Polym. Bull. (2011) 66:1191–1206
DOI 10.1007/s00289-010-0343-5

ORIGINAL PAPER

Soluble polyimides based on a novel pyridine-containing diamine *m,p*-PAPP and various aromatic dianhydrides

Shanyin Yan · Wenqiu Chen · Xiaojin Yang · Chuan Chen · Mingfu Huang · Zushun Xu · Kelvin W. K. Yeung · Changfeng Yi

Received: 6 April 2010 / Revised: 23 June 2010 / Accepted: 29 June 2010 /

Abstract A novel pyridine-containing aromatic diamine monomer, 4-phenyl-2,6-bis[3-(4-aminophenoxy)phenyl]pyridine (*m,p*-PAPP), was successfully synthesized by a modified Chichibabin reaction of benzaldehyde and a substituted acetophenone, 3-(4-nitrophenoxy)acetophenone (*m,p*-NPAP), followed by a reduction of the resulting dinitro compound 4-phenyl-2,6-bis[3-(4-nitrophenoxy)phenyl]pyridine (*m,p*-PNPP) with Pd/C and hydrazine monohydrate. The aromatic diamine was employed to synthesize a series of pyridine-containing polyimides (PIs) by polycondensation with various aromatic dianhydrides in *N*,*N*-dimethylformamide (DMF) via the conventional two-step method, and further thermal or chemical imidization forming PIs. The inherent viscosities of the resulting poly(amic acid)s and PIs were 0.59–0.73 and 0.56–0.68 dL/g; most of the PIs obtained by chemical imidization were readily soluble in common organic solvents such as DMF, *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), etc. Meanwhile, strong and flexible PI films were obtained, which had good thermal stability, with the glass transition temperature (T_g) of 204.5–237.4 °C and the temperature at 10% weight loss of 527.7–552.0 °C in nitrogen atmosphere, as well as outstanding mechanical properties with tensile strengths of 88.6–90.4 MPa, a tensile moduli of 1.04–1.56 GPa, and elongations at break of 7.2–8.7%. The PI films also were found to possess low water uptake of 0.89–0.98%.

S. Yan · W. Chen · X. Yang · C. Chen · M. Huang · Z. Xu · C. Yi (✉)
Ministry-of-Education Key Laboratory for the Green Preparation and Application of Functional Materials, Hubei University, Wuhan, China
e-mail: changfengyi@hubu.edu.cn

Z. Xu
e-mail: zushunxu@hubu.edu.cn

Z. Xu · K. W. K. Yeung · C. Yi
Division of Spine Surgery, Department of Orthopaedics and Traumatology,
The University of Hong Kong, Pokfulam, Hong Kong, China

Keywords Pyridine-containing diamine · Pyridine-containing polyimides · Solubility

Introduction

Polyimides are one of the most important classes of high-performance polymers used in the aerospace, microelectronics, and optoelectronics industries. The use of polyimides (PIs), in particular, can be attributed to their outstanding properties, such as excellent thermal and thermo-oxidative stability, solvent resistance, mechanical, and electrical properties [1–3]. However, despite the excellent combined properties, their widespread applications are often limited by their poor solubility and high processing temperature, which make it impossible for most PIs to be directly processed in their imidized forms. In order to overcome these drawbacks, many efforts on chemical modifications of PIs have been made, such as introduction of flexible linkages [4–6], bulky units [7, 8], bulky pendent substituents [9–11], and noncoplanar moieties [12], in the polymer backbone. Solubility of PIs can also be improved by incorporation of less symmetric structures such as *ortho*- or *meta*-linked aromatic units in the main chain [13, 14]. The incorporation of *ortho*- or *meta*-linked units into the polymer backbone may have interrupted the chain packing, thus leading to improved solubility.

However, as is well known, introduction of some groups, such as flexible ether and acyclic linkages, to the PI backbones will sacrifice their some advantageous properties, such as thermal stability and mechanical properties. For the PI materials, synthesis of newly heteroaromatic monomers and corresponding PIs that have both good processability and maintained thermal stability would be very interesting, e.g., new kinds of heteroaromatic diamine or dianhydride monomers are always focused and employed in the synthesis of PIs; in other words, newly synthesized aromatic monomers would play very important roles in the synthesis of advanced PI materials [15, 16]. It has been proven that introduction of rigid heteroaromatic pyridine ring to the polymer backbone could endow it with excellent thermal and thermo-oxidative stability, which should be useful to decrease the negative effects resulting from the introduction of flexible ether linkages in the poly(ether-imide)s backbone [17–19].

Pyridine is a heteroaromatic molecule with rigidity and polarizability. Among different heterocyclic rings, the advantage of using a pyridine nucleus is based on its high thermal stability derived from its molecular symmetry and aromaticity [20]. Also, the presence of nitrogen atom in the structure produces a polarized bond which improves the solubility of the prepared polymers due to increased dipole–dipole interactions in the polymer–solvent system. Therefore, the main advantage of using pyridine in the backbone of PIs is to increase their solubility while maintaining their thermal stability. New kinds of heteroaromatic diamine, dianhydride, or other monomers holding pyridine unit have been designed and synthesized, and the novel heteroaromatic polymers with good thermostability and processability have been obtained derived from those monomers containing pyridine nucleus structures at the same time [21].

Among the several methods, modified Chichibabin reaction is one of the best methods for the preparation of a pyridine ring. Tamami and Yeganeh [22, 23] and Liaw et al. [24, 25] have used this method for the preparation of novel pyridine-containing diamines. Related PIs were synthesized from polycondensation of these diamines with some dianhydrides.

Introduction of pyridine ring, incorporation of an ether linkage and *meta*-linked unit into the polymer backbone, and phenylation of the backbone have been the main structural modifications that have been used to obtain the soluble, thermally stable PIs in this article. The obtained polyimides have better solubility than the analogous polyimides reported by Wang et al. [17].

Experimental

Materials

3-Hydroxyacetophenone (98%) and palladium on activated carbon (Pd/C, 5%) were purchased from Aladdin Reagent Inc. (Shanghai, China), and *p*-chloronitrobenzene from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), which was used as received. Pyromellitic dianhydride (PMDA or **2a**) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), 4,4′-oxydiphthalic dianhydride (ODPA or **2b**) 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 **2c**) was purchased from Alfa Aesar (USA), and these aromatic tetracarboxylic dianhydrides were all recrystallized from acetic anhydride and then dried in vacuo at 150 °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 used without further purification.

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. The ^{1}H-NMR analysis was conducted on a Varian INOVA-600 spectrometer at 600 MHz. 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 *N*,*N*-dimethylformamide (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 K$_\alpha$ radiation ($\lambda = 1.5406$ Å, operating at

35 kV and 25 mA). DSC thermograms were obtained on a Perkin-Elmer DSC-7 differential scanning calorimeter; samples were performed under nitrogen atmosphere by raising the temperature from 30 to 400 °C at the 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. The tensile tests were performed on an electronic universal testing machine (Shenzhen Sans testing machine Co., Ltd., China) at 20 °C with a drawing speed of 10 mm/min. Water uptake (WU) was measured by immersing completely dried PI film samples into deionized water at room temperature for 24 h, the samples were then taken out, wiped with tissue paper, and quickly weighted on a microbalance to calculate WU, using the following equation:

$$\mathrm{WU} = \frac{W_\mathrm{s} - W_\mathrm{d}}{W_\mathrm{d}} \times 100\%$$

where W_s and W_d are the weights of swollen and dry membrane, respectively. The fluorescence spectra were recorded by Shimadzu Co. Ltd. (Japan) RF-540 fluorospectrophotometer.

Monomer synthesis

Synthesis of 3-(4-nitrophenoxy)acetophenone (m,p-NPAP)

In a 250-mL three-necked round bottom flask equipped with a nitrogen inlet, 6.81 g (0.05 mol) of 3-hydroxyacetophenone and 8.29 g (0.06 mol) of anhydrous potassium carbonate were suspended in a mixture of 50 mL of dry DMF and 20 mL of toluene. The mixture was then refluxed at 140 °C using a Dean–Stark trap to remove small amounts of water azeatropically. After most of the toluene was distilled, 7.88 g (0.05 mol) of *p*-chloronitrobenzene was added with the mixture being cooled to 60 °C. The mixture was then warmed to 120 °C and kept for 6 h. After the reaction mixture was cooled to room temperature, it was poured into a 300 mL solution of ethanol/water (volume ratio 1/9) to give brown precipitates. Filtrating and washing with water, the product was recrystallized from ethanol to afford 10.10 g of light yellow crystal *m,p*-NPAP. Yield: 78.5%. Melting point: 104.1 °C (by DSC at a scan rate of 20 °C/min).

IR (KBr, cm^{-1}): 3104, 3071 (C–H), 1686 (C=O), 1515, 1342 (–NO_2), 1242 (C–CO–C), 1181 (C–O–C), 851 (C–N). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 8.28 (d, $J = 9.0$ Hz, 2H, H1), 7.91–7.89 (m, 1H, H4), 7.69 (dt, $J = 1.8$ Hz, 8.4 Hz, 2H, H6, H5), 7.50 (d, $J = 9.6$ Hz, 1H, H3), 7.19 (d, $J = 9.0$ Hz, 2H, H2), 2.51 (s, 3H, –CH_3). Elemental analysis: calculated for $C_{14}H_{11}NO_4$: C, 65.37%; H, 4.31%; N, 5.44%; Found: C, 65.12%; H, 4.38%; N, 5.45%.

Synthesis of 4-phenyl-2,6-bis[3-(4-nitrophenoxy)phenyl]pyridine (m,p-PNPP)

A mixture of 6.43 g (0.025 mol) of *m,p*-NPAP, 1.33 g (0.0125 mol) of benzaldehyde, 12.53 g (0.1625 mol) of ammonium acetate, and 20 mL of glacial acetic acid were taken in a 100-mL three-necked flask equipped with a magnetic force stirrer and a reflux condenser. The mixture was refluxed with stirring for 16 h. The viscous solid precipitated was filtered off and stirred in 100 mL 50% acetic acid/water for 8 h. Then, the precipitated solid was filtered off and washed thoroughly with ethanol and water. After drying under vacuum at 40 °C, 3.40 g of yellow powder of *m,p*-PNPP was obtained. Yield: 46.8%. Melting point: 70.2 °C (by DSC at a scan rate of 20 °C/min).

IR (KBr, cm^{-1}): 3105, 3070 (C–H), 1577 (C=C), 1342 (–NO_2), 847 (C–N). ^1H NMR (600 MHz, DMSO-d_6, δ, ppm): 8.52 (d, $J = 8.4$ Hz, 4H, H10), 8.34 (s, 2H, H4), 8.11 (d, $J = 7.2$ Hz, 2H, H8), 8.02–8.01 (m, 4H, H5, H3), 7.95–7.93 (m, 4H, H2, H6), 7.66 (d, $J = 2.4$ Hz, 4H, H9), 7.62–7.60 (m, 2H, H7), 7.56–7.54 (m, 1H, H1). Elemental analysis: calculated for $C_{35}N_3O_6H_{23}$: C, 72.28%; H, 3.98%; N, 7.23%; Found: C, 72.03%; H, 4.13%; N, 7.26%.

Synthesis of 4-phenyl-2,6-bis[3-(4-aminophenoxy)phenyl]pyridine (m,p-PAPP)

To a 250-mL three-necked flask equipped with a dropping funnel and a reflux condenser, 2.91 g (0.005 mol) of *m,p*-PNPP, 0.2 g of palladium on activated carbon (Pd/C, 5%), and 50 mL of anhydrous ethanol were added, and after heating to refluxing temperature with stirring, 5 mL of hydrazine monohydrate was added dropwise for 1 h. After the completion of the addition of hydrazine monohydrate, the mixture was refluxed for an additional 8 h. Then, the mixture was filtered, and the resultant solid was extracted using enough ethanol. On concentrating all the ethanol solution, yellow precipitation appeared, which was filtered off, and recrystallized from ethanol to get 2.17 g of needle crystal of *m,p*-PAPP. Yield: 83.2%. Melting point: 79.4 °C (by DSC at a scan rate of 20 °C/min).

IR (KBr, cm^{-1}): 3339, 3211 (N–H), 3029 (C–H), 1578, 1505 (C=C), 1214 (C–O–C). ^1H NMR (600 MHz, DMSO-d_6, δ, ppm): 8.14 (s, 2H, H4), 8.03 (d, $J = 7.2$ Hz, 2H, H5), 7.95–7.88 (m, 4H, H8, H3), 7.56 (t, $J = 7.2$ Hz, 2H, H2), 7.50–7.44 (m, 3H, H6, H1), 6.93–6.92 (m, 2H, H7), 6.85–6.82 (m, 4H, H9), 6.64–6.61 (m, 4H, H10), 4.95 (s, 4H, –NH_2). Elemental analysis: calculated for $C_{35}N_3O_2H_{27}$: C, 80.59%; H, 5.22%; N, 8.06%; Found: C, 80.42%; H, 5.26%; N, 8.15%.

Polymer synthesis and film preparation

The general procedure for the preparation of the PIs **4a–d** (Scheme 2) was illustrated as follows. A measure of 2.0 mmol of dianhydride was gradually added to a stirred solution of 2.0 mmol of *m,p*-PAPP in 10 mL of DMF in a 150-mL three-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. Chemical imidization was carried out by adding 3 mL of a mixture of acetic anhydride/pyridine (volume ratio 2/1) into the PAA solution with stirring at room temperature for 1 h. Then, the mixture was stirred at 60 °C for 18 h to yield a homogeneous PI solution, which was poured slowly into deionized water to give a fibrous precipitate, which was collected by filtration, washed thoroughly with hot methanol, and dried at 80 °C in vacuum overnight. Yields were nearly quantitative for the polymerizations. For the thermal imidization, the PAA was poured into a ceramic trough, which was dried in an oven at 120 °C for 12 h, at 150, 200, 250, and 300 °C for 1 h each temperature. Polyimide films were stripped from the ceramic trough when the trough was cooled.

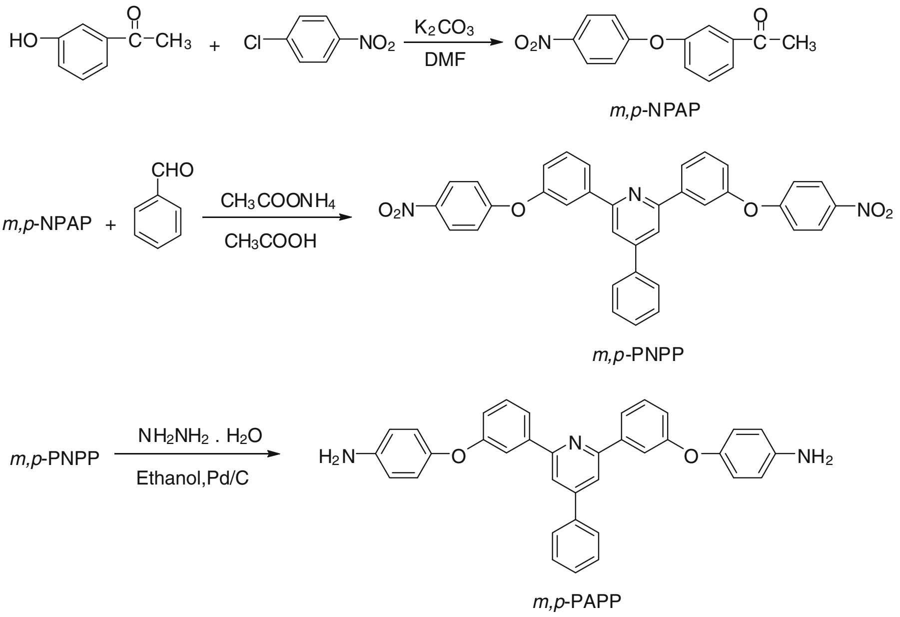
Results and discussions

Synthesis of diamine monomer

As shown in Scheme 1, the diamine monomer (*m*,*p*-PAPP) was obtained through a three-step synthetic route. First, the nucleophilic substitution reaction of 3-hydroxyacetophenone with *p*-chloronitrobenzene in the presence of potassium carbonate gives the intermediate compound *m*,*p*-NPAP. Then, the dinitro compound *m*,*p*-PNPP 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 benzaldehyde and *m*,*p*-NPAP. Finally, the novel diamine monomer *m*,*p*-PAPP was obtained in a high yield by the reduction of *m*,*p*-PNPP 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. The detailed characterizations on the diamine monomer *m*,*p*-PAPP were done using FTIR (Fig. 1), NMR techniques (Fig. 2), and elemental analyses, which support unambiguously the structure shown in Scheme 1. The analytical data of *m*,*p*-PAPP and the intermediate compounds *m*,*p*-NPAP and *m*,*p*-PNPP are given in the experimental section. The results indicate that the design and synthesis of novel diamine monomer *m*,*p*-PAPP should be successful and feasible in this study.

Synthesis of polyimides

Polyimides **4a–d** were prepared conveniently from aromatic diamine **1** and various aromatic dianhydrides **2a–d** (PMDA, ODPA, BTDA and BPADA) as shown in Scheme 2. The new PIs were synthesized using two-step methods, which were carried out via poly(amic acid)s as intermediates. 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 poly(amic acid) solutions. Thermal or chemical imidization procedures were chosen to form PIs. The merit of the former was convenient for preparation of polyimide films, whereas the latter was suitable for the preparation of soluble PIs. As shown in Table 1, the resulting poly(amic acid)s and PIs all get high yields (95–98%), and the inherent viscosity (η_{inh}) values of the poly(amic acid)s and PIs were in the range of 0.59–0.73 and 0.56–0.68 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.



Scheme 1 Synthesis of the diamine monomer *m*,*p*-PAPP

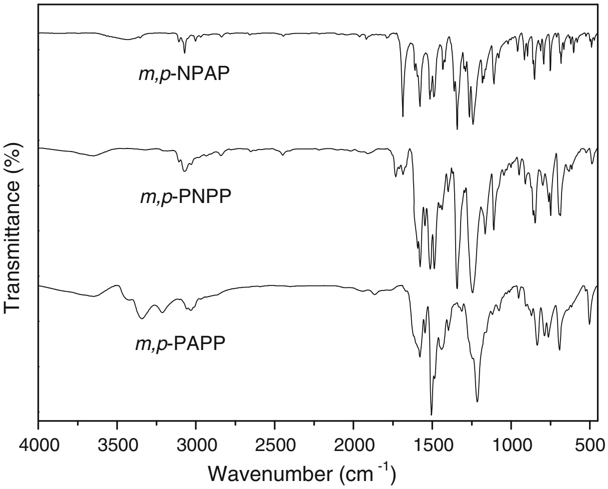
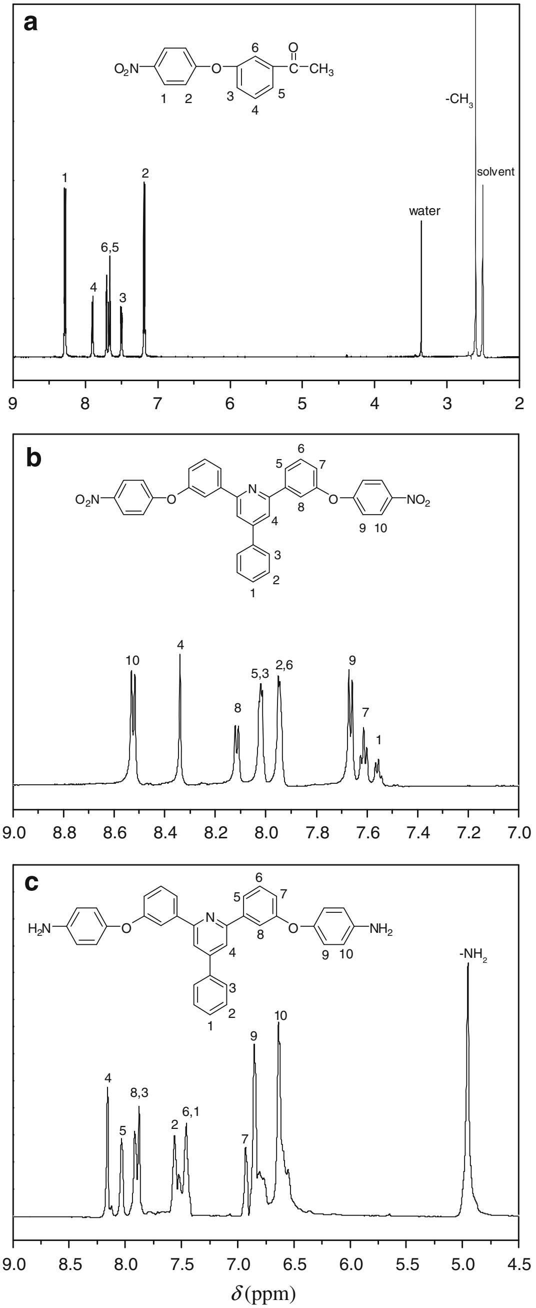


Fig. 1 FTIR spectra of *m*,*p*-NPAP, *m*,*p*-PNPP, and *m*,*p*-PAPP

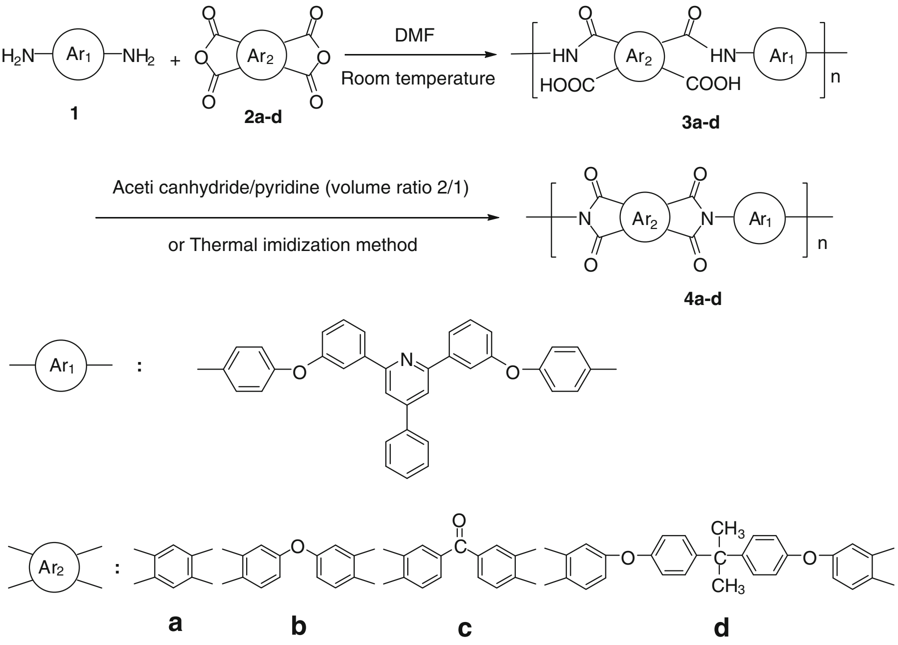
Spectroscopy of polyimides

The formation of PIs was confirmed by FTIR spectroscopy. Figure 3 shows the FTIR spectra of poly(amic acid) **3b**, the PI **4b** prepared by chemical or thermal imidization method, the latter being based on *m*,*p*-PAPP and ODPA. The complete

Fig. 2 ^{1}H NMR spectra of **a** *m*,*p*-NPAP, **b** *m*,*p*-PNPP, and **c** *m*,*p*-PAPP



conversion of amic acid to imide ring was proven by the disappearance of absorption bands at 1,714 cm^{-1} corresponding to C=O stretching of carboxylic acid and 1,660 cm^{-1} corresponding to C=O amide stretching, together by the appearance



Scheme 2 Synthesis of the pyridine-containing polyimides

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

Polymer	Yields (%)		η_{inh} (dL/g)	
	PAA	PI	PAA	PI
4a	95	95	0.59	–
4b	97	98	0.73	0.68
4c	97	96	0.71	0.56
4d	96	97	0.69	0.64

–, Not measured for insoluble in DMF at room temperature

of absorption bands at about 1,780 cm^{-1} (asymmetrical C=O stretching), 1,723 cm^{-1} (symmetrical C=O stretching), 1,375 cm^{-1} (C–N stretching), and 725 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. These results indicate that full imidization PI can be obtained using both kinds of imidization methods. The ^{1}H NMR (600 MHz) spectrum of PI showed no amide and acid protons, confirming full imidization. Also, all protons in the backbone of PI can be assigned, as shown in Fig. 4.

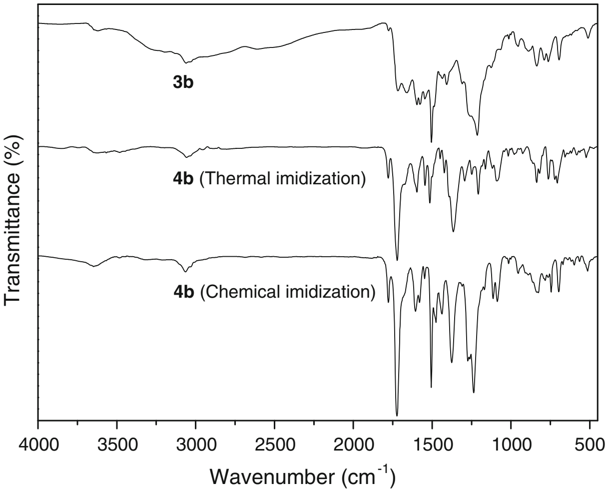


Fig. 3 FTIR spectra of the poly(amic acid) **3b** and polyimide **4b**

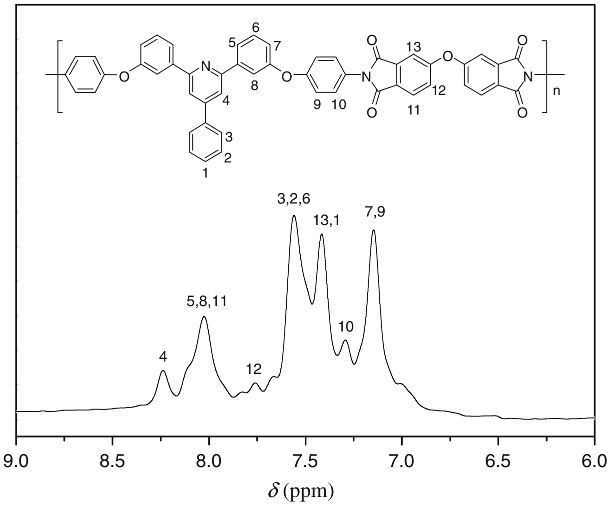


Fig. 4 ^{1}H NMR spectrum of the polyimide **4b**

Polymer solubility

The solubilities of the resulting PIs obtained by chemical imidization were investigated in different organic solvents by dissolving 10 mg of polymers in 1 mL of solvent at room temperature, as shown in Table 2. It can be seen that almost all the PIs exhibited good solubility in common organic solvents, such as *m*-Cresol, DMF, DMAc, DMSO, NMP, etc. even at room temperature. It can also be seen that the PIs **4b**, **4c**, and **4d** showed good solubility in low-boiling-point solvent THF. The good solubility should be because of the introduction of the flexible ether group and the bulk pendent phenyl group as well as the *meta*-linked unit into the polymer backbone. The incorporation of pyridine ring in the backbone of PIs also can increase their solubility.

X-ray diffraction

Morphological information of the PIs were obtained by X-ray diffraction studies. 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 poly(amic acid) in solution may allow it to obtain a more favorable conformation for packing [26]. The X-ray diffraction patterns of the PIs prepared via chemical imidization route are shown in Fig. 5. All the PIs except PI **4d** showed amorphous pattern mainly because of the introduction of *meta*-linked structure into the polymer chain. Polyimide **4d** (based on *m*,*p*-PAPP and BPADA) displayed a little of the crystalline pattern. In general, amorphous polymers have a lower softening temperature and an improved solubility with respect to their crystalline analogs, thus they had good solubility (confirmed by solubility tests in Table 2) and could be solution-cast into flexible and tough films.

Thermal properties

The thermal properties of the resulting PIs were investigated by DSC and TGA methods. The T_g values of the PIs were 204.5–237.4 °C (as shown in Fig. 6). The T_g values of the obtained PIs except **4d** (based on *m*,*p*-PAPP and BPADA) were higher than that of commercial PI, Ultem 1000 (T_g, 217 °C), based on BPADA (bisphenol-A diphthalic anhydride) and MPD (*m*-phenylene diamine). However, the T_g values of the obtained PIs were lower than that of Kapon film derived from PMDA–ODA (T_g, 390 °C). 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 PI **4a** obtained from dianhydride PMDA had the highest T_g value because of the rigid phenyl unit.

Table 2 Solubility behavior of polyimides in different organic solvents

Polymer	Organic solvents							
	m-Cresol	DMF	DMAc	DMSO	NMP	THF	Toluene	Acetone
4a	+ (++)	+ (+)	+ (+)	+ (+)	+ (++)	− (−)	− (−)	− (−)
4b	++	++	++	++	++	++	− (−)	− (−)
4c	++	++	++	++	++	++	− (−)	− (−)
4d	++	++	++	++	++	++	− (−)	− (−)

++, Soluble; +, partially soluble; −, insoluble; ( ), heating at 60 °C

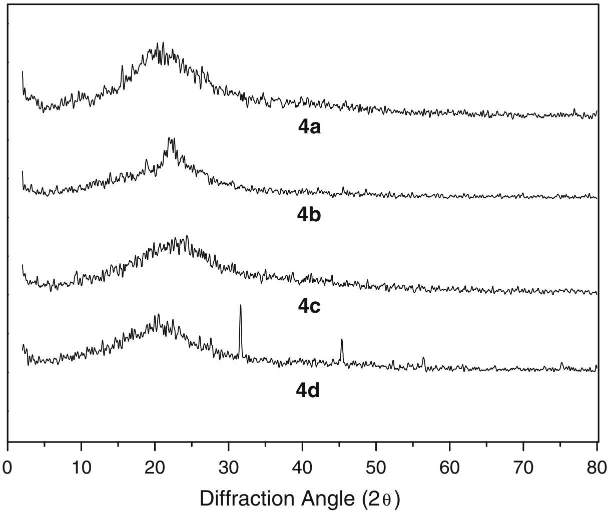
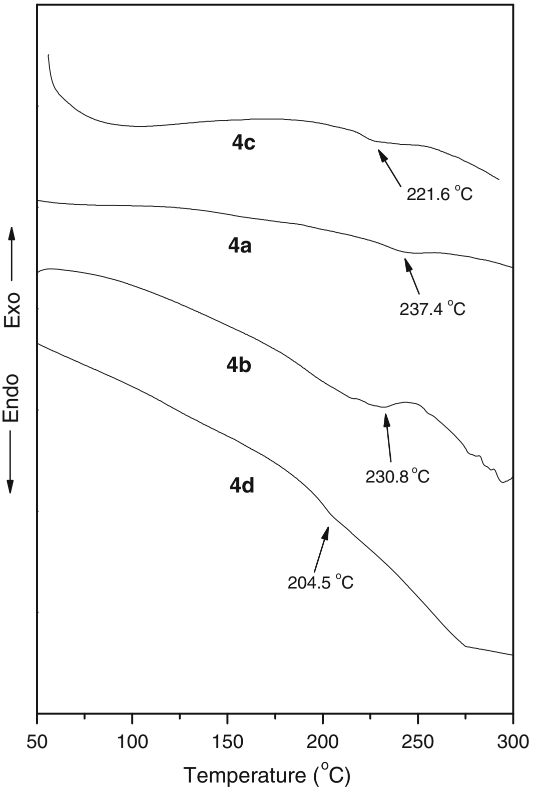


Fig. 5 X-ray diffraction patterns of the polyimides

Fig. 6 DSC curves of the pyridine-containing polyimides



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 Fig. 7. The PI films did not exhibit obvious weight loss before the scanning temperature reached up to 500 °C in nitrogen atmosphere, indicating that no thermal decomposition occurred. As shown in Table 3, the decomposition-starting temperatures of the resulting PI were in the range of 501.6–525.5 °C, and the temperatures at 5% and 10% weight loss were 479.7–534.0 and 527.7–552.0 °C in nitrogen atmosphere, respectively. In addition, the residual weight at 800 °C for the resulting PIs were 61.6–65.0% in nitrogen atmosphere, implying that all the PIs possess excellent thermal stability. The good thermal stability should be the because of the introduction of pyridine ring into the polymer backbone.

Mechanical properties and water uptake

High-quality PI films could be prepared by casting the PAA solution in a ceramic trough followed by the thermal curing as per the following procedure: 120°C for 12 h, at 150, 200, 250, and 300°C for 1 h each temperature in air. Table 4 summarizes the tensile strength and modulus of the resulting PIs. The PI films possess tensile strength of 88.6–90.4 MPa, tensile modulus of 1.04–1.56 GPa, and elongation at break of 7.2–8.7%, which indicate that they were strong and tough polymeric materials. Meanwhile, the PI films exhibited low water uptake of 0.89–0.98%.

Optical properties

Figure 8 shows the emission spectra of protonated PI **4b** with HCl. Calculated amount of HCl solution was added into the THF solution of the PI sample, and the solution was kept overnight before the fluorescence measurement. There was little

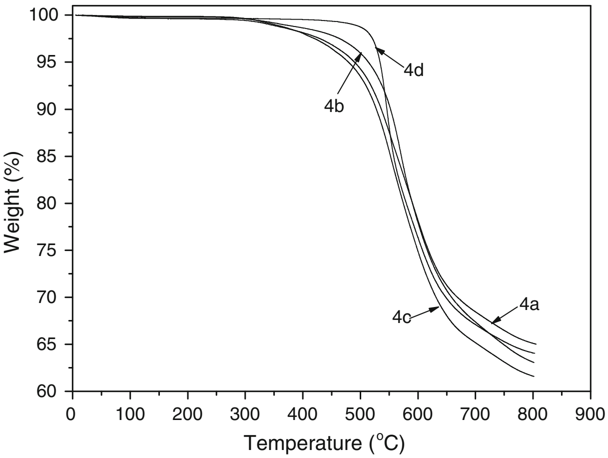


Fig. 7 TGA curves of the polyimide films in nitrogen atmosphere

Table 3 Thermal properties of the polyimide films in nitrogen atmosphere

Polymer	Thermal properties				
	T_g (°C)	T_d (°C)	T_5 (°C)	T_{10} (°C)	R_w (%)
4a	237.4	503.8	489.8	536.2	65.0
4b	230.8	506.5	513.7	552.0	63.1
4c	221.6	501.6	479.7	527.7	61.6
4d	204.5	525.5	534.0	546.2	64.2

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

Table 4 Mechanical properties and water uptake of the polyimide films

Polymer	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Water uptake (%)
4a	90.4	1.37	7.9	0.91
4b	88.6	1.04	8.7	0.89
4c	89.8	1.56	7.2	0.98
4d	88.9	1.49	8.5	0.97

fluorescence around 448 nm observed in neutral polymer solution excited at 360 nm. However, the stronger fluorescence about 439–464 nm was observed after protonation with different HCl concentrations. Compared to a benzene ring, pyridine is an electron-deficient aromatic heterocycle, with a localized lone pair of electrons in sp^2 orbital on the nitrogen atom; consequently, the derived polymers have greater electron affinity and better electron-transporting properties, and offer

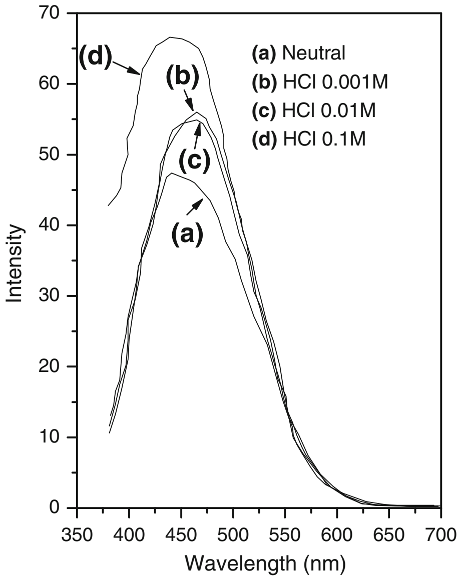


Fig. 8 Fluorescence emission spectra of polyimide **4b** in THF solution as a functional of HCl (excited at 360 nm) concentrations with a polymer concentration of 1 mg/10 mL

the possibility of protonation or alkylation of the lone pair electrons as a way of modifying their properties [9, 19, 25, 27, 28].

Conclusions

A new pyridine-containing aromatic diamine monomer, 4-phenyl-2,6-bis[3-(4-aminophenoxy)phenyl]pyridine (*m*,*p*-PAPP), was successfully synthesized and characterized, which was employed in polycondensation with various aromatic dianhydrides, to prepare a series of pyridine-containing PIs. Experimental results indicate that the resulting diamine monomer *m*,*p*-PAPP has good polymerizability, and therefore, strong and tough PI films can be obtained. The novel PIs obtained have fairly high T_g values, excellent thermal stability in nitrogen, as well as good solubility not only in polar aprotic solvents but also in some low-boiling-point solvents such as THF. Meanwhile, the films also possess low water uptake of less than 1%. The protonated polymer possessed fluorescence (439–464 nm) in THF solution after being protonated with acids excited at 360 nm.

Acknowledgments The research was financially supported by the Natural Science Foundation of Hubei Province (No. 2008CDB276), Hubei, China. The authors also acknowledge the necessary facilities provided by the Ministry of Education Key Laboratory for the Green Preparation and Application of Functional Materials for providing.

References

1. Hasegawa M, Horie K (2001) Photophysics, photochemistry, and optical properties of polyimides. Prog Polym Sci 26:259–335. doi:10.1016/S0079-6700(00)00042-3
2. Wang XL, Li YF, Gong CL, Ma T, Yang FC (2008) Synthesis and properties of new pyridine-bridged poly(ether-imide)s based on 4-(4-trifluoromethylphenyl)-2,6-bis[4-(4-aminophenoxy) phenyl]pyridine. J Fluor Chem 129:56–63. doi:10.1016/j.jfluchem.2007.08.014
3. Madhra MK, Salunke AK, Banerjee S, Prabha S (2002) Synthesis and properties of fluorinated polyimides, 2 derived from novel 2,6-bis(3′-trifluoromethyl-*p*-aminobiphenyl ether)pyridine and 2,5-bis(3′-trifluoromethyl-*p*-aminobiphenyl ether)thiophene. Macromol Chem Phys 203:1238–1248. doi:10.1002/1521-3935(200206)203:9<1238:AID-MACP1238>3.0.CO;2-R
4. Yang CP, Su YY, Wen SJ, Hsiao SH (2006) Highly optically transparent/low color polyimide films prepared from hydroquinone- or resorcinol-based bis(ether anhydride) and trifluoromethyl-containing bis(ether amine)s. Polymer 47:7021–7033. doi:10.1016/j.polymer.2006.07.066
5. Jang W, Lee HS, Lee S, Choi S, Shin D, Han H (2007) The optical and dielectric characterization of light-colored fluorinated polyimides based on 1,3-bis(4-amino-2-trifluoromethylphenoxy)benzene. Mater Chem Phys 104:342–349. doi:10.1016/j.matchemphys.2007.03.025
6. Liaw DJ, Liaw BY, Yu CW (2001) Synthesis and characterization of new organosoluble polyimides based on flexible diamine. Polymer 42:5175–5179. doi:10.1016/S0032-3861(00)00822-3
7. Yang CP, Hsiao SH, Wu KL (2003) Organosoluble and light-colored fluorinated polyimides derived from 2,3-bis(4-amino-2-trifluoromethylphenoxy)naphthalene and aromatic dianhydrides. Polymer 44:7067–7078. doi:10.1016/j.polymer.2003.08.032

8. Liaw DJ, Liaw BY (1999) Synthesis and properties of new polyimides derived from 1,1-bis[4-(4-aminophenoxy)phenyl]cyclododecane. Polymer 40:3183–3189. doi:10.1016/S0032-3861(98)00494-7
9. Wang KL, Liou WT, Liaw DJ, Chen WT (2008) A novel fluorescent poly(pyridine-imide) acid chemosensor. Dyes Pigment 78:93–100. doi:10.1016/j.dyepig.2007.10.015
10. Zhang QY, Li SH, Li WM, Zhang SB (2007) Synthesis and properties of novel organosoluble polyimides derived from 1,4-bis[4-(3,4-dicarboxylphenoxy)]triptycene dianhydride and various aromatic diamines. Polymer 48:6246–6253. doi:10.1016/j.polymer.2007.08.047
11. Hsiao SH, Yang CP, Huang SC (2004) Preparation and properties of new polyimides and polyamides based on 1,4-bis(4-amino-2-trifluoromethylphenoxy)naphthalene. J Polym Sci A 42:2377–2394. doi:10.1002/pola.20075
12. Li J, Kato J, Kudo K, Shiraishi S (2000) Synthesis and properties of novel soluble polyimides having an unsymmetric spiro tricyclic dianhydride unit. Macromol Chem Phys 201:2289–2297. doi:10.1002/1521-3935(20001101)201:17<2289:AID-MACP2289>3.0.CO;2-F
13. Chung CL, Hsiao SH (2008) Novel organosoluble fluorinated polyimides derived from 1,6-bis(4-amino-2-trifluoromethylphenoxy)naphthalene and aromatic dianhydrides. Polymer 49:2476–2485. doi:10.1016/j.polymer.2008.03.047
14. Hariharan R, Sarojadevi M (2006) Synthesis and properties of organosoluble polyimides derived from bis(4-amino-3,5-dimethyl phenyl) halo phenyl methane and various dianhydrides. J Appl Polym Sci 102:4127–4135. doi:10.1002/app.24152
15. Zhang SJ, Li YF, Yin DX, Wang XL, Zhao X, Shao Y, Yang SY (2005) Study on synthesis and characterization of novel polyimides derived from 2,6-bis(3-aminobenzoyl) pyridine. Eur Polym J 41:1097–1107. doi:10.1016/j.eurpolymj.2004.11.014
16. Wang XL, Li YF, Ma T, Zhang SJ, Gong CL (2006) Synthesis and characterization of novel polyimides derived from 2,6-bis[4-(3,4-dicarboxyphenoxy)benzoyl]pyridine dianhydride and aromatic diamines. Polymer 47:3774–3783. doi:10.1016/j.polymer.2006.03.101
17. Wang XL, Li YF, Gong CL, Zhang SJ, Ma T (2007) Synthesis and characterization of novel soluble pyridine-containing polyimides based on 4-phenyl-2,6-bis[4-(4-aminophenoxy)phenyl]-pyridine and various aromatic dianhydrides. J Appl Polym Sci 104:212–219. doi:10.1002/app.25540
18. Wang XL, Li YF, Zhang SJ, Ma T, Shao Y, Zhao X (2006) Synthesis and characterization of novel polyimides derived from pyridine-bridged aromatic dianhydride and various diamines. Eur Polym J 42:1229–1239. doi:10.1016/j.eurpolymj.2005.12.012
19. Wang KL, Liou WT, Liaw DJ, Huang ST (2008) High glass transition and thermal stability of new pyridine-containing polyimides: effect of protonation on fluorescence. Polymer 49:1538–1546. doi:10.1016/j.polymer.2008.01.039
20. Kurita K, Wiliams RL (1974) Heat resistant polymers containing bipyridyl units. III. Polyimides having *o*-, *m*-, or *p*-phenylenedioxy linkage. J Polym Sci A 12:1809–1822. doi:10.1002/pol.1974.170120821
21. Zhang SJ, Li YF, Wang XL, Zhao X, Shao Y, Yin DX, Yang SY (2005) Synthesis and properties of novel polyimides derived from 2,6-bis(4-aminophenoxy-4′-benzoyl)pyridine with some of dianhydride monomers. Polymer 46:11986–11993. doi:10.1016/j.polymer.2005.10.003
22. Tamami B, Yeganeh H (2001) Synthesis and characterization of novel aromatic polyamides derived from 4-aryl-2,6-bis(4-aminophenyl) pyridines. Polymer 42:415–420. doi:10.1016/S0032-3861(00)00276-7
23. Tamami B, Yeganeh H (2001) Preparation and properties of novel polyimides derived from 4-aryl-2,6 bis(4-amino phenyl)pyridine. J Polym Sci A 39:3826–3831. doi:10.1002/pola.10025
24. Liaw DJ, Wang KL, Chang FC, Lee KR, Lai JY (2007) Novel poly(pyridine imide) with pendent naphthalene groups: synthesis and thermal, optical, electrochemical, electrochromic, and protonation characterization. J Polym Sci A 45:2367–2374. doi:10.1002/pola.21997
25. Liaw DJ, Wang KL, Chang FC (2007) Novel organosoluble poly(pyridine-imide) with pendent pyrene group: synthesis, thermal, optical, electrochemical, electrochromic, and protonation characterization. Macromolecules 40:3568–3574. doi:10.1021/ma062546x
26. Leu WT, Hsiao SH (2006) Synthesis and properties of novel aromatic poly(ester-imide)s bearing 1,5-bis(benzoyloxy)naphthalene units. Eur Polym J 42:328–335. doi:10.1016/j.eurpolymj.2005.07.008
27. Liaw DJ, Wang KL, Pujari SP, Huang YC, Tao BC, Chen MH, Lee KR, Lai JY (2009) A novel, conjugated polymer containing fluorene, pyridine and unsymmetric carbazole moieties: synthesis, protonation and electrochemical properties. Dyes Pigment 82:109–117. doi:10.1016/j.dyepig.2008.12.004
28. Liaw DJ, Wang KL, Kang ET, Pujari SP, Chen MH, Huang YC, Tao BC, Lee KR, Lai JY (2009) Optical properties of a novel fluorene-based thermally stable conjugated polymer containing pyridine and unsymmetric carbazole groups. J Polym Sci A 47:991–1002. doi:10.1002/pola.23127