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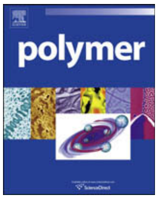

Synthesis and properties of soluble fluorinated poly(ether imide)s with different pendant groups

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ABSTRACT

Two types of new fluorinated diamine monomer, [1,4-(4-amino-2-trifluoromethyl-phenoxy)-2-(3′-trifluoromethylphenyl) benzene (III)] and [1,4-(4-amino-2-trifluoromethyl-phenoxy)-2-(3′-methylphenyl) benzene (IV)] were synthesized and polymerized with aromatic dianhydrides. A series of soluble poly(ether imide)s (PEIs) were prepared from the diamines and dianhydrides by two-step chemical imidization methods. Experimental results indicated that all the PEIs had glass transition temperature between 230 °C and 247 °C, the temperature at 5% weight loss between 527 °C and 598 °C under nitrogen. The membranes hand tensile strengths in the range of 74–101 MPa, tensile modulus in the range of 1.9–2.6 GPa, and elongation at break from 20 to 28%. The cast membranes also exhibited high optical transparency, with a UV–vis absorption edge of 354–406 nm. Moreover, these PEIs membranes possessed low dielectric constants of 2.63–3.20 (at 1 MHz) and low water uptakes ($<$0.75 wt%).

1. Introduction

It is well known that polyimides are useful high performance materials because of their excellent thermal stability, mechanical and electric properties [1–3]. High optical transparency is one of the most attractive properties of polyimides materials for a variety of applications such as electrics, optical waveguide [4,5]. However, the widespread applications of polyimides are often limited by processing difficulties because of their poor solubility and high processing temperature, which are caused by rigid polymer backbones and the strong interchain interaction. In addition, most polyimides between UV and the visible area have strong absorption, rendering their color to yellow or brown because of their highly conjugated aromatic structures and the intermolecular charge transfer complex (CTC) formation [6–11]. Therefore, the development of soluble polyimides with high optical transparency has attracted major interesting in the research of aromatic polymers. Fortunately, considerable efforts have gotten good progresses on the processability and solubility of polyimides based on structure design and modification of aromatic dianhydride and diamine monomers. Introducing noncoplanar moiety into the backbone of the polymer, contributed either from the diamine or from the dianhydride, has been proved to be a successful approach to attain solubility without sacrificing their excellent properties. It is one of the important progresses that polyimides derived from ether-bridged aromatic diamines and/or aromatic dianhydrides [12–20].

Furthermore, many aromatic dianhydrides and diamines having trifluoromethyl groups can effectively impart solubility of the polyimides. In addition, the introduction of bulky trifluoromethyl moieties into the polymers would increase the chain-packing distances and decrease intermolecular interactions. Usually, the refractive index and the birefringence do decrease with adding bulky fluorinated pendant groups. It has been demonstrated that the introduction of bulky trifluoromethyl group into polyimide backbones resulted in an enhanced solubility and optical transparency together with a lower dielectric constant, which was attributed to low polarizability of the C–F bond and the increase in free volume. Another approach to enhance solubility and/or melt processability is to incorporate flexible linkages along the backbones, either into the diamine or into the dianhydride component [14,21–29].

In this study, two new fluorinated aromatic diamines, [1,4-(4-amino-2-trifluoromethyl-phenoxy)-2-(3′-trifluoromethylphenyl) benzene (III)], and [1,4-(4-amino-2-trifluoromethyl-phenoxy)-2-(3′-methylphenyl) benzene (IV)], were designed and synthesized. A series of fluorinated PEIs (IIIa–IIId, IVa–IVd) were prepared by polycondensation of the monomers with various aromatic dianhydrides. The effect of trifluoromethyl group and methylphenyl group on solubility, thermal properties, mechanical properties, dielectric constant and optical properties of the PEIs was investigated. It is characterized that the prepared PEIs exhibited good solubility,

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excellent thermal and mechanical properties, low water uptake, low dielectric constant and high optical transparency.

2. Experimental

2.1. Materials

2-Chloro-5-nitrotrifluoromethlybenzene was obtained from Acros Organics. 1,4-Bis(3,4-dicarboxyphenoxy)benzene dianhydride (HQDPA; Acros Organics, 97%), 3,3,4,4-benzophenonetetracarboxylic dianhydride (BTDA, Acros Organics, 97%) and 4,4-oxydiphthalic anhydride (ODPA, Acros Organics, 97%) were recrystallized from acetic anhydride before use. 4,4-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA, Hoechst Celanese Corp., 99%) was used without further purification. *N*,*N*-Dimethylacetamide (DMAc) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. (3-Fluoromethylphenyl)-1,4-hydroquinone and (3-methylphenyl)-1,4-hydroquinone were synthesized according to the literature [30].

2.2. Measurements

IR spectra (KBr) were measured on a Nicolet Impact 410 Fourier transform infrared spectrometer. ^{1}H NMR was recorded on a Bruker 510 NMR spectrometer (500 MHz) with tetramethyl silane as a reference. Elemental analyses were performed on an Elemental Analyses MOD-1106. Gel permeation chromatograms (GPCs) using polystyrene as a standard were obtained on a Waters 410 instrument with tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 821^e instrument at a heating rate of 20 °C/min under nitrogen. Thermal gravimetric analyses (TGA) were determined in nitrogen atmosphere using a heating rate of 10 °C/min and polymers were contained within open aluminum pans on a Perkin Elmer TGA-7. Near infrared spectra were measured by a Jasco V-570 UV/VIS/NIR spectrophotometer. The refractive indices of the polymer films were obtained using a Gaertener L116B spectroscopic ellipsometer. UV transparencies were measured by a Shimadzu UV 2501-PC spectrophotometer. Wide-angle X-ray diffraction (WAXD) measurements at room temperature were made using a Rigaku/max-rA diffractometer equipped with a Cu Kα radiation source. The dielectric constants of the polymer films (diameter = 13 mm and thickness = 0.5 mm, prepared by compression molding, and then coated with silver by a vacuum evaporation method) were obtained using an HP 4192A LF impedance gain-phase analyzer with an HP-6047C. The polarizability and dipole moments of the model compounds were calculated using WinMOPAC 3.0 software. CNDO/S method and MOS-F program were chosen after the geometry optimization by AM1 method in MOPAC 2000 program. The equilibrium moisture absorption was determined by weighing the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days. The mechanical tests in tension were carried out using a SHIMADZU AG-I at a constant crosshead speed of 10 mm/min.

2.3. Monomer synthesis

2.3.1. 1,4-(4-nitro-2-trifluoromethyl-phenoxy)-2-(3′-trifluoromethylphenyl)benzene (I)

A mixture of 50.84 g (0.2 mol) of (3′-trifluoromethylphenyl)-1,4-hydroquinone, 45.11 g (0.4 mol) of 2-chloro-5-nitrotrifluromethlybenzene, 33.12 g (0.24 mol) of anhydrous potassium carbonate, 500 mL of dry *N*,*N*-dimethylformamide (DMF), and 70 mL of toluene was placed in a 1000-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a Dean-Stark strap, a reflux condenser and a nitrogen purge. The mixture was refluxed with stirring at 128 °C for 4 h to ensure complete dehydration. After removing toluene, the reaction mixture was heated to 151 °C and refluxed for 8 h under a nitrogen atmosphere. After being poured into water (1 L), the yellow precipitate was collected by filtration and dried under vacuum. The crude product was washed with ethanol to give a yellow powder of I (96.16 g, yield: 84%). Mp: 147 °C. IR (KBr, cm^{-1}): 1538 and 1359 (–NO$_2$ stretch), 1227 (Ph–O–Ph stretch), 1139 (C–F stretch). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 8.53 (d, $J = 8.6$ Hz, 1H), 8.54 (dd, $J = 7.4$ Hz, 1H), 8.47 (d, $J = 8.3$ Hz, 1H), 8.32 (dd, $J = 7.8$ Hz, 1H), 7.95 (s, 2H), 7.79 (m, $J = 8.5$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 1H), 7.53 (d, $J = 8.3$ Hz, 1H), 7.46 (d, $J = 7.9$ Hz, 1H), 7.43 (d, $J = 9.1$ Hz, 1H), 7.13 (d, $J = 8.8$ Hz, 1H).

Elem. Anal. Calcd for $C_{27}H_{13}F_9N_2O_6$ (632.39): C, 51.28%; H, 2.07%; N, 4.43%. Found: C, 51.42%; H, 2.13%; N, 4.50%.

2.3.2. 1,4-(4-nitro-2-trifluoromethyl-phenoxy)-2-(3′-methylphenyl)benzene (II)

1,4-(4-nitro-2-trifluoromethyl-phenoxy)-2-(3′-methylphenyl)-benzene was synthesized with similar methods. A mixture of 40.046 g (0.2 mol) of (3′-methylphenyl)-1,4-hydroquinone, 45.11 g (0.4 mol) of 2-chloro-5-nitrotrifluro-methlybenzene, 33.12 g (0.24 mol) of anhydrous potassium carbonate, 500 mL of dry *N*,*N*-dimethylformamide (DMF), and 70 mL of toluene was placed in a 1000-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a Dean-Stark strap, a reflux condenser and a nitrogen purge. The mixture was refluxed with stirring at 128 °C for 4 h to ensure complete dehydration. After removing toluene, the reaction mixture was heated to 151 °C and refluxed for 8 h under a nitrogen atmosphere. After being poured into water (1 L), the yellow precipitate was collected by filtration and dried under vacuum. The crude product was washed with ethanol to give a yellow powder of II (89.17 g, yield: 86%). Mp: 155 °C. IR (KBr, cm^{-1}): 1533 and 1336 (–NO$_2$ stretch), 1253 (Ph–O–Ph stretch), 1139 (C–F stretch). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 2.51 (s, 3H), 8.55 (d, $J = 8.5$ Hz, 1H), 8.51 (dd, $J = 6.7$ Hz, 1H), 8.44 (d, $J = 8.7$ Hz, 1H), 8.38 (dd, $J = 8.2$ Hz, 1H), 7.93 (s, 2H), 7,79 (m, $J = 8.5$ Hz, 2H), 7.70 (d, $J = 8.3$ Hz, 1H), 7.51 (d, $J = 8.3$ Hz, 1H), 7.48 (d, $J = 8.8$ Hz, 1H), 7.40 (d, $J = 9.3$ Hz, 1H), 7.16 (d, $J = 9.2$ Hz, 1H). Elem. Anal. Calcd for $C_{27}H_{16}F_6N_2O_6$ (578.42): C, 56.06%; H, 2.79%; N, 4.84%. Found: C, 56.14%; H, 2.75%; N, 4.81%.

2.3.3. Synthesis of 1,4-(4-amino-2-trifluoromethyl-phenoxy)-2-(3′-trifluoro-methylphenyl) benzene (III)

A total of 12.65 g (0.02 mol) of the previously obtained dinitro compound (I), 13.44 g (0.02 mol) of Fe powder, and 60 mL of 50% aqueous ethanol were mixed in a 250-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer and a reflux condenser. The mixture was refluxed with stirring. To this solution, a mixture of 0.704 ml of concentrated HCl and 10 ml of 50% aqueous ethanol was then slowly added. The reaction solution was refluxed for 3 h, and 0.366 g NaOH was added. The solution was filtered hot, and the filtrate was then distilled to remove the solvent in vacuo. The crude product was purified by recrystallization from ethanol to give a gray solid. Yield: 70%. Mp: 128 °C. IR (KBr, cm^{-1}): 3478 and 3386 (N–H stretch), 1230 (Ph–O–Ph stretch), 1125 (C–F stretch). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 5.44 (s, 2H), 5.37 (s, 2H), 7.89 (s, 1H), 7.80 (d, $J = 7.5$ Hz, 2H), 7.71 (d, $J = 8.1$ Hz, 1H), 7.67 (t, $J = 8.0$ Hz, 1H), 7.07 (d, $J = 8.3$ Hz, 1H), 6.96 (m, $J = 8.5$ Hz, 1H), 6.92 (m, $J = 3.5$ Hz, 1H), 6.89–6.84 (m, $J = 8.3$ Hz, 2H), 6.84–6.77 (m, $J = 7.5$ Hz, 2H), 6.74 (s, 2H). ^{13}C NMR (500 MHz, DMSO-d_6, δ, ppm) 154.31, 149.58, 146.04, 143.51, 137.88, 133.10, 131.41, 129.82, 129.57, 127.19, 125.02, 124.48, 123.04, 122.86, 121.32, 120.719, 119.51, 119.01, 118.27, 111.38. Elem. Anal. Calcd for $C_{27}H_{17}F_9N_2O_2$ (572.42): C, 56.65%; H, 2.99%; N, 4.89%. Found: C, 56.43%; H, 3.11%; N, 4.81%.

2.3.4. Synthesis of 1,4-(4-amino-2-trifluoromethyl-phenoxy)-2-(3′-methylphenyl) benzene (IV)

Monomer IV was prepared by the same procedure as the monomer III, with the dinitro monomer II instead of monomer I. Mp: 137 °C. IR (KBr, cm^{-1}): 3462 and 3375 (N–H stretch), 1223 (Ph–O–Ph stretch), 1120 (C–F stretch). ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 2.30 (s, 3H), 5.44 (s, 2H), 5.32 (s, 2H), 7.35 (s, 1H), 7.28 (d, $J = 8.3$ Hz, 1H), 7.26 (d, $J = 7.7$ Hz, 1H), 7.14 (d, $J = 6.8$ Hz, 2H), 6.95–6.89 (m, $J = 7.3$ Hz, 2H), 6.87 (d, $J = 4.1$ Hz, 1H), 6.84–6.79 (m, 9.3 Hz, 2H), 6.78–6.71 (m, 9.3 Hz, 2H), 6.69 (d, $J = 8.8$ Hz, 1H). ^{13}C NMR (500 MHz, DMSO-d_6, δ, ppm) ^{13}C NMR (500 MHz, DMSO-d_6, δ, ppm) 155.53, 150.52, 147.25, 143.63, 139.38, 135.11, 131.55, 130.05, 129.91, 127.86, 125.42, 124.79, 123.26, 122.89, 121.60, 120.76, 119.49, 119.47 119.62, 110.68. Elem. Anal. Calcd for $C_{27}H_{20}F_6N_2O_2$ (518.45): C, 62.55%; H, 3.89%; N, 5.40%. Found: C, 62.42%; H, 3.96%; N, 5.31%.

2.4. Polymer synthesis

Utilizing III and IV as diamine monomer, eight kinds PEIs were synthesized by polycondensation with dianhydride monomer HQDPA (a), ODPA (b), BTDA (c) and 6FDA (d), respectively. The resulting PEIs were abbreviated to IIIa–IIId and IVa–IVd successively.

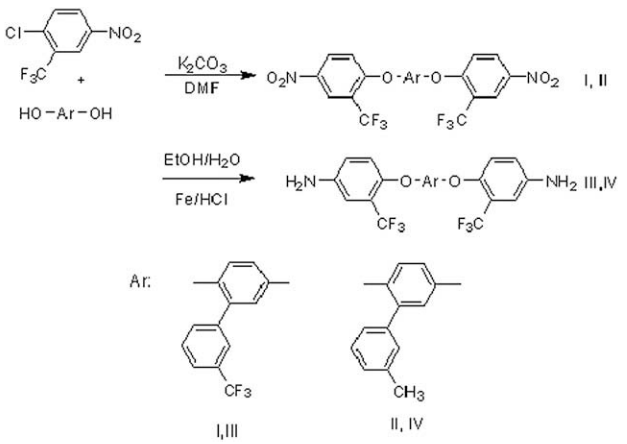
In a typical experiment, polyimide IIIb, which derived from diamine III and ODPA (b), was prepared as follows: diamine III (2.0607 g, 3.6 mmol) was dissolved in 20 mL of DMAc. To this diamine solution, ODPA (1.1117 g, 3.6 mmol) and an additional 16 mL of DMAc were added. The mixture was stirred in nitrogen at room temperature for 24 h to yield a viscous poly(amic acid) (PAA) solution with 10 wt% solid content. Chemical imidization was carried out via the addition of 7.5 mL of an acetic anhydride/pyridine (5/4 v/v) mixture into the PAA solution (with mechanical stirring) at ambient temperature. The mixture was stirred at 60 °C for 4 h to yield a polyimide solution, which was poured into methanol to give a precipitate, IIIb was collected by filtration, washed thoroughly with methanol, and dried at 80 °C in vacuo. Other PEIs were synthesized in an analogous procedure. IR (KBr, cm^{-1}): 1784 and 1730 (asymmetric, symmetric imide C=O stretch), 1619–1481 (aromatic C=C stretch), 1381 (C–N stretch), 1240 (Ph–O–Ph stretch), 1100–1300 (C–O and C–F stretching).

3. Results and discussion

3.1. Monomer synthesis

The fluorinated diamine monomers, III and IV, were prepared through the nucleophilic substitution reaction of 2-chloro-5-nitrobenzotrfluoride with (3-trifluoromethylphenyl)-1,4-hydroquinone or (3-methylphenyl)-1,4-hydroquinone in the presence of potassium carbonate in dry DMF to yield a dinitro compound, and these products underwent reduction with Fe/HCl in ethanol/water at 90 °C as shown in Scheme 1. In the nucleophilic substitution reaction, the inductive effect of the electron-withdrawing CF_3 group activated the aryl chloride group, and so the reaction could take place at a lower temperature, thus preventing coloring. The yields in each step were very high, and the obtained products in each step were confirmed by spectroscopic techniques.

FTIR and ^1H NMR were used to confirm the structures of the dinitro monomer and diamine monomer. Fig. 1 shows the IR spectra of the diamines III and IV. The pair of N–H stretching bands of the amino group was shown in the region 3300–3500 cm^{-1}. The elemental analysis of PEIs is listed in Table 1 showing that the obtained values are close to the calculated ones. As shown in Table 2, the weight–average and number–average molecular weights of the resulting PEIs were in the range of 27,000–160,000, and 16,000–87,000, respectively, relative to the polystyrene standards.



Scheme 1. Synthesis of monomers.

Fig. 2 shows the ^1H spectra of diamines III, IV. In monomer IV ^1H NMR spectra, the methyl group appeared in 2.30 ppm. ^1H NMR spectrum of diamines III, IV confirms that the nitro groups have been converted into amino groups by the high field shift of the aromatic protons at 5.44 ppm corresponding to the amino protons, respectively. After reduction, most of the resonance signals of

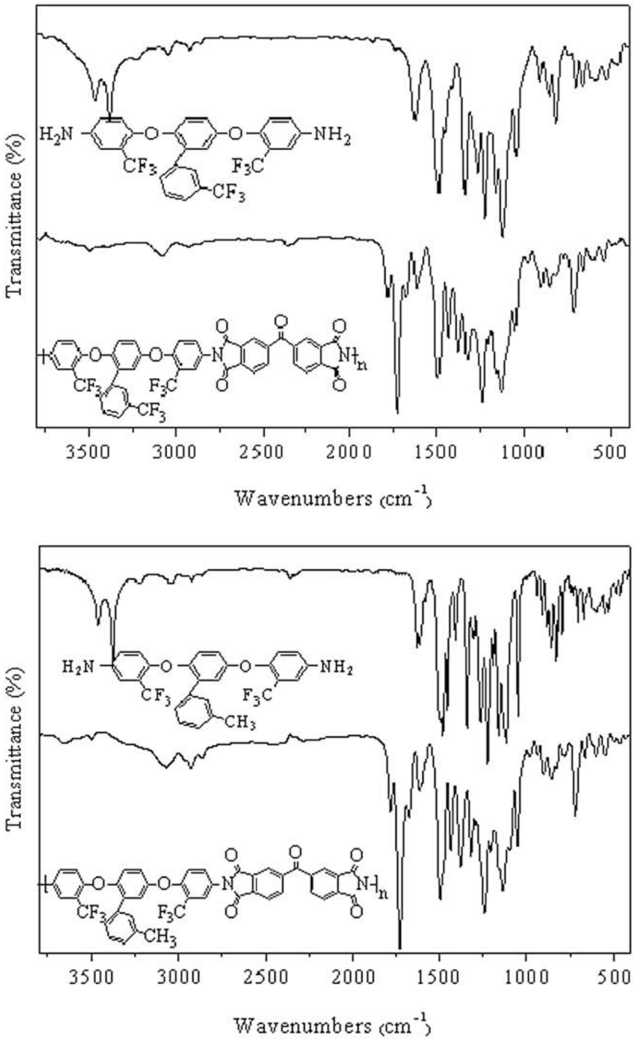


Fig. 1. IR spectra of diamino (III), (IV) and polyimide (IIIc), (IVc).

Table 1
Elemental analysis of the polyimides.

Polymer	Formula (molecular weight)	Elemental analysis (%)			
			C	H	N
IIIa	$(C_{51}H_{29}F_9N_2O_8)_n$	Calcd	63.23	3.02	2.89
	$(968.77)_n$	Found	63.84	2.95	2.81
IIIb	$(C_{45}H_{25}F_9N_2O_7)_n$	Calcd	61.65	2.87	3.20
	$(876.67)_n$	Found	62.27	2.77	3.11
IIIc	$(C_{46}H_{25}F_9N_2O_7)_n$	Calcd	62.17	2.84	3.15
	$(888.69)_n$	Found	61.35	2.51	3.32
IIId	$(C_{48}H_{25}F_{15}N_2O_6)_n$	Calcd	57.04	2.49	2.77
	$(1010.70)_n$	Found	56.06	2.31	2.86
IVa	$(C_{51}H_{32}F_6N_2O_8)_n$	Calcd	66.96	3.53	3.06
	$(914.80)_n$	Found	65.87	3.41	3.13
IVb	$(C_{45}H_{25}F_9N_2O_7)_n$	Calcd	65.70	3.43	3.41
	$(822.70)_n$	Found	66.56	3.27	3.27
IVc	$(C_{46}H_{28}F_6N_2O_7)_n$	Calcd	66.19	3.38	3.36
	$(834.71)_n$	Found	65.30	3.20	3.48
IVd	$(C_{48}H_{28}F_{12}N_2O_6)_n$	Calcd	60.26	2.95	2.93
	$(956.73)_n$	Found	61.12	2.89	3.09

aromatic protons shifted to a higher field due to the electron-donating nature of the amino group. These results clearly confirm that the diamines III and IV prepared herein are consistent with the proposed structure.

3.2. Synthesis and characterizations of polymers

The two types diamine monomers III and IV were reacted with different dianhydrides a–d with a conventional two-step procedure of ring-opening polyaddition at room temperature to form PAA and sequential chemical imidization by adding mixture of acetic anhydride and pyridine (molar ratio monomer/anhydride/pyridine 1:10:10) into PAA solution at ambient temperature for 30 min followed by heating at 60 °C for 12 h to give poly(ether imide)s IIIa–IIId and IVa–IVd as displayed in Scheme 2.

The structures of the PEIs were characterized by FTIR and ^1H NMR spectra. The FTIR spectra of PEIs IIIc and IVc exhibited characteristic imide group absorptions at around 1784 and 1730 cm^{-1} (typical of imide carbonyl asymmetrical and symmetrical stretchings) and did not show an amide carbonyl peak at 1650 cm^{-1}, thus indicating complete imidization during polycondensation. 1381 cm^{-1} (C–N stretch), 1093 and 730 cm^{-1} (imide ring deformation), together with some strong absorption bands in the region of 1100–1300 cm^{-1} due to the C–O and C–F stretchings (Fig. 1) are also clearly visible.

The ^1H NMR spectra of soluble PEIs IIIb and IVa are shown in Fig. 3. In IIIb ^1H NMR spectra, all protons resonated in the region of 7.1–8.3 ppm. The H_1, H_2 and H_3 close to the imide ring appeared at the farthest downfield region of the spectrum because of the resonance. The protons H_7 and H_8 shifted to a higher field because of the electron-donating property of aromatic ether. In IVa ^1H NMR spectra, the methyl group appeared in 2.27 ppm. The H_1 close to the imide ring appeared at the farthest downfield region of the spectrum because of the resonance. The protons H_8 and H_9 shifted to a higher field because of the electron-donating property of aromatic ether. The above results demonstrate that the diamines monomers III and IV hold a good polymerization activity to form PEIs, meanwhile, 100% chemical imidization could be achieved at lower temperatures, and this should be suitable to get soluble polyimide, and show that series III and IV were synthesized successfully.

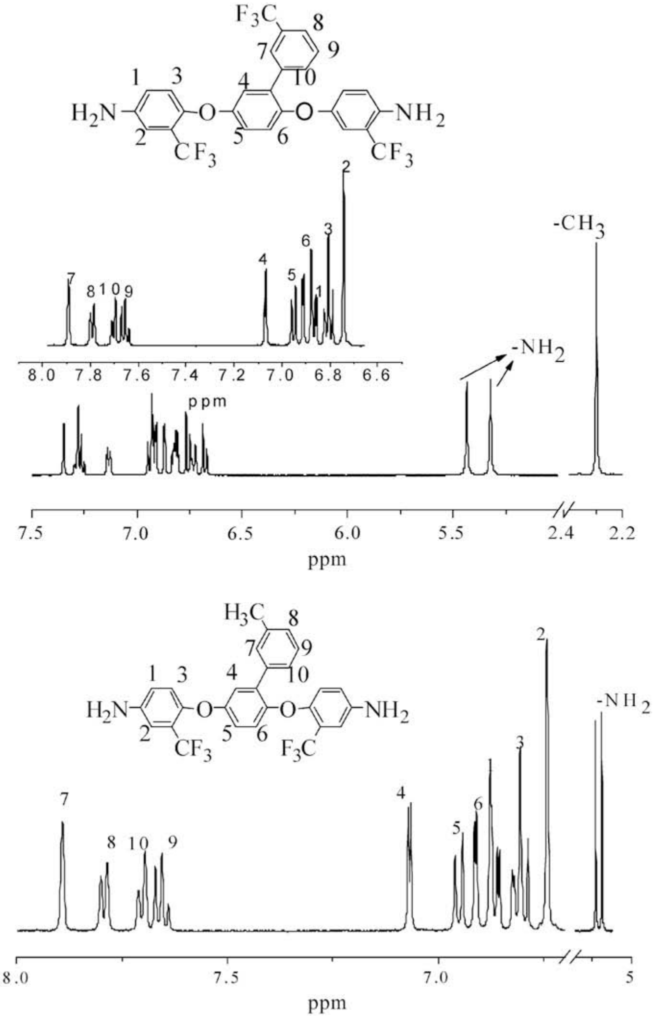


Fig. 2. ^1H NMR spectra of diamines (III,IV) in DMSO-d_6.

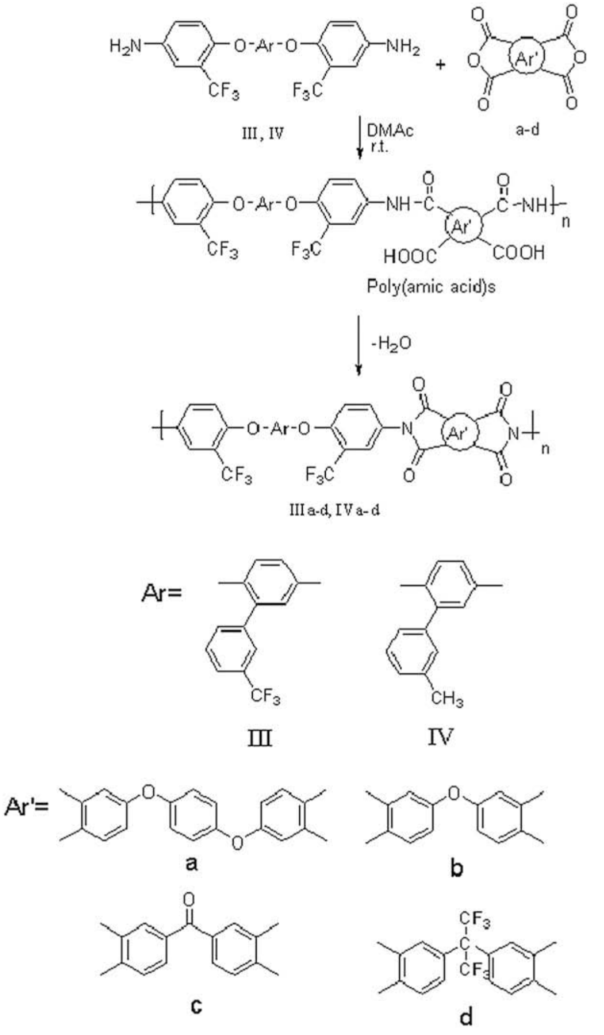
Table 2
GPC data and thermal properties of the polyimides.

Polymer	GPC data			DSC	TGA		
	M_w[a] × 10^4	M_n[a] × 10^4	M_w/M_n[a]	T_g[b] (°C)	$T^c_{5\%}$ (°C)	$T^c_{10\%}$ (°C)	Char yield[d] (%)
IIIa	2.7	1.7	1.6	230	593	615	55.739
IIIb	4.4	2.4	1.8	232	598	621	56.742
IIIc	9.0	4.3	2.1	241	586	607	53.343
IIId	2.9	1.6	1.9	236	553	578	50.870
IVa	9.2	4.5	2.0	238	538	578	59.086
IVb	16.0	8.7	1.9	240	557	580	56.757
IVc	3.8	2.0	1.9	247	538	581	59.610
IVd	5.6	2.8	2.0	243	527	559	53.299

[a] Relative to polystyrene standard, using THF as the eluent.
[b] Baseline shift in the second heating DSC traces, with a heating rate of 20 °C/min in nitrogen.
[c] Temperature at 5% and 10% weight loss were recorded by TG at a heating at 10 °C/min in nitrogen.
[d] Residual weight (%) when heated to 800 °C.

3.3. Solubilities of the polymers

The solubility of synthesized fluorinated PEIs was tested in various organic solvents and the results are summarized in Table 3. PEI series III and IV showed an excellent solubility in aprotic polar solvents such as DMSO, DMA_C, DMF and NMP and were also soluble in less polar solvents like pyridine, THF at room temperature. Most of them were soluble even in acetone. The solubility of IIIa–IIId and IVa–IVd is enhanced due to the introduction of bulky pendant trifluoromethylphenyl and methylphenyl group which could inhibit close packing and reduced the interchain interactions to enhance solubility.



Scheme 2. Synthesis of polyimides.

3.4. Thermal properties of the polymers

DSC was used to evaluate the thermal properties of the PEI films. The glass transition temperatures of PEIs are given in Table 2. The T_g of PEIs series III and IV were, respectively, in the range of 234–247 and 230–241 °C, which increased in the order of BTDA > 6FDA > OPDA > HQDPA. PEI IIIa and IVa obtained from HQDPA showed the lowest T_g because of the presence of two flexible ether linkages between the phthalimide units. From Table 2, it can be seen that the T_g of PEI series III was higher than that of the comparable PEI series IV. A possible explanation for the lower T_g values of III polymers is that the substitution of methyl with trifluoromethyl would lead to an internal plasticization in addition to the geometry and free-volume factors [30,31].

Thermal stabilities of the PEIs were evaluated by TGA under nitrogen with a 5% weight loss and 10% weight loss for comparison. These are summarized in Table 3. The decomposition temperatures at a 5% weight loss of PEIs IIIa–IIId were recorded in the range of 553–593 °C in nitrogen and those of PEIs IVa–IVd were recorded in the range of 527–557 °C. Series III possessed higher decomposition temperatures than that of Series IV. This result was attributed to the presence of stronger C–F bonds with higher stability than C–H. They left more than 50.87% char yield at 800 °C. The TGA data indicated that these PEIs had fairly high thermal stability regardless of the introduction of the pendant groups, even though they revealed high solubility and optical transparency.

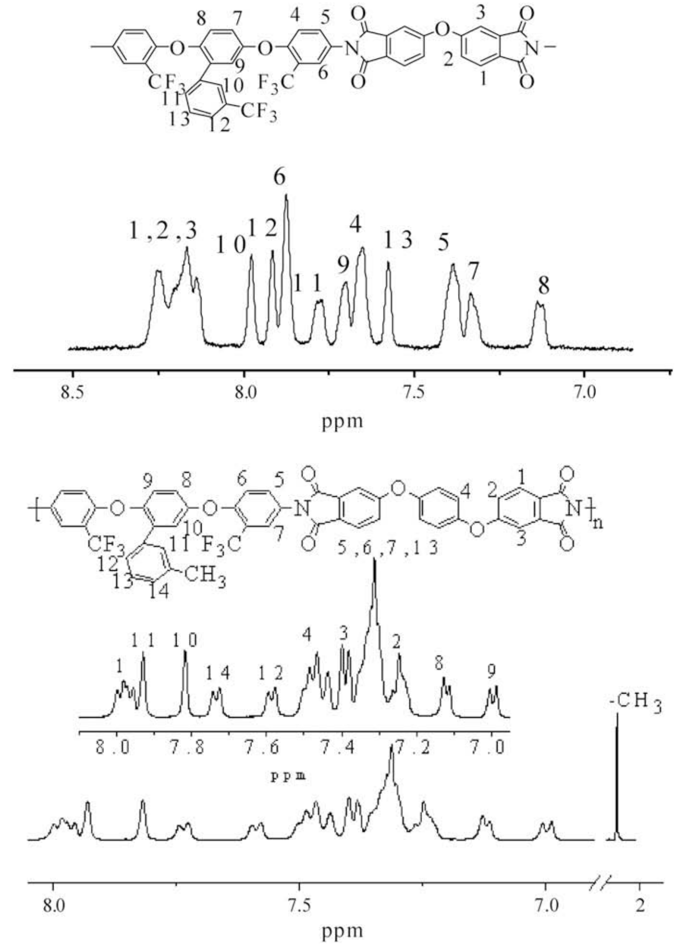


Fig. 3. ^{1}H NMR spectra of the polyimide IIIb in DMSO-d_6.

3.5. Mechanical properties of the polymers

The mechanical properties of polyimide films are summarized in Table 4. PEI series III and series IV had tensile strength, elongation at break, and Young's modulus in the ranges of 74–101 MPa, 20–28% and 1.9–2.6 GPa, respectively, indicating that they could be cast into transparent, flexible and tough films.

3.6. Morphological structure of the polymers

The morphological structure of the PEI films was analyzed by Wide-Angle X-ray Diffraction (WAXD). The curves of all the

Table 3
Solubility of the polyimides.

Polymer	Solvents[a]								
	NMP	DMAc	DMF	DMSO	THF	Py	$CHCl_3$	Acetone	Ethanol
IIIa	++	++	++	++	++	++	++	++	–
IIIb	++	++	++	++	++	++	++	+	–
IIIc	++	++	++	++	++	++	++	++	–
IIId	++	++	++	++	++	++	++	++	–
IVa	++	++	++	++	++	++	++	++	–
IVb	++	++	++	++	++	++	++	++	–
IVc	++	++	++	++	++	++	++	++	–
IVd	++	++	++	++	++	++	++	++	–

Qualitative solubility was determined with as 10 mg of polymer in 1 mL of solvent. ++: soluble at room temperature; +: soluble on heating at 100 °C.

[a] NMP, *N*-methyl-2-pyrrolidone; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine; THF, tetrahydrofuran.

Table 4
Mechanical properties and optical properties of polyimides.

Polymers	Film thickness (μm)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)	λ_0[a] (nm)	UV-transmittance[b] (%)
IIIa	44	93	28	2.3	372	95
IIIb	46	101	20	2.6	372	95
IIIc	43	85	24	2.2	405	94
IIId	44	85	21	2.1	354	95
IVa	48	74	25	1.9	388	89
IVb	47	78	20	2.2	386	89
IVc	45	75	21	2.4	406	87
IVd	42	83	25	1.9	384	90

[a] Cut-off wavelength defined as the point at which the transmittance becomes less than 1%.

[b] UV-transmittance at 800 nm (%).

Table 5
Refractive index and dielectric constant of polyimides.

Polymer	Refractive index		Dielectric constant			Water uptake (%)
	$n_{1310\ \mathrm{nm}}$	$n_{1550\ \mathrm{nm}}$	1 KHz	10 KHz	1 MHz	
IIIa	1.5713	1.5671	2.83	2.81	2.79	0.27
IIIb	1.5595	1.5542	2.73	2.71	2.70	0.29
IIIc	1.5558	1.5503	3.12	3.10	3.09	0.68
IIId	1.5497	1.5342	2.66	2.64	2.63	0.19
IVa	1.6038	1.6022	3.09	3.03	3.02	0.38
IVb	1.5994	1.5979	2.89	2.87	2.86	0.39
IVc	1.5677	1.5591	3.25	3.21	3.20	0.75
IVd	1.6162	1.5341	2.72	2.68	2.66	0.21

polymers were broad and without obvious peak features, which indicate that they are all amorphous (Fig. 4). The mean intermolecular distances calculated from the peak maximum for the reflection WAXD patterns for IIIa–IIId were 4.77 Å, 4.87 Å, 4.91 Å, 5.36 Å and those for IVa–IVd were 4.47 Å, 4.61 Å, 4.68 Å, and 5.10 Å, respectively. This was reasonable because the PEIs contained laterally attached, non-coplanar unit of diamine that sterically disrupted the chain-packing and inhibited significant chain–chain interactions. The amorphous nature of the PEIs could be attributed in part to the presence of the bulky CF_3 group and bulky pendant group, which resulted in a less dense chain-packing structure. Therefore, amorphous halo represents PI chain packed unsystematically. The amorphous phase endows some special features to polyimide, such as high solubility in solvents and lightest color.

3.7. Dielectric constants and water uptakes of the polymers

The dielectric constants and water uptakes of all the polyimides are reported in Table 5. The PEI series III and IV exhibited the dielectric constants at 1 MHz in the range of 2.63–3.09 and 2.66–3.20, respectively, which are lower than the corresponding non-fluorinated polyimides and the standard PI such as Kapton films ($\xi_{\mathrm{cap}} = 3.5$ at 1 kHz) and Ultem ($\xi_{\mathrm{cap}} = 3.5$ at 1 kHz) [32]. PEI series III had lower dielectric constants than series IV. The decreased dielectric constants could be explained by the presence of the bulky trifluoromethylphenyl pendant groups, which has lower polarizability and larger free volume of the polymer chain than methyl phenyl groups. Considering the type of dianhydride backbone, the dielectric constant form lists in the following order: $d < b < a < c$. PEI having d exhibited lowest dielectric constants because of the presence of bulky CF_3 groups. When a, b and c were considered, c had a higher dielectric constant for the reason that the carbonyl bridge (C═O) had less free volume, more polarizability and moisture absorption in the PEI backbone when compared to the –O– bridge. As expected, the fluorinated PEI series III exhibited lower water absorptions (0.19–0.68%) than IV (0.21–0.75%) due to the content of the hydrophobic CF_3 group. The low water absorptions ensure that these polymers have stable dielectric performance.

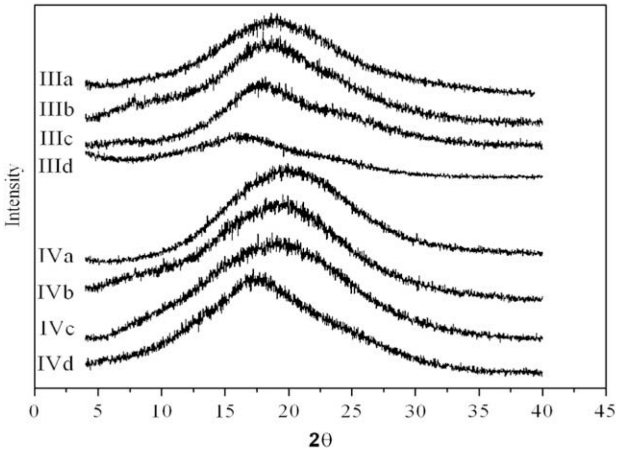


Fig. 4. Wide-angle X-ray diffractograms of the polyimides.

3.8. Optical properties of the polymers

Thin films were measured for optical transparency with UV–vis spectroscopy. Fig. 5 shows the UV–vis transmittance spectra of the PEI films, the cut-off wavelength (absorption edge, λ_0) values and the percentage transmittance at 400 nm from these spectra are listed in Table 4. Except for IIIc and IVc, the other fluorinated PEIs had shorter λ_0 than 400 nm, and all the PEI series III and IV exhibited high optical transparency of 85–95%. Because of the highly conjugated aromatic structures and intermolecular charge-transfer complex (CTC) formation of PI, most polymers between the UV and visible area have strong absorption. However, these fluorinated PEIs which have flexible group like ether linkage and CF_3 group with bulky side groups in the center of the diamine reduced the intermolecular CTC between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. The 6FDA, ODPA and HQDPA produced nearly colorless polyimide films in contrast to other dianhydrides, and these can be explained by the decreased intermolecular interactions [33]. Moreover, CF_3 group might weaken chain-to-chain cohesive force due to lower polarizability of the C–F bond. The decrease in the intermolecular CTC formation is understandable also from the significant solubility of the PEIs prepared from diamines. All the series III revealed shorter λ_0 and higher optical transparency than their respective series IV.

It has been reported that the replacement of C–H bonds with C–F bonds gives high optical transparency of the polymeric material in the near-infrared (NIR) telecommunication region [34]. As shown in Fig. 6, there are C–H bond vibrational absorption peaks ($2\nu_{\mathrm{C–H}}$ 1650 nm and $3\delta_{\mathrm{C–H}}$, 1100 nm) and related peak ($2\nu_{\mathrm{C–H}} + \delta_{\mathrm{C–H}}$, 1400 nm). However, it has small light absorption at telecommunication wavelength of 1310 and 1550 nm due to its high fluorine content. Furthermore, the near-infrared absorption of series III was weaker than that of series IV at the key telecommunication wavelengths of 1310 and 1550 nm. The wavelength of 1310 nm or 1550 nm will be used for optical telecommunication, so these PEIs are expected to be applicable for optoelectronic materials [35].

Table 5 shows the refractive index of the spin-coated fluorinated polymers at 1310 nm and 1550 nm. It is known that refractive indices of fluorine-containing polymers are smaller than those of unfluorinated polymers due to the smaller polarizability of the carbon–fluorine bond (C–F) compared to that of the carbon–hydrogen (C–H) bond.

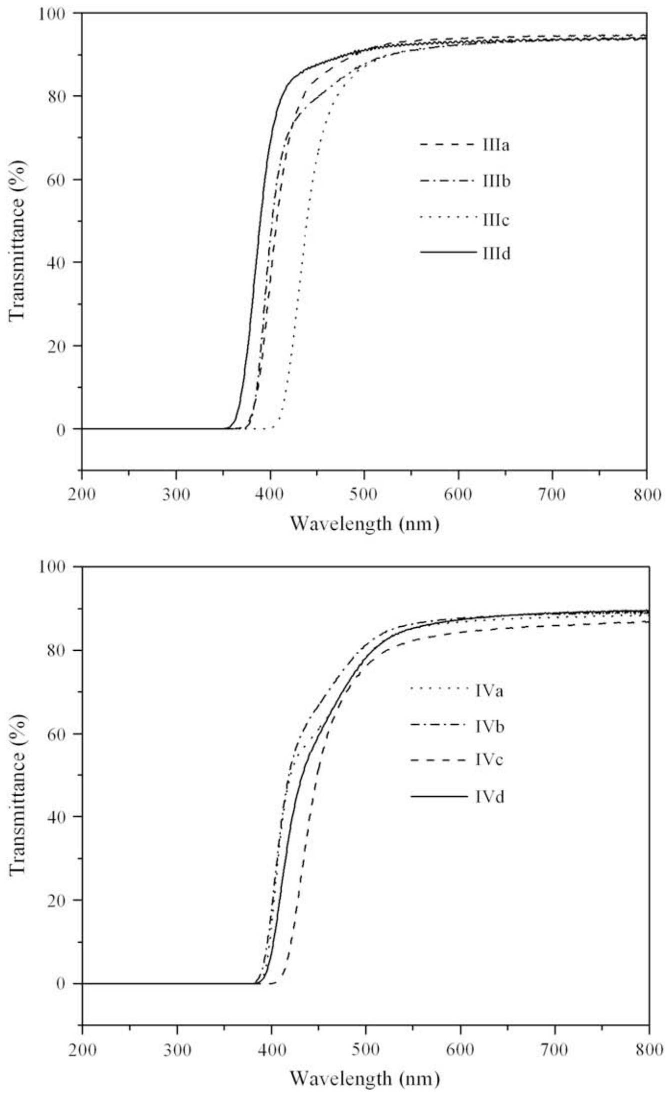


Fig. 5. UV–vis spectra of the polyimide films.

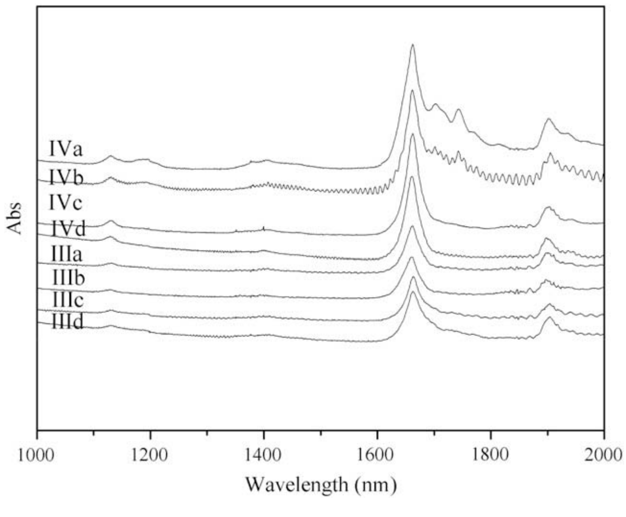


Fig. 6. Near-IR spectra of the polyimides.

4. Conclusions

Two series of fluorinated poly (ether imide)s (III and IV) were synthesized from 1,4-(4-amino-2-trifluoromethyl-phenoxy)-2-(3′-trifluoromethylphenyl) benzene and 1,4-(4-amino-2-trifluoromethyl-phenoxy)-2-(3′-methylphenyl) benzene with various aromatic dianhydrides via chemical imidization technique, respectively. The combination of these dianhydride and diamine monomers was a successful process for reducing overall charge transfer complex formation due to either inter- or intramolecular electronic interactions. Thus, the prepared PEIs displayed excellent solubility, fantastic optical property and low dielectric constant. In addition, we compared PEI series III with series IV to investigate the difference of the pendant group affecting the dielectric property of the polymers. As a result, we confirmed that both PEI series III and IV showed low dielectric constant, and PEI series III displayed lower dielectric constant than IV. PEI series III also exhibited better thermal stability, higher optical transparency and lower water absorption than series IV. The NIR absorptions at the communication window of all the polymers were as low as we expected. All the characterizations proved that the resulting fluorinated PEIs were potential candidates for optical device and microelectronic applications.

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