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Synthesis and characterization of novel soluble fluorinated aromatic polyamides derived from fluorinated isophthaloyl dichlorides and aromatic diamines

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Abstract

Two series of fluorinated aromatic polyamides derived from two novel monomers, 5-(4-trifluoromethylphenoxy)isophthaloyl dichloride (3FPC) and 5-(3,5-bistrifluoromethyl-phenoxy)isophthaloyl dichloride (6FPC) with various aromatic diamines were synthesized and characterized. Experimental results indicated that the fluorinated aromatic polyamides showed good solubility in many organic solvents. The solubility of the polyamides was affected by the trifluoromethyl substituents and the pendent phenoxy groups in the polymer backbone. The fluorinated polyamides have good thermal stability with the glass transition temperature of 206–285 °C, the temperature at 5% weight loss of 442–460 °C in nitrogen. The polyamide films also exhibited good mechanical properties and excellent electrical and dielectric properties. The fluorinated groups in the polymer backbone have played an important role in the improvement of electrical and dielectric performance of polymer.

Keywords: Fluorinated polyamides; Solubility; Dielectric property

1. Introduction

Aromatic polyamides, such as poly(*p*-phenylene terephthalamide) and poly(*m*-phenylene terephthalamide), have been recognized as one of the most successful aromatic polymer materials due to their extensive applications in high-tech industry [1–5]. Despite the excellent combined properties, including good thermal stability and mechanical properties, as well as outstanding chemical resistance and electrical insulating performance, aromatic polyamides have some drawbacks associated with infusibility and insolubility, which were caused by the highly regular and rigid polymer backbones and the formation of intermolecular hydrogen bonding, resulting in their poor processability. Moreover, the high moisture absorptions of aromatic polyamides, compared with other polymer materials, have resulted in obvious negative effect on their mechanical properties as well as electrical insulating and dielectric performance. Consequently, many efforts have been made to improve their solubility and dielectric properties without much impairing their thermal stability and mechanical properties. The successful approaches employed with those purpose include: (1) introducing flexible segments, such as ether linkage, into polymer backbone to decrease the rigidity of polymer backbone; (2) introducing side chains, such as symmetric/asymmetric bulky substituents or flexible fluorinated groups, along polymer backbone to reduce the interaction between polymer chains [6–9].

Recently, considerable attention has been devoted to the fluorinated aromatic polyamides. It was found that the incorporation of flexible fluorinated groups into polyamide backbones resulted in great benefits for improving polymer solubility as well as electrical and dielectric performance [10–15], which attributed to the small dipole and the low polarizability of the C–F band as well as the increase in free volume.

As part of the efforts to gain the high performance polymers with high thermal stability, low dielectric constant

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and dissipation factor (low-*k*) for advanced microelectronics applications, two series of fluorinated aromatic polyamides with pendent phenoxy groups and trifluoromethyl substituents were synthesized from two novel fluorinated isophthaloyl dichlorides, 5-(4-trifluoromethylphenoxy)isophthaloyl dichloride (3FPC) and 5-(3,5-bistrifluoromethylphenoxy)isophthaloyl dichloride (6FPC), with various aromatic diamines by polycondensation reaction. The solubility, thermal and mechanical properties as well as electrical insulating and dielectric behaviors were investigated.

2. Experimental

2.1. Materials

3,5-Dimethylphenol, 1-chloro-4-trifluoromethylbenzene and 1-bromo-3,5-ditrifluoro-methylbenzene were purchased from Beijing Beihua Fine Chemicals Co., China, and used as received. *p*-Phenylenediamine (PDA), 4,4′-oxydianiline (4,4′-ODA) and 3,4′-oxydianiline (3,4′-ODA) were purified by vacuum sublimation prior to use. 1,4-Bis(4-aminophenoxy)benzene (APB) were recrystallized from ethanol. 4-(4-Aminophenoxy)-3-trifluoromethylphenylamine (3FODA) was synthesized according to the literature [16]. 1,4-Bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB) was prepared in our laboratory according to the method reported previously [17]. Commercially available *N*-methyl-2-pyrrolidinone (NMP) and *N*,*N*′-dimethylacetamide (DMAc) were purified by vacuum distillation over CaH_2 prior to use.

2.2. Monomer synthesis

2.2.1. 1,3-Dimethyl-5-(4-trifluoromethylphenoxy)benzene (3FPB)

A 500-ml three-necked flask equipped with a reflux condenser, a water separator and a gas inlet tube was fitted with 3,5-dimenthylphenol (36.60 g, 0.30 mol), 1-chloro-4-trifluoromethyl benzene (57.78 g, 0.32 mol), potassium hydroxide (17.40 g, 0.31 mol), DMSO (180 ml) and toluene (60 ml). The mixture was refluxed for 12 h in nitrogen under stirring and the water produced in the reaction processing was removed by means of azeotropic method. Then, the mixture was concentrated by vacuum distillation to remove most of the DMSO followed by pouring into water (150 ml). The organic phase was separated, dried with magnesium sulphate. The purified 3FPB was obtained by vacuum distillation (49.1 g, 61.5%, bp 96.1 °C under 1 mm Hg). ^{1}H NMR ($CDCl_3$, δ): 6.67 (s, 2H), 6.82 (s, 1H), 7.01–7.04 (d, 2H), 7.54–7.57 (d; 2H). Mass spectrometry (EI, *m/e*, % relative intensity): 266 (M + , 100). Elemental analysis: calcd for $C_{15}H_{13}F_3O$: C, 67.66%; H, 4.92%. Found: C, 67.64%; H, 4.87%.

2.2.2. 5-(4-Trifluoromethylphenoxy)isophthalic acid (3FPA)

A mixture of 3FPB (39.90 g, 0.15 mol), pyridine (500 ml) and water (200 ml) was placed into a 2000-ml three-necked flask equipped with mechanical stirrer and a reflux condenser. The mixture was heated to reflux followed by addition of $KMnO_4$ (94.74 g, 0.60 mol) in portions in 4 h. After that, the mixture was refluxed with stirring for an additional 2 h and then filtered hot to remove the solid MnO_2. The filtrate was vacuum distilled to remove the solvents (pyridine and water) to give a yellow liquid. The yellow liquid was placed into a 2000-ml three-necked flask, and then, a mixture of sodium hydroxide (36.00 g, 0.90 mol) and water (800 ml) were added. The mixture was heated to reflux followed by addition of $KMnO_4$ (94.74 g, 0.60 mol) in portions in 4 h. The mixture was kept refluxing for another 2 h and then cooled to 70 °C. To this, 20 ml of ethanol was added dropwise to eliminate the unreacted $KMnO_4$. After refluxing for 1 h, the mixture was filtered hot to remove the MnO_2 to afford a colorless solution. The solution was concentrated by vacuum distillation and poured into excess aqueous hydrochloric acid to give white precipitate. The precipitate (3FPA) was collected, washed with diluted hydrochloric acid and water, respectively, and dried at 120 °C in vacuum (31.8 g, 65.0%, mp 168.1 °C determined by DSC). ^{1}H NMR (DMSO-d_6, δ): 7.26–7.29 (d, 2H), 7.76–7.78 (d, 2H), 7.80 (s, 2H), 8.28 (s, 1H). FTIR (KBr, cm^{-1}): 3424, 3065, 1709, 1595, 1543, 1459, 1231, 1086, 919. Mass spectrometry (EI, *m/e*, % relative intensity): 326 (M + , 100). Elemental analysis: calcd for $C_{15}H_9F_3O_5$: C, 55.23%; H, 2.78%. Found: C, 55.24%; H, 2.82%.

2.2.3. 5-(4-Trifluoromethylphenoxy)isophthaloyl dichloride (3FPC)

A mixture of 3FPA (19.57 g, 0.06 mol), thionyl chloride (150 ml) and two drops of *N*,*N*-dimethylformamide (DMF) was refluxed for 4 h under stirring. Then, the mixture was vacuum distilled to remove the residue thionyl chloride and cooled to 0–4 °C. The white precipitate was afforded and collected by filtration. The crude product was purified by recrystallization in anhydrous petroleum ether (18.5 g, 85.1%, mp 58.1 °C determined by DSC). ^{1}H NMR ($CDCl_3$, δ): 7.13–7.20 (d, 2H), 7.68–7.76 (d, 2H), 8.03 (s, 2H), 8.65 (s, 1H), ^{13}C NMR ($CDCl_3$, δ): 119.2, 122.4, 125.8, 126.7, 127.1, 127.3, 127.9, 128.6, 136.0, 157.5, 158.0, 166.6. FTIR (KBr, cm^{-1}): 1759, 1746, 1588, 1439, 1373, 1330, 1121, 1019, 844. Mass spectrometry (EI, *m/e*, % relative intensity): 362 (M + , 17.8), 327 (100), 243 (16.5), 75 (63.7). Elemental analysis: calcd for $C_{15}H_7Cl_2F_3O_3$: C, 49.62%; H, 1.94%; Found: C, 49.44%; H, 2.09%.

2.2.4. 5-(3,5-Bis-trifluoromethylphenoxy)isophthaloyl dichloride (6FPC)

6FPC was prepared via a similar procedure with 3FPC, except that 1-bromo-3,5-ditrifluoromethylbenzene was used instead of 1-chloro-4-trifluoromethylbenzene (68.2%, mp 54.2 °C determined by DSC). ^{1}H NMR (CDCl$_3$, δ): 7.51 (s, 2H), 7.77 (s, 1H), 8.07(s, 2H), 8.72 (s, 1H). ^{13}C NMR (CDCl$_3$, δ): δ 118.6, 119.2, 120.8, 124.4, 126.8, 128.2, 129.0, 129.4, 133.4, 133.8, 134.2, 134.6, 136.4, 156.5, 156.7, 166.4. FTIR (KBr, cm^{-1}): 1761, 1588, 1463, 1439, 1373, 1283, 1136, 1002, 931, 890. Mass spectrometry: (EI, *m/e*, % relative intensity): 430 (M + , 9.1); 395 (100), 367 (15.4) 180 (6.9), 75 (71.1). Elemental analysis: calcd for $C_{16}H_6Cl_2F_6O_3$: C, 44.58%; H, 1.40%. Found: C, 44.64%; H, 1.23%.

2.3. Polymer synthesis

In a typical experiment, polyamide PA-2, which derived from 3FPC and 4,4′-oxydianiline (4,4′-ODA), was prepared as follows: 4,4′-ODA (1.2014 g, 6.00 mmol) and pyridine (0.10 g) were dissolved in 35 ml of NMP, to which 3FPC (2.5866 g, 6.00 mmol) was added with stirring. The mixture was stirred in nitrogen at room temperature for 6 h to yield a viscous polyamide solution. Then the solution was trickled into excess ethanol with stirring to afford a precipitate. The precipitate was collected, washed with hot ethanol for three times and dried at 160 °C under vacuum for 6 h to give polyamide PA-2 (3.21 g, 96%).

The polyamides, i.e., PA-1 (3FPC/PDA), PA-3 (3FPC/3,4′-ODA), PA-4 (3FPC/APB), PA-5 (3FPC/3FODA), PA-6 (3FPC/6FAPB), PA-7 (6FPC/PDA), PA-8 (6FPC/4,4′-ODA), PA-9 (6FPC/3,4′-ODA), PA-10 (6FPC/APB), PA-11 (6FPC/3FODA) and PA-12 (6FPC/6FAPB), were also prepared via a similar procedure as described for PA-2 by the polymerization of 1 equiv. of fluorinated isophthaloyl dichloride (3FPC or 6FPC) with 1 equiv. of aromatic diamine, including *p*-phenylenediamine (PDA), 3,4′-oxydianiline (3,4′-ODA), 1,4-bis(4-aminophenoxy)benzene (APB), 4-(4-aminophenoxy)-3-trifluoromethylphenylamine (3FODA), and 1,4-bis-(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB).

2.4. Preparation of polyamide films

The polyamide films were prepared by the casting of homogenous polymer solutions in DMAc (15% solid content) on the clean glass plates, followed by heating in an oven with a programmed procedure: 80 °C/1 h, 180 °C /2 h and 220 °C/1 h, successively. The flexible polyamide films with 45–50 μm thickness were then stripped from the glass plates.

2.5. Measurements

^{1}H NMR and ^{13}C NMR spectra were performed on a Bruker DMX-300 spectrometer operating at 300 MHz in CDCl$_3$ or DMSO-d_6. FTIR spectra were obtained on a Perkin–Elmer 782 Fourier transform spectrophotometer. Mass spectra were obtained on a Micromass GCT mass spectrometer. Elemental analysis was carried out with a Flash EA1112 element analyzer. The wide angle X-ray diffraction measurement was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu Kα radiation, operated at 40 kV and 200 mA. Differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) were recorded on a Perkin–Elmer 7 series thermal analysis system in nitrogen at a heating rate of 10 °C/min. 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 measured with an Ubbelohde viscometer with a 5 wt% of polymer in NMP solution at 25 ± 0.5 °C, in which the polyamides were pretreated by drying in oven at 120 °C for 1 h to remove the adsorbed moisture. Water uptake was determined by the weighing of the changes in the polymer film ($50 \times 50 \times 0.05$ mm^3) before and after immersion in boiling water for 6 h. The electrical properties were measured on a Hewlett–Packard 4284A Presion LCR meter. The dielectric constant and dissipation factor were determined by the bridge method with an LKI-1 capacitance meter at a frequency of 1 MHz and 25 °C.

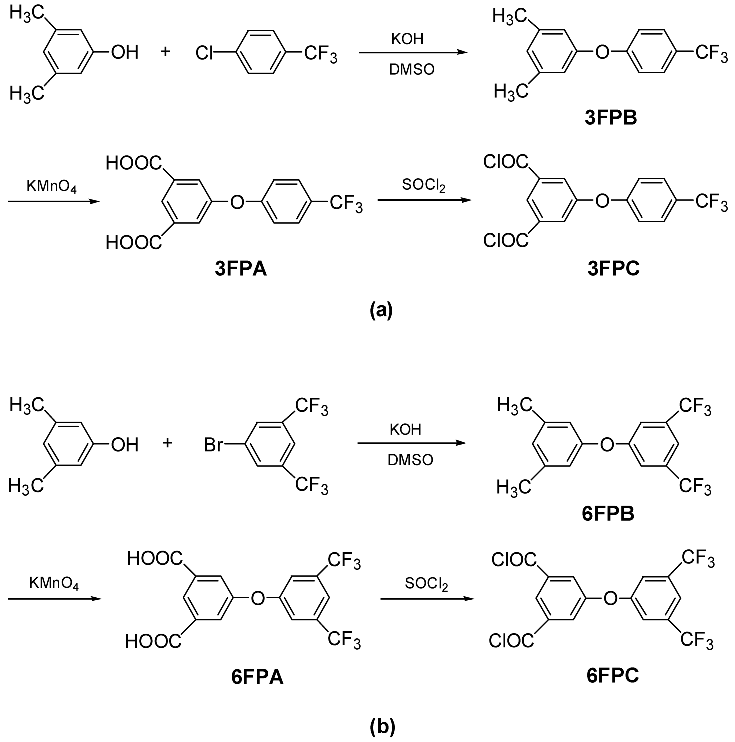
3. Results and discussion

3.1. Monomer synthesis

The fluorinated isophthaloyl dichlorides were synthesized according to a three-step procedure as shown in Scheme 1. First, 3,5-dimenthylphenol was reacted with 1-chloro-4-trifluoromethylbenzene or 1-bromo-3,5-ditrifluoromethylbenzene by the nucleophilic substitution reaction to give corresponding dimethyl compounds 3FPB and 6FPB, which were then oxidized with $KMnO_4$ to afford the dicarboxylic acids 3FPA or 6FPA in good yields. The dicarboxylic acids were reacted with thionyl chloride to give the corresponding isophthaloyl dichloride (3FPC or 6FPC). All compounds were characterized by ^{1}H NMR, ^{13}C NMR, FTIR, elemental analysis and mass spectrometry with satisfied results. Fig. 1 shows the ^{1}H NMR spectra of the monomers 3FPC and 6FPC, in which all the protons were assigned as expected. The protons H4 of 3FPC and 6FPC were observed in the downfield region (8.65–8.72 ppm), owing to the strong electron-withdrawing effect of the two carbonyl groups in *ortho*-position. In both cases, the protons H1 of 3FPC and 6FPC located at the *ortho*-position of the ether linkage appeared in the upfield region (7.13–7.51 ppm) due to the electron-donation effect of the ether group.

3.2. Polymer synthesis

The fluorinated polyamides were prepared by a one-step pathway by polycondensation reaction of 1 equiv. of



Scheme 1. Synthesis of fluorinated aromatic diacid chlorides 3FPC (a) and 6FPC (b).

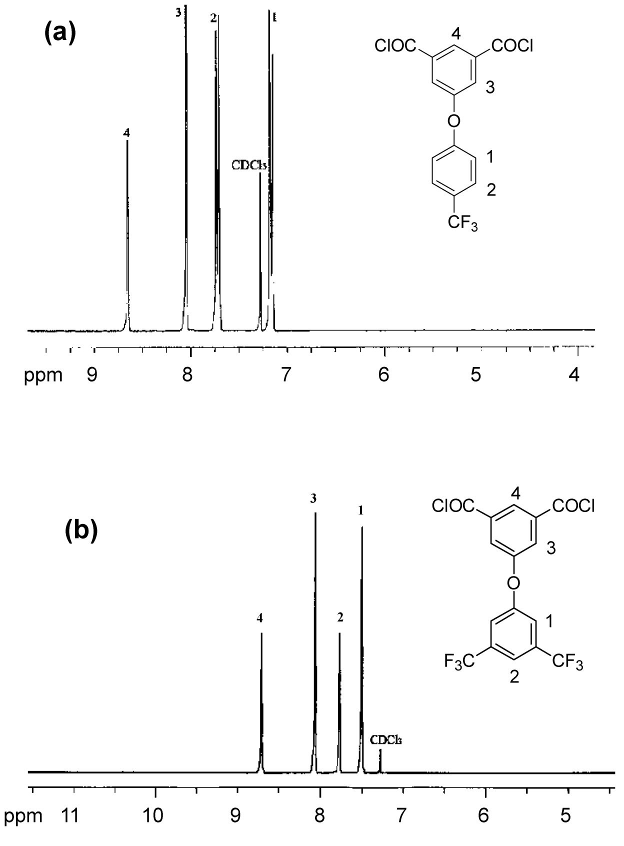
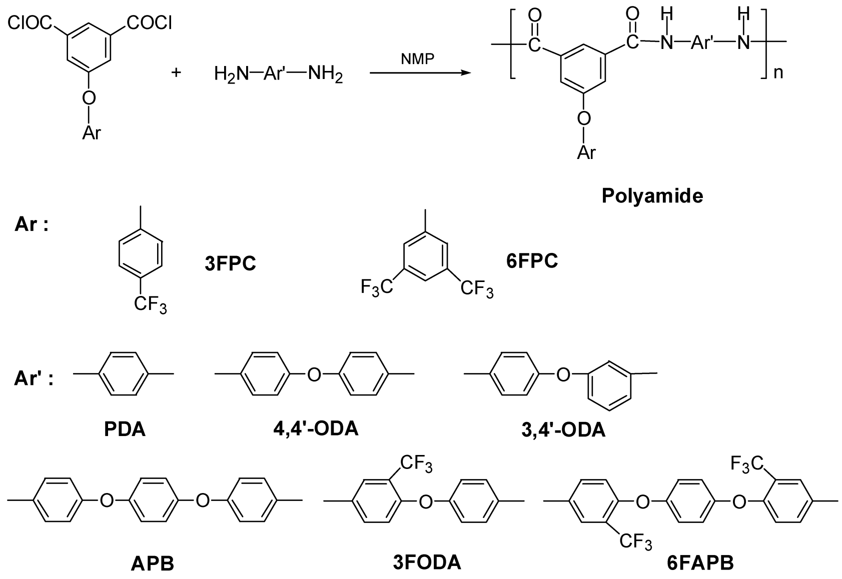


Fig. 1. ^{1}H NMR spectra of (a) 3FPC and (b) 6FPC ($CDCl_3$, 300 MHz).

fluorinated isophthaloyl dichloride and 1 equiv. of aromatic diamine in NMP catalyzed by a trace of pyridine at 10 wt% of solid content (Scheme 2). Two series of fluorinated polyamides derived from 3FPC and 6FPC with aromatic diamines, including PA-1 (3FPC/PDA), PA-2 (3FPC/4,4′-ODA), PA-3 (3FPC/3,4′-ODA), PA-4 (3FPC/APB), PA-5 (3FPC/3FODA), PA-6 (3FPC/6FAPB), PA-7 (6FPC/PDA), PA-8 (6FPC/4,4′-ODA), PA-9 (6FPC/3,4′-ODA), PA-10 (6FPC/APB), PA-11 (6FPC/3FODA) and PA-12 (6FPC/6FAPB), were prepared in good yields (91–96%). The physical properties and elemental analysis of the fluorinated polyamides were listed in Table 1. The fluorinated polyamides showed colors from white to yellow, exhibited inherent viscosities of 0.71–0.91 dl/g in NMP at 25 °C, implying that polymers have relative high molecular weights. The elemental analysis values were in good agreement with the calculated ones. Fig. 2 shows the ^{1}H NMR and ^{13}C NMR spectra of PA-2, in which all the protons and the carbons could be assigned in the polymer structure. Fig. 3 compares the FTIR spectra of the typical polyamides. It can be seen that the characteristic absorptions of polyamides at 3300–3400 cm^{-1} (N–H stretching), 1660–1670 cm^{-1} (C=O stretching), and 1500–1550 (combined N–H bending and C–N stretching) were all observed. The results demonstrated that the fluorinated polyamides have the expected chemical structures.

3.3. Polymer solubility

The fluorinated polyamides can easily dissolved in many organic solvents to afford homogeneous polymer solutions.



Scheme 2. Preparation of fluorinated aromatic polyamides.

The solubility was determined by dissolving 1.5 g of polymers in 8.5 g of solvent (15 wt% of solid content) at room temperature. Table 2 summarizes the solubility of the fluorinated polyamides. It can be seen that the polyamides could easily dissolved in both strong dipolar solvents such as NMP, DMAc, DMF or *m*-cresol and some common organic solvents such as THF and acetone. The polyamides derived from the fluorinated aromatic diamines such as 3FODA and 6FAPB exhibited better solubility than the others. For instance, PA-5, PA-6, PA-11 and PA-12 showed excellent solubility, which could completely dissolved in cyclopentanone at room temperature within 2 h. However, the other polyamides need more than 2 h to dissolve in cyclopentanone at room temperature. Moreover, when comparing the polyamides derived from 3FPC and 6FPC, it is found that the polymers based on 6FPC exhibited better solubility because of the high fluorine content. For example, PA-11 and PA-12 exhibited higher solubility, which could even be dissolved in THF at room temperature in 2 h.

The fluorinated polyamides showed different solubility behaviors in different organic solvents. The complete dissolution time for PA-6 and PA-12 depended on the kind of solvents (Fig. 4). The dissolution time for PA-6 and PA-12, defined as the time for the polymer solid being completely dissolved in the solvent, increased in the following order: acetone > THF > *m*-cresol > DMF > DMAc > NMP. For instance, PA-6 could completely dissolve in NMP to afford homogenous solution in 24 min, but needed 140 min in THF and 220 min in acetone. Moreover, when comparing the dissolving time for PA-6 and PA-12, which derived from 3FPC and 6FPC with the same diamine 6FAPB, respectively, it is found that no

Table 1
Physical properties and elemental analysis of the fluorinated polyamides

Polymer code	Polymer component	Yield (%)	Color	η_{inh}[a] (dl/g)	Formula	Elemental analysis					
						C (%)		H (%)		N (%)	
						Calcd	Found	Calcd	Found	Calcd	Found
PA-1	3FPC/PDA	95	Yellow	0.75	$(C_{21}H_{13}F_3N_2O_3)_n$	63.32	62.98	3.29	3.12	7.03	7.20
PA-2	3FPC/4,4′-ODA	96	Yellow	0.89	$(C_{27}H_{17}F_3N_2O_4)_n$	66.12	65.73	3.49	3.52	5.71	5.55
PA-3	3FPC/3,4′-ODA	93	Yellow	0.81	$(C_{27}H_{17}F_3N_2O_4)_n$	66.12	65.33	3.49	3.62	5.71	5.35
PA-4	3FPC/APB	91	White	0.85	$(C_{33}H_{21}F_3N_2O_5)_n$	68.04	67.44	3.63	3.89	4.81	4.51
PA-5	3FPC/3FODA	93	White	0.71	$(C_{28}H_{16}F_6N_2O_4)_n$	60.22	59.18	2.89	2.68	5.02	4.81
PA-6	3FPC/6FAPB	95	White	0.79	$(C_{35}H_{19}F_9N_2O_5)_n$	58.51	59.07	2.67	2.15	3.90	3.98
PA-7	6FPC/PDA	92	Yellow	0.81	$(C_{22}H_{12}F_6N_2O_3)_n$	56.66	54.98	2.59	2.48	6.01	5.94
PA-8	6FPC/4,4′-ODA	93	Yellow	0.71	$(C_{28}H_{16}F_6N_2O_4)_n$	60.22	60.87	2.89	2.67	5.02	4.94
PA-9	6FPC/3,4′-ODA	93	White	0.82	$(C_{28}H_{16}F_6N_2O_4)_n$	60.22	59.95	2.89	2.58	5.02	4.89
PA-10	6FPC/APB	92	White	0.87	$(C_{34}H_{20}F_6N_2O_5)_n$	62.77	61.84	3.10	3.02	4.31	4.23
PA-11	6FPC/3FODA	94	White	0.91	$(C_{29}H_{15}F_9N_2O_4)_n$	55.60	54.78	2.41	2.40	4.47	4.38
PA-12	6FPC/6FAPB	95	White	0.73	$(C_{36}H_{18}F_{12}N_2O_5)_n$	54.97	55.47	2.31	2.36	3.56	3.89

[a] Inherent viscosity determined at 5 wt% of polyamides in NMP at 25 °C.

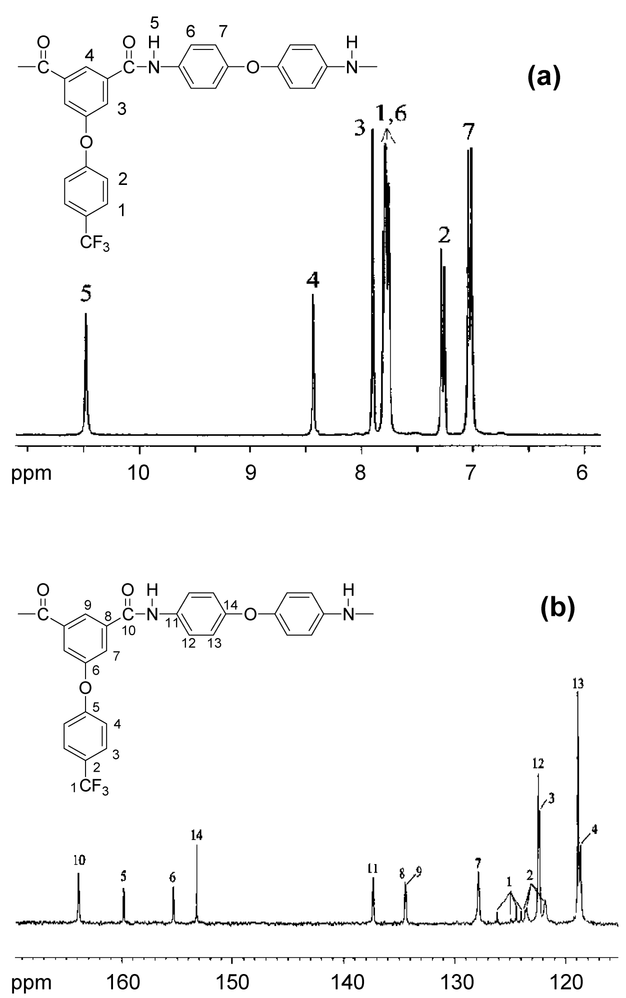


Fig. 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of the fluorinated polyamide PA-2 (DMSO-d_6, 300 MHz).

matter what solvents were employed, PA-12 showed enhanced solubility with less dissolution time than PA-6.

The homogeneous and stable polyamide solutions in solvents with low boiling point could be gained because of the excellent solubility in common organic solvents. This makes the polyamide films or coatings to be prepared at relatively low temperature. A strong and flexible polyamide film of PA-6 was obtained by casting the homogenous polymer solutions in cyclopentanone (15 wt% solid content) on a glass plate, followed by thermally baking at relative low temperature with the following procedure: 60 °C/1 h, 120 °C/2 h and 180 °C/2 h.

The crystallinity of the fluorinated polyamides was evaluated by wide-angle X-ray diffraction measurements (Fig. 5). It is found that all the fluorinated aromatic polyamides exhibited amorphous patterns. We can interpret the result by the presence of the flexible pendent phenoxy groups, which resulted in poor chain packing. The high solubility of polyamides is also affected by the amorphous structure.

Therefore, the excellent solubility of the fluorinated aromatic polyamides were attributed to the combined effects of the pendent phenoxy groups in the polymer backbone and the high CF_3 content, which resulted in the decrease in the

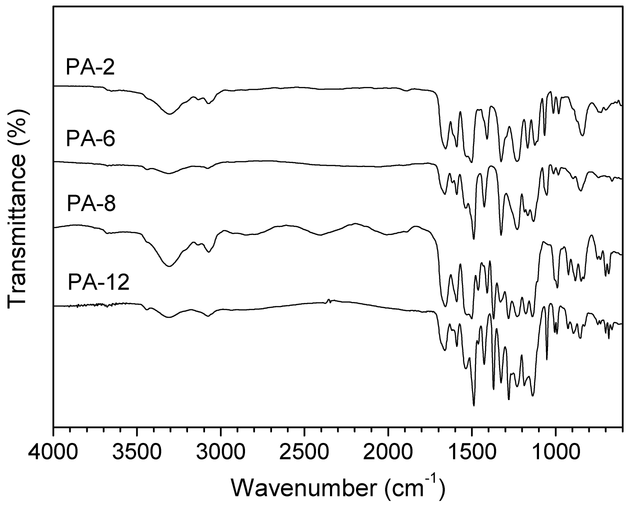


Fig. 3. FTIR spectra of the fluorinated polyamides.

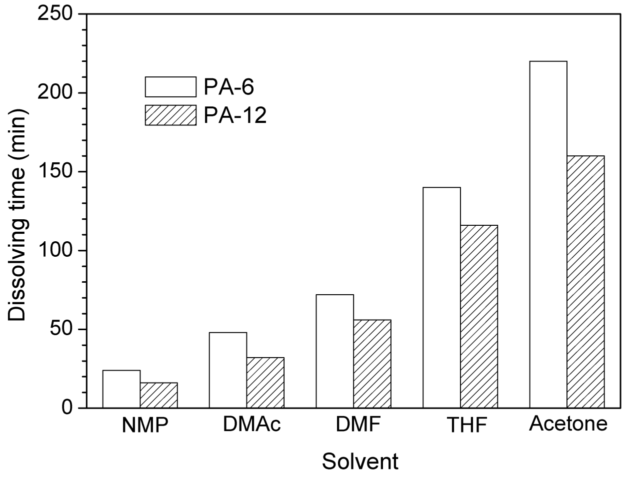


Fig. 4. Comparison on the dissolution time of PA-6 and PA-12 in different solvents.

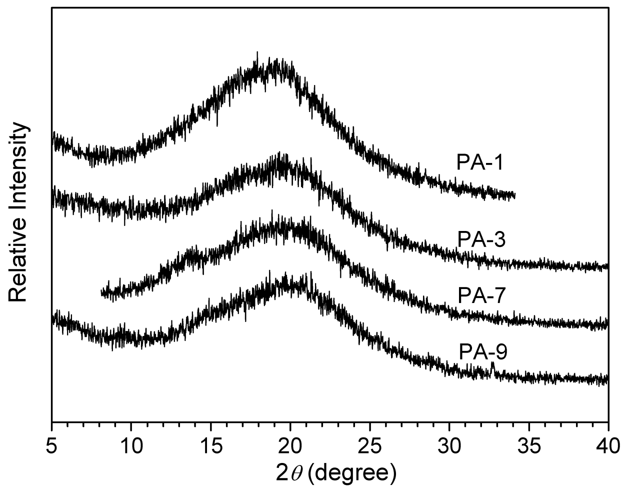


Fig. 5. X-ray diffraction patterns of the fluorinated polyamides.

Table 2
Solubility of the fluorinated polyamides

Solvent	PA-1	PA-2	PA-3	PA-4	PA-5	PA-6	PA-7	PA-8	PA-9	PA-10	PA-11	PA-12
NMP	++	++	++	++	++	++	++	++	++	++	++	++
DMSO	++	++	++	++	++	++	++	++	++	++	++	++
DMAc	++	++	++	++	++	++	++	++	++	++	++	++
DMF	++	++	++	++	++	++	++	++	++	++	++	++
m-Cresol	++	++	++	++	++	++	++	++	++	++	++	++
γ-Butyrolactone	+	+	+	++	++	++	+	+	+	++	++	++
Cyclopentanone	+	+	+	+	++	++	+	+	+	+	++	++
THF	+	+	+	+	+	+	+	+	+	+	++	++
Acetone	−	−	+	+	+	+	+	+	+	+	+	+
Ethanol	−	−	−	−	−	−	−	−	−	−	−	−

++: Soluble at room temperature in 2 h; + : soluble at room temperature in 24 h; −: insoluble.

interaction of polymer chains by increasing the distance between polymer chains.

3.4. Thermal stability

The thermal properties of the fluorinated polyamides were evaluated by DSC and TGA. The results are summarized in Table 3. The fluorinated polyamides give the glass transition temperature (T_g) in the range of 206–285 °C. PA-1 exhibited the highest T_g value (285 °C) because of the effect of the rigid polymer backbone, whereas, PA-9 gave the lowest T_g (206 °C), which probably due to the flexible polymer chain caused by the 3,4-phenoxy segment. In general, the 6FPC-based polyamides showed lower T_g values than the corresponding 3FPC-based polyamides. The T_g value of PA-7 is 42 °C lower than that of PA-1 (285 °C). This might be a result of increase in free volume caused by the introduction of the bulky CF_3 substituents.

From the TGA curves of the fluorinated polyamides exhibited in Fig. 6, we found that the these polyamides did not show obvious weight losses until the temperature reached 420 °C in nitrogen, implying that no thermal decomposition occurred. However, as the temperature over 450 °C, the polymers showed a rapid thermal decomposition. The fluorinated polyamides have the onset decomposition temperatures in the range of 427–462 °C, the temperatures at 5 and 10% weight loss in the range of 442–460 and 478–499 °C, respectively. In addition, the fluorinated polyamides remained 33.7–59.9% of the original weight at 700 °C in nitrogen. The 3FPC-based polyamides showed the residual weight retention (R_w) higher than the corresponding 6FPC-based ones, which related to the high fluorine content in the latter.

Table 3
Thermal properties of the fluorinated polyamides

Polymer code	T_g (°C)	T_d (°C)	T_5 (°C)	T_{10} (°C)	R_w (%)
PA-1	285	427	442	480	59.9
PA-2	238	453	458	486	59.1
PA-3	233	453	451	480	55.6
PA-4	226	435	452	482	56.9
PA-5	247	434	460	499	57.1
PA-6	214	448	457	497	53.2
PA-7	243	458	459	478	36.4
PA-8	220	453	458	486	42.8
PA-9	206	462	458	480	41.5
PA-10	195	435	452	482	33.7
PA-11	231	434	460	499	46.8
PA-12	209	451	454	481	38.8

T_g—determined by DSC; T_d—onset decomposition temperature; T_5, T_{10}—the decomposition temperatures at 5 and 10% weight loss, respectively; R_w—residual weight retention at 700 °C.

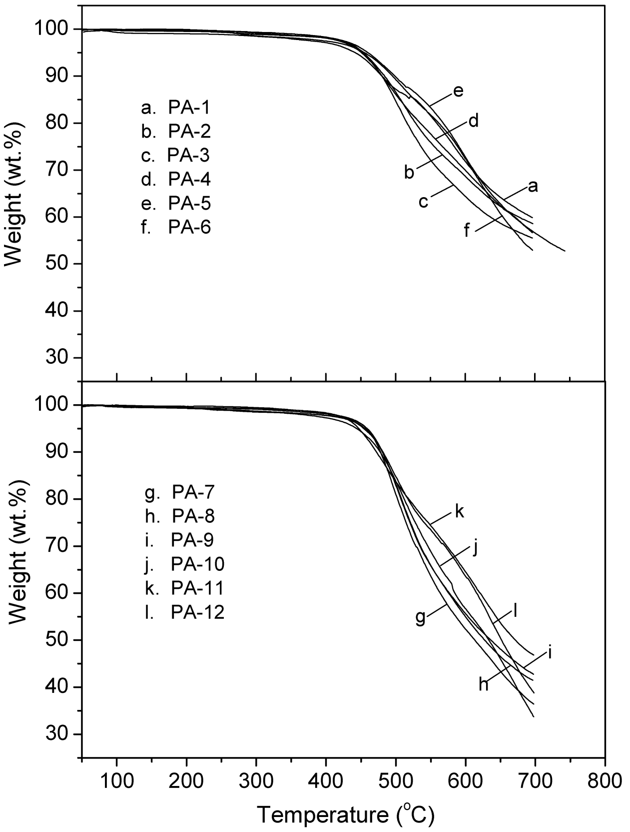


Fig. 6. TGA curves of the fluorinated polyamides (in nitrogen at a heating rate of 10 °C/min).

3.5. Mechanical properties

The unoriented polyamide films were employed to investigate the mechanical and electrical properties and the results are listed in Tables 4 and 5. The tensile strength, tensile moduli and elongation at breakage of these polyamide films were in the range of 73.8–108.3 MPa, 2.15–3.32 GPa and 5.1–7.0%, respectively. PA-1 and PA-7, which derived from aromatic diamine PDA, exhibited low elongation at breakage of 5.1 and 5.2%, respectively, due to the rigid polymer backbone. PA-2 based on 3FPC and 4,4′-ODA showed the best mechanical properties, which might be attributed to the combined effect of the reaction activity of monomers and the flexible ether linkage in the polymer backbone.

3.6. Electrical and dielectric properties

The polyamide films exhibited good electrical insulating and dielectric properties. The volume resistivity, surface resistivity and dielectric strength of the polyamide films were in the range of $1.02–4.24 \times 10^{15}$ Ω cm, $1.85–8.93 \times 10^{14}$ Ω and 79–123 kV/mm, respectively. Moreover, the dielectric constants at 1 MHz were measured in the range of 3.25–3.41 and the dielectric dissipation factor of $2.75–4.56 \times 10^{-3}$. The polyamides with high fluorine content, such as PA-6, PA-11 and PA-12, showed improved electrical insulating and dielectric properties. Particularly, PA-12 has the highest volume resistivity (4.24×10^{15} Ω cm) and surface resistivity (8.93×10^{14} Ω), as well as the lowest dielectric constant (3.24) and dissipation factor (2.75×10^{-3}). The decreased dielectric constants of the fluorinated polyamides could be attributed to the low polarizability of the C–F band and the increase in free volume. These results suggested that the CF_3 groups in the polymer chains play an important role in the electrical and dielectric performance.

The electrical and dielectric properties of polymer films were also affected by the water absorption. The polyamides derived from aromatic diamine PDA, such as PA-1 and PA-7, showed obvious high water uptakes, which are 2.50 and 2.30%, respectively. However, the polyamides derived from fluorinated aromatic diamine 6FAPB, such as PA-6 and PA-12, exhibited apparent low water uptakes, 1.30% for the former and 1.19% for the latter, which are almost half of the values of PA-1 and PA-7, respectively. The relations between water absorption and volume resistivity of PA-12 in 52% relative humidity at 25 °C are shown in Fig. 7. (The relative humidity was obtained from aqueous salt solution of $Mg(NO_3)_2 \cdot 6H_2O$ according to the literature [18].) It is observed that water uptake of film markedly increased in the initial 8 h combined with a rapid decreasing of volume resistivity and the equilibrium was achieved after 48 h. The results revealed that the electrical properties of aromatic polyamides were damaged by the high water absorption.

Table 4
Mechanical properties of the fluorinated polyamides

Polymer code	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at breakage (%)
PA-1	88.9	2.87	5.2
PA-2	108.3	3.32	7.0
PA-3	86.1	2.85	6.1
PA-4	82.3	2.31	6.8
PA-5	80.8	2.97	6.2
PA-6	79.6	2.15	5.8
PA-7	88.0	2.77	5.1
PA-8	78.5	2.63	5.4
PA-9	73.8	2.30	5.5
PA-10	81.6	2.23	6.6
PA-11	90.6	2.88	6.5
PA-12	90.1	3.07	5.3

3.7. Optical property

Fig. 8 shows the UV–vis spectra of the fluorinated polyamide films with thickness of 20–25 μm, in which the cutoff wavelength was ranged from 325 to 380 nm and the transmittance in visible region was 80–85%. In comparison, PA-6 showed a cutoff wavelength of 330, 50 nm shorter than PA-1 (380 nm). PA-12 exhibited the best transparency with cutoff wavelength at 325 nm and transmittance of 83% at 430 nm due to the effect of fluorinated substituents in the polymer backbone. This can be explained by the decrease of the intermolecular interaction because of the presence of bulky and electron-withdrawing CF_3 groups, which are effective in decreasing the formation of charge-transfer complex (CTC) between polymer chains.

4. Conclusions

Two novel fluorinated isophthaloyl dichlorides were synthesized and characterized, which were then employed to polycondense with various aromatic diamines to yield

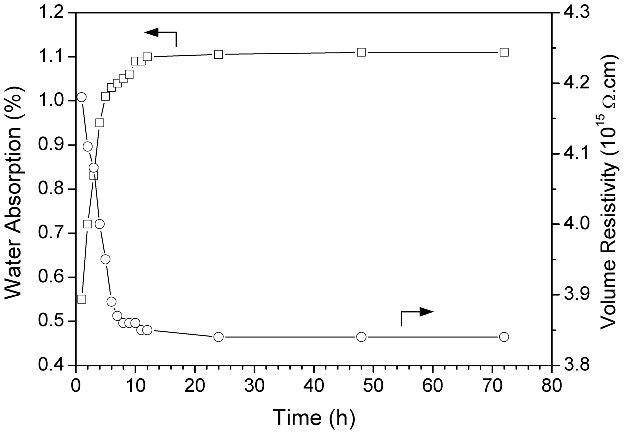


Fig. 7. Relationship between water absorption and volume resistivity of PA-12 in 52% relative humidity at 25 °C.

Table 5
The dielectric and optical properties of the fluorinated polyamides

Polymer code	$\rho_v \times 10^{-15}$ (Ω cm)	$\rho_s \times 10^{-14}$ (Ω)	D_s (kV/mm)	ε_r (1 MHz)	tan δ (10^{-3})	W_u (%)	λ_{cut} (nm)
PA-1	1.83	2.56	103	3.41	4.56	2.50	380
PA-2	1.78	1.85	114	3.39	4.38	1.71	355
PA-3	2.55	3.78	79	3.35	4.25	1.50	350
PA-4	2.34	2.96	96	3.34	3.89	1.43	340
PA-5	2.41	3.12	119	3.29	3.28	1.40	350
PA-6	2.51	6.54	123	3.25	3.19	1.30	330
PA-7	1.58	1.89	102	3.38	3.36	2.30	365
PA-8	1.02	2.56	93	3.36	3.18	1.34	345
PA-9	2.11	3.76	93	3.32	2.98	1.33	350
PA-10	2.89	4.32	89	3.30	2.85	1.33	332
PA-11	3.08	7.12	110	3.26	2.81	1.30	345
PA-12	4.24	8.93	115	3.24	2.75	1.19	325

ρ_v—volume resistivity; ρ_s—surface resistivity; D_s—dielectric strength; ε_r—dielectric constant at 1 MHz, 25 °C; tanδ—dissipation factor; W_u—water uptake; λ_{cut}—cutoff wavelength in UV–vis spectra.

two series of fluorinated aromatic polyamides. Experimental results indicated that the polyamides exhibited excellent solubility in many organic solvents. The flexible and strong polyamide films exhibited good thermal stability with the glass transition temperature of 206–285 °C, the temperature at 5% weight loss of 442–460 °C in nitrogen. The fluorinated polyamide films also showed good mechanical properties with the tensile strengths of 73.8–108.3 MPa and elongations at breakage of 5.1–7.0%. In addition, the polyamide films exhibited great electrical and dielectric properties with low water absorptions. It was concluded that the fluorinated groups in the polymer backbone have played an important role in the improvement of solubility and dielectric properties of polymer.

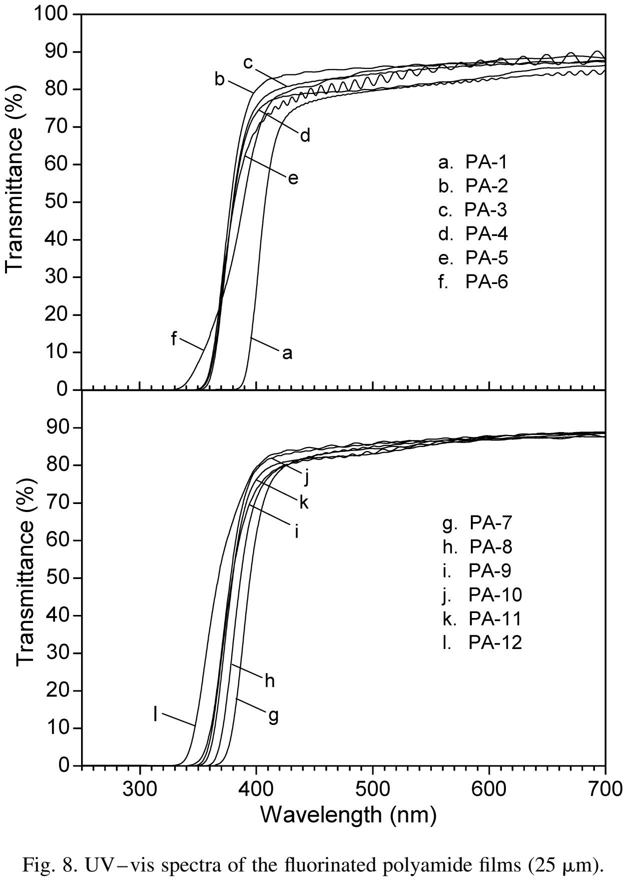


Fig. 8. UV–vis spectra of the fluorinated polyamide films (25 μm).

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