

Syntheses and Properties of Polyimides Derived from Diamines Containing 2,5-Disubstituted Pyridine Group

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ABSTRACT: A series of novel homo- and copolyimides containing pyridine units were prepared from the heteroaromatic diamines, 2,5-bis(4-aminophenyl) pyridine and 2-(4-aminophenyl)-5-aminopyridine, with pyromellitic dianhydride (PMDA), and 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) via a conventional two-step thermal imidization method. The poly(amic acid) precursors have inherent viscosities of 1.60–9.64 dL/g ($c = 0.5$ g/dL in DMAC, 30°C) and all of them can be cast and thermally converted into flexible and tough polyimide films. All of the polyimides show excellent thermal stability and mechanical properties. The polyimides have 10% weight loss temperature in the range of 548–598°C in air. The glass transition temperatures of the PMDA-based samples are in the range

of 395–438°C, while the BPDA-based polyimides show two glass transition temperatures ($T_{g,1}$ and $T_{g,2}$), ranging from 268 to 353°C and from 395 to 418°C, respectively. The flexible films possess tensile modulus in the range of 3.42–6.39 GPa, strength in the range of 112–363 MPa and an elongation at break in the range of 1.2–69%. The strong reflection peaks in the wide-angle X-ray diffraction patterns indicate that the polyimides have a high packing density and crystallinity. The polymer films are insoluble in common organic solvents exhibiting high chemical resistance. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1844–1851, 2006

Key words: heteroaromatic polyimides; pyridine; thermal stability; mechanical properties

INTRODUCTION

Polyimides based on aromatic ring structures or their copolymers are well known as high performance polymers due to their excellent thermal and thermo-oxidative stabilities, outstanding mechanical, and electrical properties; therefore, all kinds of polyimides have been widely used in the fields of adhesives, coatings, films, fibers, composite matrix resins, as well as microelectronic materials.^{1–4} For the polyimide materials, syntheses of new heteroaromatic monomers and corresponding polyimides that have both good processability and thermal stability would be very interesting.^{5,6} In general, the choice of heteroaromatic structure in the main chain of the polymer is to impart certain properties to the polymer. The selection of pyridine nucleus is based on its high thermal stability derived from its molecular symmetry and aromaticity, as well as polarizability resulting from nitrogen atom in pyridine ring.^{7,8} So, new kinds of heteroaromatic diamine, dianhydride, or other monomers holding

pyridine unit should have contributions for the thermal stability, chemical stability, and retention of mechanical property of the resulting polymer.⁹ Consequently, some researchers have focused on the adoption of monomers containing pyridine nucleus to synthesize novel heteroaromatic polymers that have good thermostability and processability.^{10–20} To improve the processability of these polymers, the heteroaromatic monomers were designed with certain chemical structures, viz the introduction of 2,6-disubstituted pyridine rings, flexible linkage, such as ether, ester, benzoyl groups, and the bulky groups, e.g., naphthalene and trifluoromethyl group. But, the resulting polymers having greater tractability showed lower thermal stability and poorer chemical resistance.

In this work, we synthesized the heteroaromatic diamines containing 2,5-disubstituted pyridine, 2,5-bis(4-aminophenyl) pyridine (**3**) and 2-(4-aminophenyl)-5-aminopyridine (**6**). The diamines were employed in polycondensations with pyromellitic dianhydride (PMDA) and tetracarboxylic dianhydride (BPDA) to afford a series of novel homo- and copolyimides. The properties of these polyimides were also investigated. The pyridine-containing diamines **3** and **6** introduced a rigid rod-like and completely aromatic structure into the polymer backbone and enhanced the thermal stability.

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EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA, Beijing Chemical Reagents, China), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA, prepared in our laboratory), and 1,4-phenylenediamine (PDA, Shanghai Chemical Reagents, China) were purified by sublimation just before use. *N,N*-dimethylacetamide (DMAc, Tianjing Chemical Reagents, China) was dried over CaH₂ and then fractionally distilled under reduced pressure and stored over 4 Å molecular sieves. 1,3-bis(piperidinyl)-trimethinium tetrafluoroborate was prepared from piperidine and 1,1,3,3-tetramethoxypropane (4MP) in our laboratory. Potassium *tert*-butoxide (Aldrich), *p*-nitrophenylacetic acid (Acros), *p*-nitroacetophenone (Acros), and other reagents and solvents (from various commercial sources) were used as received.

Syntheses of diamines containing pyridine unit

Synthesis of 2,5-bis(4-nitrophenyl) pyridine (2)

A 1-L round-bottomed flask equipped with a stirring bar and reflux condenser was charged with **1** (104.34 g, 0.3 mol) and DMF (480 mL). Potassium *tert*-butoxide (33.93 g, 0.324 mol) was added to the solution in several portions, while maintaining the internal temperature below 15°C with ice water bath. Then a solution of 4-nitroacetophenone (49.54 g, 0.3 mol) in 300 mL of DMF was added dropwise and the mixture was agitated for 2 h at 55°C. After cooling to 30°C, ammonium acetate (92.4 g, 1.2 mol) was added to the mixture in one portion. Glacial acetic acid (72 g, 1.2 mol) was then added dropwise, while maintaining the internal temperature below 30°C. The flask was placed into an oil bath at 90°C and stirred for 3 h. After cooling to room temperature, the precipitate generated was collected on a glass-sintered funnel and washed with water and ethanol, dried in vacuum to gain 69.6 g (72.0% yield) of gray yellow crystal solid. ¹H NMR δ (600 MHz, DMSO-d₆): 9.20 (d, *J* = 2.4 Hz, 1H, H₈), 8.47 (d, *J* = 9.0 Hz, 2H, H₂ and H₆), 8.42 (dd, *J* = 8.4 and 2.4 Hz, 1H, H₁₀), 8.38 (d, *J* = 4.2 Hz, 2H, H₁₄ and H₁₆), 8.37 (d, *J* = 4.2 Hz, 2H, H₁₃ and H₁₇), 8.33 (d, *J* = 8.4 Hz, 1H, H₁₁), 8.15 (d, *J* = 9.0 Hz, 2H, H₃ and H₅) ppm. ¹³C NMR δ (100 MHz, DMSO-d₆): 153.68 (C₇), 148.33 (C₈), 147.87 (C₁₅), 147.27 (C₁), 143.78 (C₄), 142.80 (C₁₂), 136.06 (C₁₀), 133.17 (C₉), 128.12 (C₃ and C₅), 127.75 (C₁₃ and C₁₇), 124.11 (C₂ and C₆), 123.94 (C₁₄ and C₁₆), 121.50 (C₁₁) ppm. IR (KBr pellet): 1599, 1515, and 1469 (C=C, C=N); 1422 (NO₂, asym); 1343 (NO₂, sym); 856 (C—NO₂); 833 (Ar—H) cm⁻¹. Elemental anal. Calcd. for C₁₇H₁₁N₄O₄: C, 63.35; H, 3.44; N, 13.04. Found: C, 63.58; H, 3.35; N, 13.14.

Synthesis of 2,5-bis(4-aminophenyl) pyridine (3)

Hydrazine hydrate (30 mL; ≥80%) was added to a refluxing suspension of 10 g (31.03 mmol) of **2** and 2.0 g of 10% palladium-charcoal catalyst (Pd/C) in 900 mL of THF under nitrogen atmosphere. After the addition, the reaction proceeded for another 5 h under refluxing then cooled to room temperature. The Pd/C was filtered and the mother liquid was evaporated to dryness in vacuum, the residue was washed with water and cold ethanol, dried in vacuum to yield 7.87 g (97.5%) of light yellow crystal solid. mp: 236–237°C. MS (EI): *m/z* = 262.3 (M⁺). ¹H NMR δ (600 MHz, DMSO-d₆): 8.74 (d, *J* = 2.4 Hz, 1H, H₈), 7.87 (dd, *J* = 2.4 Hz and 8.4 Hz, 1H, H₁₀), 7.81 (d, *J* = 9.0 Hz, 2H, H₃ and H₅), 7.73 (d, *J* = 8.4 Hz, 1H, H₁₁), 7.43 (d, *J* = 8.4 Hz, 2H, H₁₃ and H₁₇), 6.67 (d, *J* = 8.4 Hz, 2H, H₁₄ and H₁₆), 6.64 (d, *J* = 9.0 Hz, 2H, H₂ and H₆), 5.39 (s, 2H, C₁-NH₂), 5.30 (s, 2H, C₁₅-NH₂) ppm. ¹³C NMR δ (75 MHz, DMSO-d₆): 154.43 (C₇), 150.13 (C₈), 149.22 (C₁₅), 146.42 (C₁), 133.57 (C₁₀), 133.21 (C₉), 127.65 (C₃ and C₅), 127.45 (C₁₃ and C₁₇), 126.55 (C₄), 124.67 (C₁₂), 118.50 (C₁₁), 114.87 (C₁₄ and C₁₆), 114.29 (C₂ and C₆) ppm. IR (KBr pellet): 3316 (NH₂, sym); 3205 (NH₂, asym); 1600; 1520 and 1472 (C=C, C=N); 822 (Ar—H) cm⁻¹. Elemental anal. Calcd. for C₁₇H₁₅N₄: C, 78.13; H, 5.79; N, 16.08. Found: C, 79.32; H, 4.41; N, 16.13.

Synthesis of 2-(4-nitrophenyl)-5-nitropyridine (5)

Triethylamine (15 mL) was added dropwise to a solution of **4** (20.35 g, 60 mmol) and 4-nitroacetophenone (8.26 g, 50 mmol) in 30 mL of acetonitrile while the temperature was kept below 10°C. After the mixture was stirred at room temperature for 3 h, 18.15 g of glacial acetic acid was added to the suspension while the temperature was kept below 30°C, then followed by the addition of 23.1 g of ammonium acetate (AcONH₄). The reaction mixture was heated to 50°C and kept at the temperature for 5 h, then cooled to room temperature and filtered. The crude product was washed with water and ethanol and then dried under reduced pressure to give 9.64 g (80.05%) of pale gray crystal solid. ¹H NMR δ (600 MHz, DMSO-d₆): 9.49 (d, *J* = 3.0 Hz, 1H, H₂), 8.74 (dd, *J* = 3.0 and 9.0 Hz, 1H, H₅), 8.46 (d, *J* = 8.4 Hz, 2H, H₈ and H₁₀), 8.42 (d, *J* = 9.0 Hz, 1H, H₄), 8.35 (d, *J* = 8.4 Hz, 2H, H₇ and H₁₁) ppm. ¹³C NMR δ (75 MHz, DMSO-d₆): 159.07 (C₃), 149.18 (C₉), 145.59 (C₆), 144.36 (C₂), 142.84 (C₁), 133.60 (C₅), 129.38 (C₇ and C₁₁), 124.66 (C₈ and C₁₀), 122.53 (C₄) ppm. IR (KBr pellet): 1593, 1576, 1513 and 1462 (C=C, C=N); 1418 (NO₂, asym.); 1345 (NO₂, sym.); 853 (C—NO₂); 844 (Ar—H) cm⁻¹. Elemental anal. Calcd. for C₁₁H₇N₃O₄: C, 53.88; H, 2.88; N, 17.14. Found: C, 52.30; H, 2.94; N, 16.88.

Synthesis of 2-(4-aminophenyl)-5-aminopyridine (6)

2-(4-Aminophenyl)-5-aminopyridine was prepared in a similar procedure to that of **3** with **5** instead of **2**, obtained as light yellow solid in 98% yield. mp: 194–196°C. MS (EI): $m/z = 186.2$ (M^+). $^1\text{H NMR } \delta$ (600 MHz, DMSO- d_6): 7.93 (d, $J = 3.0$ Hz, 1H, H_2), 7.59 (d, $J = 9.0$ Hz, 2H, H_7 and H_{11}), 7.41 (d, $J = 9.0$ Hz, 1H, H_4), 6.93 (dd, $J = 3.0$ and 9.0 Hz, 1H, H_5), 6.57 (d, $J = 9.0$ Hz, 2H, H_8 and H_{10}), 5.17 (s, 2H, $C_1\text{-NH}_2$), 5.12 (s, 2H, $C_6\text{-NH}_2$) ppm. $^{13}\text{C NMR } \delta$ (75 MHz, DMSO- d_6): 148.52 (C_3), 145.79 (C_9), 143.01 (C_1), 136.20 (C_2), 128.04 (C_6), 126.46 (C_7 and C_{11}), 121.63 (C_4), 118.98 (C_5), 114.38 (C_8 and C_{10}) ppm. IR (KBr pellet): 3317 (NH_2 , sym), 3204 (NH_2 , asym); 1607, 1515, and 1479 ($\text{C}=\text{C}$, $\text{C}=\text{N}$); 834 ($\text{Ar}=\text{H}$) cm^{-1} . Elemental anal. Calcd. for $\text{C}_{11}\text{H}_{11}\text{N}_3$: C, 71.33; H, 5.99; N, 22.68. Found: C, 71.22; H, 5.51; N, 22.59.

General procedure for the syntheses of polymers

The polyimides were synthesized from the two diamines (**3** or **6**) with PMDA and BPDA via a conventional two-step thermal imidization method. The synthesis of PI-3 is described as an example of the general synthetic route for the polyimides. To a solution of 0.5227 g (2 mmol) of **3** and 0.2162 g (2 mmol) of PDA in 31 mL of CaH₂-dried DMAc under nitrogen atmosphere 0.8728 g (4 mmol) of PMDA was added in one portion. The mixture was stirred at ambient temperature for about 24 h under nitrogen atmosphere to afford a highly viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) was 7.41 dL/g as measured in DMAc at a concentration of 0.5 g/dL at 30°C.

The proper quantity of the poly(amic acid) solution was cast on a glass plate and placed in an oven maintained at 60°C overnight to remove most of the solvent. The semidried poly(amic acid) film was converted into the polyimide film by sequential heating at 80°C for 1 h and at 150, 200, 250, 300, 350, and 400°C each for 0.5 h under vacuum. The film was removed from the glass plate by soaking in hot water.

Measurements

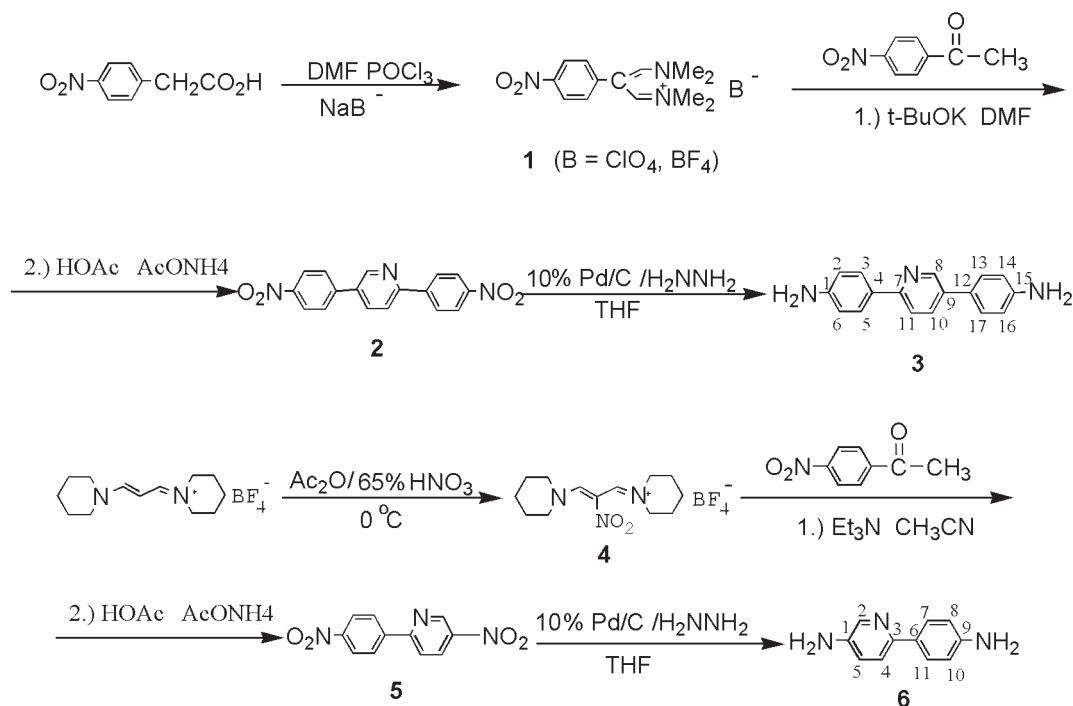
$^1\text{H NMR}$ (600 MHz) and $^{13}\text{C NMR}$ (75 or 100 MHz) were taken on a Varian Unity spectrometer with tetramethylsilane as an internal standard. Fourier transform infrared (FTIR) spectra were obtained with Bio-Rad Digilab Division FTS-80 FTIR spectrometer. Elemental analyses were measured with an elemental analyzer MOD-1106 (Italyd). MS spectra were given by a Bruker BIFLEX mass spectrometer. The melting points of the prepared monomers were determined on an XT-4 melting point apparatus (Beijing Taike Apparatus) and were uncorrected. The inherent viscosities

of the polymers were measured with an Ubbelohde viscometer at a concentration of 0.5 g/dL in DMAc at 30°C. Thermogravimetric analysis (TGA) was done with a Perkin-Elmer TGA-2 at a heating rate of 10°C/min in air. Dynamic mechanical thermal analysis (DMTA) was performed on a dynamic mechanical analyzer (Rheometric Scientific Inc.) using film samples in tensile mode at a heating rate of 5°C/min and a frequency of 1 Hz. The wide-angle X-ray diffraction (WAXD) measurements were undertaken on a Rigaku max 2500 V PC X-ray diffractometer (Japan) with Cu $K\alpha$ radiation (40 kV 200 mA) with a scanning rate of 2°/min from 2° to 60°. The tensile measurements were carried out at room temperature in air using an Instron model 1122 at a drawing rate of 5 mm/min.

RESULTS AND DISCUSSIONS

Syntheses of diamines containing pyridine unit

The heteroaromatic diamines **3** and **6** were synthesized by three-step reactions according to Schemes 1 and 2, respectively. **1**^{21,22} and **4**^{23,24} were prepared according to the reported methods. The annulations of 4-nitroacetophenone with the vinamidinium salts in the presence of hot ammonium acetate/acetic acid give the 2,5-disubstituted pyridines in excellent yields.^{25–27} The nitro compounds were converted into the diamines **3** and **6** by the Pd-catalyzed hydrazine reduction. NMR, IR spectroscopy, elemental analysis, and MS spectrometry were employed to confirm the structures of **3** and **6**. The values of elemental analysis are in good agreement with the calculated ones. The molecular weight determined by mass spectrometry was 262.3 and 186.2, which agreed with the calculated ones (M^+). In the FTIR spectrum, **2** displayed the absorption bands representative of the nitro group at 1422 (asymmetric stretching) and 1343 cm^{-1} (symmetric stretching). After reduction, the aromatic primary amine absorption at 3316 and 3205 cm^{-1} were identified and the bands for nitro group disappeared. The structures of **2** and **3** were also corroborated by high-resolution NMR spectra. The $^1\text{H NMR}$ demonstrated that the nitro groups were completely converted into amino groups by the high-field shift of the aromatic protons and by the signals at 5.39 and 5.30 peculiar to amino protons. In the $^{13}\text{C NMR}$ spectra, upfield shifts of the phenyl carbon resonance were observed in diamine **3** because of the resonance effect caused by the electron-donating amino group. The $^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra of **2** and **3** also confirm that they have completely aromatic structure containing pyridine ring. The two ring compounds **5** and **6** exhibited the similar characteristic peaks. Thus, all the spectroscopic data obtained are in good agreement with the proposed chemical structures.



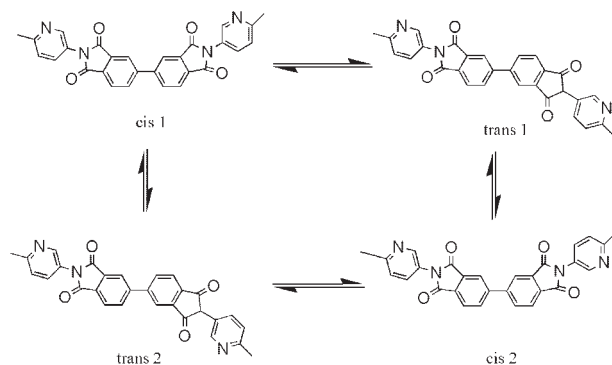
Scheme 1 Syntheses of pyridine containing diamines 3 and 6.

Syntheses and characterization of polymers

The novel polyimides were prepared by a two-stage method. The homo-polyimides were prepared by the polycondensation of 3 (or 6) and PMDA (or BPDA). In the case of the copolymers, a mixture of diamines at a designated ratio with PMDA or BPDA was used. The inherent viscosities of PAA precursors based on 3 were 2.04–9.64 dL/g ($c = 0.5$ g/dL, in DMAc, 30°C), while the inherent viscosities of PAA based on 6 were 1.60–6.78 dL/g ($c = 0.5$ g/dL, in DMAc, 30°C). All of the PAA precursors could be cast into flexible and tough PAA films, which could be subsequently converted into tough polyimide films by extended heating at elevated temperature. The inherent viscosities

of PAA precursors are summarized in Table I along with the thermal properties of the PI films.

The PAA solution afforded flexible and tough films in all cases after being cast and cured. The structures of the PIs are shown in Figure 1. The complete imidization was confirmed by the FTIR spectroscopy as shown in Figure 2, where the characteristic bands of the imide carbonyl were at around 1772–1782 cm^{-1} (asym C=O, stretching), 1705–1714 cm^{-1} (sym C=O, stretching), 1342–1360 cm^{-1} (C–N, stretching), 1073–1095 cm^{-1} , and 719–735 cm^{-1} (imide ring formation). The disappearance of amide and carbonyl bands at 1700–1650 cm^{-1} and 3500–2800 cm^{-1} indicate a virtually complete conversion of PAA precursor into the PIs. The colors of the PMDA-based polyimide films were deep yellow; whereas, the polyimide films based on BPDA were light yellow.



Scheme 2 The transformations of different conformations of polyimides based on BPDA.

Solubility of polyimides

The solubility behavior of the polyimides generally depends on their chain packing density and intermolecular interactions, which are affected by the rigidity symmetry and regularity of the molecular backbone. All of the films are almost insoluble in the organic solvents examined in this study and exhibit high chemical resistance. This nature can be explained by the strong interaction between polymer chains that are highly stacked on each other because of the rigidity of the polymer backbone. All of the PI films based on

TABLE I
Thermal Properties of Polyimides

Code	PIs	η^a_{inh} (dL/g) of PAA	T_{β} (°C) ^b	T_g1 (°C) ^b	T_g2 (°C) ^b	In air ^c	
						T_5 (°C)	T_{10} (°C)
PI-1	PMDA-PDA/3 (0/100)	9.64	Ud ^d	Ud	405	549	566
PI-2	PMDA-PDA/3 (25/75)	9.03	Ud	Ud	419	527	548
PI-3	PMDA-PDA/3 (50/50)	7.41	Ud	Ud	438	545	569
PI-4	PMDA-PDA/3 (75/25)	7.25	180	Ud	425	539	562
PI-5	BPDA-PDA/3 (0/100)	3.23	178	353	417	558	578
PI-6	BPDA-PDA/3 (25/75)	2.44	172	322	407	573	588
PI-7	BPDA-PDA/3 (50/50)	2.38	162	268	395	572	582
PI-8	BPDA-PDA/3 (75/25)	2.04	176	292	418	577	598
PI-9	PMDA-PDA/6 (0/100)	6.78	Ud	Ud	395	532	548
PI-10	PMDA-PDA/6 (25/75)	6.20	Ud	Ud	410	550	565
PI-11	PMDA-PDA/6 (50/50)	5.71	159	Ud	413	545	564
PI-12	PMDA-PDA/6 (75/25)	5.49	174	Ud	411	540	561
PI-13	BPDA-PDA/6 (0/100)	1.99	192	336	414	552	574
PI-14	BPDA-PDA/6 (25/25)	1.78	185	320	403	560	580
PI-15	BPDA-PDA/6 (50/50)	1.68	177	325	ud	547	567
PI-16	BPDA-PDA/6 (75/25)	1.60	175	325	ud	550	569

^a Inherent viscosity of PAA measured with 0.5g/dL in DMAc at 30°C.

^b Obtained from DMTA at a heating rate of 5°C/min at 1Hz.

^c 5% and 10% weight loss in air obtained from TGA at a heating rate of 10°C/min.

^d Undetected.

BPDA could be dissolved in concentrated sulfuric acid at room temperature, which suggests that these polyimide films have no crosslinked structure and weaker interaction between polymer chains caused by the flexible dianhydride moiety. In the case of PI films prepared from PMDA after being immersed in the concentrated H₂SO₄ at room temperature for 3 days, the films of PI-1, PI-2, PI-9, and PI-10 were dissolved completely while PI-3, PI-4, PI-11, and PI-12 were broken into small pieces. The difference in solubility behavior of the copolyimides might be caused by the concentration of the pyridine units in the backbone. The basicity of the pyridine makes it easier to be dissolved in the sulfuric acid.

Thermal properties of polyimides

The thermal stability of the polyimide films were estimated by the 5% (T_5) and 10% (T_{10}) weight loss temperature measured by a thermogravimetric ana-

lyzer (TGA) at a heating rate of 10°C/min in air atmosphere. The results are tabulated in Table I and the typical TGA curves are reproduced in Figure 3. The polyimides have a 10% weight loss temperature in the range of 548–598°C in air, while some of them showed 5% weight loss temperature over 570°C, indicating that the heteroaromatic structure enhances the thermal and thermooxidative stability of the polyimides. In general, the high thermal stability is due to the presence of the rigid backbone structure in the polyimides. But T_5 and T_{10} do not change much with the increase of the molar ratio of rigid rod-like PDA, confirming that the pyridine units may have critical influence on the thermal stability of the polymer.

The glass transition temperature (T_g) was determined in air using dynamic mechanical thermal analyzer with a heating rate of 5°C/min in air. The typical DMTA curves are shown in Figure 4 and the results are listed in Table I. All of the homo- and copolyimides do not show discernible glass transitions on the

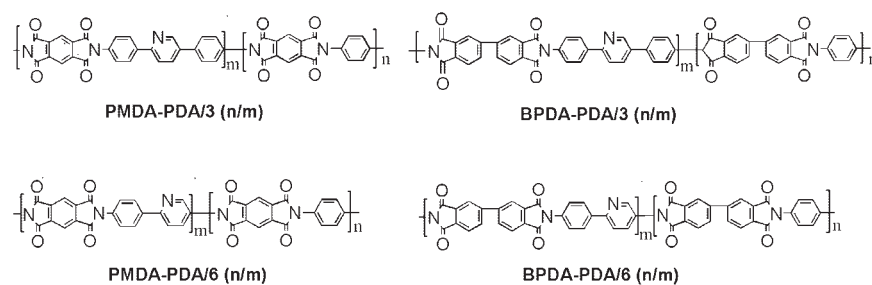


Figure 1 Chemical structures of polyimides (n/m : molar ratio).

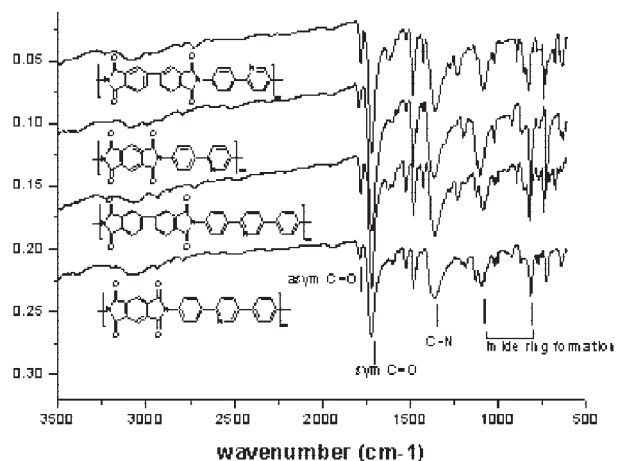


Figure 2 Thin film FTIR spectra for PI-1, PI-5, PI-9, and PI-13.

DSC thermograms possibly because of the low thermal effect during the transition of some rigid rod polyimides and their high level of crystallinity. The T_g values of the PMDA-based polyimide films range from 395 to 438°C, while the BPDA-based polyimides (except PI-15 and PI-16) show two glass transition temperatures (T_{g1} and T_{g2}) ranging from 268 to 353°C and from 395 to 418°C, respectively. Most of the polyimides exhibit T_{β} ranging from 159 to 205°C except PI-1, PI-2, PI-3, PI-9, PI-10. That the BPDA-based polyimides exhibited two T_g may be attributed to the flexible BPDA moiety that can rotate around the main chain of polymers. As shown in Scheme 2, the kinked (cis) conformation of BPDA could be transformed into the extended (trans) conformation by rotation around the central single bond during the thermal process at elevated temperature.²⁸ The pyridine ring has one nitrogen atom that decreases the symmetry elements of the polyimides containing pyridine units, so the

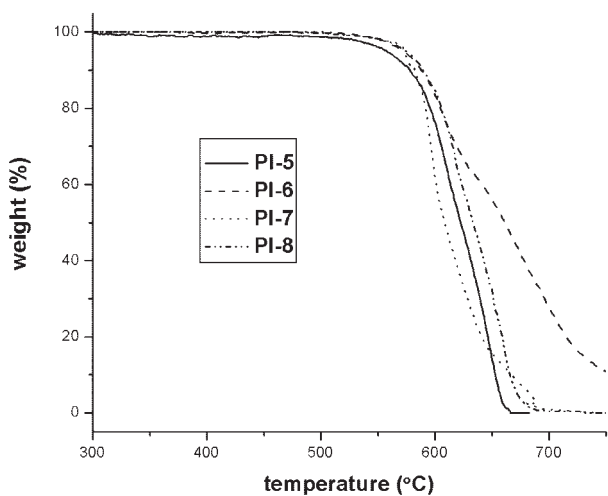


Figure 3 Typical TGA curves of polyimides.

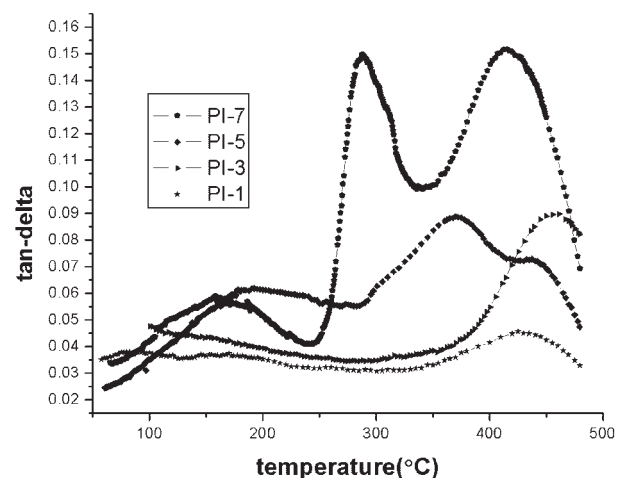
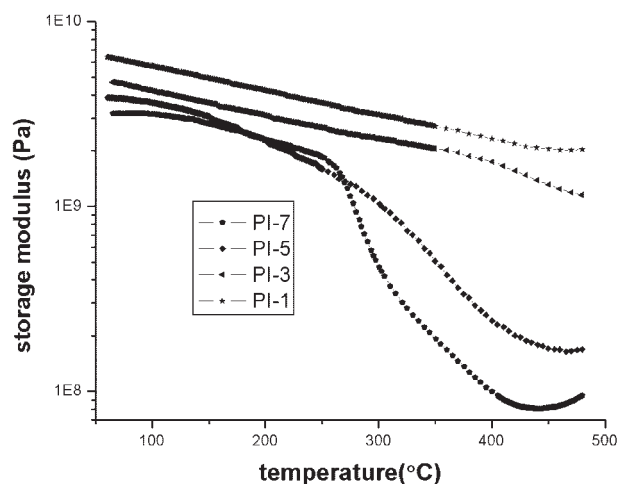


Figure 4 Typical dynamics mechanical thermal analysis (DMTA) plots for polyimides.

polyimides based on the relative flexible dianhydride (BPDA) may show the transformation between four conformations at high temperature resulting in two glass transition temperatures. It is a pity that we have not found a scientific proof to verify our explanation yet due to the very poor solubility of these polyimides.

Mechanical properties of polyimides

The mechanical properties of the polyimide films were determined using a tensile tester and were evaluated using their stress-strain profiles. The results are reported in Table II. The polyimides have tensile strength at break of 112–363 MPa elongations at break of 1.2–69% and initial modulus of 3.42–6.39 GPa, indicating the PIs containing pyridine have excellent mechanical properties. As shown in Table II, the elongations and strength of polyimides based on BPDA are much higher than those of polyimide films based on PMDA while there is no obvious difference be-

TABLE II
Mechanical Properties of Polyimides

Code	Pis	Elongation at break ^a (%)	Strength at break ^a (MPa)	Tensile modulus ^a (GPa)
PI-1	PMDA-PDA/3 (0/100)	16	202	4.71
PI-2	PMDA-PDA/3 (25/75)	22	137	3.82
PI-3	PMDA-PDA/3 (50/50)	20	232	4.46
PI-4	PMDA-PDA/3 (75/25)	8.6	241	6.00
PI-5	BPDA-PDA/3 (0/100)	58	304	4.06
PI-6	BPDA-PDA/3 (25/75)	69	349	4.29
PI-7	BPDA-PDA/3 (50/50)	49	207	3.42
PI-8	BPDA-PDA/3 (75/25)	45	316	4.59
PI-9	PMDA-PDA/6 (0/100)	5.8	183	4.95
PI-10	PMDA-PDA/6 (25/75)	4.1	167	5.96
PI-11	PMDA-PDA/6 (50/50)	4.0	134	6.39
PI-12	PMDA-PDA/6 (75/25)	1.9	112	6.8
PI-13	BPDA-PDA/6 (0/100)	41	363	5.2
PI-14	BPDA-PDA/6 (25/25)	52	300	3.42
PI-15	BPDA-PDA/6 (50/50)	50	239	3.71
PI-16	BPDA-PDA/6 (75/25)	50	322	4.00

^a Measured at room temperature in air using an Instron model 1122 at a drawing rate of 5 mm/min.

tween the polyimides based on the same dianhydride, implying the difference of elongations may be due to the relatively flexible dianhydride component. As shown in DMTA curves (Fig. 4), the storage modulus decrease slightly at high temperature, especially for the polyimides prepared from PMDA, and the polyimides without PDA moiety exhibit the highest storage modulus above 400°C, indicating that the pyridine component strengthen the mechanical properties of polyimides at high temperature.

X-ray diffraction data of polyimides

The crystallinity of the prepared polyimides was evaluated by WAXD scans. The representative WAXD patterns of the thermally cured polyimide films are presented in Figure 5. As expected, all of the polyimides except PI-16 reveal a strong peak reflection at 2θ values of about 20°. This indicates that these polyimides have a high packing density. PI-5, PI-6, PI-13, and PI-14 exhibit two strong peak reflections at 2θ values of about 15° and 25°, which are indicative of higher crystallinity. These results confirm the rigid structure of the polyimides; also offer an explanation for the poor solubility and high T_g values of them.

CONCLUSIONS

Heteroaromatic diamines **3** and **6** were synthesized by the annulations reaction of vinamidium salts and 4-nitroacetophenone, followed by hydrazine palladium catalyzed reduction in the reasonable high yield. The diamines were polycondensed with aromatic tetracarboxylic dianhydrides in DMAc. The polymerization proceeded homogeneously and gave the poly(amic

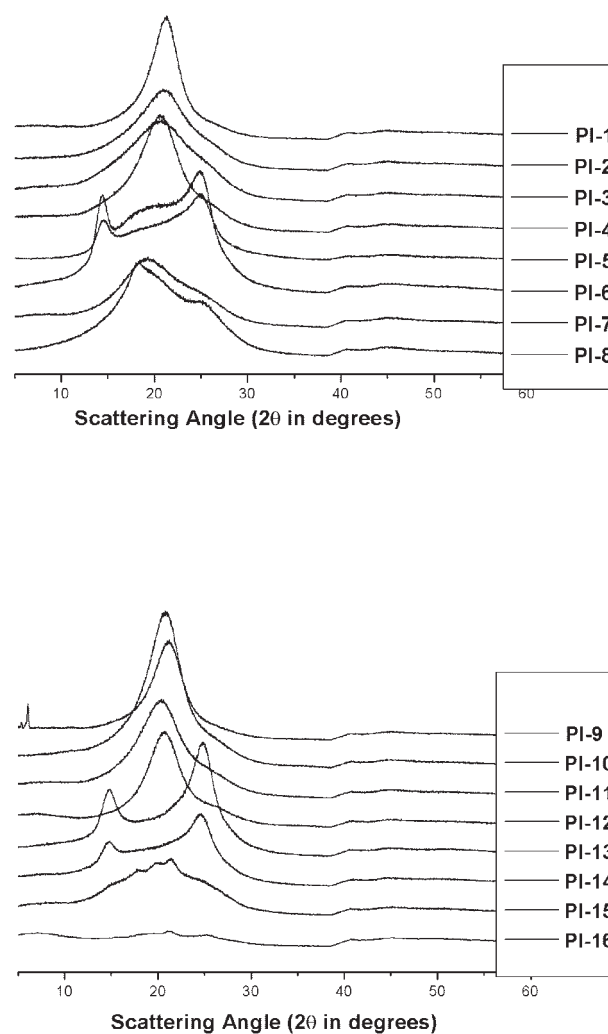


Figure 5 WAXD curves for polyimides.

acid)s that showed an inherent viscosity range of 1.60–9.64 dL/g ($c = 0.5$ g/dL in DMAC, 30°C). The corresponding polyimides were obtained as flexible films by curing the semidried poly(amic acid) films. The polyimide films show excellent thermal stability and mechanical properties. The characteristics were considered to be due to the introduction of the aromatic and rigid structure containing pyridine into the polymer backbone. The films were insoluble in common organic solvents, exhibiting high chemical resistance.

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