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Synthesis and characterization of novel polyimides derived from 1,1-bis[4-(4′-aminophenoxy)phenyl]-1-[3″,5″-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane

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Abstract

A novel fluorinated aromatic diamine monomer, 1,1-bis[4-(4′-aminophenoxy)phenyl]-1-[3″,5″-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane(9FTPBA), was synthesized by coupling 3′,5′-bis(trifluoromethyl)-2,2,2-trifluoroacetophenone with 4-nitrophenyl phenyl ether under the catalysis of trifluoromethanesulfonic acid, followed reduced by reductive iron and hydrochloric acid. A series of new fluorine-containing polyimides having inherent viscosities of 0.96–1.23 dl/g was synthesized from the novel diamine with various commercially available aromatic dianhydrides using a standard two-stage process with thermal imidization and chemical imidization of poly(amic acid) films. All the fluorinated polyimides were soluble in many polar organic solvents such as NMP, DMAc, DMF, and *m*-cresol, as well as some of low boiling point organic solvents such as chloroform and acetone. The polymer films have good thermal stability with the glass transition temperature of 223–225 °C, the temperature at 5% weight loss of 535–568 °C in nitrogen, and have outstanding mechanical properties with the tensile strengths of 68–89 MPa, initial moduli of 2.14–2.19 GPa, and elongations at breakage of 3.2–10.5%.

Keywords: Fluorine-containing diamine; Fluorine-containing polyimide; Solubility

1. Introduction

Aromatic polyimide exhibit excellent thermal stability, chemical stability, mechanical strength, low dielectric constants, and have been widely used in microelectronic encapsulation, aviation and separation, etc. [1–4]. However, aromatic polyimides are usually difficult to process because of their poor solubility in organic solvents and high melting temperature. There are not suitable to develop further polyimides employed in the advanced materials. Many attempts have been made to improve the processability (melt processing properties and/or solubility in organic solvent) of polyimides without sacrificing their thermal and mechanical properties. The strategies that enhance the solubility of polyimides should include that the flexible linkages or monomer unites, bulky lateral groups or non-coplanar structures were introduced into the polymer backbone, as well as the monomers of fluorine-containing aromatic diamine or dianhydride were synthesized by the molecular design of the monomer and polymer chain [5–11]. For the polyimide family, fluorinated aromatic polyimides [12–15], specially trifluoromethyl-containing polyimides, have been identified as one of the polyimide materials having great potential foreground, because the bulky trifluoromethyl groups both inhibit efficiently to form regular chain structure and increase the molecular polarity correspondingly, so the resulting polyimides tends to contain a high free volume, and exhibits good solubility in organic solvents without sacrificing the above excellent properties. Since the fluorine-containing polyimides have the desirable characteristic of the lowering dielectric constants, excellent optic property, and lowering adsorption for moisture, therefore, many fluorinated polyimides have

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been prepared derived from various fluorinated aromatic diamines [16–19] or fluorinated aromatic dianhydrides [20–22]. On the other hand, the polyimides with aryl ether and bulky triphenylethane also show good solubility in polar organic solvents because of the bulky lateral groups or non-coplanar structures [23,24].

In this paper, a novel fluorinated aromatic diamine, 1,1-bis[4-(4′-aminophenoxy)phenyl]-1-[3″,5″-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane (9FTPBA), was synthesized in our laboratory, and three kinds of novel fluorinated aromatic polyimides were prepared by polycondensation of 9FTPBA with various commercially available aromatic dianhydrides. For the resulting polyimides, and the solubility in less polar and polar organic solvents was observed by comparing each other; the polycondensation process, corresponding composition and structure, thermal, optic and mechanical properties were investigated.

2. Experimental

2.1. Materials

1-Bromo-3,5-bis(trifluoromethyl)benzene was purchased from Liaoning Tianhe Fine Chemical Corp., Ltd, China, and was purified by distillation. Magnesium was purchased from ACROS Chemicals, Corp., and used as received. Anhydrous lithium trifluoroacetic acid was prepared by reaction of lithium hydroxide and trifluoroacetic acid, and was dried at 130 °C for 24 h under vacuum. Trifluoromethanesulfonic acid (triflic acid, 98%, Aldrich) was used as received. Tetrahydrofuran (THF) and ethyl ether were freshly distilled under nitrogen over sodium prior to use. Lithium hydroxide, phenol, 1-chloro-4-nitrobenzene, trifluoroacetic acid, 1,2-dichloroethane, reductive iron, anhydrous potassium carbonate, hydrochloric acid, ethanol and iodine were purchased from Beijing Chemical Reagents Corp., China, and used as received. Pyromellitic dianhydride (PMDA, Beijing Chemical Reagents Corp.) was purified by sublimation at 200–215 °C under vacuum. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA, Beijing Chemical Reagents Corp.) was recrystallized from acetic anhydride/acetic acid and dried at 120 °C for 8 h and at 180 °C for 10 h under vacuum. 4,4′-oxydiphthalic anhydride (ODPA, Shanghai Nanxiang Chemical Co.) was recrystallized from acetic anhydride prior to use. *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), and *N*-methyl-2-pyrrolidinone (NMP) were purchased from Beijing Chemical Reagents Corp., China; DMAc and DMF were purified by distillation under reduced pressure over calcium hydride, while NMP were purified by distillation under reduced pressure over P_2O_5, and were stored in the presence of 4 Å molecular sieves.

2.2. Monomer synthesis

2.2.1. 3′,5′-Bis(trifluoromethyl)-2,2,2-trifluoroacetophenone (9FAP)

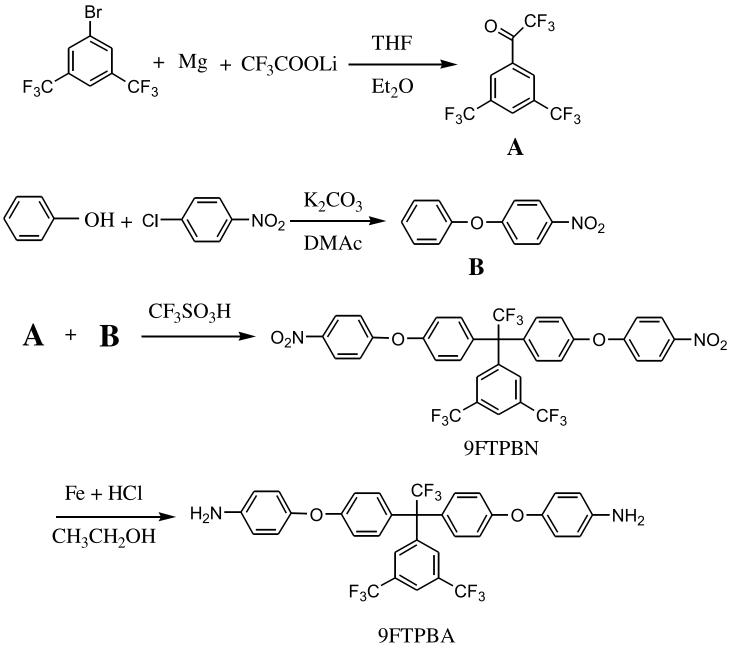
A mixture consisting of anhydrous lithium trifluoroacetic acid (31.2 g, 0.26 mol), magnesium (5.52 g, 0.23 mol), iodine (0.2 g) and freshly anhydrous THF (200 ml) was added to a 500 ml of three-necked round-bottom flask fitted with a dropping funnel, thermometer, reflux condenser with drying tube and magnetic stirrer. To which, 1-bromo-3,5-bis(trifluoromethyl)benzene (5.9 g, 0.02 mol) and freshly anhydrous ethyl ether (50 ml) were added until the anhydrous lithium trifluoroacetic acid was dissolved completely. The mixture was slowly heated at 60 °C ensuring the reaction was started. Then a mixture of 52.6 g (0.18 mol) of 1-bromo-3,5-bis(trifluoromethyl)benzene and 50 ml of freshly anhydrous THF was dropwise. After completion of the addition, the mixture was refluxed for 8 h, it was cooled down to room temperature, the mixture of concentrated hydrochloric acid (36%, 30 ml) and distilled water (30 ml) was put into slowly with shaking. Then, the aqueous phase was removed by the separation, and the organic phase was washed well with 5% aqueous solution of sodium bicarbonate and distilled water, respectively. Finally, the organic solution obtained was dried by anhydrous magnesium sulfate, and was distilled to remove the solvent, and the resulting crude product was purified by distillation to give 3′,5′-bis(trifluoromethyl)-2,2,2-trifluoroacetophenone (9FAP, 46.5 g, 75%), a colorless liquid, and its bp is about 150–151 °C. Anal. calcd for $C_{10}H_3F_9O$ (310.00): C, 38.73%; H, 0.98%. Found: C, 38.70%; H, 0.99%.

2.2.2. 4-Nitrophenyl phenyl ether

A mixture of phenol (47 g, 0.50 mol), 1-chloro-4-nitrobenzene (78 g, 0.50 mol), anhydrous potassium carbonate (55 g, 0.40 mol), and anhydrous DMAc (300 ml) was added to a 500 ml of three-necked round-bottom flask fitted with a mechanical stirrer, thermometer, and reflux condenser. The mixture was heated to 140 °C for 24 h. Then, the part of the solvent (DMAc) was removed by vacuum distillation, cooling, and the reaction mixture was poured into 2000 ml of distilled water. The precipitate formed was collected by filtration, washed with distilled water, and dried in air. The resulting crude product was recrystallized from ethanol to give yellow crystals, i.e. 4-nitrophenyl phenyl ether (95 g, 88%), and mp 54–56 °C. Anal. calcd for $C_{12}H_9NO_3$ (215.06): C, 66.97%; H, 4.22%; N, 6.51%. Found: C, 66.95%; H, 4.21%; N, 6.54%.

2.2.3. 1,1-Bis[4-(4′-nitrophenoxy)phenyl]-1-(3″,5″-bis(trifluoromethyl)phenyl)-2,2,2-trifluoroethane (9FTPBN)

A mixture of 9FAP (31 g, 0.10 mol), 4-nitrophenyl phenyl ether (47 g, 0.22 mol) and anhydrous 1,2-dichloroethane (150 ml) was added to 250 ml of round-bottom



Scheme 1. Synthesis of diamine monomer 9FTPBA.

flask fitted with a dropping funnel, drying tube, and magnetic stirrer, and trifuoromethanesulfonic acid (16.5 g, 0.11 mol) was dropwise at room temperature. After completion of the addition, the mixture was stirred at the room temperature for 72 h. The mixture was poured into excess distilled water, and a precipitate was formed and collected by filtration, washing with 5% of aqueous solution of sodium bicarbonate, distilled water and methanol, respectively. The precipitate obtained was dried in air to get a yellow solid, i.e. 9FTPBN (56 g, 78%), mp 131–132 °C. Anal. calcd for $C_{34}H_{19}F_9N_2O_6$ (722.11): C, 56.52%; H, 2.63%; N, 3.88%. Found: C, 56.50%; H, 2.64%; N, 3.90%.

2.2.4. *1,1-Bis[4-(4′-aminophenoxy)phenyl]-1-[3″,5″-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane (9FTPBA)*

A mixture of 1.5 ml of concentrated hydrochloric acid and 10 ml of 50% aqueous ethanol was added slowly to a mixture of 43.3 g of 9FTPBN (0.06 mol), reductive iron (20 g, 0.36 mol), and 30 ml of 50% aqueous ethanol in a 250 ml of three-necked round-bottom flask equipped with a mechanical stirrer and thermometer. The mixture was stirred with refluxing for 3 h, and 1 ml of ammonium hydroxide solution (10 wt%) was added slowly to the mixture during 10 min. The mixture was hot-filtered to remove solvent, a light brown solid was got, it should be 9FTPBA, which was further purified by recrystallization from ethanol, and given 32 g of 9FTPBA (80%), and mp 94–96 °C. Anal. calcd for $C_{34}H_{23}F_9N_2O_2$ (662.16): C, 61.64%; H, 3.50%; N, 4.23%. Found: C, 61.60%; H, 3.53%; N, 4.20%.

2.3. *Polymer synthesis*

Utilizing 9FTPBA as diamine monomer, three kinds of novel polyimides were synthesized by polycondensation of 9FTPBA with BTDA, ODPA and PMDA, respectively, and the resulting polyimides were abbreviated to 9FTPBA/BTDA, 9FTPBA/ODPA and 9FTPBA/PMDA, successively.

In a typical experiment, polyimide 9FTPBA/BTDA, which derived from 9FTPBA and BTDA, was prepared as follows: 9FTPBA (3.3108 g, 50 mmol) was dissolved in 28 ml of NMP in a 100 ml of three-necked flash fitted with a nitrogen inlet pipet and mechanical stirrer, then BTDA (1.6100 g, 50 mmol) was added to the solution with stirring, then the reaction was allowed to carry through 24 h at room temperature to yield a viscous polyamide acid solution (PAA solution) with 15% of solid content. PAA solution was gradually converted into a polyimide by imidization, the PAA solution was coated to a clean glass plate and heated according as temperature procedure of 80 °C/3 h, 120 °C/1 h, 150 °C/1 h, 180 °C/1 h, 250 °C/2 h, 300 °C/2 h, a polyimide film was obtained by full imidization. Meanwhile, the polyimide can also be obtained by chemical-imidization method, a mixture of 6 ml acetic anhydride and 4 ml pyridine was added into the PAA solution and was remained 24 h with stirring at room temperature, and the PAA was altered to a polyimide by catalysis imidization of acetic anhydride and pyridine. The solution containing polyimide was poured into ethanol to produce a precipitate, the precipitate was collected by filtration and washed with ethanol thoroughly, and then it was dried at 80 °C for 24 h and 120 °C for 6 h under vacuum, successively.

Polyimide 9FTPBA/ODPA, and polyimide

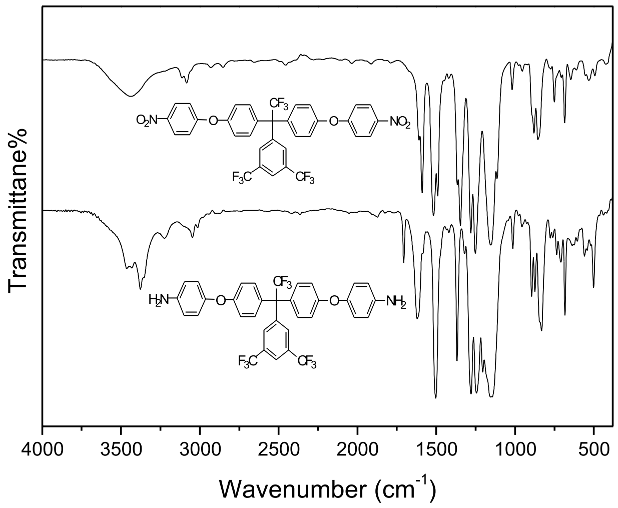


Fig. 1. FT-IR spectra of dinitro-compound and diamine compound.

9FTPBA/PMDA, were synthesized from the polymerization of 1 equiv. 9FTPBA and 1 equiv. of ODPA, PMDA, respectively, at 15% solid content in NMP in the same method as polyimide 9FTPBA/BTDA.

2.4. Measurements

^{1}H NMR and ^{13}C NMR spectra were performed on a Varian UNITY 400 spectrometer operating at 400 MHz in dimethyl sulfoxide-d_6 (DMSO-d_6). Differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) were recorded on a Pinkin–Elmer 7 series thermal analysis system in nitrogen at a heating rate of 20 °C/min. Fourier transform infrared (FT-IR) spectra were obtained on a Perkin–Elmer 782 Fourier transform spectrophotometer. UV–vis spectra were recorded on a Hitachi U-3210 spectrophotometer. The mechanical properties were measured on an Instron 1122 testing instrument with 120×5 mm specimens in accordance with GB1040-79 at a drawing rate of 50 mm/min. Inherent viscosity was carried out with an Ubblohde viscometer in NMP at 25±0.5 °C, in which the samples were dried at 120 °C for 1 h to remove absorbed moisture. Water uptake was determined by the weighing of the changes in the polymer film ($50\times50\times0.05$ mm^3) before and after immersion in boiling water for 6 h. moisture intake was determined by the weighing of the changes in the polymer film ($50\times50\times0.05$ mm^3) before and after placement in air of relative humidity 80% for 6 h.

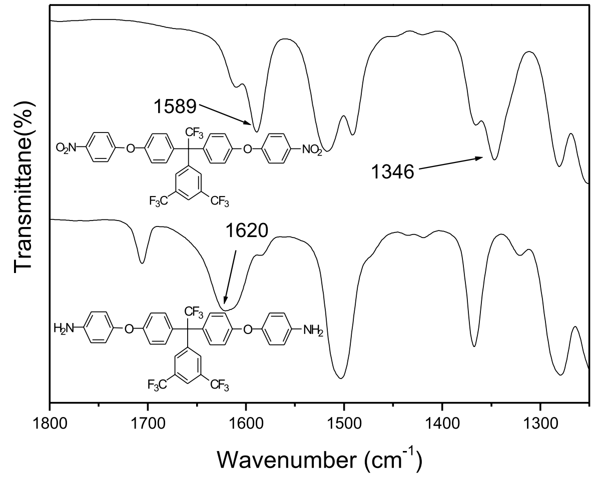


Fig. 2. The contrast of IR characteristic bands dinitro-compound and diamine-compound.

3. Results and discussion

3.1. Synthesis of monomer

The diamine monomer 9FTPBA was prepared by the reaction sequence as shown in Scheme 1. First, 3′,5′-bis(trifluoromethyl)-2,2,2-trifluoroacetophenone (9FAP) was obtained by Grignard reaction of anhydrous lithium trifluoroacetic acid, 1-bromo-3,5-bis(trifluoromethyl)benzene and magnesium in a mixing solvent anhydrous THF and ethyl ether to get satisfaction yield; next, the dinitro-compound (9FTPBN) was prepared by reaction of 9FAP and 4-nitrophenyl phenyl ether in 1,2-dichloroethan under the catalysis of trifuoromethanesulfonic acid; finally, 9FTPBN was reduced by hydrochloric acid and reductive iron to form the diamine monomer, 1,1-bis[4-(4′-aminophenoxy)phenyl]-1-[3″,5″-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane, being abbreviated to 9FTPBA.

For the resulting 9FTPBA, the composition and structure were confirmed by using FT-IR, ^{1}H NMR, ^{13}C NMR and elemental analysis methods. The elemental analysis data presented in the above experimental section have indicated that the dinitro-compound 9FTPBN and diamine monomer 9FTPBA hold the composition of $C_{34}H_{19}F_9N_2O_6$ and $C_{34}H_{23}F_9N_2O_2$, respectively, and that found were correspond to that calculated. Fig. 1 is FT-IR spectra of the resulting 9FTPBN and 9FTPBA, and the characteristic bands of their IR absorption were enlarged partly to get Fig. 2. By comparing with two IR spectra, the absorption bands presented at 1589 and 1346 cm^{-1} resulting from asymmetric and symmetric stretching vibration of $-NO_2$ group disappeared after 9FTPBN was reduced, whereas the characteristic bands of the $-NH_2$ group were presented at 3463–3377 cm^{-1} (N–H stretching) and 1620 cm^{-1} (N–H banding), this should be an evidence which indicates that the nitro group was changed into the amine group. ^{1}H NMR and ^{13}C NMR spectra of diamine monomer 9FTPBA dissolved in DMSO-d_6 are shown in Figs. 3 and 4. According to ^{1}H NMR spectrum, the chemical shift of proton from amino group should be at 4.38 ppm (s, 4H, H_1), and the signal presented at 2.48 ppm should represent that of residual proton in DMSO-d_6, while chemical shifts presented at 6.58 ppm H_2 (d, 4H, $J_{H2-H3}=11.76$ Hz); 6.77 ppm H_3 (d, 4H, $J_{H2-H3}=8.7$ Hz); 6.87 ppm H_4 (d, 4H, $J_{H4-H5}=8.9$ Hz); 6.95 ppm H_5 (d, 4H, $J_{H4-H5}=8.9$ Hz); 7.54 ppm H_6 (s, 2H)

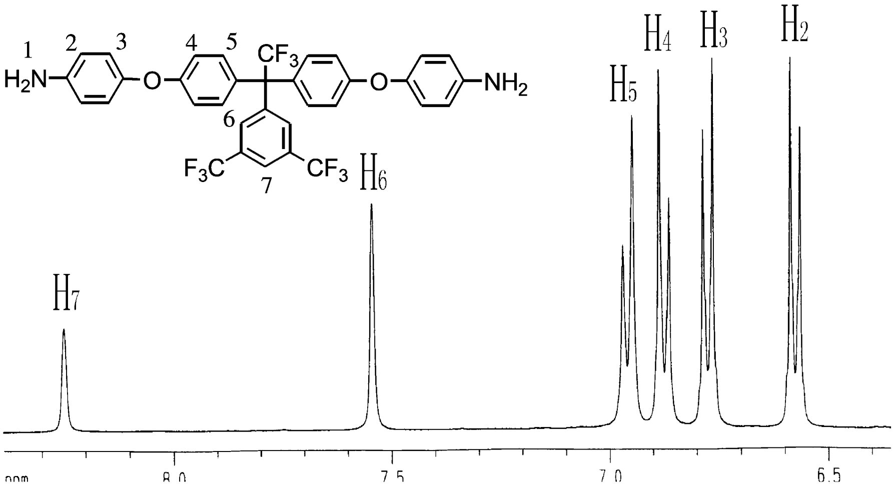


Fig. 3. ^{1}H NMR spectra of diamine monomer 9FTPBA.

Table 1
The experimental data of three polyimides obtained

Polyimide no.	Yield (%)	Color	Formula (formula weight)	Elemental analyses			
					C	H	N
9FTPBA/BTDA	83	Yellow	$C_{51}H_{25}F_9N_2O_7$ (872.75)	Calcd	64.56	2.66	2.95
				Found	64.55	2.65	2.96
9FTPBA/ODPA	80	Yellow	$C_{50}H_{25}F_9N_2O_7$ (860.75)	Calcd	64.11	2.69	2.99
				Found	64.13	2.68	2.98
9FTPBA/ PMDA	85	Yellow	$C_{44}H_{21}F_9N_2O_6$ (784.65)	Calcd	62.57	2.51	3.32
				Found	62.56	2.50	3.33

and 8.24 ppm H_7 (s, 1H). H_2, H_3, H_4 and H_5 all show a doublet peak because of the spin–spin coupling each other. ^{13}C NMR spectrum of diamine monomer 9FTPBA (Fig. 4) exhibits 15 peaks in the range from 64 to 159 ppm as differences of chemical environment located carbon atoms. According as Fig. 4, C_5, C_{12}, C_{13} and C_{14} all show clear quartet peaks because of the spin–spin coupling between carbon and fluorine atoms, meanwhile, other signals of ^{13}C NMR will be attributed to: C_1, 159.4; C_2, 146.2; C_3, 145.1; C_4, 143.2; C_5, 64.0(m); C_6, 115.3; C_7, 116.7; C_8, 131.2; C_9, 124.7; C_{10}, 129.8; C_{11}, 122.0; C_{12}, 124.8–126.2(m); C_{13}, 119–129(m); C_{14}, 122–131(m);

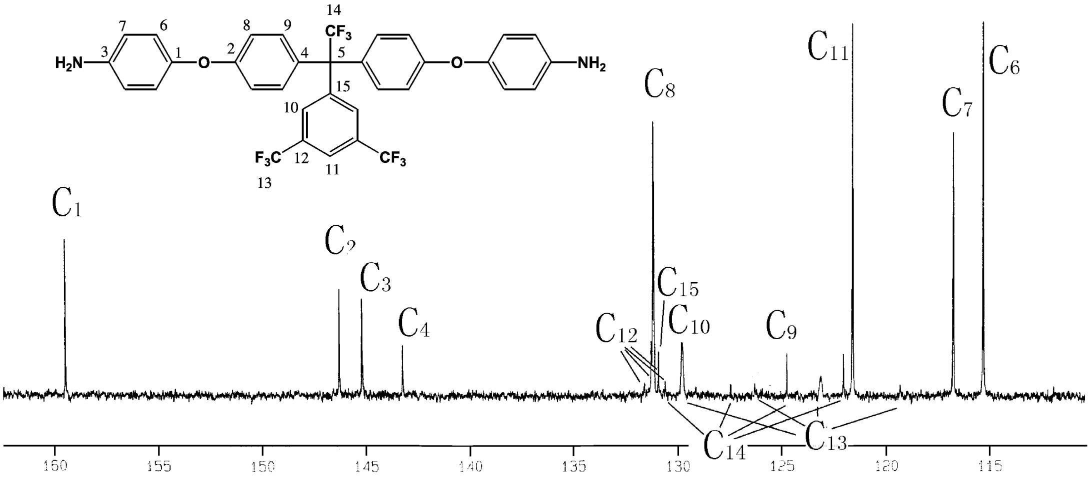


Fig. 4. ^{13}C NMR spectra of diamine monomer 9FTPBA.

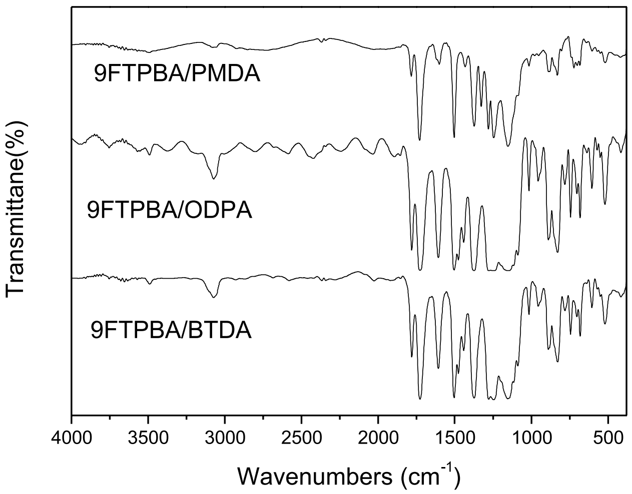
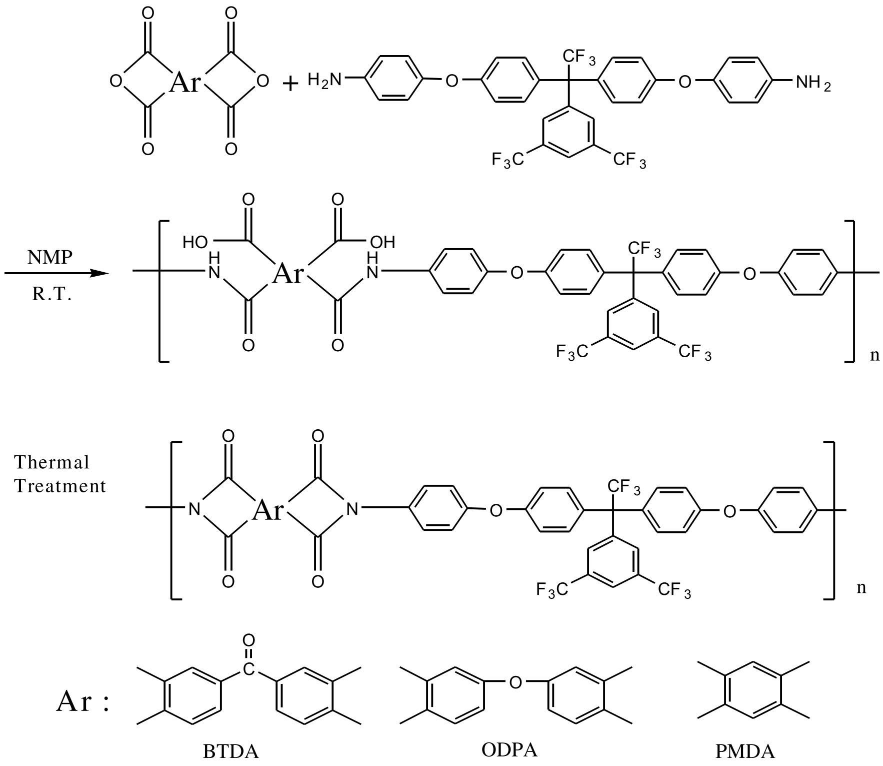


Fig. 5. FT-IR spectra of the resulting polyimides.

C_{15}, 130.6–131.6(m). The analysis results of ^1H NMR and ^{13}C NMR further confirm that the structure of 9FTPBA corresponds to that designed.

3.2. Synthesis of polyimides

When 9FTPBA was used as diamine monomer, the polycondensation of it with dianhydride monomer of BTDA, ODPA and PMDA will form three kinds of new polyimides, i.e. 9FTPBA/BTDA, 9FTPBA/ODPA, and 9FTPBA/PMDA. The experimental data listed in Table 1 show that the resulting polyimides could attain yields of 83–85%; the composition of chain unit of three polyimides was confirmed by elemental analysis results because those found are in accordance with those calculated. FT-IR spectra (Fig. 5) of the resulting polyimides exhibit characteristic absorption bands for the imide ring at 1780–1783 and 1726–1729 cm^{-1}, which shows asymmetric and symmetric stretching vibrations of imide ring C=O. The absorption bands of C–N stretching vibration (1373–1374 cm^{-1}) and



Scheme 2. Synthesis chemistry of polyimides based on diamine monomer 9FTPBA.

Table 2
Mechanical properties of three polyimides

Polyimide No.	Film	Tensile strength (MPa)	Elongation to break (%)	Initial modulus (GPa)
9FTPBA/BTDA	Good	68.1	3.2	2.19
9FTPBA/ODPA	Good	89.7	10.5	2.05
9FTPBA/PMDA	Brittle	/	/	/

Table 3
The water absorption and intrinsic viscosity of polyimides

Polyimide No.	Moisture intake (%)	Water intake (%)	Intrinsic viscosity (dl/g)
9FTPBA/BTDA	1.30	1.74	1.10
9FTPBA/ODPA	1.40	1.80	0.96
9FTPBA/PMDA	1.26	1.40	1.23

Table 4
The data of thermal analysis of polyimide films

Polyimide no.	Glass-transition temperature (DSC, °C)	Temperature at 5% weight loss (TGA, °C)	Temperature at 10% weight loss (TGA, °C)
9FTPBA/BTDA	223	535	558
9FTPBA/ODPA	224	568	590
9FTPBA/PMDA	225	537	561

imide-ring deformation vibrations (1153–1155 and 730–750 cm^{-1}) indicate that the expecting polyimides containing fluorine have gotten by polycondensation of novel diamine monomer 9FTPBA with aromatic dianhydrides through the general two-stage process, as shown in Scheme 2.

3.3. Mechanical properties of polyimides

The mechanical properties of films from the resulting polyimides are summarized in Table 2. The data presented in Table 2 indicate that the resulting polyimides from 9FTPBA/BTDA and 9FTPBA/ODPA can afford good quality films by thermal-imidization, while the film based on 9FTPBA/PMDA is brittle, which is perhaps due to the rigidity of chain structure derived from polyimide of 9FTPBA/PMDA. According to Table 2, the tensile strength and elongation to break of the films from 9FTPBA/ODPA reach 10.5% and 89.7 Mpa, and are better than those of one based on 9FTPBA/BTDA, and the values of their initial modulus will be near basically, the data exhibit that the resulting polyimides hold good mechanical properties. The data presented in Table 3 show that the moisture and water intake of the polyimide films are 1.26–1.40 and 1.40–1.80%, and the corresponding sequence is 9STPBA/ODPA > 9FTPBA/BTDA > 9FTPBA/PMDA. The low moisture and water intake of the polyimide films will be suitable for the applications in the microelectronic encapsulation. The intrinsic viscosities of the resulting polyimides show that their molecular weights can also satisfy the requirement for film formation (Table 3).

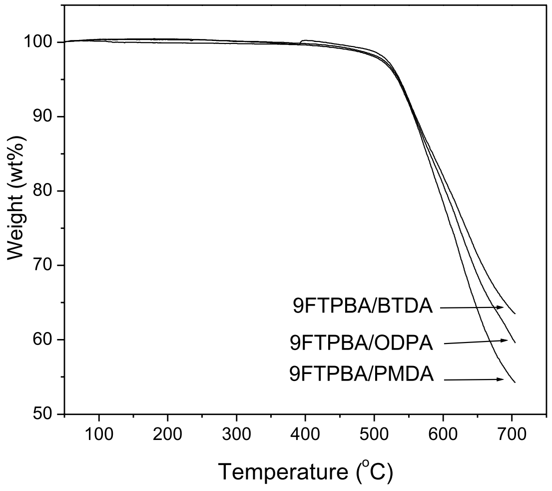


Fig. 6. The TGA curves of three polyimides.

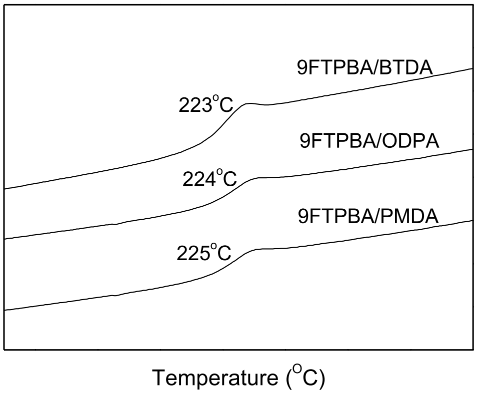


Fig. 7. DSC curves of three polyimides.

3.4. Thermal properties of polyimides

Figs. 6 and 7 are TGA and DSC curves of the resulting polyimides, and the corresponding data of thermal analysis are listed in Table 4. The TGA curves and data in Table 4 show that there are not weight loss before 450 °C, the

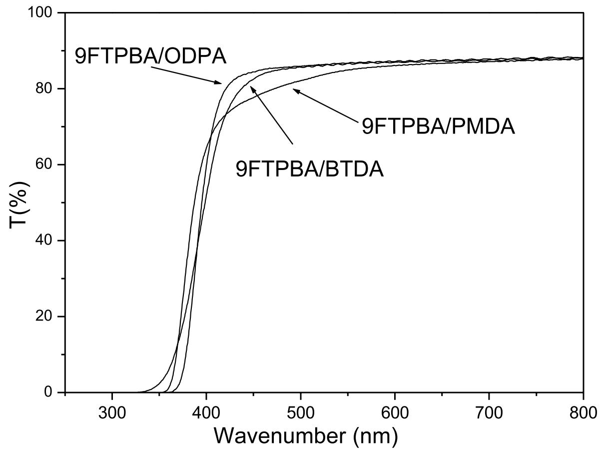


Fig. 8. UV spectra of three polyimides films (20 nm).

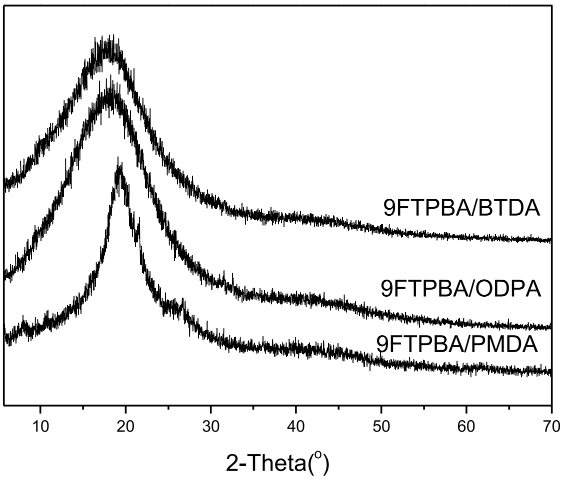


Fig. 9. Wide-angle X-ray diffraction patterns of three polyimides.

temperature of 5% weight loss is at 535–568 °C (in N_2), while that of 10% weight loss would be at 558–590 °C (in N_2), and their T_g values have reached to 223–225 °C (Fig. 7). The results of thermal analysis demonstrate that the resulting polyimides should hold excellent thermal stability and melting fluidity, these would be suitable to their application and processing.

3.5. Morphologies of polyimides

The UV spectra shown by Fig. 8 show that the films of the polyimides have good spectral transmittances over 450 nm, that is to say the resulting polyimides should have amorphous morphology. Furthermore, the measurement of wide-angle X-ray diffraction of the film sampling also confirms that there is only a broad peak that indicates amorphous morphology, as shown in Fig. 9. This perhaps results from the effect of the large volume of trifluoromethyl and triphenylethane on regularity of the polyimides obtained.

Table 5
Solubility of polyimides

Solvent	9FTPBA/ BTDA	9FTPBA/ ODPA	9FTPBA/ PMDA
NMP	+	+	+
DMF	+	+	+
DMAc	+	+	+
THF	+	+	+
Acetone	+	+	+
Cyclopentanone	−	+	−
m-Cresol	+	+	−
4-butyrolactone	−	+	×
Toluene	×	×	×
cyclohexene	×	×	×
CH_3OH	×	×	×

The solubility was determined at 15% solid content. +, The polymer was completely dissolved in the solvent at room temperature; −, the polymer was completely dissolved in the solvent on heating; ×, the polymer did not dissolve in the solvent.

3.6. Solubility of polyimides

The solubility of three polyimides was determined in the common organic solvents, and the data are summarized in Table 5. Most of polymers were soluble both in aprotic dipolar solvents and in common organic solvents such as NMP, DMF, DMAc, THF, cyclopentanone, acetone, *m*-cresol and 4-butyrolactone, 9FTPBA/ODPA has the best solubility in this solvent at room temperature, three of polyimides dissolve slowly at room temperature until it was heated at 80 °C, but 9FTPBA/PMDA was insoluble in 4-butyrolactone. All the new polyimides were insoluble in methanol, toluene and cyclohexene. When three polyimides obtained were dissolved in the above solvents at room temperature or heated, a homogeneous polymer solution with a solid content of 15 wt% would be formed, the polyimide solutions (including the solution that were heated) was stable for more than 2 months of storage, and no phase separation, gelation, or precipitation was observed during the storage period.

4. Conclusions

1,1-Bis[4-(4′-aminophenoxy)phenyl]-1-[3″,5″-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane(9FTPBA), a novel aromatic diamine monomer containing fluorine, was synthesized successfully from 1-bromo-3,5-bis(trifluoromethyl)benzene, and three kinds of soluble fluorine-containing polyimides were prepared by polycondensation of 9FTPBA with BTDA, ODPA and PMDA. The introduction of the bis(trifluoromethyl)phenyl and triphenylethane groups would improve the solubility of polyimides obtained. Meanwhile, the resulting polyimides still remained good thermal stability, mechanical properties, and spectral transmittances, as well as low moisture and water intakes.

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References

[1] Mittal KL, editor. Polyimide: synthesis, characterization, and application. New York: Plenum; 1984.
[2] Kricheldorf HR, editor. Progress in polyimide chemistry I. Berlin: Springer; 1990.
[3] Wilson D, Stenzenberger HD, Hergenrother PM, editors. Polyimides. London: Blackie; 1990.
[4] Leng WN, Zhou YM, Xu QH, Liu JZ. Polymer 2001;42:9253.
[5] Zhou HW, Liu JG, Qian ZG, Zhang SY, Yang SY. J Polym Sci, A: Polym Sci 2001;39:2404.

[6] Liew DJ, Hus PN, Chen WH, Liew BY. J Polym Sci, A: Polym Chem 2001;39:3498.
[7] Yamashita M, Kakimoto M, Imai Y. J Polym Sci, A: Polym Chem 1993;31:1513.
[8] Liou GS, Hsiao SH, Ishida M, Kakimoto M, Imai Y. J Polym Sci, A: Polym Chem 2002;40:2810.
[9] Maglio G, Palumbo R, Vignola MG. Macromol Chem Phys 1995;196:775.
[10] Yang CP, Wei CS. Polymer 2001;42:1837.
[11] Qian ZG, Ge ZY, Li ZX, He MH, Liu JG, Pang ZZ, et al. Polymer 2002;43:6057.
[12] Yang CP, Su YY, Hsiao FZ. Polymer 2004;45:7529.
[13] Yang CP, Hsiao SH, Wu KL. Polymer 2003;44:7067.
[14] Yang CP, Hsiao SH, Chen KH. Polymer 2002;43:5095.
[15] Ge ZY, Yang SY, Tao ZQ, Liu JG, Fan L. Polymer 2004;45:3627.
[16] Chern YT, Shiue HC. Macromolecules 1997;30:4646.
[17] Xie K, Zhang SY, Liu JG, Yang SY. J Polym Sci, A: Polym Chem 2001;39:2581.
[18] Liu JG, He MH, Li ZX, Qian ZG, Yang SY. J Polym Sci, A: Polym Chem 2002;40:1572.
[19] Yang CP, Hsiao SH, Wu KL. Polymer 2003;44:7067.
[20] Clair S, Anne K, Terry L. J Flourine Chem 1986;55:395.
[21] Hu AJ, Hao JY, He T, Yang SY. Macromolecules 1999;32:8046.
[22] Myung BY, Kim JJ, Yoon TH. J Polym Sci, A: Polym Chem 2002;40:4217.
[23] Hsiao SH, Chen WT. J Polym Sci, A: Polym Chem 2003;41:420.
[24] Hsiao SH, Chen WT. J Polym Sci, A: Polym Chem 2001;41:914.