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Soluble fluoro-polyimides derived from 1,3-bis(4-amino-2-trifluoromethyl- phenoxy) benzene and dianhydrides

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Abstract

Soluble fluoro-polyimides have been synthesized by reacting of a fluorine-containing aromatic diamine, 1,3-bis(4-amino-2-trifluoromethylphenoxy) benzene(diamine **3**), with aromatic dianhydrides to yield poly(amic acid)s which were then cyclized to yield polyimide by either thermal or chemical imidization method. The new tri-aromatic ring diamine, with trifluoromethyl groups at β position of amine group and bridged by ether bonds, was obtained by reduction of the corresponding dinitro-compound which was synthesized by coupling of 2-chloro-5-nitro-1-trifluoromethylbenzene with 1,3-hydroquinone in presence of strong base. Homogeneous and stable polyimide solutions with >12–15 wt.% of solid content were obtained. High quality and purity polyimide films have been prepared which exhibited excellent thermal stability, low moisture absorption and high hygrothermal stability. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Fluoro-containing diamine; Soluble polyimides; Polycondensation

1. Introduction

Aromatic polyimide materials have been widely employed in microelectronic applications such as the substrates of flexible printed circuit boards, dielectric and insulating layers in multilayer structures and multichip modules, passivation layer in IC surface, buffer and conformal coatings in electronic packaging, since they have low dielectric constant and dissipation factor, high thermal stability, good mechanical properties and easy processability [1–8]. However, most commercial polyimides are usually insoluble in common organic solvents and infusible which posed the limitation on their extensive applications.

Many soluble fluorinated polyimides have been synthesized in recent years [9–12]. The introduction of fluoroalkyl groups, especially trifluoromethyl group (CF_3) has been demonstrated to ensure polyimides with desirable dielectric properties, exceptional thermal and mechanical properties. However, the strong electron-withdrawing ability of CF_3 could reduce the reactivity of the monomer (i.e. aromatic diamine) such that it was sometimes difficult to produce a high-molecular-weight polyimide. If the CF_3 is located at the ortho position of amine group, the reactivity is further reduced due to the steric hindrance. High concentration of fluorinated groups in polyimide would induce other negative influence on polymer properties due to its amphiphaticity. Hence, the molecular structure of the fluorinated monomer (aromatic diamine or dianhydride) should be carefully designed to gain a polyimide with desirable combined properties.

Another concern of polyimides for applications in microelectronics and optical devices were the moisture absorption, hygrothermal resistance and adhesion on inorganic substrate surface. With development of semiconductor and electronic packaging technology, the new designed, higher pin-count electronic devices are most often housed in moisture sensitive packages such as PBGA, TQFP, SCP etc. where assembly and reliability risks are usually limited by the ‘popcorning’ problem, which was due to the absorbed moisture in polymer packaging materials. The moisture vaporized at the high solder reflow temperature (220–240°C) and induced high steam pressure throughout the package to produce popcorning in packages [13–16]. Good adhesion was also important for polyimide materials to be used in microelectronics devices. Hence, polyimides with features of low moisture absorption, good dielectric and insulating property as well as outstanding mechanical strength are desirable.

The present article describes a series of soluble fluoro-polyimides with low moisture uptake and good hygrothermal stability, which were synthesized with

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1,3-bis(4-amino-2-trifluoromethylphenoxy) benzene and aromatic tetracarboxylic dianhydrides by chemical or thermal imidization method.

2. Experimental section

2.1. Materials

1,3-hydroquinone were purchased from Beijing Chemical Reagents Co., and used as received. Commercially obtained *N*,*N*′-dimethylformamide (DMF) and toluene were purified by distillation under reduced pressure prior to use. 1-Methyl-2-pyrrolidinone (NMP) was vacuum distilled from P_2O_5 and stored in nitrogen. Pyromellitic dianhydride (PMDA) was purified by sublimation in vacuum at 200–215°C. 3,3′4,4′-benzophenonetetracarboxylic dianhydride (BTDA) was recrystallized from acetic anhydride/acetic acid and then dried in a vacuum oven at 120°C for 8 h and then 180°C for 10 h. 4,4′-oxydiphthalic anhydride (ODPA, Shanghai Chemspec) was recrystallized from acetic anhydride before use. 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) (99%, Hoechst Celanese) was recrystallized from acetic anhydride and dried at 100°C for 12 h and then 160°C for 10 h.

2.2. Measurements

^{1}H-NMR and ^{13}C-NMR spectra were performed on a Varian Unity 300 spectrometer operating at 300 MHz in $CDCl_3$, or DMSO-d_6. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Perkin–Elmer 7 series thermal analysis system in air or nitrogen at a heating rate of 10°C min^{-1}. FTIR spectra were obtained on a Perkin–Elmer 782 Fourier transform spectrophotometer. Mechanical properties were measured on Instron 8810 with 0.60 cm wide specimens in accordance with GB 1447-83 at a rate of 5.0 mm min^{-1}.

2.3. Isothermal aging

Thin films ($1.0 \times 3.0 \times 0.05$ cm^3) were placed in an air or nitrogen circulating oven at 371°C with an inlet air flow of 100 ml min^{-1}. All samples were weighed after aging for schedule time intervals.

2.4. Water uptakes

Thin film ($1.0 \times 3.0 \times 0.05$ cm^3) was immersed in water at 23°C for 24 h (method 1) or at 100°C for 30 min. (method 2), which was then dried immediately and weighed to determine the water uptakes.

2.5. Monomer synthesis

2.5.1. 1,3-bis(4-nitro-2-trifluoromethylphenoxy) benzene (2)

A mixture of 55.0 g (0.50 mol) of 1,3-hydroquinone, 120 g of anhydrous potassium carbonate, 150 ml of toluene and 1000 ml of DMF in a three-necked, 2 l, round-bottom flask fitted with a nitrogen inlet, a thermometer and a mechanical stirrer was heated to 130–135°C under nitrogen for 1.5 h. The mixture was cooled to 60–70°C, and then 248 g (1.10 mol) of 2-chloro-4-nitro-trifluoromethylbenzene was added and refluxed for 4 h. Some of the solvent (toluene and DMF) was removed under reduced pressure to give a viscous liquid material, which was then poured on excess amount of ice water. The yellow precipitate was collected by filtration, washed with water and air-dried to give a crude product, which was recrystallized from ethyl alcohol to yield a yellow crystal: 195.0 g (80%); mp 111.8°C (DSC in air); IR (KBr): 3091, 1623, 1586, 1531, 1478, 1438, 1336, 1290, 1260, 1117, 1050, 897, 881, 844, 794 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 8.62 (d, 2H), 8.38 (q, 2H), 7.56 (t, 1H), 7.08 (d, 2H), 7.04 (d, 2H), 6.95 (t, 1H) ppm. MS (EI, *m*/*e*, % relative intensity): 488 (M + , 100). Anal. Calcd for $C_{20}H_{10}F_6N_2O_6$: C, 49.18; H, 2.05; N, 5.74. Found: C, 48.73; H, 2.25; N, 5.52.

2.5.2. 1,3-Bis(4-amino-2-trifluoromethylphenoxy) benzene (3)

A mixture of 3.6 ml of concentrated HCl and 15 ml of 50% aqueous ethanol was added slowly to a mixture of 73.2 g (0.15 mol) of compound (**2**), 50.3 g of reduced iron and 150 ml of 50% aqueous ethanol in a three-necked, 1 l, round-bottom flask equipped with a mechanical stirrer and thermometer. The mixture was stirred under refluxing for 2 h. To the mixture was then slowly added 8 ml of ammonium hydroxide solution (10 wt. %) over 30 min. The mixture was filtered hot and then cooled in ice-bath. To which was added slowly aqueous HCl (5%) to produce a solid, diamine **3** dihydrochloride. Pure diamine **3** was obtained by adding aqueous ammonium hydride to the solution of diamine **3** dihydrochloride in methylene chloride, which was then purified by column chromatograph: 39.8 g (62%); m. p. 41.2°C (DSC in air); IR (KBr): 3468, 3389, 3225, 3051, 1634, 1597, 1505, 1481,1455, 1341, 1261, 1123, 1047, 908, 871, 834, 774, 686 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.18 (t, 1H), 6.94–6.78 (m, 6H), 6.60–5.58 (m, 4H), 3.60 (s, 4H) ppm; ^{13}C-NMR ($CDCl_3$): 159.2, 144.8, 143.1, 131.2, 130.1, 125.8, 123.2, 123.1, 122.8, 122.2, 121.8, 120.7, 119.1, 115.0, 112.3, 111.6, 107.0 ppm. MS (EI, *m*/*e*, % relative intensity) 428 (M+, 100). Anal. Calcd for $C_{20}H_{14}F_6N_2O_2$: C, 56.07; H, 3.27; N, 6.54. Found: C, 56.24; H, 3.33; N, 6.46.

2.6. Synthesis of polyimides

Polyimide **1** Diamine **3** (21.049 g, 67.70 mmol) was dissolved in 315 ml of NMP. To this solution was added ODPA (15.245 g, 67.7 mmol). The mixture was stirred at room temperature in argon for 12 h to yield a viscous poly(amic acid) solution (10 wt.%) with an inherent viscosity of 1.32 dl g^{-}. The poly(amic acid) was converted into polyimide using either thermal or chemical imidization method. For thermal imidization method, the poly(amic acid) solution was cast onto a clean glass plate and heated (80°C/1 h, 120°C/1 h, 180°C/1 h, 250°C/4 h, and 300°C/1 h) to produce a polyimide film. The chemical imidization was carried out by adding a mixture of acetic anhydride and pyridine (1:1) into the above-mentioned poly (amic acid) solution (with mechanical stirring) at ambient temperature for 2 h, and then at 60°C for 4 h. The polyimide solution was poured into methanol to precipitate solid polyimide which was collected by filtration, washed thoroughly with methanol and dried at 80°C in vacuum to give solid polyimide **1**, which was then postcured at 200°C for 2 h. ^{1}H-NMR ($CDCl_3$): δ 8.06 (d, 2H), 7.80(s, 2H), 7.62 (d, 2H), 7.60 (d, 2H), 7.50 (d, 2H), 7.40 (t, 1H), 7.18 (d, 2H), 6.92 (d, 2H), 6.86 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$): 165.6, 161.0, 157.4, 154.5, 141.6, 134.2, 131.2, 127.0, 126.5, 125.5, 125.2, 122.0, 122.2, 121.8, 119.8, 115.8, 114.1, 111.4 ppm. Anal. Calcd for $C_{36}H_{16}F_6N_2O_7$: C, 61.53; H, 2.28; N, 3.99. Found: C, 61.38; H, 2.05; N, 4.12.

Polyimide **2** (6FDA/diamine **3**), polyimide **3** (BTDA/diamine **3**) and polyimide **4** (PMDA/diamine **3**) were synthesized from polymerization of 1 equiv. of diamine **3** and 1 equiv. of 6FDA, BTDA, or PMDA, respectively, at 10% solid content in NMP in the same method as polyimide **1**.

Polyimide 1′, 2′, 3′ and 4′ were prepared by polycondensation of 1 equiv. of 1,3-bis(4-aminophenoxy)benzene (1,3-APB) and 1 equiv. of ODPA, 6FDA, BTDA, or PMDA, respectively, at 10% solid content in NMP in the same method as described above.

3. Results and discussion

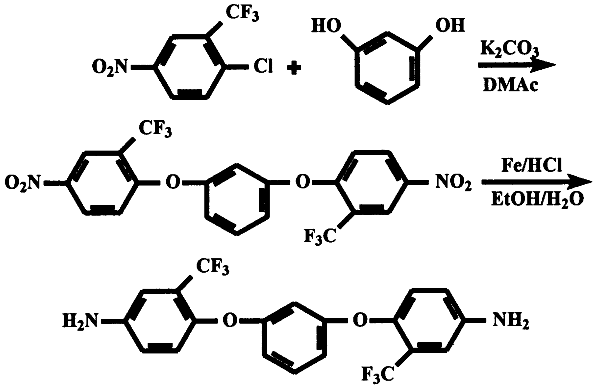
3.1. Monomer synthesis

Diamine **3** has been synthesized by coupling of 2-chloro-5-nitro-1-trifluoromethylbenzene (**1**) with 1,3-hydroquinone in the presence of strong base to yield 1,3-bis(4-nitro-2-trifluoromethylphenoxy) benzene (**2**) which was then reduced with Fe/HCl in ethanol/water to afford 1,3-bis(4-amino-2-trifluoromethyl-phenoxy) benzene (Scheme 1). Pure compound was obtained by converting the crude product to a salt of diamine **3** 2HCl followed by releasing it with aqueous ammonium hydroxide. Further purification can be performed by column chromatograph. It was found that diamine **3** was not very stable in air. In storing in air, a color change was observed. Hence, freshly prepared diamine **3** was employed for the synthesis of polyimides.

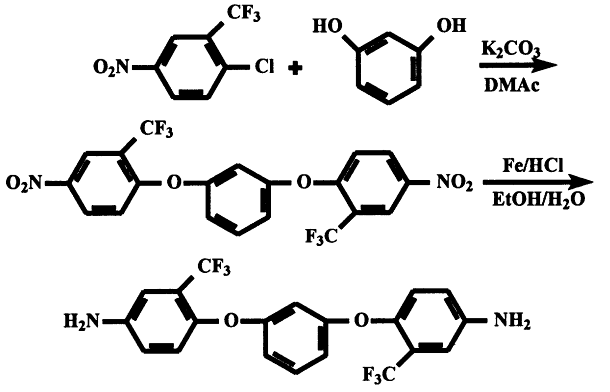
3.2. Polyimide synthesis

Diamine **3** was polycondensed with four different dianhydrides: OPDA, 6FDA, BTDA, or PMDA in NMP at room temperature to produce homogeneous viscous poly(amic acid) (PAA) solutions (Scheme 2). The intrinsic viscosities of the poly(amic acid)s were in the range 0.69–1.32 dl g^{-} in NMP at 25°C (Table 1). PAA **1**, derived from diamine **3** and ODPA, exhibited the highest value in inherent viscosity (1.32) while PAA **3** (diamine **3**/BTDA) showed the lowest value (0.69). The differences in inherent viscosity might be attributed to the length of polymer chains and the aggregating state in solution. The poly (amic acid)s were then converted to polyimides either by thermal or chemical imidization method. Using the thermal imidization method, PAA (10%, w/w) was thermally imidized to polyimide by a multi-step temperature programmed schedule (80°C/1 h, 120°C/1 h, 180°C/1 h, 250°C/4 h, and 300°C/1 h). The chemical imidization was carried out by mixing a mixture of acetic anhydride and pyridine (1:1) with PAA solution at ambient temperature for 2 h followed by heating at 60°C for 4 h, which usually produce a homogeneous polyimide solution. After precipitated by pouring the polymer solution into methanol, pure solid polymer was obtained.

Table 1 depicted the elemental analysis data of the polyimides prepared by chemical imidization method and the inherent viscosities of poly(amic acid)s and polyimides. The elemental analysis results of polyimides were well in agreement with that calculated. The inherent viscosity of polyimide ranged in 0.72–1.27 dl g^{-1}, in which polyimide **2** showed the highest value (1.27 dl g^{-1}). Fig. 1 compares the FTIR spectra of the chemically and thermally imidized polyimide **1** derived from diamine **3** and ODPA. It can be



Scheme 1.



Scheme 2.

Table 1
Inherent viscosity and the elemental analysis of the chemically imidized polyimides

PI	Inherent viscosity		Elemental Anal. of polyimide			
	PI	PAA		C	H	N
			Calculated	61.53	2.28	3.99
Polyimide **1**	0.72	1.32	Found	61.38	2.05	4.12
			Calculated	55.98	1.92	3.35
Polyimide **2**	1.27	1.13	Found	55.72	2.28	3.39
			Calculated	62.19	2.26	3.92
Polyimide **3**	0.77	0.69	Found	61.98	2.39	3.77
			Calculated	59.02	1.97	4.59
Polyimide **4**	0.87	1.21	Found	58.86	2.08	4.35

seen that the polyimides prepared by different pathways exhibited definitely same FTIR spectra. The imide carbonyl peaks at 1781 and 1727 cm^{-1} were observed. ^{1}H-NMR and ^{13}C-NMR of polyimide **1** in DMSO-d_6 are shown in Figs. 2 and 3, respectively. The absorption peaks at 6.9–8.1 ppm (Fig. 2) are assigned to the aromatic protons in polymer backbone. No any absorption was detected in the range of >8.3 ppm, indicating that the concentration of amide group (–C(O)NH–) in polymer chains was lower than the detection limit of ^{1}H-NMR (<5%). In other words, the chemically imidized polyimide possesses an imidization degree of >95%. ^{13}C-NMR spectrum of polyimide **1** (Fig. 3) exhibited 18 peaks in the range of 110–166 ppm. The C_{15} and C_{13} showed clear quartet absorption at 120–142 and 121–123 ppm, respectively, probably due to the $^{2}J_{C-F}$ and $^{3}J_{C-F}$ couplings of the carbons with fluorine atoms in the polymer segments.

3.3. Solubility

The polyimides showed great solubilities in common organic solvents. Table 2 showed the solubilities of polyimides prepared by thermal imidization method. The solubility was determined at 0.5 g of cured polyimide dissolved in 10 ml of solvent (5 wt.%) at room temperature. The polyimides cured both at 250 and 300°C were all soluble in NMP, DMAc and DMF. However, it was difficult to obtain a polyimide solution with solid content of >10% due to the diffusion limitation of solvent into the compact polymer film. The chemical imidization method could yield loose solid polyimide, which showed better solubility than that prepared by thermal imidization method (Table 3). The chemically imidized polyimides are dissolved not only in strong polar solvents such as NMP, DMAc, DMF or m-Cresol, but also in common low boiling point solvents such as THF, Chloroform. Thermal imidization method usually produces a polymer material with compact aggregation, while chemical imidization gives a loose polyimide solid. The chemically imidized polyimides, after being precipitated from the imidization solution and purified, could be re-dissolved in NMP or DMAc at room temperature to form a homogenous solution with solid content as high as 15–20%. Experimental results indicated that the polyimide solutions are very stable in room temperature, in which no precipitation, gelation or phase separation occurred in a storage period of more than two months.

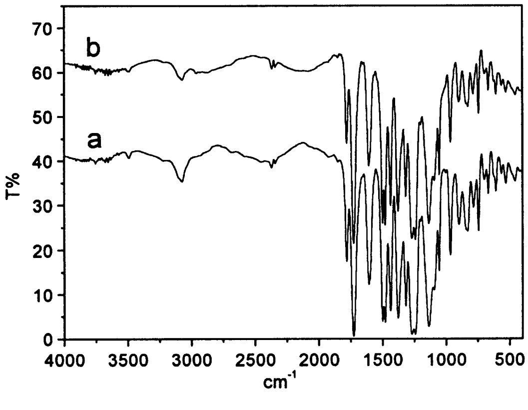


Fig. 1. FTIR spectra of polyimide **1** prepared by thermal imidization (a) and chemical imidization (b).

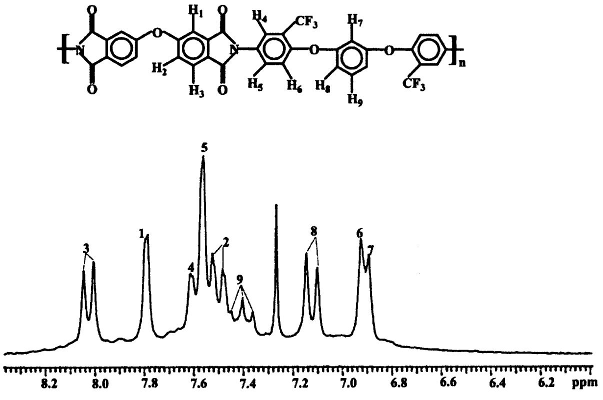


Fig. 2. ^{1}H-NMR spectrum of polyimide **1** prepared by chemical imidization method.

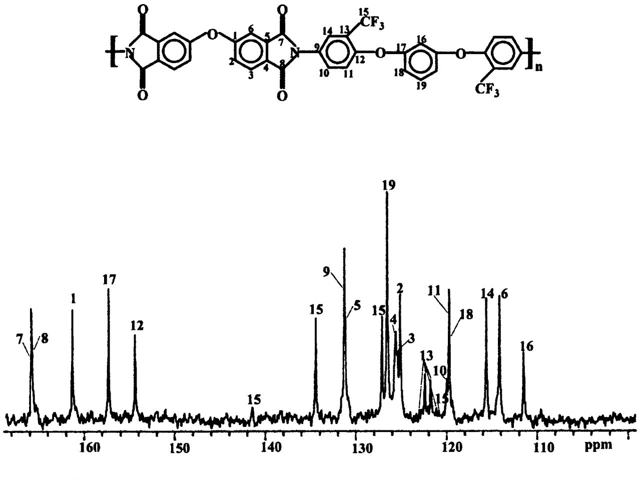


Fig. 3. ^{13}C-NMR spectrum of polyimide **1** prepared by chemical imidization method.

Table 2
Solubility of polyimide prepared by thermal imidization method (Note: ○-soluble, △-partially soluble, ×-insoluble)

Solvent	Polyimide **1** cured at		Polyimide **2** cured at		Polyimide **3** cured at		Polyimide **4** cured at	
	250°C	300°C	250°C	300°C	250°C	300°C	250°C	300°C
NMP	○	○	○	○	○	○	○	○
DMAc	○	○	○	○	○	○	○	○
DMF	○	○	○	○	○	○	○	○
m-cresol	○	△	○	△	△	△	△	△
THF	△	△	△	△	△	△	△	△
Chloroform	△	△	△	△	△	×	△	×
Acetone	△	△	△	△	△	×	△	×
MeOH	×	×	×	×	×	×	×	×

Table 3
Solubility of polyimides prepared by chemical imidization method (Note: ○-soluble, △-partially soluble, ×-insoluble)

Solvent	Polyimide **1**	Polyimide **2**	Polyimide **3**	Polyimide **4**
NMP	○	○	○	○
DMAc	○	○	○	○
DMF	○	○	○	○
m-cresol	○	○	○	○
THF	○	○	○	○
Chloroform	○	○	○	○
Acetone	○	○	△	△
MeOH	×	×	×	×

Fig. 4 compared TGA curves of the polyimides prepared by chemically and thermally imidization. It can be seen that the chemically imidized polyimide post-baked at 220°C showed further 2–3% of weight loss from 200–350°C, while the thermally imidized polymer did not loss any weight before 500°C, implying that the weight loss (2–3%) of the chemically imidized polyimide might be attributed to the incomplete imidization. Thus, the chemically imidized polyimide has an imidization degree of 97–98%, which might be one of the reason it showed great solubility.

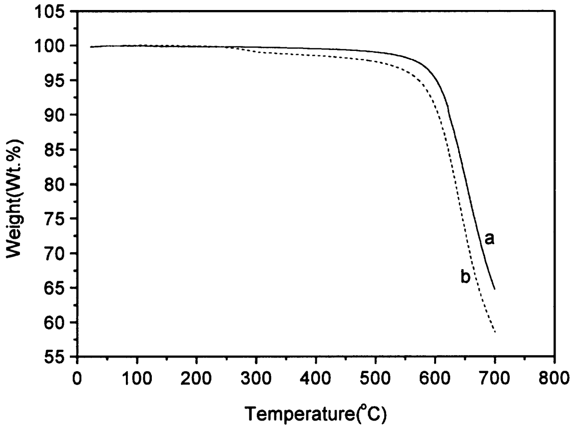


Fig. 4. TGA curves (1st run) of the thermally (a) and chemically (b) imidized polyimide **1** in N_2 at scanning rate of 20°C min^{-1}.

3.4. Mechanical properties

Tough, flexible films were obtained by casting the chemically imidized polyimide solution on glass surface, followed by thermal baking in a schedule of 80°C /1 h, 120°C/1 h, 180°C/2 h and 220°C/2 h to remove the solvents. Films were also prepared by casting poly(amic acid) solutions on a glass plate followed by thermal curing at a schedule of 80°C/2 h, 120°C/1 h, 180°C/1 h, 250°C/4 h and finally 300°C/1 h. Table 4 showed mechanical properties of the thermally imidized polyimides. The polyimide films exhibited tensile strengths of 97–119 MPa, elongation at break of 13–27%, and tensile Modulus of 1.41–1.98 GPa.

3.5. Thermal stability

Thermal properties of the thermally imidized polyimides were investigated by means of TGA and DSC. The polyimides did not lose appreciable weight until the temperature scanned to 500°C in air (Fig. 4). Table 5 summarized the thermal properties of the polymers. In nitrogen, the initial decomposition temperatures for polyimide **1**, **3** and **4** ranged 598–608°C, which was 33–43°C higher than that of polyimide **2** (565°C). In air, the decomposition temperature was increased in the order of polyimide **2** (513°C) < polyimide **3** (527°C) < polyimide **4** (543°C) < polyimide **1** (561°C). The 5% weight loss temperatures were 559–587°C in nitrogen and 482–534°C in air, and the10% weight loss temperatures were 582–622°C in nitrogen and 538–589°C in air, respectively. Glass transition temperatures of the polymers, determined by DSC in 1st run (Fig. 5), were in the range of

Table 4
Mechanical properties of the thermally imidized polyimides

	Polyimide **1**	Polyimide **2**	Polyimide **3**	Polyimide **4**
Elongation at break (%)	13	27	15	24
Tensile strength (MPa)	96.7	115.1	119.2	99.6
Young's modulus (GPa)	1.52	1.83	1.98	1.41

Table 5
Thermal properties of polyimides prepared by thermal imidizition method (the polyimide samples were prepared by thermal imidization method at a curing schedule of 80°C/2 h, 120°C/1 h, 180°C/1 h, 250°C/4 h and 300°C/1 h)

	Polyimide **1**		Polyimide **2**		Polyimide **3**		Polyimide **4**	
	in air	in N_2	in air	in N_2	in air	in N_2	in air	in N_2
Initial decomposition temperature (°C)	561	603	513	565	527	598	543	608
Temperature at 5% weight loss (°C)	534	560	482	559	497	587	507	578
Temperature at 10% weight Loss (°C)	589	622	538	582	558	614	552	610
Glass transition temperature (DSC, 1st run) (°C)	203.1		228.1		216.0		246.7	

203 to 247°C. Polyimide 2 (6FDA-diamine **3**) showed the lowest Tg value of 203°C, while polyimide **4** (PMDA-diamine **3**) give the highest Tg (247°C). It seems that the differences in Tgs were attributable to the rigidity and packing of polymer chains.

Fig. 6 showed the thermal and thermo-oxidative stability of the polyimides. The weight losses of the polymers increased linearly with increasing isothermal aging time at 371°C in flowing air or in nitrogen. In air, the thermo-oxidative stability of the polyimides decreased in the following order: polyimide **2** > polyimide **4** > polyimide **3** > polyimide **1**. After isothermal aging at 371°C in air for 96 h, polyimide **2** and polyimide **1** lost weight of 7 and 17%, respectively, implying that polyimide **2** possessed better thermo-oxidative stability than polyimide **1**. In nitrogen, polyimide **2** also showed the best thermal stability than others. It can be seen that the weight loss of polyimide **2** was only 3% after isothermal aging for 170 h at 371°C, compared with 8–10% of other polymers. In summary, although polyimide **2** showed relative low decomposition temperature (TGA) and low glass transition temperature (DSC), it exhibited the best thermal and thermo-oxidative stability.

3.6. Moisture absorption and hygrothermal stability

Table 6 depicted the moisture uptakes of the polyimides measured in two different methods. The method 1 is the

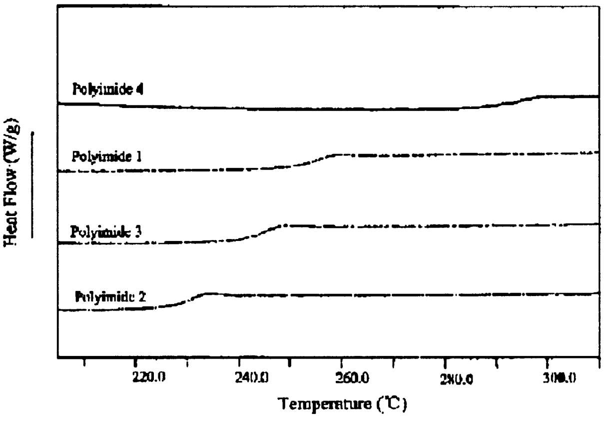


Fig. 5. DSC curves (first run) of the thermally imidized polyimide **1–4** in air at a scanning rate of 20°C $\min^{-1}$.

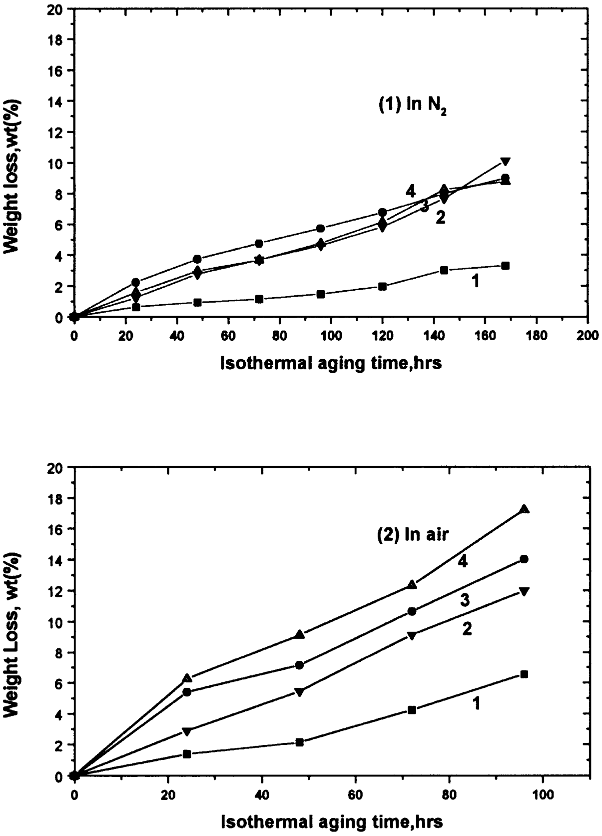


Fig. 6. Thermal (upper, in N_2) and thermo-oxidative (bottom, in air) stability of polyimide **1–4** measured by isothermal aging at 371°C; Curve 1: polyimide **2** (6FDA/diamine **3**); Curve 2: polyimide **4** (PMDA/diamine **3**); Curve 3: polyimide **3** (BTDA/diamine **3**); Curve 4: polyimide **1** (ODPA/diamine **3**).

Table 6
Water absorption of the chemically imidized polyimides

	Method 1	Method 2	Average value	Growth rate (%)
Polyimide **1**	0.43	0.40	0.42	
Polyimide 1′	0.93	0.88	0.91	116
Polyimide 2	0.62	0.51	0.56	
Polyimide 2′	0.86	0.90	0.88	57
Polyimide 3	0.81	0.74	0.78	
Polyimide 3′	1.09	1.13	1.11	42
Polyimide 4	0.45	0.37	0.41	
Polyimide 4′	0.92	0.98	0.95	132

immersion of a film in water at 23 ± 0.5°C for 24 h, followed by weighing. The method 2 is the boiling of a film in water at 100°C for 30 min, then weighing. Experimental results indicated that the moisture uptakes of polyimides were low, ranged in 0.43–0.81%. Polyimide **3** (BTDA-diamine **3**) showed an obvious high water uptakes (0.74–0.81%), almost doubled that of other polyimides. In comparison, the polyimides derived from the corresponding non-fluoromethyl group-containing, aromatic diamines, 1,3-bis(4-aminophenoxy)benzene(1,3-APB), and aromatic diahydrides exhibited higher moisture uptakes than polyimide **1–4**. For instance, polyimide 1′ (ODPA-1,3-APB) has a moisture uptake of 0.91, which is 116% of polyimide **1**. The low moisture absorption of the fluoro-polyimides might be mainly interpreted by the increase in hydrophobicity of the polymer due to the introducing of trifluoromethyl groups. The increased hydrophobicity inhibited adsorption of moisture molecule on the surface of fluorinated polymers.

Hygrothermal stability was investigated by boiling polyimide films in water at 120°C/2 atm for 30 h. Fig. 7 compared the DSC curves of polyimide **2** and polyimide **3** before and after hygrothermal exposure. It can be seen that no obvious difference was observed in DSC (1st run) scanned to 260°C. Polyimide **2** and polyimide **3** showed Tgs of 213.7 and 226°C, respectively, which were changed 0.55–0.94°C compared to the hygrothermally treated samples. Fig. 8 compared the TGA curves of polyimide **2** and polyimide **3** with and without hygrothermal treatment. The decomposition temperatures and 10% weight loss temperature of polyimide **2** were 570.8 and 586.1°C, respectively, only 8–12°C of decreases in comparison with that of the hygrothermally treated sample. Similarly, polyimide **3** showed a decrease in decomposition temperature of 18–25°C after hygrothermal exposure. Hence, a slight influence of hygrothermal exposure on the thermal stability of polyimide was detected. After thermal and accelerated hydrolytic exposures, the polyimide film surface did not loss its gloss. No surface cracks, voids or other defects in the hygrothermally treated samples were observed in SEM photographs.

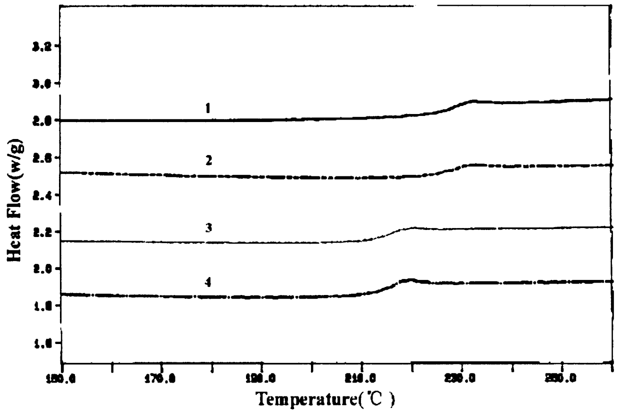


Fig. 7. Comparison on DSC curves (1st run) of the thermally cured polyimides before and after hygrothermally treated at 120°C under 2 atm: curve 1: freshly prepared polyimide **2** (6FDA-diamine **3**); curve 2: hygrothermally treated polyimide **2**; curve 3: freshly prepared polyimide **3** (BTDA/diamine **3**); curve 4: hygrothermally treated polyimide **3**.

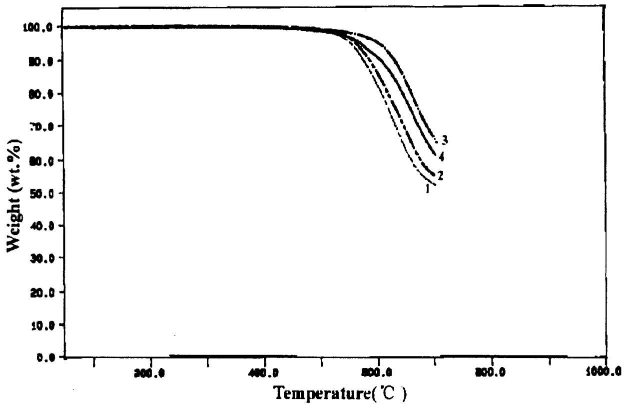


Fig. 8. Influence of hygrothermal treating on TGA (1st run) of the thermally cured polyimides; curve 1: hygrothermally treated polyimide **2**; curve 2: freshly prepared polyimide **2**; curve 3: freshly prepared polyimide **3**; curve 4: hygrothermally treated polyimide **3**.

4. Conclusions

A series of soluble fluoro-polyimides were synthesized using 1,3-bis(4-amino-2- trifluoromethylphenoxy) benzene and dianhydrides by two different methods. Experimental results indicated good mechanical property, low moisture absorption and high hygrothermal resistance, good thermal and thermo-oxidative stabilities at elevated temperature as high as 371°C.

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