

## Synthesis and Characterization of Ternary-Copolymer of Soluble Fluorinated Polyimides Based on 1,4-bis(4-amino-2-trifluoromethylphenoxy) benzene

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**ABSTRACT:** A series of novel ternary-copolymer of fluorinated polyimides (PIs) were prepared from 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (pBATB), commercially available aromatic dianhydrides, and aromatic diamines via a conventional two-step thermal or chemical imidization method. The structures of all the obtained PIs were characterized with FTIR,  $^1\text{H-NMR}$ , and element analysis. Besides, the solubility, thermal stability, mechanical properties, and moisture uptakes of the PIs were investigated. The weight-average molecular weight ( $M_w$ ) and the number-average molecular weight ( $M_n$ ) of the PIs were determined using gel-permeation chromatography (GPC). The PIs were readily dissolved not only in polar solvents such as DMF, DMAc, and NMP, but also in some common organic solvents, such as acetic ester, chloroform, and acetone. The glass transition temperatures of these PIs ranged from 201 to 234°C and the 10% weight loss temperatures ranged from 507 to 541°C in nitrogen. Meanwhile, all the PIs left around 50% residual even at 800°C in nitrogen. The GPC results indicated that the PIs possessed moderate-to-high number-average molecular weight ( $M_n$ ), ranging from 9609 to 17,628. Moreover, the polymer films exhibited good mechanical properties, with elongations at break of 8–21%, tensile strength of 66.5–89.8 MPa, and Young's modulus of 1.04–1.27 GPa, and low moisture uptakes of 0.54–1.13%. These excellent combination properties ensure that the polymer could be considered as potential candidates for photoelectric and microelectronic applications. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** copolymers; fluoropolymer; polyimides; solubility; 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene

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### INTRODUCTION

Aromatic polyimides (PIs) have been widely employed in many applications such as aerospace, microelectronics, gas separation, optoelectronics, and composites due to their prominent thermal stability, excellent mechanical properties, good chemical resistance, and low dielectric constants.<sup>1–4</sup> However, the wholly aromatic PIs are usually insoluble and infusible because of their rigid chain characteristics and strong interchain interactions, which posed limitation on their extensive applications.

To overcome these drawbacks, much effort has been focused on the design and synthesis of soluble and processable PIs without sacrificing their prominent thermal stability. Thus, many approaches have been applied to improve their solubility, thermal stability, and processability through introducing flexible aryl-ether linkages,<sup>5–7</sup> noncoplanar structures,<sup>8–10</sup> unsymmetrical structures,<sup>11–13</sup> or bulky substituents<sup>14–16</sup> into the polymer backbone. One of the most successful approaches is to incorpo-

rate fluorine-containing groups,<sup>17,18</sup> especially the trifluoromethyl groups into the polyimide structure.<sup>17–27</sup> Although many properties such as processability, moisture uptakes, and the dielectric properties could be improved through fluorination, which might be due to the small dipole and low polarizability of the C–F bond, the solubility of fluorinated PIs did not improve dramatically. In many common solvents, fluorinated PIs are still not readily soluble. The incorporation of trifluoromethyl groups and aryl-linkages into the polymer structure simultaneously might solve this problem.

Thus, in this study, a series of novel ternary-copolymer of PIs were prepared from 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (pBATB), commercially available aromatic dianhydrides and aromatic diamines via a two-step procedure. All the prepared PIs exhibit good solubility not only in polar solvents, but also in common solvents. Moreover, the thermal stability, mechanic properties, and moisture uptakes of the polymer were investigated.

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## EXPERIMENTAL

### Materials

Commercially available hydroquinone (Chengdu Chemical Regents, China), 2-chloro-5-nitrobenzotrifluoride (Matrix Scientific, Columbia, SC), hydrazine monohydrate (Shanghai Chemical Regents, China), anhydrous potassium carbonate (Shanghai Chemical Regents), 5% palladium on activated carbon (Shanghai Chemical Regents), 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6FHP) (98%, Matrix Scientific) and 2,2'-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) (97%, Aldrich, St. Louis, MO) were used without further purification. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) (97%, Matrix Scientific) and 4,4'-(4,4'-isopropylidenediphenoxy)-bis(phthalic anhydride) (BPADPA) (97%, Aldrich) were recrystallized from acetic anhydride before use. *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidinone (NMP) were purified by distillation under reduced pressure from calcium hydride prior to use. All other solvents were obtained from various commercial resources and used without further purification.

### Measurements

All the melting points were carried on a WRS-2A melting point apparatus. Fourier transform infrared (FTIR) spectra (KBr) were obtained on a Bruker Tensor27 FTIR spectrophotometer. <sup>1</sup>H-NMR spectra were performed on a Bruker 300 MHz spectrometer using CDCl<sub>3</sub> or dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) as solvents and tetramethylsilane (TMS) as internal standard. The <sup>19</sup>F-NMR spectra of the PIs were performed on a BRUKER AVANCE III 500 MHz spectrometer using DMSO-*d*<sub>6</sub> as solvent. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Netzsch Simultaneous DSC-TG Instrument in nitrogen at a heating rate of 10 °C/min. Elemental analyses were determined with an Elementar Vario EL system. The number-average molecular weight (*M*<sub>n</sub>), weight-average molecular weight (*M*<sub>w</sub>), and molecular weight distribution of the PIs were measured with a Agilent GL-gel-permeation chromatography (GPC) with tetrahydrofuran as an eluent at a flow rate of 1.0 mL/min and calibrated with monodispersed polystyrene (PS). The tensile properties were performed on an Instron 4446 Tensile apparatus with a 5-kg load cell at a cross-head speed of 5 mm/min on polyimide film strips approximately 0.08 mm thick and 5 mm wide with a 20 mm gauge length. For the measurement of moisture uptakes, polyimide film specimens were immersed in deionized water at 25 °C, and the weight difference was calculated after 24 h.

### Monomer Synthesis

**Synthesis of 1,4-Bis(4-nitro-2-trifluoromethylphenoxy)benzene.** Hydroquinone (1.100 g, 10 mmol) and 2-chloro-5-nitrobenzotrifluoride (4.511 g, 20 mmol) were first dissolved in 40 mL of DMF in a three-necked, 100-mL, round-bottom flask fitted with a magnetic stirring bar, condenser, and thermometer. After the mixture was completely dissolved, anhydrous potassium carbonate (4.146 g, 30 mmol) was added to the flask in one portion. After 30 min of stirring at room temperature, the mixture was heated to 135 °C for 24 h. Some of the solvent (DMF) was removed by reduced pressure distillation at 70 °C.

Then the mixture was poured into 50 mL distilled water to afford brown precipitate, which was then collected by filtration and washed with acetone and vacuum dried at 80 °C for 12 h. After recrystallization from ethanol, 3.8 g of the natural needle-like crystals was obtained in a yield of 78%.

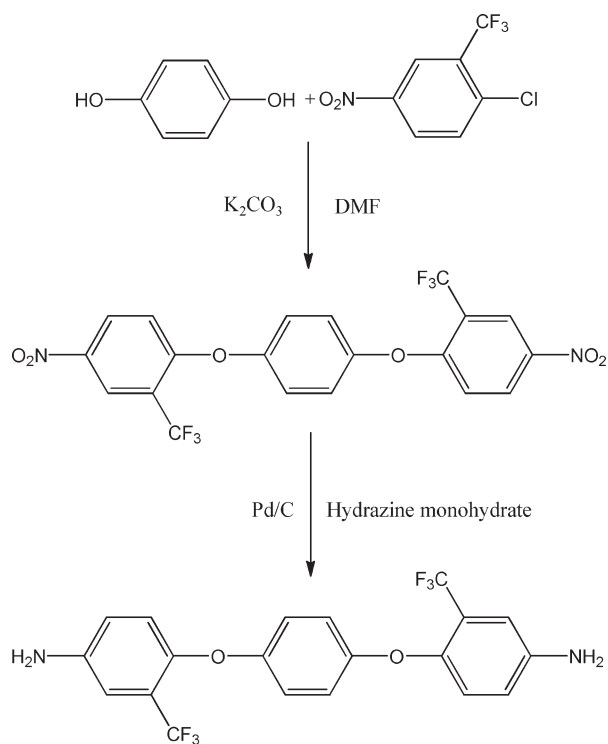
The melting point is 218 °C, according to WRS-2A melting point apparatus. IR (KBr): 1531 cm<sup>-1</sup>, 1334 cm<sup>-1</sup> (Ar—NO<sub>2</sub>), 1251 cm<sup>-1</sup> (C—O—C), 1350 cm<sup>-1</sup>–1138 cm<sup>-1</sup> (CF<sub>3</sub>). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 8.637 (s, 2H), 8.388–8.359 (t, 2H), 7.252 (s, 4H), 7.033–7.003 (d, 2H). These results are comparable with literature data.<sup>24</sup>

**Synthesis of 1,4-Bis(4-amino-2-trifluoromethylphenoxy)benzene.** A mixture of 1,4-bis(4-nitro-2-trifluoromethylphenoxy)benzene (pBNTB) (0.45 g, 0.92 mmol), 5% palladium on activated carbon (0.045 g) and ethanol (30 mL) was added into a three-necked, 50-mL, round-bottom flask equipped with a magnetic stirring bar and heated to reflux at 78 °C. Hydrazine monohydrate (5 mL) was then added dropwise to the mixture. After the addition, the mixture was heated to reflux for 6 h. The light yellow solution was obtained by removing the Pd/C catalyst through filtering the hot mixture. Then, the removal of the excess ethanol and hydrazine monohydrate afforded the crude product. After recrystallization from ethanol, 0.365 g of the light yellow solid was obtained in a yield of 81%.

The melting point is 133 °C, according to WRS-2A melting point apparatus. IR (KBr): 3476 cm<sup>-1</sup>, 3449 cm<sup>-1</sup> (Ar—NH<sub>2</sub>), 3053 cm<sup>-1</sup> (Ar—H), 1260 cm<sup>-1</sup> (C—O—C), 1350–1138 cm<sup>-1</sup> (CF<sub>3</sub>). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 6.962 (s, 2H), 6.906 (s, 4H), 6.854–6.823 (d, 2H), 6.799–6.773 (d, 2H), 3.723 (s, 4H). These results are comparable with literature data.<sup>24</sup>

### Polymerization

The PIs were synthesized from pBATB, various dianhydrides, and diamines via a two-step method. The synthesis of pFPI-3 is used as an example to illustrate the general synthetic route used to yield the PIs. The polymerization was conducted in a three-necked, 50-mL, nitrogen-flushed, round-bottom flask equipped with a magnetic stirrer, reverse Dean-star trap and reflux condenser filled dry xylene. 6FDA (0.2222 g, 0.5 mmol), 6FHP (0.0915 g, 0.25 mmol), and pBATB (0.1070 g, 0.25 mmol) were completely dissolved in 2 mL of DMF, 1 mL of DMF, and 1 mL of DME, respectively. The 6FDA solution was first added into the flask at 0 °C, followed by the addition of diamines solutions. The mixture was then warmed to room temperature and stirred for 24 h under nitrogen atmosphere to form a viscous poly(amino acid) (PAA) solution. Two methods were used to convert PAA into a polyimide. For the thermal-imidization method, the PAA solution was cast onto a clean glass plate and heated (60 °C/20 min, 120 °C/30 min, 165 °C/2 h, 200 °C/30 min, 250 °C/20 min, 300 °C/10 min) to produce a fully imidized polyimide film, which was then also used to test its mechanical property and moisture uptake. Chemical imidization was carried out by adding 2.5 mL dry xylene into the afore-mentioned PAA solution at room temperature and heating at 165 °C for 5 h. During the heating process, the solvent was evaporated continuously. The crude product was obtained by pouring the remaining PAA solution into a mixture of methanol/water (1 : 1, v/v, 50 mL) and 2N HCl (5 mL). The precipitate was collected by filtration,



Scheme 1. Synthesis of pBATB.

washed thoroughly with methanol, and dried at  $80^\circ C$  to yield the light-yellow solid pFPI-3. Elemental analysis calculated for  $C_{65}H_{30}O_{12}N_4F_{24}$ : C, 51.52; H, 1.98; N, 3.70. Found: C, 54.17; H, 2.17; N, 3.27.

pFPI-1 (pBATB + 6FDA + BPADA) was synthesized from the polymerization of 2 equiv of pBATB, 1 equiv of 6FDA, and 1 equiv of BPADA in DMF in the same method as mentioned before. Elemental analysis calculated for  $C_{82}H_{46}O_{14}N_4F_{18}$ : C, 61.27; H, 2.86; N, 3.47. Found: C, 61.35; H, 2.9; N, 3.41.

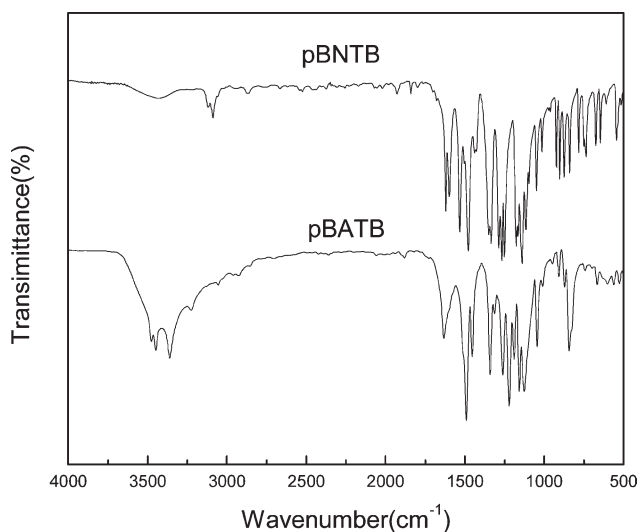


Figure 1. FTIR spectra of pBNTB and pBATB.

pFPI-2 (pBATB + 6FDA + BAPP) was synthesized from the polymerization of 1 equiv of pBATB, 2 equiv of 6FDA, and 1 equiv of BAPP in DMF in the same method as mentioned before. Elemental analysis calculated for  $C_{77}H_{38}O_{12}N_4F_{18}$ : C, 61.03; H, 2.51; N, 3.70. Found: C, 62.18; H, 2.85; N, 3.62.

pFPI-4 (pBATB + BPADA + 6FHP) was synthesized from the polymerization of 1 equiv of pBATB, 2 equiv of BPADA, and 1 equiv of 6FHP in DMF in the same method as mentioned before. Elemental analysis calculated for  $C_{89}H_{58}O_{16}N_4F_{12}$ : C, 64.11; H, 3.48; N, 3.36. Found: C, 64.75; H, 3.46; N, 3.25.

pFPI-5 (pBATB + BPADA + BAPP) was synthesized from the polymerization of 1 equiv of pBATB, 1 equiv of BPADA, and 1 equiv of BAPP in DMF in the same method as mentioned before. Elemental analysis calculated for  $C_{101}H_{72}O_{16}N_4F_6$ : C, 70.88; H, 4.21; N, 3.27. Found: C, 72.82; H, 4.18; N, 3.38.

## RESULTS AND DISCUSSION

### Monomer Synthesis and Characterization

pBATB was synthesized by a two-step synthetic route as illustrated in Scheme 1. pBATB was obtained by the reduction of pBNTB with hydrazine monohydrate and  $Pd/C$  catalyst. The structure of pBNTB and pBATB was confirmed by FTIR and  $^1H$ -NMR as indicated in the experimental section. Figure 1 compares the IR spectra of pBNTB and pBATB. As shown in the Figure 1, the absorption peaks due to the asymmetric and symmetric stretching of the  $\text{NO}_2$  group disappeared after reduction, whereas the characteristic absorption peaks of the  $\text{NH}_2$  group appeared at about  $3476\text{ cm}^{-1}$  and  $3449\text{ cm}^{-1}$ . The  $^1H$ -NMR of pBATB in  $CDCl_3$  is shown in Figure 2. The

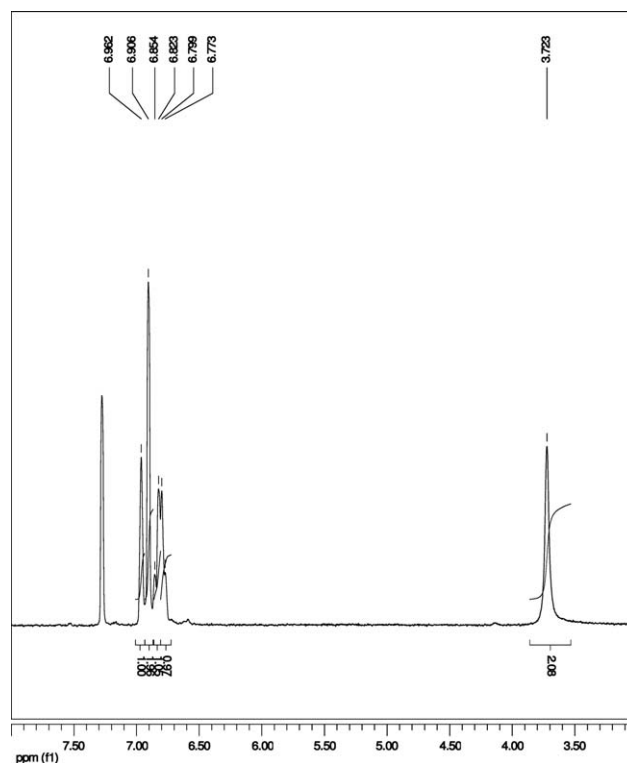
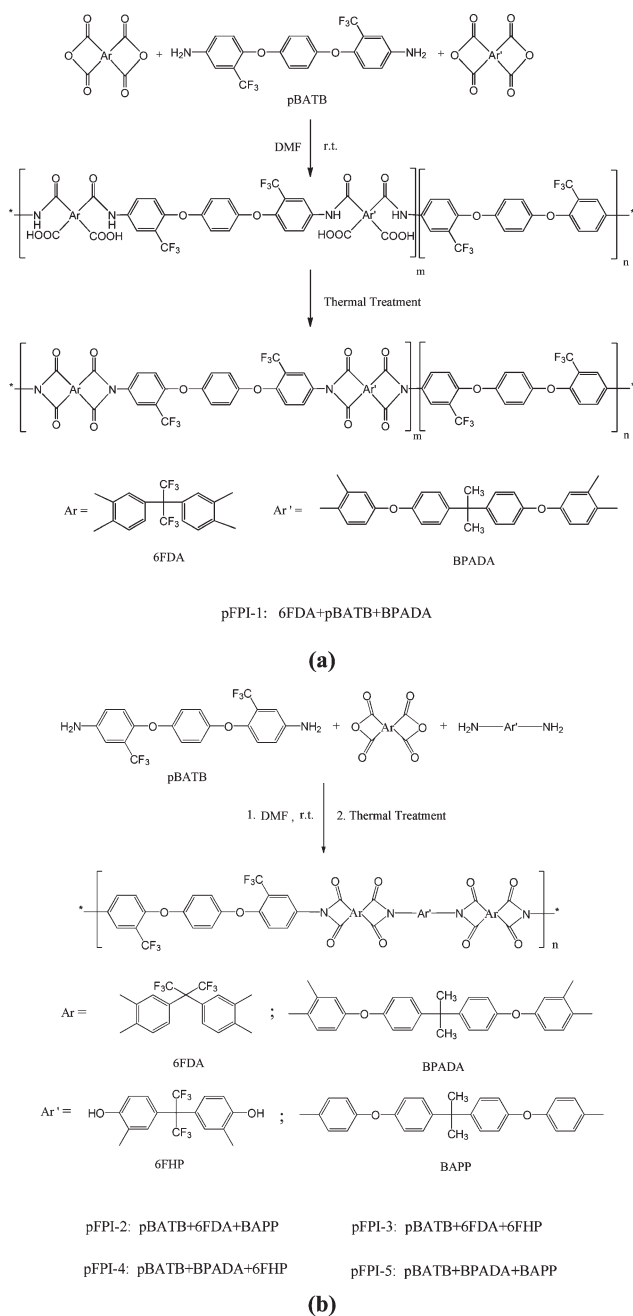


Figure 2.  $^1H$ -NMR spectrum of pBATB.



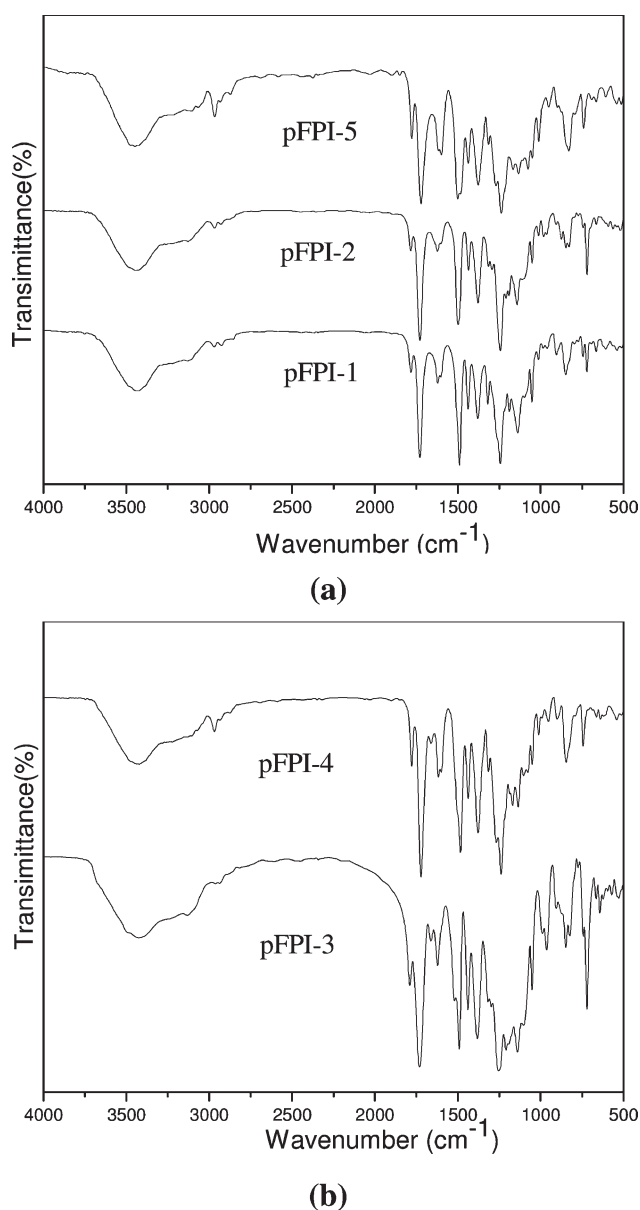
**Scheme 2.** Synthesis of PIs.

signal at 3.723 ppm of the  $^1\text{H-NMR}$  spectrum of pBATB is peculiar to the  $-\text{NH}_2$  group.

### Polymerization

A series of novel ternary-copolymer of fluorinated PIs were prepared from pBATB, commercially available aromatic dianhydrides, such as 6FDA and BPADA, and aromatic diamines, such as 6FHP and BAPP, via a two-step procedure, as illustrated in Scheme 2. The polymerization was carried out through the reaction of pBATB with diamines monomers and dianhydrides monomers in DMF. The ring-opening polyaddition at room temperature for 24 h yielded PAAs. Then the formed PAAs were thermally imidized to polyimide ( $60^\circ\text{C}/20$  min,  $120^\circ\text{C}/30$  min,

$165^\circ\text{C}/2$  h,  $200^\circ\text{C}/30$  min,  $250^\circ\text{C}/20$  min,  $300^\circ\text{C}/10$  min) or chemically imidized by adding appropriate amount of dry xylene into the PAAs solutions and heating at  $165^\circ\text{C}$  for 5 h. The chemical structures of all PIs were characterized by FTIR,  $^1\text{H-NMR}$ , and element analysis. The FTIR spectra of pFPI-1–5 are shown in Figure 3. The FTIR spectra showed the characteristic absorption peaks of asymmetrical and symmetrical stretching of imide carbonyl at around  $1780\text{ cm}^{-1}$  and  $1730\text{ cm}^{-1}$ , C–N stretching at  $1380\text{ cm}^{-1}$ , imide ring deformation at  $1050\text{ cm}^{-1}$  and  $740\text{ cm}^{-1}$ . And the multiple stretching absorption peaks of C–O–C and C–F were also observed in the range of  $1300$ – $1100\text{ cm}^{-1}$ . The disappearance of the characteristic absorption peaks of  $-\text{NH}_2$  group near  $3200$ – $3350\text{ cm}^{-1}$  and of  $-\text{C}=\text{O}$  near  $1650$ – $1674\text{ cm}^{-1}$  indicates a complete formation of imide structure. As a typical example, the  $^1\text{H-NMR}$  spectrum of the



**Figure 3.** FTIR spectra of pFPI-1–5.

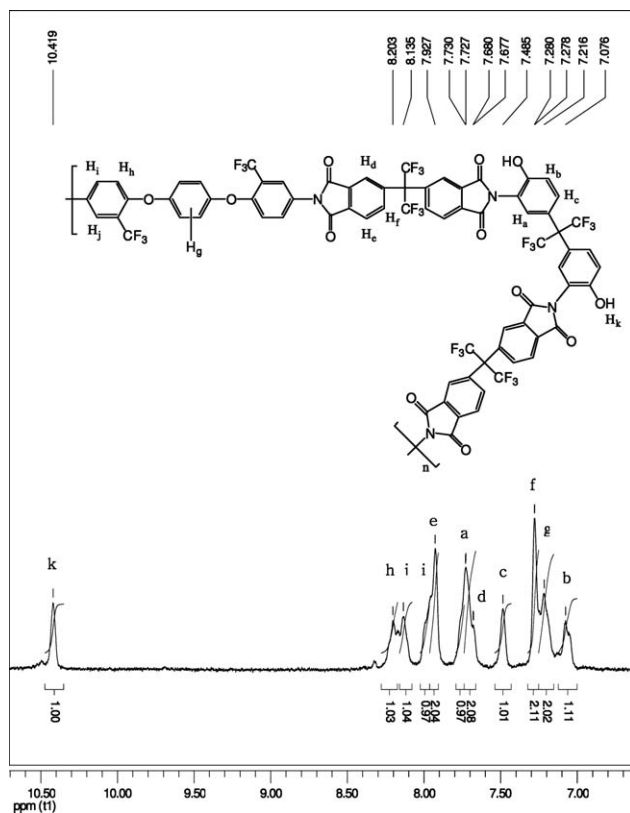


Figure 4.  $^1\text{H-NMR}$  spectrum of pFPI-3.

pFPI-3 in  $\text{DMSO-}d_6$  was illustrated in Figure 4. The assignments of all the protons are in complete agreement with the proposed polyimide structure. The absorption peaks at 7.0–8.1 ppm are assigned to the aromatic protons in polyimide backbone. And the absorption peak at 10.419 ppm is assigned to the protons of  $-\text{OH}$  group. No characteristic absorption peak of  $-\text{NH}_2$  group was detected at about 3.7 ppm, indicating that the imidization was complete. Meanwhile, the  $^{19}\text{F-NMR}$  spectrum of the pFPI-3 in  $\text{DMSO-}d_6$  was illustrated in Figure 5. As can be seen in Figure 5, there are only three obvious signal peaks, which is due to that there are only three different types of

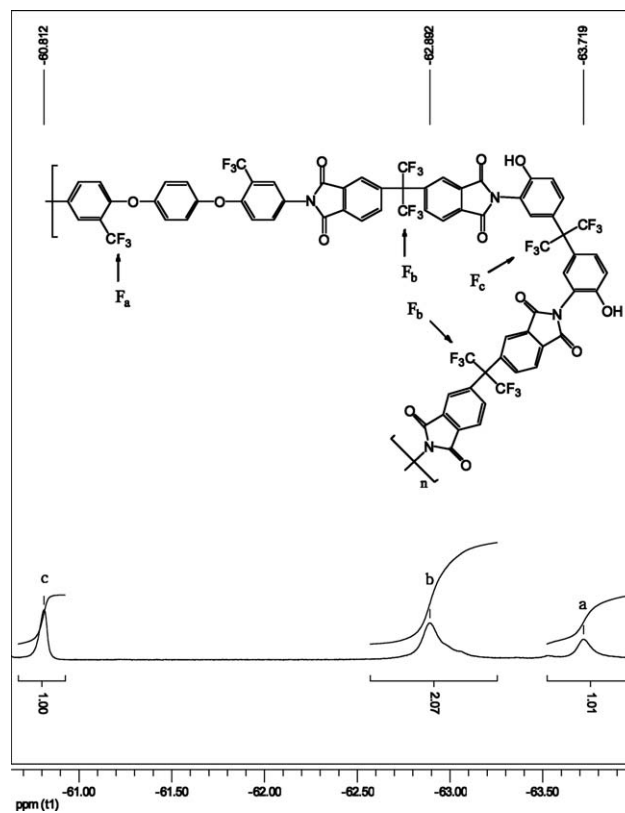


Figure 5.  $^{19}\text{F-NMR}$  spectrum of pFPI-3.

fluorine in the backbone structure of pFPI-3. According to the book “Guide to fluorine NMR for organic chemists” written by William R. Dolbler, the signal at  $-63.719$  ppm,  $-62.892$  ppm, and  $-60.812$  ppm in the Figure 5 is assigned to  $F_a$ ,  $F_b$ , and  $F_c$ , respectively. Thus the assignments of all the fluorine are in complete agreement with the proposed polyimide structure. These results clearly confirm that the obtained products are consistent with the proposed structure. The elemental analysis data of the pFPI-1–5 (Table I) are also in accordance with the calculated value. These results clearly confirm that the obtained products are consistent with the proposed structure.

Table I. Elemental Analysis of pFPI-1–5

Polyimide	Formula (formula weight)		Elemental analysis (%)		
			C	H	N
pFPI-1	$(\text{C}_{82}\text{H}_{46}\text{O}_{14}\text{N}_4\text{F}_{18})_n$ (1606) $_n$	Calcd.	61.27	2.86	3.47
		Found	61.35	2.9	3.41
pFPI-2	$(\text{C}_{77}\text{H}_{38}\text{O}_{12}\text{N}_4\text{F}_{18})_n$ (1514) $_n$	Calcd.	61.03	2.51	3.70
		Found	62.18	2.85	3.62
pFPI-3	$(\text{C}_{65}\text{H}_{30}\text{O}_{12}\text{N}_4\text{F}_{24})_n$ (1514) $_n$	Calcd.	51.52	1.98	3.70
		Found	54.17	2.17	3.27
pFPI-4	$(\text{C}_{89}\text{H}_{58}\text{O}_{16}\text{N}_4\text{F}_{12})_n$ (1666) $_n$	Calcd.	64.11	3.48	3.36
		Found	64.75	3.46	3.25
pFPI-5	$(\text{C}_{101}\text{H}_{72}\text{O}_{16}\text{N}_4\text{F}_6)_n$ (1710) $_n$	Calcd.	70.88	4.21	3.27
		Found	72.82	4.18	3.38



**Table II.** Thermal Properties of pFPI-15 Obtained by Chemical Imidization

Polymer	$T_{d(5\%)} (^{\circ}\text{C})^a$	$T_{d(10\%)} (^{\circ}\text{C})^a$	$T_g (^{\circ}\text{C})^a$	Char yield (%) <sup>b</sup>	$M_n^c$	$M_w/M_n^c$
pFPI-1	513.4	535.7	201.5	56	13370	2.08
pFPI-2	523.1	543.2	233.3	62	17628	2.25
pFPI-3	430.0	507.5	262.6	48	9814	1.70
pFPI-4	487.2	522.3	211.3	56	17391	2.04
pFPI-5	533.3	540.8	212.4	53	9609	1.40

<sup>a</sup> $T_{d(5\%)}$ ,  $T_{d(10\%)}$ , and  $T_g$  determined on Netzsch Simultaneous DSC-TG Instrument in nitrogen at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ ., <sup>b</sup>Residual weight retention (%) at 800 $^{\circ}\text{C}$  in nitrogen., <sup>c</sup>Determined by GPC eluted with THF based on polystyrene standards.

Furthermore, the number-average molecular weight ( $M_n$ ) and molecular weight distribution of the resulting PIs prepared by the chemical imidization are listed in Table II. The GPC results indicated that the PIs possessed moderate-to-high  $M_n$ , ranging from 9609 to 17,628, which were high enough to prepare flexible and tough films. As shown in Figure 6, the PAA is synthesized through a nucleophilic substitution in which the diamines donate an electron to dianhydride. And after that, the PAA is converted into corresponding polyimide by using thermal or chemical method. Therefore, the reactivity of the diamine and dianhydride should be considered as a crucial factor which could affect the molecular weight of synthesized polyimide. Even though the introduction of trifluoromethyl group ( $\text{CF}_3$ ) will improve the solubility and other properties of the PIs, it

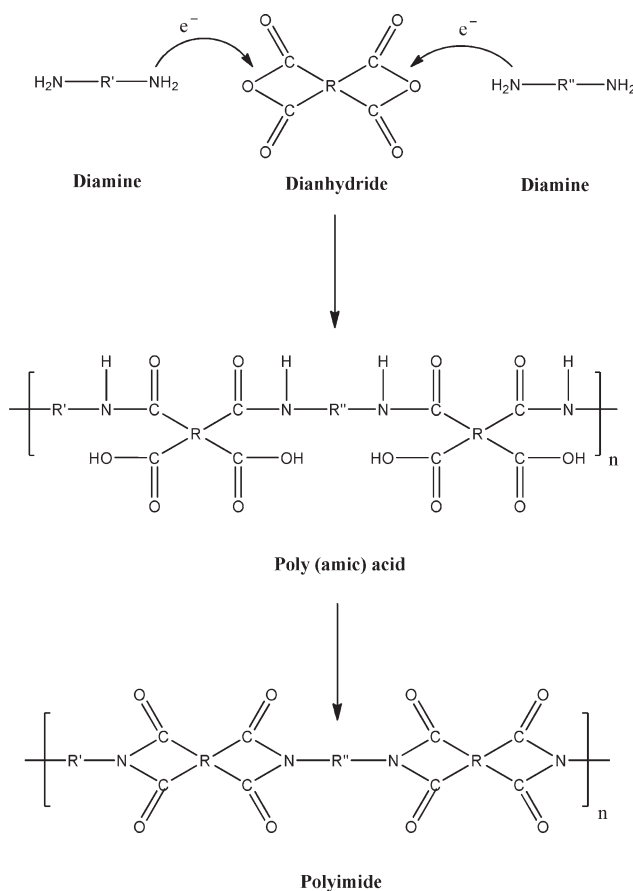
will somehow affect the reactivity of the monomer (i.e., aromatic diamine and dianhydride) due to its strong electron-withdrawing ability. As shown in Figure 7, pFPI-3 was synthesized from 6FDA, 6FHP, and pBATB. Even though the trifluoromethyl group will increase the reactivity of 6FDA, the reactivity of both 6FHP and pBATB will be decreased more severely. Thus, it may be a plausible explanation why the molecular weight of pFPI-3 is relatively low compared to other synthesized PIs. The pFPI-5 was synthesized from BPADA, BAPP, and pBATB. In term of reactivity, BPADA is weaker than 6FDA, because there is no fluorine-containing group in BPADA. Besides, the trifluoromethyl group decreases the reactivity of pBATB. Therefore, the molecular weight of pFPI-5 is also relatively low.

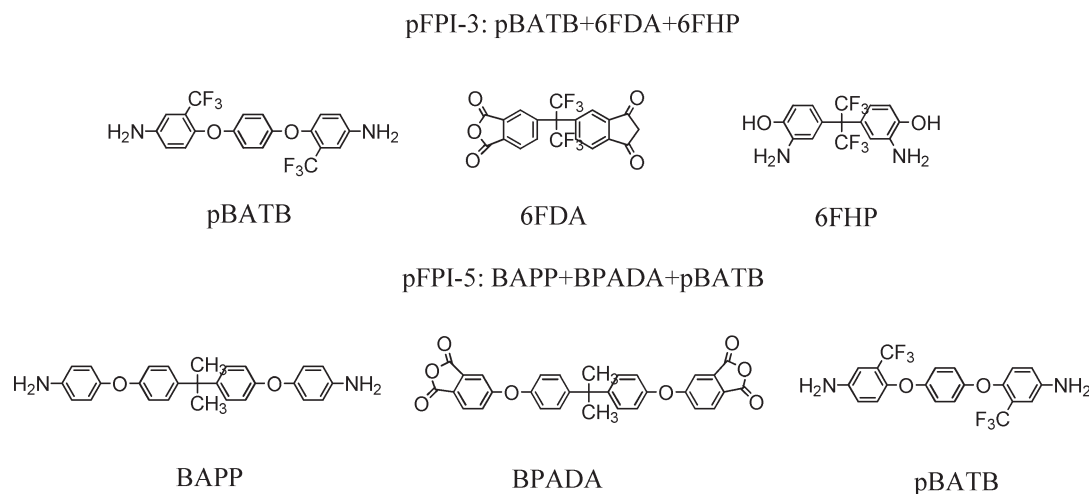
#### Polymer Solubility

The solubility of pFPI-1–5 was tested in various organic solvents, and the results were listed in Table III. It is well known that polyimide generally shows poor solubility in organic solvents due to their rigid chain characteristics and strong interchain actions, which posed limitation on their applications in extensive fields. Unlike those insoluble PIs, the prepared pFPI-1–5 exhibit excellent solubility not only in some strong polar solvents, such as dimethyl sulfoxide (DMSO), DMF, and NMP, but also in common organic solvents, including some low-boiling solvents, such as dichloromethane, chloroform, and acetone. Obviously, the improved solubility of these PIs could be partly attributed to the introduction of trifluoromethyl, which decreases the packing density and intermolecular interactions of the polymer chains and also allows solvent molecules to diffuse into polymer chains. Besides, the introduction of ether linkage could decrease the coplanarity of the polymer chains, which could also loosen the packing density of the polymer chains. In a word, the introduction of trifluoromethyl and ether linkage could reduce the chain–chain interactions to enhance the solubility.

#### Polymer Thermal Properties

TGA and DSC were used to evaluate the thermal properties of pFPI-1–5 obtained by chemical imidization, and the results are listed in Table III. As a typical example, the TGA and DSC curves of pFPI-1 in nitrogen are shown in Figure 8. The  $T_g$  values of pFPI-1–5 were in the range of 201–234 $^{\circ}\text{C}$ . pFPI-3 derived from pBATB, 6FDA, and 6FHP showed the highest  $T_g$  value (234 $^{\circ}\text{C}$ ), whereas pFPI-1 prepared from pBATB, 6FDA, and BPADA gave the lowest  $T_g$  value (201 $^{\circ}\text{C}$ ). No ether linkage exists in 6FDA or 6FHP, as a result, in term of rigidity, pFPI-3 should rank the first, which might make it possess the highest  $T_g$  value. Clearly, the difference in  $T_g$ 's was due to the rigidity

**Figure 6.** Synthesis of polyimide.



**Figure 7.** The structure of monomer used in synthesizing pFPI-3 and pFPI-5.

and packing density of the polymer chains. The 5% and 10% weight loss temperatures were also given in Table III. In nitrogen, the temperature at 5% weight loss was from 430 to 534°C, while the temperature at 10% weight loss was from 507 to 541°C. Besides, pFPI-1–5 left around 50% char yield at 800°C in nitrogen.

#### Mechanical Properties and Moisture Uptakes

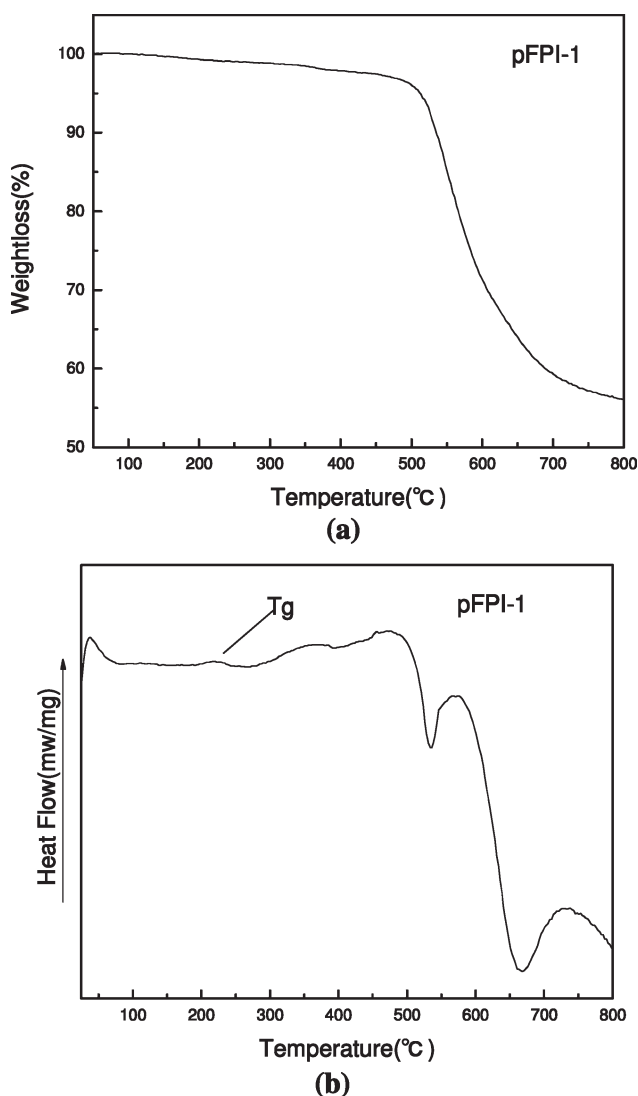
Tough and flexible films were obtained by casting PAA solutions on a glass plate followed by thermal curing at a schedule of 60°C/20 min, 120°C/30 min, 165°C/2 h, 200°C/30 min, 250°C/20 min, 300°C/10 min. The mechanical properties of the polyimide films are summarized in Table IV. The PIs films had elongations at break of 8–21%, tensile strength of 66.5–89.8 MPa, and Young's modulus of 1.04–1.27 GPa. And among those prepared PIs, pFPI-3 exhibits the highest tensile strength, whereas, pFPI-5 exhibits the lowest tensile strength. The plausible explanation is that no ether linkage exists in

6FDA or 6FHP, as a result, in term of rigidity, pFPI-3 should rank the first, which might make it possess the highest tensile strength and Young's modulus value. Both BPADA and BAPP has ether linkage, in term of rigidity, pFPI-5 should rank the last, which might explain why it exhibits the lowest tensile strength. The moisture uptakes of pFPI-1–5 are also listed in Table IV. Polyimide materials usually exhibit higher moisture uptake than the hydrocarbon polymers due to the presence of imide groups.<sup>28</sup> The moisture uptake of aromatic PIs could be up to 3.0–3.5% depending on the chemical structure of polymer and the relative humidity of the environments.<sup>12</sup> Thus, the introduction of trifluoromethyl groups, on one hand could inhibit the moisture uptake of the fluorinated PIs due to their hydrophobic features; on the other hand could loosen the packing density of the polymer backbone chains, thus increasing the moisture uptake of the polymers due to its bulky volume. Although the fluorine content of pFPI-3 ranked the most, its moisture uptake was not the lowest. Therefore, there

**Table III.** Solubility of pFPI-15 Prepared by Chemical Imidization<sup>a</sup>

Solvent	pFPI-1	pFPI-2	pFPI-3	pFPI-4	pFPI-5
DMSO	++	++	++	++	++
NMP	++	++	++	++	++
DMAc	++	++	++	++	++
DMF	++	++	++	++	++
Dichloromethane	++	++	+	++	++
THF	++	++	++	++	++
Acetic ester	++	++	++	++	+
Chloroform	++	++	+	+	++
Acetone	++	++	++	++	++
Cyclopentanone	++	++	++	++	++
Methanol	–	–	–	–	–

<sup>a</sup>The solubility was measured at a concentration of 1.0% wt solid content. ++: diffuent; the solid polymer was quickly dissolved in the solvent to afford a homogenous solution without heating or stirring. +: soluble; the solid polymer was completely dissolved in the solvent to afford a clean solution with stirring. –: insoluble; the solid polymer did not dissolve in the solvent even with heating.



**Figure 8.** TGA (a) and DSC (b) curve of pFPI-1 in nitrogen.

was not a quantitative linear relationship between the fluorine content and moisture uptake of polyimide materials. But due to the effect of trifluoromethyl groups, pFPI-1–5 still exhibited relatively low water absorption, which is desirable for advanced microelectronics applications.

**Table IV.** Mechanical Properties and Moisture Uptake of pFPI-1–5

Polymer	pFPI-1	pFPI-2	pFPI-3	pFPI-4	pFPI-5
Elongation at break (%)	13	9	8	14	21
Tensile strength (MPa)	74.7	89.1	89.8	70.5	66.5
Young's modulus (GPa)	1.13	1.21	1.27	1.04	1.18
Moisture uptake (%)	0.54	0.63	0.75	0.67	1.13

## CONCLUSION

A series of novel ternary-copolymer of fluorinated PIs were prepared from pBATB, commercially available aromatic dianhydrides and aromatic diamines via a two-step procedure. All the obtained PIs revealed good solubility and low moisture uptakes due to introduction of trifluoromethyl groups and ether linkage in PIs. Besides, the prepared moderate-to-high molecular weight PIs displayed good thermal stability and mechanical properties. Therefore, these PIs exhibited excellent combination properties could be considered as potential candidates for photoelectric and microelectronic applications.

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