

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

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ABSTRACT: A new kind of pyridine-containing aromatic diamine monomer, 4-phenyl-2,6-bis[4-(4-aminophenoxy)phenyl]-pyridine (PAPP), was successfully synthesized by a modified chichibabin reaction of benzaldehyde and a substituted acetophenone, 4-(4-nitrophenoxy)-acetophenone (NPAP), followed by a reduction of the resulting dinitro compound 4-phenyl-2,6-bis[4-(4-nitrophenoxy)phenyl]-pyridine (PNPP) with Pd/C and hydrazine monohydrate. The aromatic diamine was employed to synthesize a series of new pyridine-containing polyimides by polycondensation with various aromatic dianhydrides in *N*-methyl-2-pyrrolidone (NMP) via the conventional two-step method, 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 0.79–1.13 dL/g, and most of them

were soluble in common organic solvents such as *N,N*-dimethylacetamide (DMAc), NMP, and tetrahydrofuran (THF), etc. Meanwhile, strong and flexible polyimide films were obtained, which had good thermal stability, with the glass transition temperatures (T_g) of 268–338°C and the temperature at 5% weight loss of 521–548°C in air atmosphere, as well as outstanding mechanical properties with tensile strengths of 89.2–112.1 MPa and elongations at break of 9.5–15.4%. The polyimides also were found to possess low dielectric constants ranging from 2.53 to 3.11. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 212–219, 2007

Key words: high performance polymers; pyridine-containing polyimides; solubility; thermal properties; dielectric constant

INTRODUCTION

Polyimides have found a variety of applications in aerospace, microelectronics, optoelectronics, composites and so on, which can be contributed to their excellent properties, such as outstanding thermal and thermo oxidative stability, solvent resistance, mechanical and electrical properties.^{1–5}

However, with the quick development of high technology fields especially in microelectronic industry, common polyimides cannot meet the sharply increasing demands for polyimides with outstanding combined properties because of their shortcoming in processability owing to their insolubility in organic solvents and high melting temperature.^{6,7} Thus, to utilize the thermal stability of polyimides for further applications and also to take advantage of other properties of polyimide such as high chain rigidity, packing density, and polar chain interactions, it will be desira-

ble to synthesize soluble and/or melt-processable polyimides.

Solubilization of the polyimides has been targeted by several methods, such as introduction of flexible linkages,^{8,9} bulky units in the polymer backbone,^{10,11} bulky pendent substituents,^{12,13} or noncoplanar moieties.^{14,15} Among these approaches, introducing bulky pendent substituents and heteroaromatic rings into polyimide chains has been considered to be efficient, which can provide not only enhanced solubility but also good thermal and thermo-oxide stability.

The selection of a pyridine nucleus is based on its high thermal stability derived from its molecular symmetry and aromaticity.^{16–19} The rigidity based on the symmetry and aromaticity of the pyridine ring would contribute to the thermal stability, chemical stability, retention of mechanical property of the resulting polymer at elevated temperature, and the polarizability resulting from the nitrogen atom in pyridine ring would be suitable to improve their solubility in organic solvents.^{20,21} Considering this, the polyimides with good thermostability and processability have been prepared from pyridine-containing diamine and dianhydride monomers.^{22–25} In continuation of our work, this article reported the successful synthesis and detailed charac-

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terization of four new pyridine-containing polyimides derived from a novel diamine monomer, 4-phenyl-2,6-bis[4-(4-aminophenoxy) phenyl]-pyridine (PAPP), and various aromatic dianhydrides.

EXPERIMENTAL

Materials

4-Hydroxyacetophenone (TCI) and *p*-chloronitrobenzene (TCI) were used as received. 4,4'-Oxydiphthalic anhydride (ODPA; Shanghai Nanxiang Chemical, China), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA; Beijing Chemical Reagents, China), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA; Aldrich) were recrystallized from acetic anhydride before use. Pyromellitic dianhydride (PMDA; Beijing Chemical Reagents, China) was purified by sublimation at 200–220°C. *N,N*-Dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP) were purified by distillation under reduced pressure over calcium hydride and were stored over 4-Å molecular sieves. Reagent-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

¹H NMR (400 MHz) and ¹³C NMR (400 MHz) spectra were measured on a Mercury-plus400 spectrometer using tetramethylsilane as the internal reference. Fourier transform infrared (FTIR) spectra of the monomer and intermediates were obtained on a Micolet NEXUS 670 spectrometer (KBr disks). Gel permeation chromatography was performed with an Agilent HP1100 instrument. Tetrahydrofuran (THF) was used as eluent, and ODS2 Hypersil column was employed. The molecular weight and polydispersity are reported versus monodisperse polystyrene standard. Elemental analyses were determined by 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. *T*_g was taken as the midpoint of the inflection observed on the curve of heat capacity versus temperature. Melting points were measured by the DSC method. 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 25°C on a Siemens Kristalloflex D5000 X-ray diffractometer, using nickel-filtered Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$, operating at 40 kV and 30 mA). The mechanical prop-

erties were measured on an Instron 1122 testing instrument with $100 \times 5 \text{ mm}^2$ specimens in accordance with GB 1040-79 at a drawing rate of 50 mm/min. The values of inherent viscosity (η_{inh}) were determined by an Ubbelohde viscosimeter at 30°C using DMAc as a solvent, and the polymer solution was given a concentration of 0.5 g/dL. Solubility was determined qualitatively by placing 10 mg of polymer into 1 mL of solvent at room temperature for 24 h, or heating at 80°C. The dielectric constants were determined on an Agilent 4291B instrument with 25- μm thick specimens at frequencies of 1 MHz and 10 MHz at room temperature. Water uptake was measured by weighting the changes of a sample ($30 \times 30 \text{ mm}^2$) before and after immersion in water at 25°C for 24 h.

Synthesis of diamine monomer

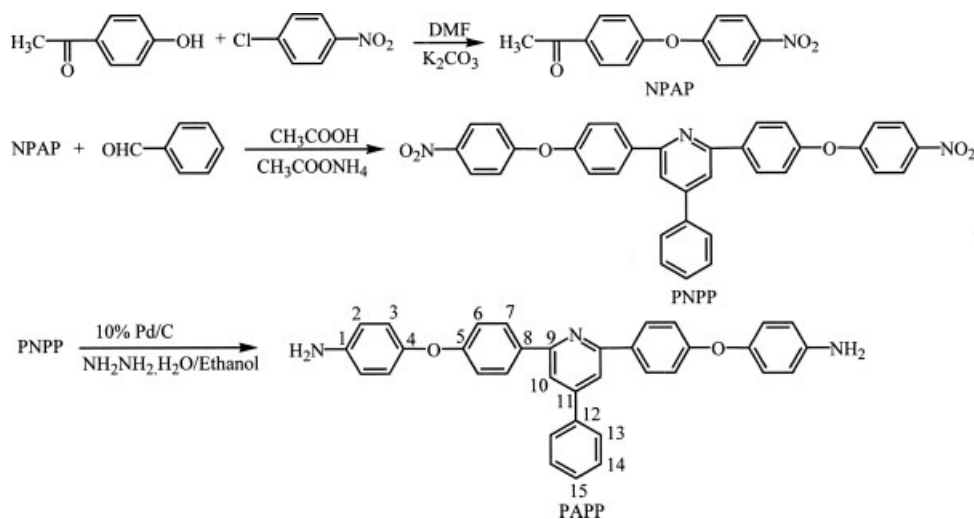
Synthesis of 4-(4-nitrophenoxy)-acetophenone (NPAP)

In a 250-mL three-necked round bottom flask equipped with a nitrogen inlet, 13.62 g (0.1 mol) of 4-hydroxyacetophenone and 29.02 g (0.21 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 using a Dean–Stark trap to remove small amounts of water azeotropically. After most of the toluene was distilled, 15.76 g (0.1 mol) of *p*-chloronitrobenzene was added when the mixture was 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 500 mL of ice/water to give brown precipitates. Filtrating and washing with water, the product was recrystallized from ethanol to afford 21.66 g of light yellow crystal NPAP. Yield: 84.2%. Melting point: 79°C.

¹H NMR (CDCl₃): δ (ppm) 8.27–8.23 (d, *J* = 8 Hz, 2H), 8.06–8.02 (d, *J* = 8 Hz, 2H), 7.16–7.12 (d, *J* = 8 Hz, 2H), 7.13–7.09 (d, *J* = 8 Hz, 2H), 2.62 (s, 3H). ¹³C NMR (CDCl₃): δ (ppm) 196.49, 161.70, 159.05, 146.21, 133.81, 130.83, 126.01, 119.45, 118.35, 26.51. Elemental analysis of (C₁₄H₁₁NO₄)_{*n*} (257.24)_{*n*} calculated: C 65.37%, H 4.31%, N 5.44%. Found: C 65.32%, H 4.40%, N 5.39%.

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

12.86 g (0.05 mol) of NPAP, 2.65 g (0.025 mol) of benzaldehyde, 25.05 g (0.325 mol) of ammonium acetate, and 40 mL of glacial acetic acid were placed into a 100-mL three-necked flask equipped with a mechanical stirrer and a reflux condenser. The mixture was refluxed with stirring for 4 h. Then the precipitated solid was filtered off and washed thoroughly with water. After drying under vacuum at 60°C, 6.08 g of yellow powder of PNPP was obtained. Yield: 41.8%. Melting point: 226°C.



Scheme 1 Synthesis of the diamine monomer PAPP.

IR (KBr) (cm^{-1}): 3106, 3075 (C—H), 1586, 1339 (C—NO₂), 1319 cm^{-1} (C—N). ¹H NMR (DMSO-*d*₆): δ (ppm) 8.30–8.25 (d, *J* = 10 Hz, 4H), 8.09–8.06 (d, *J* = 6 Hz, 4H), 7.93–7.79 (m, 5H), 7.45 (s, 2H), 7.33–7.25 (m, 8H). ¹³C NMR (DMSO-*d*₆): δ (ppm) 161.93, 159.13, 144.56, 143.52, 141.66, 135.11, 131.80, 129.63, 128.85, 126.72, 122.29, 120.18, 119.22, 118.13. Elemental analysis of (C₃₅H₂₃N₃O₆)_{*n*} (581.57)_{*n*} calculated: C 72.28%, H 3.99%, N 7.23%. Found: C 72.17%, H 4.08%, N 7.19%.

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

To a 250-mL three-necked flask equipped with a dropping funnel and a reflux condenser, 5.81 g (0.01 mol) of PNPP, 0.2 g of palladium on activated carbon (Pd/C, 10%), and 100 mL of anhydrous ethanol were added, and after heating to refluxing temperature with stirring, 10 mL of hydrazine monohydrate was added drop wise for 2 h. After the addition of hydrazine monohydrate was finished, 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 4.54 g of needle crystal of PAPP. Yield: 83.0%. Melting point: 191°C.

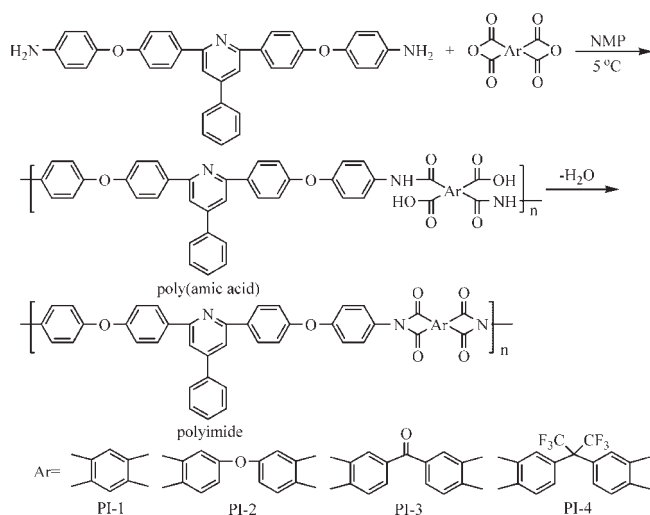
IR (KBr) (cm^{-1}): 3425, 3351 (N—H), 3037, 3011 (C—H), 1603–1500 (C=C), 1277, 1230 (C—O—C). ¹H NMR (DMSO-*d*₆): δ (ppm) 8.29–8.24 (d, *J* = 10 Hz, 4H, H7), 8.06 (s, 2H, H10), 8.01–7.98 (d, *J* = 6 Hz, 2H, H13), 7.60–7.50 (m, 3H, H14, H15), 7.03–6.98 (d, *J* = 10 Hz, 4H, H6), 6.88–6.84 (d, *J* = 8 Hz, 4H, H3), 6.63–6.67 (d, *J* = 8 Hz, 4H, H2), 5.07 (s, 4H, —NH₂). ¹³C NMR (DMSO-*d*₆): δ (ppm) 160.05 (C9), 156.00 (C5), 149.41 (C11), 145.73 (C4), 145.21 (C1), 137.93 (C12), 132.53 (C8), 129.06 (C14, C15), 128.48 (C13), 127.27 (C7), 121.08 (C3), 116.39 (C10), 115.38 (C6), 114.91 (C2). Ele-

mental analysis of (C₃₉H₂₇N₃O₂)_{*n*} (521.61)_{*n*} Calculated: C 80.59%, H 5.22%, N 8.06%. Found: C 80.43%, H 5.29%, N 7.94%.

Synthesis of polyimides

The typical two-step polymerization method was employed in the synthesis of objective polyimides. An equimolar amount of diamine and dianhydride monomers was used in all cases. A representative polymerization procedure is as follows.

A measure of 0.4362 g (2.0 mmol) of PMDA was gradually added to a stirred solution of 1.0432 g (2.0 mmol) of PAPP in 8.5 mL of NMP in a 50-mL three-necked flask equipped with a nitrogen inlet at 5°C. The mixture was stirred at room temperature under nitrogen atmosphere for 24 h, forming a viscous solution of poly(amic acid) (PAA) precursor in NMP. The



Scheme 2 Synthesis of the pyridine-containing polyimides.

TABLE I
Physical Properties and Elemental Analysis of the Polyimides

Polymer	Yield (%)	η_{inh}^a (dL/g)		M_n^b	PDI ^c	Elemental analysis (%)			Film quality	
		PAA	PI			C	H	N		
PI-1	96	1.55	– ^d	–	–	Calcd.	76.81	3.58	5.97	C, F, & T ^e
						Found	76.62	3.66	5.96	
PI-2	98	1.63	0.92	–	–	Calcd.	76.97	3.67	5.28	C, F, & T
						Found	76.79	3.77	5.30	
PI-3	97	0.97	0.79	–	–	Calcd.	77.32	3.62	5.20	C, F, & T
						Found	77.09	3.71	5.14	
PI-4	98	1.67	1.13	33450	1.88	Calcd.	69.75	3.14	4.52	C, F, & T
						Found	69.58	3.25	4.46	

^a Measured on 0.5% polymer solution in DMAc, at 30.0°C ± 0.1°C; PAA, poly(amic acid); PI, polyimide.

^b M_n , number-average molecular weight.

^c Polydispersity index.

^d Not detected.

^e C, clear; F, flexible; T, tough.

PAA was subsequently converted into polyimide 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 (6/4, v/v) into the PAA solution with stirring at ambient temperature for 1 h. Then the mixture was stirred at 100°C for 4 h to yield a homogeneous polyimide solution, which was poured slowly into ethanol 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 all polymerizations. For the thermal imidization, the PAA was poured into a glass plate, which was dried in an oven at 80°C for 8 h, at 150, 200, 250, and 300°C for 1 h each temperature. Polyimide films were stripped from the glass substrate by immersing the glass plates in hot water.

RESULTS AND DISCUSSION

Monomer synthesis

As shown in Scheme 1, the diamine monomer (PAPP) was obtained through a three-step synthetic route. First, the nucleophilic substitution reaction of 4-hydroxyacetophenone with *p*-chloronitrobenzene in the presence of potassium carbonate gives the intermediate compound NPAP. Then the dinitro compound 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,²⁶ from benzaldehyde and NPAP. Finally, the novel diamine monomer PAPP was obtained in a high yield by the reduction of 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 polyimides. The detail characterizations on the diamine monomer

PAPP were done by elemental analyses, FTIR, and NMR techniques, which support unambiguously the structure shown in Scheme 1. The analytical data of PAPP and the intermediate compounds NPAP and PNPP are given in Experimental section. The results indicate that the design and synthesis of novel diamine monomer PAPP should be successful and feasible in this work.

Synthesis of polyimides

The diamine PAPP reacted with PMDA, ODPA, BTDA, and 6FDA to give the corresponding polyimides as shown in Scheme 2.

The new polyimides were synthesized using two-step methods, which were carried out via poly(amic acid)s intermediate. First, the diamine was dissolved in a measured amount of dry NMP and the equimolar

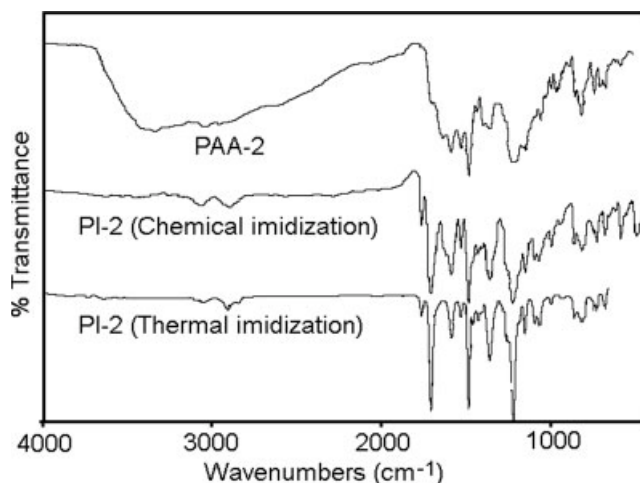


Figure 1 FTIR spectra of poly(amic acid) and the polyimide derived from PAPP and ODPA.

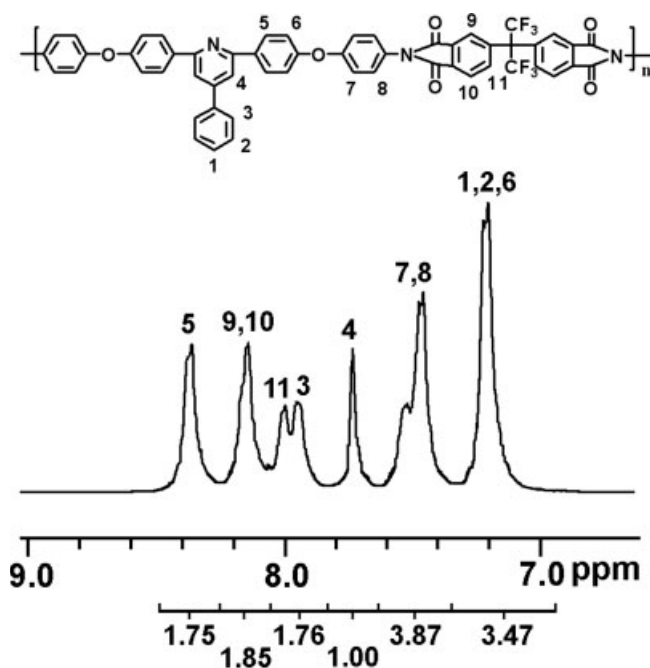


Figure 2 ^1H NMR spectrum of polyimide PI-4 (chemical imidization) (400 MHz, $\text{DMSO}-d_6$).

amount of dianhydride monomers were added to the solution slowly. After completing the addition, the solution was stirred for 24 h at room temperature, forming viscous poly(amic acid) solutions. Thermal or chemical imidization procedures were chosen to form polyimides. The merit of the former was ease for preparation of polyimide films, whereas the latter was suited for the preparation of soluble polyimides. The experimental data of the isolated polyimides obtained have been summarized in Table I. According to the data from Table I, the resulting polyimides all get high yields (96–98%), and the inherent viscosity values of these poly(amic acid)s and polyimides were in the range of 0.97–1.67 and 0.79–1.13 dL/g, respectively, which indicated formation of high molar masses. This is consistent with the fact that tough and flexible films could be obtained by coating and solvent evaporation of polymer solutions. Gel permeation chromatography of polyimide PI-4 was run in THF solvent; values

presented in Table I also indicate the formation of high molar mass.

Spectroscopy

The formation of polyimides was confirmed by FTIR spectroscopy. Figure 1 compares representative FTIR spectra of poly(amic acid), the polyimide prepared by chemical imidization method, and the polyimide prepared by thermal imidization method which is based on PAPP-6FDA. The complete conversion of amic acid to imide ring was proved by the disappearance of absorption bands at 1716 cm^{-1} corresponding to C=O stretching of carboxylic acid and 1650 cm^{-1} corresponding to C=O amide stretching, together by the appearance of absorption bands at about 1780 cm^{-1} (asymmetrical C=O stretching), 1730 cm^{-1} (symmetrical C=O stretching), 1374 cm^{-1} (C–N stretching), and 722 cm^{-1} (C=O bending) corresponding to the characteristic of imide bands. Compared with FTIR spectra of polyimides, there exist similar absorption bands for the polyimide obtained either by thermal or by chemical imidization methods. These results indicate that full imidization polyimide can be obtained using both kinds of imidization methods. The ^1H NMR (400 MHz) spectrum of polyimide PI-4 showed no amide and acid protons, confirming full imidization. Also, all protons in the backbone of polyimide PI-4 can be assigned, as shown in Figure 2.

Polymer solubility

The solubilities of the resulting polyimides were investigated in different organic solvent by dissolving 10 mg of polymers in 1 mL of solvent at room temperature or upon heating, as shown in Table II. It can be seen that almost all the polyimides exhibited good solubility in common organic solvents, such as NMP, DMAc, DMF, *m*-cresol, even at room temperature. The good solubility should be the result of the introduction of the flexible ether groups and the bulk pendent phenyl group in polymer backbone. In addition, the solubility varies depending upon the dianhydride used. Polyimide PI-4 exhibited good solubility behav-

TABLE II
Solubility of the Polyimides

Polymer ^a	Organic solvents ^b							
	<i>m</i> -Cresol	NMP	DMAc	DMF	DMSO	Toluene	THF	CHCl_3
PI-1	+-	+-	+-	+-	+-	-	-	-
PI-2	++	++	++	+	+-	-	+-	+-
PI-3	+	++	++	+	+-	-	+-	+-
PI-4	++	++	++	++	++	-	++	++

^a Measured by chemical cyclization polyimide derived from the corresponding poly(amic acid)s.

^b 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 at 80°C ; +-, partially soluble on heating at 80°C ; -, insoluble.

TABLE III
Thermal Properties of the Polyimide Films

Polymer ^a	Thermal properties ^b				
	T_g^b (°C)	T_d^c (°C)	T_5^c (°C)	T_{10}^c (°C)	R_w^c (%)
PI-1	338	558	548	571	41.5
PI-2	268	541	530	552	40.0
PI-3	276	552	527	551	37.0
PI-4	292	527	521	537	26.5

^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 N₂.

^c T_d , decomposition-starting temperature in air; T_5 and T_{10} , temperature at a 5% or 10% weight loss in air; R_w , residual weight at 700°C in air.

ior in common organic solvents. A comparison of the solubility of PI-4 polymer with the other three polymers shows that the polymer have better solubility in NMP, DMAc, DMF, THF, CHCl₃, *m*-cresol at room temperature. It can also be seen that they showed good solubility in some low boiling-point solvents, such as THF and CHCl₃, which indicates that they should have potential applications in areas where temperature is sensitive.

Thermal properties

The thermal properties of the resulting polyimides, which were investigated by DSC and TGA methods, are listed in Table III. The data in Table III represent that T_g values of these polyimides ranged from 268 to 338°C (as shown in Fig. 3), which depended on the chemical structure of the aromatic dianhydrides used. Polyimide PI-1 derived from PAPP and PMDA exhibited the highest T_g value because of the effect of the highest rigidity of PMDA among the four dianhydrides. On the contrary, polyimides PI-2, PI-3, and PI-4 showed lower T_g values due to the relative flexible polymer chain. However, it was found that PI-4 (derived from 6FDA and PAPP) showed higher T_g value than that of PI-2 and PI-3. This could be

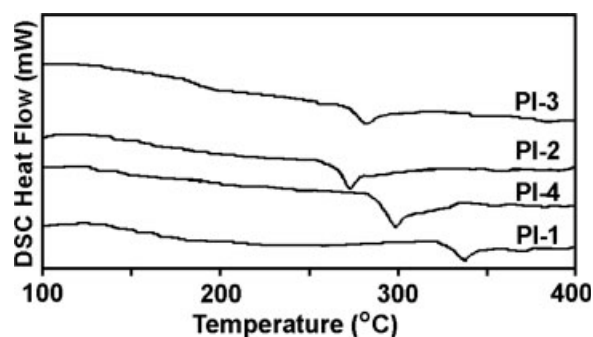


Figure 3 DSC curves of the pyridine-containing polyimides.

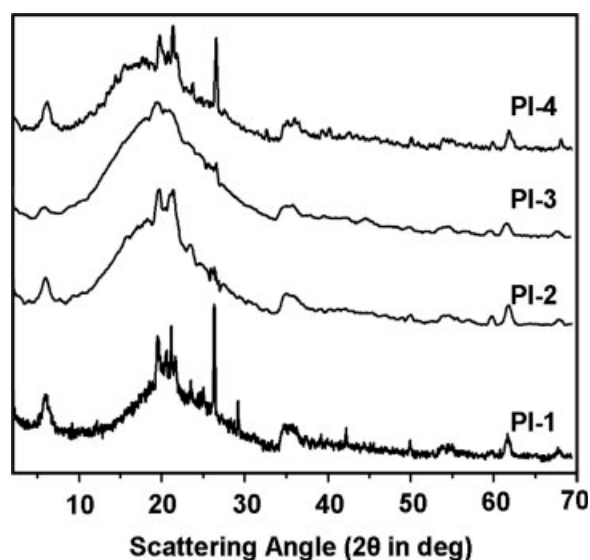


Figure 4 X-ray diffraction patterns of the polyimides.

explained that the presence of hexafluoropropane might inhibit the free rotation of the polymer chain. These results are also confirmed by X-ray diffraction patterns of these polyimides shown in Figure 4, in which polyimides PI-1 and PI-4 (based on PMDA and 6FDA, respectively) displayed a little of the crystalline pattern, whereas other polyimides showed the amorphous patterns.

The T_g values of these polyimides are higher than commercial polyimide, Ultem 1000 (T_g , 217°C), based on bisphenol-A diphthalic anhydride and *m*-phenylene diamine.²⁷ However, the T_g values of these polyimides are lower than Kapon films derived from PMDA-ODA (T_g , 390°C).²⁷

The thermal stabilities of these polyimides were evaluated by TGA. The TGA curves for polyimides prepared by the thermal imidization method are shown in Figure 5. The results are summarized in Table III. These polyimides did not exhibit obvious weight loss before the scanning temperature reached up to 500°C in air atmosphere, indicating that no thermal decom-

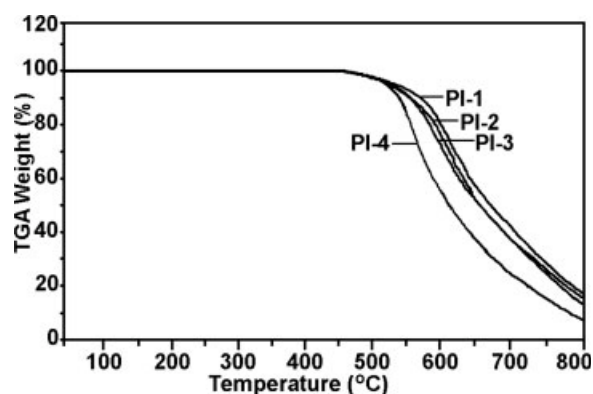


Figure 5 TGA curves of the polyimides.

TABLE IV
Mechanical, Dielectric Properties, and Water Uptake of the Polyimides

Polymer ^a	Mechanical properties ^b			Dielectric properties ^c				Water uptake (%)
	TS	TM	E%	E	$\tan \delta \times 10^3$	ϵ'	$\tan \delta' \times 10^3$	
PI-1	112.1	1.21	13.2	3.02	8.8	2.77	8.6	0.72
PI-2	104.4	1.12	15.4	3.06	7.4	2.71	7.5	0.64
PI-3	105.2	1.88	10.7	3.11	8.7	2.87	8.9	0.79
PI-4	89.2	1.22	9.5	2.53	7.7	2.35	7.6	0.51

^a Polyimide film samples were obtained by thermal imidization method.

^b TS, tensile strength; TM, tensile modulus; E%, elongation at break.

^c ϵ , $\tan \delta$: dielectric constant and dielectric dissipation factor at 1 MHz; ϵ' , $\tan \delta'$: dielectric constant and dielectric dissipation factor at 10 MHz; thickness of polyimide films: 25 μm .

position occurred. As shown in Table III, the decomposition-starting temperature of the resulting polyimides were in the range of 527–558°C, and the temperature at 5% and 10% weight loss was in the range of 521–548°C and 537–571°C in air atmosphere, respectively. In addition, the residual weight retentions at 700°C for the resulting polyimides were 26.5–41.5% in air atmosphere, implying that these polyimides possess excellent thermal and thermo oxidative stability.

Mechanical properties

High-quality polyimide films could be prepared by casting the PAA solution on glass plates followed by the thermal curing in the following procedure, 80°C for 8 h, 150, 200, 250, and 300°C for 1 h each temperature in air. Table IV summarizes the tensile strength and modulus of these resulting polyimides. The polyimide films possess tensile strength of 112.1–89.2 MPa, tensile modulus of 1.12–1.88 GPa, and elongation at break of 9.5–15.4%, which indicate that they are strong and tough polymeric materials.

Dielectric properties

The dielectric properties of these polyimide films were detected at 1 and 10 MHz at 25°C, which is summarized in Table IV. The dielectric constants of these polyimides at 1 and 10 MHz were in the range of 2.53–3.11 and 2.35–2.87, and the dielectric dissipation factor ($\tan \delta$) was in the range of $7.4\text{--}8.8 \times 10^{-3}$ and $7.5\text{--}8.9 \times 10^{-3}$, respectively. Polyimide PI-4 exhibited the lowest dielectric constant, which can be explained by the contribution of the $-\text{CF}_3$ groups in polyimide backbone. 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 are comparable to those of many semifluorinated polyimides (6FDA-MPD: 3.0; 6FDA-7FMDA: 2.9; TFDA-p-APB:

2.89).^{16,28} The results suggested that $-\text{CF}_3$ groups in the polymer chain could improve the dielectric performance, and the polar pyridine moieties may also contribute to the dielectric constant because of its low polarizability resulting from the polar pyridine ring.²⁹

The water uptake of these polyimides was investigated, and the results are listed in Table IV. The data indicate that these polyimides exhibited low water uptake of 0.51–0.79%, which presents the negative influence of the moisture from the surrounding environment on dielectric properties. It can also be seen that polyimide PI-4 showed the lowest water uptake. The reason should be the introduction of the hydrophobic trifluoromethyl groups in the polyimide backbone.

CONCLUSION

A new pyridine-containing aromatic diamine monomer, 4-phenyl-2,6-bis[4-(4-amino-phenoxy)phenyl]-pyridine (PAPP), was successfully synthesized and characterized in the present work, which was employed in polycondensation of it with various aromatic dianhydrides, to prepare a series of pyridine-containing aromatic polyimides. Experimental results indicate that the resulting diamine monomer PAPP has good polymerizability, and transparent and tough polyimide films could be obtained. The novel polyimides 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, chloroform. Meanwhile, the films exhibited good dielectric properties and less than 1% water uptake.

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