

# Synthesis and Properties of Fluorinated Polyamideimides with High Solubility

Sun-Yuan Tsay,<sup>1,2</sup> Meng-Feng Tsai,<sup>1</sup> Bor-Kuan Chen<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, National Cheng Kung University, Tainan, 70101, Taiwan, Republic of China

<sup>2</sup>Department of Polymer Materials, Kun Shan University of Technology, Tainan, 71003, Taiwan, Republic of China

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**ABSTRACT:** A series of fluorinated polyamideimides (PAIs) were synthesized by the direct polycondensation of a novel diimide-diacid, 1,4-bis(trimellitimidido-2-trifluoromethylphenoxy) benzene (BTTFB), with aromatic diamines by using triphenyl phosphite (TPP) and pyridine as condensation agents in a medium consisting of *N*-methyl-2-pyrrolidone (NMP) and CaCl<sub>2</sub>. Most of the resulting polymers showed an amorphous nature. All the fluorinated PAIs were readily soluble in a variety of organic solvents such as NMP, *N,N*-dimethyl acetamide, dimethylformamide, and dimethyl sulfoxide and could even be dissolved in less polar solvents such as THF and *m*-cresol. The PAIs had inherent

viscosities of 0.77–0.93 dL/g, depending on the diamines. All the soluble PAIs afforded transparent, flexible, and tough films that exhibited excellent thermal stability, good mechanical properties, and low moisture absorption. The glass transition temperatures of these PAIs ranged from 244 to 272°C and the 5% weight loss temperatures were >525°C in nitrogen. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 321–327, 2005

**Key words:** fluorinated polymer; polyamide; synthesis polyimides; Yamazaki process

## INTRODUCTION

Polyimides have been used extensively in the aerospace and electronics fields because of their thermal stability and excellent mechanical and electrical properties. Usually, polyimides are difficult to fabricate because of their infusibility and insolubility in most organic solvents.<sup>1</sup> Much attention has been focused on the research of soluble polyimides to expand their applications.<sup>2</sup> One approach is to incorporate fluorine-containing groups into polyimide structure.<sup>3</sup> Because of the unique properties associated with fluorine (e.g., high electronegativity, high C—F bond energy, low intermolecular cohesive energy, and high hydrophobicity), the introduction of fluorine atoms into polyimide was shown to increase processibility and solubility and decrease moisture absorption and the dielectric constant.<sup>4</sup>

Although many properties can be improved by the incorporation of fluorine atoms into polyimides, the improvement in solubility is still limited. In many common solvents, modified polyimides are not readily soluble. To overcome this drawback, the incorporation of amide groups into the polyimide backbone to form polyamideimides<sup>5</sup> has been shown to improve

the solubility and preserve the many outstanding properties of polyimides.

Various synthetic methods for the preparation of polyamideimides have been disclosed in many reports. Among them, the direct polycondensation was the most convenient approach for synthesizing high molecular weight polyamideimides on a laboratory scale. Yamazaki et al. developed direct polycondensation by using triphenyl phosphite as the condensation agent for the synthesis of polyamides.<sup>6</sup>

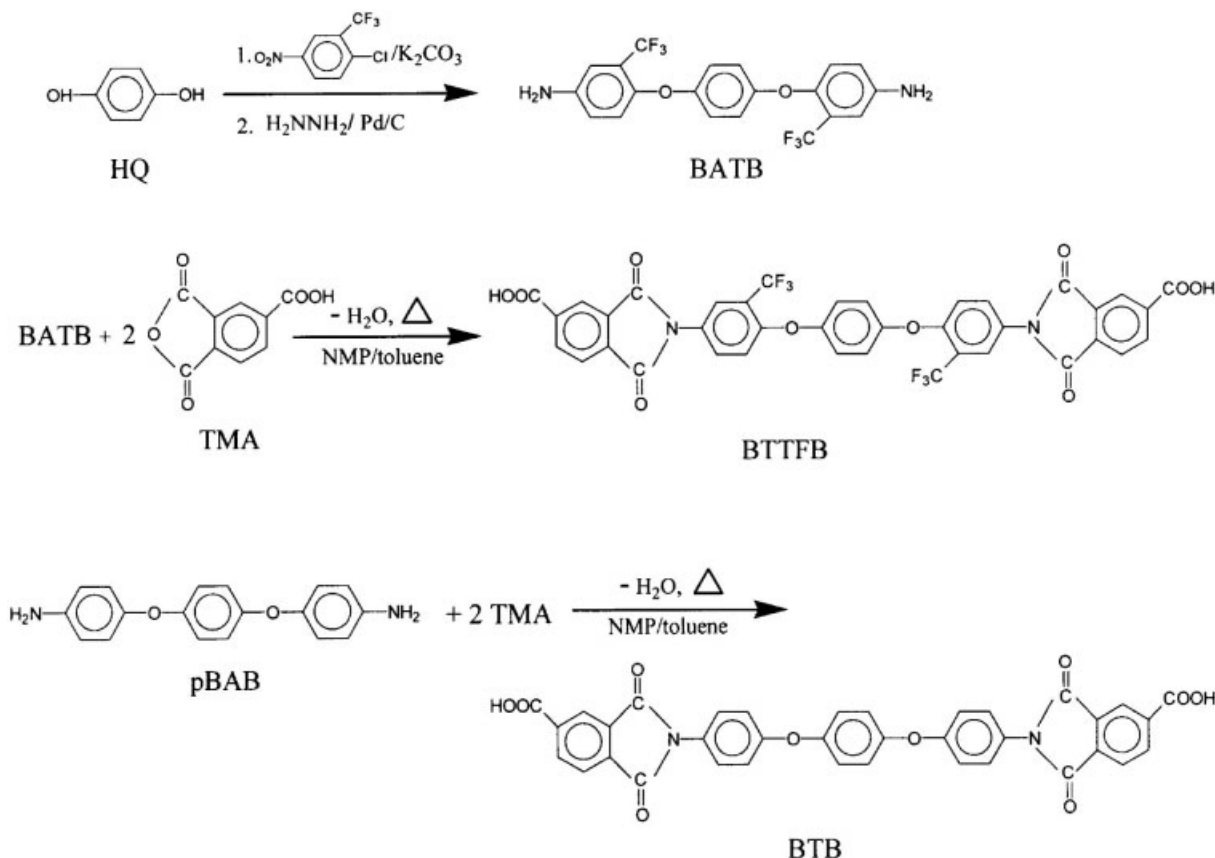
In this study, we synthesized a series of novel polyamideimides with fluorinated diacids and various diamines via the Yamazaki process. The primary aim of this work was to illustrate that the new polyamideimides could possess the high solubility of polyamides as well as the excellent properties of fluorinated polyimides. We also investigated the effect of fluorinated groups on various properties of polymers, which included processibility, inherent viscosity, moisture absorption, and thermal, transparent, and mechanical properties.

## EXPERIMENTAL

### Materials

Chemicals of high purity were obtained from various commercial sources, which consisted of 2-chlorobenzotrifluoride (Acros), 10% palladium on activated carbon (Acros), trimellitic anhydride (TMA; Lancaster), hydrazine monohydrate (Kanto, Japan), calcium chlo-

Correspondence to: S.-Y. Tsay (sytsay@mail.ncku.edu.tw).



Scheme 1 Synthesis of diacids.

ride (Showa, Japan), triphenyl phosphite (TPP; Lancaster), pyridine (Acros), and 4,4'-oxydianiline (ODA; Fluka). Other unfluorinated diamines with ether group, 1,4-bis(4-aminophenoxy)benzene (pBAB) and 1,3-bis(4-aminophenoxy)benzene (mBAB), were synthesized following literature procedures.<sup>7</sup> Solvents including *N*-methyl-2-pyrrolidone (NMP), methanol, tetrahydrofuran (THF), *N,N*-dimethyl acetamide (DMAc), and dimethyl sulfoxide (DMSO) were purchased from Tedia. NMP and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. TPP was purified by vacuum distillation. Calcium chloride was dried under a vacuum at 150°C for 6 h. The other reagents were used as received without any further purification.

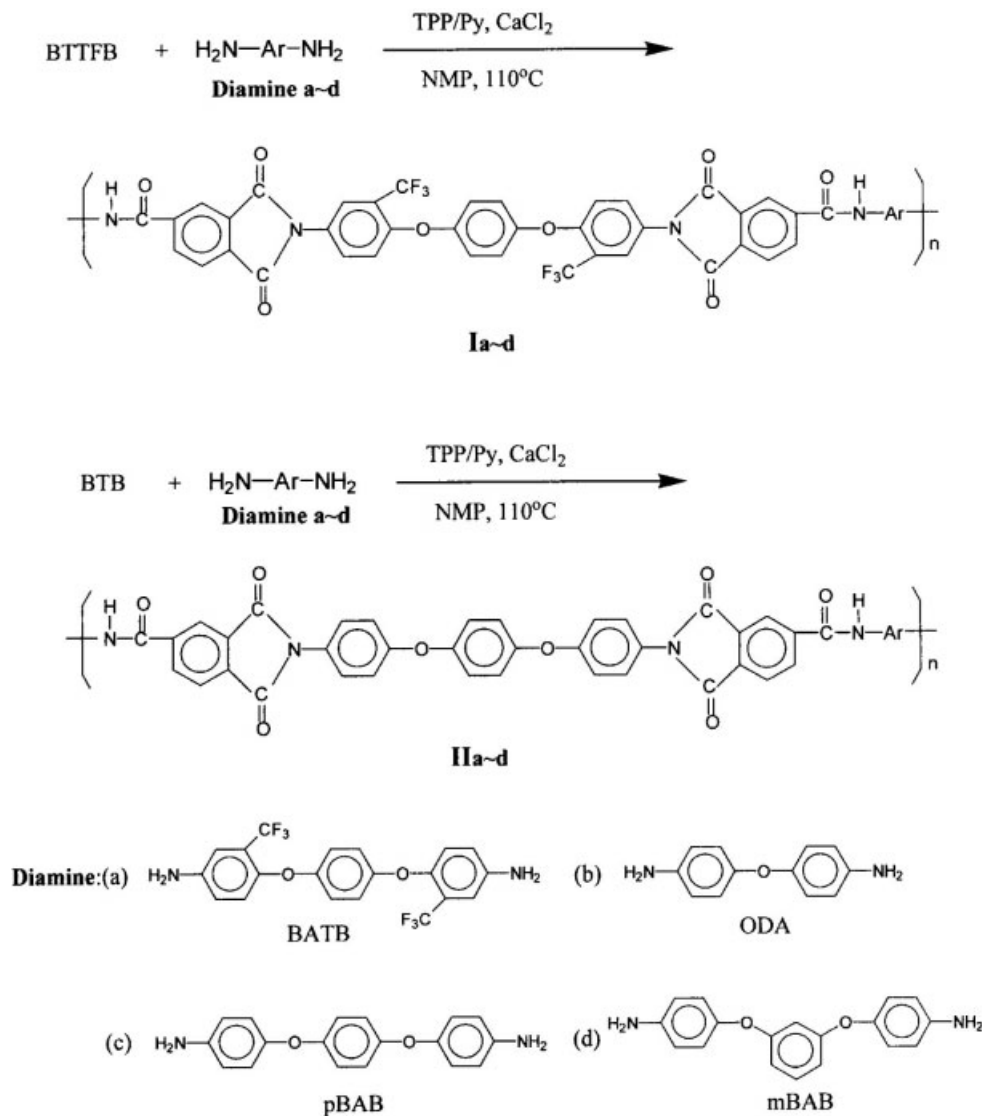
#### Synthesis of 1,4-Bis(4-amino-2-trifluoromethylphenoxy)benzene (BATB)

1,4-Hydroquinone was coupled with 2-chloro-5-nitrobenzotrifluoride (CNB) in the presence of  $K_2CO_3$  in DMAc to yield 1,4-bis(4-nitro-2-trifluoromethylphenoxy)benzene (BNTB) as illustrated in Scheme 1. The dinitro compound BNTB 45 g (0.092 mol), 10% Pd on activated carbon 0.5 g, and 300 mL of ethanol were introduced into a four-necked flask and heated to

reflux at 78°C. Hydrazine monohydrate (100 mL) was added dropwise to this solution over a period of 30 min. After the addition was completed, the reaction mixture was held at reflux for an additional 4 h. The Pd/C catalyst was removed by filtering the hot reaction mixture. Then, the filtrate was heated to recover the ethanol. The crude product was obtained by removing excess hydrazine and ethanol and was washed with water. Further recrystallization from ethanol produced a white crystalline product of 29.5 g. Melting point (m.p.): 134°C. The yield was 75%. IR (KBr): 3449  $cm^{-1}$ , 3477  $cm^{-1}$  (Ar—NH<sub>2</sub>), 1248  $cm^{-1}$  (C—O—C), 1350–1120  $cm^{-1}$  (CF<sub>3</sub>). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 6.945 (2H), 6.889 (4H), 6.753 (2H), 6.746 (2H), 3.707 (4H). These results are comparable with literature data.<sup>8</sup>

#### Synthesis of 1,4-Bis(trimellitimido-2-trifluoromethylphenoxy)benzene (BTTFB)

Fluorinated diimine-diacid BTTFB was synthesized by reacting BATB with TMA as shown in Scheme 1. Diamine compound BATB 31 g (0.0724 mol) was dissolved in 200 mL NMP in a reactor. The solution was cooled with ice and stirred until all of the diamine was dissolved. TMA 27.8 g (0.145 mol) was charged in several portions and stirred at room temperature for



Scheme 2 Polymerization of polyamideimides.

7 h. Toluene (25 mL) was added and the mixture was heated to 180°C at reflux for 6 h until the water was azeotropically distilled off via a Dean–Stark trap. Heating was continued to distill off the residual toluene. After cooling, the bright yellow precipitate was isolated by filtration, washed several times with water and methanol, and dried at 120°C under vacuum overnight to give 55 g of diimide-diacid BTTFB (98% yield).

m.p.: 336°C (by DSC). IR (KBr) 1728  $\text{cm}^{-1}$ , 1778  $\text{cm}^{-1}$  (imide C=O), 3460  $\text{cm}^{-1}$  (—OH).  $^1\text{H-NMR}$  (DMSO- $d_6$ )  $\delta$  8.415 (Hf, 2H), 8.316 (Hd, 2H), 8.085 (He, 2H), 7.950 (Hb, 2H), 7.738 (Hc, 2H), 7.264 (Ha, 6H).

### Polymerization

A typical example of polymerization was executed as follows. A mixture of 13.35 g (0.0172 mol) of diimide-

diacid BTTFB and 70 g NMP (solid content 15%) was stirred under nitrogen gas and heated to 70°C to dissolve BTTFB. Pyridine (2.7 g), 10.7 g TPP, and 1.34 g  $\text{CaCl}_2$  were charged. The mixture was stirred and heated to 110°C. An equal molar amount of diamine (BATB, 0.0172 mol) was then added gradually to this mixture. The resulting mixture was reacted at 110°C for 5 h. More NMP was added during the polymerization to maintain the viscosity of the reaction mixture, which allowed the solution to be stirred. After the completion of polymerization, the viscous mixture was poured into methanol. The precipitated polymer was filtered and washed thoroughly with methanol and water and then dried under a vacuum.

Other polyamideimides (PAIs) in this study (with diamine ODA, pBAB, and mBAB) were prepared by similar procedures (see Scheme 2).

### Preparation of polyamideimide films

PAIs were dissolved in an adequate amount of NMP, and the polymer solutions were spread on a glass plate by using a spin-coater to control the film thickness at 50–90  $\mu\text{m}$ . The film on the glass was dried in an oven by heating to 300°C to remove all solvents. The PAI film was then cooled to room temperature and stripped from the plate.

### Measurements

Fourier transfer infrared (FTIR) spectra were recorded on a Bio-Rad FTS-40A spectrometer.  $^1\text{H-NMR}$  spectra were performed on a Bruker AMX-400 spectrometer with  $\text{DMSO-}d_6$  or  $\text{CDCl}_3$  as solvent. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 thermal analyzer at a heating rate of 20°C/min in  $\text{N}_2$  within the temperature range of 30–800°C. Differential scanning calorimetry (DSC) data were obtained from a Perkin-Elmer DSC-7. Samples of 5–10 mg were sealed in hermetic aluminum pans and scanned in the calorimeter at a heating rate of 20°C/min in the range of 30–400°C under  $\text{N}_2$  atmosphere. The glass-transition temperature ( $T_g$ ) values were taken as the change of the specific heat in the heat flow curves. Wide-angle X-ray diffractograms were obtained at room temperature with film specimens  $\sim 0.2$  mm thick on a Rigaku Geiger Flex D-Max IIIa X-ray diffractometer, using Ni-filtered  $\text{CuK}\alpha$  radiation (40 kV, 15 mA). The inherent viscosities were determined by using an Ubbelohde viscometer (Schott Geräte AVS310) at 30°C. An Instron universal tester model 4467 was used to study the stress-strain behavior of the samples. Qualitative solubility was determined by dissolving 0.05 g of polymer in 5 g of solvent. For the measurement of moisture absorption rates, specimens were exposed to air at room temperature, and the weight difference was calculated after 3 days. UV-vis spectra of the polymer films were recorded on a Perkin-Elmer Lambda 10 spectrophotometer at room temperature.

## RESULTS AND DISCUSSION

### Diamine and diacid syntheses

The synthesis of fluorinated diamine BATB is illustrated in Scheme 1. BATB was readily obtained with a high yield by the catalytic reduction of dinitro compound BNTB with hydrazine hydrate and Pd/C catalyst in refluxing ethanol. The structure of BATB was confirmed by IR and  $^1\text{H-NMR}$  as indicated under Experimental. Absorption bands at 3449 and 3447  $\text{cm}^{-1}$  are the result of asymmetric and symmetric stretching of the  $\text{Ar-NH}_2$ . Absorption at 1248  $\text{cm}^{-1}$  shows C—O—C presence. The signal at 3.707 ppm of

the  $^1\text{H-NMR}$  spectrum of BATB is peculiar to the amino group.

The imide-diacid BTTFB was synthesized (Scheme 1) via a two-stage procedure that included ring-opening addition of diamine BATB to two equivalent amounts of TMA, followed by cyclodehydration of imidodicarboxylic acid by means of toluene–water azeotropic distillation. The FTIR spectrum of BTTFB is depicted in Figure 1(a). It exhibited characteristic imide group absorptions at 1778 and 1728  $\text{cm}^{-1}$  (typical of imide carbonyl asymmetrical and symmetrical stretch). The wide absorption band around 3460  $\text{cm}^{-1}$  corresponded to the stretching vibration of carboxyl—OH. Figure 1(b) shows the  $^1\text{H-NMR}$  spectrum of BTTFB. The characteristic peaks correlate well with the proposed structure.

### Polymerization

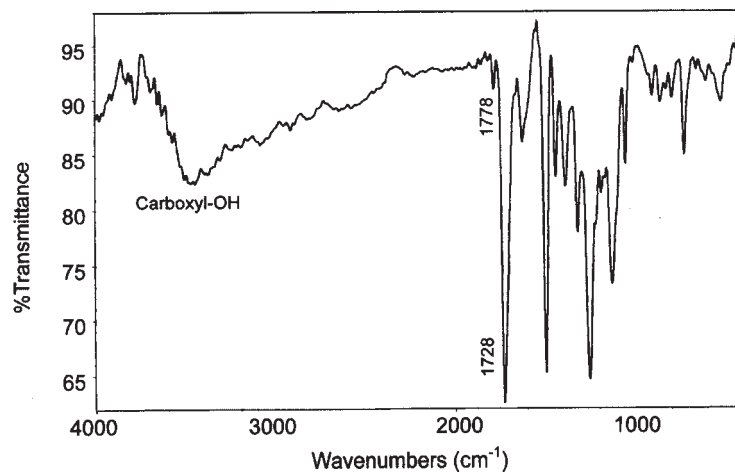
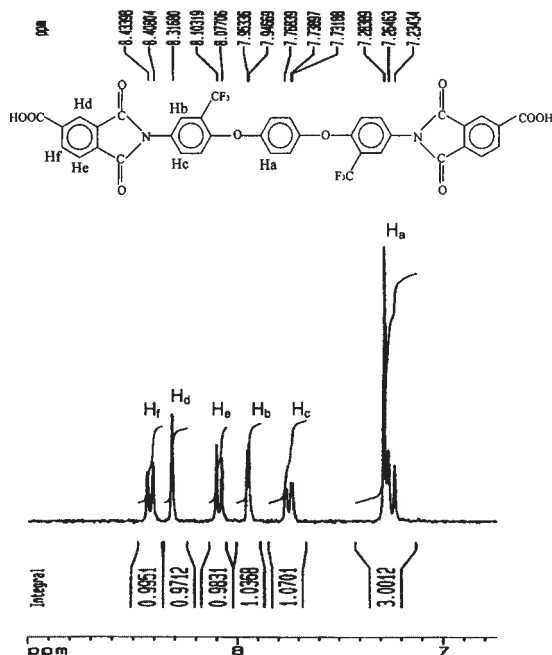
A series of novel PAIs as listed in Table I were prepared from diimide-diacid BTTFB and various aromatic diamines (BATB, ODA, pBAB, and mBAB) by the direct condensation reaction by using triphenyl phosphite and pyridine as condensing agents (Yamazaki process; Scheme 2). Figure 2 is the IR spectrum of synthesized BTTFB-BATB (PAI-Ia). It displays characteristic absorption bands for the imide ring at 1780 and 1720  $\text{cm}^{-1}$  because of the asymmetrical and symmetrical C=O stretching vibration and at 720  $\text{cm}^{-1}$  because of tertiary amine structure. The absorption of the amide group appears at around 3300  $\text{cm}^{-1}$  (N—H stretching) and 1680  $\text{cm}^{-1}$ . Other PAIs had similar functional groups. To study the effect of the fluorinated group on various properties of polymers, **Ia–d** with unfluorinated diimide-diacid were prepared for comparison.

### Properties of polyamideimides

The qualitative solubility of PAIs in various solvents is also shown in Table I. Most PAIs were soluble in aprotic polar solvents such as NMP, DMAc, dimethylformamide, and DMSO, and in even less polar solvents such as *m*-cresol and THF. **Ia** had the highest solubility. The superior solubility of these PAIs may be due to combined favorable effects of the pendent —CF<sub>3</sub> group, which hinders close packing and allows solvent molecules to diffuse into polymer chains, and the flexible aromatic ether linkages. On the other hand, **Ic** derived from linear, *para*-, and symmetric structure of unfluorinated BTB and pBAB was virtually insoluble.

X-ray diffractograms of some representative PAIs are shown in Figure 3. Most of the PAIs derived from fluorinated BTTFB exhibit amorphous patterns. **Ic** shows better crystalline character in comparison with others, which may be due to more efficient packing of

(a) FT-IR spectrum

(b)  $^1\text{H}$  NMR spectrumFigure 1 FTIR and  $^1\text{H}$ -NMR spectra of BTTFB

polymer chain containing symmetric pBAB diamine. This results in a slightly poor solubility. If an unfluorinated diacid BTB is polymerized with a fluorinated diamine BATB to form **IIa**, its solubility is better than that of **Ic**. The X-ray diffractograms also show that **IIa** has less crystallinity than **Ic**. This illustrates that the effect on the improvement of solubility from the fluorinated group in the diamine is more significant than that in the diimide-diacid. If the fluorinated groups were presented in both the diamine and the diacid as

in **Ia**, the solubility was improved synergically. The semicrystalline behavior of the **IIc** may be attributed to its rigid structure and caused the insoluble nature as mentioned above. This observation is in agreement with the general rule that solubility decreases as crystallinity increases.

For the transmittance of visible light, Figure 4 compares the UV-visible absorption spectra of three PAI films. **Ia** has highest transmittance for visible light, whereas **IIa** has lowest transmittance. Based on the

TABLE I  
Solubility of Polyamideimides

Polymer code	Solvent					
	NMP	DMAc	DMF	DMSO	THF	<i>m</i> -Cresol
Ia	++	++	++	++	++	+h
Ib	++	++	++	++	+h	+h
Ic	++	++	++	+h	-h	-h
Id	++	++	++	++	+h	+h
IIa	++	++	++	+h	+h	+h
IIb	+h	—	—	—	—	—
IIc*	—	—	—	—	—	—
IId	+h	—	—	—	—	—

\* Reference PAI.

++ = soluble at room temperature; +h = soluble in hot solvent (80°C),

-h = slightly soluble in hot solvent, — = insoluble.

data, one can determine that the introduction of fluorinated groups into diacid is the primary reason for improved transparency of PAIs. This is consistent with the finding in an earlier article.<sup>9</sup>

The thermal properties of the PAIs were evaluated by TGA and DSC, and the results are summarized in Table II. The temperatures of 5% weight loss ( $T_{d-5\%}$ ) in a nitrogen atmosphere were determined from original TGA thermograms. The  $T_d$  values of these PAIs stayed in the range of 525–588°C. They left more than 53% char yield at 800°C in nitrogen. The TGA data indicate that these PAIs have fairly high thermal stability. **Ib** has the highest  $T_d$  among all evaluated **Ia–d**, the PAIs derived from fluorinated diacid. This can be attributed to the fact that diamine ODA in **Ib** has the shortest molecular chain, and the diimide-diacid proportion is highest in the entire polymer molecular structure. **Ia** also has a relatively high  $T_d$ . This demonstrates the contribution of the imide group in the diacid to the thermal stability of PAIs. However, **IIc** is

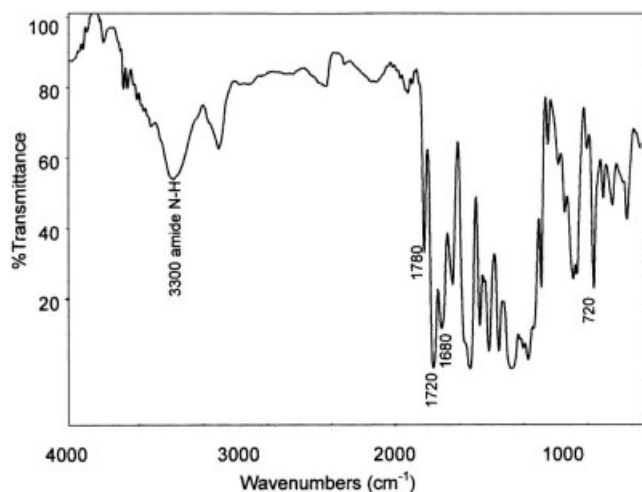


Figure 2 FTIR spectrum of PAI-Ia.

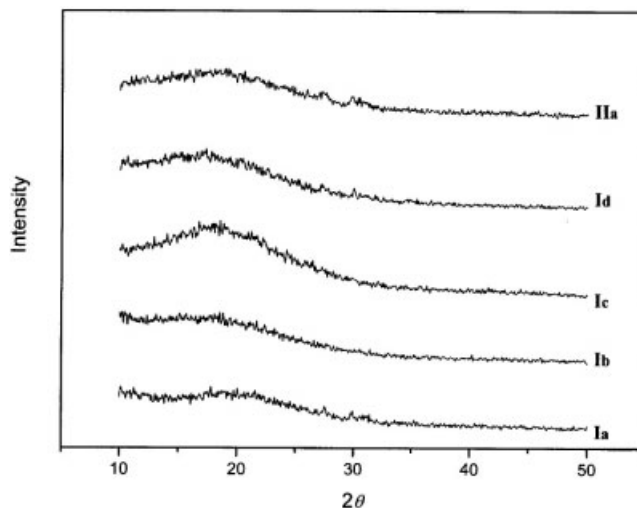


Figure 3 Wide-angle X-ray diffractograms of some PAIs.

unable to form high molecular weight polymer and has the lowest  $T_d$ , 432°C.

Because residual water or solvent can sometimes influence the first heating run of DSC, samples were first heated to 350°C and the  $T_g$  was determined by the second heating.  $T_g$  values of these fluorinated PAIs were recorded in the range of 244–272°C. The most thermal stable **Ib** according to TGA also had the highest  $T_g$ .

Because of the asymmetric nature of diamine mBAB, **Id**'s  $T_g$  is lower than other PAI-I's. The order of  $T_g$  values correlates to the decreasing order of stiffness of the polymer backbones (% elongation to break in the mechanical properties). As discussed above, **IIc** has a lower molecular weight, which results in a lowest  $T_g$ .

Other physical properties, such as inherent viscosity and moisture absorption, are listed in Table III. There

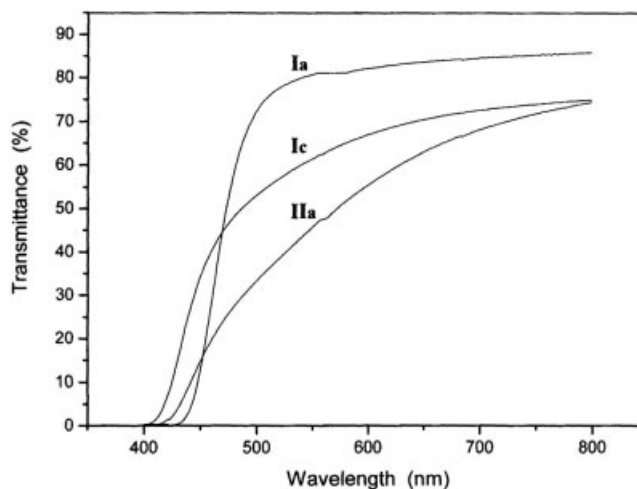


Figure 4 UV-vis spectra of the fluorinated PAIs.

is no viscosity measurement for **Ib–d** because of its insolubility in solvents. All diamines in PAIs contain ether structures, which increase nucleophilicity and hence the reactivity, resulting in an increase of viscosity. The inherent viscosity of fluorinated PAIs ranges from 0.77 to 0.93 dL/g measured at a concentration of 0.5 g/dL. All PAIs have a moisture absorption rate of <2.5%. Although amide groups can form hydrogen bonds with water molecules, the hydrophobic fluorinated groups prevent a high absorption rate. **Ia** exhibited the lowest moisture absorption because of its higher fluorine content in the polymer molecule.

Table III also lists the mechanical properties of the PAI films. These films had tensile strengths of 76–90 MPa and elongation at break of 7–15%. All these PAIs possessed good mechanical properties with high tensile strength. **Ib** and **Ic** had higher elongation than other fluorinated diacid PAIs. This may be attributed to the flexible bonding between oxygen and the *para* position of phenyl groups.<sup>10</sup> **Id** had the lowest elongation due to its *meta* bonding structure. However, unfluorinated diacid **IIa** elongated more than its fluorinated counterparts. This demonstrated that the incorporation of fluorine into the polyamideimide diacid molecule reduced its elongation ability.

## CONCLUSION

A novel fluorinated diimide-diacid, BTTFB, was synthesized from imidization between BATB and TMA and used as a PAI building block. PAIs having mod-

TABLE II  
Thermal Properties of Polyamideimides

Polymer	$T_{d-5\%}$ (°C)	Char yield (%)	$T_g$ (°C)
<b>Ia</b>	563	53	249
<b>Ib</b>	588	73	272
<b>Ic</b>	525	57	255
<b>Id</b>	537	62	244
<b>IIa</b>	558	63	257
<b>IIc*</b>	432	—	207

\* Reference PAI.

TABLE III  
Physical and Mechanical Properties of PAIs

Polymer	Inherent viscosity (dL/g)	Moisture absorption (%)	Elongation at break (%)	Tensile strength (MPa)
<b>Ia</b>	0.77	2.03	7.03	76
<b>Ib</b>	0.93	2.17	9.17	86
<b>Ic</b>	0.84	2.07	8.41	79
<b>Id</b>	0.82	2.15	6.96	89
<b>IIa</b>	0.82	2.25	15.07	90
<b>IIb–d*</b>	—	—	—	—

\* **IIb–d** does not dissolve in solvents and cannot make film.

erate-to-high molecular weight were successfully prepared by direct polycondensation of the diimide-diacid with various aromatic diamines by using triphenyl phosphite and pyridine. The introduction of trifluoromethyl groups to PAIs resulted in dramatic changes in their properties, especially in the improvement of their solubility. The  $T_g$ 's ranged from 244 to 272°C and the 5% weight loss temperatures were recorded higher than 525°C in nitrogen, indicating excellent thermal stability. PAIs with fluorinated diimide-diacid showed high solubility, good transparency, and low moisture absorption, whereas the contribution of fluorinated diamine improved thermal and mechanical properties.

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