

# Synthesis and characterization of polyimides from 4,4'-(3-(*tert*-butyl)-4-aminophenoxy)diphenyl ether

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**Abstract** A novel diamine 4,4'-(3-(*tert*-butyl)-4-aminophenoxy)diphenyl ether (**4**) was synthesized from 2-*tert*-butylaniline and 4,4'-oxydiphenol through iodination, acetyl protection, coupling reaction and deacetylation protection. Then some polyimides (PIs) were obtained by one-pot polycondensation of diamine **4** with several commercial aromatic dianhydrides respectively. They all exhibit enhanced solubility in organic solvents (such as NMP, DMF, THF and CHCl<sub>3</sub> etc.) at room temperature. Their number-average molecular weights are in the range of  $(2.1\text{--}3.7) \times 10^4$  g/mol with PDI from 2.25 to 2.74 by GPC. They can form transparent, tough and flexible films by solution-casting. The light transparency of them is higher than 90% in the visible light range from 400 nm to 760 nm and the cut-off wavelengths of UV-vis absorption are below 370 nm. They also display the outstanding thermal stability with the 5% weight loss temperature from 525 °C to 529 °C in nitrogen atmosphere. The glass transition temperatures ( $T_g$ s) are higher than 264 °C by DSC. XRD results demonstrate that these PIs are amorphous polymers with the lower water absorption (<0.66%). In summary, the incorporation of *tert*-butyl groups and multiple phenoxy units into the rigid PI backbones can endow them excellent solubility and transparency with relatively high  $T_g$ s.

**Keywords** *tert*-Butyl · Multiple phenoxy units · Polyimides · Solubility · Transparency

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## Introduction

As one of famous high performance polymers, aromatic polyimides are widely used in many high-tech fields, such as automobile, membrane separation, adhesives, aerospace and micro-electronics etc. [1–6]. Due to the rigid backbones of traditional polyimides, most of them are difficult to process in solution or melting state, which limits their wide applications [7]. So many attentions have been focused on design and synthesis of PIs with excellent processability without sacrificing their inherent properties. Up to date, there are two main approaches to improve their processability. One is to improve their solubility by using aromatic monomers with asymmetric units, bulky side-groups or fluorine atoms [8–15]. The other is to improve their thermoplasticity by introducing flexible linkages into their backbone [16–20]. For example, Tamai et al. synthesized a series of PIs based on aromatic ether diamines having different numbers of benzene rings and found the  $T_g$ s of these PIs decrease with increasing numbers of benzene rings in diamines. In other words, the thermostability of PIs decrease with increasing the number of flexible linkages in backbone. On the other hand, our previous studies demonstrated that the solubility of PIs was improved greatly by attaching bulky *tert*-butyl groups to the polyimide backbones, while their inherent thermal property was still kept [21–25]. Thus, highly soluble, transparent and thermo-stable PIs would be obtained if we introduce *tert*-butyl groups into aromatic ether diamine with four benzene rings. In this paper, a novel diamine containing *tert*-butyl groups and multiphenoxy units, 4,4'-(3-(*tert*-butyl)-4-aminophenoxy)diphenyl ether, was synthesized and polymerized with several commercial aromatic dianhydrides to produce a series of PIs via one-step polycondensation. The effects of *tert*-butyl groups and multiple phenoxy units on the physical-chemical properties of PIs were investigated and discussed in detail.

## Experimental

### Materials

2-*tert*-butylaniline (Wuxi TPW Pharmaceutical Technology Co. Ltd.) and *m*-Cresol (Sinopharm Chemical Reagent Co. Ltd.) was purified by the vacuum distillation before use. Pyromellitic dianhydride (PMDA, Sinopharm Chemical Reagent Co. Ltd.), 3,3',4,4'-diphenylether tetracarboxylic dianhydride (OPDA, TCI Chemicals), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, J&K Chemical Co. Ltd.) and 2,2-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA, J&K Chemical Co. Ltd.) were purified by recrystallization from acetic anhydride before use. Isoquinoline, triethylamine, 4,4'-oxydiphenol, I<sub>2</sub>, *o*-phenanthroline, CuI, K<sub>3</sub>PO<sub>4</sub> and other materials were purchased and used without further purification.

### Measurement

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a 400 MHz Varian NMR spectrometer with DMSO-*d*<sub>6</sub> and CDCl<sub>3</sub> as solvent. The mechanical property of the polyimide films was determined by a CMT-4104 (SANS, Shenzhen, China) tensile tester at a drawing speed of 1 mm/min. The FTIR spectra were recorded on a Perkin-Elmer Fourier transform infrared spectrometer. The X-ray diffraction measurement was carried out on a Rigaku D/max-2200/PC X-ray diffractometer with Cu/K- $\alpha$  radiation. The number-average molecular weights and polydispersity index of the resulting PIs were determined by a TOSOH HLC-8320 gel permeation chromatography (GPC) analyzer (polystyrene calibration). Solubility was determined qualitatively by placing 10 mg polymer into 1 mL solvent at room temperature. The transparency of the polyimide films were performed on a Perkin-Elmer Lambda 20 UV-vis spectrometer. Differential scanning calorimetry (DSC) curves were obtained on a PE Pyris-1 thermal analyzer under N<sub>2</sub> atmosphere at a heating rate of 20 °C/min from 40 °C to 430 °C. Thermogravimetric analysis (TGA) was performed on a PE Pyris-7 thermal analyzer under nitrogen at a heating rate of 20 °C/min from 50 °C to 800 °C. The molecular weight of diamine **1** was determined by a waters Q-ToF Premier mass spectrometry. The rates of water absorption was determined by immersing the dry films (about 250 mg) in 25 °C water for 24 h and calculated from the differences of the weights.

### Monomer synthesis

#### 2-*tert*-Butyl-4-iodophenylamine (**1**)

**1** was synthesized from 2-*tert*-butylaniline according to our previous report [23]. Yield: 93%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):

7.47 (d, *J* = 2 Hz, 1H; Ar H), 7.29 (dd, *J*<sub>1</sub> = 8, *J*<sub>2</sub> = 2 Hz, 1H; Ar H), 6.42 (d, *J* = 8 Hz, 1H; Ar H), 1.39 (s, 9H; CH<sub>3</sub>).

#### *N*-(2-*tert*-butyl-4-iodophenyl)acetamide (**2**)

2.75 g (10 mmol) compound **1**, 20 mL CH<sub>2</sub>Cl<sub>2</sub>, 1.11 g (11 mmol) triethylamine were added into 100 mL single-necked flask under magnetic stirring and the mixture was cooled to 0 °C. A solution of acetyl chloride (11 mmol acetyl chloride in 5 mL CH<sub>2</sub>Cl<sub>2</sub>) was dropped into the mixture within 15 min. After the addition, the reaction was further conducted at the room temperature for 8 h. Then, 20 mL saturated NaHCO<sub>3</sub> solution was added to the mixture to quench the reaction and the mixture were extracted with 20 mL CH<sub>2</sub>Cl<sub>2</sub> to get the organic layer, which was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the filtration, the dark oil was obtained by the rotating evaporation. The crude product was recrystallized from ethanol to afford 2.57 g compound **2**. Yield: 81%; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 9.22 (s, 1H; -NH-), 7.64 (s, 1H; Ar H), 7.55 (d, *J* = 8.0 Hz, 1H; Ar H), 6.83 (d, *J* = 8.2 Hz, 1H; Ar H), 2.02 (s, 3H; CH<sub>3</sub>), 1.34–1.23 (m, 9H; CH<sub>3</sub>).

#### 4,4'-(3-(*tert*-butyl)-4-acetamidophenoxy) diphenyl ether (**3**)

3.49 g (11 mmol) compound **2**, 1.01 g (5 mmol) 4,4'-oxydiphenol, 0.95 g (5 mmol) CuI, 1.80 g (10 mmol) *o*-phenanthroline, 6.37 g (30 mmol) K<sub>3</sub>PO<sub>4</sub> and 50 mL DMF were added to the three-necked flask under magnetic stirring. After the air in the three-necked flask was replaced with nitrogen, the mixture was warmed up to 120 °C to react under a closed system for 36 h. The mixture was cooled to room temperature and 50 mL ethyl acetate was added into it. After filtration by Buchner funnel, the mixture was concentrated under reduced pressure to get the black oil. Then it was purified by column chromatography with silica gel with a petroleum ether/ethyl acetate (v/v = 3/1, 2/1, 1/1, in sequence) as the eluent to give 1.68 g compound **3**. Yield: 58%; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 9.13 (s, 2H; -NH-), 7.06 (s, 8H; Ar H), 7.03 (d, *J* = 2.8 Hz, 2H; Ar H), 6.99 (d, *J* = 8.6 Hz, 2H; Ar H), 6.74 (dd, *J*<sub>1</sub> = 8.5, *J*<sub>2</sub> = 2.8 Hz, 2H; Ar H), 2.02 (s, 6H; CH<sub>3</sub>), 1.29 (s, 18H; CH<sub>3</sub>).

#### 4,4'-(3-(*tert*-butyl)-4-aminophenoxy)diphenyl ether (**4**)

5.80 g (10 mmol) compound **3**, 25 mL concentrated hydrochloric acid and 25 mL ethanol was added to a 200 mL single-neck flask under magnetic stirring. The reaction was conducted under reflux for 12 h. After the reaction finished, it was cooled to room temperature and the right amount of saturated NaOH aqueous solution was added to it to neutralize (pH = 7–8). After extraction with 20 mL ethyl acetate for three times, the combined organic layer was concentrated under reduced pressure to get the black oil. Then the crude product was

purified by column chromatography with silica gel for two times with a petroleum ether/ethyl acetate (v/v = 6/1, 5/1, 4/1, in sequence) as the eluent to give 3.92 g compound **4**. Yield: 79%;  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 6.92 (d,  $J = 9.1$  Hz, 4H; Ar H), 6.85 (d,  $J = 9.2$  Hz, 4H; Ar H), 6.79 (d,  $J = 2.1$  Hz, 2H; Ar H), 6.67 (d,  $J = 8.5$  Hz, 2H; Ar H), 6.61 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 2.1$  Hz, 2H; Ar H), 4.65 (s, 4H;  $-\text{NH}_2$ ), 1.31 (s, 18H;  $\text{CH}_3$ ).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ ): 154.96 (Ar C), 152.38 (Ar C), 147.35 (Ar C), 143.13 (Ar C), 134.47 (Ar C), 120.21 (Ar C), 118.68 (Ar C), 118.61 (Ar C), 118.49 (Ar C), 118.28 (Ar C), 34.64 (C), 29.69 (C). HPLC-MS (ESI, m/z):  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{32}\text{H}_{37}\text{N}_2\text{O}_3$ , 497.2726; found, 497.2798.

### Polymer synthesis

A typical synthesis procedure was displayed as follows (e.g., **4-OPDA**). 496.3 mg (1 mmol) **1**, 10 mL *m*-cresol, 310.2 mg (1 mmol) OPDA and two drops of isoquinoline was added to a 50 mL three necked flask charged with a nitrogen inlet and a mechanical stirring under  $\text{N}_2$  atmosphere. The reaction mixture was heated to 80 °C under stirring and kept at this temperature for another 12 h. Then the reaction temperature was raised successively to 120 °C for 12 h, 150 °C for 12 h and 180 °C for 12 h. The mixture was cooled to room temperature and diluted by 8 mL  $\text{CHCl}_3$  under stirring. Then the resulting viscous mixture was poured into 300 mL methanol under stirring to afford a fiber-like precipitate. The precipitate was collected by filtration through Buchner funnel and dried under vacuum at 160 °C for 24 h. At last, the crude product was reprecipitated twice from DMF into methanol to give the polyimide **4-OPDA**.

Yield is 717 mg (93%); IR ( $\text{cm}^{-1}$ ):  $\nu = 2965$  ( $\text{CH}_2\text{-H}$ ), 1779 ( $\text{C=O}$ ), 1725 ( $\text{C=O}$ ), 1610, 1489, 1373 (C-N), 1236, 1213, 1099, 943, 814.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.01

(d,  $J = 8.2$  Hz, 2H; Ar H), 7.59 - 7.54 (m, 2H; Ar H), 7.50 (dd,  $J_1 = 8.2$ ,  $J_2 = 1.9$  Hz, 2H; Ar H), 7.28 (d,  $J = 2.7$  Hz, 2H; Ar H), 7.07 (dd,  $J_1 = 9.1$  Hz,  $J_2 = 2.3$  Hz, 8H; Ar H), 6.93 (d,  $J = 8.6$  Hz, 2H; Ar H), 6.83 (dd,  $J_1 = 8.6$  Hz,  $J_2 = 2.7$  Hz, 2H; Ar H), 1.30 (s, 18H;  $\text{CH}_3$ ).

### 4-PMDA

Yield: 95%; IR ( $\text{cm}^{-1}$ ):  $\nu = 2966$  ( $\text{CH}_2\text{-H}$ ), 1780 ( $\text{C=O}$ ), 1730 ( $\text{C=O}$ ), 1600, 1491, 1374 (C-N), 1231, 1106, 943, 807, 732.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.50 (d,  $J = 7.2$  Hz, 2H; Ar H), 7.31 (d,  $J = 2.5$  Hz, 2H; Ar H), 7.08 (d,  $J = 9.1$  Hz, 8H; Ar H), 6.96-6.91 (m, 2H; Ar H), 6.84 (d,  $J = 8.9$  Hz, 2H; Ar H), 1.30 (s, 18H;  $\text{CH}_3$ ).

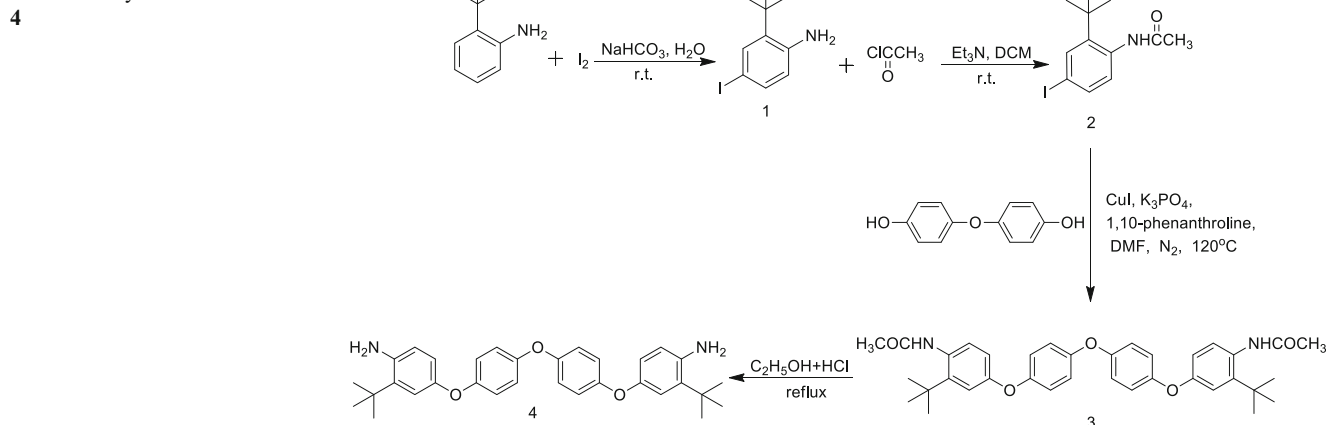
### 4-6FDA

Yield: 92%; IR ( $\text{cm}^{-1}$ ):  $\nu = 2968$  ( $\text{CH}_2\text{-H}$ ), 1786 ( $\text{C=O}$ ), 1729 ( $\text{C=O}$ ), 1609, 1493, 1372 (C-N), 1238, 1104, 944, 846, 725.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.04 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.7$  Hz, 2H; Ar H), 7.98 (s, 2H; Ar H), 7.89 (t,  $J = 7.0$  Hz, 2H; Ar H), 7.29 (d,  $J = 2.5$  Hz, 2H; Ar H), 7.12 - 7.03 (m, 8H; Ar H), 6.93 (dd,  $J_1 = 8.6$  Hz,  $J_2 = 3.1$  Hz, 2H; Ar H), 6.83 (dd,  $J_1 = 8.6$  Hz,  $J_2 = 2.6$  Hz, 2H; Ar H), 1.31 (s, 18H;  $\text{CH}_3$ ).

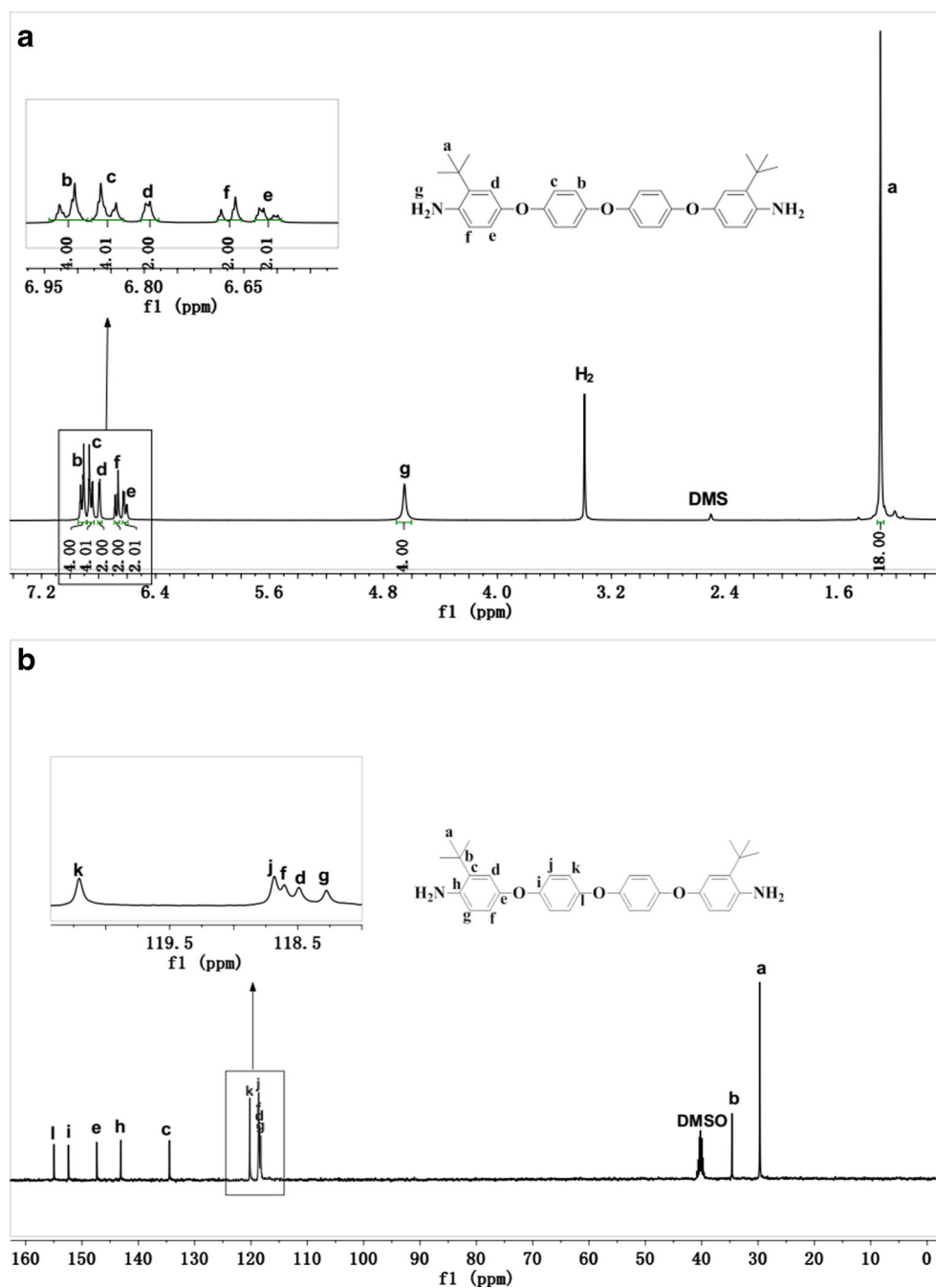
### 4-BPDA

Yield: 97%; IR ( $\text{cm}^{-1}$ ):  $\nu = 2966$  ( $\text{CH}_2\text{-H}$ ), 1777 ( $\text{C=O}$ ), 1723 ( $\text{C=O}$ ), 1600, 1491, 1370 (C-N), 1232, 1099, 943, 843, 745.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.25 (s, 2H; Ar H), 8.13 - 8.07 (m, 4H; Ar H), 7.31 (d,  $J = 2.6$  Hz, 2H; Ar H), 7.08 (dd,  $J_1 = 19.2$  Hz,  $J_2 = 9.1$  Hz, 8H; Ar H) 6.96 (d,  $J = 8.6$  Hz, 2H; Ar H), 6.84 (dd,  $J_1 = 8.6$  Hz,  $J_2 = 2.6$  Hz, 2H; Ar H), 1.32 (s, 18H;  $\text{CH}_3$ ).

**Scheme 1** Synthesis of diamine



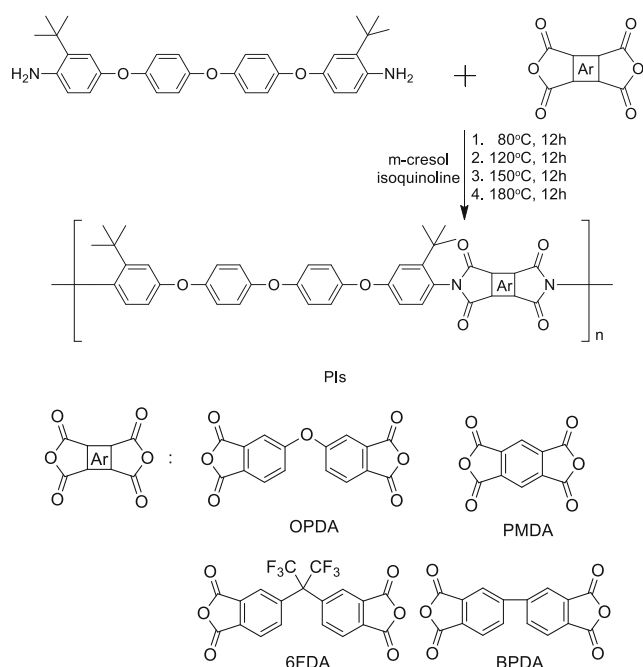
**Fig. 1**  $^1\text{H}$  (a) and  $^{13}\text{C}$  (b) NMR spectra of diamine **4**



### Membrane preparation

PI membranes with the different thickness were prepared as follows: PI solution (0.8 wt.% in NMP) was cast onto a clean glass plate ( $3 \times 3$  cm) and then dried at  $100^\circ\text{C}$  in the air oven until NMP was removed. After cooling to room temperature, the membranes were soaked in deionized water and peeled off from the substrates and further dried at  $180^\circ\text{C}$  under vacuum for 20 h. The thickness of membranes

was from 5 to  $10\ \mu\text{m}$ , which were used to FTIR and UV-vis spectra measurement. Similarly, PI solution (1 wt.%) was cast onto the clean glass plates ( $2 \times 3$  cm) to prepare the transparent membrane with thickness from  $20\ \mu\text{m}$  to  $30\ \mu\text{m}$ , which was used to XRD measurement. PI solution (5 wt.%) was cast onto a clean glass plates ( $6 \times 6$  cm) to prepare transparent membrane with thickness from  $30$  to  $45\ \mu\text{m}$ , which was used to measure the mechanical property and water absorption of PIs.



**Scheme 2** Synthesis of the PIs

## Results and discussion

### Monomer synthesis

The synthetic route of the novel diamine **4**, 4,4'-(3-(*tert*-butyl)-4-aminophenoxy)diphenyl ether, was outlined in Scheme 1.

Firstly, 2-*tert*-butyl-4-iodophenylamine (**1**) was prepared from 2-*tert*-butylaniline by the iodination reaction. Then intermediate **1** was reacted with acetyl chloride to protect the amino group on the benzene ring to produce N-(2-*tert*-butyl-4-iodophenyl)acetamide (**2**). Next, in the presence of  $K_3PO_4$  and DMF under the nitrogen atmosphere, the intermediate **3** was obtained from the intermediate **2** and 4,4'-oxydiphenol through Ullman coupling reaction with CuI as a catalyst and

1,10-phenanthroline as a ligand. This is the key step to significantly influence the yield of diamine **4**. Thus the reaction time of Ullman coupling reaction was prolonged to 36 h to insure the high yield of intermediate **3**. At last the diamine **4** was produced through the deprotection of acetyl in intermediate **3** and purified by recrystallization two times. The title diamine **4** was characterized by  $^1H$  NMR,  $^{13}C$  NMR, MS and DSC. The  $^1H$  and  $^{13}C$  NMR spectra of diamine **4** were presented in Fig. 1.

As shown in Fig. 1a, the proton signals of amino group ( $H_g$ ) appeared around 4.65 ppm, and five proton signals of benzene ring ( $H_b$ ,  $H_c$ ,  $H_d$ ,  $H_e$ ,  $H_f$ ) were found from 6.61 to 6.92 ppm, whereas the proton signals of *tert*-butyl were observed at 1.31 ppm. Also, twelve carbon signals were found in the range from 29 to 155 ppm in Fig. 1b, which was in agreement with all carbon atoms in diamine **4**. Furthermore, the molecular weight of diamine **4** was 496.2798 measured by MS, which was consistent with its theoretical value. The melting point of diamine **4** was around 110 °C, which was obtained from DSC analysis. All above results confirmed the chemical structure of diamine **4**.

### Polymer synthesis and characterization

Generally, polyimides can be synthesized from a diamine and a dianhydride through two-step procedure or one-pot approach [1]. According to our previous studies, the polymerization activity of the diamine will dramatically decrease due to the steric hindrance when *tert*-butyl groups are introduced into the ortho-position of the amino group [21, 22]. Thus, the two-step approach is not suitable for preparing polyimides with high molecular weights from diamine **4** with various dianhydrides. Here all the polyimides were synthesized from diamine **4** and a few commercial dianhydrides through the one-pot method in solution at high temperature as outlined in Scheme 2.

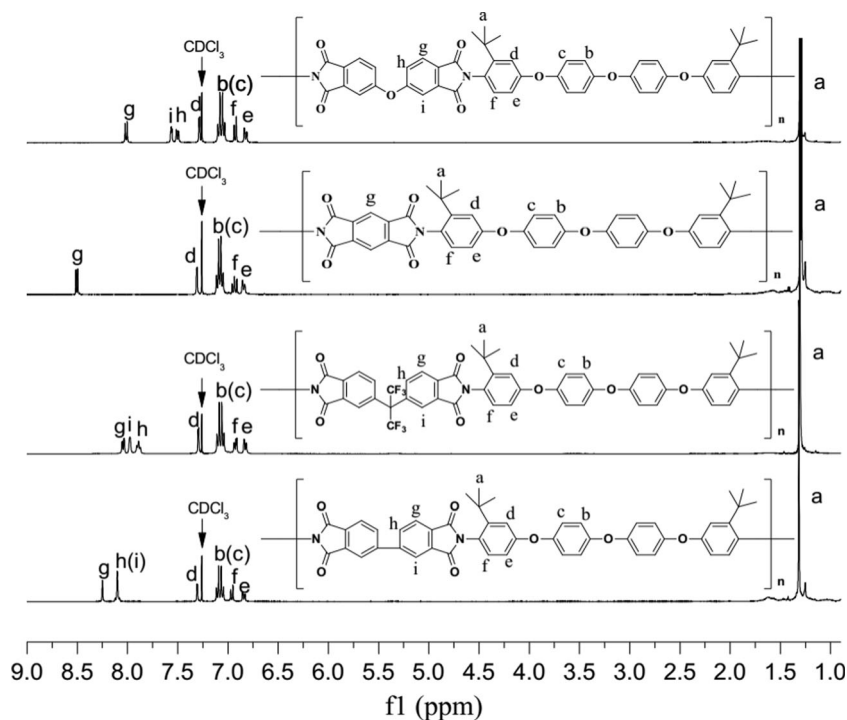
**Table 1** Characterization of the resulting PIs

Polyimides	$M_n$ ( $\times 10^{-4}$ )	PDI	$T_g$ (°C)	$T_5$ (°C)	Char Yield (%)	Element analysis (%)				
						Elemental formula	C	H	N	
4-PMDA	3.3	2.71	300	525	47.7	$C_{42}H_{34}N_2O_7$	Calculated	74.32	5.05	4.13
							Found	73.79	5.30	4.09
4-BPDA	3.2	2.74	283	529	54.6	$C_{48}H_{38}N_2O_7$	Calculated	76.38	5.07	3.71
							Found	76.10	5.42	3.67
4-OPDA	3.7	2.25	264	527	43.9	$C_{48}H_{38}N_2O_8$	Calculated	74.79	4.97	3.63
							Found	74.14	5.26	3.61
4-6FDA	2.1	2.42	266	525	51.6	$C_{51}H_{38}F_6N_2O_7$	Calculated	67.70	4.23	3.10
							Found	67.32	4.59	3.18

$M_n$ : number-averaged molecular weight, PDI: polydispersity index,  $T_g$ : glass transition temperature,  $T_5$ : temperature at 5% weight loss, —: not obtained



**Fig. 2**  $^1\text{H}$  NMR spectra of the resulting PIs



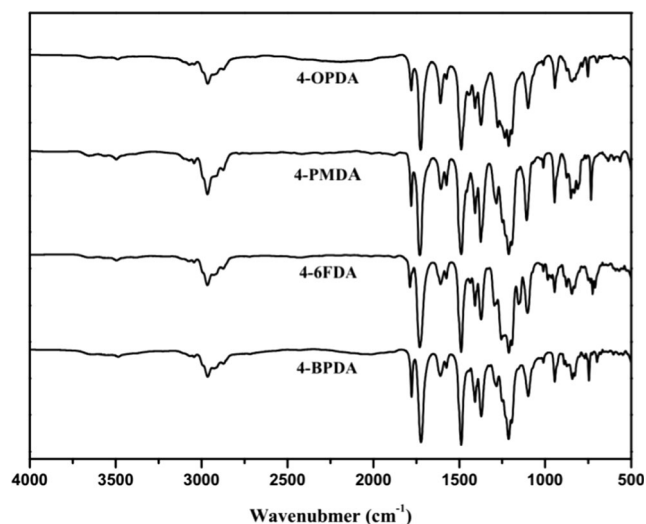
When diamine **4** polymerized with the aromatic dianhydrides PMDA, BPDA, OPDA and 6FDA in *m*-cresol through the one-pot method, the process was carried out smoothly at the solid content of 10 wt % and the soluble PIs with high molecular weights were produced with the high yields (>90%). The resulting PIs was characterized by the means of GPC,  $^1\text{H}$  NMR, FT-IR and EA.

As was shown in Table 1, the number-average molecular weights ( $M_n$ ) of the PIs were in the range from  $2.1 \times 10^4$  to  $3.7 \times 10^4$  with the polydispersity indices (PDIs) from 2.25 to 2.74. Apparently, the aromatic PIs with high molecular weight and relatively narrow PDI were still obtained by a one-pot

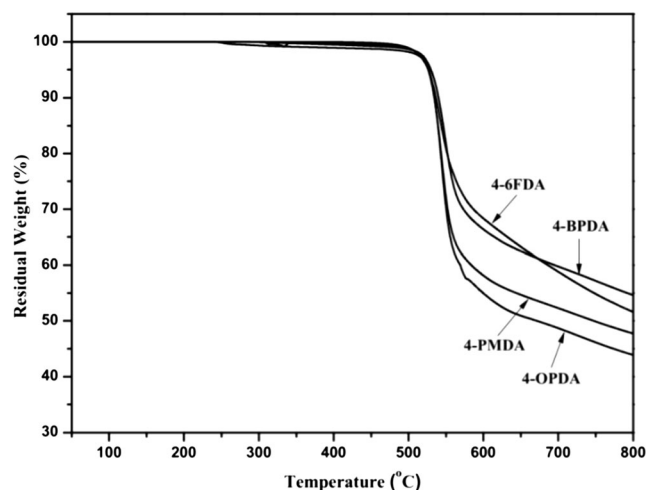
method at high temperature even though the relatively low reactivity of the hindered aromatic diamine **4**.

Figure 2 displayed the  $^1\text{H}$  NMR spectra of four resulting PIs in  $\text{CDCl}_3$  and all the signals were labeled. The results agreed with the chemical structure of the resulting PIs. In addition, no obvious signals of  $-\text{OH}$  or  $-\text{NH}$  were observed in the  $^1\text{H}$  NMR spectra, which indicated the imidization process was complete in the polymerization.

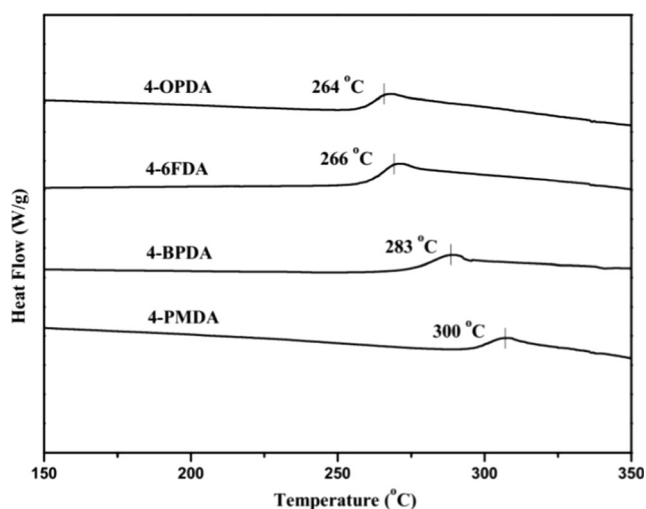
The FT-IR spectra of the resulting PIs were displayed in Fig. 3. For all PI samples, the characteristic  $\text{C}=\text{O}$  vibration bands of imide ring could be observed at the wave number of  $1778\text{--}1787\text{ cm}^{-1}$  and  $1725\text{--}1730\text{ cm}^{-1}$ , whereas the  $-\text{OH}$  vibration band and the  $\text{C}=\text{O}$  vibration band of poly(amic acid)



**Fig. 3** FT-IR spectra of the resulting PIs



**Fig. 4** TGA curves of the resulting PIs



**Fig. 5** DSC curves of the resulting PIs

were not detected at the wave number of about  $3000\text{ cm}^{-1}$  and  $1650\text{ cm}^{-1}$ , respectively. These evidences also confirmed the imidization of the resulting PIs catalyzed by isoquinoline was completed at the one-pot method. All of the other characteristic bands were observed at wave number of  $2965\text{--}2967\text{ cm}^{-1}$  for C-H in *tert*-butyl,  $1371\text{--}1375\text{ cm}^{-1}$  for C-N,  $1015\text{--}1104\text{ cm}^{-1}$  and  $724\text{--}752\text{ cm}^{-1}$  for imide-ring. In addition, the elemental analysis results were consistent with the theoretically calculated values.

### Thermal properties

The thermal behavior of the resulting PIs was studied by means of TGA and DSC measurements. The TGA curves of all PIs were shown in Fig. 4 and the temperature at 5% weight loss of these PIs was shown in Table 1. Obviously, all the PIs were stable up to  $450\text{ }^{\circ}\text{C}$ . The weight loss temperature of 5% was in the range of  $525\text{--}529\text{ }^{\circ}\text{C}$  at nitrogen atmosphere. The char yields of all PIs at  $800\text{ }^{\circ}\text{C}$  were higher than 43 wt%. Compared with the previous PIs containing *tert*-butyl and

**Table 2** Solubility of the resulting PIs

Solvents	4-OPDA	4-PMDA	4-6FDA	4-BPDA
<i>m</i> -cresol	++	++	++	++
DMAc	++	++	++	++
DMF	++	++	++	++
NMP	++	++	++	++
THF	++	++	++	++
$\text{CHCl}_3$	++	++	++	++
Toluene	(+)	(+)	++	(+)

++: soluble at room temperature, (+): partially soluble at  $60\text{ }^{\circ}\text{C}$

NMP N-methyl-2-pyrrolidone, DMAc N,N-dimethylacetamide, DMF N,N-dimethylformamide, THF tetrahydrofuran,  $\text{CHCl}_3$  trichloromethane

**Table 3** Mechanical property and water absorption of the resulting PI films

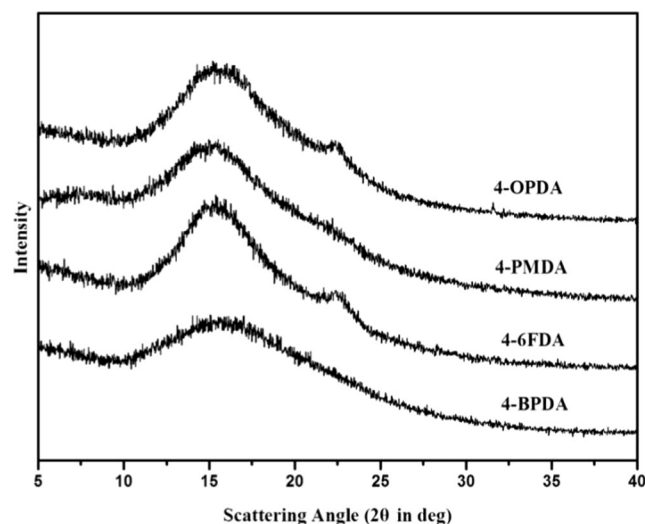
Polyimide	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Water absorption (%)
4-OPDA	52.2	2.48	6.1	0.66
4-PMDA	57.3	2.16	12.1	0.52
4-6FDA	52.8	1.94	4.3	0.45
4-BPDA	50.0	2.17	10.2	0.48

phenoxy units, the inherent thermal stability of the resulting PIs was not sacrificed by introducing bulky pendant groups and multiple phenoxy units into their backbones [26–28].

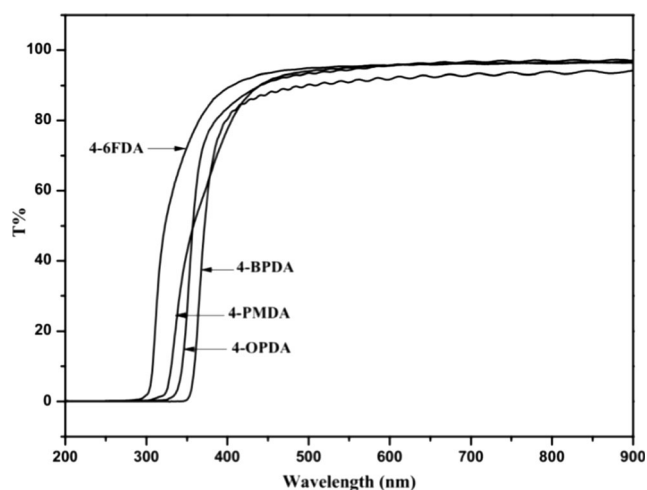
The DSC curves of all PIs were presented in Fig. 5 and the corresponding  $T_g$ s were also summarized in Table 1. According to our previous studies, the incorporation of *tert*-butyl into the polyimide backbone could retain its high  $T_g$ , but multiple phenoxy units decreased its  $T_g$ . Combining the effects of these two different units, the  $T_g$ s of the resulting PIs were still in the range of  $264\text{--}300\text{ }^{\circ}\text{C}$ , which depended on the stiffness and polarity of the corresponding dianhydride. For example, 4-PMDA had a highest  $T_g$  of  $300\text{ }^{\circ}\text{C}$  while 4-OPDA had a lowest  $T_g$  of  $264\text{ }^{\circ}\text{C}$ .

### Solubility

Generally, the solubility of polyimides depends on their chain packing ability and intermolecular interactions. Here we investigated the effect of *tert*-butyl group and multiple phenoxy units on the solubility of the resulting PIs at  $10\text{ mg/mL}$  (PI/solvent) and room temperature or  $60\text{ }^{\circ}\text{C}$  in various solvents. The results were summarized in Table 2. The solubility of the



**Fig. 6** X-ray diffraction curves of the resulting PI films



**Fig. 7** UV-vis spectra of the resulting PI films

resulting PIs was obviously enhanced and all of them could be dissolved in conventional organic solvents, such as NMP, DMF, DMAc, THF and  $\text{CHCl}_3$  at room temperature, including 4-PMDA with the most rigid dianhydride. Especially, 4-6FDA exhibited the most excellent solubility and even dissolved in toluene at room temperature. The enhanced solubility can be attributed to *tert*-butyl groups reducing the interaction between polyimide chains and multiple phenoxy units improving the flexibility of main chains of PIs. These two factors synchronously helped to the solvent molecules permeating into PI molecular chains and the solubility was indeed improved distinctly.

### Mechanical behaviors and Water Absorption Rates

The mechanical property of the resulting PI films with the thickness about 40  $\mu\text{m}$  was measured by CMT-4104 tensile tester at room temperature and the results were summarized in Table 3. All the resulting PI films had the tensile strength from 50 to 57.3 MPa, the tensile modulus from 1.94 to 2.48 GPa and the elongation at break of 4.3 to 12.1%. The relatively low elongation at break was attributed to amorphous glassy states of these PIs, because

**Table 4** Optical properties of the resulting PI films

Polyimide	Film thickness ( $\mu\text{m}$ )	Transparency <sup>a</sup> (%)	Cut-off wavelength (nm)
4-OPDA	10	94	331
4-PMDA	9	94	313
4-6FDA	10	95	296
4-BPDA	10	91	352

<sup>a</sup> In the visible region (400–760 nm)

such kinds of polymers are usually somewhat brittle at the temperature far below  $T_g$ . Furthermore, the water absorption rates of the resulting PIs were determined below 1% (Table 3). This can be attributed to the strong hydrophobic properties of *tert*-butyl. These PI films may have potential applications in the electrical fields due to their low water absorption rates [29].

### X-ray diffraction data

The morphology of the resulting PI films (film thickness about 30  $\mu\text{m}$ ) was examined by X-ray diffractometer with  $2\theta$  from 5 to  $40^\circ$  and the diffraction spectra were exhibited in Fig. 6. All of them showed amorphous patterns in their X-ray diffraction curves. This indicated that the incorporation of *tert*-butyl and multiple phenoxy units into PIs increased the distance of PI main chains, reduced the stacking density and also enhanced the solubility of PIs [30].

### Optical properties

The UV-vis spectra of the resulting PI films with similar thickness (about 10  $\mu\text{m}$ ) are shown in Fig. 7 and their optical properties were outlined in Table 4. All of the resulting PI films showed an excellent transmission above 90% in the visible region (400–760 nm) and their cut-off wavelengths ranged from 296 to 352 nm. This can be attributed to the bulky *tert*-butyl groups, which increased the intermolecular distance, weakened the PIs chain packing and restrained CTC formation, thus improving the optical transparency of PIs films.

### Conclusions

A series of soluble PIs with high transparency were prepared by introducing the bulky pendant groups *tert*-butyl and flexible multiple phenoxy units into their backbone. Our results further confirmed that the incorporation of bulky side groups and multiple phenoxy units could enhance solubility and improve transparency of the resulting PIs. In addition, multiple phenoxy units didn't deteriorate heavily the inherent thermal properties of PIs. The strong and tough PI films could be prepared by solution-casting, which are potential candidates for micro-electronic or optical applications.

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