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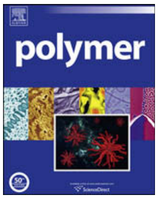

Synthesis and properties of fluorinated poly(ether ketone imide)s based on a new unsymmetrical and concoplanar diamine: 3,5-Dimethyl-4-(4-amino-2-trifluoromethylphenoxy)-4′-aminobenzophenone

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ABSTRACT

A new unsymmetrical and concoplanar aromatic diamine monomer containing trifluoromethyl and dimethyl groups, 3,5-dimethyl-4-(4-amino-2-trifluoromethylphenoxy)-4′-aminobenzophenone (**3**), was synthesized in a three-step reaction using 2,6-dimethylphenol and 4-nitrobenzoyl chloride as starting materials. A series of fluorinated poly(ether ketone imide)s (PEKIs) (**5a**–**d**) were prepared from diamine **3** with four aromatic dianhydrides via a one-step high-temperature polycondensation procedure. The obtained PEKIs were readily soluble in some organic solvents and could be solution cast into flexible and tough films. These PEKI films exhibited high optical transparency with a cutoff wavelength of 354–375 nm and low dielectric constants (2.26–2.45 at 1 MHz). They also showed good thermal stability with glass-transition temperatures (T_gs) above 289 °C, 10% weight loss temperatures in the range of 518–531 °C, and the weight residue more than 52% at 800 °C in nitrogen. Moreover, the PEKI films possessed tensile strengths and initial modulus ranged from 91 to −128 MPa and 1.7 to 2.4 GPa, respectively. Due to their properties, these fluorinated PEKIs could be considered as photoelectric and microelectronic materials.

1. Introduction

It is well known that polyimides (PIs) are useful high performance materials because of their excellent thermal stability, mechanical and electric properties [1–6]. However, most PIs are generally difficult to process due to their poor solubility and high processing temperature, which limit their widespread application. Such difficulty mainly results from their strong interchain forces, inherent macromolecular rigidity, or semicrystallinity. Therefore, many studies have been made to enhance their processabilities and solubilities either by introducing bulky groups, flexible linkages or molecular asymmetry into the polymer backbones [7–12]. In a similar manner, incorporation of kink concoplanar and unsymmetrical structures to PIs macromolecule was quite effective to improve the solubility of PIs without deteriorating their inherent excellent properties [13–16].

Furthermore, high optical transparency is also one of the most attractive properties of PI materials for a variety of applications such as electrics and optical waveguide [17,18]. However, the standard wholly aromatic PIs often have strong absorption in the visible region of their UV–visible spectra and are pale yellow or deep reddish yellow because of their highly conjugated aromatic structures and/or the intermolecular charge–transfer complex (CTC) formation [19]. The intermolecular CTC formation can be reduced by introducing a bulky pendant group to prevent the polyimide chains from being well stacked [20,21]. Reducing conjugation or introducing aliphatic dianhydride/diamine is another method to lighten the color of PIs [22]. However, the level of thermal stability of these PIs would be reduced in this way, because the aliphatic segments are less stable. Recently, some efforts have been made on preparing fluorinated aromatic PIs, especially the trifluoromethyl-containing poly(ether imide)s (PEIs) [23–32]. These fluorinated PEIs are usually prepared from the trifluoromethyl-substituted bis(ether amine)s. It has been proved that the introduction of bulky trifluoromethyl group into PI backbones resulted in an enhanced solubility and optical transparency together with a lowered dielectric constant, which was attributed to the low polarizability of the C–F bond and the increase in the free volume [33]. However, some of these fluorinated PEIs derived from PMDA and BPDA still showed a limited solubility. For example, Yang studied a series of fluorinated PEIs derived from 4,4′-bis(4-amino-2-trifluoromethylphenoxy)-benzophenone, 1,4-bis(4-amino-2-trifluoromethylphenoxy)naphthalene and 2,5-bis(4-amino-2-trifluoromethylphenoxy)-*tert*-butylbenzene [24–26]. These materials derived from BPDA were almost

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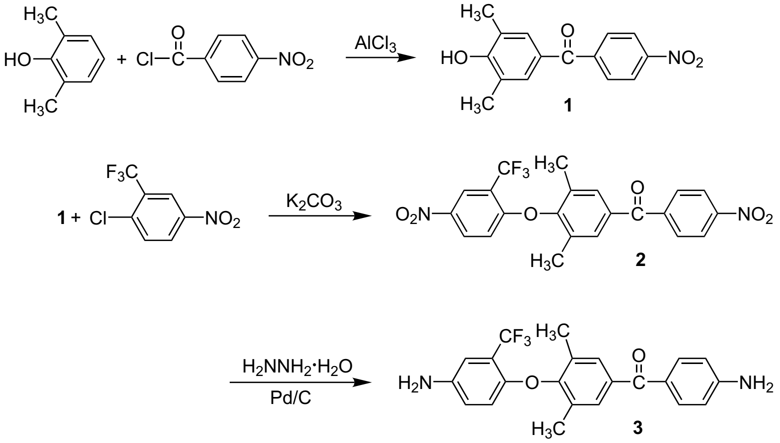


Scheme 1. Synthesis of aromatic unsymmetrical diamine **3**.

insoluble in most common solvents. Moreover, the T_g of these PEIs also have a much decreased value compared with the standard aromatic PIs because of introducing amount of flexible ether linkages into polymer backbones (two ether linkages in each repeated unit). Insulating materials for microelectronics should not only have low dielectric constant and moisture absorption, but also should possess high T_g to withstand the elevated processing temperatures [34].

As part of the efforts to gain soluble PIs with eminent combination properties for photoelectric and microelectronic applications, this paper mainly reported a series of new fluorinated PEKIs based on an unsymmetrical and concoplanar diamine containing trifluoromethyl and dimethyl pendant groups. The solubility, optical and dielectric properties, and other physical properties of these fluorinated PEKIs were investigated and discussed.

2. Experimental

2.1. Materials

2,6-Dimethylphenol, 2-chloro-5-nitrobenzotrifluoride and 4-nitrobenzoylchloride purchased from Alfa Aesar were used as received. Commercially available aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA or **4a**), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA or **4b**), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA or **4c**) and 4,4′-oxydiphthalic dianhydride (ODPA or **4d**) were all purified by recrystallization from acetic anhydride and then dried in vacuo at 120 °C for 24 h. Commercially available *N*-methyl-2-pyrrolidinone (NMP), *m*-cresol, *N*,*N*-dimethylacet amide (DMAc), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and other solvents were purified by distillation prior to use.

2.2. Measurements

NMR spectra were measured on a Bruker AV400 instrument with dimethyl sulfoxide-d_6 (DMSO-d_6) or $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrometer. Elemental analysis was carried out on a Carlo-Erba 1106 system. Weight-average molecular weights (M_w) and number average molecular weights (M_n) were obtained via gel permeation chromatography (GPC) on the basis of polystyrene calibration using PL-GPC 50 as an apparatus and $CHCl_3$ as the eluent. Differential scanning calorimetric (DSC) analysis was performed on a PE Diamond DSC instrument at a heating rate of 20 °C/min in nitrogen atmosphere. Glass-transition temperatures were read at the middle of the transition in the heat capacity from the second heating scan after quick cooling from 380 °C at a cooling rate of 20 °C/min. Thermogravimetric analysis (TGA) of the polymer samples was measured on a Netzsch TG 209F1 instrument at a heating rate of 20 °C/min in nitrogen atmosphere. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a PerkinElmer Lambda 35 UV–vis spectrophotometer at room temperature. The dielectric constant was determined on an Agilent 4291B instrument at a frequency region from 1 MHz to 1.1 GHz at 25 °C. Prior to test, the polymer film samples were dried at 150 °C for 10 h. The tensile properties were performed on an Instron 3365 Tensile Apparatus with a 5-kg load cell at a crosshead speed of 5 mm/min on strips approximately 60–90 μm thick and 0.5 cm wide with a 2-cm gauge length. An average of at least five individual determinations was used. The equilibrium water absorption was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days.

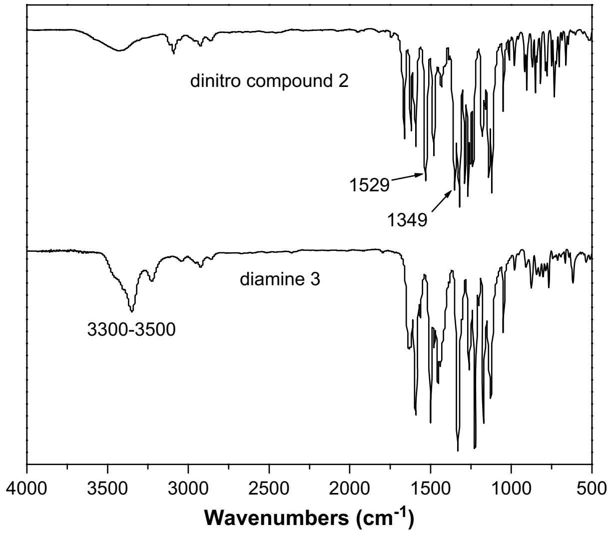


Fig. 1. FT-IR spectra of dinitro compound **2** and diamine **3**.

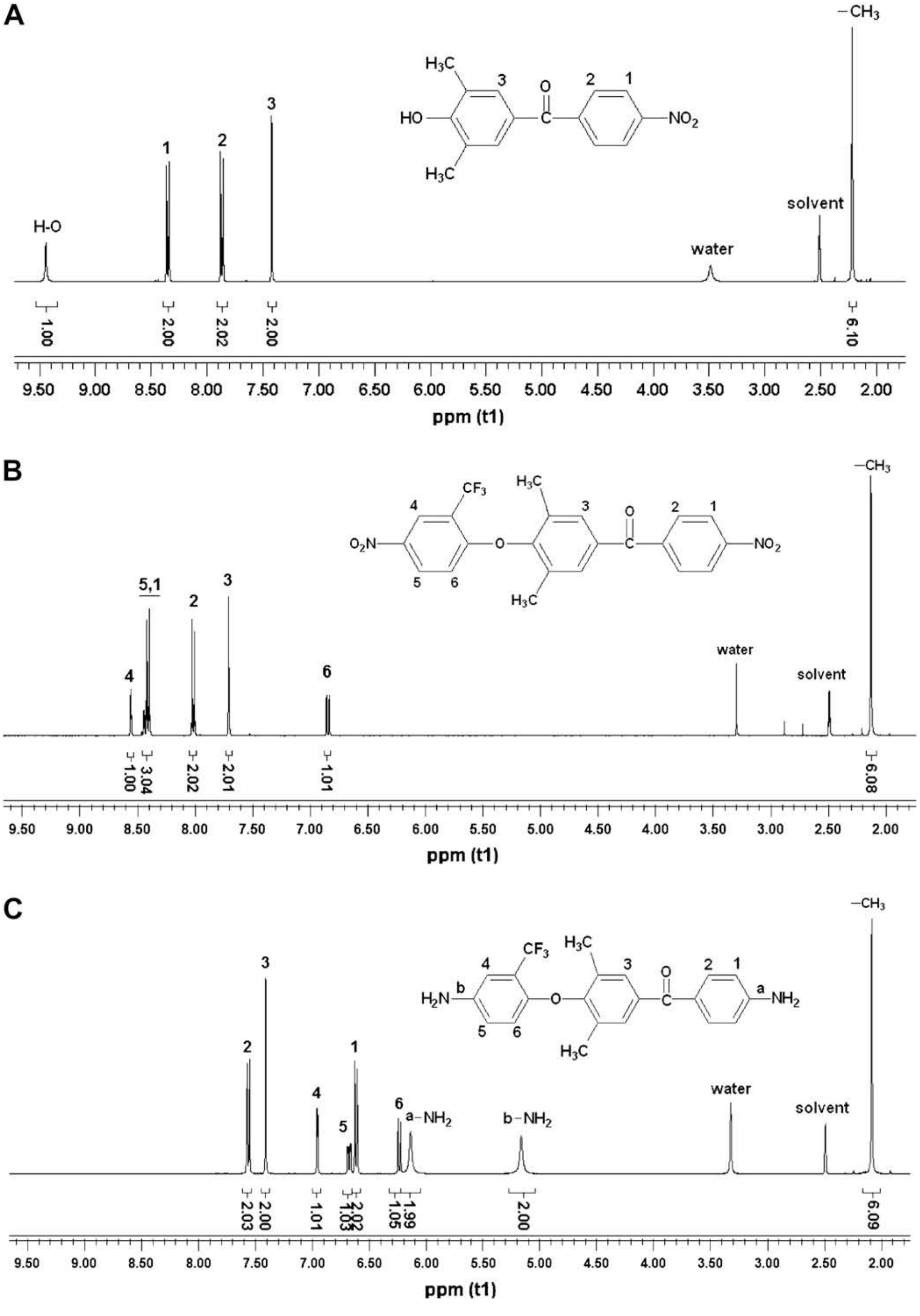


Fig. 2. ^{1}H NMR spectra of compounds **1**, **2** and diamine **3** in DMSO-d_6.

2.3. Monomer synthesis

*2.3.1. 4-Hydroxy-3,5-dimethyl-4′-nitrobenzophenone (**1**)*

In a 500 mL, four-necked, round-bottomed flask equipped with a mechanical stirrer, a condenser and a thermometer, 12.2 g (0.1 mol) of 2,6-dimethylphenol and 46.7 g (0.35 mol) of anhydrous $AlCl_3$ were dissolved in 150 mL of 1,2-dichloroethane at −5 to 0 °C. After stirring for 1 h, the mixture was cooled to −15 °C using ethanol bath. Subsequently, 18.6 g (0.1 mol) of 4-nitrobenzoyl chloride was added to the solution slowly in several portions over 2 h periods and stirred intensively for 1 h at this temperature. Then the resulting mixture was heated to 0 °C stirring for 3 h and 15 °C for another 10 h, and was poured into hydrochloric acid (37.5 wt%, 40 mL) containing crushed ice. The light brown powder was obtained from steam distillation followed by filtration. This crude product could be further purified by recrystallization for two times in ethanol. About 19.5 g of compound **1** was obtained (yield 72%; mp 185–186 °C by DSC at a scan rate of 10 °C/min). FT-IR (KBr): 3434 (O–H), 1655 (C=O), 1523, 1350 (NO_2) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.44 (s, 1H), 8.35 (d, J = 8.8 Hz, 2H), 7.87 (d,

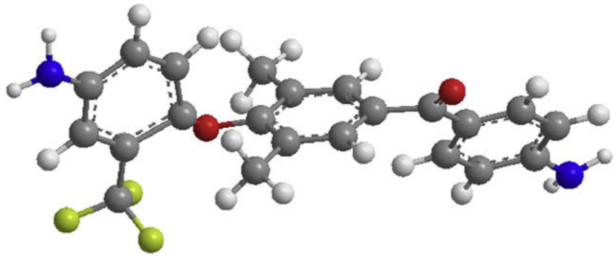


Fig. 3. Minimum energy models of diamine **3**.

$J = 8.8$ Hz, 2H), 7.42 (s, 2H), 2.23 (s, 6H). Elemental analysis: Calcd for $C_{15}H_{13}NO_4$ (271.27): C, 66.41%; H, 4.83%; N, 5.16%. Found: C, 66.31%; H, 4.97%; N, 5.20%.

*2.3.2. 3,5-Dimethyl-4-(4-nitro-2-trifluoromethylphenoxy)-4′-nitrobenzophenone (**2**)*

A mixture of intermediate compound **1** (16.3 g, 0.06 mol), 2-chloro-5-nitrobenzotrifluoride (13.6 g, 0.06 mol), potassium carbonate (12.4 g, 0.09 mol) and DMF (100 mL) was heated to 130 °C for 12 h and then poured into methanol/water (1:3 by volume). The crude product was recrystallized from DMF/ethanol (4:1) to provide brown needle crystal solid (24.0 g, 87%), mp 181–182 °C by DSC at a scan rate of 10 °C/min. FT-IR (KBr): 1662 (C=O), 1529, 1349 (NO_2), 1266 (C–O–C), 1120 (C–F) cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz) δ: 8.56 (d, $J = 2.8$ Hz, 1H), 8.45 (dd, $J_1 = 2.8$ Hz, $J_2 = 9.2$ Hz, 1H), 8.40 (d, $J = 9.2$ Hz, 2H), 8.01 (d, $J = 9.2$ Hz, 2H), 7.71 (s, 2H), 6.85 (d, $J = 9.2$ Hz, 1H), 2.15 (s, 6H). Elemental analysis: Calcd for $C_{22}H_{15}F_3N_2O_6$ (460.36): C, 57.40%; H, 3.28%; N, 6.09%. Found: C, 57.47%; H, 3.38%; N, 6.31%.

*2.3.3. 3,5-Dimethyl-4-(4-amino-2-trifluoromethylphenoxy)-4′-aminobenzophenone (**3**)*

The intermediate dinitro compound **2** (18.4 g, 0.04 mol) and 5% Pd/C (0.4 g) were suspended in 200 mL of ethanol in a 500-mL flask. The suspension solution was heated to refluxing, and 85% hydrazine monohydrate (15 mL) was added dropwise to the mixture over 0.5 h. After a further 4 h of refluxing, the resultant clear, darkened solution was filtered hot to remove Pd/C, and the filtrate was distilled to remove some solvent. The obtained mixture was poured into 100 mL of stirring water, giving rise to a pale yellow product. The crude product was purified by column chromatography over silica gel (dichloromethane), and white powder diamine **3** was obtained (11.9 g, 74%), mp 138–139 °C by DSC at a scan rate of 10 °C/min. FT-IR (KBr): 3300–3500 (NH_2), 1634 (C=O), 1226 (C–O–C), 1127 (C–F) cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz) δ: 7.56 (d, $J = 8.6$ Hz, 2H), 7.41 (s, 2H), 6.96 (d, $J = 2.6$ Hz, 1H), 6.68 (dd, $J_1 = 2.6$ Hz, $J_2 = 8.8$ Hz, 1H), 6.62 (d, $J = 8.7$ Hz, 2H), 6.24 (d, $J = 8.8$ Hz, 1H), 6.15 (s, 2H), 5.17 (s, 2H), 2.10 (s, 6H). Anal. Calcd for $C_{22}H_{19}F_3N_2O_2$ (400.39): C, 65.99; H: 4.78; N, 7.00. Found: C, 65.71; H, 4.90; N, 7.07.

Table 1
Inherent viscosities[a] and GPC molecular weights of the PEKIs.

Polymers	η_{inh} (dL/g)	GPC data		
		$M_n \times 10^4$	$M_w \times 10^4$	PDI
5a	0.84	–[b]	–	–
5b	0.97	3.25	5.36	1.65
5c	0.91	2.81	4.47	1.59
5d	0.68	2.58	4.46	1.73

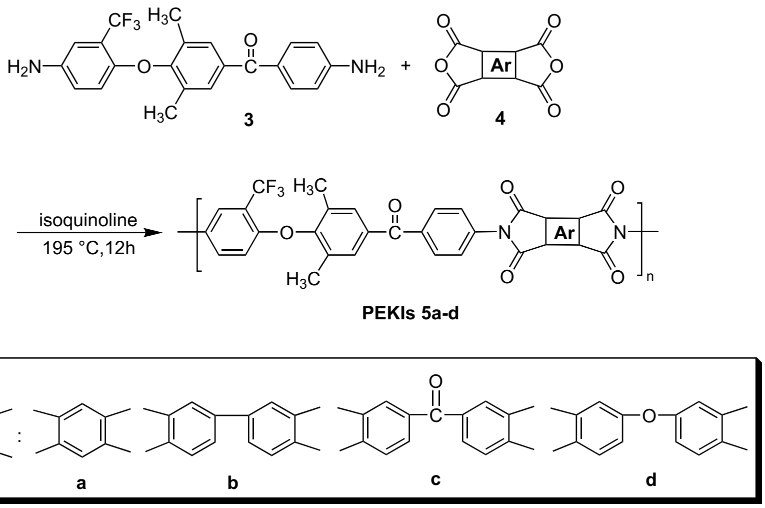
[a] Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.
[b] PEKI **5a** was only partly soluble in $CHCl_3$.

2.4. Polymer synthesis

The general procedure for the preparation of the PEKIs **5a–d** was illustrated as follows. Diamine **3** (2.0 mmol) and dianhydride monomer **4a–d** (2.0 mmol) were first dissolved in 20.0 mL of *m*-cresol in a 50 mL three-necked round-bottomed flask. After the mixture was stirred at room temperature for 30 min, isoquinoline (ca. 8 drops) was added, and further stirred for 3 h at 120 °C. Then the mixture was heated at 195 °C for 12 h. Water formed during the imidization was continuously removed with a stream of nitrogen. At the end of the reaction, the mixture was cooled and precipitated into 300 mL ethanol. The polymer was separated by filtration and washed with ethanol for several times and dried in a vacuum oven at 120 °C for 10 h.

PEKI **5a**. FT-IR (KBr): 1780, 1731, 1664, 1371, 1235, 1130, 1054, 725 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz) δ: 8.44 (m, 2H), 8.01 (m, 3H), 7.71–7.78 (m, 5H), 6.85 (d, $J = 8.4$ Hz, 1H), 2.21 (s, 6H). Anal. Calcd for $(C_{32}H_{17}F_3N_2O_6)_n$ $(582.48)_n$: C, 65.98; H: 2.94; N, 4.81. Found: C, 64.67; H, 3.30; N, 4.51.

PEKI **5b**. FT-IR (KBr): 1778, 1721, 1658, 1371, 1235, 1127, 1054, 739 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.28 (dd, $J_1 = 5.0$ Hz, $J_2 = 11.6$ Hz, 2H), 8.15 (m, 4H), 8.00 (d, $J = 8.4$ Hz, 2H), 7.85 (s, 1H), 7.70 (d, $J = 7.6$, 2H), 7.66 (s, 2H), 7.50 (d, $J = 8.8$ Hz, 1H), 6.63 (d,



Scheme 2. Synthesis of fluorinated PEKIs **5a–d**.

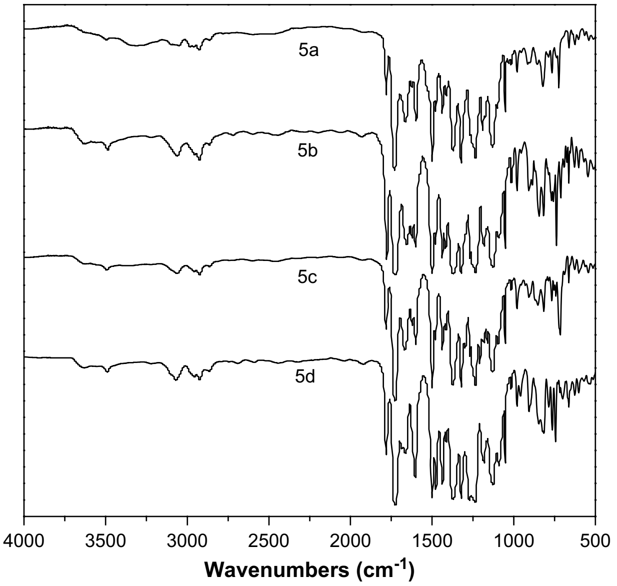


Fig. 4. FT-IR spectra of PEKIs **5a–d**.

J = 8.8 Hz, 1H), 2.25 (s, 6H). Anal. Calcd for $(C_{38}H_{21}F_3N_2O_6)_n$ $(658.58)_n$: C, 69.30; H: 3.21; N, 4.25. Found: C, 68.74; H, 3.35; N, 4.26.

PEKI **5c**. FT-IR (KBr): 1781, 1728, 1668, 1372, 1235, 1132, 1054, 716 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.28 (m, 4H), 8.17 (d, $J = 9.2$ Hz, 2H), 8.02 (d, $J = 11.6$ Hz, 2H), 7.82 (s, 1H), 7.67 (d, $J = 7.6$, 2H), 7.64 (s, 2H), 7.48 (d, $J = 8.0$ Hz, 1H), 6.62 (d, $J = 8.8$ Hz, 1H), 2.23 (s, 6H). Anal. Calcd for $(C_{39}H_{21}F_3N_2O_7)_n$ $(686.59)_n$: C, 68.22; H: 3.08; N, 4.08. Found: C, 67.76; H, 3.25; N, 3.97.

Table 2
Solubility behavior of the fluorinated PEKIs.[a]

Polymers	NMP	DMAc	DMF	DMSO	$CHCl_3$	CH_2Cl_2	THF	Acetone
5a	++	++	+	+	+−	+−	+−	−
5b	++	++	++	+	++	++	+	S
5c	++	++	++	++	++	++	++	S
5d	++	++	++	++	++	++	++	+−

[a] The qualitative solubility was determined with 10 mg of the polymer in 1 mL of the solvent. ++, soluble at room temperature; +, soluble on heating; +−, partly soluble on heating; S, swelling on heating; −, insoluble even on heating.

PEKI **5d**. FT-IR (KBr): 1781, 1728, 1666, 1371, 1237, 1127, 1054, 744 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.05 (m, 2H), 7.97 (d, $J = 8.4$ Hz, 2H), 7.81 (s, 1H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.64 (s, 2H), 7.57–7.61 (m, 2H), 7.52 (m, 2H), 7.46 (d, $J = 8.8$ Hz, 1H), 6.61 (d, $J = 8.8$ Hz, 1H), 2.24 (s, 6H). Anal. Calcd for $(C_{38}H_{21}F_3N_2O_7)_n$ $(674.58)_n$: C, 67.66; H: 3.14; N, 4.15. Found: C, 66.70; H, 3.19; N, 4.08.

3. Results and discussion

3.1. Monomer synthesis

The new unsymmetrical aromatic diamine, 3,5-dimethyl-4-(4-amino-2-trifluoromethylphenoxy)-4′-aminobenzophenone, was synthesized in a three-step reaction using 2,6-dimethylphenol and 4-nitrobenzoyl chloride as starting materials (Scheme 1). First, the intermediate **1** was synthesized from 2,6-dimethylphenol and 4-nitrobenzoyl chloride via a Friedel–Crafts acylation reaction at a relatively low temperature catalyzed by anhydrous $AlCl_3$. Then, the dinitro compound **2** was synthesized by a nucleophilic substitution reaction of **1** and 2-chloro-5-nitrobenzotrifluoride in the presence of potassium carbonate in DMF. Finally, dinitro compound **2** was

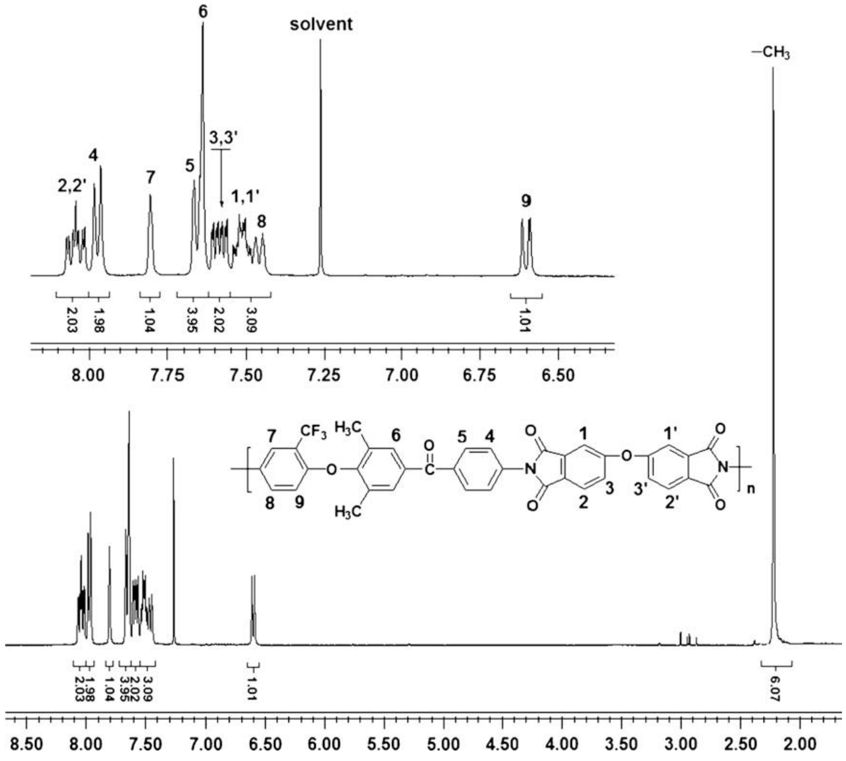


Fig. 5. ^{1}H NMR spectrum of PEKI **5d** in $CDCl_3$.

Table 3
Optical and mechanical properties of the PEKI films.

Polymers	λ_{cutoff} (nm)	T_{450} (%)	Tensile strength (MPa)	Elongation to break (%)	Initial modulus (GPa)
5a	361	78	97	10.9	2.4
5b	375	82	128	11.4	2.3
5c	355	81	104	12.7	2.1
5d	354	84	91	18.5	1.7

Table 4
Dielectric properties and water absorption of the PEKI films.

Polymers	Film thickness (μm)	Dielectric Constant (Dry)					Water absorption (%)
		1 MHz	10 MHz	100 MHz	500 MHz	1 GHz	
5a	62	2.45	2.38	2.34	2.34	2.35	0.55
5b	51	2.26	2.23	2.21	2.20	2.20	0.33
5c	63	2.29	2.21	2.18	2.15	2.14	0.51
5d	68	2.33	2.25	2.22	2.19	2.20	0.42
PMDA-ODA	45	3.59	3.51	3.48	3.46	3.45	0.56

converted to the corresponding diamine monomer **3** by hydrazine Pd/C-catalyzed reduction.

FT-IR and ^{1}H NMR were used to confirm the structures of the intermediates **1**, **2** and diamine **3**. Fig. 1 shows the FT-IR spectra of **2** and **3**. Dinitro compound **2** gave two characteristic bands at 1529 and 1349 cm^{-1} (NO_2 asymmetric and symmetric stretching). After reduction, the characteristic absorptions of the nitro groups disappeared, and the amino groups showed the pair of N–H stretching bands at the region of 3300–3500 cm^{-1}. Fig. 2 shows ^{1}H NMR spectra of **1**, **2** and **3**, and the assignments of each proton are given in the figure. The spectral results are in good agreement with the proposed molecular structures of **1**, **2** and **3**, and the unsymmetrical protons in the amino groups of **3** appear in 5.17 and 6.15 ppm. Furthermore, the elemental analysis results also agree with the calculated values for the all proposed chemical compositions.

Because of the introduction of bulky pendant groups (trifluoromethyl and dimethyl groups) at the ortho-position of ether linkage in diamine **3**, to attain the minimum energy of conformation, it is no doubt that the diamine monomer would possess a large kink concoplanar structures and large dihedral angles between aromatic phenyl rings. As shown in Fig. 3, the molecular model of diamine **3**, simulated by semiempirical computations of Cambridge Software, exhibited remarkable twisting and concoplanar structures. Thus, the structure of diamine **3** was designed to impart several desirable properties to obtained PIs, such as good solubility, high optical transparency and low dielectric constants.

3.2. *Polymer synthesis*

Generally, there are two main synthetic methods to PIs, namely one-step and two-step polymerizations. In the one-step polymerization, completely cyclized PIs were obtained directly from their corresponding teteracarboxylic acid dianhydride and diamine, using high boiling solvents. This method was usually used when working with soluble PIs and is considered more practical for polymerizing less reactive dianhydrides and diamines. In the two-step polymerization, the poly(amic acid) (PPA) was first prepared from dianhydride and diamine in a polar aprotic solvent, then the PPA was cyclodehydrated at elevated temperatures or by adding a cyclizing agent such as acetic anhydride. However, the PAA was an unstable polymer; the hydroxyl group of the carboxylic acid group and amino group of amide in PAA all could cause a nucleophilic substitution reaction to take place with the carbonyl group of PAA at room temperature or in the heating process. Meanwhile, the ketone group in BTDA or diamine was an electrophilic group and could condense to the amine group to form an imine group. Therefore, PAA with the ketone group would be connected with imine linkage to form nonlinear or crosslinking PI during thermal imidization [24–26,35]. Considering the structure of diamine **3**, these fluorinated PEKIs were prepared via a one-step high-temperature polycondensation procedure (Scheme 2). Despite the amino group in the diamine **3** was less basic than a normal dramatic amine because of the inductive deactivation of the trifluoromethyl and carbonyl group, the diamine **3** was still sufficiently reactive to obtain fibroid or strip-like polymers by one-step polymerizations at relatively high temperature (195 °C). As shown in Table 1, these polymers had inherent viscosities ranging from 0.68 to 0.97 dL/g. According to GPC data (Table 1), the M_w and M_n values of these polymers dissolved in $CHCl_3$ were 44 600–53 600 and 25 800–32 500, respectively. The polydispersity index (PDI) of the **5** series was in the range of 1.59–1.73.

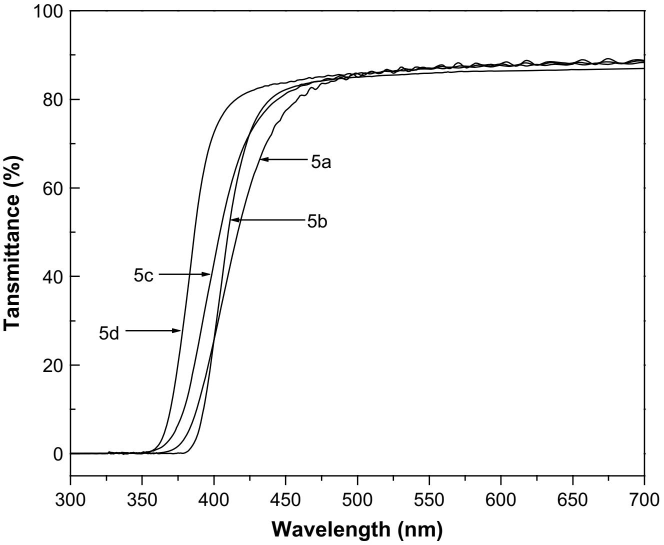


Fig. 6. UV–vis spectra of the PEKI films.

The complete imidization between diamine and dianhydride was confirmed by FT-IR and ^{1}H NMR spectra. Fig. 4 depicts the FT-IR spectra of PEKIs **5a–d**. They all showed characteristic imide absorption bands around 1780 and 1730 cm^{-1} (imide carbonyl asymmetrical and symmetrical stretchings), 1371 cm^{-1} (C–N stretching), and 1054 and 720 cm^{-1} (imide ring deformation), together with strong C–F stretching absorption peak at about 1130 cm^{-1}, while the amino group at the region of 3300–3500 cm^{-1} disappeared. A representative of ^{1}H NMR spectrum of PEKI **5d** is illustrated in Fig. 5. The assignments of each proton are given in the figure, and the spectrum is in complete agreement with the

Table 5
Thermal properties of polyimides.

Polymers	T_g[a] (°C)	T_{10}[b] (°C)		Char yield (%)[c]
		In N_2	In air	
5a	NO	531	471	52
5b	329	522	483	55
5c	307	518	493	56
5d	289	519	468	54

[a] From the second trace of DSC measurements conducted at a heating rate of 20 °C/min.

[b] 10% weight loss temperature in TGA at 20 °C/min heating rate.

[c] Residual weight retention at 800 °C.

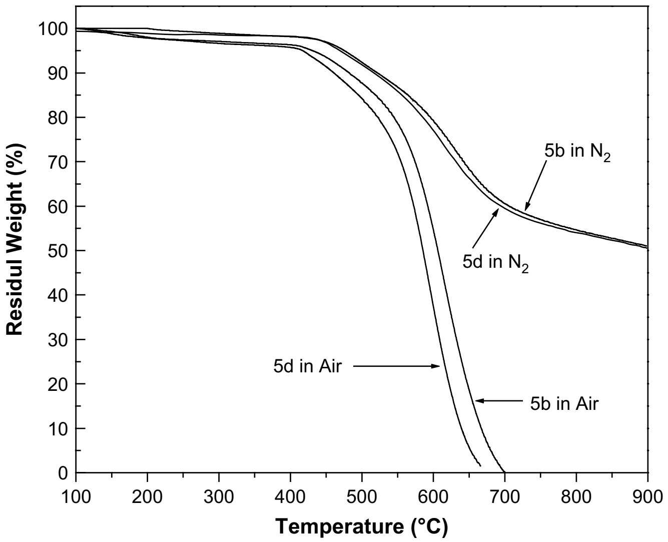


Fig. 7. TGA curves of PEKIs **5b** and **5d** at a heating rate of 20 °C/min.

proposed polymer structure. In addition to FT-IR and ^{1}H NMR spectra, the elemental analysis results of these PEKIs also generally agree with the calculated values for the proposed structures.

3.3. Polymer solubility

The solubility of these fluorinated PEKIs was tested in various organic solvents, and the results are listed in Table 2. It is well known that aromatic PIs generally show rather poor solubility in organic solvents, especially for those derived from rigid dianhydrides such as PMDA and BPDA. Unlike those insoluble PIs, all the obtained PEKIs were soluble in NMP, DMAc, DMF and DMSO at room temperature or at heating. The PEKI **3b**, **3c** and **3d** even could be soluble in $CHCl_3$, CH_2Cl_2, and THF. Apparently, PEKI **3b** showed an improved solubility compared with some fluorinated PEIs derived from the trifluoromethyl-substituted bis(ether amine)s and BPDA, especially in some low-boiling-point solvents [23–26,28]. It should be noted that good solubility in low-boiling-point solvents is critical for preparing PI films or coatings at a relatively low processing temperature, which is desirable for advanced microelectronics manufacturing applications. The good solubility of these fluorinated PEKIs was governed by the structural modification through incorporation of the bulky groups (trifluoromethyl and dimethyl groups) and concoplanar structures into their macromolecular backbone. This kind of macromolecular architecture could decrease the packing density and intermolecular interactions of macromolecular chains, so that it improves the solubility of resultant polymers.

3.4. Optical and mechanical properties

All the fluorinated PEKIs could be processed to transparent, flexible and tough films conveniently by casting from polymer solutions. The optical properties of the PEKI films are given in Table 3, and corresponding UV–Vis spectra of these PEKI films about 30 μm thickness are shown in Fig. 6. It could be seen from Fig. 6 that these fluorinated PEKI films exhibited good transparency, the cutoff wavelength (λ_{cutoff}) was in the range of 354–375 nm, and the transparency at 450 nm (T_{450}) was higher than 78%. These results mainly attributed to the reduction of intermolecular CTC between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. The electron-withdrawing trifluoromethyl and carbonyl groups in the diamine moieties were presumably effective to decrease the CTC formation between polymer chains in virtue of inductive effect (by decreasing the electron-donating behavior of the diamine moieties). Meanwhile, the bulky groups (trifuoromethyl and dimethyl groups) at the ortho-position of ether linkage and concoplanar structures, were effective to break the conjugation along the backbone and provide enhanced optical transparency.

These PEKI films were subjected to tensile tests, and the results are also reported in Table 3. The films had tensile strengths of 91–128 MPa, elongations at break of 10.9–18.5%, and initial moduli of 1.7–2.4 GPa. These results indicate that the incorporation of the bulky groups (trifuoromethyl and dimethyl groups) and concoplanar structure into the polymer backbone not only improves solubility and optical transparency but also retains the good mechanical properties.

3.5. Dielectric constant and water absorption

The dielectric constants and water absorption of all the PEKIs are presented in Table 4. For comparison, the data of a standard PEI film from PMDA and 4,4′-oxydianiline (ODA) are also listed in Table 4. These PEKIs showed dielectric constants in the range of 2.26–2.45 at 1 MHz and in the range of 2.14–2.35 at 1 GHz, respectively, which were much lower than that of the standard PEI film. The low dielectric constants could mainly be attributed to the trifluoromethyl group in the polymer chains. The low polarizability of trifluoromethyl group, combined with the bulky free volumes and concoplanar structure, endowed these PEKIs with low dielectric constants. It presents potential utility for the microelectronics industry, in which a low dielectric constant is desired to prevent crosstalk between conducting paths. As expected, these PEKIs also exhibited low water absorptions (0.33–0.55%) due to the hydrophobic nature of the trifluoromethyl and dimethyl pendant groups. The low water absorptions also ensure that these PEKIs have stable dielectric performance.

3.6. Thermal properties

The thermal properties of the fluorinated PEKIs are summarized in Table 5. It was inspiring that these PEKIs showed extra high T_g, and the values were all above 289 °C. PEKI **5a** based on rigid dianhydride **PMDA** even show no distinctly T_g at determined temperature region. Apparently, all these PEKIs showed higher T_g values (30–50 °C) compared with some fluorinated PEIs derived from the trifluoromethyl-substituted bis(ether amine)s and corresponding dianhydrides [23–32]. High T_g values mainly originated from the introduction of trifluoromethyl and dimethyl groups into the ortho-position of the ether linkages, which hinder the rotation around C–O–C bond of the two phenyl rings, and further increase the chain rigidity and T_g values of these polymers. Moreover, because the ketone linkage in the polymer backbone is more rigid than the ether linkage, it also makes these PEKIs show a higher T_g values than those of some fluorinated PEIs derived from the trifluoromethyl-substituted bis(ether amine)s. The thermal and thermooxidative stabilities of all the PEKIs were evaluated by TGA measurements in both nitrogen and air atmospheres. Typical TGA curves for PEKIs **5b** and **5d** are reproduced in Fig. 7. These PEKIs showed good thermal stability and had no notable weight loss below 500 °C in nitrogen atmosphere. The 10% weight loss temperatures (T_{10}) in nitrogen and in air atmospheres were in the range of 518–531 °C and 468–493 °C, respectively. They left more than 52% char yield at 800 °C in nitrogen. As mentioned above, these PEKIs possessed sufficiently high T_g and eminent thermal stability which could withstand the elevated processing temperatures as insulating materials for microelectronics.

4. Conclusions

A series of fluorinated PEKIs containing trifluoromethyl and dimethyl pendant groups, were prepared from a newly synthesized unsymmetrical diamine **3** and various aromatic dianhydrides by the one-step high-temperature polycondensation. The introduction of bulky pendant groups and concoplanar structure was an effective way to improve their solubility, optical and dielectric properties without substantial diminution of their physical properties. All the PEKIs exhibited good solubility, high optical transparency, and low dielectric constants and water absorption. Meanwhile, they also retained good thermal stability and mechanical properties. Thus, these PEKIs demonstrated eminent combination properties and could be considered as potential high-temperature resistant materials for photoelectric and microelectronic applications.

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References

[1] Chern YT, Shiue HC. Macromolecules 1997;30:4646.
[2] Hsiao SH, Li CT. Macromolecules 1998;31:7213.
[3] Liaw DJ, Chang FC, Leung MK, Chou MY, Muellen K. Macromolecules 2005;38:4024.
[4] Zhu YQ, Zhao PQ, Cai XD, Meng WD, Qing FL. Polymer 2007;48:3116.
[5] Choi H, Chung IS, Hong K, Park CE, Kim SY. Polymer 2008;49:2644.
[6] Ding MX. Prog Polym Sci 2007;32:623.
[7] Maya EM, Lozano AE, Campa JGI, Abajo J. Macromol Rapid Commun 2004;25:592.
[8] Zhang QY, Li SH, Li WM, Zhang SB. Polymer 2007;48:6246.
[9] Liu Y, Zhang YH, Guan SW, Li L, Jiang ZH. Polymer 2008;49:5439.
[10] Liaw DJ, Chang FC. J Polym Sci Part A Polym Chem 2004;42:5766.
[11] Hsiao SH, Lin KH. J Polym Sci Part A Polym Chem 2005;43:331.
[12] Shao Y, Li YF, Zhao X, Wang XL, Ma T, Yang FC. J Polym Sci Part A Polym Chem 2006;44:6836.
[13] Lin SH, Li FM, Stephen Z, Cheng D, Harris FW. Macromolecules 1998;31:2080.
[14] Qiu ZM, Zhang SB. Polymer 2005;46:1693.
[15] Hu ZQ, Wang MH, Li SJ, Liu XY, Wu JH. Polymer 2005;46:5278.
[16] Wang JY, Liao GX, Liu C, Jian XG. J Polym Sci Part A Polym Chem 2004;42:6089.
[17] Matsuura T, Yoshinori H, Nishi S, Yamada N. Macromolecules 1991;24:5001.
[18] Ando S, Sawada T, Inoue Y. Electron Lett 1993;29:2143.
[19] Hasegawa M, Horie K. Prog Polym Sci 2001;26:259.
[20] Yang CP, Su YY. J Polym Sci Part A Polym Chem 2006;44:3140.
[21] Lin CH, Lin CH. J Polym Sci Part A Polym Chem 2007;45:2897.
[22] Liu JG, He MH, Zhou HW, Qian ZG, Wang FS, Yang SY. J Polym Sci Part A Polym Chem 2002;40:110.
[23] Xie K, Zhang SY, Liu JG, He MH, Yang SY. J Polym Sci Part A Polym Chem 2001;39:2581.
[24] Yang CP, Su YY. J Polym Sci Part A Polym Chem 2004;42:222.
[25] Hsiao SH, Yang CP, Huang SC. J Polym Sci Part A Polym Chem 2004;42:2377.
[26] Yang CP, Su YY, Wu KL. J Polym Sci Part A Polym Chem 2004;42:5424.
[27] Yang CP, Hsiao FZ. J Polym Sci Part A Polym Chem 2004;42:2272.
[28] Hsiao SH, Chang YH. J Polym Sci Part A Polym Chem 2004;42:1255.
[29] Yang CP, Hsiao SH, Wu KL. Polymer 2003;44:7067.
[30] Jang WB, Lee HS, Lee SK, Choi SY, Shin DY, Han H. Mater Chem Phys 2007;104:342.
[31] Liaw DJ, Huang CC, Chen WH. Polymer 2006;47:2337.
[32] Qiu ZQ, Wang JH, Zhang QY, Zhang SB, Ding MX, Gao LX. Polymer 2006;47:8444.
[33] Yang CP, Su YY, Wen SJ, Hsiao SH. Polymer 2006;47:7021.
[34] Chung IS, Park CE, Ree M, Kim SY. Chem Mater 2001;13:2801.
[35] Yang CP, Hsiao FZ. J Polym Res 2003;10:181.