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Synthesis and characterization of novel polyimides derived from 2,6-bis[4-(3,4-dicarboxyphenoxy)benzoyl]pyridine dianhydride and aromatic diamines

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Abstract

A novel pyridine-containing aromatic dianhydride monomer, 2,6-bis[4-(3,4-dicarboxyphenoxy)benzoyl]pyridine dianhydride, was synthesized from the nitro displacement of 4-nitrophthalonitrile by the phenoxide ion of 2,6-bis(4-hydroxybenzoyl)pyridine, followed by acidic hydrolysis of the intermediate tetranitrile and cyclodehydration of the resulting tetraacid. A series of new polyimides holding pyridine moieties in main chain were prepared from the resulting dianhydride monomer with various aromatic diamines via a conventional two-stage process, i.e. ring-opening polycondensation forming the poly(amic acid)s and further thermal or chemical imidization forming polyimides. The inherent viscosities of the resulting polyimides were in the range of 0.51–0.68 dL/g, and most of them were soluble in aprotic amide solvents and cresols, such as *N*,*N*-dimethylacetamide, *N*-methyl-2-pyrrolidone, and *m*-cresol, etc. Meanwhile, some strong and flexible polyimide films were obtained, which have good thermal stability with the glass transition temperatures of 221–278 °C, the temperature at 5% weight loss of 512–540 °C, and the residue at 800 °C of 60.4–65.3% in nitrogen, as well as have outstanding mechanical properties with the tensile strengths of 72.8–104.4 MPa and elongations at breakage of 9.1–11.7%. The polyimides also were found to possess low dielectric constants.

Keywords: Dianhydride monomer; Polyimides; Pyridine moieties

1. Introduction

Polyimides (PIs), as aromatic polymers, have exhibited a series of outstanding characters, e.g. excellent thermostability, mechanical and electrical properties, as well as ability of solvent-resistance, so that they are being widely employed in the aerospace, microelectronics, optoelectronics, composites and so on [1,2]. Because many of them are insoluble and infusible, however, their applications in some fields were limited. It is well known that the poor properties of PIs have a close connection with its chemical composition and chain structure, in other words, the chemical composition and chain structure of PIs will be a head ingredient leading them to infusible within processing temperature and insoluble in organic solvents. Thus, incorporating new functionalities to make polyimides more tractable without decreasing their many desirable properties has become one important target of polyimides chemistry [3,4]. So far, many efforts on chemical modifications of polyimides structure have been done, such as introduction of flexible linkages in the polymer backbone, or incorporation of bulky side groups, which result in good solubility and processibility of the polyimides [5–10].

Considering heteroaromatic rings introduced into the main chain of a synthetic polymer could provide certain properties presumed upon them, pyridine ring with heteroaromatic structure has been applied to design and synthesis of some monomers, as well as preparation of advanced polymers because its excellent stability resulting from corresponding molecular symmetry and aromaticity [11,12]. In fact, those pyridine-containing polymers also possess excellent thermal stability, chemical stability, and retention of mechanical property at elevated temperature, as well as good solubility in organic solvents [13–15]. Consequently, the studies utilizing monomers containing pyridine nucleus structures to synthesize novel heteroaromatic polymers have been focused widely [15–20]. It was found that the incorporation of pyridine ring to

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the polyimide backbone should be contributed to increase its solubility while maintaining its excellent thermal properties [21]. Comparing with pyridine-containing diamine monomers [20,21], unfortunately, pyridine-containing dianhydride monomers, which are need for synthesis polyimides containing pyridine moieties were reported very few so far, which should be due to purification hardness of pyridine-containing tetraacid intermediates. The investigation to overcome the above hardness and synthesize pyridine-containing dianhydride monomers, however, will be very interesting.

In this work, a new kind of pyridine-containing aromatic dianhydride monomer, 2,6-bis[4-(3,4-dicarboxyphenoxy)benzoyl]pyridine dianhydride, was synthesized successfully, meanwhile, a series of novel polyimides holding pyridine moieties in main chain were prepared from the resulting dianhydride monomer with various aromatic diamines via a conventional two-stage process undergoing ring-opening polycondensation to form the poly(amic acid)s and further thermal or chemical imidization to form polyimides. And the composition, structure and properties of the resulting pyridine-containing polyimides and dianhydride monomer are characterized by means of ^{1}H ^{13}C NMR, FT-IR (KBr plate), elemental analysis, DSC, TGA and Wide-angle X-ray diffraction (WXRD), as well as an Instron 1122 testing instrument, Ubbelohde wiscosimeter and Agilent 4291B instrument.

2. Experimental

2.1. Materials

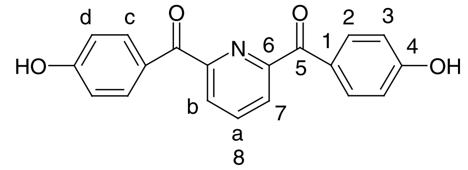
2,6-Pyridinedicarboxyl chloride (TCI), 4-nitrophthalonitrile (TCI) were used as received. Phenyl ethyl ether (Chemspec Inc., Shanghai, China) was purified by distillation from calcium hydride and stored over anhydrous sodium sulfate. *N*-Methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylacetamide (DMAc) was distilled under reduced pressure over calcium hydride prior to use and stored over 4 Å molecular sieves. *p*-Phenylenediamine (PDA) and 4,4′-oxydianiline (ODA) were purified by vacuum sublimation prior to use. 1,4-Bis(4-aminophenoxy) benzene (PAPB) and 1,3-bis(4-aminophenoxy) benzene (MAPB) were recrystallized from ethanol. 1,4-Bis(2-trifluoromethyl-4-aminophenoxy) benzene (PFAPB) was prepared in our laboratory according to the method previously reported [22].

2.2. Monomer synthesis

2.2.1. 2,6-Bis(4-hydroxybenzoyl)pyridine (BHBP)

24.5 g (0.12 mol) of 2,6-pyridinedicarboxyl chloride was gradually added to a mixture of 60 mL of benzene, 30.5 g (0.25 mol) of phenyl ethyl ether and 64.0 g (0.48 mol) of anhydrous aluminum chloride at 10–12 °C with continuous stirring. After addition, the mixture was slowly heated to 40 °C and stirred for 2 h. Finally, the resulting reaction mixture was allowed to cool to room temperature and poured into 500 mL of a water solution of hydrochloric acid (5%) to precipitate out white solids. The solids was collected by filtrating, and washed with hot methanol to give 31.0 g of white powder of compound 2,6-bis(4-hydroxybenzoyl)pyridine (BHBP). The yield is 81%, and the melting point is 277 °C.

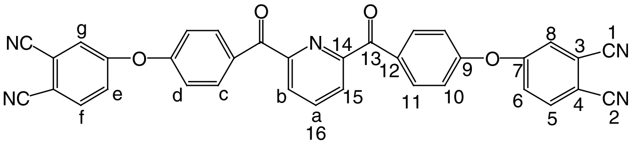
FT-IR (KBr): 3352–3251 (O–H stretching), 1645 (C=O stretching) and 1326 cm^{-1} (C–N stretching). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 10.50 (s, 2H, –OH), 8.24 (t, $J=8.4$ Hz, 1H, H_a), 8.07 (d, $J=7.4$ Hz, 2H, H_b), 7.92 (d, $J=8.6$ Hz, 4H, H_c), 6.84 (d, $J=8.4$ Hz, 4H, H_d). ^{13}C NMR (300 MHz, DMSO-d_6): δ (ppm) 190.9 (C^5), 162.4 (C^4), 154.2 (C^6), 138.8 (C^8), 133.3 (C^2),126.7 (C^1), 125.8 (C^7), 115.0 (C^3). Elem. Anal. Calcd for $C_{19}H_{13}NO_4$ (319.08): C 71.47, H 4.10, N 4.39. Found: C 71.26, H 4.20, N 4.32.



2.2.2. 2,6-Bis[4-(3,4-dicyanophenoxy)benzoyl]pyridine (BCNP)

In a 250 mL round-bottom flask, 16.0 g (0.05 mol) of BHBP and 16.6 g (0.12 mol) of anhydrous potassium carbonate were suspended in a mixture of 100 mL of dry DMF and 40 mL of toluene. The mixture was then refluxed at 140 °C for 4 h using a Dean–Stark trap to facilitate dehydration. After most toluene was distilled, 17.3 g (0.1 mol) of 4-nitrophthalonitrile was added to the mixture when it was cooled to 60 °C. The mixture was then allowed to warm to 90 °C and stirred for 5 h. After the resulting reaction mixture cooling to room temperature, it was poured into 600 mL of ice/water to give white precipitates. Filtrating and washing with water, the crude product was recrystallized twice from acetonitrile to afford 16.6 g of white crystals 2,6-bis[4-(3,4-dicyanophenoxy)benzoyl]pyridine (BCNP). The yield is 58%, while the melting point is 196 °C.

FT-IR (KBr): 2231 (C≡N stretching), 1248 cm^{-1} (C–O–C stretching). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 8.32 (t, $J=10.5$ Hz, 1H, H_a), 8.17 (d, $J=10.5$ Hz, 2H, H_b), 7.89 (d, $J=12.9$ Hz, 4H, H_c), 7.36 (d, $J=9.3$ Hz, 2H, H_f), 7.30 (d, $J=9.3$ Hz, 2H, H_e), 7.26 (s, 2H, H_g), 7.10 (d, $J=13.2$ Hz, 4H, H_d). ^{13}C NMR (300 MHz, DMSO-d_6): δ (ppm) 195.0 (C^{13}), 163.6 (C^9), 162.3 (C^7), 157.0 (C^{14}), 143.2 (C^{16}), 140.2 (C^5), 137.5 (C^{11}), 136.2 (C^{12}), 130.9 (C^{15}), 127.7 (C^6), 127.2 (C^8), 123.1 (C^{10}), 121.8 (C^1), 120.7 (C^2), 119.5 (C^3), 113.1 (C^4). Elem. Anal. Calcd for $C_{35}H_{17}N_5O_4$ (571.54) C 73.55%, H 3.00%, N 12.25%. Found C 73.32%, H 2.83%, N 12.21%.

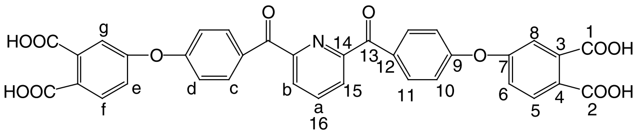


2.2.3. 2,6-Bis[4-(3,4-dicarboxylphenoxy)benzoyl]pyridine (BACP)

11.4 g (0.02 mol) of BCNP and 130 mL of 85% phosphoric acid were put into a 250 mL flask and refluxed for 2.5 h. After cooling to room temperature, the mixture was poured into

1200 mL of cold, dilute aqueous potassium hydroxide (10%). The mixture was stirred at room temperature for 6 h after modulating the pH value to 11, and then it was neutralized with 6M hydrochloric acid to pH 3–4, followed by stirring for 6 h. The product was collected by filtration and dried in a vacuum at room temperature. After recrystallization from aqueous acetic acid (30%) using activated charcoal, 10.9 g of light yellow solid was obtained. The yield is 84%, and the melting point is 226 °C.

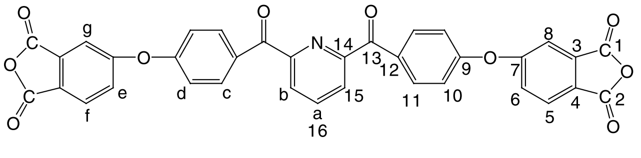
FT-IR (KBr): 2500–3500 (C(O)O–H stretching), 1709 (C=O stretching), 1267 cm^{-1} (C–O–C stretching). ^1H NMR (300 MHz, DMSO-d_6): δ (ppm) 8.34 (t, $J=5.7$ Hz, 1H, H_a), 8.25 (d, $J=5.7$ Hz, 2H, H_b), 8.12 (d, $J=6.3$ Hz, 4H, H_c), 7.91 (d, $J=6.0$ Hz, 2H, H_f), 7.39 (s, 2H, H_g), 7.25 (d, $J=6.3$ Hz, 2H, H_e), 7.19 (d, $J=6.6$ Hz, 4H, H_d). ^{13}C NMR (300 MHz, DMSO-d_6): δ (ppm) 191.34 (C^{13}), 167.86 (C^1), 167.41 (C^2), 159.85 (C^7), 157.33 (C^9), 153.45 (C^{14}), 139.28 (C^{16}), 136.69 (C^3), 133.41 (C^5), 132.25 (C^{11}), 131.31 (C^{12}), 128.14 (C^{15}), 126.73 (C^4), 120.52 (C^6), 119.12 (C^{10}), 118.24 (C^8). Elem. Anal. Calcd for $C_{35}H_{21}NO_{12}$ (647.54) C 64.92%, H 3.27%, N 2.16%. Found C 64.84%, H 3.20%, N 2.13%.



2.2.4. 2,6-Bis[4-(3,4-dicarboxyphenoxy)benzoyl]pyridine dianhydride (BPDA)

6.5 g (0.01 mol) of the tetraacid precursor 2,6-bis[4-(3,4-dicarboxylphenoxy)benzoyl] pyridine (BACP) was refluxed in the mixture 100 mL of acetic anhydride and 200 mL of acetic acid for 12 h in a 500 mL round-bottom flask. After cooling to room temperature, the white solid was removed by filtration and dried overnight at 150 °C under reduced pressure, which was then purified by recrystallization from acetic anhydride to yield 5.1 g of white crystals. The yield is 83%, and the melting point is 229 °C.

FT-IR (KBr): 1845 and 1782 (C=O stretching), 1282 cm^{-1} (C–O–C stretching). ^1H NMR (300 MHz, DMSO-d_6): δ (ppm) 8.38 (t, $J=9.3$ Hz, 1H, H_a), 8.34 (d, $J=9.3$ Hz, 2H, H_b), 8.19 (d, $J=9.3$ Hz, 4H, H_c), 8.07 (d, $J=8.7$ Hz, 2H, H_f), 7.62 (s, 2H, H_g), 7.28 (d, $J=8.7$ Hz, 2H, H_e), 7.20 (d, $J=9.0$ Hz, 4H, H_d). ^{13}C NMR (300 MHz, DMSO-d_6): δ (ppm) 191.30 (C^{13}), 168.05 (C^1), 167.45 (C^2), 162.44 (C^7), 159.72 (C^9), 158.47 (C^{14}), 139.40 (C^{16}), 136.33 (C^3), 134.01 (C^5), 132.41 (C^{11}), 131.32 (C^{12}), 127.83 (C^{15}), 125.64 (C^4), 120.43 (C^6), 119.18 (C^{10}), 118.41 (C^8). Elem. Anal. Calcd for $C_{35}H_{17}NO_{10}$ (611.51) C 68.74%, H 2.80%, N 2.29%. Found C 68.71%, H 2.73%, N 2.26%.

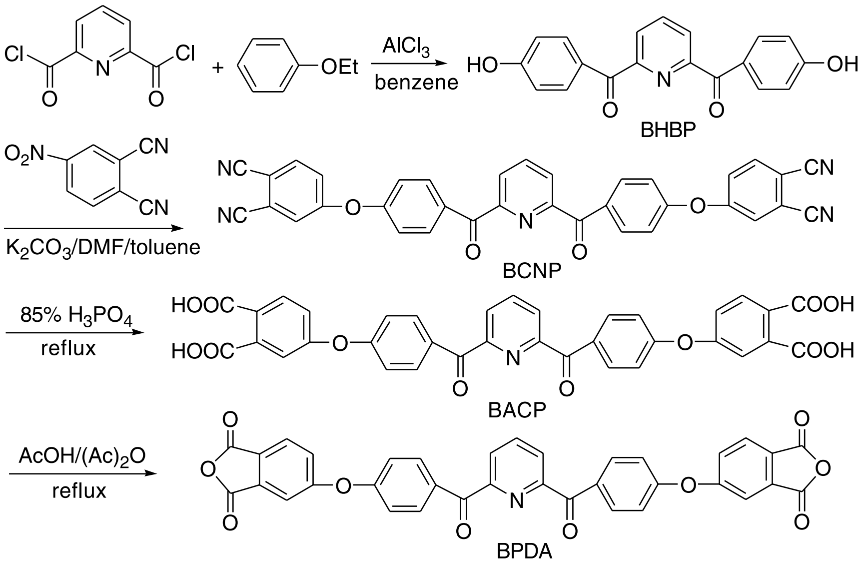


2.3. Polyimide synthesis

A typical polymerization is as follows: 2.4460 g (4.0 mmol) of dianhydride monomer, 2,6-bis[4-(3,4-dicarboxyphenoxy)benzoyl]pyridine dianhydride (BPDA), was gradually added to a stirred solution of 0.8009 g (4.0 mmol) of 4,4′-oxydianiline (ODA) in 18.5 mL of NMP in a 50 mL three-necked flask equipped with a nitrogen inlet at 0–5 °C. The mixture was stirred for 24 h at room temperature under nitrogen atmosphere to form a viscous solution of poly(amic acid) (PAA) precursor solution in NMP. The PAA was converted into polyimide by either thermal or chemical imidization method. For the thermal imidization method, the PAA solution was cast on a clean glass plate, followed by thermal curing with a programmed procedure (80 °C/2 h, 120 °C/1 h, 150 °C/1 h, 180 °C/1 h, 250 °C/1 h, 280 °C/2 h) to produce a fully imidized polyimide film. The chemical imidization was carried out by adding 5 mL of a mixture of an acetic anhydride/pyridine (6/4 v/v) to the above-mentioned PAA solution with stirring at room temperature for 1 h, then the mixture was heated to 100 °C and stirred for 4 h. After cooling, the homogeneous polyimide solution was subsequently poured into 300 mL of ethanol to produce a solid polymer precipitate, which was removed by filtration, washed thoroughly with hot ethanol, and finally dried in a vacuum oven at 100 °C overnight.

2.4. Measurements

^1H and ^{13}C NMR spectra were measured on a JEOL EX-300 spectrometer using tetramethylsilane as the internal reference. Fourier transform infrared (FT-IR) spectra of intermediates, monomer and polyimides were obtained on a Micolet NEXUS 670 spectrometer (KBr disks). Elemental analysis was determined on a Perkin–Elmer model 2400 CHN analyzer. Differential scanning calorimetry (DSC) analyses were performed on a Perkin–Elmer differential scanning calorimeter DSC 7 at a heating rate of 20 °C/min under flowing nitrogen. Glass transition temperature (T_g) was taken as the midpoint of the inflection observed on the curve of heat capacity versus temperature. Melting points were measured by DSC. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050, and experiments were carried out on approximately 10 mg of samples under controlled flux of nitrogen at 20 °C/min. Wide-angle X-ray diffraction measurements were performed at room temperature on a Siemens Kristalloflex D5000 X-ray diffractometer, using nickel-filtered Cu K, radiation ($\lambda=1.5418$ Å, operating at 40 kV and 30 mA). The mechanical properties were measured on an Instron 1122 testing instrument with 100×5 mm^2 specimens in accordance with GB 1040–79 at a drawing rate of 50 mm/min. Inherent viscosities were determined at 30 °C with an Ubbelohde wiscosimeter with DMAc as a solvent on polymer solutions with a concentration of 0.5 g/dL. Qualitative solubility was determined with 10 mg of polymer in 1 mL of solvent at room temperature after 24 h or heating until dissolution for samples



Scheme 1. Synthesis procedure of the dianhydride monomer BPDA.

soluble on heating. The dielectric constants were determined on an Agilent 4291B instrument with 25 μm thickness specimens at frequencies of 1 and 10 MHz at room temperature.

3. Results and discussion

3.1. Synthesis of dianhydride monomer

To date, reports on the synthesis of pyridine-containing dianhydride monomers that can be used to prepare polyimide have appeared very few in the literature. In the present work, the new pyridine-containing dianhydride, 2,6-bis[4-(3,4-dicarboxy phenoxy)benzoyl]pyridine dianhydride (BPDA), was successfully synthesized through a four-step synthetic route starting from 2,6-pyridinedicarbonyl chloride, as shown in Scheme 1. First, diphenol 2,6-bis(4-hydroxybenzoyl)pyridine (BHBP) was prepared by Friedel–Crafts acylation of phenyl ethyl ether with 2,6-pyridinedicarbonyl chloride using anhydrous aluminum chloride as a catalyst. Then the tetranitrile intermediate 2,6-bis[4-(3,4-dicyanophenoxy)benzoyl]pyridine (BCNP) was readily synthesized from the nitro displacement of 4-nitrophthalonitrile by the phenoxide ion of BHBP in a good yield, according to the procedure of Takekoshi [23]. After that,

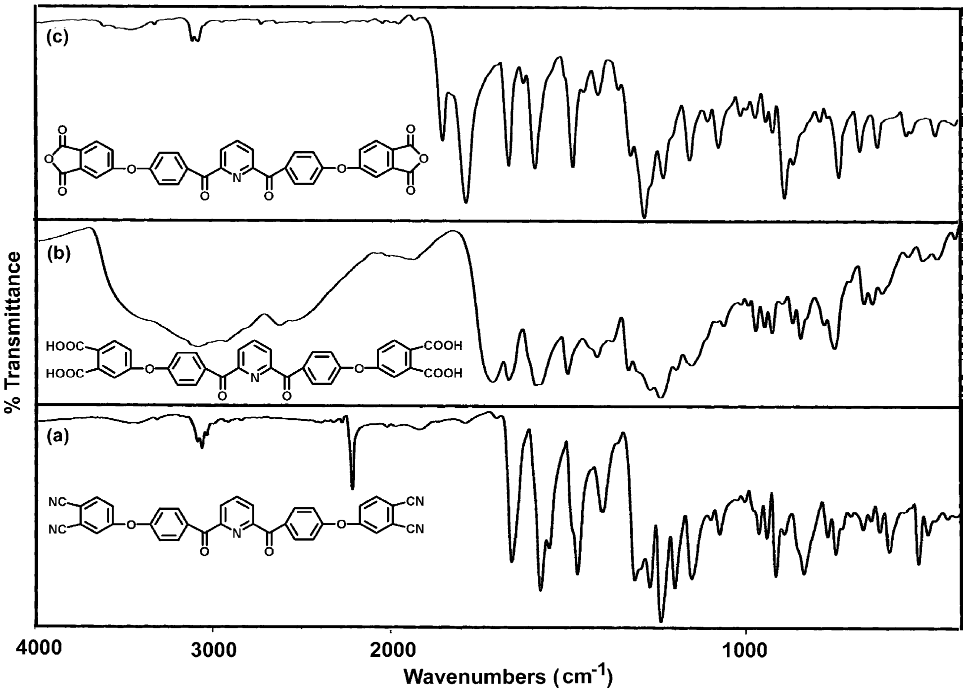
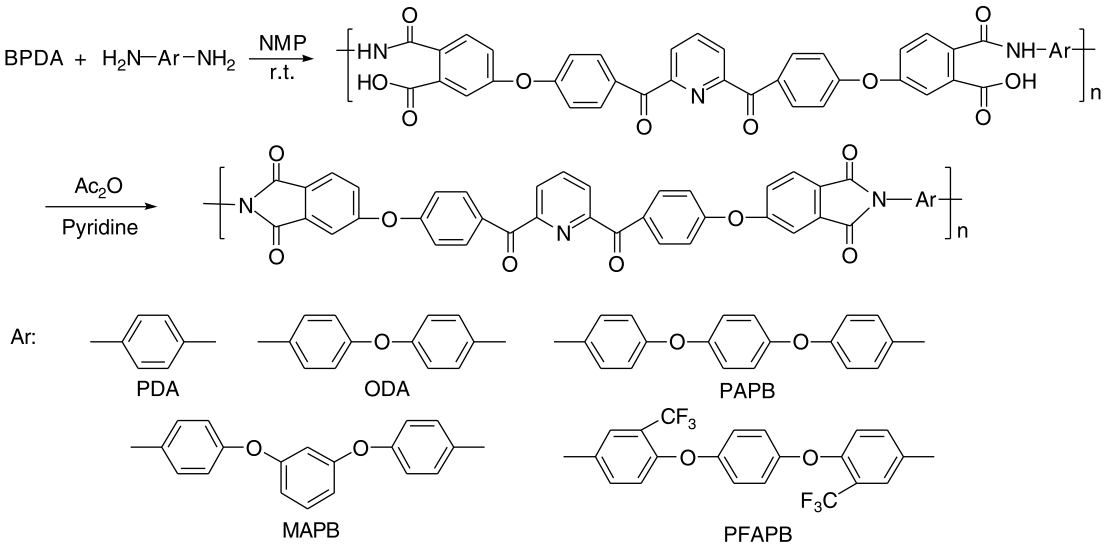


Fig. 1. FT-IR spectra of intermediate compound BCNP (a) and BACP (b) and dianhydride BPDA (c).



Scheme 2. Synthesis of the polyimides.

hydrolysis of the tetranitrile compound BCNP, which was carried out by the method of phosphoric acid [24], afforded the tetraacid compound 2,6-bis[4-(3,4-dicarboxyl phenoxy)benzoyl]pyridine (BACP), which was further purified by recrystallization in 30% of aqueous acetic acid using activated charcoal. Finally, the pyridine-containing pyridine diaanhydride, 2,6-bis[4-(3,4-dicarboxyphenoxy)benzoyl]pyridine dianhydride (BPDA), was obtained by chemical cyclodehydration of tetraacid precursor BACP with acetic anhydride. The synthesis route was confirmed by the FT-IR spectrum of the dianhydride monomer BPDA, and the intermediate BCNP and BACP, as shown in Fig. 1. The IR spectrum of intermediate tetranitrile BCNP is characterized by absorption at 2231 cm^{-1} because of the cyano group. The most characteristic bands of tetraacid precursor BACP can be observed near 1709 cm^{-1} (C=O stretching) and in the region of 2500–3500 cm^{-1} (O–H stretching). The disappearance of the characteristic cyano stretching band on the IR spectrum revealed completion of hydrolysis. The IR spectrum of dianhydride BPDA shows two characteristic cyclic anhydride absorptions near 1845 and 1782 cm^{-1}, attributed to the asymmetrical and symmetrical stretching vibrations of C=O. The disappearance of the characteristic bands of tetraacid precursor BACP, as well as the appearance of two characteristic cyclic anhydride absorptions indicated the conversion from tetraacid to dianhydride. According to the date from FT-IR, ^1H, and ^{13}C NMR spectroscopy presented in Section 2.2, the dianhydride monomer BPDA, and the intermediates BHBP, BCNP and BACP hold the structure as uniform as that shown in Scheme 1. All intermediate compounds and the dianhydride BPDA were also confirmed by elemental analysis, which were in good agreement with the calculated values. The results indicate that the design and synthesis of the novel pyridine-containing aromatic dianhydride monomer BPDA should be successful and feasible in this work. Furthermore, the yield of BHBP, BCNP, BACP and BPDA was 81, 58, 84 and 83%, successively, and the white crystal pyridine-containing aromatic dianhydride in this work was stable in air at room temperature and pure enough to be employed for polycondensation with diamine. This is to say that the dianhydride monomer could satisfy the requirement of preparation of polyimides with high molecular weight.

Table 1
Physical properties and elemental analysis of the polyimides

Polyimide	Yield (%)	η_{inh}[a] (dL/g)	Composition of repeating unit	Elemental analysis (%)			
					C	H	N
BPDA–PDA	97	–	$C_{41}H_{21}N_3O_8$	Calcd	72.03	3.10	6.15
				Found	71.86	3.17	5.98
BPDA–ODA	98	0.68	$C_{47}H_{25}N_3O_9$	Calcd	72.77	3.25	5.42
				Found	72.63	3.29	5.38
BPDA–PAPB	98	0.54	$C_{53}H_{29}N_3O_{10}$	Calcd	73.35	3.37	4.48
				Found	73.31	3.28	4.51
BPDA–MAPB	96	0.51	$C_{53}H_{29}N_3O_{10}$	Calcd	73.35	3.37	4.48
				Found	73.41	3.33	4.46
BPDA–PFAPB	95	0.60	$C_{55}H_{27}F_6N_3O_{10}$	Calcd	65.81	2.71	4.19
				Found	65.77	2.73	4.22

[a] Measured on 0.5% polymer solution in DMAc, at 30.0±0.1 °C; –, not dissolved.

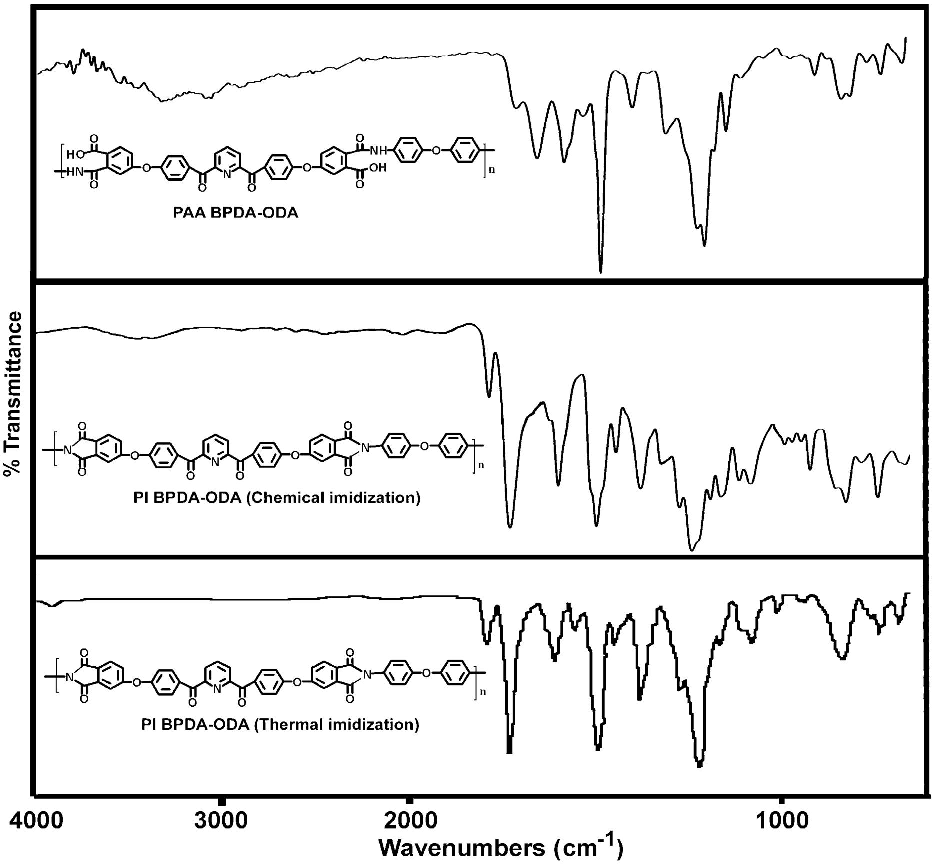


Fig. 2. FT-IR spectra of PAA and PI derived from BPDA and ODA.

3.2. Synthesis chemistry of the polyimides

Pyridine-containing polyimides (PIs) were obtained from pyridine-containing aromatic dianhydride BPDA and various aromatic diamines by the conventional two-step polymerization method in NMP, that is, poly(amic acid)s (PAAs) were first prepared by gradually adding dianhydride BPDA to NMP solution of diamines to give viscous resin solutions, which were converted into polyimide either by the chemical or thermal imidization method, as shown in Scheme 2. A series of pyridine-containing polyimides were synthesized by polymerization of 1 equiv. BPDA and 1 equiv. of aromatic diamines, including PDA, ODA, PAPB, MAPB and PFAPB at almost 15% solid content in NMP, respectively. The experimental data of the isolated polyimides obtained have been summarized in Table 1. According to the data from Table 1, the resulting polyimides all get high yields (95–98%), and elemental analyses show that compositions found of the repeating unit of them can agree with those calculated of that of them well as shown in Scheme 2. The resulting polyimides exhibited inherent viscosities of 0.51–0.68 dL/g in DMAc at 30 °C, which imply that polyimides with moderate molecular weights were obtained. The inherent viscosities of the resulting polyimides were comparable to previously reported polyimides with similar structures, which derived from pyridine-containing diamines, 2,6-bis(3-aminobenzoyl) pyridine (inherent viscosities, 0.37–0.58 dL/g in DMAc at 30 °C) [20] and 2,6-bis(4-aminophenoxy-4′-benzoyl)pyridine (inherent viscosities, 0.58–0.81 dL/g in DMAc at 30 °C) [21], and according to inherent viscosity data reported for soluble polyimides [25], molecular weights (M_w) of the resulting polyimides should be ranged from 40,000 to 80,000. Fig. 2 compares FTIR spectra of PAA and related polyimide based on BPDA–ODA. The complete conversion of amic acid to imide ring was shown by the disappearance of the amic acid bands at 1650–1700 and 2500–3500 cm^{-1} (including N–H at ~3400 cm^{-1}), together with the appearance of characteristic imide absorption bands at 1778 (asymmetrical C=O stretch), 1722 (symmetrical C=O stretch), 1376 (C–N stretch), 1113, and 743 cm^{-1} (imide ring deformation). Meanwhile, comparing with the FT-IR spectra of polyimide derived from BPDA–ODA (Fig. 2), there exist

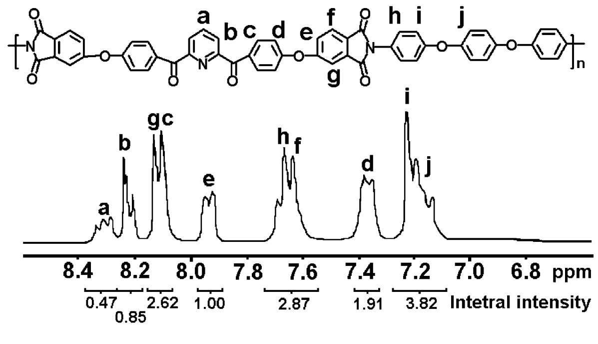


Fig. 3. ^{1}H NMR spectra of polyimide BPDA–PAPB (chemical imidization) (300 MHz, DMSO-d_6).

Table 2
Solubility of the polyimides

Polyimide[a]	Solvent				
	m-Cresol	NMP	DMAc	DMF	DMSO
BPDA–PDA[b]	−−	−−	−−	−−	−−
BPDA–ODA[b]	−−	−−	−−	−−	−−
BPDA–PAPB[b]	+	+	−−	−−	−−
BPDA–MAPB[b]	+	+	−−	−−	−−
BPDA–PFAPB[b]	+	+	+	−−	−−
BPDA–PDA[c]	++	+	+	−−	−−
BPDA–ODA[c]	++	++	++	+	+
BPDA–PAPB[c]	++	++	++	++	+
BPDA–MAPB[c]	++	++	++	++	+
BPDA–PFAPB[c]	++	++	++	++	++

[a] Qualitative solubility was determined by dissolving 10 mg of polyimide in 1 mL of solvent at room temperature or upon heating; ++, soluble at room temperature; +, soluble on heating; and −−, insoluble even on heating.

[b] Measured by thermal cyclization polyimide derived from the corresponding poly(amic acid)s.

[c] Measured by chemical cyclization polyimide derived from the corresponding poly(amic acid)s.

similar absorption bands for the polyimide obtained either by thermal or by chemical imidization method, these indicate that the conversion from PAA to PI were basically complete by using the two kinds of imidization methods. Fig. 3 shows a typical ^{1}H NMR spectrum of the pyridine-containing polyimide derived from BPDA and PAPB, in which all the protons in the polymer backbone can be assigned and no signal at δ (ppm) 10–12 (C(O)O–H) appears, indicating that complete imidization was really achieved. The characterization by FTIR, ^{1}H NMR, and elemental analysis confirmed that all the polymers had the expected chemical structures, and complete imidization was really achieved.

3.3. Solubility of the resulting polyimides

The new pyridine-containing aromatic polyimides, except BPDA–PDA, prepared by the two-step chemical imidization procedures can easily be dissolved in organic polar solvents to afford homogeneous polymer solution. The solubility of the polymers was determined by dissolving 10 mg of polymers in 1 mL of solvent at room temperature or upon heating, as shown in Table 2. It can be seen that all the polyimides, except BPDA–PDA and BPDA–ODA, could be dissolved in organic polar solvents, such as *m*-cresol, NMP, or DMAc, even at room temperature in most cases. The solubility varies depending upon the diamine used. Polyimide based on BPDA and PFAPB containing pendent trifluoromethyl was dissolved readily in *m*-cresol, NMP, DMAc, DMF and DMSO at room temperature. Similarly, polyimides BPDA–ODA, BPDA–PAPB and BPDA–MAPB obtained by chemical cyclization of poly(amic acid) were also soluble in given solvents, whereas polyimide BPDA–PDA with symmetric *p*-phenylene units showed poor solubility. The good solubility of these polyimides can be attributed to the presence of trifluoromethyl and flexible aryl ether linkages, together with the high polarity pyridine ring along the polymer backbone. The insolubility of BPDA–PDA can be explained by the rigid nature of its diamine moiety, which is symmetric *p*-phenylene and regularity. These results show that introduction of trifluoromethyl, flexible linkages and polar pyridine moieties should be contributed to the solubility of polymer. The solubility data listed in Table 2 show that the polyimides obtained by thermal imidization method hold a poor solubility. Comparing with that of PIs obtained by chemical imidization, the poor solubility of PI obtained by thermal imidization was possibly due to the presence of partial inter molecular crosslinking during the thermal imidization stage [26,27].

3.4. Crystallinity of the polyimides

The crystallinity of the prepared pyridine-containing polyimides was determined on wide-angle X-ray diffraction

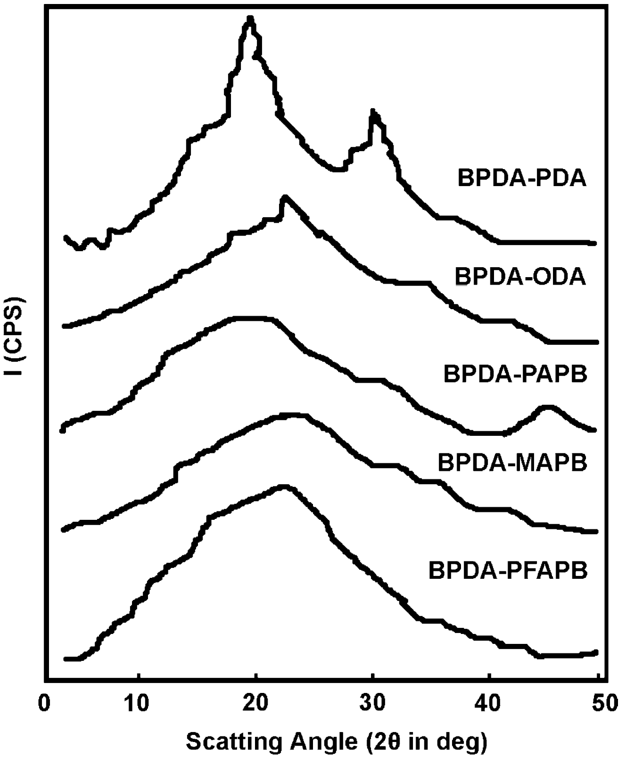


Fig. 4. X-ray diffraction pattern of the polyimides.

Table 3
Thermal properties of the polyimides

Polyimide[a]	Thermal properties				
	T_g[b] (°C)	T_d[c] (°C)	T_5[c] (°C)	T_{10}[c] (°C)	R_w[c] (%)
BPDA–PDA	278	526	530	562	65.3
BPDA–ODA	230	524	512	553	60.5
BPDA–PAPB	223	523	540	561	63.9
BPDA–MAPB	224	525	524	558	61.7
BPDA–PFAPB	221	529	521	557	60.4

[a] Measured samples were obtained by thermal imidization method.
[b] T_g was measured by DSC at a heating rate of 10 °C/min in N_2.
[c] T_d, decomposition-starting temperature; T_5 and T_{10}, temperature at a 5 or 10% weight loss. Residual weight (%) at 800 °C in nitrogen.

scans with graphite monochromatized Cu Kα radiation, 2θ ranging from 0 to 50°, using the PI films obtained by thermal cyclodehydration as samples, and the results were shown in Fig. 4. The X-ray diffraction patterns for polyimides BPDA–ODA, BPDA–PAPB, BPDA–MAPB, and BPDA–PFAPB show a diffuse halo, which tends to an amorphous structure. However, the X-ray diffraction curve of polyimide BPDA–PDA shows that there are small crystal peaks. It shows a little of crystalline morphologies (peak around 31°), which maybe relate to rigidity structure of the polyimide, and this should be a reason that it became brittle during thermal imidization.

3.5. Thermal properties of the polyimides

The thermal properties of the pyridine-containing polyimides were determined with DSC and TGA methods, and the results are listed in Table 3. Fig. 5 shows the DSC curves of these polyimides. It shows that the values of glass transition temperature (T_g) of these polyimides were ranged from 221 to 278 °C, which depended on the chemical structure of aromatic diamine component. Polyimide based on BPDA–PDA exhibited the highest T_g value because of the effect of the rigid polymer backbone. On the contrary, polyimide derived from BPDA and PFAPB showed the lowest T_g due to the relative flexible polymer chain. These results are also confirmed by X-ray diffraction patterns of these polyimides (Fig. 4), in which polyimide BPDA–PDA displayed a semicrystalline pattern, whereas other polyimides showed the amorphous patterns. Although polyimide based on BPDA–PAPB and BPDA–MAPB have a similar chemical structure, the T_g value of the former is 16 °C higher than that of the latter. This could be explained by the linear para-oriented linkages in BPDA–PAPB, which caused a more well-packed structure than meta-oriented BPDA–MAPB [28]. The T_g values of the resulting polyimides are higher than commercial polyimides, Ultem 1000 (T_g, 217 °C), based on bisphenol-A(diphthalic anhydride) and *m*-phenylene, which, however, are lower than Kapton films derived from PMDA–ODA (T_g, 390 °C) [29].

Fig. 6 compares the TGA curves of the resulting pyridine-containing polyimides prepared by thermal imidization method. These polyimides did not exhibit obvious weight loss before the scanning temperature reached up to 500 °C in nitrogen, indicating that no thermal decomposition occurred. As shown in Table 3, the decomposition-starting temperature of the pyridine-containing polyimides was in the range of 523–529 °C, and the temperature at 5 and 10% weight loss was in the range of 512–540 and 553–562 °C, respectively. In addition, the residual weight retentions at 800 °C for the pyridine-containing polyimides were 60.4–65.3%, implying that the pyridine-containing polyimides possess excellent thermal stability.

The 5% weight loss temperatures (T_5) of the resulting polyimides are higher than previously reported polyimides derived from pyridine-containing diamines, 2,6-bis(3-aminobenzoyl)pyridine (T_5, 495–549 °C) [20], 2,6-bis(4-

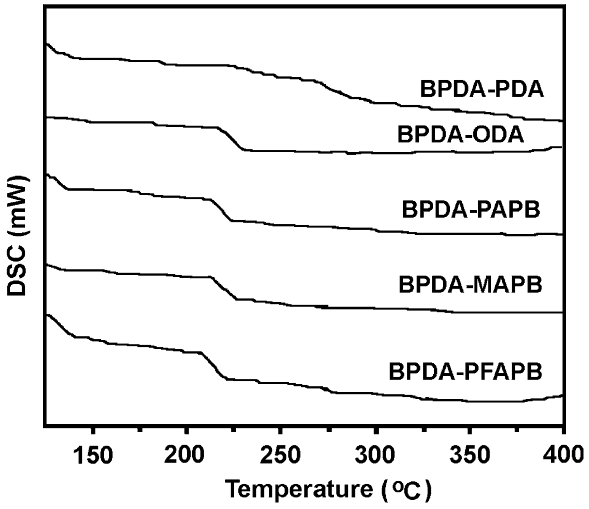


Fig. 5. DSC thermograms of PIs at heating rate of 20 °C/min in nitrogen.

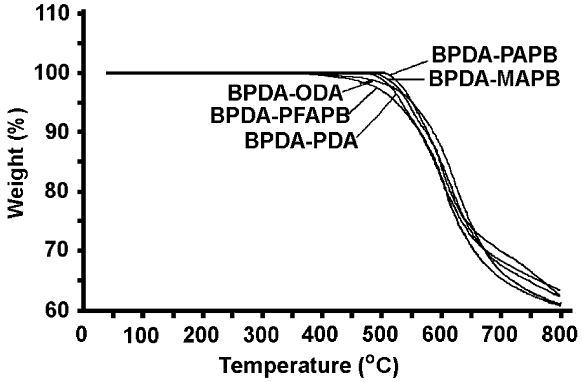


Fig. 6. TGA curves of the polyimides.

aminophenoxy- 4′-benzoyl)pyridine (T_5, 439–509 °C) [21] and 2,6-bis(3′-trifluoromethyl-*p*-amino biphenylether)pyridine (T_5, 503–518 °C) [19]. Similarly, comparing with polyimides holding similar structure but benzene ring instead of pyridine ring, which derived from 1,3-bis[3′-trifluoromethyl-4′(4″-aminobenzoxyl)benzyl]benzene (T_5, 491–516 °C) [30], these polymers possess higher 5% weight loss temperatures, and this should be contributions of polarity and rigidity of pyridine ring.

3.6. Mechanical properties of the polyimides

High-quality polyimide films, except BPDA–PDA, could be prepared by casting the PAA solution on glass plates followed by the thermal curing in the following procedure, 80 °C/2 h, 120 °C/1 h, 150 °C/1 h, 180 °C/1 h, 250 °C/1 h, 280 °C/2 h in air. Table 4 summarizes the tensile strength and modulus of these resulting pyridine-containing polyimides. Because of the rigid nature of its diamine moiety, polymer BPDA–PDA, which became brittle during thermal imidization, could not obtain strong and flexible film. The PI films have tensile strength of 72.8–104.4 MPa, tensile modulus of 1.29–2.77 GPa, and elongation at breakage of 9.1–10.4%, which indicate that they are strong and tough polymeric materials. It is noticed that the tensile modulus of the polyimide BPDA–PFAPB (1.29 GPa), derived from the pyridine-containing dianhydride BPDA and fluorinated aromatic diamine PFAPB, is two times lower than that of polyimides BPDA–ODA (2.77 GPa) and BPDA–PAPB (2.68 GPa). It is obvious that the high fluorine concentration in the polymer backbone would be responsible to the reduction in the tensile modulus.

The mechanical property values of the resulting polyimides are comparable to those of many commercial polyimides (Ultem 1000: tensile strength, 105 MPa; tensile modulus, 3.0 GPa; elongation at break, 60%. Avimid N: tensile strength, 110 MPa; tensile modulus, 4.13 GPa; elongation at break, 6%) [29], and polyimides derived from pyridine-based diamine and benzene-based diamine with similar structure to pyridine-based diamine, i.e. 2,6-bis(3′-trifluoromethyl-*p*-amino biphenylether)pyridine (tensile strength, 105–115 MPa; tensile modulus, 2.5–2.8 GPa; elongation at break, 6–12%) and 1,3-bis[3′-trifluoromethyl-4′(4″-aminobenzoxyl)benzyl]benzene (tensile strength, 87–98 MPa; tensile modulus, 2.1–2.5 GPa; elongation at break, 9–11%) [30].

Table 4
Mechanical properties of the polyimides

Polyimide[a]	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at breakage (%)
BPDA–ODA	104.4	2.77	10.4
BPDA–PAPB	92.7	2.68	11.7
BPDA–MAPB	95.3	2.43	9.6
BPDA–PFAPB	72.8	1.29	9.1

[a] Measured by thermal imidization polyimides from the corresponding poly(amic acid)s.

Table 5
Dielectric properties of the polyimide films

Polyimide[a]	1 MHz		10 MHz	
	ε	tan $\delta \times 10^3$	ε'	tan $\delta' \times 10^3$
BPDA–PDA	3.02	8.2	2.97	8.5
BPDA–ODA	2.94	7.8	2.89	7.9
BPDA–PAPB	2.56	7.6	2.39	7.6
BPDA–MAPB	2.55	7.3	2.36	7.4
BPDA–PFAPB	2.48	6.1	2.29	6.4

[a] ε, tan δ, dielectric constant and dielectric dissipation factor at 1 MHz; ε', tan δ', dielectric constant and dielectric dissipation factor at 10 MHz; thickness of polyimide films obtained by thermal imidization method, 25 μm.

3.7. Dielectric properties of the polyimides

The dielectric properties of the pyridine-containing polyimide films were detected at 1 and 10 MHz at 25 °C (Table 5). The dielectric constants of these polyimides at 1 and 10 MHz were in the range of 2.48–3.02, and 2.29–2.97, and the dielectric dissipation factor (tan δ) in the range of 6.1–8.2 × 10^3, and 6.4–8.5 × 10^3, respectively. In comparison with polyimide BPDA–PAPB, polyimide BPDA–PFAPB exhibited a lower dielectric constant and dissipation factor; moreover, it also gave the lowest ε and tan δ values, which can be explained by the presence of CF_3 groups in the polyimide chains. For each polyimide, the dielectric constant at 1 MHz is higher than that at 10 MHz. This variation is attributed to the frequency dependence of the polarization mechanisms, which comprise the dielectric constant. The dielectric constant values of these films are lower than Kapton H (3.3 at 10 MHz), and comparable to those of many semifluorinated polyimides (6FDA–MPD: 3.0; 6FDA–7FMDA: 2.9; TFDA-*p*-APB: 2.89) [19,27]. The results suggested that CF_3 groups in the polymer chain could improve the dielectric performance, and the polar pyridine moieties maybe also have contribution to dielectric constant due to its low polarizability resulting from polar pyridine ring [31].

4. Conclusions

A new kind of pyridine-containing aromatic dianhydride was firstly synthesized and characterized, which was employed to polycondense with various aromatic diamines to prepare a series of novel aromatic polyimides containing pyridine ring. Experimental results indicated that the resulting polyimides that hold inherent viscosities of 0.51–0.68 dL/g could easily be dissolved in many organic solvents to give homogeneous and stable polyimides solution. Strong and flexible polyimide films could be obtained by casting the resulting PAA solution on glass substrate, followed by thermal dehydration with a programmed procedure. The resulting polyimide films exhibited not only good thermal stability with a glass transition temperature of 221–278 °C, and an initializing decomposition temperature of 523–529 °C in nitrogen, but also outstanding mechanical properties with the tensile strengths of 72.8–104.4 MPa, as well as elongation at breakage of 9.1–10.4%. In addition, the pyridine-containing polyimides have fairly low dielectric constants of 2.48–3.02 at 1 MHz, and 2.29–2.97 at 10 MHz.

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