

## Synthesis and Characterization of Novel Aromatic Polyimides from Bis(3-aminophenyl)3,5-bis(trifluoromethyl)phenyl Phosphine Oxide

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**Abstract** : A novel diamine monomer, containing fluorine and phosphine oxide, bis(3-aminophenyl) 3,5-bis(trifluoromethyl)phenyl phosphine oxide (mDA6FPPO), was prepared via Grignard reaction, and utilized to prepare polyimides with dianhydrides such as PMDA, 6FDA, BTDA or ODPA, by the conventional two-step route; preparation of poly(amic acid), followed by solution imidization. The polyimides were characterized by FT-IR, NMR, and DSC with intrinsic viscosity and refractive index also being evaluated. A phosphine oxide containing monomer, bis(3-aminophenyl)phenyl phosphine oxide (mDAPPO) and a commercial 3,3-diaminodiphenyl sulfone (mDDS) were also used for comparison. The polyimides derived from mDA6FPPO exhibited high  $T_g$ , excellent solubility and low birefringence.

### Introduction

Polyimides have been utilized in high performance composites and electronic packaging applications for the past decades due to their excellent dielectric, adhesive and mechanical properties, thermal and chemical resistance, and dimensional stability.<sup>1</sup> Among these, the low dielectric constant is one of the decisive factors in minimizing electrical power loss and delay of signal transmission in thin film insulators,<sup>2</sup> thus allowing smaller and lighter electronic devices. Therefore, there has been an extensive investigation in fluorination<sup>3-5</sup> and nano-foam technology<sup>6,7</sup> and more recently, the utilization of organic-inorganic hybrid nano-composites and poly(silsesquioxane).<sup>8</sup>

Since the fluorination of polyimide was attempted in 1972,<sup>9</sup> fluorine containing diamines and dianhydrides have been introduced to prepare fluorinated polyimides with properties of low water up-take, low refractive index and low dielectric constant<sup>3</sup> and also excellent solubility even in chloroform, toluene or tetrachloroethane (TCE), despite full imidization.<sup>10</sup> However, fluorinated polyimides

also have drawbacks such as poor adhesion, low mechanical strength and high coefficient of thermal expansion (CTE).<sup>3</sup>

Since the adhesive property of polyimides is critical factor in microelectronic applications, especially for fluorinated polyimides,<sup>3</sup> adhesion promoters such as silane coupling agents were utilized to improve adhesion, which has an adverse effect on the performance of devices and increases processing cost.<sup>11</sup> On the other hand, phosphine oxide containing polyimides and polysulfones are proven to have excellent adhesive properties<sup>12</sup> with the added benefits of excellent thermal stability<sup>13</sup> and miscibility owing to strong hydrogen bonding.<sup>14</sup> It was also reported that triphenyl phosphine oxide moieties in the polyimide have non-coplanar structure, possibly providing low birefringence.<sup>12</sup>

Therefore, in this study, a novel diamine monomer containing phosphine oxide and fluorine, bis(3-aminophenyl) 3,5-bis(trifluoromethyl)phenyl phosphine oxide (mDA6FPPO), was prepared via Grignard reaction and utilized to synthesize polyimides with low dielectric constant as well as good adhesive properties, solubility and mechanical properties. Polyimides were synthesized by the conventional two-step method and were subjected

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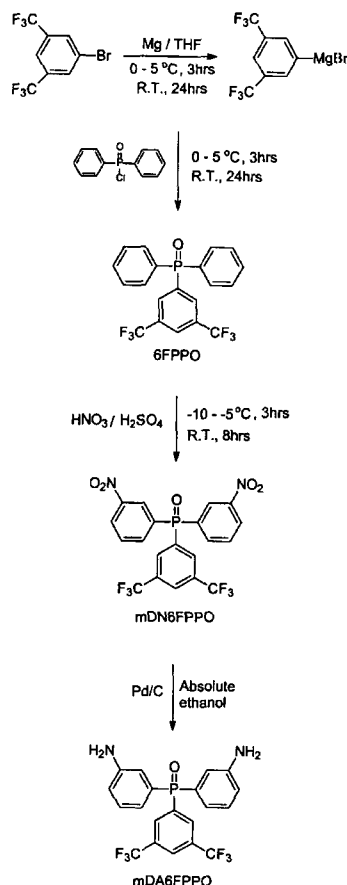
to thermal and optical property measurements, and compared to polyimides prepared from bis(3-aminophenyl) phenyl phosphine oxide (mDAPPO), or a commercial monomer, 3,3-diaminodiphenyl sulfone (mDDS).

## Experimental

**Materials.** Diphenylphosphinic chloride (98%), 3,5-bis(trifluoromethyl)bromobenzene (99%), triphenylphosphine oxide (98%), Mg turning, sulfuric acid and nitric acid were obtained from Aldrich and used as received. Phthalic anhydride (99%), purchased from Aldrich was vacuum sublimed twice prior to use. N-methylpyrrolidinone (NMP) and 1,2-dichlorobenzene (*o*-DCB) obtained from Fisher, were stirred over P<sub>2</sub>O<sub>5</sub> (phosphorus pentoxide) overnight, and then vacuum distilled. N,N-dimethylacetamide (DMAc), toluene, absolute ethyl alcohol and chloroform from Fisher and tetrachloroethane (TCE) from Yakuri (Japan) were used as received. Tetrahydrofuran (THF, Aldrich) was purified by distillation after stirring over calcium hydride.

Bis(3-nitrophenyl) 3,5-bis(trifluoromethyl)phenyl phosphine oxide (mDN6FPPO), containing fluorine and phosphine oxide moiety was synthesized and utilized to prepare polyimides. A monomer containing only phosphine oxide, bis(3-aminophenyl)phenyl phosphine oxide (mDAPPO), was also synthesized as reported in the literature<sup>15</sup> for comparison. A commercial monomer, 3-aminophenyl sulfone (mDDS) from Aldrich was purified by recrystallization in deoxidized ethanol. All anhydrides such as pyromellitic dianhydride (PMDA), 3,3,4,4-benzophenone tetracarboxylic dianhydride (BTDA), 5,5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-bis-1,3-isobenzofuranedione (6FDA) and 4,4-oxydiphthalic dianhydride (ODPA) were obtained from Chriskev and used as received. Cu foils (0.035 mm in thickness, bare and Cr/silane coated) were provided by Ijin (Korea).

**Synthesis of 3,5-Bis(trifluoromethyl)phenyl diphenyl Phosphine Oxide (6FPPO).** 3,5-Bis(trifluoromethyl)phenyl diphenyl phosphine oxide (6FPPO) was synthesized via the Grignard reaction (Scheme 1). 4.23 g (0.1746 mol) of Mg turning (99%) and 120 mL of THF were charged into



**Scheme 1.** Synthesis of bis(3-aminophenyl) 3,5-bis(trifluoromethyl)phenyl phosphine oxide (mDA6FPPO).

a flame dried 3-neck round bottom flask, equipped with magnetic stirrer, addition funnel, condenser, drying tube, thermometer and nitrogen inlet. The solution was first cooled to below 5°C in an ice bath, then 23.5 mL (0.1346 mol) of 3,5-bis(trifluoromethyl)bromobenzene (99%) was added dropwise over a period of 3-4 hrs under N<sub>2</sub> flow, while stirring vigorously. The mixture was allowed to react overnight, while the ice in the bath slowly melted and the temperature of the reaction mixture reached room temperature. Then, ice was again added to the bath to afford 5°C or lower, and 23.5 mL (0.1207 mol) of diphenylphosphinic chloride (98%) was added dropwise over 3-4 hrs. After reacting for another 24 hrs without adding more ice in the bath, a brown solution resulted.

Aqueous sulfuric acid (10%) was added to the

solution to obtain a pH of 1, followed by the addition of water and diethyl ether to form an aqueous layer and an organic layer. After decanting the organic layer, the aqueous layer was washed twice with diethyl ether and all organic parts were collected and dried by evaporation, resulting in light brown solid 6FPPO. This was dissolved in chloroform and washed with 10% sodium bicarbonate and with water. The organic part was condensed by a rotary evaporator, followed by precipitation into 2 L of boiling hexane. After hot filtration, the solution was condensed by a rotary evaporator, and stored at room temperature overnight and in a freezer overnight. The fibrous off-white crystal was collected by vacuum filtration then further purified by recrystallization in hexane.

**Nitration and Reduction of 6FPPO.** 6FPPO was subjected to nitration using sulfuric acid and nitric acid to afford bis(3-nitrophenyl) 3,5-bis(trifluoromethyl)phenyl diphenyl phosphine oxide (mDN6FPPO) (Scheme I). 30 g (0.0724 mol) of 6FPPO was added into 1 L three-neck flask and 300 mL of concentrated sulfuric acid was charged to make approximately 10 wt% solid concentration. After dissolving 6FPPO at room temperature, the solution was cooled to  $-5^{\circ}\text{C}$  with an ice/salt-water bath. Fuming nitric acid (14 mL) in sulfuric acid (43 mL) was added dropwise to the solution over a period of three hrs, while stirring vigorously and maintaining  $-5^{\circ}\text{C}$ . The mixture was allowed to react for 8 hrs without adding more ice, then poured into 2 kg of ice and yellowish oil was extracted with chloroform, followed by washing with sodium bicarbonate aqueous solution until pH reached 7. The solvent was removed by a rotary evaporator and the remaining solid was crystallized twice in absolute ethanol, resulting in pale yellow crystals, mDN6FPPO.

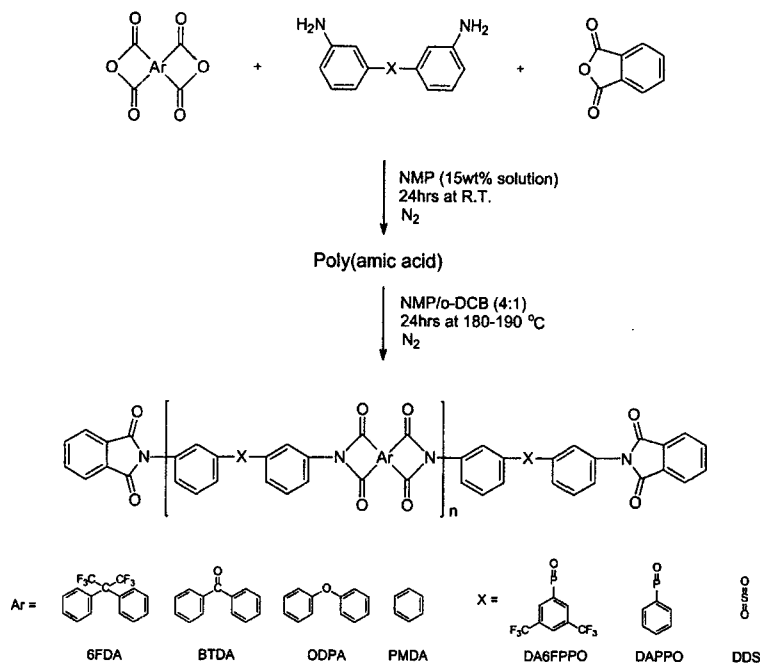
25 g (0.0496 mol) of mDN6FPPO, 200 mL of absolute ethanol, and 200 mg of Pd/C catalyst were charged into the flame-dried pressure reactor. The hydrogenation was carried out at  $50^{\circ}\text{C}$  under the hydrogen pressure of 0.69 MPa (100 psi) for 24 hrs at 200 rpm in a high pressure reactor (Parr Instrument Co., U.S.A.) as shown in Scheme I. Quantitative hydrogenation was confirmed by thin layer chromatography. After filtering off the catalyst over celite, the solution was dried by

evaporation, leaving yellow crystals. mDA6FPPO crystals obtained were recrystallized in water/ethanol (90:10) mixture and further purified by sublimation to obtain white crystals of mDA6FPPO.

**Characterization of Monomers.** 6FPPO, mDN6FPPO and mDA6FPPO were characterized by FT-IR, NMR, EA, titrator, and melting point measurements. FT-IR spectra were recorded with KBr pellets and Perkin Elmer IR 2000 spectrometer, while  $^1\text{H-NMR}$ ,  $^{31}\text{P-NMR}$  and  $^{19}\text{F-NMR}$  spectra were obtained using 300 MHz FT-NMR (JEOL JNM-LA 300 WB). Chemical shifts were given in parts per million with tetramethylsilane as the internal reference for  $^1\text{H-NMR}$ ,  $\text{H}_2\text{PO}_3$  for  $^{31}\text{P-NMR}$  and  $\text{CFCl}_3$  for  $^{19}\text{F-NMR}$ , respectively.  $\text{CDCl}_3$  or deuterated DMSO was used as a solvent. Elemental analysis was carried out with EA-1108 (Carlo Erba Instrument, Italy), while the titration was performed with an Auto-titrator 670 (Metrohm). Melting temperature of monomers was determined with a digital melting point apparatus (Model 1A9100, Fisher).

**Synthesis and Characterization of Polyimides.** All polyimides were prepared from two step route; synthesizing poly(amic acid) precursor, followed by solution imidization (Scheme II). The number average molecular weight was controlled to 20,000 g/mol by adding mono-functional phthalic anhydride (PA). The poly(amic acid) was synthesized by dissolving diamine monomer in NMP, followed by adding PA and dianhydride. The mixture was reacted for 24 hrs at room temperature at 15 wt% solid concentration. The solution imidization was carried out with an azeotropic agent o-DCB (20 v/v%) at  $180\text{--}190^{\circ}\text{C}$  for 24 hrs under nitrogen flow. The reaction mixture was then cooled to room temperature and isolated into water/methanol mixture, followed by filtration and drying.

The polyimides were analyzed by FT-IR (IR 2000, Perkin Elmer) and FT-NMR (300 MHz, JEOL), and further characterized via thermal analysis, intrinsic viscosity measurement and optical property measurements. The solubility was determined by dissolving the polyimide film in a solvent at a concentration of 10 wt% at room temperature for 24 hrs. Intrinsic viscosities were measured with Canon Ubbelohde viscometer in NMP at  $25^{\circ}\text{C}$ .



**Scheme II.** Synthesis of polyimides via two step route.

The thermal properties such as  $T_g$  and thermal stability were measured via differential scanning calorimetry (DSC, TA-2910) and thermogravimetric analyzer (TGA, TA-2980) in air or nitrogen at a heating rate of  $10^\circ\text{C}/\text{min}$ , respectively. The refractive indices of polyimides were measured using thin films on silicon wafer by Metricon Prism Coupler (Model 2010) with  $1.55\ \mu\text{m}$  laser diode. The thin film was prepared by spin coating polyimide solution in TCE. The in-plane ( $n_{TE}$ ) and out of plane ( $n_{TM}$ ) refractive indices of polyimides were measured and the birefringence ( $n_{TE} - n_{TM} = \Delta n$ ) was calculated.

## Results and Discussion

**Synthesis and Characterization of mDA6FPPO.** mDA6FPPO was prepared by nitrating 6FPPO to mDN6FPPO, followed by hydrogenation. After purification at each step, the yield was 85% for 6FPPO, 95% for mDN6FPPO and 90% for mDA6FPPO, resulting in an overall yield of 72.7%, compared to the overall yield of 30% for mDAPPO.<sup>16</sup> The monomers were either white crystals (6FPPO, mDA6FPPO), or pale yellow crystal

(mDN6FPPO), and exhibited a very narrow melting point range:  $94.2\text{--}95.1^\circ\text{C}$  (6FPPO);  $174.5\text{--}175.0^\circ\text{C}$  (mDN6FPPO) and  $225.5\text{--}226.5^\circ\text{C}$  (mDA6FPPO), indicating high purity.

The chemical structures of 6FPPO, mDN6FPPO and mDA6FPPO were identified by FT-IR,  $^1\text{H-NMR}$ ,  $^{31}\text{P-NMR}$  and  $^{19}\text{F-NMR}$ , while mDA6FPPO was further characterized by elemental analyzer and titrator. In the IR spectrum of 6FPPO, P=O stretching absorption appeared at  $1187\ \text{cm}^{-1}$ , while C-F multiple stretch bending absorptions from trifluoromethyl groups were observed between  $1300$  and  $1100\ \text{cm}^{-1}$  (Figure 1). mDN6FPPO exhibited the nitro absorption peaks at  $1534\ \text{cm}^{-1}$  and at  $1350\ \text{cm}^{-1}$  from  $\text{NO}_2$  asymmetric and symmetric stretch, respectively, which were not observed from 6FPPO. However, mDA6FPPO showed typical N-H stretching absorptions at  $3423$  and  $3347\ \text{cm}^{-1}$ , N-H bending at  $1598\ \text{cm}^{-1}$  and N-H out-of plane bending at  $778\ \text{cm}^{-1}$  due to the amine groups.

In the  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-}d_6$ ) spectrum of 6FPPO, protons in 3,5-bis(trifluoromethyl)phenyl moiety appeared at 8.44 ppm (triplet, 1H) and 8.20 ppm (quartet, 2H), while protons in

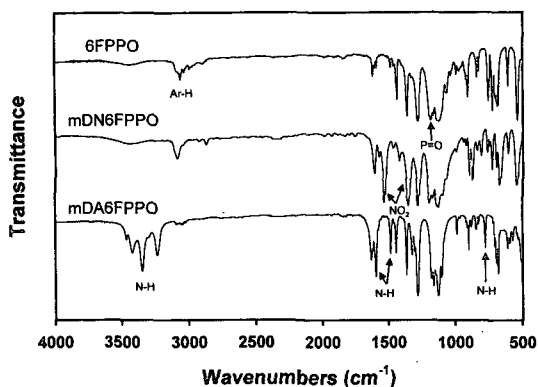


Figure 1. FT-IR spectra of mDA6FPPO.

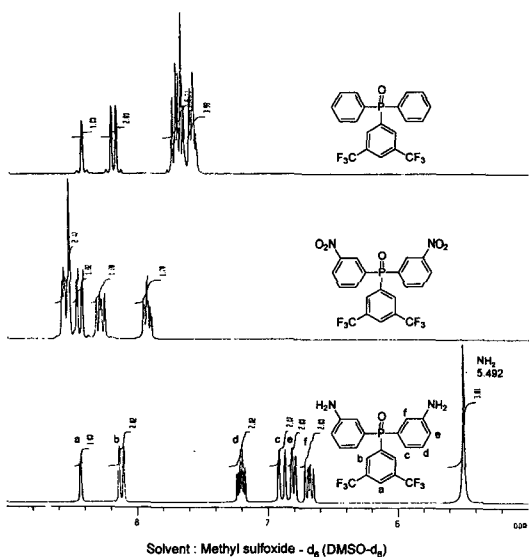


Figure 2. <sup>1</sup>H-NMR spectra of mDA6FPPO.

diphenyl moiety appeared at 7.68 ppm (multiplet, 6H) and 7.59 ppm (multiplet, 4H) (Figure 2). By nitrating 6FPPO, four groups of peaks were observed from mDN6FPPO: 8.53-8.57 ppm (multiplet, 5H); 8.44 ppm (doublet, 2H); 8.28 ppm (quartet, 2H) and 7.92 ppm (multiplet, 2H). The hydrogen peaks from the nitro phenyl moieties were shifted down-field, compared with those of 6FPPO, due to the deshielding effect of electron-withdrawing nitro groups.

The electron-donating effect of amino groups in mDA6FPPO was demonstrated by the seven groups of peaks; 8.42 ppm (singlet, 1H) and 8.12 ppm (doublet, 2H) for protons in 3,5-bis(trifluoromethyl)

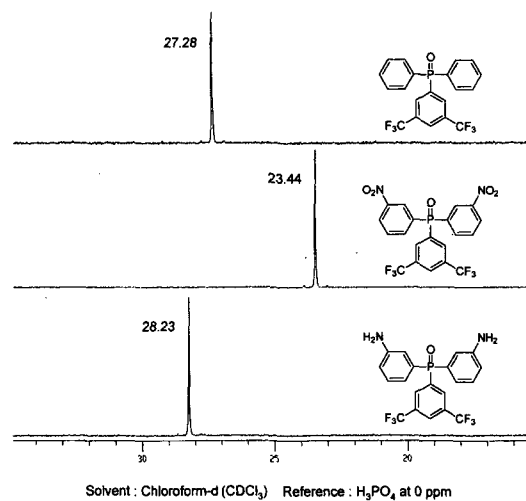
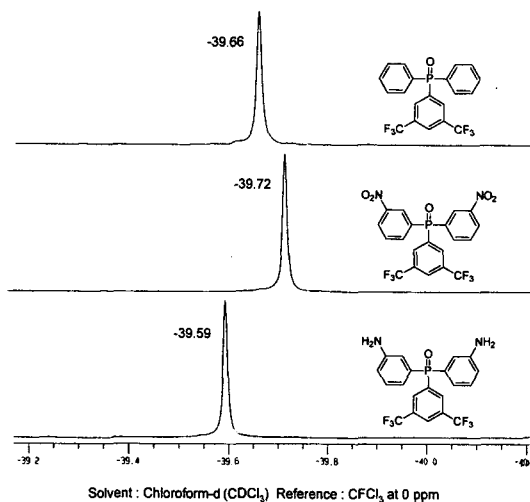


Figure 3. <sup>31</sup>P-NMR spectra of mDA6FPPO.

phenyl pendant group, 7.20 ppm (multiplet, 2H), 6.89 ppm (doublet, 2H), 6.80 ppm (doublet, 2H) and 6.67 ppm (quartet, 2H) for hydrogens in amino phenyl moieties, and 5.49 ppm (singlet, 4H) for hydrogens in amino groups (Figure 2). The hydrogen peaks of amino phenyl moieties were shifted up-field, compared to those of 6FPPO and mDN6FPPO, indicating the shielding effect of the electron donating amino group. But the shifts of hydrogen peaks from 3,5-bis(trifluoromethyl) phenyl pendant group were again negligible due to the distance from the electron donating amino functions.

<sup>31</sup>P-NMR (300.4 MHz, CDCl<sub>3</sub>) analysis provided a sharp single peak at 27.28 ppm for 6FPPO, 23.44 ppm for mDN6FPPO and 28.23 ppm for mDA6FPPO (Figure 3). As noted the peak shifted up-field upon nitration and down-field upon hydrogenation, which is opposite the <sup>1</sup>H-NMR results. In <sup>19</sup>F-NMR (282.65 MHz, CDCl<sub>3</sub>) all the peaks were found in similar positions; -39.66 ppm (6FPPO), -39.72 ppm (mDN6FPPO) and -39.59 ppm (mDA6FPPO), indicating that F was not affected by nitration and hydrogenation, as expected from <sup>1</sup>H-NMR (Figure 4). However, sharp single peaks indicate the high purity of monomers. Further characterization of mDA6FPPO and mDAPPO with elemental analyzer and titrator revealed that experimental results were well matched to the theoretical values, confirming the

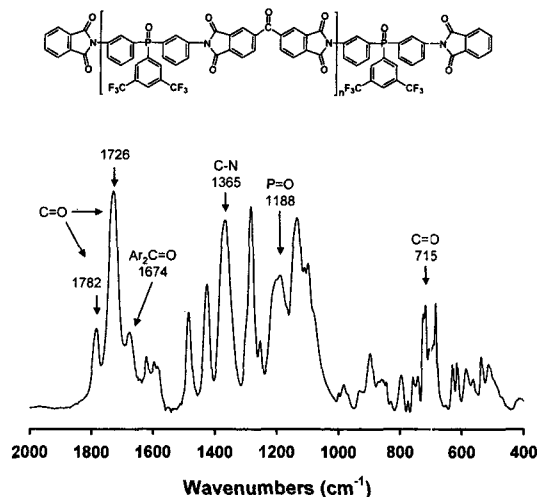


**Figure 4.**  $^{19}\text{F}$ -NMR spectra of mDA6FPPO.

successful synthesis of high purity monomers (Table I).

#### Synthesis and Characterization of Polyimides.

**Structure of Polyimides:** Fully imidized polyimides were characterized by FT-IR,  $^1\text{H}$ -NMR,  $^{31}\text{P}$ -NMR and  $^{19}\text{F}$ -NMR. The IR spectra of BTDA-mDA6FPPO-PA polyimide showed imide carbonyl peaks at  $1782\text{ cm}^{-1}$  (C=O asymmetric stretching), at  $1726\text{ cm}^{-1}$  (C=O symmetric stretching) and at  $715\text{ cm}^{-1}$  (C=O banding), with the C-N peak at  $1365\text{ cm}^{-1}$ , but no amide-carbonyl peak at  $1650\text{ cm}^{-1}$ , suggesting complete imidization (Figure 5). As expected, P=O stretching and C-F multiple stretching bands appeared at  $1188\text{ cm}^{-1}$  and  $1300\text{--}1100\text{ cm}^{-1}$ , respectively. The  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum of BTDA-mDA6FPPO-PA polyimide revealed that all hydrogen peaks were in good agreement with the proposed polymer structure (Figure 6). A single peak was also observed at  $23.04\text{ ppm}$  in  $^{31}\text{P}$ -NMR (300.4 MHz,  $\text{CDCl}_3$ ) and at  $-39.55\text{ ppm}$  in  $^{19}\text{F}$ -NMR



**Figure 5.** FT-IR spectra of polyimide with BTDA and mDA6FPPO.

( $282.65\text{ MHz}$ ,  $\text{CDCl}_3$ ), respectively, as expected.

**Solubility and Solution Viscosity of Polyimides:** The solubility of polyimides was greatly enhanced by the incorporation of phosphine oxide moiety and further by trifluoromethyl phenyl group (Table II). mDDS based polyimides showed solubility only in NMP and DMAc, but mDAPPO-based polyimides were soluble in NMP, DMAc, TCE,  $\text{CHCl}_3$ , while some mDA6FPPO-based polyimides exhibited solubility even in THF, toluene and acetone. The excellent solubility of mDA6FPPO-based polyimides could be attributed to the presence of bulky  $\text{CF}_3$  groups, leading to increased free volume, and also to the phosphine oxide segments providing strong intermolecular forces with solvent molecules.<sup>14</sup>

Since most of the polyimides prepared in this investigation showed good solubility in NMP, the intrinsic viscosity was measured in NMP at  $25^\circ\text{C}$ . The intrinsic viscosity of mDA6FPPO-based polyimides ranged from  $0.20$  to  $0.28\text{ dL/g}$ , suggesting

**Table I. Titrated Molecular Weight and Melting Point of Monomers**

	M.W. (g/mol)			m.p. ( $^\circ\text{C}$ )		Color
	Calculated	Measured		MPA <sup>b</sup>	DSC	
		E. A. <sup>a</sup>	Titration			
mDA6FPPO	444.31	444.04	444.50	226.0	229.7	White
mDAPPO	308.31	307.95	309.02	203.0	210.6	White

<sup>a</sup>Elemental Analyzer. <sup>b</sup>Melting Point Apparatus.

a reasonably high molecular weight (Table III). The intrinsic viscosity of mDAPPO-based and mDDS-based polyimides was in the range of 0.20-0.30, and 0.23-0.26 dL/g, respectively, which were similar to 0.20-0.28 dL/g of mDA6FPPO-based

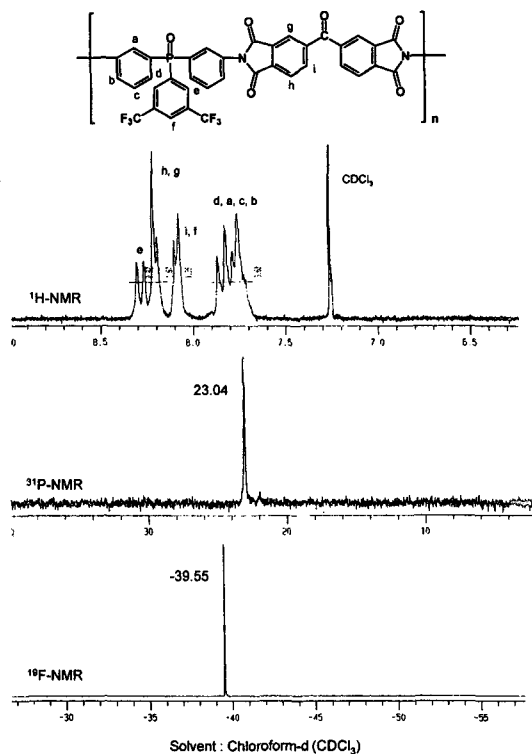


Figure 6. NMR spectra of polyimide with BTDA and mDA6FPPO.

polyimides. Therefore, the target molecular weight of 20,000 g/mole seemed to be attained.

**Thermal Properties of Polyimides:** mDA6FPPO-PMDA polyimide showed a  $T_g$  of 281°C, followed by 247°C (with 6FDA), 243°C (with BTDA) and 228°C (with ODPa) (Figure 7). DMA analysis resulted in a slightly higher  $T_g$  than DSC, but showed a similar trend: mDAPPO-based polyimides showed slightly higher  $T_g$  than mDA6FPPO-based polyimides, exhibiting 271°C (6FDA-mDAPPO), compared to 247°C (6FDA-mDA6FPPO). This could be attributed to more free volume present in mDA6FPPO, due to bulky  $CF_3$  moieties and non-coplanarity of mDA6FPPO compared to mDAPPO. The mDDS-based polyimides showed higher  $T_g$  than mDA6FPPO-based

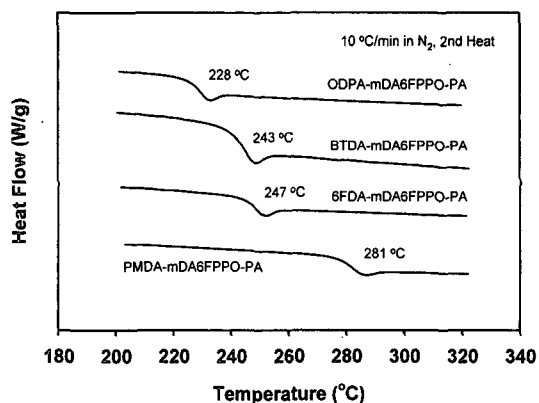


Figure 7. DSC thermograms of mDA6FPPO-based polyimides.

Table II. Solubility of Polyimides

		NMP	DMAc	TCE	CHCl <sub>3</sub>	THF	Toluene	Acetone
mDA6FPPO	6FDA	S	S	S	S	S	I	S
	BTDA	S	S	S	S	P	S	I
	ODPA	S	S	S	S	S	P	I
	PMDA	S	S	S	S	P	I	I
mDAPPO	6FDA	S	S	S	S	S	I	P
	BTDA	S	S	S	S	I	S	I
	ODPA	S	S	S	S	P	I	I
	PMDA	S	S	S	P	I	I	I
mDDS	6FDA	S	S	P	P	I	I	I
	BTDA	S	S	I	I	I	I	I
	ODPA	S	S	I	I	I	I	I
	PMDA	I	I	I	I	I	I	I

\*at R.T. for 24 hrs.

\*S : Soluble, P : Partially soluble, I : Insoluble.

**Table III. Characteristics of Polyimides**

		[ $\eta$ ] <sup>a</sup> (dL/g)	$T_g$ (°C)		$T_d$ (°C) <sup>c</sup>		Residue(wt%) <sup>d</sup>	
			DSC <sup>b</sup>		in Air	in N <sub>2</sub>	in Air	in N <sub>2</sub>
mDA6FPPO	ODPA	0.22	228		533	546	10	55
	BTDA	0.28	243		530	532	5	58
	6FDA	0.24	247		517	521	3	50
	PMDA	0.20	281		522	530	5	53
mDAPPO	ODPA	0.27	251		526	532	13	56
	BTDA	0.30	273		506	510	23	60
	6FDA	0.29	271		524	527	5	60
	PMDA	0.20	331		479	479	50	67
mDDS	ODPA	0.23	250		557	557	0	57
	BTDA	0.26	266		548	551	0	59
	6FDA	0.24	268		532	536	0	59

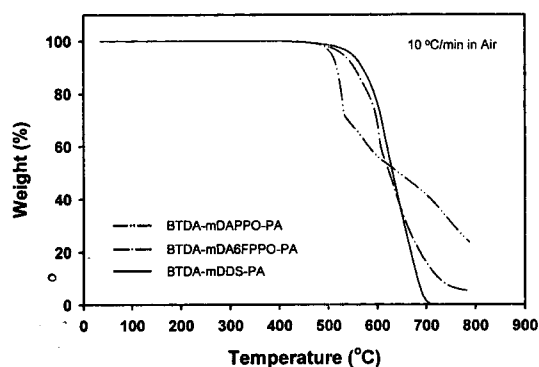
<sup>a</sup>At 25 °C in NMP. <sup>b</sup>second heat at 10 °C/min in N<sub>2</sub>. <sup>c</sup>by TGA, 5 wt% loss. <sup>d</sup>by TGA at 800 °C.

polyimides, possibly due to the bulky CF<sub>3</sub> groups, but similar  $T_g$  to mDAPPO-based polyimides (Table III).

Polyimides with mDA6FPPO showed excellent thermal stability, exhibiting initial decomposition temperature at around 500 °C in air and also in nitrogen (Figure 8), and 5-15% char yield at 800 °C in air and 53-58% in nitrogen. The polyimides with mDAPPO exhibited the highest char yield in air, followed by mDA6FPPO and mDDS-based polyimides. The high char yield could be explained by relatively high phosphine oxide content in mDAPPO, compared to mDA6FPPO and mDDS.

**Optical Properties of Polyimides:** In-plane ( $n_{TE}$ ) refractive index of 1.5351 and out of plane ( $n_{TM}$ ) refractive index of 1.5340 were obtained from 6FDA-mDA6FPPO polyimide, compared to

1.5805 ( $n_{TE}$ ) and 1.5787 ( $n_{TM}$ ) for 6FDA-mDAPPO polyimide, 1.5836 ( $n_{TE}$ ) and 1.5803 ( $n_{TM}$ ) for BTDA-mDA6FPPO, and 1.5835 ( $n_{TE}$ ) and 1.5818 ( $n_{TM}$ ) for ODPA-mDA6FPPO polyimide. Thus, the calculated birefringence was 0.0011 for 6FDA-mDA6FPPO, 0.0017 for 6FDA-mDAPPO, 0.0017 for ODPA-mDA6FPPO and 0.0033 for BTDA-mDA6FPPO polyimides. As expected, 6FDA-mDA6FPPO-based polyimides exhibited lower refractive index and birefringence than other polyimides prepared in this investigation, owing to high fluorine content (26.78%) which is from the pendant 3,5-bis(trifluoromethyl) phenyl moiety. The refractive index and birefringence of 6FDA-mDA6FPPO polyimide could be compared to those of 6FDA-TFDB polyimide in the literature.<sup>17</sup> As noted, 6FDA-TFDB polyimide exhibited a higher refractive index (1.548 vs. 1.5345) and birefringence (0.0066 vs. 0.0011) than 6FDA-mDA6FPPO polyimide, despite the higher fluorine content (31.3% vs. 26.78%). This unusual behavior could be explained by the non-coplanarity of phosphine oxide moiety in mDA6FPPO.<sup>29</sup> Higher fluorine content of 6FDA-mDA6FPPO (26.78%) might be responsible for the lower refractive index, while other polyimides having similar fluorine content exhibited similar refractive indices and birefringence, except BTDA-mDA6FPPO (Table IV). Therefore, it can be said that the effect of CF<sub>3</sub> may be dependent on the structure of the polyimides.



**Figure 8.** TGA thermograms of BTDA-based polyimides.



Table IV. Optical Properties of Polyimides

		F (wt%)	$n_{TE}$	$n_{TM}$	$n_{TE} - n_{TM}$
mDA6FPPO	6FDA	26.78	1.5351	1.5340	0.0011
	BTDA	15.60	1.5836	1.5803	0.0033
	ODPA	15.87	1.5835	1.5818	0.0017
mDAPPO	6FDA	15.15	1.5804	1.5787	0.0017
	BTDA	-	1.6432	1.6418	0.0014
	ODPA	-	1.6432	1.6408	0.0024
	PMDA	-	1.6827	1.6800	0.0027

\*Measured at 1.55 mm with a film of 2.5-3.0 mm thick.

## Conclusions

1. A novel diamine, containing phosphine oxide and fluorine, mDA6FPPO (bis(3-aminophenyl) 3,5-bis(trifluoromethyl)phenyl phosphine oxide), was successfully synthesized via Grignard reaction from diphenylphosphinic chloride and 3,5-bis(trifluoromethyl) bromobenzene, followed by nitration and reduction.

2. Polyimides prepared from mDA6FPPO and dianhydrides such as PMDA, 6FDA, BTDA and ODPA exhibited excellent solubility, high  $T_g$  (228-281 °C) and good thermal stability.

3. Polyimides from mDA6FPPO and 6FDA provided small birefringence (0.0011) due to the bulky 3,5-bis(trifluoromethyl)phenyl pendent groups and non-coplanarity of mDA6FPPO, as well as  $CF_3$  moiety in the 6FDA monomer.

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