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Journal of Fluorine Chemistry 129 (2008) 56–63

JOURNAL OF FLUORINE CHEMISTRY

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Synthesis and properties of new pyridine-bridged poly(ether-imide)s based on 4-(4-trifluoromethylphenyl)-2, 6-bis[4-(4-aminophenoxy)phenyl]pyridine

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Received 10 August 2007; received in revised form 30 August 2007; accepted 30 August 2007
Available online 4 September 2007

Abstract

A novel pyridine-containing aromatic diamine monomer, 4-(4-trifluoromethylphenyl)-2,6-bis[4-(4-aminophenoxy)phenyl]pyridine (FAPP), was synthesized via the modified Chichibabin pyridine synthesis of 4-(4-nitrophenoxy)-acetophenone with 4-trifluoromethyl-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 process. The resulting polyimides exhibited good solubility in aprotic amide solvents and *m*-cresol, such as *N*,*N*-dimethylacetamide, *N*-methyl-2-pyrrolidone, and *m*-cresol, *etc*., which possessed the inherent viscosities of 0.76–0.91 dL/g. Strong and flexible poly(ether-imide) films were obtained, which showed excellent thermal properties with the glass transition temperatures of 268–353 °C, the temperature at 5% weight loss of 547–595 °C, and the residue at 700 °C of 65–74% in nitrogen, good mechanical properties with the tensile strengths of 87.6–104.2 MPa and elongations at breakage of 8.9–12.6%, and good optical transparency with the cut-off wavelengths of 357–380 nm, as well as low dielectric constants in the range of 2.49–3.04 at 1 MHz and low water uptake 0.43–0.69%. Furthermore, the resulted polyimides derived from FAPP were compared with non-fluorinated analogous polyimides and fluorinated analogous polyimides with trifluoromethyl groups in different positions, and the effects of substituents were also investigated and discussed.

Keywords: Fluorinated polyimides; Polyimides; Diamine monomer; Pyridine moieties

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1. Introduction

Aromatic polyimides are one of the most important classes of high-performance polymers used in the aerospace, microelectronics, and optoelectronics industries because of their excellent thermal, mechanical and electrical properties as well as outstanding chemical resistance [1–3]. However, despite the excellent combined properties, their widespread applications are often limited by their poor processability, limited solubility in common organic solvents and high melting point, which make it impossible for most polyimides to be directly processed in their imidized forms. In order to overcome these limitations, soluble polyimides have been targeted by many efforts, including introduction of flexible linkages [4–6], bulky units [7,8], bulky pendent substituents [9–11], or non-coplanar moieties [12,13], in the polymer backbone. Recently, considerable attention has been devoted to the fluorinated aromatic poly(ether-imide)s, especially trifluoromethyl-containing poly(ether-imide)s, with excellent solubility and low refractive indices, water uptake, and dielectric constant [14–17]. It was found that the incorporation of bulky –CF_3 into poly(ether-imide) 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 increase in free volume. The fluorinated polyimides also provided other merits such as good thermal and thermo-oxidative stability and low moisture absorption.

However, as is well known, introduction of some groups, such as flexible ether and acyclic linkages, *etc*., to the polyimide backbones will sacrifice their some advantageous properties, such as thermal stability and mechanical properties. It has been proved that introduction of rigid heteroaromatic

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0022-1139/$ – see front matter
doi:10.1016/j.jfluchem.2007.08.014

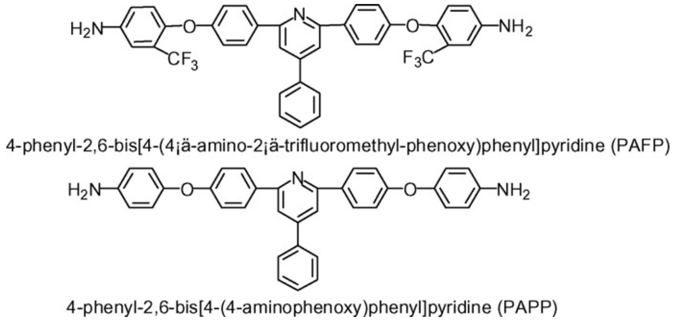


Fig. 1. PAFP and PAPP diamine monomers.

pyridine ring to the polymer backbone could endow it excellent thermal and thermo-oxidative stability, which should be useful to decrease the negative effects resulted from the introduction of flexible ether linkages in the poly(ether-imide)s backbone [18–25].

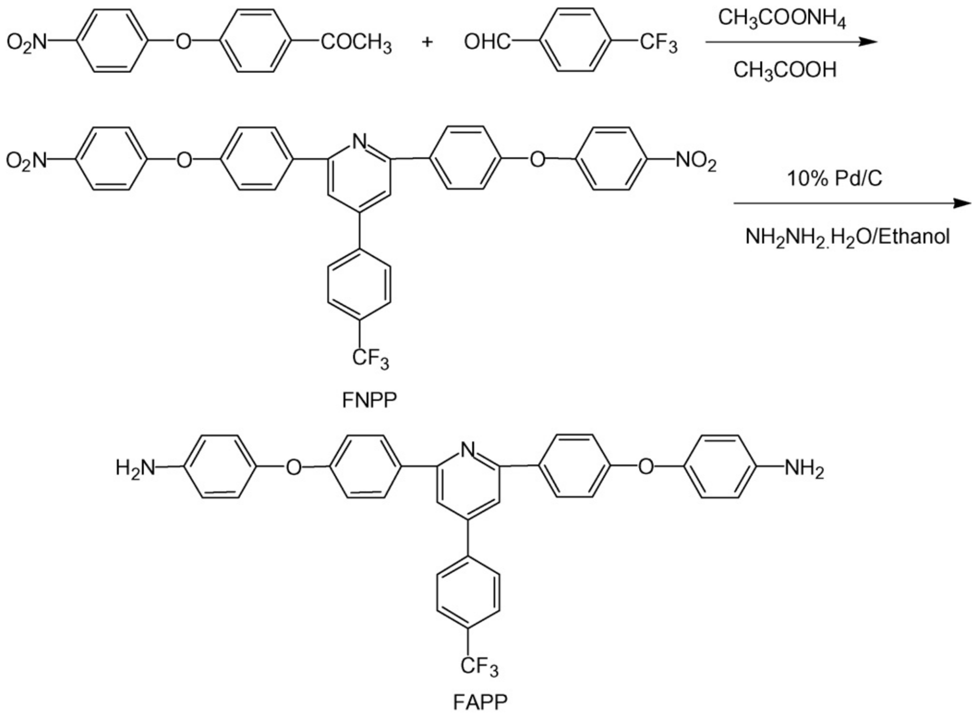
As part of our continuing efforts on soluble polyimides with high thermal stability and low dielectric constant for advanced microelectronics applications [26,27], this work deals with the synthesis and characterization of a series of fluorinated pyridine-bridged poly(ether-imide)s from 4-(4-trifluoromethylphenyl)-2,6-bis[4-(4-aminophenoxy)phenyl]pyridine (FAPP) and various commercially available aromatic dianhydrides. The solubility, moisture absorption, and thermal, mechanical, optical, and dielectric properties of the resulting polyimides were investigated. Since the designed poly(ether-imide)s are composed of flexible ether linkages, rigid pyridine rings, pendent phenyl groups, and bulky trifluoromethyl groups, they should be expected to exhibit an enhanced solubility, excellent thermal properties, outstanding mechanical properties, and good optical and dielectric properties. Furthermore, to investigate the effect of trifluoromethyl substituents on the polymer properties, the polyimides derived from FAPP were compared with analogous polyimides derived from a pyridine-containing diamine monomer with two $–CF_3$ groups in *meta*-position of $–NH_2$ group, 4-phenyl-2,6-bis[4-(4′-amino-2′-trifluoromethyl-phenoxy)phenyl]pyridine (PAFP), reported by Shang et al. [28], and polyimides derived from a non-fluorinated pyridine-containing diamine, 4-phenyl-2,6-bis[4-(4-aminophenoxy)phenyl]pyridine (PAPP) [29], as shown in Fig. 1.

2. Results and discussion

2.1. Synthesis of diamine

The diamine monomer, 4-(4-trifluoromethylphenyl)-2,6-bis[4-(4-aminophenoxy)phenyl]pyridine (FAPP), was prepared in a high yield by the catalytic reduction of a intermediate dinitro compound, 4-(4-trifluoromethylphenyl)-2,6-bis[4-(4-nitrophenoxy)phenyl]pyridine (FNPP), which was obtained by the modified Chichibabin pyridine synthesis of 4-(4-nitrophenoxy)-acetophenone (NPAP) with 4-trifluoromethyl-benzaldehyde in the presence of ammonium acetate and acetic acid, as shown in Scheme 1. The new aromatic pyridine-containing diamine was stable in atmosphere at room temperature and pure enough to prepare polyimides via polymerization with commerce aromatic dianhydride monomers.

FTIR, ^{1}H NMR, and elemental analysis were used to confirm the structure of the intermediate FNPP and diamine monomer FAPP. The results of elemental analysis of FNPP and FAPP shown in Section 3 showed that the measured values match the calculated ones. The FTIR spectrum of FNPP showed two



Scheme 1. Synthesis of the diamine monomer FAPP.

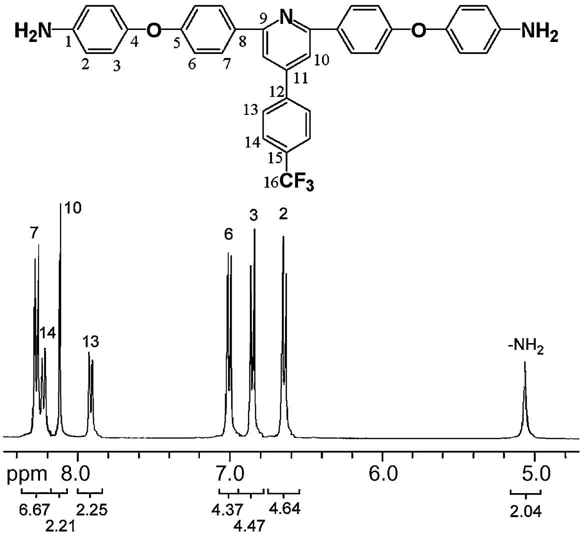


Fig. 2. ^{1}H NMR spectrum of FAPP in DMSO-d_6 (400 MHz).

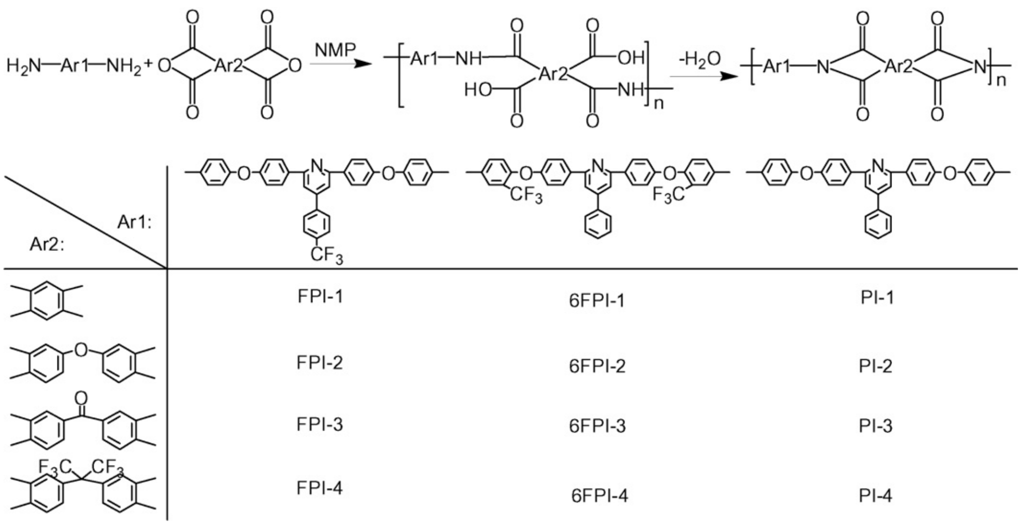
characteristic bands at 1529 and 1345 cm^{-1} (–NO_2 asymmetric and symmetric stretching), while the characteristic absorptions of the nitro groups disappeared and the amino group showed a pair of N–H stretching absorptions in the region of 3300–3500 cm^{-1} in the FTIR spectrum of FAPP. Fig. 2 presents the ^{1}H NMR spectrum of the diamine monomer FAPP in DMSO-d_6, in which signals in the range of 6.64–8.28 ppm were ascribed to the protons of the aromatic rings and the signal in 5.06 ppm was ascribed to the protons of –NH_2 group. All the results support unambiguously the structure shown in Scheme 1.

2.2. Synthesis of polyimides

The diamine monomer was reacted with four kinds of commercially available aromatic dianhydrides, PMDA, ODPA, BTDA, and 6FDA, 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(amide acid)s intermediate. Firstly, the diamine was dissolved in measured amount of dry NMP and the equimolar amount of dianhydride monomers were added to the solution slowly. After completing the addition, the solutions were stirred for 24 h at room temperature, forming viscous poly(amide acid) solutions. 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 are summarized in Table 1. According to the data from Table 1, the resulting polyimides all get high yields (95–98%), and the inherent viscosities values of these poly(amide acid)s and polyimides were in the range of 1.22–1.43 and 0.76–0.91 dL/g, respectively, which indicated formation of high molar masses. This is consistent with the fact that tough and flexible films could be obtained by coating and solvent evaporation of polymer solutions. Gel permeation chromatography of polyimide FPI-4 was run in THF solvent, was ca. 30,000.

The formation of polyimides was confirmed by FTIR spectroscopy. Fig. 3 compares representative FTIR spectra of poly(amide acid), polyimide FPI-4 resin prepared by chemical imidization method and polyimide FPI-4 film prepared by thermal imidization method, which based on FAPP and 6FDA. The complete conversion of amic acid to imide ring was proved by the disappearance of absorption bands at 1718 cm^{-1} corresponding to C=O stretching of carboxylic acid and 1661 cm^{-1} corresponding to C=O amide stretching, together with the appearance of absorption bands at about 1785 cm^{-1} (asymmetrical C=O stretching), 1728 cm^{-1} (symmetrical C=O stretching), 1377 cm^{-1} (C–N stretching), and 722 cm^{-1} (C=O bending) corresponding to the characteristic of imide bands. According to Fig. 3, the FTIR spectrum of polyimides FPI-4 obtained either by thermal or by chemical imidization method exist similar absorption except in the region of 3100–3700 cm^{-1}. The absorption band of FPI-4 obtained by chemical imidization at 3100–3700 cm^{-1} should be due to the contribution of rudimental solvent, while there is no rudimental



Scheme 2. Synthesis of the polyimides FPIs, and structure of PIs and 6FPIs.

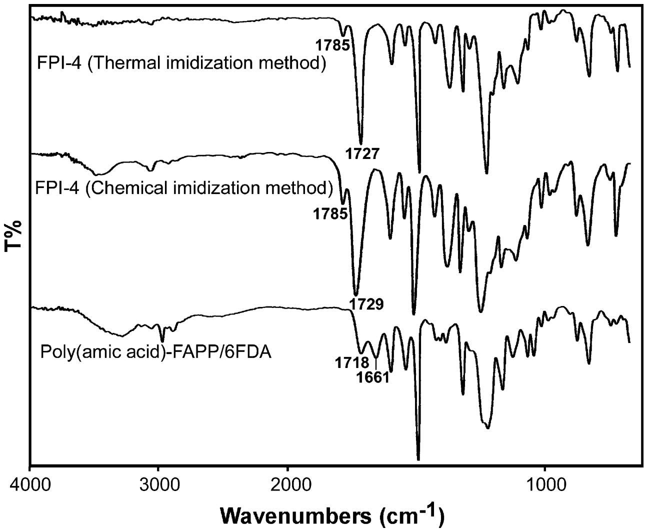


Fig. 3. FTIR spectra of poly(amide acid), chemical imidization polyimide FPI-4, and thermal imidization FPI-4 derived from FAPP and 6FDA.

solvent exist in FPI-4 film obtained by thermal imidization because of the high temperature process. These results indicate that full imidization polyimide can be obtained using both kinds of imidization methods.

2.3. Solubility of polymers

The solubilities of the resulting poly(ether-imide)s were investigated in different organic solvents by dissolving 100 mg of polymers in 900 mg of solvent (10 wt.%) at room temperature or upon heating. Table 2 summarized the results and compared with polyimides reported previously [28,29]. It can be seen that almost all the resulted FPIs except FPI-1 exhibited good solubility in common organic solvents, such as NMP, DMAc, DMF, *m*-cresol, even at room temperature. The good solubility should result from the introduction of the flexible ether groups and the bulk pendent trifluoromethylphenyl group in polymer backbone, which decreased the interaction between polymer chains. In addition, the solubility varies depending upon the dianhydride used. A comparison of the solubility of FPIs shows that FPI-2 and FPI-4 have better solubility in strong polar solvents such as *m*-cresol, NMP, DMAc, and DMF at room temperature. It can also be seen that they showed good solubility in some low boiling-point solvents, such as THF and $CHCl_3$, which indicates that they should have potential applications in areas where temperature is sensitive. According to the comparison in Table 2, FPIs and 6FPIs exhibited comparable solubilities, which were better than that of PIs. This indicates that introduction of trifluoromethyl group, despite its position, can enhance solubility of polyimides.

Table 2
Solubility of the poly(ether-imide)s, and their comparison with previously reported polyimides [28,29]

Polymer	Organic solvents[a]							
	m-Cresol	NMP	DMAc	DMF	DMSO	THF	$CHCl_3$	MeOH
FPI-1[b]	+−	+−	+−	+−	+−	−−	−−	−−
FPI-2[b]	++	++	++	+	+	++	++	−−
FPI-3[b]	+	+	+	+	+	+−	+−	−−
FPI-4[b]	++	++	++	++	++	++	++	−−
PI-1[b]	+−	+−	+−	+−	+−	−−	−−	−−
PI-2[b]	+	+	+	+−	+−	+−	+−	−−
PI-3[b]	+−	+−	+−	+−	+−	+−	+−	−−
PI-4[b]	++	++	++	+−	+−	+	+	−−
6FPI-1[c]	+−	+−	+−	+−	+−	−−	−−	−−
6FPI-2[c]	++	++	++	++	++	++	++	−−
6FPI-3[c]	+	+	+	+	+	+−	+−	−−
6FPI-4[c]	++	++	++	++	++	++	++	−−

[a] Qualitative solubility was determined by dissolving 100 mg of polyimide in 900 mg of solvent at room temperature or upon heating; ++, soluble at room temperature; +, soluble on heating at 80 °C or reflux for THF, $CHCl_3$, and MeOH; +−, partially soluble on heating at 80 °C or reflux for THF, $CHCl_3$, and MeOH; and −−, insoluble.

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

[c] Results reported by Shang et al. in the literature [28].

2.4. DSC measurements

These FPIs exhibited no crystallization or melting transaction temperature in DSC measurements, as shown in Fig. 4. The glass transition temperature (T_g) values of these poly(ether-imide)s are summarized in Table 3, which ranged from 268 to 353 °C. Among the resulted FPIs, FPI-1 derived from FAPP and

Table 1
Physical properties and elemental analysis of the poly(ether-imide)s

Polymer	Yield (%)	η_{inh}[a] (dL/g)		$\bar{M}_n$[b]	PDI[c]	Elemental analysis(%)				Film quality[d]
		PAA	PI				C	H	N	
FPI-1	95	1.35	0.76	–	–	Calcd.	71.59	3.13	5.45	C, F and T
						Found	71.47	3.22	5.40	
FPI-2	97	1.43	0.81	–	–	Calcd.	72.30	3.47	4.86	C, F and T
						Found	72.14	3.61	4.69	
FPI-3	96	1.22	0.84	–	–	Calcd.	72.68	3.22	4.80	C, F and T
						Found	72.59	3.33	4.67	
FPI-4	98	1.31	0.91	29,740	1.79	Calcd.	66.20	2.83	4.21	C, F and T
						Found	66.08	2.91	4.09	

[a] Measured on 0.5% polymer solution in DMAc, at 30.0 ± 0.1 °C. PAA, poly(amide acid); PI, polyimide.

[b] $\bar{M}_n$, number-average molecular weight.

[c] Polydispersity index.

[d] C, clear; F, flexibal; T, tough.

Table 3
Thermal properties of the poly(ether-imide) films, and their comparison with previously reported polyimides [28,29]

Polymer	Thermal properties				
	T_g (°C)	T_d[a] (°C)	T_5[b] (°C)	T_{10}[b] (°C)	R_w[c] (%)
FPI-1[d]	353	572	595	611	72
FPI-2[d]	277	569	575	605	74
FPI-3[d]	268	579	581	610	73
FPI-4[d]	295	535	547	572	65
PI-1[d]	338	543	561	594	72
PI-2[d]	268	528	553	583	72
PI-3[d]	276	515	545	579	70
PI-4[d]	292	542	562	597	68
6FPI-1[e]	312	589	583	617	70
6FPI-2[e]	258	582	578	613	70
6FPI-3[e]	271	611	601	640	75
6FPI-4[e]	281	554	561	587	66

[a] T_d, onset decomposition temperature.
[b] T_5, and T_{10}, temperature at 5% and 10% weight loss.
[c] R_w, residual weight retention at 700 °C.
[d] Measured samples were obtained by thermal imidization method.
[e] Results reported by Shang et al. [28].

PMDA exhibited the highest T_g value because of the effect of the highest rigidity of PMDA among the four dianhydrides, on the contrary, FPI-2, FPI-3 and FPI-4 showed the lower T_g values due to the relative flexible polymer chain. However, it was also found that FPI-4 (derived from 6FDA and FAPP) showed higher T_g value than that of FPI-2 and FPI-3. This could be interpreted that the presence of hexafluoropropane might inhibit the free rotation of the polymer chain. According to the T_g values of polyimides PIs, FPIs, and 6FPIs in Table 3, FPIs exhibited higher glass transition temperatures than PIs without –CF_3, which might result from enhancement of large pendent trifluoromethylphenyl group to the rigidity of polymer chain, while 6FPIs exhibited the lowest T_g values, which might because the introduction of the bulky –CF_3 side groups in the polymer backbone decreased the intermolecular interactions, thus leading to a decreased T_g value [30]. That is to say that –CF_3 groups in the pendent phenyl groups in polyimide backbone showed positive effects on its thermal resistance while –CF_3 groups in the *meta*-positions of nitrogen showed negative effects on its thermal resistance in this case, which might be explained that the former enhanced the rigidity of polymer chain by inhibiting its free rotation while the later decreased the intermolecular interactions.

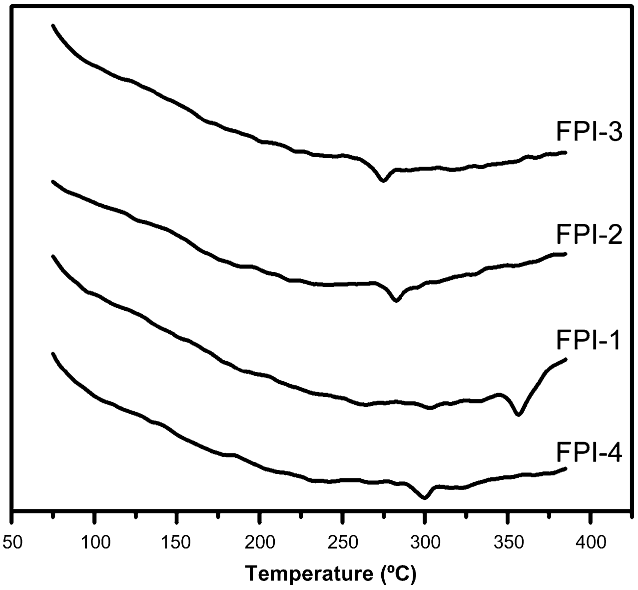


Fig. 4. DSC curves of the polyimide films.

The T_g values of the resulted poly(ether-imide)s are higher than commercial poly(ether-imide), Ultem 1000 (T_g, 217 °C), based on bisphenol-A diphthalic anhydride and *m*-phenylene diamine [31], and comparable to polyimide based on BTDA and ODA (T_g, 279 °C) [32]. However, the T_g values of these poly(ether-imide)s are lower than Kapton films derived from PMDA–ODA (T_g, 390 °C) [33].

2.5. Thermal stability

The thermal stability properties of the poly(ether-imide) films were evaluated by TGA. The TGA curves for these polymers are shown in Fig. 5, and the results are summarized in Table 3. These polymer films did not show obvious weight loss before the scanning temperature reached up to 530 °C implying that no thermal decomposition occurred and the onset decomposition temperatures were as high as above 535 °C. The 5% and 10% weight loss temperatures (T_5 and T_{10}), which were usually considered as the criterion in determining the thermal stability of high temperature polymers, were in range of 547–595 °C and 572–611 °C, respectively. Furthermore, the residual weight retentions at 700 °C in nitrogen were in the range of 65–74%. All the results indicated that the obtained poly(ether-imide) films exhibited excellent thermal stability. According to data in Table 3, almost all the trifluoromethyl-containing polyimides, FPIs and 6FPIs, showed higher or comparable onset decomposition temperatures, and 5% and 10% weight loss temperatures than non-fluorinated polyimides PIs implying that FPIs and 6FPIs exhibited better thermal stability than PIs. This can be explained that introduction of the strong electron negativity of –CF_3 groups might enhanced the polarity of the polymer, which should restrict the movement of polymer-link and lead better thermal stability [34].

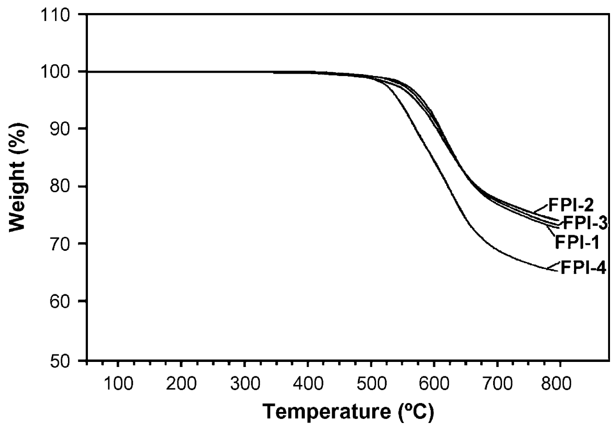


Fig. 5. TGA curves of the polyimide films.

Table 4
Mechanical properties of the polyimide films [28,29]

Polymer	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
FPI-1	99.1	9.4	1.57
FPI-2	97.8	12.6	1.43
FPI-3	104.2	11.8	1.74
FPI-4	87.6	8.9	1.17
PI-1[a]	112.1	13.2	1.21
PI-2[a]	104.4	15.4	1.12
PI-3[a]	105.2	10.7	1.88
PI-4[a]	89.2	9.5	1.22
6FPI-1[b]	88.3	5.5	2.23
6FPI-2[b]	103.4	8.5	1.94
6FPI-3[b]	96.9	6.6	2.12
6FPI-4[b]	73.1	4.5	1.63

[a] Results reported in the literature [29].

[b] Results reported by Shang et al. [28].

According to the data presented in Table 3, these poly(ether-imide) films showed higher onset decomposition temperatures, 5% and 10% weight loss temperatures, and char residues than many fluorinated poly(ether-imide)s [14–17,35]. This should be resulted from the introduction of pyridine ring into the polymer backbone, whose rigidity based on its symmetry and aromaticity should have contributions to the polymer thermal stability [20,21].

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 for 8 h, 120, 150, 200, and 250 °C for 1 h at each temperature. Mechanical properties of the resulted polymer films were investigated, and the results were summarized in Table 4. Polyimide FPIs had tensile strength, elongation at break, and tensile modulus in the ranges of 87.6–104.2 MPa, 8.9–12.6%, and 1.17–1.74 GPa, respectively, indicating that they are strong and tough polymeric materials. For the three series of polyimides PIs, FPIs, and 6FPIs, their mechanical properties were comparable, which showed that all of them exhibited good mechanical properties.

2.7. Optical and dielectric properties

Optical transparency properties of the resulted poly(ether-imide) films were investigated using UV–vis spectroscopy. The cut-off wavelengths (λ_0) of these polymers were summarized in Table 5, which ranged from 357 to 380 nm. The λ_0 of FPIs were affected by dianhydride moieties: λ_0 of FPI-3 is the maximum, FPI-1 and FPI-2 exhibit a lower λ_0, and FPI-4 shows the lowest λ_0. Both PIs and FPIs exhibited lower λ_0 than Kapton indicating their good transparency. It can also be seen that the fluorinated polyimides FPIs showed a lower cut-off wavelength and higher optical transparency than their respective CF_3-free analogs. This may be interpreted by reduction in the intermolecular charge-transfer complex (CTC) between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. Bulky and electron-withdrawing $-CF_3$ group in diamine moieties was effective in decreasing the intermolecular CTC formation between polymer chains through steric hindrance and the inductive effect [36]. A secondary positive effect of the $-CF_3$ groups on the film transparency was the weakened intermolecular cohesive force due to the lower polarizability of the C–F bond.

Furthermore, the obtained poly(ether-imide) films exhibited good dielectric properties. As shown in Table 5, the dielectric constants (ε) and dielectric dissipation factors ($\tan\delta$) of FPIs at 1 MHz were in the range of 2.49–3.04 and $(5.7–8.1) \times 10^{-3}$, respectively. The dielectric constants of FPIs vary depending on the dianhydride moieties: FPI-4 revealed lower dielectric constant than other three FPIs. Compared with CF_3-free analogs, 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. As a result, the fluorinated polyimides FPIs showed lower dielectric constants than non-fluorinated polyimides PIs, and the dielectric constants of the two series of polyimides were lower than that of Kapton H derived from PMDA–ODA (3.43 at

Table 5
Optical and dielectric properties and water uptake

Polymer	Film thickness (μm)	λ_0[a] (nm)	ε[b] (1 MHz)	$\tan\delta \times 10^{3}$[b] (1 MHz)	Water uptake (%)
FPI-1	40	373	2.99	7.9	0.64
FPI-2	31	376	2.92	6.8	0.55
FPI-3	35	380	3.04	8.1	0.69
FPI-4	39	357	2.49	5.7	0.43
PI-1	28	379	3.02	8.8	0.72
PI-2	33	375	3.06	7.4	0.64
PI-3	30	386	3.11	8.7	0.79
PI-4	23	360	2.53	7.7	0.51
Kapton	38	443	3.43	9.2	–

[a] λ_0, the cut-off wavelength.

[b] ε, $\tan\delta$, dielectric constant and dielectric dissipation factors at 1 MHz.

1 MHz) and comparable to those of many fluorinated polyimides (6FDA–MPD: 3.0; 6FDA–7FMDA: 2.9; TFDA-*p*-APB: 2.89) [21,37].

3. Experimental

3.1. Materials

4-(4-Nitrophenoxy)-acetophenone (NPAP) was prepared as described in a previous article [31]. 4-Trifluoromethyl-benzaldehyde (TCI) and hydrazine monohydrate (Beijing Chemical Reagents Corp., China) were used as received. 4,4′-Oxydiphthalic anhydride (ODPA, Shanghai Nanxiang Chemical Co., China), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, Beijing Chemical Reagents Corp., China) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA, Aldrich) were recrystallized from acetic anhydride before use. Pyromellitic dianhydride (PMDA, Beijing Chemical Reagents Corp., China) was purified by sublimation at 200–220 °C. 4,4′-Oxydianiline (ODA) was purified by vacuum sublimation prior to use. *N*,*N*-Dimethylacetamide (DMAc) and *N*-methy-2-pyrrolidone (NMP) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. All other solvents were obtained from various commercial sources and used without further purification.

3.2. Measurements

^{1}H NMR spectra were measured on a Mercury-plus400 spectrometer using tetramethylsilane as the internal reference. Fourier transform infrared (FTIR) spectra were obtained on a Nicolet NEXUS 670 spectrometer (KBr disks). Gel permeation chromatography was performed with an Agilent HP1100 instrument. Tetrahydrofuran (THF) was used as eluent, and ODS2 Hypersil column was employed. The molecular weight and polydispersity are reported versus monodisperse polystyrene standard. Elemental analyses were determined by a Perkin-Elmer model 2400 CHN analyzer. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Lambda 35 UV–vis spectrophotometer. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer differential scanning calorimeter DSC 7 at a heating rate of 20 °C/min under flowing nitrogen. T_g was taken as the midpoint of the inflection observed on the curve of heat capacity versus temperature. Melting points were measured by DSC method. Thermogravimetric analysis (TGA) was conducted with a instruments NETZSCH STA 449C, and experiments were carried out on approximately 10 mg of samples under controlled flux of nitrogen at 50 mL/min. The mechanical properties were measured on an Instron 1122 testing instrument with 100 × 5 mm specimens in accordance with GB 1040-79 at a drawing rate of 50 mm/min. The values of inherent viscosity (η_{inh}) were determined by an Ubbelohde viscosimeter at 30 °C using DMAc as a solvent, and polymer solution concentration was 0.5 g/dL. Solubility was determined qualitatively by placing 100 mg of polymer into 900 mg of solvent at room temperature for 24 h, or heating at 80 °C. The dielectric constants were determined on an Agilent 4291B instrument with film specimens at a frequency of 1 MHz at room temperature.

3.3. Synthesis of 4-(4-trifluoromethylphenyl)-2,6-bis[4-(4-nitrophenoxy)phenyl]pyridine (FNPP)

12.86 g (0.05 mol) of NPAP, 3.35 g (0.025 mol) of 4-trifluoromethyl-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 viscous solid precipitated was filtered off and stirred in 200 mL 50% acetic acid/water for 8 h. The resulted yellow solid was collected by filtration and dried under vacuum at 60 °C, then 7.31 g of yellow powder of 4-(4-trifluoromethyl-phenyl)-2,6-bis[4-(4-nitrophenoxy)phenyl]pyridine (FNPP) was obtained. The yield is 45.0%, and the melting point is 68 °C.

FT-IR (KBr, cm^{-1}): 1515 and 1345 (–NO_2 stretching), 1247 (C–F stretching), 1165 (C–O–C stretching). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.29–8.26 (d, $J = 8.4$ Hz, 4H), 8.14–8.12 (d, $J = 7.2$ Hz, 4H), 7.78–7.76 (d, $J = 7.6$ Hz, 2H), 7.71–7.69 (d, $J = 7.6$ Hz, 2H), 7.63 (s, 2H), 7.22–7.20 (d, $J = 7.2$ Hz, 4H), 7.15–7.13 (d, $J = 8.4$ Hz, 4H). Anal. Calcd. for $C_{36}H_{22}N_3F_3O_6$: C, 66.56; H, 3.41; N, 6.47. Found: C, 66.37; H, 3.22; N, 6.49%.

3.4. Synthesis of 4-(4-trifluoromethylphenyl)-2,6-bis[4-(4-aminophenoxy)phenyl]pyridine (FAPP)

To a 250 mL three-necked flask equipped with a dropping funnel, and a reflux condenser, 6.50 g (0.01 mol) of FNPP, 0.2 g of palladium on activated carbon (Pd/C, 10%), 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 filtrate was subsequently poured into 600 mL of water to produce a solid precipitate, which was removed by filtration, washed with water, and dried. Recrystallization from 75% ethanol/water can offer 5.10 g of needle crystal of 4-(4-trifluoromethylphenyl)-2,6-bis[4-(4-aminophenoxy)phenyl]pyridine (FAPP). The yield is 86.5%, and the melting point is 136 °C.

FT-IR (KBr, cm^{-1}): 3441 and 3363 (N–H stretching), 1236 (C–F stretching), 1168 (C–O–C stretching). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.28–8.26 (d, $J = 8.8$ Hz, 4H), 8.23–8.21 (d, $J = 8.4$ Hz, 2H), 8.12 (s, 2H), 7.92–7.90 (d, $J = 8.4$ Hz, 2H), 7.02–6.99 (d, $J = 8.8$ Hz, 4H), 6.87–6.84 (d, $J = 8.4$ Hz, 4H), 6.66–6.64 (d, $J = 8.4$ Hz, 4H), 5.06 (s, –NH_2). Anal. Calcd. for $C_{36}H_{26}N_3F_3O_2$: C, 73.33; H, 4.44; N, 7.13. Found: C, 73.27; H, 4.51; N, 7.08%.

3.5. Synthesis of polymers

The typical two-step polymerization method was employed in synthesis of objective polyimides. An equimolar amount of diamine and dianhydride monomers were used in all cases. A representative polymerization procedure is as follows.

0.6204 g (2.0 mmol) of ODPA was gradually added to a stirred solution of 1.1792 g (2.0 mmol) of FAPP in 10.5 mL of NMP in a 50 mL three-necked flask equipped with a nitrogen inlet at 5 °C. The mixture was stirred at room temperature under nitrogen atmosphere for 24 h, forming a viscous solution of poly(amide acid) (PAA) precursor in NMP. The PAA was subsequently converted into polyimide by either a thermal or chemical imidization process. Chemical imidization was carried out by adding 2 mL of a mixture of acetic anhydride/pyridine (6/4, 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. Yields were nearly quantitative for all polymerizations. For the thermal imidization, the PAA was poured into a glass plate, which was dried in an oven at 80 °C for 8 h, 120, 150, 200, and 250 °C for 1 h at each temperature. Polyimide film was stripped from the glass substrate by immersing the glass plates in hot water.

4. Conclusions

A new diamine monomer, 4-(4-trifluoromethylphenyl)-2,6-bis[4-(4-aminophenoxy)phenyl]pyridine was successfully synthesized, which led to a number of novel fluorinated poly(ether-imide)s (FPIs) by two-step polycondensation method via reacting with various aromatic dianhydrides. The resulted polymers exhibited good solubility in many organic solvents. Transparent, flexible and tough poly(ether-imide) films were obtained, which showed excellent thermal and mechanical properties, good dielectric properties, and lower water uptake. The resulted FPIs exhibited better solubility, thermal and dielectric properties, and transparency than their non-fluorinated analogies, and better thermal properties than their analogies with trifluoromethyl groups in the *meta*-positions of imide nitrogen. Such improvement in the properties could be attributed to the introduction of the bulky trifluoromethyl groups into the pendent phenyl groups of the polyimide chain.

Acknowledgements

The authors thank the State Key Laboratory of Applied Organic Chemistry for financial support and Yingxia Ma for providing necessary facilities.

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