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Design and preparation of novel fluorescent polyimides containing *ortho*-linked units and pyridine moieties

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A novel pyridine-containing aromatic diamine monomer, 4-[4-hydroxyphenyl]-2,6-bis[4-(2-aminophenoxy)phenyl]pyridine (*p*,*o*-HAPP), was synthesized by a modified Chichibabin reaction of *p*-Hydroxybenzaldehyde and a substituted acetophenone, 4-(2-nitrophenoxy)acetophenone (*p*,*o*-NPAP), followed by a reduction of the resulting dinitro compound 4-[4-hydroxyphenyl]-2,6-bis[4-(2-nitrophenoxy)phenyl]pyridine with Pd/C and hydrazine monohydrate. The aromatic diamine was employed to prepare a series of pyridine-containing polyimides (PIs) by polycondensation with various aromatic dianhydrides in *N*,*N*-dimethylformamide (DMF) via the conventional two-step method. The inherent viscosities of the resulting poly(amic acids) and PIs were in range of 0.62–0.76 and 0.52–0.64 dL/g, respectively. The obtained novel PIs exhibited high solubility in common organic solvents, such as *m*-Cresol, DMF, *N*,*N*-dimethylacetamide, dimethylsulfoxide, *N*-methylpyrrolidone (NMP), tetrahydrofuran, and chloroform. Meanwhile, flexible PI films were obtained, which had excellent thermal stability, with the glass transition temperature (T_g) of 259.8–323.4 °C and the temperature at 10% weight loss of 485.5–576.4 °C in nitrogen atmosphere. The protonated polymer showed UV–vis absorption in the region 200–400 nm and displayed strong fluorescence intensity (470 nm) in NMP solution.

Keywords: pyridine-containing diamine; fluorescence; polyimides; design; solubility

1. Introduction

Linear aromatic polyimides (PIs) have been studied extensively as high performance materials due to their outstanding thermal and thermo oxidative stabilities, chemical resistance, and excellent mechanical and electrical properties. They have been widely utilized in the traditional field of gas separation, microelectronics, aerospace devices, integrated electronic circuits, passivation coatings, substrate components, adhesives, composites, and so on [1–8]. Recently, some research have focused on π-conjugated PIs, which offer potential applications both in optoelectronics and photonics owing to their unique luminescence and electron properties [9–13]. In particular, pyridine and its derivatives have attracted more attention because pyridine is an electron-deficient aromatic heterocyclic substituent with a localized lone pair electrons in sp2 orbital on the nitrogen atom [14–16]. Therefore, the pyridine-containing PIs

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can increase electron affinity to improve electron-transporting properties and offer the possibility of protonation of the lone pair electrons as a way of modifying their luminescence properties [17–23]. Liaw and others have synthesized some conjugated polymers containing pyridine in the main chain and these materials exhibit excellent optical properties for the development of polymeric photoelectricity and organic photoluminescence materials [16–23]. However, their products still exhibit some drawbacks, such as insoluble nature and low glass transition temperature, which limit their applications.

To overcome poor solubility, many efforts on chemical modifications of PIs have been made, such as introduction of flexible linkages [24,25], bulky units or bulky pendent substituents [26–29], and noncoplanar moieties [30], in the polymer backbone. However, such groups often reduce glass transition temperature, compromising ultimate performance. Recently, a novel approach to increasing solubility of PIs without sacrificing their thermal stability has been found [31–33]. Eastmond and others have shown that the incorporation of *ortho*-linked unit into the polymer backbone may interrupt the chain packing and improve the solubility [34–39]. In addition, the incorporation of *ortho*-linked units can induce important new properties, such as high glass transition temperature for the resulting polymers [38,39]. As stated above, synthesizing a kind of pyridine-containing PIs with bulky pendent substituents, *ortho*-linked unit and flexible ether linkage may be an innovative way to obtain soluble and high glass transition temperature fluorescent PIs.

In this work, a novel aromatic diamine, 4-[4-hydroxyphenyl]-2,6-bis[4-(2-aminophenoxy) phenyl]pyridine (*p*,*o*-HAPP) with pyridine rings, pendant hydroxyphenyl side group, and ether linkage was synthesized and then polymerized with four commercial dianhydrides to produce a series of conjugated pyridine-containing PIs. The obtained polymers were then systematically investigated to measure the general physical properties, such as solubility, thermal stability, UV–vis absorption properties, and fluorescence emission properties.

2. Experimental

2.1. Materials

o-Chloronitrobenzene (GR), *p*-Hydroxyacetophenone (99%), *p*-Hydroxybenzaldehyde (AR), and palladium on activated carbon (Pd/C, 5%) were purchased from Aladdin Reagent Inc. (Shanghai, China). Pyromellitic dianhydride (PMDA or **2a**) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), 4,4′-oxydiphthalic dianhydride (ODPA or **2c**) and 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA or **2d**) were purchased from Shanghai Research Institute of Synthetic Resins (Shanghai, China), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA or **2b**) was purchased from Alfa Aesar (Ward Hill, Massachusetts, USA), and these aromatic tetracarboxylic dianhydrides were all recrystallized from acetic anhydride and then dried in vacuums at 120 °C for 12 h before use. *N*,*N*-dimethylformamide (DMF) and toluene were purified by distillation under reduced pressure over calcium hydride and were stored over 4-Å molecular sieves. Analytical-grade potassium carbonate was dried in vacuo at 130 °C for 12 h before use. All other solvents were obtained from various commercial sources and purified by distillation before using.

2.2. Measurements

Fourier transform infrared (FTIR) spectrometer (Spectrum One, Perkin-Elmer, USA) was used to identify the structure of the monomer and intermediates. Solid samples were coated on KBr disks. ^{1}H and ^{13}C NMR spectra were conducted on a Varian INOVA-600 spectrometer at 600 MHz. dimethylsulfoxide (DMSO)-d_6 was used as solvent and tetramethylsilane as internal reference. Elemental analysis was carried out on a Vario EL III system. Solubility was determined qualitatively by placing 10 mg of polymer into 1 mL of solvent at room temperature for 24 h. The inherent viscosities were determined at a 0.5% concentration in DMF with an Ubbelohde capillary viscometer at 25 °C. A crystallographic study of PI was performed at room temperature (about 25 °C) on a D/MAX-IIIC X-ray diffractometer (Akishima-shi, Tokyo, Japan). The X-ray diffraction (XRD) pattern was taken from 2 to 80° (2θ value) with Cu Kα radiation ($\lambda = 1.5406$ Å, operating at 35 kV, and 25 mA). Differential scanning calorimeter (DSC) thermograms were obtained on a Perkin-Elmer DSC-7 DSC, samples were performed under nitrogen atmosphere by raising the temperature from 30 to 400 °C at a rate of 20 °C/min. Thermogravimetric analysis (TGA) of the PI was performed under nitrogen atmosphere at temperatures ranging from 25 to 800 °C at the heating rate of 10 °C /min using a Perkin-Elmer TGA-7 thermogravimetric analyzer. UV–vis spectra of the PIs **4c** based on ODPA and *p*,*o*-NPAP between 200 and 400 nm in *N*-methylpyrrolidone (NMP) solution (10^{-4}g mL^{-1}) were studied by Perkin-Elmer Co. Ltd. (USA) λ–17 UV–vis spectrophotometer with NMP reference. The fluorescence spectra were recorded by Shimadzu Co. Ltd. (Kyoto, Japan) RF-540 fluorospectrophotometer in NMP solution with excited wavelength of 360 nm between 375 and 650 nm.

2.3. Monomer synthesis (Scheme 1)

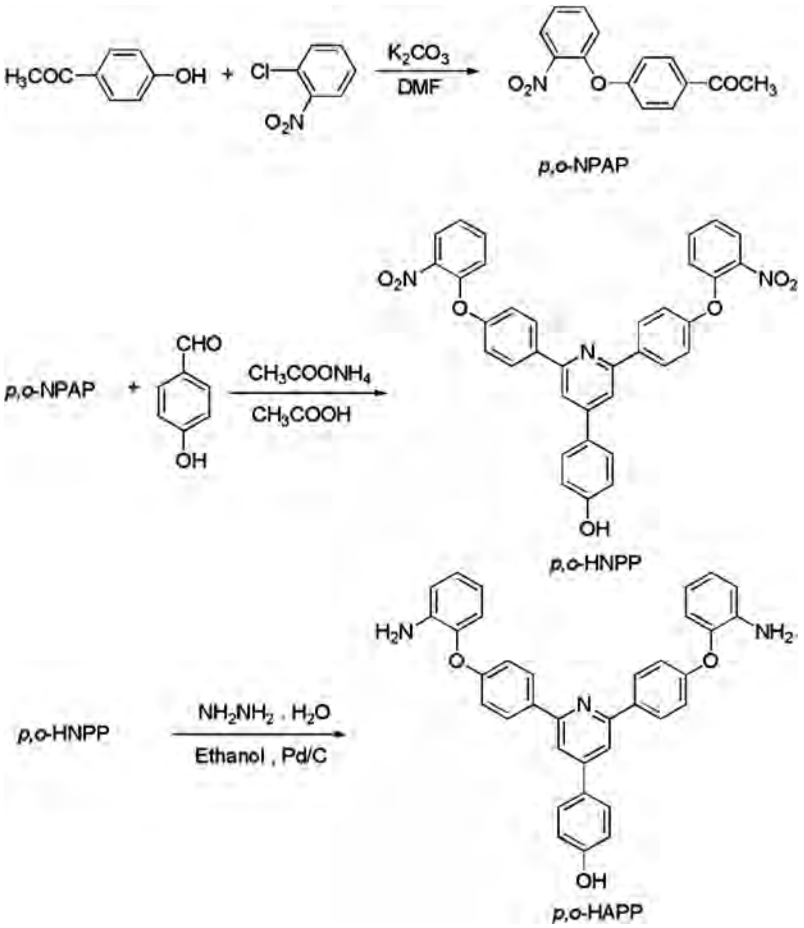
2.3.1. Synthesis of 4-(2-nitrophenoxy)acetophenone (*p*,*o*-NPAP)

In a 250 mL three-necked round bottom flask equipped with a nitrogen inlet, 6.808 g (0.050 mol) of *p*-Hydroxyacetophenone and 8.638 g (0.063 mol) of anhydrous potassium carbonate were suspended in a mixture of 50 mL of dry DMF and 10 mL of toluene. The mixture was then refluxed at 120–130 °C using a Dean–Stark trap to remove small amounts of water azeatropically. After most of the toluene was distilled, 7.878 g (0.050 mol) of *o*-chloronitrobenzene was added when the mixture was cooled to 60 °C. The mixture was then warmed to 120–130 °C and kept for 8 h. After the reaction mixture was cooled to room temperature, it was poured into 500 mL of ice water to give yellow precipitates. The precipitate was collected by filtration, washed with water, and dried. The light yellow crystal 4-(2-nitrophenoxy)acetophenone (*p*,*o*-NPAP) was obtained after the precipitate purified by recrystallization in ethanol (10.85 g). Yield: 84.4%. Melting point: 104.6 °C (by DSC at a scan rate of 20 °C/min).

FTIR (KBr, cm^{-1}): 3081 (C–H), 1668 (C = O), 1529 and 1344 (NO_2), 1168 (C–O–C). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 8.10 (d, $J = 8.1$ Hz, 1H), 7.96 (d, $J = 8.7$ Hz, 2H), 7.74 (t, $J = 7.8$ Hz, 1H), 7.45 (t, $J = 7.8$ Hz, 1H), 7.32 (d, $J = 8.2$ Hz, 1H), 7.07 (d, $J = 8.6$ Hz, 2H), 2.51 (s, 3H). Elemental analysis: calculated for $C_{14}H_{11}NO_4$: C, 65.37%, H, 4.31%, N, 5.44%; Found: C, 65.10%, H, 4.37%, N, 5.48%.

2.3.2. Synthesis of 4-[4-hydroxyphenyl]-2,6-bis[4-(2-nitrophenoxy)phenyl]pyridine (*p*,*o*-HNPP)

12.86 g (0.05 mol) of *m,p*-NPAP, 3.05 g (0.025 mol) of *p*-Hydroxybenzaldehyde, 25.05 g (0.325 mol) of ammonium acetate, and 40 mL of glacial acetic acid were placed into a 200-mL three-necked flask equipped with a magnetic force stirrer and a reflux condenser. The mixture was refluxed with stirring for 6 h. After the reaction mixture was cooled to room temperature. The precipitate was collected by filtration, washed with water, and dried. The light



Scheme 1. Synthesis of the diamine monomer *p*,*o*-HAPP.

yellow powder *p*,*o*-HNPP was obtained after the precipitate purified by recrystallization in glacial acetic acid (4.5 g). Yield: 60.2%. Melting point: 104.6 °C (by DSC at a scan rate of 20 °C/min).

FTIR (KBr, cm^{-1}): 1597 (C=C), 1527 and 1344 (NO_2), 829 (C–N). ^1H NMR (600 MHz, DMSO-d_6, δ, ppm): 9.83 (s, 1H), 8.33 (d, $J = 8.7$ Hz, 4H), 8.13–8.02 (m, 4H), 7.88 (d, $J = 8.6$ Hz, 2H), 7.71 (t, $J = 8.4$ Hz, 2H), 7.38 (t, $J = 7.4$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 8.7$ Hz, 4H), 6.89 (d, $J = 8.4$ Hz, 2H). Elemental analysis: calculated for $C_{35}N_3O_7H_{23}$: C, 70.35%, H, 3.88%, N, 7.03%; Found: C, 70.18%, H, 4.09%, N, 7.19%.

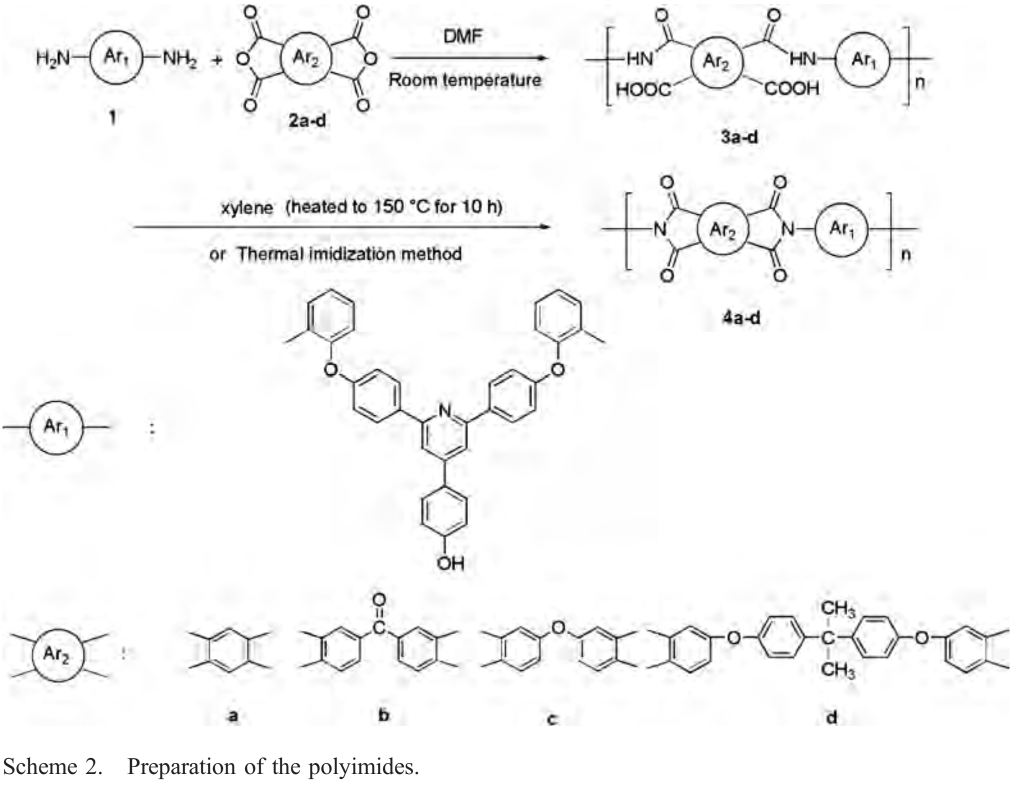
2.3.3. *Synthesis of p,o-HAPP*

To a 250 mL two-necked flask equipped with a dropping funnel and a reflux condenser, 5.98 g (0.01 mol) of *p*,*o*-HNPP, 0.4 g of palladium on activated carbon (Pd/C, 5%), and 100 mL of anhydrous ethanol were added and after heating to refluxing temperature with stirring, 10 mL of hydrazine monohydrate was added dropwise for 2 h. After the completion of the addition of hydrazine monohydrate, the mixture was refluxed for an additional 12 h. Then, the mixture was filtered and the filtrate was subsequently poured into 600 mL of water to produce a solid precipitate, which was removed by filtration, washed with water, and dried. The white powder *p,o*-HAPP was obtained after the precipitate purified by recrystallization in ethanol (4.5 g). Yield: 95.2%. Melting point: 104.6 °C (by DSC at a scan rate of 20 °C/min).

FTIR (KBr, cm^{-1}): 3458 and 3369 (N–H), 3209 (O–H), 829 (C–N). ^1H NMR (600 MHz, DMSO-d_6, δ, ppm): 9.87 (s, 1H, H1), 8.26 (d, $J = 8.6$ Hz, 4H, H5), 8.0 (s, 2H, H4), 7.87 (d, $J = 8.5$ Hz, 2H, H3), 7.01 (d, $J = 8.4$ Hz, 4H, H6), 6.97 (t, $J = 7.4$ Hz, 2H, H9), 6.93 (d, $J = 8.6$ Hz, 2H, H2), 6.88 (d, $J = 7.8$ Hz, 2H, H7), 6.84 (d, $J = 8.0$ Hz, 2H, H10), 6.59 (t, $J = 7.6$ Hz, 2H, H8), 5.00 (s, 4H, –NH_2). ^{13}C NMR (600 MHz, DMSO-d_6, δ, ppm): 158.73 (C1), 158.61 (C11), 155.86 (C7), 149.21 (C5), 141.07 (C12), 140.72 (C17), 133.14 (C8), 128.58 (C3), 128.42 (C9), 128.31 (C4), 125.43 (C15), 120.81 (C6), 116.47 (C10), 116.42 (C13), 115.95 (C14), 115.84 (C2), 114.60 (C16). Elemental analysis: calculated for $C_{35}N_3O_3H_{27}$: C, 78.19%, H, 5.06%, N, 7.82%; Found: C, 78.01%, H, 5.12%, N, 7.94%.

2.4. Preparation of polymer

The general procedure for the preparation of the PIs **4a–4d** (Scheme 2) was illustrated as follows. A measure of 1.0 mmol of dianhydride was gradually added to a stirred solution of 1.0 mmol of *p,o*-HAPP in 10 mL of DMF in a 50 mL two-necked flask equipped with a nitrogen inlet. The mixture was stirred at room temperature under nitrogen atmosphere for 24 h, forming a viscous solution of poly(amic acid) PAA precursor in DMF. The PAA was subsequently converted into PI by either a thermal or a chemical imidization process. Following the thermal imidization method, the PAA was collected by filtration and then dried in an oven



Scheme 2. Preparation of the polyimides.

at 80 °C. Finally, the PI resin was obtained by temperature programming under 150, 200, 250, and 300 °C for 2 h each temperature. For the film preparation, the PAA was poured into a glass plate and dried in an oven at 120 °C for 12 h, at 150, 200, 250, and 300 °C for 2 h each temperature. PI film was stripped from the glass plate when it was cooled. The chemical imidization method was as follows, 10 mL of DMF and 10 mL of xylene were added, and the reaction mixture was heated to 150 °C for 10 h with a Dean–Stark trap. The xylene was removed off under reduced pressure. After cooling to room temperature, the mixture was precipitated from 400 mL ethanol. The polymers were collected by filtration and dried under vacuum at 80 °C for 24 h.

3. Results and discussions

3.1. Monomer synthesis

As shown in Scheme 1, the diamine monomer *p*,*o*-HAPP was obtained through a three-step synthetic route. First, the nucleophilic substitution reaction of *p*-Hydroxyacetophenone with *o*-chloronitrobenzene in the presence of potassium carbonate gives the intermediate compound *p*,*o*-NPAP. Then, the intermediate dinitro compound *p*,*o*-HNPP was prepared via a modified Chichibabin reaction, which is one of the best methods among the several ones for the preparation of a pyridine ring, from *p*,*o*-NPAP and p-Hydroxybenzaldehyde. Finally, the novel diamine monomer *p*,*o*-HAPP was obtained in a high yield by the reduction of *p*,*o*-HNPP using hydrazine monohydrate catalyzed by Pd/C. The new aromatic diamine monomer is stable in atmosphere at room temperature and pure enough for polymerization with commercial aromatic dianhydride monomers to prepare PIs.

FTIR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis were used to identify the structures of the intermediates *p*,*o*-NPAP, *p*,*o*-HNPP, and the diamine *p*,*o*-HAPP. The spectra FTIR (as shown in Figure 1) of *p*,*o*-NPAP and *p*,*o*-HNPP showed nitro group characteristic bands at 1530 (asymmetrical stretching) and 1344 cm^{-1} (symmetrical stretching), while the characteristic absorptions of the nitro group disappeared and the amino group showed a typical N–H stretching absorption pair at 3458 and 3369 cm^{-1} in the FTIR spectrum of diamine *p*,*o*-HAPP. The structures of intermediates and the diamine were also confirmed by high-resolution NMR spectra. Figure 2 shows the ^{1}H and ^{13}C NMR spectra of diamine *p*,*o*-HAPP. In the ^{1}H NMR spectroscopy, the signals in the range of 8.26–6.59 ppm were ascribed to the protons of the aromatic rings, the signal in 9.87 ppm was ascribed to the protons of hydroxy group, and the signal in 5.00 ppm was ascribed to the protons of $-NH_2$ group. There are 17 resonance signals in the regions of 158.73–114.60 ppm in the ^{13}C NMR spectrum for the diamine *p*,*o*-HAPP and three ^{13}C NMR signals [14] (115.86, 149.21, and 120.81 ppm) confirmed the formation of pyridine ring. All the spectroscopic data obtained and the elemental analysis values were in good agreement with the proposed structures.

3.2. Preparation of polymer

New PIs were prepared from diamine **1** and commercially available aromatic dianhydrides, such as **2a–2d** (PMDA, BTDA, ODPA, and BPADA), via a conventional two-step procedure as shown in Scheme 2. First, the diamine was dissolved in a measured amount of dry DMF and the equimolar amount of dianhydride monomer was added to the solution slowly. After completing the addition, the solution was then stirred for 24 h at room temperature, forming viscous PAA solutions. Thermal or chemical imidization procedures were chosen to form PIs. The merit of the former was convenient for preparation of PI films, whereas the latter was

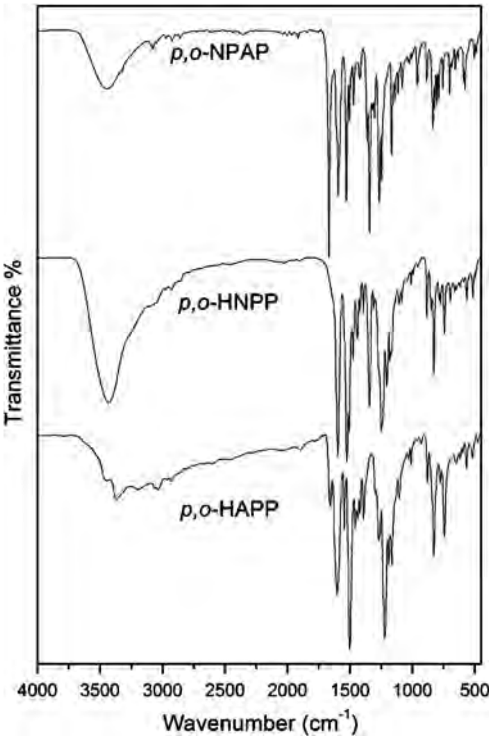


Figure 1. FTIR spectra of *p*,*o*-NPAP, *p*,*o*-HNPP, and *p*,*o*-HAPP.

suited for the preparation of soluble PIs. As shown in Table 1, the resulting PAAs and PIs all get high yields (94–98%), and the inherent viscosity (η_{inh}) values of the PAAs and PIs were in the range of 0.62–0.76 and 0.52–0.64 dL/g, respectively, which indicated the formation of high molar masses. This is consistent with the fact that tough and flexible films could be obtained by solvent evaporation of polymer solutions.

The formations of PIs were confirmed by FTIR and ^{1}H NMR spectroscopy. Figure 3 shows the FTIR spectra of PAAs and PIs. The complete conversion of the amic acid to imide ring was proved by the disappearance of absorption bands at 1719 cm^{-1} corresponding to C=O stretching of carboxylic acid and 1666 cm^{-1} corresponding to C=O amide stretching, together by the appearance of absorption bands at about 1780 cm^{-1} (asymmetrical C=O stretching), 1720 cm^{-1} (symmetrical C=O stretching), 1380 cm^{-1} (C–N stretching), and 740 cm^{-1} (C=O bending) corresponding to the characteristic of imide bands. Compared with FTIR spectra of PIs, there exist similar absorption bands for the PI obtained either by thermal or by chemical imidization methods. Figure 4 shows the ^{1}H NMR spectroscopy of the PI **4c**, the signals in the range of 8.18–6.87 ppm were ascribed to the protons of the aromatic rings, the signal in 9.83 ppm was ascribed to the protons of hydroxy group, while the signal at 5.00 ppm owing to the amino group of the monomer disappeared implying the high degree of PI. These results indicate that full imidization PI can be obtained by using both kinds of imidization methods.

3.3. Polymer solubility

The solubility of the resulting PIs obtained by chemical (C) or thermal (T) imidization was investigated in different organic solvents by dissolving 10 mg of polymers in 1 mL of solvent

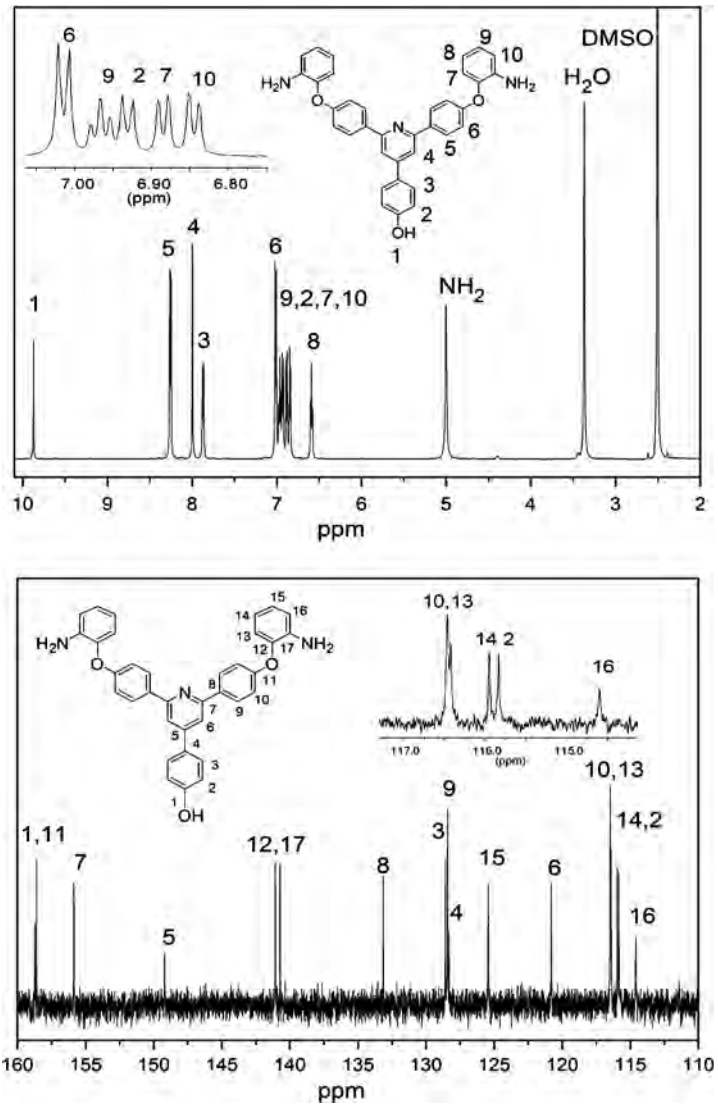


Figure 2. ^{1}H and ^{13}C NMR spectra of *p*,*o*-HAPP.

Table 1. Yields and inherent viscosities of poly(amic acid)s and polyimides.

	Yields (%)		η_{inh} (dL/g)	
Polymer	PAA	PI	PAA	PI
4a	98	97	0.72	0.61
4b	95	94	0.69	0.59
4c	96	98	0.76	0.64
4d	97	95	0.62	0.52

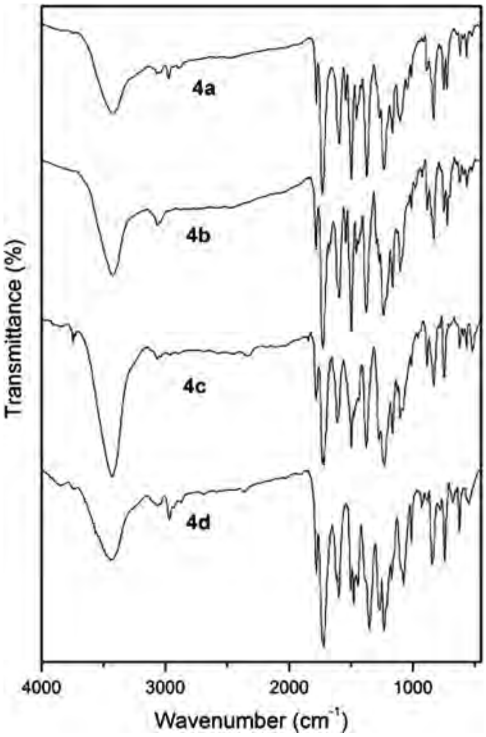


Figure 3. FTIR spectra of polyimides.

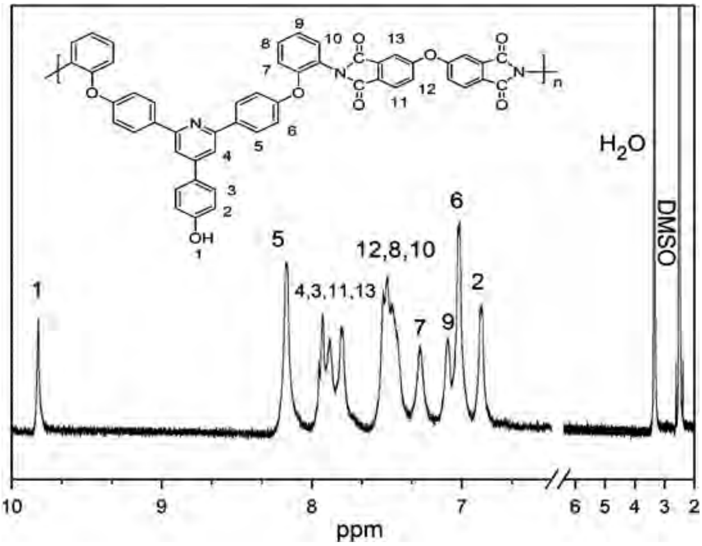


Figure 4. ^{1}H NMR spectrum of the polyimide **4c**.

at room temperature or upon heating. As shown in Table 2, almost all the PIs exhibited good solubility in common organic solvents, such as *m*-Cresol, DMF, *N*,*N*-dimethylacetamide (DMAc), DMSO, and NMP, even at room temperature. In general, the good solubility should

Table 2. Solubility behavior of polyimides in different organic solvents.

Polymer	Organic solvents							
	m-Cresol	NMP	DMF	DMAc	DMSO	THF	$CHCl_3$	Toluene
4a^{C}	++	++	++	++	++	++	–	–
4b^{C}	++	++	++	++	++	++	–	–
4c^{C}	++	++	++	++	++	++	+	–
4d^{C}	++	++	++	++	++	++	+	–
4a^{T}	++	++	+	+	+	–	–	–
4b^{T}	++	++	+	+	+	–	–	–
4c^{T}	++	++	++	++	++	++	–	–
4d^{T}	++	++	++	++	++	++	–	–

C: the polyimides obtained from chemical-imidization method; T: the polyimides obtained from thermal-imidization method; (++) soluble, meaning completely dissolved in the solvent within 1 h at room temperature; (+) soluble, meaning completely dissolved in the solvent when heated at 80 °C; and (–) insoluble, meaning not dissolved in the solvent.

be the result of the introduction of the flexible ether group and the bulk pendent hydroxyphenyl group as well as the *ortho*-linked unit into the polymer backbone. The incorporation of pyridine ring in the backbone of PIs also can increase their solubility. Most of the chemically imidized PIs (the PIs **4a–4d)** showed a better solubility in low boiling point solvent such as tetrahydrofuran (THF) and chloroform ($CHCl_3$) than those prepared by the thermal imidization method. The difference in solubility of PI between thermal and chemical imidization can be explained by the imidization reaction mechanism [24]. In addition, the solubility varies depending upon the dianhydride used. The PIs **4c and 4d** possesses the better solubility, because of the presence of the flexible ether groups, respectively.

3.4. X-ray diffraction

The morphological structure of the PIs was analyzed by wide-angle XRD. In most cases, the degree of crystallinity of the PI depended on the imidization methods. In general, the chemical imidization method can yield a material with a higher degree of crystallinity than that obtained from the thermal imidization method. This implies that imidization of the PAA in solution may allow it to obtain a more favorable conformation for packing [25]. The XRD patterns of the PIs prepared via chemical imidization route are shown in Figure 5. All the PIs showed amorphous pattern, this is mainly because the presence of flexible ether linked and the introduction of *ortho*-linked structure into the polymer chain induces looser chain packing and reveals a large decrease in crystallinity. In general, amorphous polymers have a lower softening temperature and improved solubility with respect to their crystalline analogs. Therefore, the amorphous nature of the resulting PIs would endow them a good solubility (confirmed by solubility tests in Table 2).

3.5. Thermal properties

The thermal behavior data of the PIs, collected from DSC and TGA curves, are summarized in Table 3. DSC revealed that rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so that T_g of the polymer could be easily read in the second heating trace of DSC. The T_g values of the PIs **4a–4d** were in the range of 259.8–323.4 ° C (as shown in Figure 6). The high T_g values might be attributed to the substitution of phenoxy units in the position *ortho* to an imide ring, which increasingly inhibited the rotation of

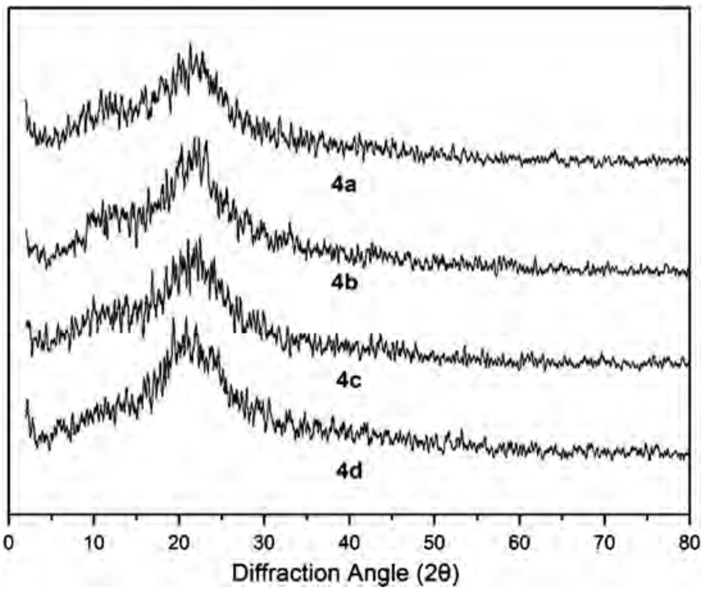


Figure 5. XRD patterns of the polyimides.

Table 3. Thermal properties of the PI films in nitrogen atmosphere.

	Thermal properties				
Polymer	T_g (°C)	T_d (°C)	T_5 (°C)	T_{10} (°C)	R_w (%)
4a	317.1	431.3	475.4	527.4	65.6
4b	313.7	514.6	529.5	576.4	69.7
4c	323.4	480.2	517.8	555.7	62.4
4d	259.8	381.2	431.5	485.5	52.2

T_d, decomposition-starting temperature in nitrogen; T_5 and T_{10}, temperature at 5% or 10% weight loss in nitrogen; and R_w, residual weight at 800 °C in nitrogen atmosphere.

the nitrogen atom along the phenyl ring, resulting in more rigid polymer chains that in turn increased the Tg values of the polymers [38,39]. In addition, the increasing order of T_g generally correlated with the structure of the dianhydride component. As expected, the PI **4d** derived from dianhydride BPADA showed the lowest T_g value due to the increase in flexibility of polymer chain determined by the ether linkage between the phenyl rings, whereas the PIs **4a** and **4b** had the highest T_g value because of the rigid phenyl unit.

The thermal stabilities of the obtained PIs were evaluated by TGA. The TGA curves for PIs prepared by the thermal imidization method are shown in Figure 7. The PI films did not exhibit obvious weight loss before the scanning temperature reached up to 400 °C in nitrogen atmosphere, indicating that no thermal decomposition occurred. As shown in Table 3, the decomposition-starting temperatures of the resulting PIs were in range of 380.2–514.6 °C and the temperatures at 5 and 10% weight loss were in range of 431.5–529.5 °C and 485.5–576.4 °C in nitrogen atmosphere, respectively. In addition, the residual weight at 800 °C for the resulting PIs was in range of 52.2–69.7% in nitrogen atmosphere, implying that all the

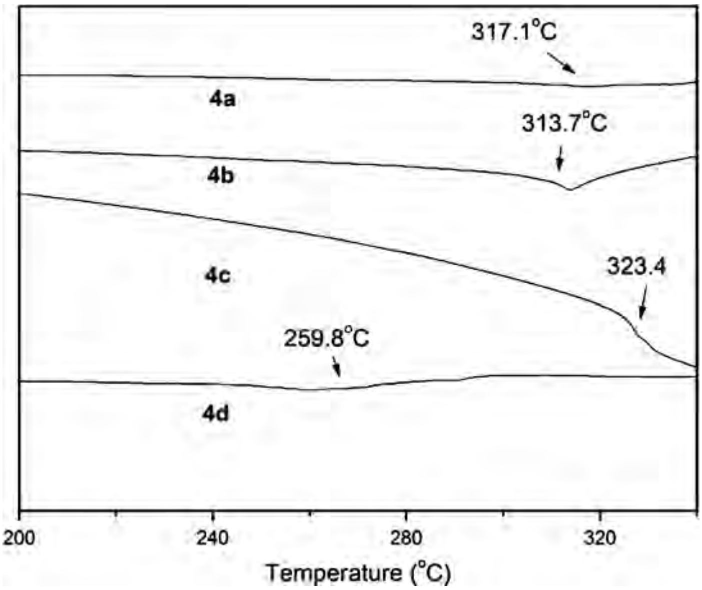


Figure 6. DSC curves of the polyimides.

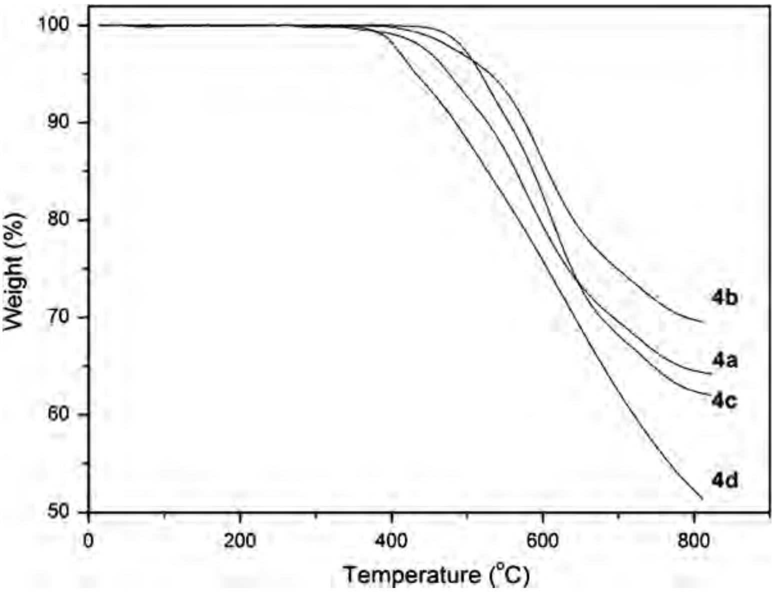


Figure 7. TGA curves of the polyimides in nitrogen atmosphere.

PIs possess excellent thermal stability. All the results indicated that the obtained PIs films exhibited excellent thermal stability, these should be the result of the introduction of pyridine ring into the polymer backbone.

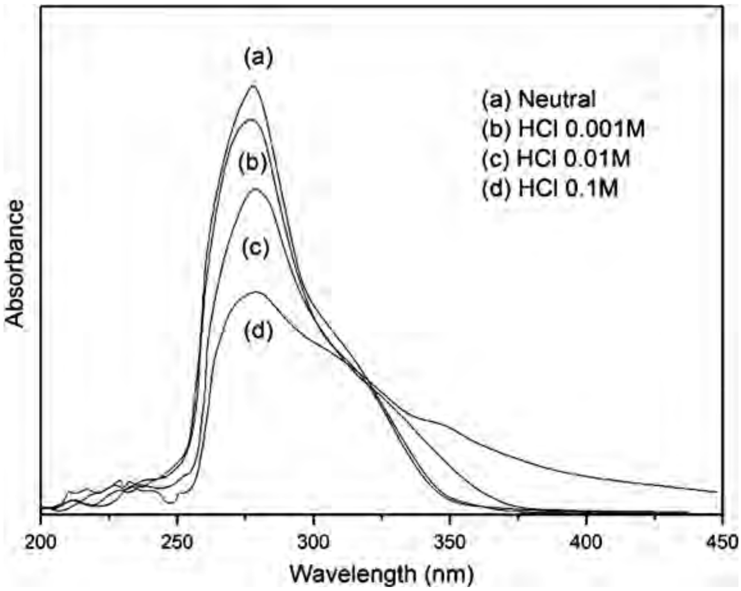


Figure 8. UV–vis spectra of the polyimide **4c** with concentration of 10^{-4}g mL^{-1} in NMP solution and protonated with HCl.

3.6. Optical properties

The optical properties of the resulting novel PI (**4c**) based on *p*,*o*-HAPP and ODPA were investigated by UV–vis spectra and fluorescence spectra with concentration of 10^{-4}g mL^{-1} in NMP solution and protonated with HCl. The PI (**4c**) exhibits absorption bands in the region

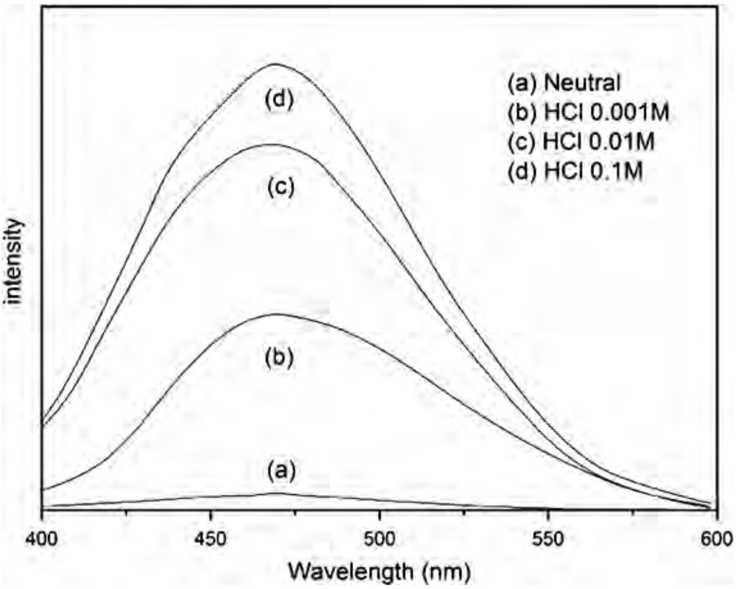


Figure 9. Fluorescence spectra of the polyimide **4c** with concentration of 10^{-4}g mL^{-1} in NMP solution and protonated with HCl (excited at 360 nm).

of 200–400 nm, and the absorption maximum ($\lambda_{\max}$) at 278 nm is due to the n–π^* transition of pyridine group, as shown in Figure 8. Upon protonation with HCl, the intensity of the pyridine chromophore (278 nm) decreased, but a new absorption band appeared at 348 nm when HCl concentration is higher than 0.01 M. The absorption intensity at 278 nm (n–π^*) decreases after protonation, because the lone pair electron of the nitrogen on pyridine is quaternated by protic acid. However, the new band around 348 nm could be attributed to the formation of an aggregate after protonation that caused a longer conjugation length. The spectral behavior suggests a lower π–π^* transition energy for the protonated polymer.

Figure 9 shows the emission spectra of the PI **4c** with concentration of 10^{-4}g mL^{-1} in NMP solution, and the solution was kept overnight before the fluorescence measurement. There was a weak fluorescence peak observed in neutral polymer solution excited at 360 nm. However, strong fluorescence at 470 nm was observed after protonation with different HCl concentrations. Specially, the emission intensity of protonated polymer exhibits an acid concentration dependent increase in the concentration range of 0.001–0.1 M. This phenomenon suggests the formation of an aggregate and excimer emission at a high concentration of the acid. Because the pyridine-containing PIs have greater electron affinity and better electron-transporting properties, and offer the possibility of protonation of the lone pair electrons as a way of modifying their properties [17–23].

4. Conclusions

A series of novel PIs with *ortho*-linked units and pyridine moieties were readily prepared from the newly synthesized *p*,*o*-HAPP with various aromatic dianhydride via the polycondensation reaction. The obtained PIs exhibited high solubility in common organic solvents, such as *m*-Cresol, DMF, DMAc, DMSO, NMP, THF, and $CHCl_3$. The polymers showed excellent glass transition temperature (T_g, 259.8–323.4 °C) and thermal stability ($T_{10\%}$, 485.5–576.4 °C) in nitrogen atmosphere. The polymer containing pyridine structure exhibited UV–vis absorption bands in the near ultraviolet region, as well as possessed stronger blue fluorescence intensity (470 nm) in NMP solution after protonation with protic acid (excited at 360 nm). These characteristics indicated that the obtained novel organosoluble pyridine-containing PIs were promising high temperature resistant materials for organic photoluminescence and photoelectric applications.

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