based Polyimides



-Ar-	**Target M_n**	**M_n (K)$^+$ (avg.)**	**M.W.D.**	**T_g (C)***
DAPI	1:1	27.5	2.4	288**
m-PDA	1:1	27.1	1.9	254
BPEDA:BPADA(1:1)/ *m*-PDA	1:1	18.5	2.1	234



-Ar-	**Target M_n**	**M_n (K)$^+$ (avg.)**	**M.W.D.**	**T_g (C)***
DAPI	1:1	29.9	1.7	247**
m-PDA	20K (offset)	17.2	1.9	215

+ via GPC, mobile phase was NMP + 0.02MP_2O_5, 60ºC

* 2nd heating; heating rate of 10ºC/min

** 2nd heating; heating rate of 20ºC/min

BPEDA based polyimides, a difference of 32°C was observed by changing the diamine from DAPI to *m*-PDA.

Substituting BPEDA for BPADA in the BPADA/*m*-PDA polyimide, the glass transition temperature increases by 19°C due to the less flexible biphenyl link. The copolymer of BPEDA:BPADA (1:1) with *m*-PDA has a T_g approximately equidistant from the T_g reported for each of the homopolymers, 254ºC (BPEDA/*m*-PDA) and 215ºC (BPADA/*m*-PDA).

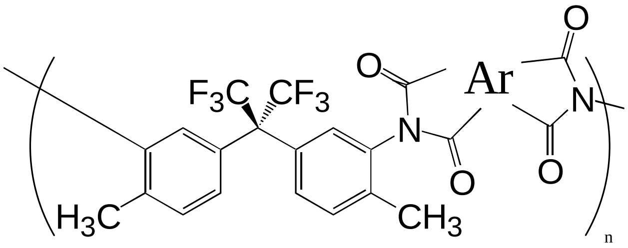
4.2.5 Polyimides Based on 2,2-Bis(3-amino-4-methylphenyl)hexafluoropropane (Bis-AT-AF)

Polyimides based on Bis-AT-AF were synthesized via high temperature solution imidization methods using NMP. The bulkiness and nonpolar nature of the hexafluoropropane moiety was expected to increase gas permeability, decrease the dielectric constant and yield soluble polyimides when combined with a variety of dianhydrides. The methyl substituent is also a potential site for crosslinking through UV initiated mechanisms.

Three dianhydrides were chosen in combination with Bis-AT-AF to yield soluble polyimides. These were: BPADA, BTDA and 6FDA. Table 4.2.5.1 details the molecular weight characterization and the thermal analysis of these materials. Analysis by GPC revealed high molecular weights for each of the polymers. Solution cast films from NMP were tough and creaseable.

The glass transition temperature for each of the polymers was found to be above 220°C (Table 4.2.5.1). The most flexible dianhydride, BPADA, had the lowest glass transition in the series due to the two ether links and the isopropylidene bridge. The more rigid dianhydride, 6FDA, had the highest T_g. Polyimides formed from Bis-AT-AF have T_gs in the following order: BPADA<BTDA<6FDA. Decrease in polyimide thermal stability occurred due to the presence of more labile functionalities in the polyimide backbone (i.e., benzylic hydrogens). The pendant methyl groups present in the Bis-AT-

Table 4.2.5.1 Molecular Weight and Thermal Analysis of 2,2-bis(3-amino-4-methylphenyl)hexafluoropropane (Bis-AT-AF) Based Polyimides



-Ar-	**Target M_n**	**M_n (K)$^+$ (avg.)**	**M.W.D.**	**T_g (°C)***	**TGA (°C)****
BPADA	1:1	26.4	2.1	224	456
BTDA	1:1	28.2	3.0	239	462
6FDA	1:1	27.7	2.2	270	457

+ via GPC, mobile phase was NMP + 0.02MP_2O_5, 60°C

* 2nd heating; heating rate of 10°C/min

** in air, 10°C/min

AF polyimides reduced the 5% weight loss values typical of most polyimides (>500°C) to around 460°C.

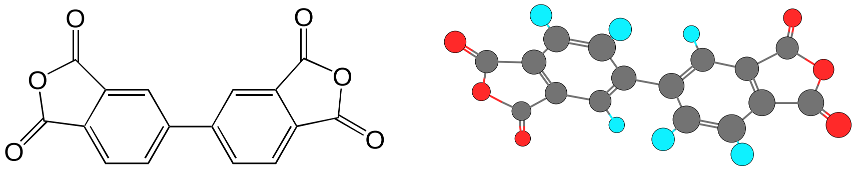
4.2.6 5,5’-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzenefurandione (6FDA) Based Polyimides

Polyimides containing 6FDA were of interest due to their excellent properties such as good solubility, low dielectric constant, low moisture sorption, good optical clarity and high gas permeability. Three dimensional models of 6FDA and biphenyl dianhydride (BPDA) molecules are shown in Figure 4.2.6.1. Clearly, the 6FDA structure appears to be much more bulky and bent when compared to BPDA. This structural difference often imparts solubility of 6FDA systems over BPDA polyimide analogs. Three diamines were chosen in combination with 6FDA to yield soluble, high T_g systems.

In Table 4.2.6.1, the molecular weight characteristics and thermal behavior are shown for these materials. The high temperature solution imidization route was used to form high molecular weight polymers from an equimolar ratio of diamine and dianhydride. Molecular weight distributions of 2.0 are shown in each case. In combination with *m*-phenylenediamine (*m*-PDA), 6FDA produced a polyimide having a T_g of 295°C. By increasing the chain rigidity with a bulky, highly rigid diamine, 9,9-bis(4-aminophenyl) fluorene (FDA), the T_g increased quite dramatically from 295°C to 369°C. Although *m*-PDA and FDA have comparable rigidities, the higher molecular weight diamine, FDA, contributed a greater amount of its “rigid” character to the polymer repeat unit as opposed to the smaller *m*-PDA. Thus, observation of higher T_g is the usual effect, which results from incorporating a higher molecular weight diamine was the observed increase in T_g. Another factor, which may also play a role in producing the high T_g of FDA/6FDA, is the inherent bulkiness of fluorene. The bulky substituent may hinder interchain molecular rotation and thereby increase the T_g.

The diamine, DDBT, is rigid and also posseses some bulky characteristics from the methyl groups and the two oxygens which protrude out of plane. The T_g of DDBT/6FDA was not obtainable due to initiation of polymer degradation in the DSC.

BPDA



6FDA

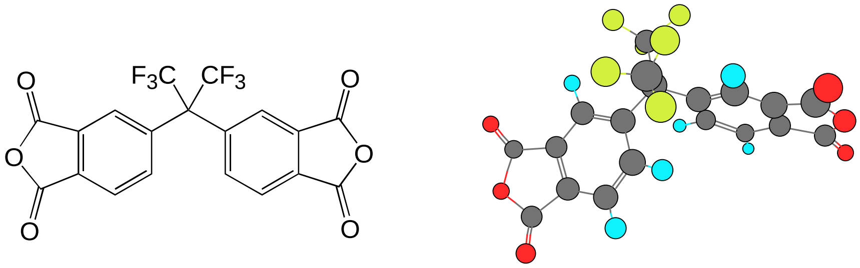


Figure 4.2.6.1 Three Dimensional Projections of 6FDA and BPDA

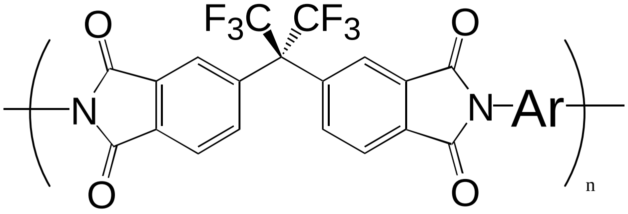


Table 4.2.6.1 Molecular Weight and Thermal Analysis of 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzenefurandione (6FDA) Based Polyimides

-Ar-	**Target M_n**	**M_n (K)$^+$ (avg.)**	**M.W.D.**	**T_g (°C)***	**TGA (°C)****
m-PDA	1:1	50	2.0	295	520
DDBT	1:1	31.7	2.0	>350	472
FDA	1:1	28.2	1.9	369	522

+ via GPC, mobile phase was NMP + 0.02MP_2O_5, 60°C

* 2nd heating; heating rate of 10°C/min

** in air, 10°C/min

The TGA results, as expected, showed good thermal stability for *m*-PDA/6FDA and FDA/6FDA, and a correspondingly reduced stability for DDBT/6FDA, which was partly attributable to abstractable benzylic protons.

4.2.7 Polyimides Derived from 3,7-diamino-2,8-dimethyl-dibenzothiophene-5,5-dioxide (DDBT)

Homopolyimides containing DDBT were expected to yield high T_gs due to the inherent monomer rigidity. It was unclear if these polyimides would be soluble. Two dianhydrides, which are known to produce soluble polyimides in many cases, were chosen in combination with DDBT. The two systems, BPADA/DDBT and 6FDA/DDBT, were synthesized using high temperature solution imidization methods. Both polymers were soluble in the reaction solvent, NMP.

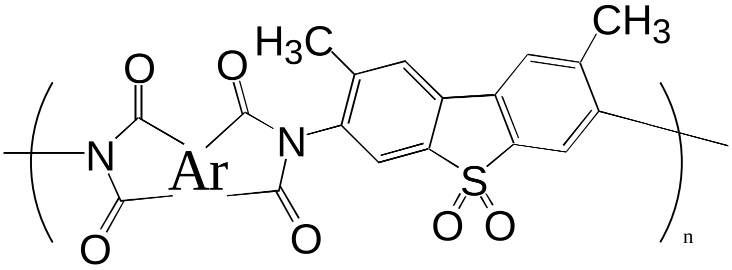
Molecular weight and thermal characterization is presented in Table 4.2.7.1. Even though the molecular weight for the BPADA/DDBT system was not high, i.e., <20,000g/mol, th polyimide could be solution cast from NMP to form creasable and ductile films. The glass transition temperature of BPADA/DDBT was found to be 313°C, which was about 95°C higher than that of the BPADA/m-PDA system. The rationale behind such a dramatic increase must be related to the extended rigid and planar nature of DDBT.

Each of these polymers had a 5% weight loss in air below 500°C resulting from, at least in part, the abstractable benzylic protons present in DDBT.

4.3 Gas Permselectivity Studies Performed on Novel Polyimides

Gas permeability through a semipermeable membrane is a product of the diffusion coefficient (a mobility factor) and solubility constant, which is the specific interaction of

Table 4.2.7.1 Molecular Weight and Thermal Analysis of 3,7-diamino-2,8-dimethyl-dibenzothiophene-5,5-dioxide (DDBT)



-Ar-	Target M_n	M_n (K)$^+$ (avg.)	M.W.D.	T_g (°C)*	TGA (°C)**
BPADA	1:1	11.2	1.8	313	431
6FDA	1:1	31.7	2.0	>350	472

\+ via GPC, mobile phase was NMP + 0.02MP_2O_5, 60°C
* 2nd heating; heating rate of 10°C/min

** in air, 10°C/min

the gas with the membrane. Gases traverse the membrane at different rates based on these two parameters. The gas pair investigated in this research was oxygen/nitrogen (O_2/N_2), which each have kinetic diameters of 3.46Å and 3.64Å, respectively. For this gas pair, the dominating factor for the rate of gas permeation is the diffusion coefficient. Since the diffusion coefficient is highly dependent on the mobility of gas through the free-volume and the free-volume distribution of the semipermeable membrane, it remains a challenge to increase the permeation rate of one species, while essentially holding the permeation rate of the other constant.

Membranes, which display both a high permeability and high selectivity toward gases, are desirable. A polymer with combined permeability and selectivity properties above the upper bound[231] (discussed in section 2.4.3.4) is rare. The data in this research will be referenced to the upper bound.

One approach to yield highly permeable and yet highly selective membranes is to utilize monomers which increase interchain spacing while simultaneaously maintaining a rigid backbone.[233-236] One such application of this method is discussed in section 2.5.1.

The approach taken in this research was to incorporate either diamines or dianhydrides which are both rigid and bulky. Monomer rigidity and bulkiness will translate into a polymer backbone which is also rigid and bulky. The bulky moieties will sterically hinder polymer-polymer interactions and serve to increase interchain spacing.

4.3.1 Permselective Behavior of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) Based Polyimides

Diaminophenylindane is a diamine which satisfies the rigid and bulky requirements for improving gas permselectivity (Figure 4.2.1.1). The three dimensional projection clearly shows the planarity and inherent rigidity of the parent indane structure. Out from this plane are four bulky groups which cause an increased spacing between adjacent polymer chains. Three of the groups are methyls and the other is the pendant phenyl ring which bears the amine. The 3-D projection also shows the kinked structure of this monomer centered about the carbon bridging the indane structure and the phenyl ring. The semi-rigid kink and bulky substituents will frustrate close packing between polymer chains and increase the gas permeability through thin polymer films of this material.

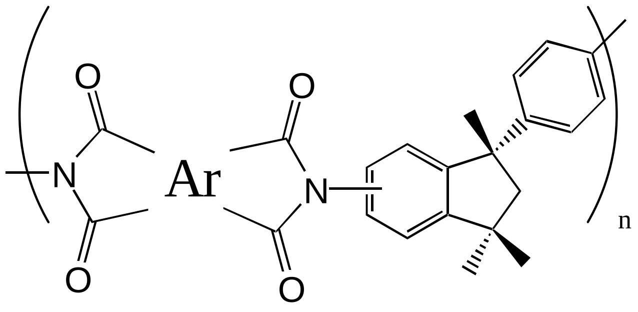
Oxygen permeability and O_2/N_2 selectivity for the homopolyimides containing DAPI are provided in Table 4.3.1.1. The first two entries, PMDA and BPDA, are considered rigid dianhydrides. Rigid repeat units may have the ability to pack well with each other and decrease the gas permeation rate. Based on this interpretation alone, PMDA, which has the greatest rigidity, should conceiveably yield a thin film which has the lowest permeability when compared to the other, more flexible, dianhydrides. However, the thin film of PMDA/DAPI has the highest permeability. By changing the dianhydride to BPDA, a less rigid monomer, the oxygen permeability decreases from 34.6Ba to 5.8Ba. Although BPDA is not as rigid as PMDA, because it is a higher molecular weight semi-rigid dianhydride, it contributes a greater amount of its character to the repeat unit. Therefore, in the case of PMDA/DAPI it appears that the bulky, kinked nature of DAPI dominates the gas permeation characteristics of the thin film, i.e., allows gases to permeate rapidly which may be attributable to an increase in free volume.

A selectivity comparison between PMDA/DAPI and BPDA/DAPI reveals the less permeable polymer, BPDA/DAPI, also has the greater selectivity. This is in agreement with the inverse relationship between permeability and selectivity that has been commonly observed in gas permeation science.[232]

The gas permeation characteristics of BPADA/DAPI reveal a continued decrease in oxygen permeability and a concomitant increase in O_2/N_2 selectivity. Perhaps with this combination of monomers the more flexible dianhydride allows for more tightly packed conformations to be achieved. The polyimide BTDA/DAPI displayed a good combination of O_2 permeablity and O_2/N_2 selectivity, 2.8Ba and 7.3, respectively. This polyimide may have commercial utility due to its good combination of permeability and selectivity values.

The permselectivity behavior of DAPI containing homopolyimides is plotted in Figure 4.3.1.1 against the upper bound.

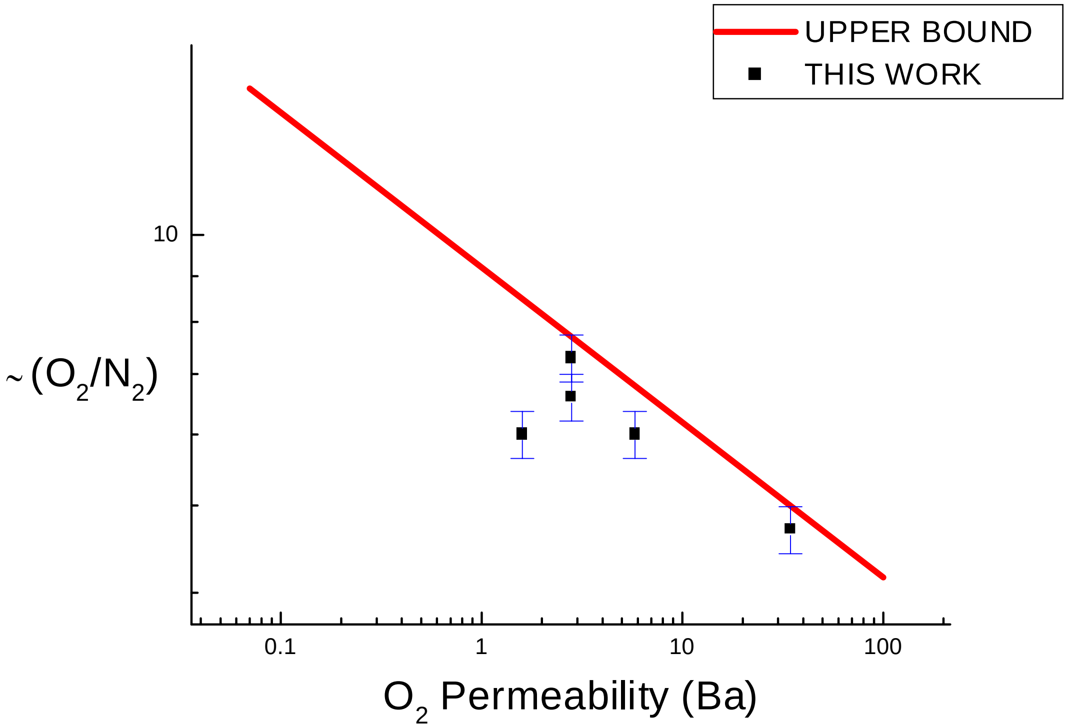
Table 4.3.1.1 Oxygen Permeability and Oxygen/Nitrogen Selectivty Values for 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI) Based Polyimides



Dianhydride	O_2 Perm. (Ba)*	O_2/N_2 Selectivity**
PMDA	34.6	4.7
BPDA	5.8	6.0
BPADA	2.8	6.6
BPEDA	1.6	6.0
BTDA	2.8	7.3

T=30°C

* ±3% error
** ±6% error



*error bars for α(O_2/N_2) values in blue (±6%); error bars for O_2 permeability values were omitted due to being indistinguishable from the data points on this scale (±3%)

Figure 4.3.1.1 Permselectivity Behavior of DAPI Containing Homopolyimides Relative to the Upper Bound

4.3.2 Effect of the DAPI Isomeric Ratio on Polymer Permeability and Selectivity

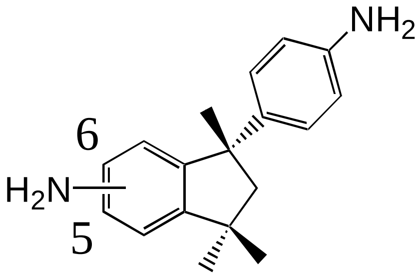
The effect of the DAPI isomeric ratio on polymer permselectivity was investigated in combination with benzophenone dianhydride (BTDA). The results of this study are presented in Table 4.3.2.1. The difference in these results for the first two systems, i.e., 30:70 and 50:50 (6:5), are within experimental error, which is typically ±4%. However, the 60:40 isomeric DAPI ratio with BTDA has ~43% increase in O_2 permeability and a decrease of ~57%in O_2/N_2 selectivity. Since the selectivity value dropped significantly, even though the increase in permeability was high, this polyimide would not be a good candidate for gas separation. However, further experiments are needed to verify the behavior of this polymer. The overall conclusion concerning the BTDA/DAPI systems studied thus far is that alteration of the DAPI isomeric ratio had no significant effect on the permselective properties.

4.3.3 Permselective Behavior of 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzenefurandione Dianhydride (6FDA) Based Polyimides

A second monomer, which satisfies the two criteria of being bulky and rigid, is 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzenefurandione dianhydride (6FDA). In Figure 4.2.6.1, the structure of 6FDA is compared with that of BPDA. The bulky structure of the two $-CF_3$ groups of 6FDA and its kinked structure would hinder close packing between adjacent polymer chains. This monomer is also rigid due to steric hinderance between fluorine atoms and aromatic protons ortho to the hexafluoroisopropylidene linkage, which restricts free rotation about the $(CF_3)_2C-C(Ar)$ bond. In addition, 6FDA is known to impart solubility to polyimides.

The permselectivity values of polyimides derived from 6FDA are given in Table 4.3.3.1. The polyimide *m*-PDA/6FDA has both a relatively low O_2 permeability and O_2/N_2 selectivity. By replacing the diamine with FDA, the O_2 permeability increases by more than five fold. Both of the diamines, *m*-PDA and FDA, are quite rigid. However,

Table 4.3.2.1 Isomeric Ratio Effect on 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI)/3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) Oxygen Permeability and Oxygen/Nitrogen Selectivity Values

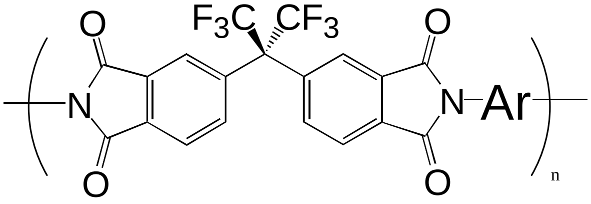


6:5 Isomeric Ratio	O_2 Perm. (Ba)	O_2/N_2 Selectivity
30:70	2.5	7.0
50:50	2.8	7.4
60:40	4.0	4.7

T=30°C

* ±3% error
** ±6% error

Table 4.3.3.1 Oxygen Permeability and Oxygen/Nitrogen Selectivty Values for 6FDA Based Polyimides



-Ar-	O_2 Perm. (Ba)	O_2/N_2 Selectivity
m-PDA	3.0	5.5
FDA	15.3	5.8
DDBT	22.2	6.1

T=30°C

* ±3% error
** ±6% error

the difference in bulkiness is quite large. The very bulky FDA significantly increases the O_2 permeability due to its ability to impart a more open polymer conformation. Surprisingly, the O_2/N_2 selectivity for this system also increases slightly over that of *m*-PDA/6FDA.

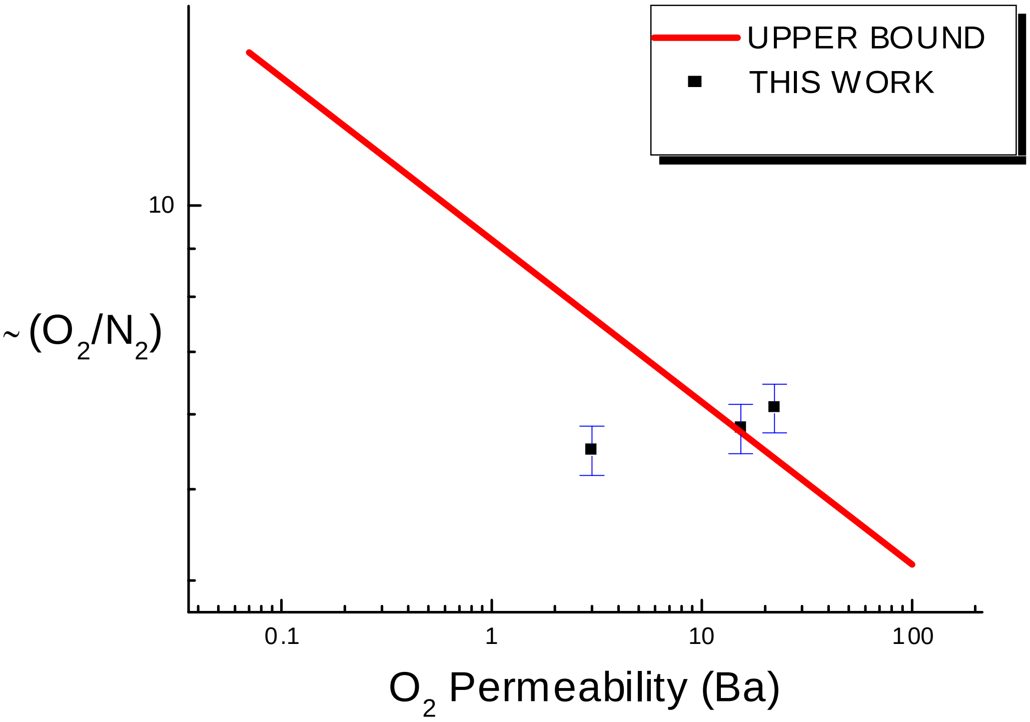
The polyimide containing the diamine, 3,7-diamino-2,8-dimethyl-dibenzothiophene-5,5-dioxide (DDBT), in combination with 6FDA shows an increase in O_2 permeability and O_2/N_2 selectivity over FDA/6FDA (Table 4.3.3.1). The marked increase in both permeability and selectivity is rarely observed in polymer science. The rigid structure of DDBT and its slightly bulky groups (methyl and SO_2) in combination with the possible electronic interactions of SO_2 groups are thought to impart these gas permeation characteristics. The permselectivity properties of this polymer, as well as those of the other DDBT-based polyimides, are plotted in relation to the upper bound in Figure 4.3.3.1.

4.3.4 Polymer Permeability and Selectivity of Polyimides Derived from 3,7-diamino-2,8-dimethyl-dibenzothiophene-5,5-dioxide (DDBT)

The sulfone linked diamine, DDBT, was shown in the previous section to give high O_2 permeability and moderate selectivity values. This diamine was also condensed with BPADA and tested for its gas permselectivity behavior. In contrast to 6FDA/DDBT, BPADA/DDBT has lower O_2 permeability and O_2/N_2 selectivity values (Table 4.3.4.1). The more flexible BPADA presumably allows the polymer chains to “seek-out” a tighter conformation, which reduces O_2 permeability.

4.4 Molecular Weight and Thermal Characterization of Polyimides Containing Hydroxyl Moieties

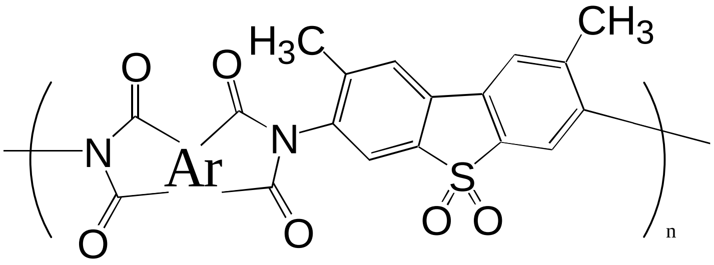
One of the objectives of this research was to investigate polyimide systems which contain hydroxyl moieties in the repeat unit. Once these materials were successfully synthesized, the influence of hydroxyl groups on thermal properties and permeability



*error bars for $\alpha(O_2/N_2)$ values in blue (±6%); error bars for O_2 permeability values were omitted due to being indistinguishable from the data points on this scale (±3%)

Figure 4.3.3.1 Permselectivity Behavior of 5,5’-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzenefurandione (6FDA)-Containing Homopolyimides as Compared to the Upper Bound

Table 4.3.4.1 Oxygen Permeability and Oxygen/Nitrogen Selectivty Values for 3,7-Diamino-2,8-dimethyl-dibenzothiophene-5,5-dioxide (DDBT) Based Polyimides



Diamine	O_2 Perm. (Ba)	O_2/N_2 Selectivity
BPADA	1.9	5.5
6FDA	22.1	6.1

T=30C

* ±3% error
** ±6% error

behavior was measured. The impetus for designing such systems was based on the hypothesis that hydrogen bonding may increase chain rigidity and favorably influence gas selectivity (Figure 4.4.1).[249]

Introducing a hydroxyl group into the backbone of a polyimide may easily be accomplished by using a monomeric diamine as the carrier. Three different diamines were investigated and have been presented in the following sections.

4.4.1 Characterization of Polyimides Containing 4,4'-diamino-3,3'-dihydroxybenzidine (HAB)

Polyimides derived from HAB were expected to yield soluble polymers with the proper dianhydrides. Due to the inherently rigid structure of HAB, flexible dianhydrides were chosen to promote solubility. These were: BPADA, DSDA and 6FDA.

Polyimides incorporating HAB were synthesized by high temperature solution imidization techniques. Each of the polyimides remained soluble in the reaction solvent (NMP) even after being cooled to ~60°C before precipitating the polymer in methanol. Molecular weight and thermal characteristics of these systems are shown in Table 4.4.1.1. HAB in combination with BPADA, a more flexible dianhydride, was soluble in the reaction solution but did not dissolve in hot NMP once it had been precipitated and attempts were made to redissolve it. Therefore, molecular weight characterization of the polyimide was not possible for this system. The insolubility of HAB/BPADA was most likely due to a combination of diamine rigidity and strong intermolecular hydrogen bonding which prevents polymer redissolution.

In order to obtain a soluble system, a comonomer, DSDA, was utilized with HAB. High molecular weight polymer was achieved for this system, as determined by GPC. The molecular weight distribution of 3.3 was a little higher than the expected value of 2.0. Even though the GPC method operates under dilute solution conditions, it may have been possible in this case that the strong hydrogen bond association between chains was not sufficiently disrupted by the NMP mobile phase. Insolubility due to light crosslinking, i.e., ester formation, may also be possible. The glass transition temperature

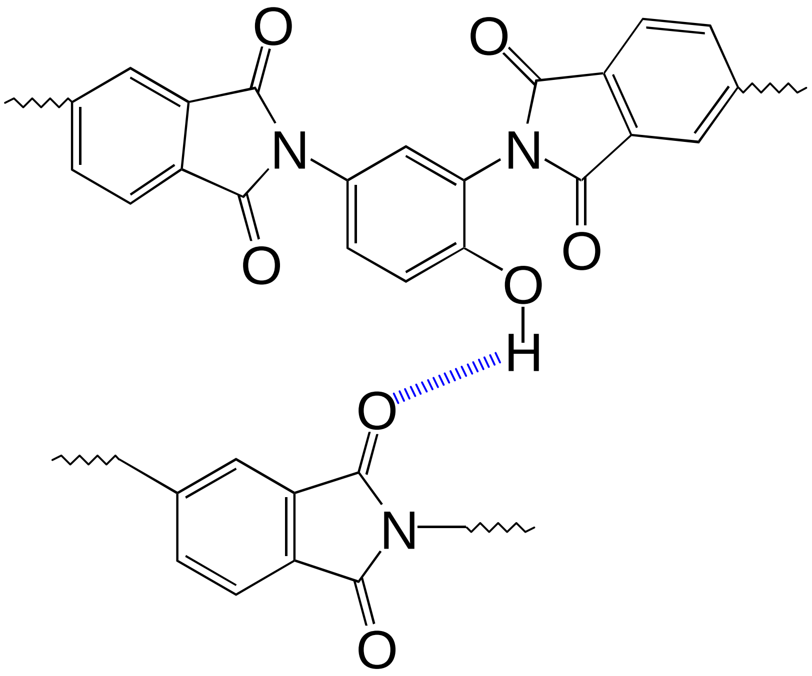
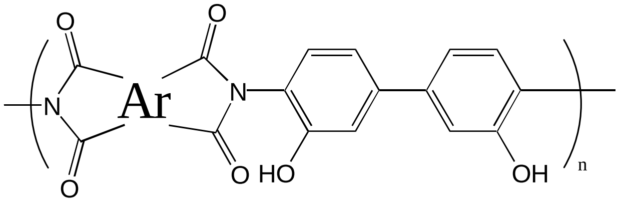


Figure 4.4.1 One Possible Type of Hydrogen Bonding in Polyimides which Contain Hydroxyl Moieties in the Backbone

Table 4.4.1.1 Molecular Weight and Thermal Analysis of 4,4'-diamino-3,3'-dihydroxybenzidine (HAB)



Dianhydride	**Target M_n**	**M_n (K)$^+$ (avg.)**	**M.W.D.**	**T_g (°C)***	**TGA (°C)****
BPADA	1:1	insol.	---	287	419
BPADA:DSDA(1:1)	1:1	83.8	3.3	---	428
6FDA	1:1	42.1	4.6	314	458

+ via GPC, mobile phase was NMP + 0.02MP_2O_5, 60°C

* 2nd heating; heating rate of 20°C/min

** in air; heating rate of 10°C/min

for BPADA:DSDA(1:1)/HAB was undetectable. The FTIR spectrum of a thin film showed the absorption bands typical for polyimides, as well as a broad absorption due to the phenolic -OH (~3400cm^{-1}) (Figure 4.4.1.1).

The polymer of HAB/6FDA had high molecular weight and was soluble when re-dissolving the precipitate in NMP to prepare a solution. This system also had a higher molecular weight distribution than was expected. By replacing BPADA with 6FDA in the HAB-based polyimides, the T_g increased by 27°C resulting from the more rigid hexafluoroisopropylidene linkage. FTIR analysis of this polymer showed absorptions typical for polyimides (Figure 4.4.1.2).

Figure 4.4.1.3 shows percent water sorption versus time under two different conditions. Under atmospheric humidity (~50%) 6FDA/HAB absorbs ~4 weight % water after eight days. However, after being totally immersed in water for eight days the film showed >7 weight % water absorption. A typical commercial polyimide, such as Kapton, will absorb 2-3 weight % water under atmospheric conditions. The increase in water absorption for 6FDA/HAB is attributable to an increase in the hydrophilic nature of the polymer backbone due to the hydroxyl groups.

Thermogravimetric analysis of polyimides containing HAB indicates a 5% weight loss well below 500°C. Premature degradation results from the more oxidatively unstable phenol moieties.

All of these polymers yielded tough, creasable films when cast from NMP. Films of HAB/BPADA were cast from the reaction solution due to the fact that the polyimide could not be redissolved once it had been precipitated.

4.4.2 Polyimides Derived from 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (Bis-AP-AF)

In view of the spurious molecular weight distributions found for HAB containing polyimides, Bis-AP-AF, a more flexible diamine containing hydroxyl groups, was introduced in an effort to reduce intermolecular chain association. Polyimides based on Bis-AP-AF were synthesized via high temperature solution imidization methods in NMP.

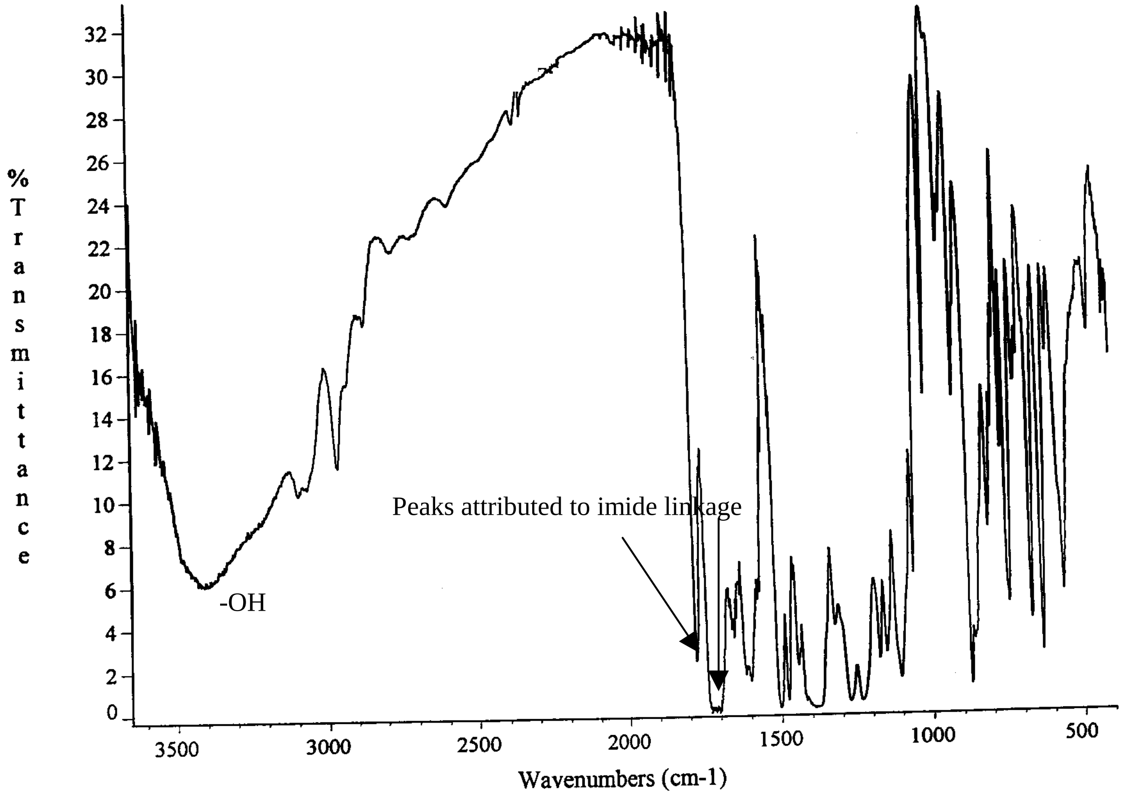


Figure 4.4.1.1 FTIR Spectrum of BPADA:DSDA(1:1)/HAB

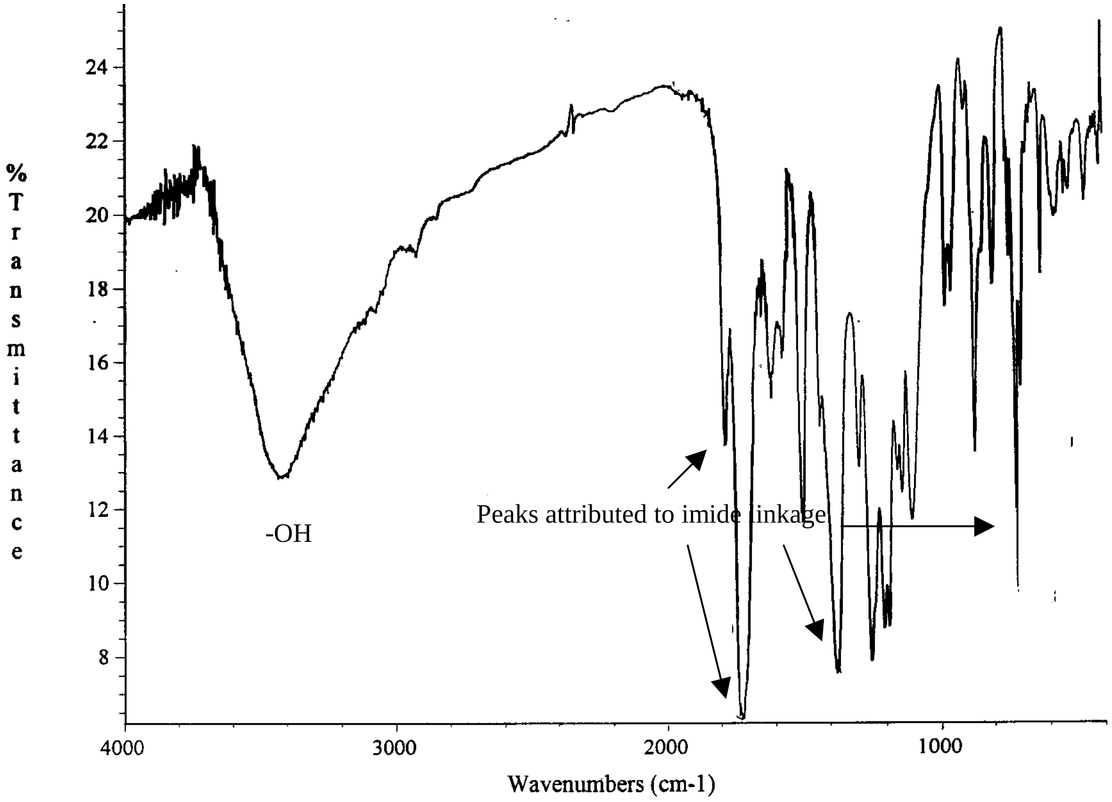
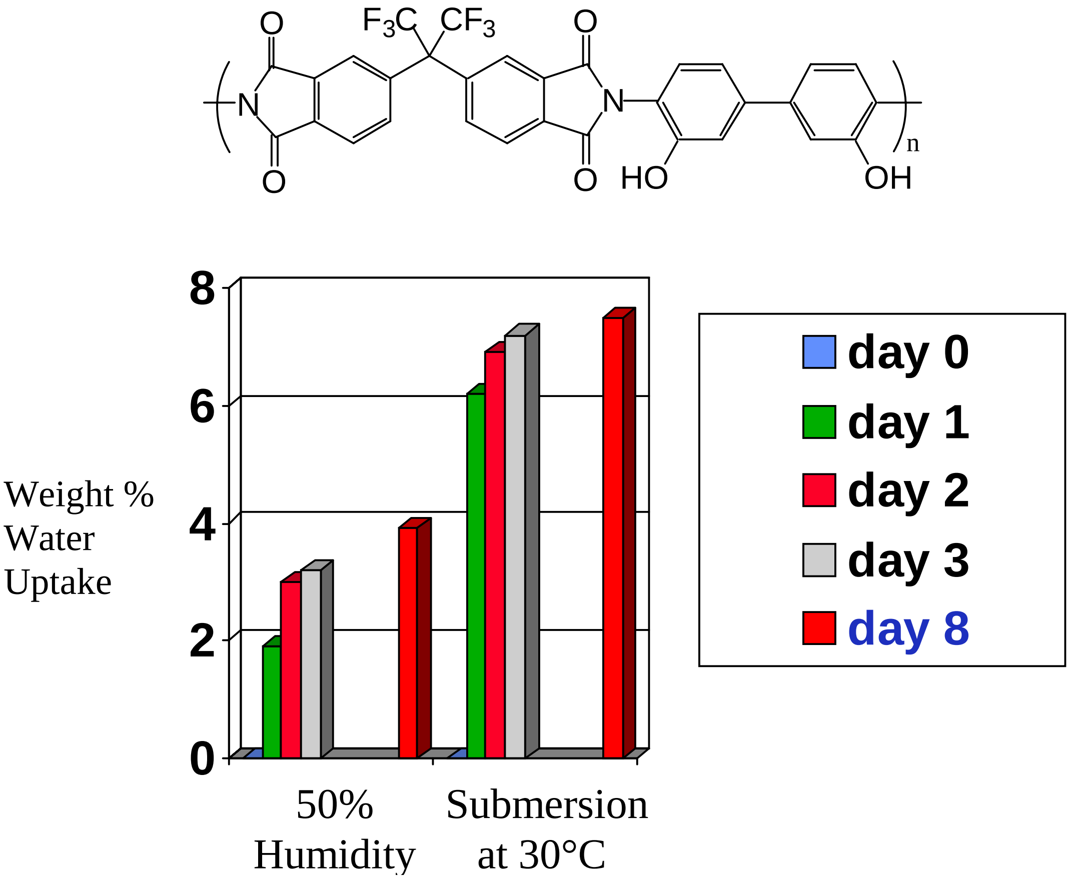


Figure 4.4.1.2 FTIR Spectrum of 6FDA/HAB



* initial film was 70µm thick
** 250°C under vacuum for 3 days was needed to remove trace amounts of water
*** control: Kapton polyimides typically uptake ~2-3 wt% water under atmospheric conditions

Figure 4.4.1.3 Percent Water Sorption Versus Time for 6FDA/HAB

Prior to precipitation, tough, creasable films were cast from the reaction solutions. The precipitated polymers were fibrous and insoluble in hot NMP, which was most likely due to a large degree of hydrogen bonding.

It was only possible to obtain the glass transition temperature for one of these materials because of an overlap between the T_g and polymer decomposition (Table 4.4.2.1). Figure 4.4.2.1 compares the T_g of Bis-AP-AF/BPADA with that of Bis-AT-AF/BPADA which has a similar backbone. A T_g increase of 28°C has been observed for Bis-AP-AF/BPADA over Bis-AT-AF/BPADA and can be attributed to intermolecular hydrogen bonding which decreases chain mobility. The thin film FTIR spectrum of Bis-AP-AF/BPADA shows absorption bands typical for polyimides as well as a broad absorption due to the phenolic -OH (~3400cm^{-1}) (Figure 4.4.2.2).

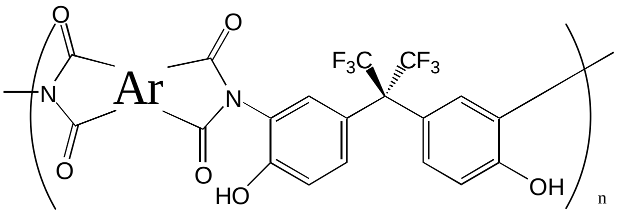
4.4.3 Polyimides Based on 2,4-Diaminophenol (DAP)

Synthetic incorporation of DAP was conducted in an attempt to arrive at soluble polyimides which contain hydroxyl groups. Unlike the two previously described diamines, HAB and Bis-AP-AF, the DAP monomer contains only one hydroxyl group. A decrease in the number of hydroxyls per repeat unit was projected to decrease the degree of hydrogen bonding and, if present, reduce crosslinking, which may lead to a more soluble systems.

Diaminophenol (DAP) was condensed with BPADA, 6FDA, BTDA and DSDA using high temperature solution imidization techniques. Molecular weight characterization and thermal behavior of these systems is provided in Table 4.4.3.1. The two soluble polyimides, DAP/BPADA and DAP/6FDA, were of high molecular weight as determined by GPC (DAP/BPADA-Figure 4.4.3.1). They also formed tough, creasable films which gave infrared absorptions typically found for polyimides, as well as a single broad peak due to the phenolic -OH (~3400cm^{-1}) (Figure 4.4.3.2). The molecular weight distribution, as expected, was around 2.0.

The homopolyimides of DSDA and BTDA were soluble in the reaction solution. Once precipitated, however, they could not be redissolved in hot NMP. This

Table 4.4.2.1 Molecular Weight and Thermal Analysis of 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (Bis-AP-AF)



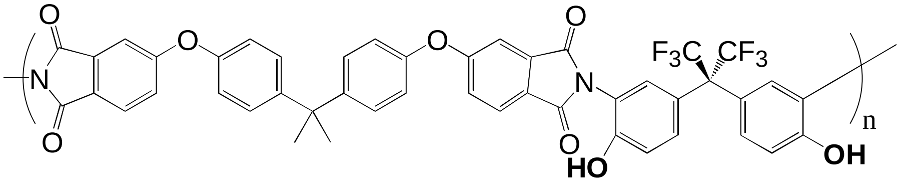
Dianhydride	**Target M_n**	**M_n (K)$^+$ (avg.)**	**M.W.D.**	**T_g (°C)***	**TGA (°C)****
BPADA	1:1	insol.	---	252	415
BTDA	1:1	insol.	---	>275	448
6FDA	1:1	insol.	---	>310	403

\+ via GPC, mobile phase was NMP + 0.02MP_2O_5, 60°C

* 2nd heating; heating rate of 20°C/min

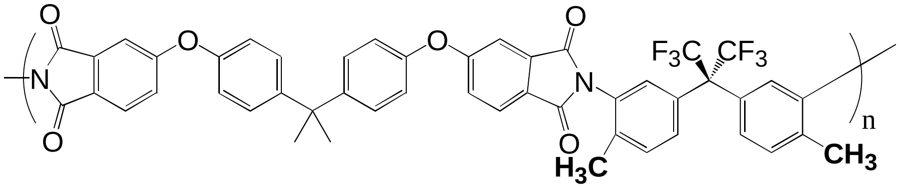
** in air; heating rate of 10°C/min

T_g(°C)



252

Bis-AP-AF/BPADA



224

Bis-AT-AF/BPADA

Figure 4.4.2.1 Chemical Structures and T_g of Bis-AP-AF/BPADA and Bis-AT-AF/BPADA

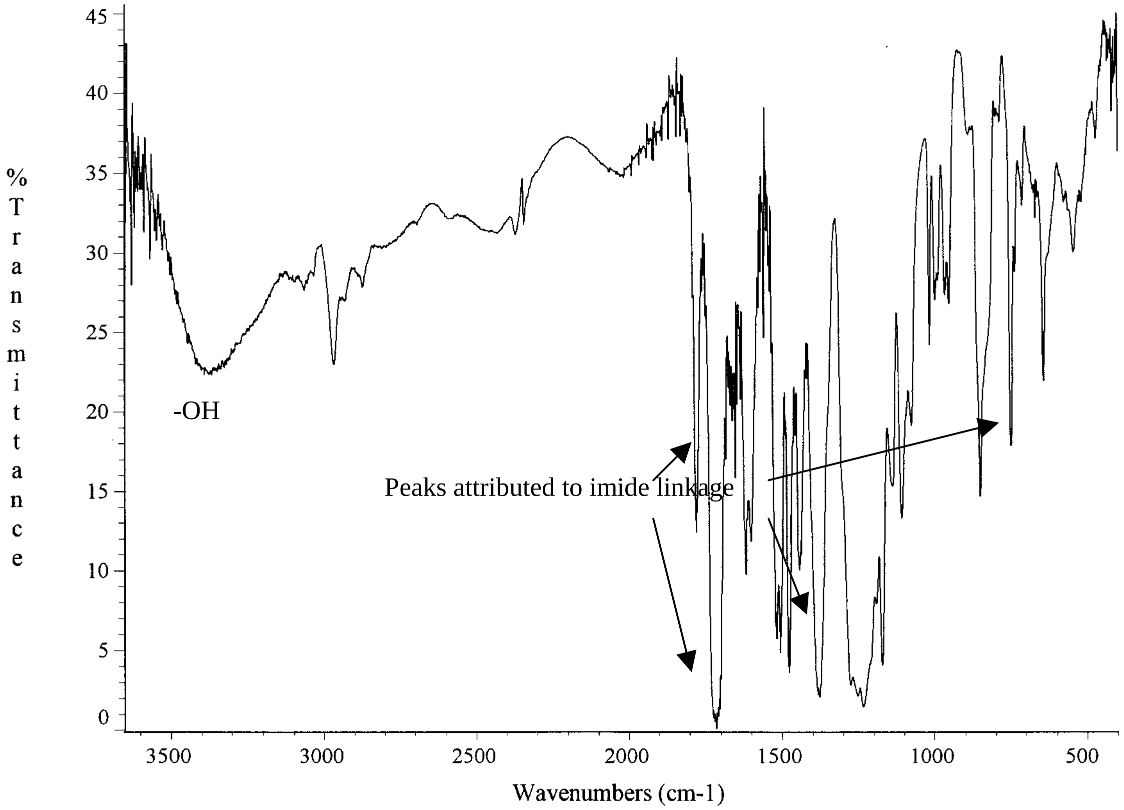
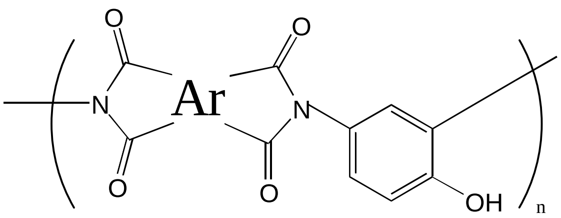


Figure 4.4.2.2 FTIR Spectrum of Bis-AP-AF/BPADA

Table 4.4.3.1 Molecular Weight and Thermal Analysis of 2,4-diaminophenol (DAP) Based Polyimides



-Ar-	Target M_n	M_n (K)$^+$ (avg.)	M.W.D.	T_g (°C)*	TGA (°C)**
BPADA	1:1	37.2	2.2	247	435
6FDA	1:1	23.0	2.0	338	450
DSDA	1:1	insol.	---	>325	480
BTDA	1:1	insol.	---	>340	435

+ via GPC, mobile phase was NMP + 0.02MP_2O_5, 60°C

* 2nd heating; heating rate of 20°C/min

** in air; heating rate of 10°C/min

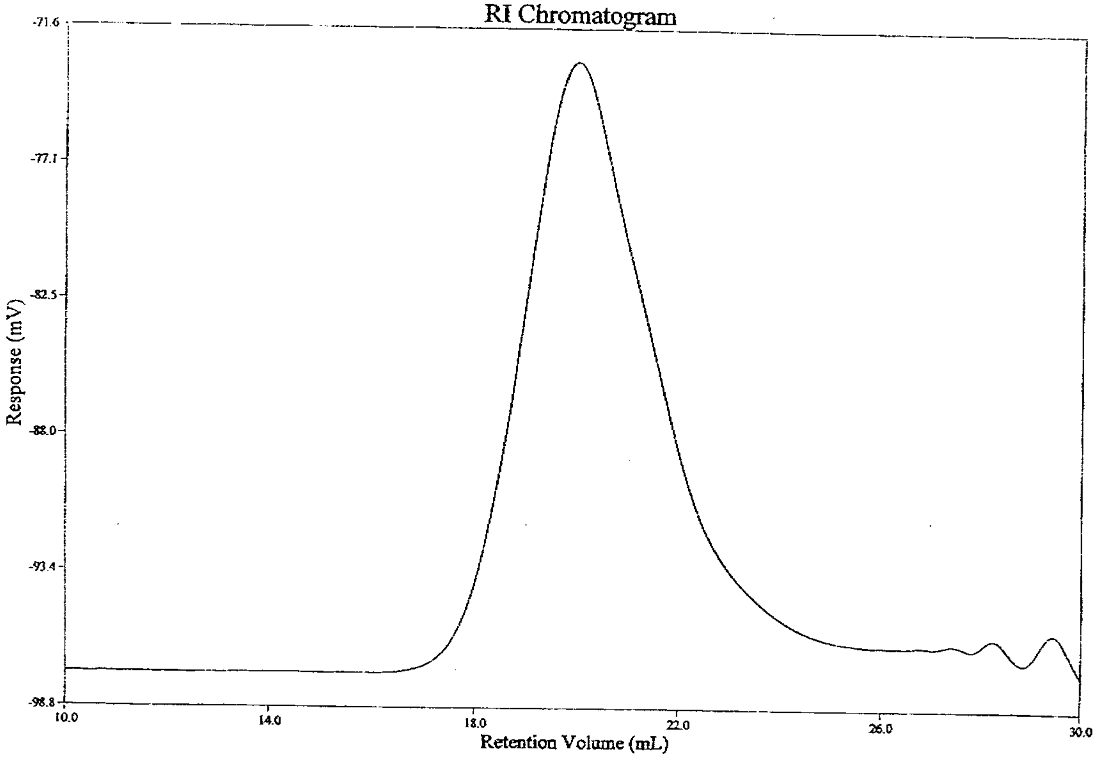


Figure 4.4.3.1 Gel Permeation Chromatogram of DAP/BPADA Based Polyimide (mobile phase was NMP + $0.02MP_2O_5$, 60°C)

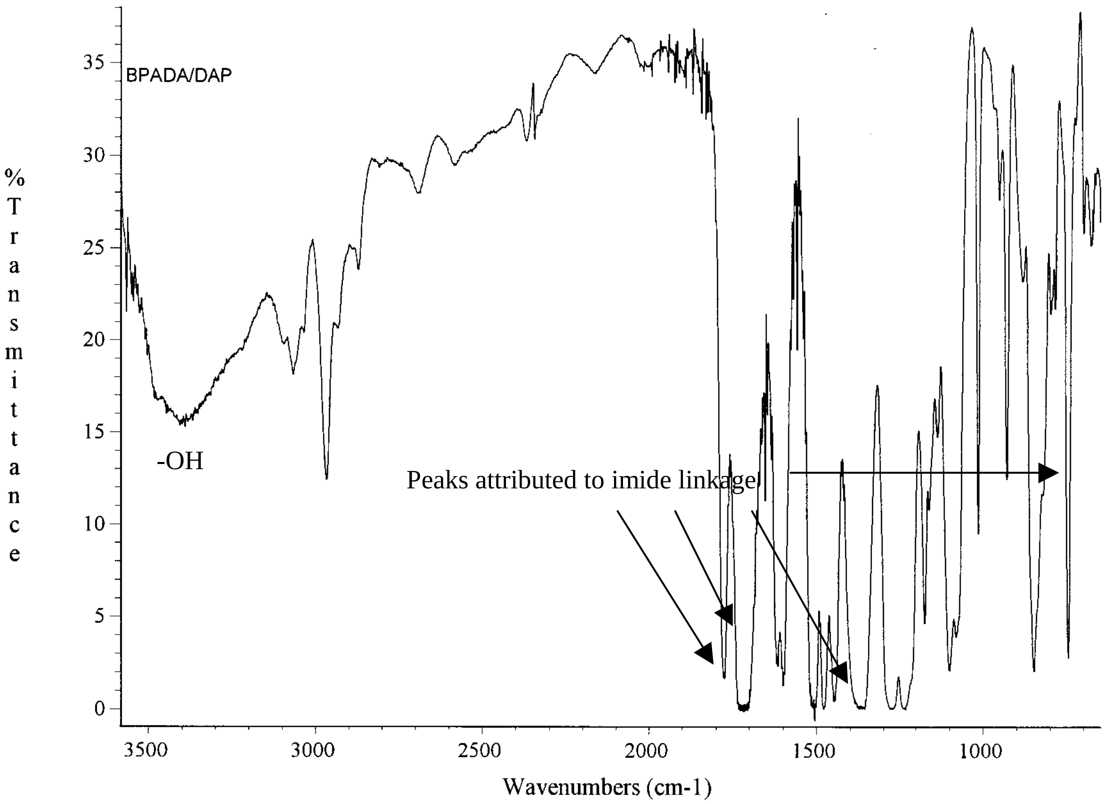


Figure 4.4.3.2 FTIR Spectrum of DAP/BPADA

phenomenon may result from a combination of strong intermolecular hydrogen bonding, light crosslinking (i.e., ester formation), and partial crystallinity, although the latter two have not been verified.

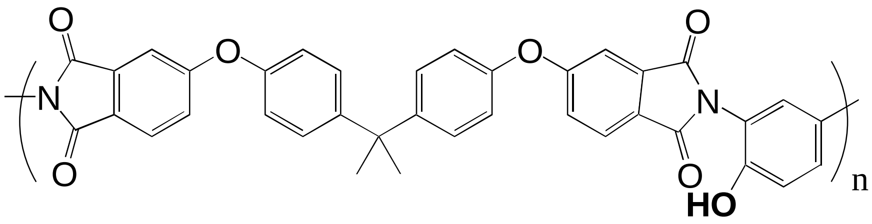
Glass transition temperatures of BPADA and 6FDA polyimides containing DAP were found to be 247°C and 338°C, respectively. Comparison of BPADA/DAP with BPADA/*m*-PDA, whose repeat unit differs by the absence of a hydroxyl group, showed the T_g to be increased by 30°C for the DAP system. Comparing 6FDA/DAP with 6FDA/*m*-PDA shows an increase in T_g of 43°C was observed (Figure 4.4.3.3) for the DAP based polyimide. In each system, the T_g has increased due to additional interaction between polymer chains through hydrogen bonding. Increasing polymer-polymer interactions via hydrogen bonding increased chain rigidity, which in-turn increased the relaxation temperature, T_g.

Determination of a glass transition temperature for DSDA/DAP and BTDA/DAP polyimides was not possible due to the transition occurring above the initial polymer degradation temperature.

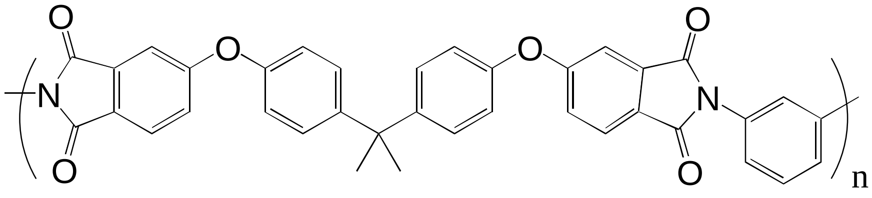
Thermogravimetric analysis in air revealed lower degradation temperatures when compared to the non-hydroxyl containing analogs. Weight loss values below 500°C resulted from the oxidatively more unstable phenolic sites.

4.5 Gas Permselectivity Studies Performed on Polyimides Containing Hydroxyl Moieties

Polyimides containing pendant phenol groups were of interest in this research for gas separation. It was hypothesized that by increasing intermolecular chain rigidity may result in an increase in gas permselectivity. Polymers containing 4,4’-diaminobiphenyl-3,3’-diol (HAB) and 2,4-diaminophenol (DAP) were tested to determine their semipermeable behavior toward gaseous O_2 and N_2.



DAP/BPADA



m-PDA/BPADA

	T_g(°C)	M_n (g/mol)
DAP/BPADA	247	37K
m-PDA/BPADA	217	20K

Figure 4.4.3.3 Chemical Structure and Glass Transition Temperature of 6FDA/DAP and 6FDA/m-PDA Based Polyimide

4.5.1 Permselective Behavior of 4,4’-diaminobiphenyl-3,3’-diol (HAB) Based Polyimides

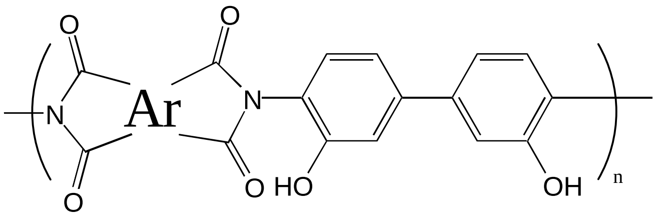
Homopolyimides based on HAB were investigated for their permselective behavior. HAB was chosen for two reasons: first, it has the ability to form intermolecular hydrogen bonds through the pendant phenol moiety and, secondly, it is a rigid diamine which facilitates a reduction in permeability.

The gas permeation values for these systems are given in Table 4.5.1.1. The BPADA/HAB system shows excellent O_2/N_2 selectivity and moderate permeability. Due to the relative insolubility of the BPADA/HAB polyimide, a soluble copolymer derived from BPADA and DSDA (50/50) was selected for comparison. DSDA, compared to BPADA, is a more rigid dianhydride and was expected to decrease O_2 permeability and increase O_2/N_2 selectivity. As shown in Table 4.5.1.1, this was indeed observed.

The hexafluoro bridge present in 6FDA is known to yield soluble systems and impart good permeability characteristics to semipermeable membranes. The 6FDA/HAB based polyimide was indeed soluble and had permeability characteristics which were quite interesting. Compared to BPADA/HAB, the 6FDA/HAB polyimide film decreases slightly in O_2/N_2 selectivity and increases greatly in O_2 permeability. The O_2/N_2 selectivity decreases by ~7% (within %error), while the O_2 permeability increases by 5 fold. As was discussed in section 4.3.3, 6FDA hinders chain packing and generally increases permeability. However, such a large increase in permeability is often accompanied by a greater decrease in O_2/N_2 selectivity, which was not found in this case. The difference in permselectivity values between BPADA/HAB and 6FDA/HAB may result from the greater phenol concentration present in 6FDA/HAB (moles OH/gram repeat unit), which may facilitate an increase in rigidity and lead to a higher selective system.

Gas permeability characteristics of polyimides based on HAB are plotted against the upper bound in Figure 4.5.1.1.

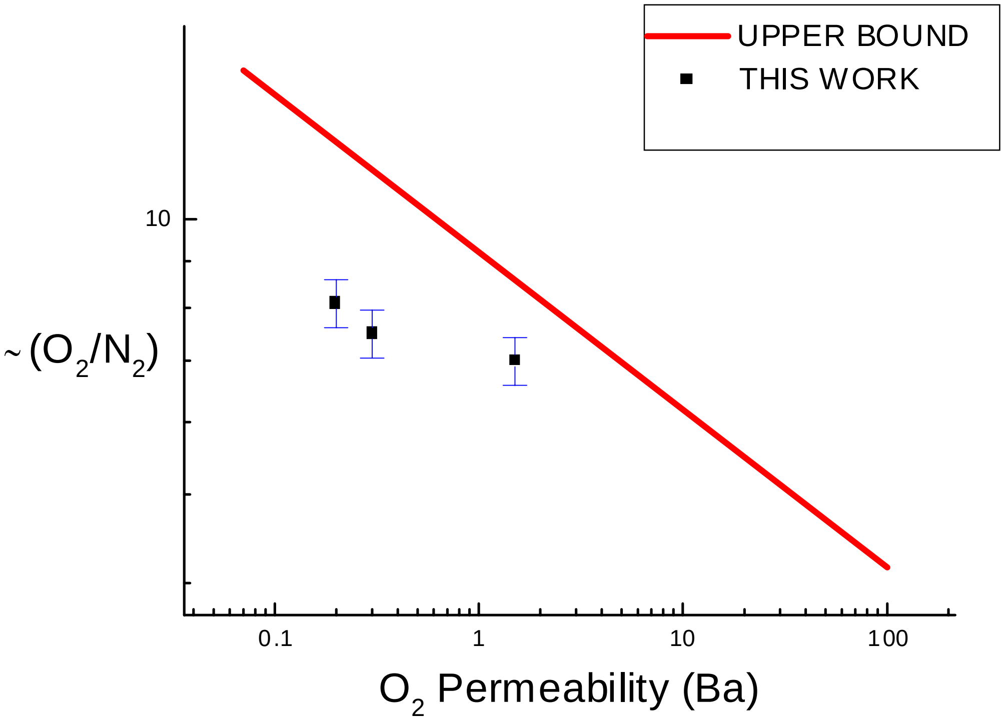
Table 4.5.1.1 Oxygen Permeability and Oxygen/Nitrogen Selectivty Values for 3,3’-dihydroxy-4,4’-diamino-biphenyl (HAB) Based Polyimides



Dianhydride	O_2 Perm. (Ba)	O_2/N_2 Selectivity
BPADA	0.3	7.5
BPADA:DSDA(50:50)	0.2	8.1
6FDA	1.5	7.0

T=30ºC

* ±3% error
** ±6% error



*error bars for α(O_2/N_2) values in blue (±6%); error bars for O_2 permeability values were omitted due to being indistinguishable from the data points on this scale (±3%)

Figure 4.5.1.1 Permselectivity Behavior of HAB Containing Homopolyimides as Compared to the Upper Bound

4.5.2 Polymer Permeability and Selectivity of Polyimides Derived from 2,4-Diaminophenol

It was also of interest in this research to make a direct comparison between polyimide repeat units, both with and without phenolic sites. One such system was prepared and is shown in Figure 4.5.2.1. Both the O_2 permeation and O_2/N_2 selectivity values are similar to each other within experimental error (±2%). It is clear from the T_g data for these two systems that the polyimide containing DAP has a greater degree of intermolecular attraction (the T_g increase by ~30°C). The tight polymeric structure, in this case, may be offset by the bulky phenolic moieties, which increases interchain spacing and result in the overall observation of negligible differences in permselectivity values.

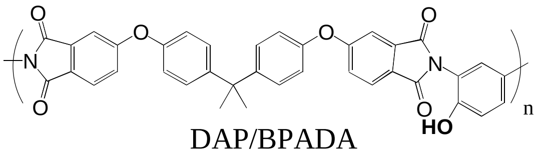
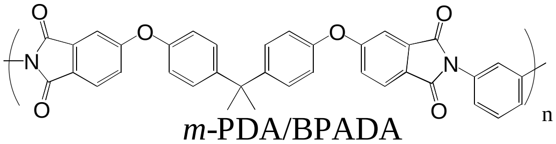
4.6 Applicable Crosslinking Mechanisms for Hollow Fiber Technology

Another objective of this research was to design and synthesize a polyimide system which could be cured at a moderately elevated temperature to yield a lightly crosslinked network. It was thought that light crosslinking might alter selectivity and permeability characteristics. Crosslinked materials have also been known to exhibit an increased resistance to solvents and contaminants, which would be an advantage for many applications.

The crosslinking reaction criteria had two important limitations: the reaction temperature must not exceed 150°C and must be completed within a time period of 2 hours. The reaction restrictions were imposed because of the need to maintain the proper polymer configuration for achieving high fluxes, i.e., hollow fibers.

Four reactive candidates were investigated. The candidates were amine-terminated, acetylene-terminated and phenol-terminated polyimides, as well as a polyimide with a pendant phenol group in the polymer repeat unit. The amine and phenol

Table 4.5.2.1 Oxygen Permeability and Oxygen/Nitrogen Selectivty Values for 2,4-diaminophenol (DAP) and 1,3-phenylenediamine (*m*-PDA) Derived Polyimides

Polymer Structure	O_2 Perm. (Ba)	O_2/N_2 Selectivity
 DAP/BPADA	**0.4**	**8.0**
 *m*-PDA/BPADA	**0.5**	**7.8**

T = 30ºC

* ±3% error
** ±6% error

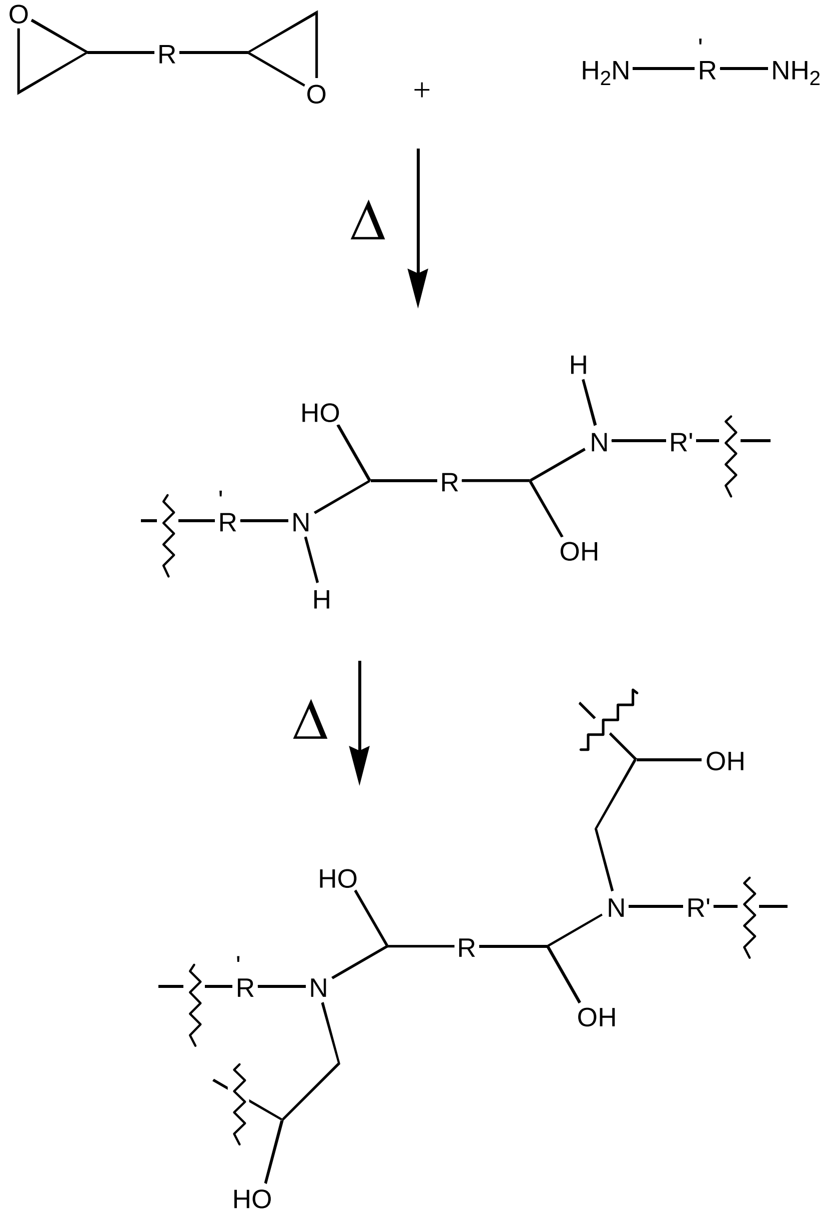
containing polyimides were reacted with epoxy and the acetylene-terminated system was reacted as a neat material. The following sections discuss how the four candidates were synthesized, characterized and evaluated for their reactivity, under the given reaction restrictions.

4.6.1 Curing Studies of Amine Terminated Oligomers with Epoxy-Cast from Chloroform

Curing of an epoxy with an amine is depicted in Scheme 4.6.1.1, which is known to undergo chain extention prior to crosslinking. A typical cure schedule for an epoxy/amine system, such as 4,4'-diaminodiphenylsulfone/Epon 828 (a difunctional epoxy), is 170°C for 1 hour prior to doing a post cure at 230°C for 30 minutes. Cure temperatures of 170°C and 230°C are required to impart sufficient molecular mobility to the system.

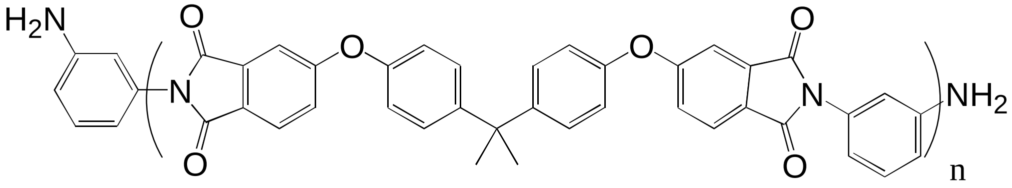
The first two systems investigated in this research were amine terminated oligomers of five and fifteen thousand grams per mol molecular weight having a backbone comprised of BPADA/*m*-PDA. The molecular weight and thermal behavior of these two polymers, which had been synthesized by the ester-acid route, are shown in Table 4.6.1.1. The T_g for these polymers was found to be 199°C and 215°C for the five and fifteen thousand grams per mol molecular weight oligomers, respectively. Curing of these two polymers must be effected, if possible, at 150°C within 2 hours. This presents quite a challenge considering the cure temperature is ~50°C below T_g.

The amine terminated oligomer based on BPADA/*m*-PDA oligomer of ~15,000g/mol was cured using a difunctional epoxy, Epon 828. The endgroup titration values obtained for the polyimide oligomer and epoxy were used to calculate a 1:1 mole ratio of reactive groups (1 amine/2 epoxide rings) for the blend. The polyimide and epoxy were then mixed together in chloroform (wt. Epoxy/ wt. Oligomer=5.2%). Bubble-free films of this reactive blend were cast from chloroform (~30wt%) dried at 100°C for 24 hours until little or no chloroform remained in the films.



Scheme 4.6.1.1 Typical Chain Extension/Curing of Epoxy Resins with Amines

Table 4.6.1.1 Molecular Weight and Thermal Characterization of Amine Terminated Oligomers



m-PDA/BPADA

Target M_n (K)	Titration M_n (K)* (avg.)	M_n (K)** (avg.)	M.W.D.	T_g (°C)***
5.0	5.99	8.3	1.6	199
15.0	14.21	16.6	1.8	215

* HBr/AcOH, ±1.0%
(multiple runs)
** via GPC, mobile phase NMP + 0.02MP_2O_5, 60°C

*** 2nd heating; heating rate of 20°C/min

Differential scanning calorimetry of a film dried at 100°C showed an initial T_g of 133°C, followed by a cure exotherm of 149°C. A second T_g for this system appeared at 189°C, followed by a second cure exotherm at 217°C (Figure 4.6.1.1). The T_g of the final cured blend was 191°C. A dynamic DSC scan was made after "curing" at 150°C for two hours in a convection oven. The system remained soluble with no molecular weight increase, and the cure exotherm occurred at 170°C in the DSC, which is well above the desired cure temperature of 150°C.

The molecular mobility in the system was increased by lowering the molecular weight of the oligomer to 5,000g/mole (Table 4.6.1.1). Moreover, the difunctional epoxy, Epon 828, was replaced with the normally tetrafunctional epoxy, MY721. An epoxy with a greater functionality may increase the likelihood of chain extension and/or crosslinking.

Following the procedure above, a five thousand gram per mol molecular weight BPADA/*m*-PDA polyimide was blended with 7.5% MY721 (1:1). Then the blend was solution cast from chloroform and was dried at 100°C under vacuum for ~24 hours before curing at 150°C for 2 hours. At the end of 2 hours curing time there were no detectable differences in the film by DSC, IR, GPC or in solubility, signifying that no reaction had occurred. This same system was taken to 210°C and periodically monitored by solubility in chloroform and GPC. Figure 4.6.1.2 shows the GPC results of this system as a function of time. Even after 15 minutes of reaction, a detectable increase in molecular weight was observed, which suggested that the crosslinking reaction occurs at this higher temperature.

4.6.2 Curing Studies of Amine, Phenol and Acetylene Containing Polymers-Cast from NMP

The previous section details the curing behavior of amine terminated polyimide oligomers cast from chloroform. In summary, the crosslinking reaction was not detected at 150°C by a number of analytical techniques. This section records the investigation of reactive oligomers cast from NMP. The higher boiling point solvent, NMP, was chosen to increase molecular mobility at the reaction temperature of 150°C. Figure 4.6.2.1

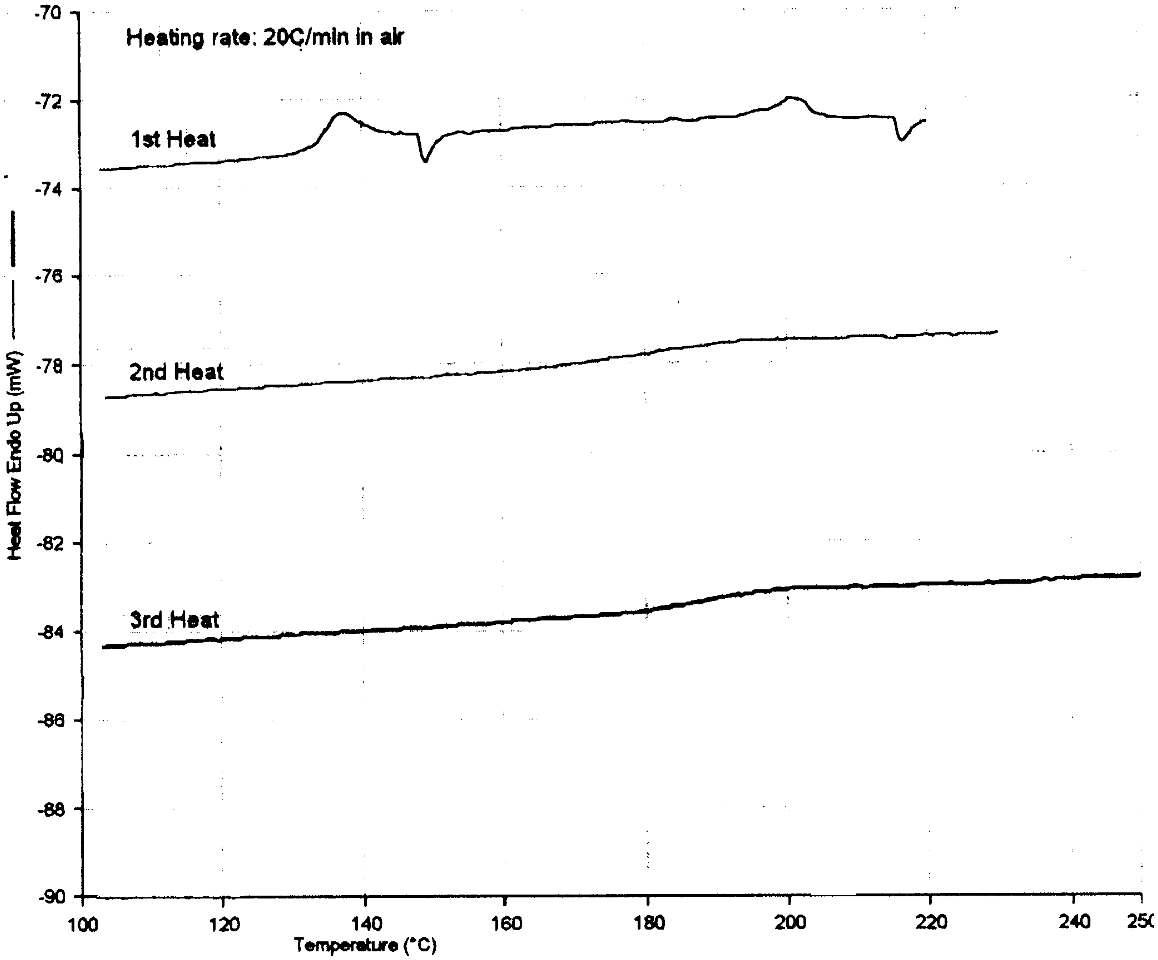


Figure 4.6.1.1 DSC Thermogram of 15kg/mole Amine Terminated Polyimide with Epon 828

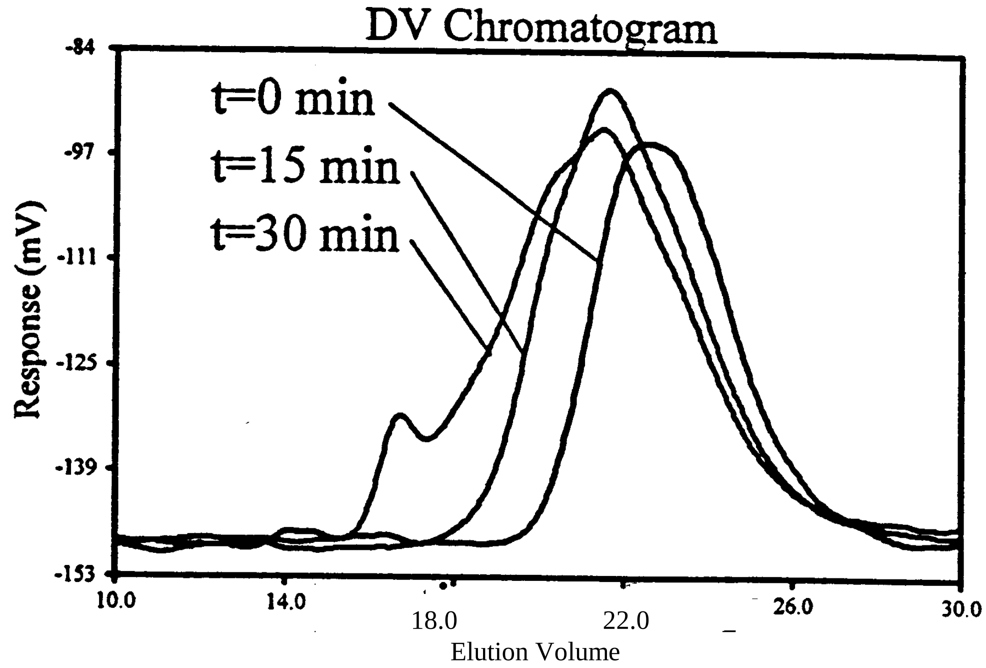
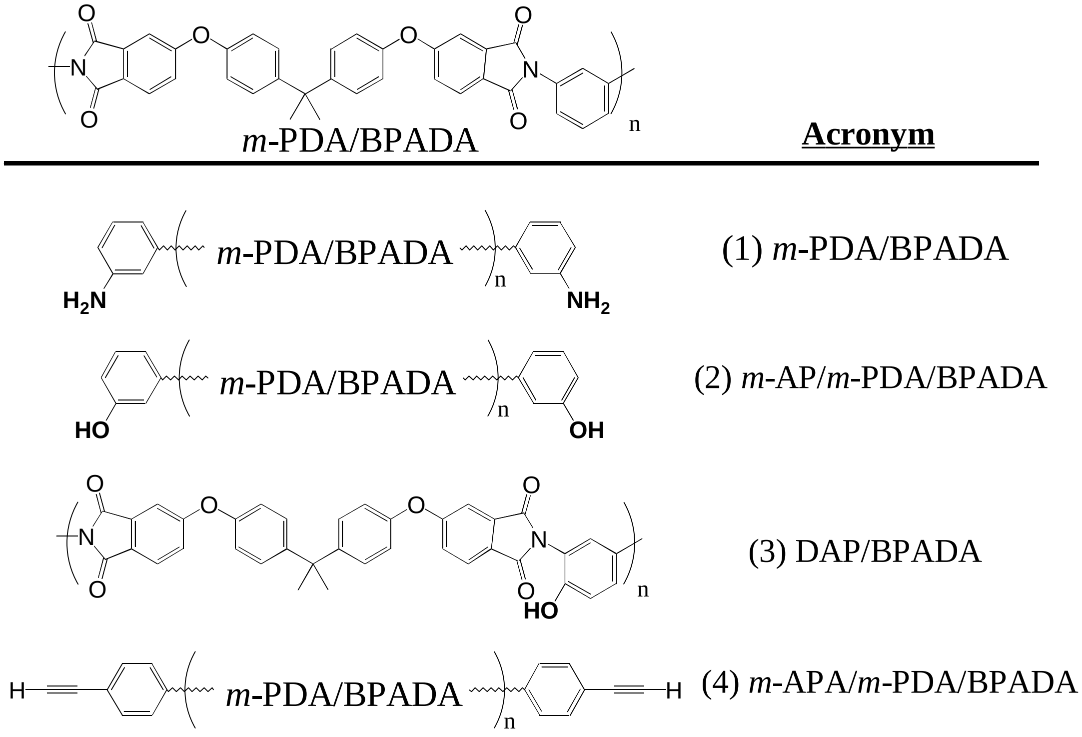


Figure 4.6.1.2 Elution Volume as a Function of Cure Time at 210°C (mobile phase was NMP + 0.02MP_2O_5, 60°C)

Figure 4.6.2.1 Chemical Structures of the Four Reactive Polymers Investigated



depicts the chemical structure of the four polymers investigated. Each of these polymers were synthesized via the ester-acid route except BPADA/DAP, which was synthesized by high temperature solution imidization methods. Molecular weight and thermal characterization, as well as titration values, are shown in Table 4.6.2.1.

Three of the four polymers were blended with epoxy (MY721), f=4. These were: BPADA/*m*-PDA (7.3wt% epoxy), BPADA/*m*-PDA/*m*-AP (4.5wt% epoxy) and BPADA/DAP (1.2wt% epoxy) (Table 4.6.2.2). A catalyst, triphenylphosphine, was also added to the two polymers which contained pendant phenol moieties. Triphenylphosphine catalyzes epoxy/phenol reactions by nucleophilic addition to the epoxidized ring, followed by proton transfer and S_N2 displacement by the phenoxide anion. The acetylene terminated oligomer was cured without epoxy or catalyst. The four polymer systems were solution cast from NMP (15wt%) and dried at 100°C under vacuum for 12 hours and were estimated to contain ~5-15wt% residual NMP.

The curing reaction of these systems at 150°C was monitored as a function of time by GPC. For the amine and acetylene terminated oligomers, no molecular weight increase was observed within a 2 hour time period. However, for the catalyzed phenol terminated oligomer, as well as for the catalyzed high molecular weight polyimide with phenolic sites in the repeat unit, molecular weight increase was found by GPC. Figures 4.6.2.2 and 4.6.2.3 show the GPC traces of these two thermosetting systems as a function of time. The phenol terminated oligomer undergoes a chain extension reaction after 120 minutes (Figure 4.6.2.2). The polymer with the phenol moieties in the repeat unit reacts within 15 minutes, beyond which time it becomes insoluble (Figure 4.6.2.3).

Clarification is needed regarding the factors leading to the observed crosslinking reaction which takes place 100°C below the T_g of these materials. It is thought that the presence of both a higher boiling point solvent and the epoxy resin facilitates sufficient molecular mobility in the system to allow a chemical reaction to occur. The nature of this crosslinking mechanism can be optimized and controlled by a number of variables such as the concentration of the phenolic moiety, catalyst and epoxy, as well as residual NMP content. The effects of crosslinking on the permselectivity of these films is suggested for future study.

Table 4.6.2.1 Molecular Weight and Thermal Characterization of Functional Polyimides

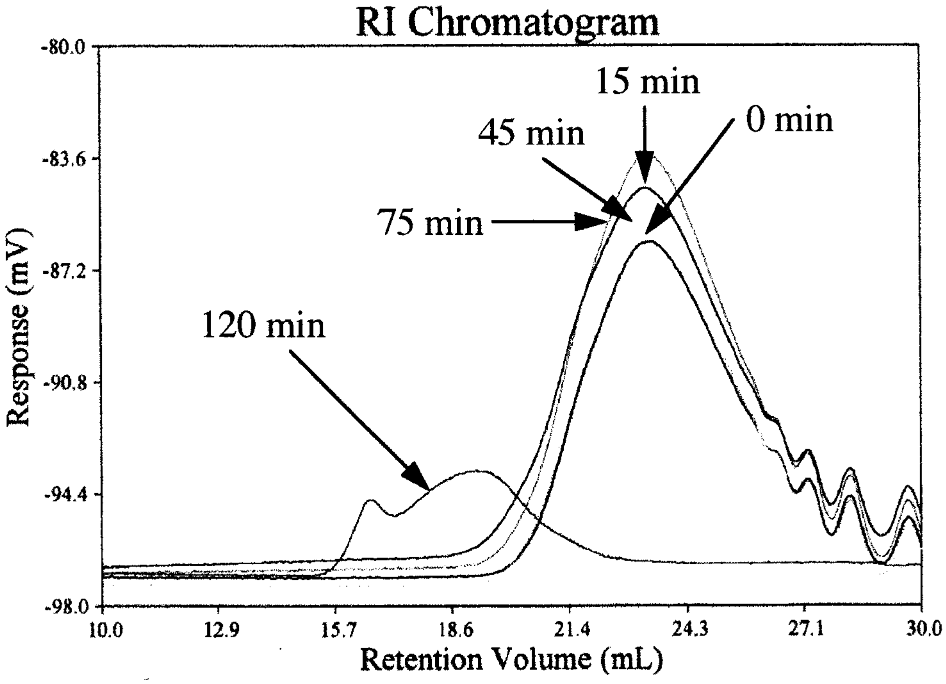
Polyimide	**Target M_n (K)**	**Titration M_n (K)* (avg.)**	**M_n (K)** (avg.)**	**M.W.D.**	**T_g (°C)*** **
***m*-PDA/BPADA**	5.0	5.99	8.3	1.6	199
***m*-AP/*m*-PDA/BPADA**	5.0	6.0^{∇}	6.7	---	---
DAP/BPADA	1:1	---	37.2	2.2	247
***m*-APA/*m*-PDA/BPADA**	5.0	$5.1^{\nabla\nabla}$	4.9	1.5	191

* HBr/AcOH, ±1.0% (multiple runs)
** via GPC, mobile phase was NMP + 0.02MP$_2$O$_5$, 60°C
*** 2nd heating; heating rate of 20°C/min
∇ via ^{13}C NMR
∇∇ via ^{1}H NMR

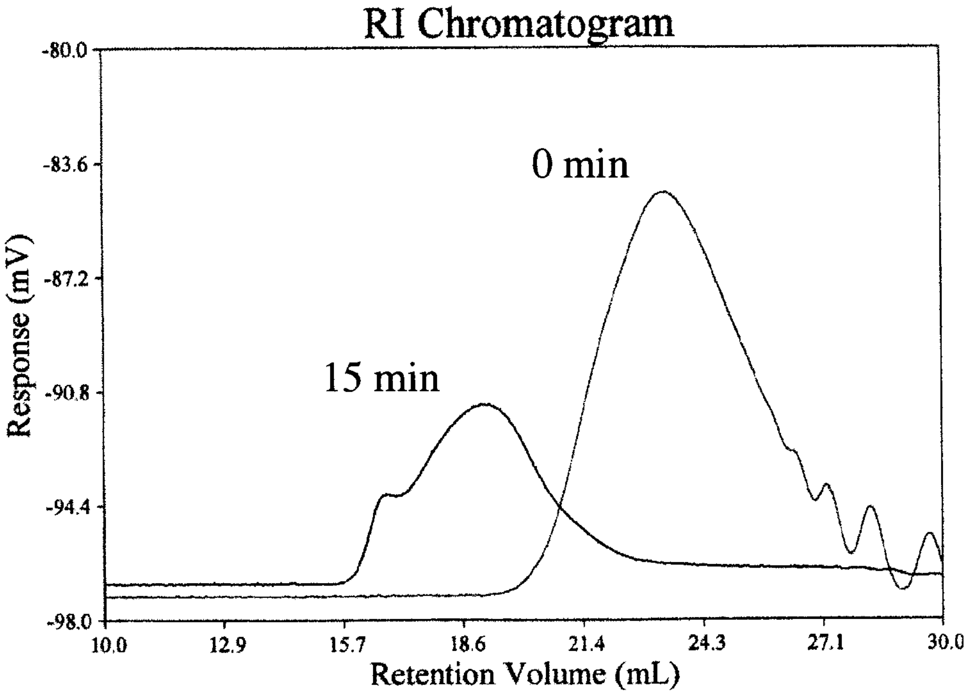
Table 4.6.2.2 Cure System Compositions

Polyimide	**Epoxy Conc.(wt%)** (MY721)	**Catalyst Conc.(wt%)*** **(TPP**)**
***m*-PDA(offset)/BPADA (amine term.), ~5K**	7.3 (N-H/epoxy ring) (1:1)	---
***m*-AP/*m*-PDA/BPADA (phenol term.), ~5K**	4.5 (O-H/epoxy ring) (1:1)	0.5
DAP/BPADA (1/1), ~37K	1.2 (O-H/epoxy ring) (~300:1)	0.8
***m*-APA/*m*-PDA/BPADA (acetylene term.), ~5K**	**---**	---

* based on epoxy wt%
** triphenylphosphine



Figures 4.6.2.2 GPC Chromatograms of 5kg/mole Phenol Terminated Polyimide Cured at 150°C with MY721 (mobile phase was NMP + $0.02MP_2O_5$, 60°C)



* insoluble after 15 min

Figures 4.6.2.3 GPC Chromatograms of 37kg/mole BPADA/DAP Cured at 150°C with MY721 (mobile phase was NMP + 0.02MP_2O_5, 60°C)