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Synthesis and characterization of soluble polyimides based on a new fluorinated diamine: 4-Phenyl-2,6-bis[3-(4′-amino-2′-trifluoromethyl-phenoxy) phenyl] pyridine

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A B S T R A C T

A new kind of pyridine-containing aromatic diamine monomer, 4-phenyl-2,6-bis[3-(4′-amino-2′-trifluoromethyl-phenoxy) phenyl] pyridine (*m*-PAFP), was successfully synthesized by a modified Chichibabin reaction of 3-(4′-nitro-2′-trifluoro-methyl-phenoxy)-acetophenone with benzaldehyde, followed by a catalytic reduction. A series of fluorinated pyridine-bridged aromatic poly(ether-imide)s were prepared from the resulting diamine monomer with various aromatic dianhydrides via a conventional two-step thermal or chemical imidization method. The inherent viscosities values of these polyimides were in the range of 0.56–1.02 dL/g, and they could be cast and thermally converted into transparent, flexible, and tough polyimide films. The polyimides displayed higher solubility in polar solvents such as NMP, DMSO and *m*-cresol. The polyimides had good thermal stability, with the glass transition temperatures (T_g) of 187–211 °C, the temperatures at 5% weight loss of 511–532 °C, and the residue at 800 °C in air was higher than 50%. These films also had dielectric constants of 2.64–2.74 at 10 MHz and low water uptake 0.53–0.66%. Wide-angle X-ray diffraction measurements revealed that these polyimides were predominantly amorphous. Moreover, the polymer films of these novel polyimides showed outstanding mechanical properties with the tensile strengths of 90.1–96.6 MPa, elongations at breakage of 8.9–10.7% and tensile modulus of 1.65–1.98 GPa.

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1. Introduction

Aromatic polyimides are well known as materials of high performance for their excellent thermal stabilities, chemical resistance and electric properties [1–4]. During the past decade, interests in these polymers have risen in response to increasing technological applications in a variety of fields such as aerospace, automobile, and microelectronics, etc. [5–8]. However, their applications have been limited in some fields because aromatic polyimides are normally insoluble in common organic solvents and high melting point.

Solubilization of the polyimides has been targeted by several methods, such as introduction of flexible linkage [9,10], bulky units in the polymer backbone [11,12], bulky pendent substituents [13,14], or noncoplanar moieties [15,16]. Among these approaches, introduction of bulky pendent substituents and heteroaromatic rings into polyimide chains has been considered to be efficient, which can provide not only enhanced solubility but also good thermostability and processability.

Pyridine is a heteroaromatic molecule with rigidity and polarizability. New kinds of heteroaromatic diamine or dianhydride holding pyridine unit have been designed and synthesized, and the novel heteroaromatic polymers with good thermostability and processability have been obtained derived from those monomers containing pyridine nucleus structures at the same time [17–23]. Considering the rigidity based on pyridine ring have contributions for the thermal stability, chemical stability of the resulting polymer at elevated temperature [24], as well as polarizability resulting from nitrogen atom in pyridine ring could be suitable to improve their solubility.

Polyimides containing hexafluoroisopropylidene or pendent trifluoromethyl groups are of special interest [25,26]. It was found that the incorporation of CF_3 into polymer backbones resulted in an enhanced solubility and optical transparency together with a lowered dielectric constant, which attributed to low polarizability of the C–F bond and the increasing in free volume. The fluorinated polyimides also provided other merits such as good thermal and low moisture absorption.

In this paper, a new aromatic, pyridine-containing ether diamine with trifluoromethyl pendent group, 4-phenyl-2,6-bis[3-(4′-amino-2′-trifluoromethyl-phenoxy) phenyl] pyridine (*m*-PAFP), had been designed and synthesized as a potentially

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convenient condensation monomer to form pyridine-containing polyimides. Meanwhile, a new series of pyridine-containing polyimides were synthesized from the resulting diamine monomer with several aromatic dianhydrides by a two-step procedure, and the polyimides obtained were characterized in detail. Furthermore, to investigate the effect of trifluoromethyl substituents and the nonlinear structure on the polymer solubility, the polyimides derived from *m*-PAFP were compared with analogous polyimides derived from a pyridine-containing diamine monomer, PAFP [27], and polyimides derived from a non-fluorinated pyridine-containing diamine monomer, PAPP, reported by Wang et al. [28], as shown in Fig. 1.

2. Results and discussion

2.1. Monomer synthesis

Among several methods for the preparation of a pyridine ring, modified Chichibabin is one of the best methods that offer some advantages such as good yield, available starting materials, and the potential for introducing different substituents in the pyridine ring [19]. As shown in Scheme 1, the diamine monomer (*m*-PAFP) was obtained through a three-step synthetic route. Firstly, the nucleophilic substitution reaction of 3-hydroxyacetophenone with 2-chloro-5-nitrotrifluoromethylbenzene in the presence of potassium carbonate in DMF gave the intermediate compound *m*-NFAP. Then the dinitro compound *m*-PNFP was prepared via a modified Chichibabin reaction from benzaldehyde and *m*-NFAP. Finally, the novel diamine monomer *m*-PAFP was obtained by the reduction of *m*-PNFP with hydrazine monohydrate catalyzed by Pd/C. The new aromatic diamine monomer is pure enough for polymerization with commercial aromatic dianhydride monomers to prepare polyimides.

The structures of *m*-PAFP and the intermediates were confirmed by elemental analysis, mass spectrometry, IR spectra, and ^{1}H NMR and ^{13}C NMR spectroscopy. Fig. 2 shows the FT-IR spectra of *m*-NFAP, *m*-PNFP and the diamine monomer (*m*-PAFP). The FT-IR spectrum of *m*-PNFP showed two characteristic bands at 1531 and 1351 cm^{-1} ($-NO_2$ asymmetric and symmetric stretching), while the characteristic absorptions of the nitro groups disappeared and the amino group showed a pair of N–H stretching absorptions in the region of 3300–3500 cm^{-1} in the FT-IR spectrum of diamine. Fig. 3 presents the ^{1}H NMR and ^{13}C NMR spectra of the diamine monomer *m*-PAFP in $CDCl_3$. In the ^{1}H NMR spectroscopy of the diamine, the signals in the range of 7.58–6.81 ppm were ascribed to the protons of the aromatic rings and the signal in 3.81–3.40 ppm were ascribed to the protons of $-NH_2$ group. In the ^{13}C NMR spectra, all the carbon-13 atoms of diamine showed 20 main signals, which resonated in the regions of 158.8–113.0 ppm. The ^{13}C NMR spectroscopy showed one quartet because of heteronuclear C–F coupling. The quartet was centered at 114 ppm by the CF_3 carbon C^{20}, and the one-bond C–F coupling constant was 268 Hz. The CF_3-attached carbon C^{19} was centered at 120 ppm, and the constant was about 90 Hz by two-bond C–F coupling. All the spectroscopic data obtained and the elemental analyses were in good agreement with the expected structures.

2.2. Polymer synthesis

The diamine monomer was reacted with three kinds of commercially available aromatic dianhydrides, PMDA, ODPA, and BTDA, to give the corresponding poly(ether-imide)s as shown in Scheme 2.

The new polyimides were synthesized using two-step methods, which were carried out via poly(amic acid)s intermediate. In our case, the poly(amic acid)s were prepared by gradually adding the solid dianhydride monomer into the equimolar amounts of diamines in anhydrous NMP, and stirred for 24 h at room temperature. Either thermal or chemical imidization procedures were chosen to form polyimides. Merits of the former were easy for preparation of polyimide films, whereas the latter was suited for the preparation of soluble polyimides. The experimental data of the isolated polyimides obtained have been summarized in Table 1. According to the data from Table 1, the resulting polyimides all get

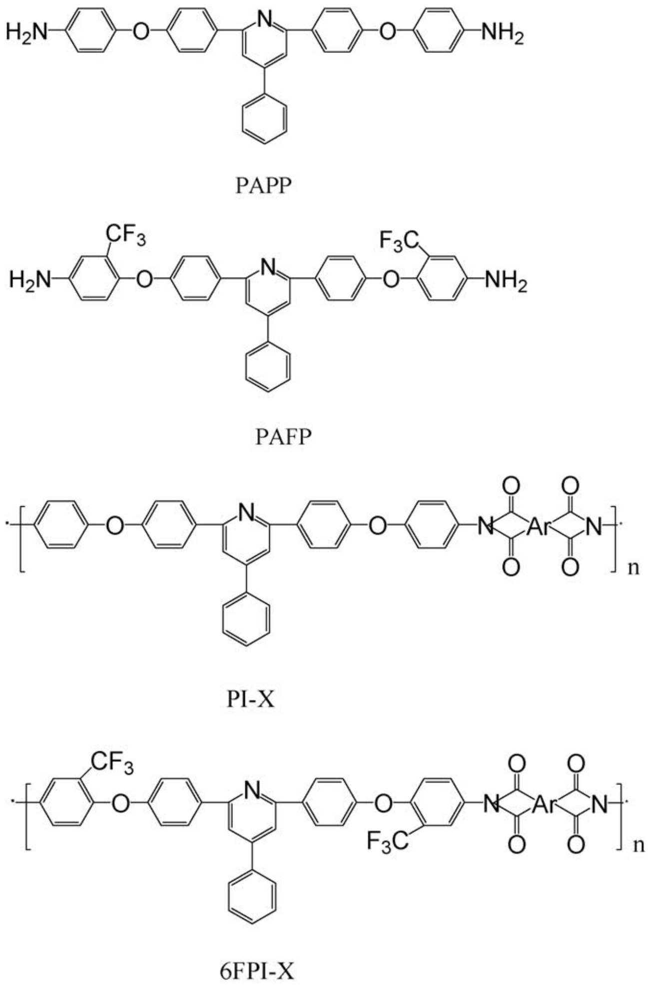
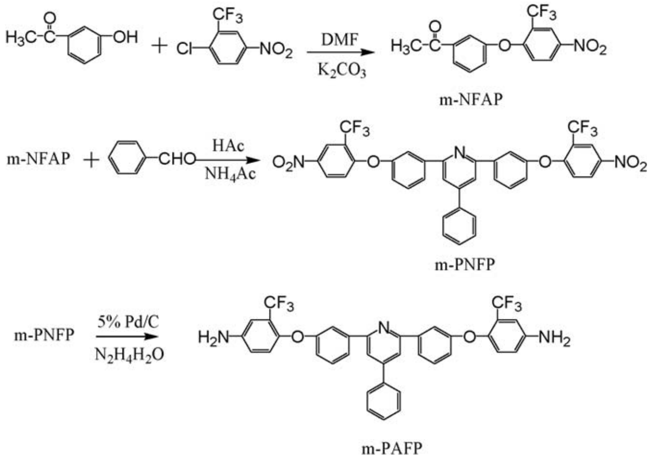


Fig. 1. PAPP and PAFP diamine monomers and polyimides.



Scheme 1. Preparation of diamine monomers.

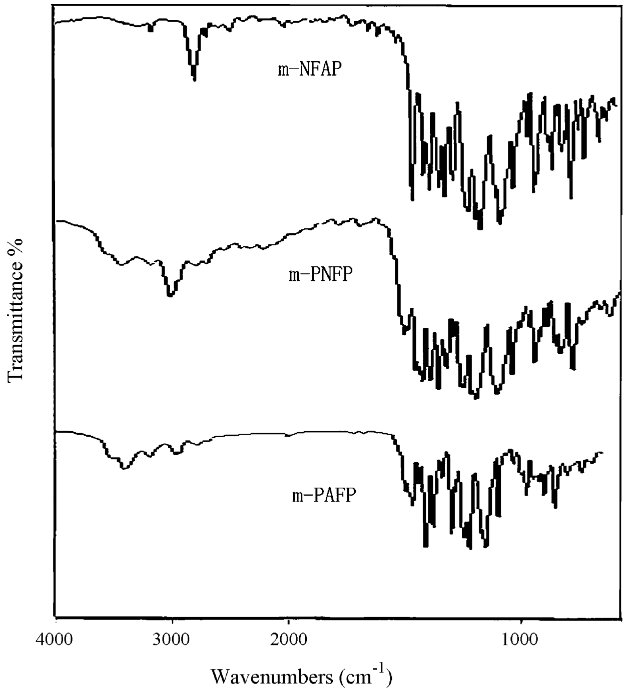
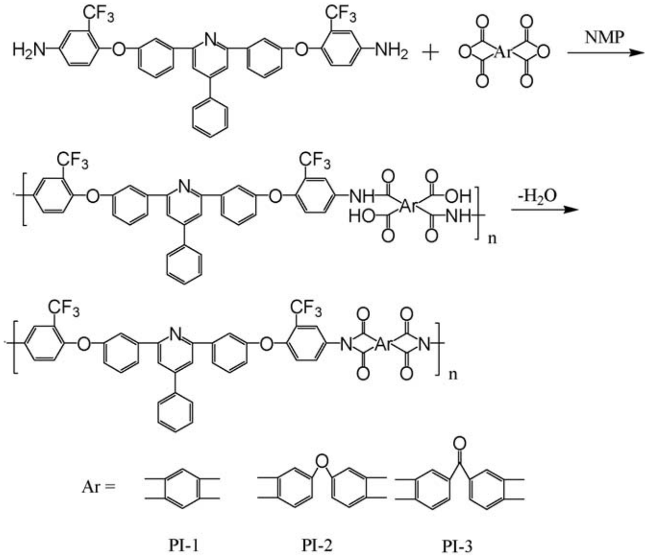


Fig. 2. FT-IR spectra of *m*-NFAP, *m*-PNFP, and *m*-PAFP.



Scheme 2. Synthesis of the polyimides.

high yields (95–98%), and elemental analyses show that compositions found of the repeating unit of them can agree with those calculated of that of them well as shown in Scheme 2. Meanwhile, the inherent viscosities values of these polyimides ranged from 0.56 to 1.02 dL/g, which indicated formation of high molar masses. Fig. 4 demonstrates IR spectra of polyimides. All the polyimides exhibited characteristic imide group absorptions around 1770 (asymmetrical C=O stretching) and 1715 cm^{-1} (symmetrical C=O stretching), 1375 cm^{-1} (C–N stretching), and together with some strong absorption bands in the region of 1300–1100 cm^{-1} (C–O stretching). There was no existence of the characteristic absorption bands of the amide group near 3200–3365 cm^{-1} (N–H stretching), indicating polymers had been fully imidized.

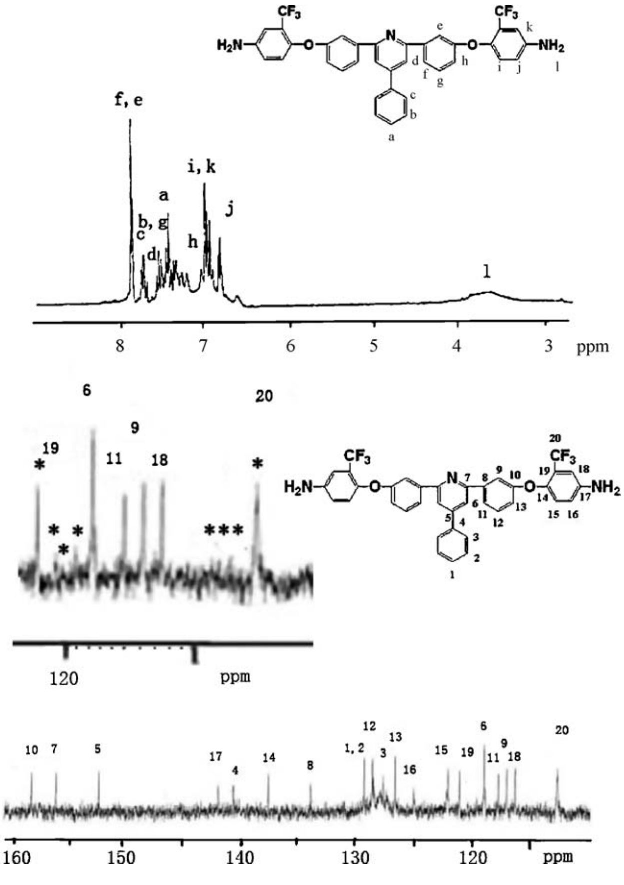


Fig. 3. ^{1}H and ^{13}C NMR spectra of *m*-PAFP.

2.3. Solubility of the resulting polyimides

The solubility of the PIs was determined by dissolving 10 mg of polymers into 1 mL of organic solvent at room temperature or upon heating, as shown in Table 2. It can be seen that all the polyimides exhibited good solubility in common organic solvents, such as NMP, DMSO, DMAc, DMF and *m*-cresol, even at room temperature in most cases. The good solubility should be resulted from both the flexibility of ether groups and the bulk pendent trifluoromethylphenyl group in the polyimide structure, which decreased the interaction between polymer chains. In addition, the solubility varies depending upon the dianhydride used. PI-2 possesses the better solubility at room temperature, because of the presence of the flexible ether groups, respectively. It can be seen that the good solubility of PI-2 in THF indicates their potential applications in areas where temperature is sensitive.

As shown in Table 2, the PI series obtained via chemical imidization could be dissolved in organic polar solvents even at room temperature in most cases. However the PI series prepared via thermal imidization had poorer solubility than those prepared

Table 1
Physical properties and elemental analysis of the polyimides.

Polyimide	Yield (%)	η_{inh} (dL/g)	Composition of repeating unit	Elemental analysis (%)			
					C	H	N
PI-1	95	0.56	$C_{47}H_{23}N_3F_6O_6$	Calcd. Found	67.93 68.01	2.77 2.60	5.06 5.11
PI-2	98	1.02	$C_{53}H_{27}N_3F_6O_7$	Calcd. Found	68.30 68.46	2.90 3.20	4.51 4.50
PI-3	96	0.98	$C_{54}H_{27}N_3F_6O_7$	Calcd. Found	68.48 68.56	2.85 2.68	4.44 4.77

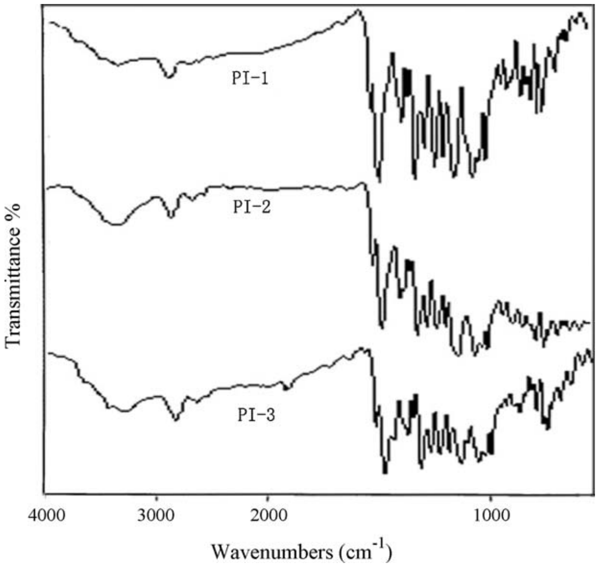


Fig. 4. FT-IR spectra of polyimides.

chemical. The difference insolubility of PI between thermal and chemical imidization can be explained by the imidization reaction mechanism [29,30].

From Table 2, we summarized the results and compared with polyimides reported [27,28]. It can be seen all the resulted FPIs exhibited good solubility in common organic solvents. A comparison of the solubility of FPIs shows that PI-1, PI-2 and PI-3 have better solubility in strong polar solvents, even at room temperature. According to the comparison in Table 2, FPI exhibited comparable solubility, which was better than that of non-fluorinated PIs. This indicates that introduction of trifluoromethyl group, despite its position, can enhance solubility of polyimides.

2.4. X-ray diffraction data

The crystallinity of the polyimides was examined by wide-angle X-ray diffraction analysis with graphite monochromatized Cu Kα radiation, 2θ ranging from 0° to 80°, using the polyimide films obtained by thermal cyclodehydration as samples, and the results were shown in Fig. 5. The X-ray diffraction curves of the polyimides express a set of wider diffraction peaks, these should be evidences that indicate the polyimides holding heterogenous morphology, and should also be a reason that could obtain transparent films from these polyimides. The polyimide based on PI-1 shows some crystalline character and exhibits two peaks around 14° and 17°, which indicate a little of crystalline morphologies in the resulting polyimide. These should be related to rigidity and planar structure of the polymer chains, as well as due to the more efficient packing of polymer chains containing pyromellitimide unit. The polyimides based on PI-2 and PI-3 show amorphous patterns, and this is because the presence of flexible ether link induces looser chain packing and reveals a large decrease in crystallinity. Therefore, the amorphous nature of the resulting polyimides would endow them a good solubility.

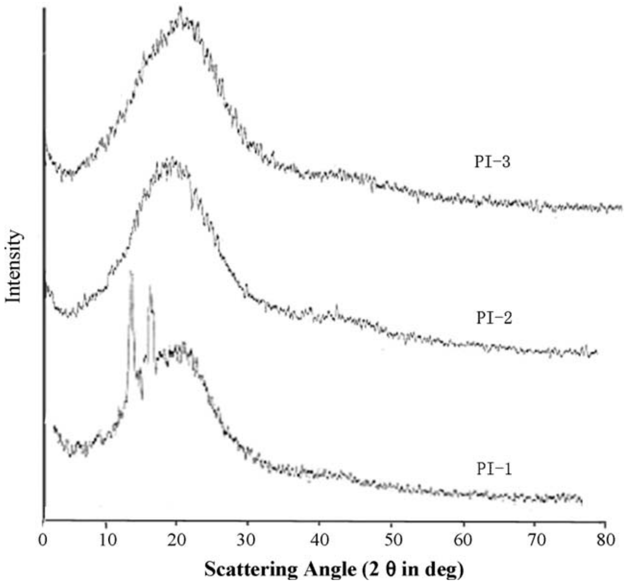


Fig. 5. Wide-angle X-ray diffraction curves of the polyimides.

Table 2
Solubility of polyimides[a].

Polymer	Solvent[b]						
	NMP	DMSO	DMAc	DMF	*m*-Cresol	$CHCl_3$	THF
PI-1[c]	++	+	++	++	+–	+–	+–
PI-2[c]	++	+	++	++	+–	+	+
PI-3[c]	++	+	++	++	+–	+–	+–
PI-1[d]	+	+–	+–	+–	+–	––	––
PI-2[d]	++	+–	+–	+–	+–	––	+–
PI-3[d]	+	+–		+–	+–	––	––
6FPI-1[e]	+–	+–	+–	+–	+–	––	––
6FPI-2[e]	++	++	++	++	++	++	++
6FPI-3[e]	+	+	+	+	+	+–	+–
PI-a[f]	+–	+–	+–	+–	+–	––	––
PI-b[f]	+	+–	+	+–	+	+–	+–
PI-c[f]	+–	+	+–	+–	+–	+–	+–

[a] Qualitative solubility was determined with 10 mg of polymer in 1 mL of solvent; ++, soluble at room temperature; +, soluble on heating; +–, partially soluble on heating; ––, insoluble.

[b] NMP, *N*-methylpyrrolidone; DMAC, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethylsulfoxide.

[c] Measured by chemical cyclization polyimide derived from the corresponding poly(amic acid)s.

[d] Measured by thermal cyclization polyimide derived from the corresponding poly(amic acid)s.

[e] Results reported by Shang et al. in the literature [27].

[f] Results reported by Wang et al. in the literature [28].

2.5. Thermal properties of the polyimides

DSC and TGA were applied to evaluate the thermal properties of the polyimides, the DSC and TGA curves of the polyimides are shown in Figs. 6 and 7, respectively, and thermal analysis data from the TGA and DSC curves of the polyimides are summarized in Table 3. DSC revealed that rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so that T_g of polymer could be easily read in the second heating trace of DSC. The data in Table 3 represents that T_g values of these PIs are in the range of 187–211 °C. As we expected, the T_g values of these polyimides depended on the structure of the dianhydride component and decreased with increasing flexibility of the polyimide backbones according to the applied structure of the dianhydride. PI-2, obtained from ODPA, showed a lower T_g because of the presence of a flexible ether linkage between the phthalimide units. PI-1, derived from PMDA, exhibited the highest T_g because of the effect of the rigid polymer backbone. In comparison with analogous polyimides derived from a pyridine-containing diamine monomer, PAFP and PAPP, reported by Shang et al. and Wang et al. [27,28]. The T_g values of these polyimides are lower than analogous polyimides (T_g, 268–338 and 258–312 °C), which suggests that the nonlinear structure in the polymer

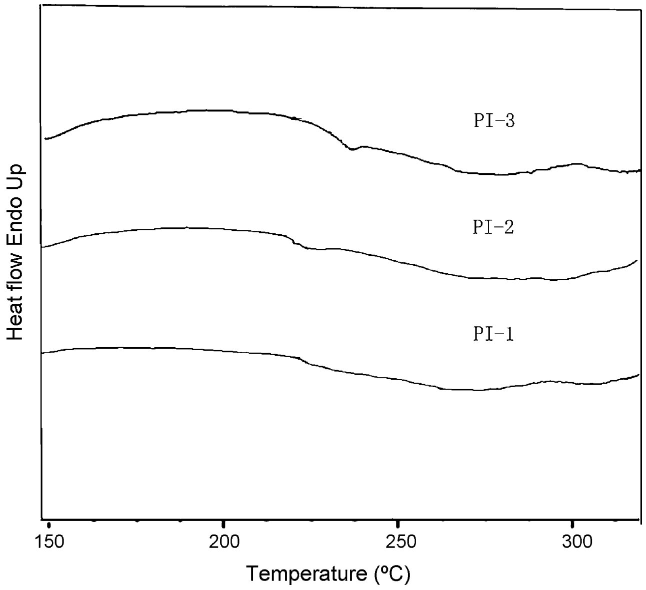


Fig. 6. DSC curves of the polyimides.

backbone decreased the intermolecular interactions, thus leading to a decreased T_g value.

For the thermal stability of the polyimides, Table 3 gives the temperature of 5% and 10% weight loss in air, respectively, i.e. T_5 and T_{10} values. The T_5 and T_{10} values of the polyimides were in the range 511–532 and 550–596 °C in air, and the amount of residue of all polyimides at 800 °C in air was higher than 50%, especially, the polyimide derived from *m*-PAFP–BTDA had the highest residue yield up to 58%. The data from thermal analysis show that the resulting polyimides have fairly high thermal stability.

2.6. Mechanical properties

High-quality polyimide films could be prepared by casting the poly(amide acid) solutions on glass plates followed by the thermal curing in the following procedure 80 °C overnight, 110, 150, 180, 210, 230, and 250 °C for 30 min at each temperature. These films were subjected to tensile tests. Table 4 shows the mechanical properties of the polyimides, including the tensile strength, tensile modulus, and elongation at break. Polyimide films had tensile strengths, elongation at break, and tensile modulus in the ranges of 90.1–96.6 MPa, 8.9–10.7%, and 1.65–1.98 GPa, respectively, indicating that they are strong and tough materials.

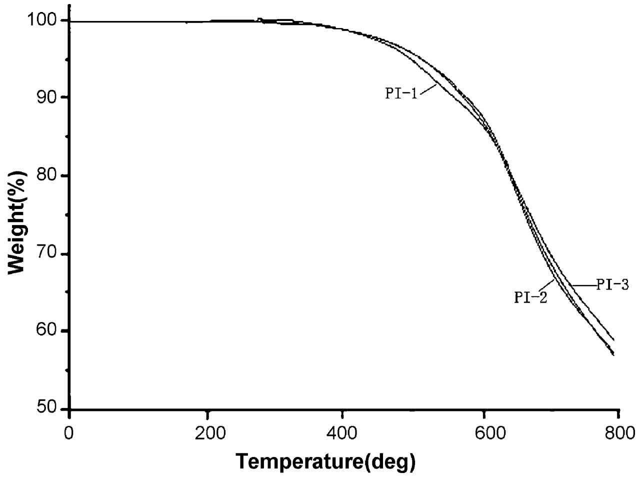


Fig. 7. TGA curves of the polyimides.

Table 3
Thermal properties of the polyimides.

Polyimides	Thermal properties[a]				
	T_g (°C)	T_d (°C)	T_5 (°C)	T_{10} (°C)	Rw (%)
PI-1	211	364	511	550	57
PI-2	187	382	532	596	57
PI-3	203	370	531	588	58

[a] T_g: determined by DSC curve; T_d: decomposition-starting temperature; T_5: the temperature at 5% weight loss in air; T_{10}: the temperature at 10% weight loss in air; Rw: residual weight retention at 800 °C.

2.7. Dielectric properties

The dielectric constant values of the polyimide films at 1 MHz and 10 MHz at 25 °C, which is summarized in Table 5. As shown in Table 5, the dielectric constants of FPIs at 1 and 10 MHz were in the range of 2.84–2.98 and 2.64–2.74, respectively. In this study, all polyimide samples were prepared with the same curing process. Obviously, the dielectric constants for each sample are quite different, and strongly depend on the chemical structure. The fluorinated polyimide films FPIs exhibited lower dielectric constants. This may be explained by the increase in free volume and decrease in polarizability. The incorporation of the bulky trifluoromethylphenyl group prohibits close packing of the polymer chains and reduces interchain charge transfer of the highly polar dianhydride groups, in addition, the large fluorine atoms increase the free volume fraction in the polymer, thereby essentially reducing the number of polarizable groups in a unit volume. The large electron negativity of the C–F bond also lowered the electronic polarization in the polymer. Polyimides based on *m*-PAFP have lower dielectric constants compared with conventional polyimides such as PMDA/ODA polyimide film (3.44 at 10 MHz) and those of many fluorinated polyimides (6FDA–MPD: 3.0; 6FDA–7FMDA: 2.9; TFDA-p-APB: 2.89) [4,30].

The water uptake of these polyimides was investigated, and the results are listed in Table 5. The data indicate that polyimides exhibited low water uptake. The reason is the structure of the CF_3 group.

Table 4
Mechanical properties of the polyimides.

Polyimide	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at breakage (%)
PI-1	90.1	1.98	8.9
PI-2	96.6	1.65	10.7
PI-3	95.5	1.84	9.9

Table 5
Dielectric properties and water uptake.

Polyimide	Dielectric constant (1 MHz)[a]	Dielectric constant (10 MHz)[a]	Water uptake[b] (%)
PI-1	2.91	2.69	0.63
PI-2	2.84	2.64	0.52
PI-3	2.98	2.74	0.66

[a] Measured by Agilent 4291B at room temperature (dry dielectric constant).

[b] Water uptake was the immersion of the films in water at 25 °C for 24 h, followed immediately by weighing.

3. Conclusions

A new pyridine-containing aromatic diamine monomer, 4-phenyl-2,6-bis[3-(4′-amino-2′-trifluoromethyl-phenoxy) phenyl] pyridine (*m*-PAFP) was successfully synthesized, which led to a number of novel fluorinated polyimides by two-step polycondensation method via reacting with various aromatic dianhydrides. The resulted polyimides exhibited good solubility in many organic solvents and could be cast into transparent, tough, and flexible films. The novel polyimides obtained have fairly high T_g values, excellent thermal stability in air, as well as good dielectric properties.

4. Experimental

4.1. Materials

Commercially available 3-hydroxyacetophenone (Shanghai Chemical Reagents Corp., China), 2-chloro-5-nitrotrifluoromethylbenzene (Acros), benzaldehyde (Beijing Chemical Reagents Corp., China), potassium carbonate (Fuchen Chemical Reagents Corp., Tianjin, China), hydrazine monohydrate (Shanghai Chemical Reagents Corp., China), and 10% Pd/C (Acros) were used without further purification. 4,4′-Oxydiphthalic anhydride (ODPA; Shanghai Nanxiang Chemical, China) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA; Beijing Chemical Reagents, China) were recrystallized from acetic anhydride before use. Pyromellitic dianhydride (PMDA; Beijing Chemical Reagents, China) was purified by sublimation at 200–220 °C. *N*,*N*-Dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP) were purified by distillation under reduced pressure over calcium hydride and were stored over 4-Å molecular sieves. Reagent-grade potassium carbonate was dried in vacuo at 130 °C for 12 h before use. All other solvents were obtained from various commercial sources and used without further purification.

4.2. Measurements

^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL EX-400 spectrometer and JEOL EX-300 spectrometer using tetramethylsilane as the internal reference. FT-IR spectra (KBr) were recorded on a Nicolet Nexus 670 FT-IR spectrometer. Elemental analyses were determined by a PerkinElmer model 2400 CHN analyzer. DSC testing was performed on a PerkinElmer DSC 7 or Pyris 1 differential scanning calorimeter at a scanning rate of 20 °C/min in flowing nitrogen (30 cm/min), and the T_g values were read at the DSC curves at the same time. TGA was conducted with a TA Instruments TGA 2050, and the experiments were carried out with approximately 10-mg samples in flowing air (flow rate = 100 cm^3/min) at a heating rate of 20 °C/min. WaXD measurements were performed at room temperature (ca. 25 °C) on a Siemens Kristalloflex D5000 X-ray diffractometer with nickel-filtered Cu Kx radiation (wavelength = 1.5418 Å) at 40 kV and 30 mA.

4.3. Synthesis of the monomer

4.3.1. 1,3-(4′-Nitro-2′-trifluoromethyl-phenoxy)-acetophenone (m-NFAP)

In a 250 mL three-necked flask equipped with a nitrogen inlet, 6.82 g (0.05 mol) of 3-hydroxyacetophenone, 11.2 g (0.05 mol) of 2-chloro-5-nitro trifluoromethyl-benzene, 6.9 g (0.05 mol) of potassium carbonate, and 100 mL of *N*,*N*-dimethylformamide (DMF) was stirred at 100 °C for 8 h. Then, it was poured into 500 mL of ice/water to give brown precipitates. The crude product was obtained by filtration, washed with water, and dried in vacuum overnight. After recrystallization from ethanol, 15.4 g of *m*-NFAP was obtained. The yield is 95%, and the melting point is 64–68 °C.

FT-IR (KBr): 1691 cm^{-1} (C=O stretching) and 1521, 1349 cm^{-1} (C–NO$_2$ stretching) and 1335 cm^{-1} (C–N stretching) and 1161, 1135, 1114 cm^{-1} (C–F and C–O stretching). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 8.61 (s, 1H), 8.31 (d, *J* = 2.4 Hz, 1H), 7.69 (d, *J* = 1.2 Hz, 1H), 7.66 (s, 1H), 7.58 (t, J_1 = 8.4, J_2 = 7.2 Hz, 1H), 6.30 (d, *J* = 9.0 Hz, 2H), 2.59 (s,3H). ^{13}C NMR (400 MHz, CDCl$_3$): δ (ppm) 196.53, 160.34, 154.57, 142.17, 139.54, 130.88, 128.86, 125.98, 125.06, 123.95, 119.85, 117.36, 114.81 MS (EI): 325(M$^+$). Elem. Anal. Calcd. for $C_{15}H_{10}F_3NO_4$: C 55.39%, H 3.10%, N 10.29%, while Found C 54.96%, H 2.98%, N 9.95%.

4.3.2. 2,4-Phenyl-2,6-bis[3-(4′-nitro-2′-trifluoromethyl-phenoxy) phenyl] pyridine (m-PNFP)

31.68 g (0.05 mol) of *m*-NFAP, 2.65 g (0.025 mol) of benzaldehyde, 25.05 g (0.325 mol) of ammonium acetate and 40 mL of glacial acetic acid were placed into a 100 mL three-necked flask equipped with a mechanical stirrer and a reflux condenser. The mixture was refluxed with stirring for 4 h. Then the precipitated solid was filtered off and washed thoroughly with water. After drying under vacuum at 60 °C, 8.96 g of yellow powder of *m*-PNFP was obtained. The yield is 50%, and the melting point is 95–97 °C.

FT-IR (KBr): 3086 cm^{-1} (C–H stretching) and 1531, 1351 cm^{-1} (C–NO$_2$ stretching) and 1334 cm^{-1} (C–N stretching) and 1160, 1137, 1116 cm^{-1} (C–F and C–O stretching). ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm) 8.45 (s, 2H), 8.32 (d, *J* = 10.5 Hz, 2H), 8.26 (d, *J* = 1.2 Hz, 2H), 8.20 (s, 2H), 8.03 (d, *J* = 8.8, 2H), 7.93 (s, 2H) 7.86 (t, J_1 = 5.4, J_2 = 4.2 Hz, 2H), 7.68 (t, J_1 = 2.4, J_2 = 2.7 Hz, 2H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.38 (d, *J* = 4.4 Hz, 2H), 7.16 (t, *J* = 4.8 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d6): δ (ppm) 160.23, 159.66, 157.61, 155.04, 149.99, 144.78, 141.90, 131.28, 131.20, 130.54, 128.83, 124.91, 123.64, 122.03, 121.65, 120.16, 119.46, 118.31, 117.50, 114.57. MS (EI): 717(M$^+$). Elem. Anal. Calcd. for $C_{37}H_{21}F_6N_3O_6$: C 61.93%, H 2.95%, N 5.86%, while Found C 61.02%, H 2.88%, N 5.78%.

4.3.3. 3,4-Phenyl-2,6-bis[3-(4′-amino-2′-trifluoromethyl-phenoxy) phenyl] pyridine (m-PAFP)

To a 250 mL three-necked flask equipped with a dropping funnel and a reflux condenser, 7.17 g (0.01 mol) of *m*-PNFP, 0.2 g of palladium on activated carbon (Pd/C10%), and 100 mL of anhydrous ethanol were added, and after heating to refluxing temperature with stirring, 10 mL of hydrazine monohydrate was added dropwise in 2 h. After addition of hydrazine monohydrate was finished, the mixture was refluxed for additional 8 h. Then, the mixture was filtered and the resultant solid was extracted using enough ethanol. On concentrating all the ethanol solution, yellow precipitation was appeared, which was filtered off and recrystallized from ethanol to get 5.71 g of needle crystal of *m*-PAFP. The yield is 87%, and the melting point is 81–83 °C.

FT-IR (KBr): 3453, 3379 cm^{-1} (N–H stretching) and 1156, 1127, 1116 cm^{-1} (C–F and C–O stretching). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 7.58 (d, *J* = 2.4, 2H, Hf), 7.84 (s, 2H, He), 7.73 (d, *J* = 1.8 Hz, 2H, Hc), 7.71 (s, 2H, Hd), 7.49–7.42 (m, 4H, Hb, Hg), 7.38 (s, 1H, Ha), 7.11 (d, *J* = 5.1 Hz, 2H, Hh), 7.02–6.95 (m, 4H, Hi, Hk), 6.81 (d, *J* = 3.9 Hz, 2H, Hj), 3.81–3.40 (m, 4H, Hl). ^{13}C NMR (400 MHz, CDCl$_3$): δ (ppm) 158.76 (C10), 156.67 (C7), 154.10 (C5), 142.54 (C17), 141.23 (C4), 138.78 (C14), 134.84 (C8), 129.84 (C1, C2), 129.14 (C12), 128.21 (C3), 127.18 (C13), 125.57 (C16), 122.78 (C15), 122.58–119.70 (C19), 119.06 (C6), 118.40 (C11), 117.16 (C9), 116.68 (C18), 113.00–114.81 (C20). MS (EI): 657(M$^+$). Elem. Anal. Calcd. for $C_{37}H_{25}F_6N_3O_2$: C 67.58%, H 3.83%, N 6.39%, while Found C 66.96%, H 3.98%, N 6.95%.

4.4. Polyimide synthesis

The diamine monomer was reacted with three kinds of commercially available aromatic dianhydrides, PMDA, ODPA, and

BTDA to give the corresponding poly(ether-imide)s, as shown in Scheme 2. A typical example of polymerization is as follows.

To a stirred solution of 1.3146 g (2.0 mmol) of *m*-PAPP in 3.4 mL NMP was added 0.6444 g (2.0 mmol) of BTDA. The mixture was stirred at room temperature for 24 h under nitrogen atmosphere, forming a viscous solution of poly(amide acid) (PAA) precursor in NMP. Either thermal or chemical imidization procedures were chosen to form polyimides. Chemical imidization was carried out by adding 3 mL of a mixture of acetic anhydride/pyridine (2/1, v/v) into the PAA solution with stirring at ambient temperature for 1 h, then the mixture was stirred at 100 °C for 4 h to yield a homogeneous polyimide solution, which was poured slowly into ethanol to give a fibrous precipitate, which was collected by filtration, washed thoroughly with hot methanol, and dried at 80 °C in vacuum overnight. For the thermal imidization, the PAA solution was spread on a glass plate and the solvent was removed at 80 °C overnight. Imidization was carried out by thermalcyclodehydration of the poly(amic acid) film by sequential at 110, 150, 180, 210, 230 and 250 °C for 30 min each. Polyimide film was stripped from the glass substrate by immersing the glass plates in hot water.

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