

Synthesis, Characterization, Thermal and Optical Properties of Soluble Polyimides Derived from an Unsymmetrical Diamine

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ABSTRACT: A new unsymmetrical diamine monomer, 2,4-diaminophenyl [4'-(2'',6''-diphenyl-4''-pyridyl)phenyl]ether, was successfully synthesized by nucleophilic substitution of 1-chloro-2,4-dinitrobenzene with 4-(2',6'-diphenyl-4'-pyridyl) phenol. The diamine monomer was characterized by FTIR, ¹H and ¹³C NMR, and elemental analysis techniques and used for the preparation of novel polyimides (PIs) by reaction with commercially available tetracarboxylic dianhydrides such as pyromellitic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, and bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride. These PIs with in-

herent viscosities ranged from 0.43 to 0.48 dL/g were readily soluble in many organic solvents and afforded tough and flexible films by solution casting. These polymers exhibited T_g s between 237 and 294°C, and 10% weight loss temperatures in excess of 500°C with up to 56% char yield at 600°C in air. Their maximum fluorescence emission in dilute (0.2 g/dL) NMP solution appeared at 450 nm. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3407–3415, 2010

Key words: polyimide; polycondensation; thermal properties; solubility

INTRODUCTION

Aromatic PIs generally possess excellent thermal, mechanical, electrical, and chemical properties. Therefore, they are being used in many applications such as electrics, coatings and adhesives, composite material, and membranes. However, these polymers are difficult to process because of their high transition temperatures (T_g , T_m) and limited solubility in organic solvents.^{1,2} To overcome these problems, much of research efforts have been focused on the enhancing the solubility of PIs, and this has included the incorporation of flexible linkages,^{3–5} the introduction of noncoplanar groups,⁶ or unsymmetrical structure into the polymer backbone.^{7,8} Generally, one of the successful approaches to increase the solubility and processability of PIs without sacrificing high thermal stability is the introduction of bulky pendent groups into polymer backbone.^{9–16} 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 thermooxidative stability. On the other hand, some reports have concerned the incorporation of pyridine

and its derivatives into polymeric frameworks.^{17–21} The rigidity based on the symmetry and aromaticity of the pyridine ring would contribute to the thermal and chemical stability, retention of mechanical properties of the resulting polymer at elevated temperatures, and the polarizability resulting from the nitrogen atom in pyridine ring would be suitable to improve their solubility in organic solvents.²² The meta-catenation is one of the aspects of improvement in processability and solubility. However, the introduction of these kinds of monomers, so that monomeric units become symmetrically nonequivalent, and the unequal reactivity of monomer unit functional groups leads to the formation of different size sequences which influences the final polymer properties.²³

Most of aromatic PIs are prepared by reaction between symmetric diamine and dianhydride monomers, whereas PIs from asymmetrically substituted *m*-phenylene diamine monomers have been relatively less explored. So to prepare novel processable PIs with enhanced thermal stability, new asymmetric diamine monomer containing pyridine ring bearing bulky aromatic groups in the 2, 4, 6 positions as pendent was synthesized and used in polycondensation with three tetracarboxylic dianhydrides. The PIs were characterized by spectroscopic and elemental analysis techniques and also their inherent viscosity, solubility, thermal and optical properties were studied.

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EXPERIMENTAL

Materials

N-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), acetic anhydride, and pyridine were purchased from Merck and purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieve. Pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), and bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCDA) were dried in a vacuum oven at 110°C for 5 h. All other solvents such as *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), pyridine, and dimethyl sulfoxide (DMSO), and materials such as 1-chloro-2,4-dinitro benzene, ammonium acetate, hydrazine monohydrate, and 10% palladium on activated carbon were purchased from Merck and used as received.

Measurements

Melting points were recorded on an electrothermal Stuart SMP3. FTIR spectra were recorded by using a Bruker Tensor 27 spectrometer on KBr pellets. The ¹H NMR and ¹³C NMR spectra were recorded on a 500 MHz Bruker Advance DRX instrument using DMSO-*d*₆ as solvent and tetramethylsilane as an internal reference. Elemental analyses were run in a Flash EA 1112 series. Thermogravimetric analysis (TGA) in the temperature range of 50–600°C was carried out with TGA-50 analyzer at a heating rate of 10°C/min under air atmosphere. Differential scanning calorimeter (DSC) was recorded on a Perkin Elmer pyris 6 DSC under nitrogen atmosphere (20 cm³/min) at a heating rate of 10°C/min. The inherent viscosities ($\eta_{inh} = \ln \eta_{rel}/C$) of the PIs were determined for the solutions of 0.5 g/dL in NMP at 25°C using an Ubbelohde viscometer. UV-vis spectra of the PIs dilute (0.2 g/dL) solutions in NMP were recorded on a Cecil 5503 spectrophotometer, and the fluorescence spectra were recorded on a Perkin Elmer LS-3B spectrophotometer. X-ray powder diffraction (XRD) patterns of the PIs were recorded by an X-ray diffractometer (XRD, GBC MMA Instrument) with Be-filtered Cu K α radiation (1.5418 Å) operating at 35.4 kV and 28 mA. The scanning range of 2 θ was set between 4° and 50° with a scan rate of 0.05 degree/second.

Monomer synthesis

4-(2',6'-Diphenyl-4'-pyridyl) phenol

OHP was synthesized according to the procedure given in the literature.²⁴

2,4-Dinitrophenyl [4'-(2'',6''-diphenyl-4''-pyridyl) phenyl] ether

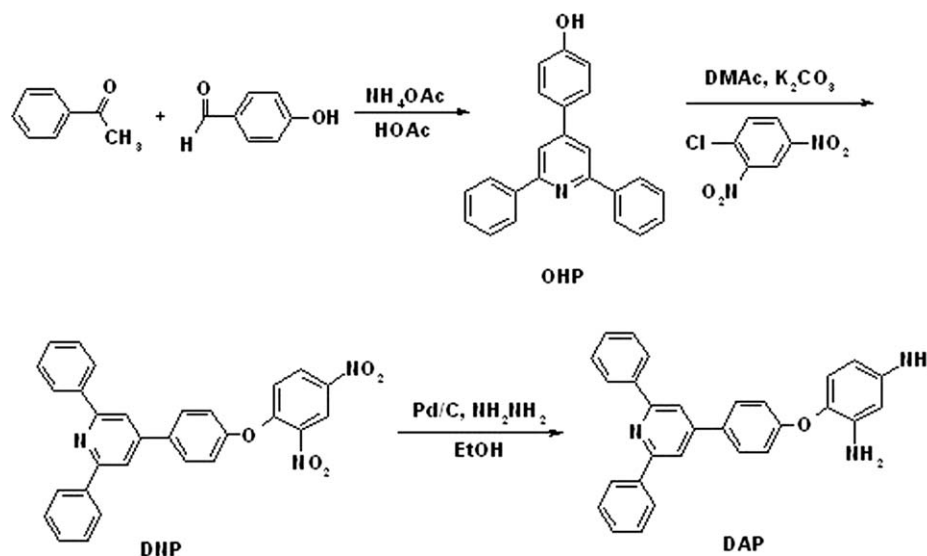
In a 250 mL three-necked round-bottomed flask equipped with a magnetic stirring bar, a condenser with guard tube, and a nitrogen inlet tube, 6.43 g (0.02 mol) OHP and 4.1 g (0.02 mol) 1-chloro-2,4-dinitrobenzene were dissolved in 50 mL DMAc, and 4.14 g (0.03 mol) potassium carbonate was added to the solution. After 30 min stirring at room temperature, the mixture was heated at 110°C for 8 h. The mixture was poured in 100 mL of methanol, and the yellow precipitate was filtered off, washed with water and dried. The crude product was recrystallized from methanol and after collection by filtration and drying; 8.9 g (yield 93%) product with melting point of 215–217°C was obtained. Anal. Calcd for C₂₉H₁₉N₃O₅: C, 71.16%; H, 3.91%; N, 8.58%. Found: C, 71.02%; H, 3.56%; N, 8.45%. FTIR(KBr, cm⁻¹): ν 1602 (C=N), 1540 and 1344 (NO₂), and 1200 (C—O—C). ¹H NMR (DMSO-*d*₆, ppm): δ 8.95 (s, 1H), 8.51 (d, 1H, *J* = 9.2 Hz), 8.36 (d, 4H, *J* = 7.2 Hz), 8.25 (m, 4H), 7.57 (m, 4H), 7.48 (d, 2H, *J* = 8.7 Hz), 7.51 (d, 2H, *J* = 8.7 Hz), 7.33 (d, 1H, *J* = 9.2 Hz).

2,4-Diaminophenyl [4'-(2'',6''-diphenyl-4''-pyridyl) phenyl] ether

In a 250 mL three-necked round-bottomed flask equipped with magnetic stirring bar, a condenser with guard tube, a dropping funnel, and a nitrogen inlet tube, a mixture of 9.8 g (0.02 mol) DNP and 0.2 g palladium on activated carbon (Pd/C, 10%) was dispersed in 100 mL ethanol. The suspension solution was heated to reflux, and 9 mL hydrazine monohydrate was added drop-by-drop to the mixture. After a further 5 h reflux, the solution was filtered hot to remove Pd/C, and the filtrate was cooled to precipitate white crystals, which were collected by filtration and dried in vacuum at 80°C. The yield was 72% (6.2 g) and mp. 168–170°C. Anal. Calcd for C₂₉H₂₃N₃O: C, 81.09%; H, 5.40%; N, 9.78%. Found: C, 80.84%; H, 5.26%; N, 9.45%. FTIR (KBr cm⁻¹): ν 3442 and 3357 (NH₂), 1622 (C=N) and 1229 (C—O—C). ¹H NMR data (DMSO-*d*₆, ppm): δ 8.32 (d, 2H, *J* = 7.1 Hz), 8.14 (s, 2H), 7.98 (d, 2H, *J* = 8.8 Hz), 7.55 (t, 6H), 7.49 (d, 2H, *J* = 7.1 Hz), 6.61 (d, 1H, *J* = 8.3 Hz), 6.09 (s, 1H), 5.88 (d, 1H, *J* = 8.3 Hz), 4.76 (s, 2H, —NH₂), 4.62 (s, 2H, —NH₂).

Polyimide synthesis

A typical two-step method was applied for preparation of the PIs. In a 50 mL three-necked round-bottomed flask equipped with a nitrogen gas inlet tube, a condenser with guard tube, and a magnetic stirrer bar, 0.8 mmol dianhydride was gradually added to a stirred solution of 1.03 g (0.8 mmol) 2,4-



Scheme 1 Synthesis of 2,4-diaminophenyl [4'-(2'',6''-diphenyl-4''-pyridyl) phenyl] ether, DAP.

diaminophenyl [4'-(2'',6''-diphenyl-4''-pyridyl)phenyl] ether (DAP) in 15 mL NMP at 5°C. The mixture was stirred for 24 h at room temperature under nitrogen atmosphere to obtain a viscous poly (amic acid) (PAA) solution. To above solution was added 2 mL acetic anhydride and 1 mL pyridine. The stirring was continued for 1 h at room temperature and 8 h at 130°C. The polymer was precipitated by pouring the solution into 500 mL methanol, and the precipitated polymer was then filtered, washed with hot water and methanol repeatedly, and then dried in a vacuum oven at 120°C for 24 h.

PI-a

Yield = 90%, $\lambda_{\text{max(ab)}}$ = 307 nm, and $\lambda_{\text{max(em)}}$ = 453 nm. FTIR (KBr, cm^{-1}): 3059 (aromatic C—H stretching), 1779 (C=O asymmetric stretching), 1732 (C=O symmetric stretching), 1548 (C=N stretching), 1498 (C=C stretching), 1368 (C—N stretching), 1244 (C—O—C stretching), 1170, 1021, 828, 724 (imide ring deformation). ^1H NMR (DMSO-*d*₆, ppm): δ 7.08–8.61 (m, aromatic H). Anal. calcd for $(\text{C}_{39}\text{H}_{21}\text{N}_3\text{O}_6)_n$: C, 76.59; H, 3.46; N, 6.87. Found: C, 76.14; H, 3.61; N, 6.47.

PI-b

Yield = 92%, $\lambda_{\text{max(ab)}}$ = 307 nm, and $\lambda_{\text{max(em)}}$ = 456 nm. FTIR (KBr, cm^{-1}): 3060 (aromatic C—H stretching), 1782 (C=O asymmetric stretching), 1729 (C=O symmetric stretching), 1682 (C=O), 1547 (C=N), 1500 (C=C stretching), 1359 (C—N stretching), 1244 (C—O—C stretching), 1097, 1020, 852, 722 (imide ring deformation). ^1H NMR (DMSO-*d*₆, ppm): δ 7.05–8.82 (m, aromatic H). Anal. calcd for $(\text{C}_{46}\text{H}_{25}\text{N}_3\text{O}_6)_n$: C, 77.20; H, 3.52; N, 5.87. Found: C, 76.95; H, 3.66; N, 5.41.

PI-c

Yield = 88%, $\lambda_{\text{max(ab)}}$ = 292 nm, and $\lambda_{\text{max(em)}}$ = 440 nm. FTIR (KBr, cm^{-1}): 3054 (aromatic C—H stretching), 2958 (C—H aliphatic), 1780 (C=O asymmetric stretching), 1718 (C=O symmetric stretching), 1595 (C=N), 1368 (C—N stretching), 1251 (C—O—C stretching), 1114, 915, 767, 721 (imide ring deformation). ^1H NMR (DMSO-*d*₆, ppm): δ 7.08 (m, 19H), 6.12 (m, 2H), 2.75 (m, 4H), 2.51 (m, 2H). Anal. calcd for $(\text{C}_{41}\text{H}_{27}\text{N}_3\text{O}_5)_n$: C, 76.74; H, 4.24; N, 6.55. Found: C, 76.48; H, 4.36; N, 6.29.

RESULTS AND DISCUSSION

Monomer synthesis and characterization

The starting material, 4-(2'',6''-diphenyl-4''-pyridyl) phenol (OHP), was synthesized according to the literature with a yield of 80%.²⁴ The dinitro compound, 2,4-dinitrophenyl [4'-(2'',6''-diphenyl-4''-pyridyl) phenyl] ether (DNP), was synthesized by the nucleophilic substitution reaction of OHP with 1-chloro-2,4-dinitrobenzene. The DNP compound was subsequently reduced to afford the DAP monomer. The reaction pathway is shown in Scheme 1. The structure of DAP monomer was confirmed by FTIR, ^1H NMR, and ^{13}C NMR spectroscopy. The FTIR spectrum of DNP compound, Figure 1(a), shows characteristic absorption bands at 1540 and 1344 cm^{-1} due to asymmetric and symmetric —NO₂ stretching vibration which disappeared after reduction. The FTIR spectrum of DAP monomer, Figure 1(b), shows the characteristic absorption bands at 3442, 3357 cm^{-1} which are related to N—H stretching. Figure 2 shows ^1H NMR spectrum of DNP compound, in which all the protons were assigned. In addition, the elemental analysis values were in

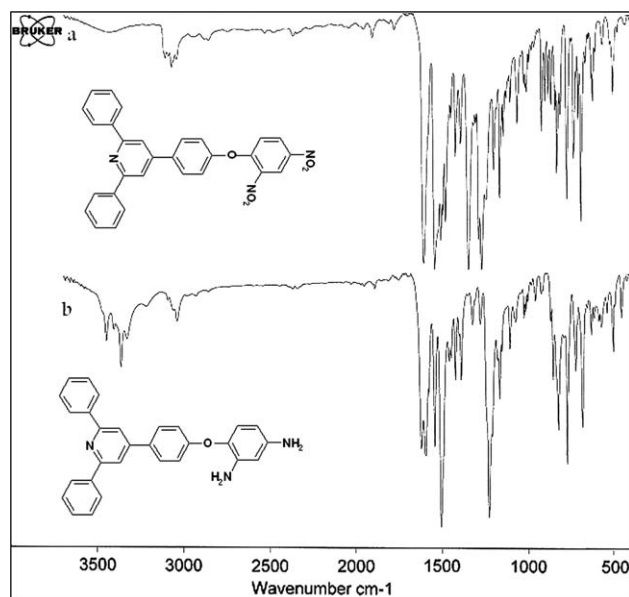


Figure 1 FTIR spectra of DNP and DAP.

close agreement with the calculated ones. The ^1H and ^{13}C NMR spectra of DAP monomer are shown in Figures 3 and 4, respectively. ^1H NMR signals at δ : 4.76 and 4.62 ppm correspond to $-\text{NH}_2$ protons. Aromatic protons are appeared at range of 5.88–8.32 ppm and protons of H_3 and H_4 resonated at the higher field than other aromatic protons because of the electron-donating property of the amino groups.

The ^{13}C NMR spectrum of DAP monomer show 17 signals, which resonated in the regions of 102.1–161.0 ppm. The assignments of each proton and carbon agree well with the proposed molecular structure of DAP monomer.

Polyimides synthesis and characterization

The new PIs were prepared in good yields by polycondensation of equal molar amounts of DAP with commercially available dianhydrides such as PMDA, BTDA, and BCDA as outlined in Scheme 2. The polycondensation was carried out in NMP at room temperature for 24 h to form PAAs, followed by chemical imidization with acetic anhydride and pyridine is a convenient method on a laboratory scale.²⁵ The inherent viscosity of the polyimides, as a suitable criterion for evaluation of molecular weight, was measured at a concentration of 0.5 g/dL in NMP at 25°C. The inherent viscosities of PIs were in the range of 0.43–0.46 dL/g, which indicate moderate molecular weight.²⁰ The FTIR spectra of the resulting PIs revealed the characteristic strong absorption bands at 1783 and 1729 cm^{-1} which are related to the asymmetric and symmetric vibrations of the two carbonyl groups of imide rings indicating the complete formation of the imide ring. The ^1H NMR spectrum of the representative polyimide (PI-b) is shown in Figure 5. As it can be seen, the signals of aromatic

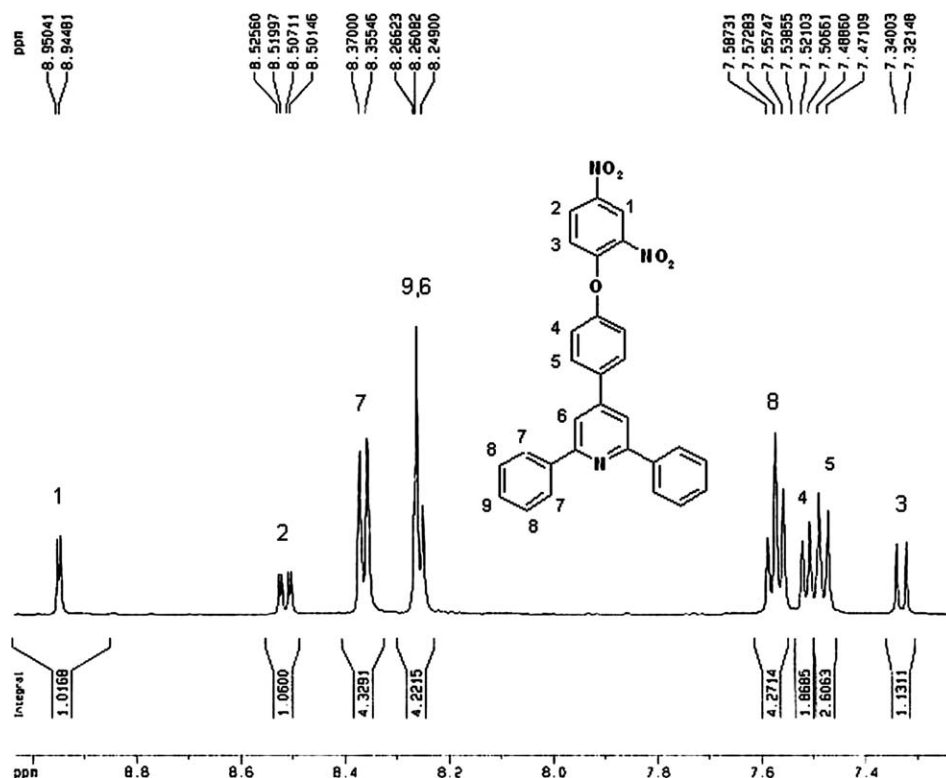
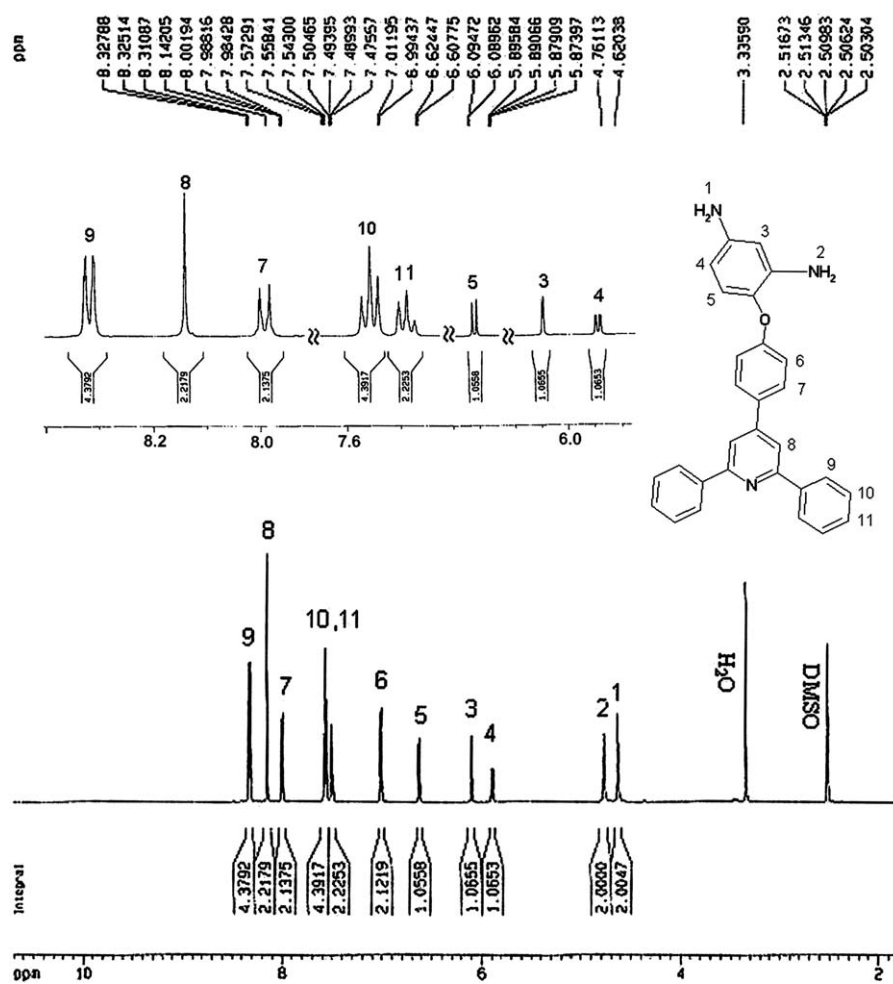
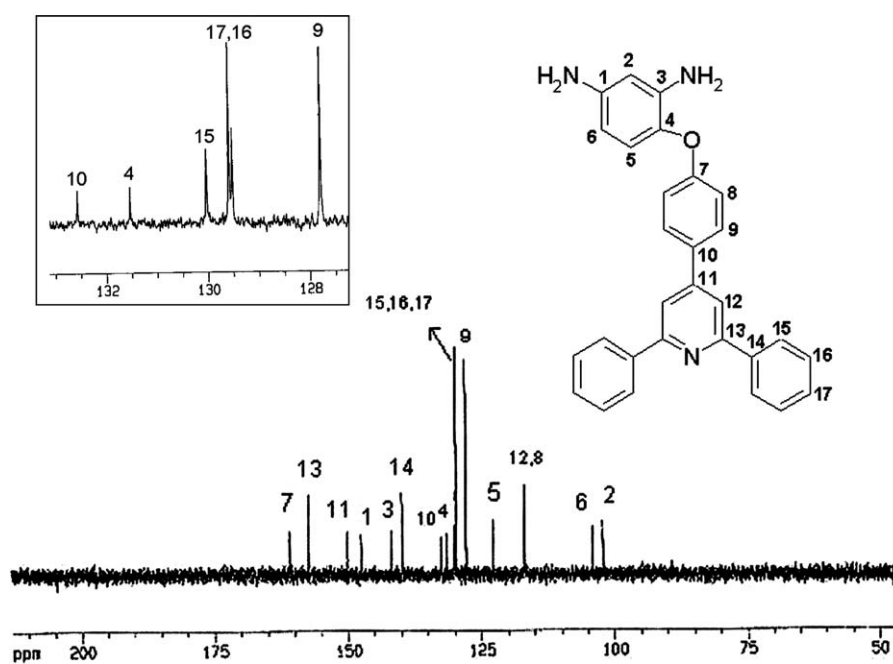
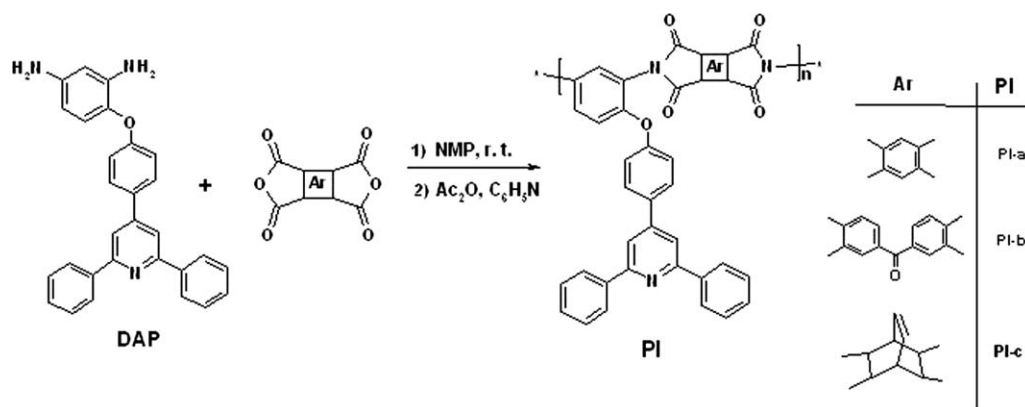


Figure 2 ^1H NMR spectrum of DNP.

Figure 3 ^1H NMR spectrum of DAP.Figure 4 ^{13}C NMR spectrum of DAP.



Scheme 2 Synthesis of polyimides from DAP with different dianhydrides.

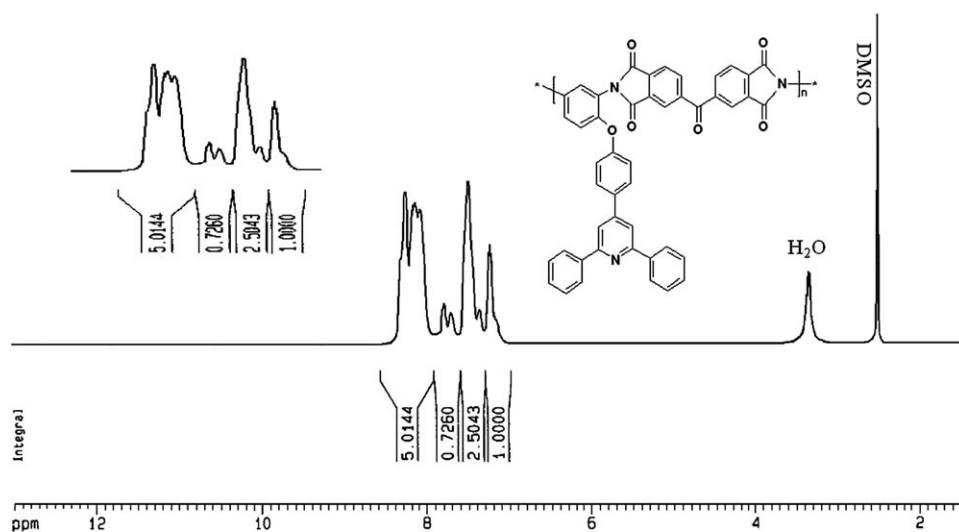


Figure 5 ^1H NMR spectrum of polyimide (PI-b).

protons were appeared at 7.05–8.5 ppm. Meanwhile, no proton signal was detected in the range greater than 8.5 ppm which indicates the complete imidization. The yields of these polymers were in the range of 88–92%. This could be due to formation of some low molecular weight oligomers as a result of different reactivity of the amino groups in the asymmetric diamine monomer, the amino group at the “ortho” position to the ether linkage is less reactive due to steric effect. Therefore, some of the low molecular weight oligomers were possibly washed out during hot extraction of the PIs with a mixture of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (50/50, v/v). The results from XRD test, x-ray diffraction patterns in Figure 6, reveal the amorphous nature of these polyimides which can be attributed to their asymmetric structural units and bulky pendent group which hindered regular macromolecular packing and decreased the intra and inter-chain interaction.

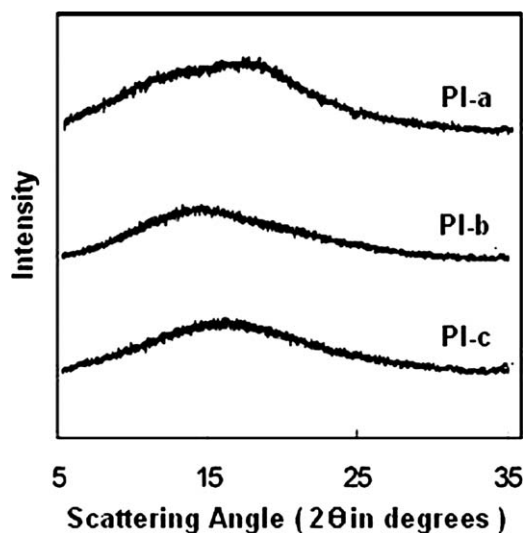


Figure 6 X-ray diffraction patterns of PIs.

TABLE I
Inherent Viscosity and Solubility of Polyimides

PI code	dianhydride	η_{inh} (dL/g)	DMAc	DMF	NMP	DMSO	DO	PY	<i>m</i> -cresol	THF	CCl ₄
PI-a	PMDA	0.45	++	++	++	++	±	++	++	-	-
PI-b	BTDA	0.46	++	++	++	++	±	++	++	-	-
PI-c	BCDA	0.43	++	++	++	++	++	++	++	±	-

DMAc, *N,N*-dimethyl acetamide; DMF, *N,N*-dimethyl formamide; NMP, *N*-methyl pyrrolidone; DMSO, dimethyl sulfoxide; DO, dioxane; Py, pyridine; THF, tetrahydro furan.

++, Soluble at room temperature; +, Soluble on heating at 60°C; ±, partially soluble on heating at 60°C; -, Insoluble on heating at 60 °C.

Polyimides solubility and optical properties

One of the major objectives of this study was to produce modified PIs with improved solubility. The solubility behavior of the new PIs was determined at concentration of 5% (W/V) in a number of solvents and the results were tabulated in Table I. As it is shown in this table, the prepared PIs were readily soluble in polar aprotic solvents such as NMP, DMAc, DMF, DMSO, and even in less polar solvents like pyridine and *m*-cresol at room temperature but showed poor solubility in dioxane and THF due to the low value of dielectric constant of the solvent. The good solubility should be the result of formation of some intermolecular spacing due to introduction of the bulky pendent group in polymer backbone, unsymmetrical structure coming from diamine monomer which interrupts the regular packing of polymer chains, and polarizability resulting from the nitrogen atom in pyridine ring. The amorphous nature of the PIs was also reflecting their good organosolubility. In addition, the solubility varies depending upon the dianhydride used. The PI was synthesized from cycloaliphatic dianhydride (PI-c)

exhibited better solubility behavior in less polar solvents such as dioxane and THF. The cycloaliphatic units instead of rigid phenyl improve the solubility of this polyimide.

Ultraviolet spectroscopy was used to study the optical properties of polymers in dilute (0.2 g/dL) NMP solution. This spectrum provides information about the conjugation along the polymer backbone. The typical UV-vis and emission spectra of PIs and diamine monomer in NMP solution were given in Figure 7. The monomer and PIs exhibited high-energy absorption band with maxima from 290 to 305 nm which can be attributed to the π - π^* transitions resulting from the conjugation between the aromatic rings and nitrogen atoms. By comparing the diamine spectrum with those of PIs, a red shift is shown which can be due to expanding of π system. The fluorescence emission of the cycloaliphatic polyimide PI-c, Figure 7(b), exhibited blue shift compared with the aromatic polyimides PI-a and PI-b which can be attributed to the effectively reduced conjugation and capability of charge-transfer complex formation by aliphatic diacids with the electron-donating diamine moiety in comparison with

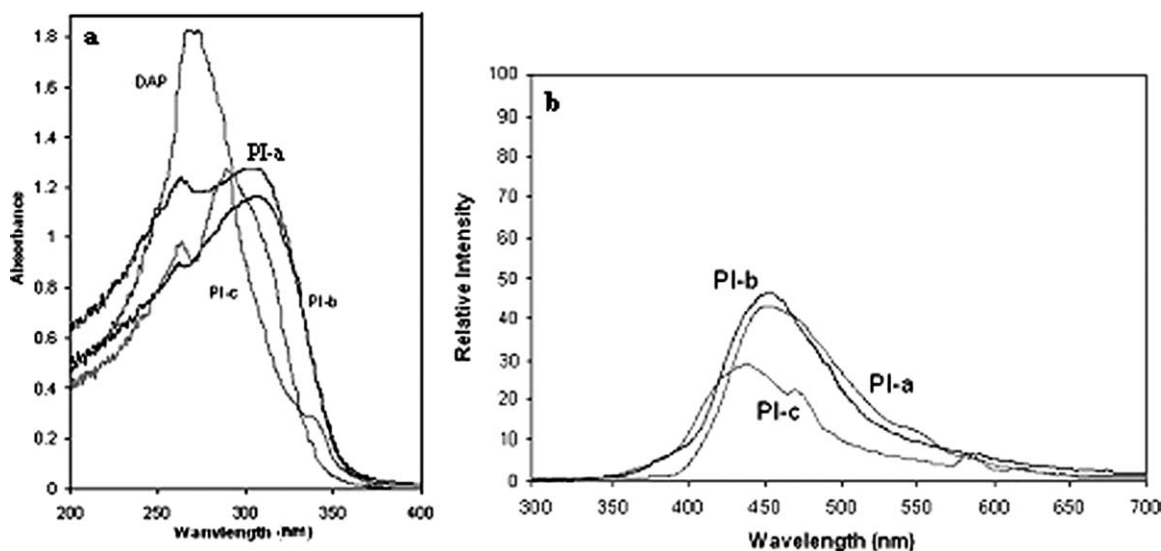


Figure 7 Uv-vis absorption spectra (a) for DAP and PIs; and (b) emission spectra for PIs in NMP solution.

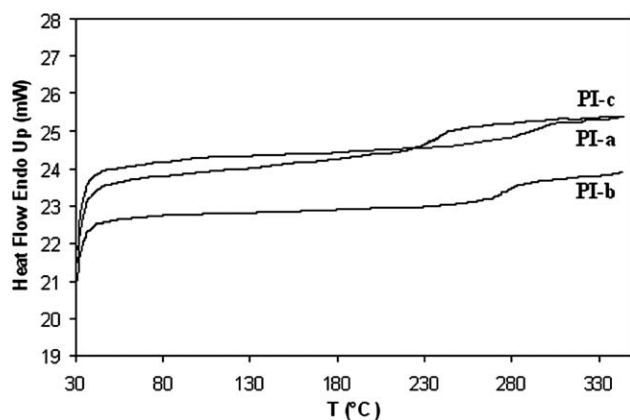


Figure 8 DSC thermograms of PIs.

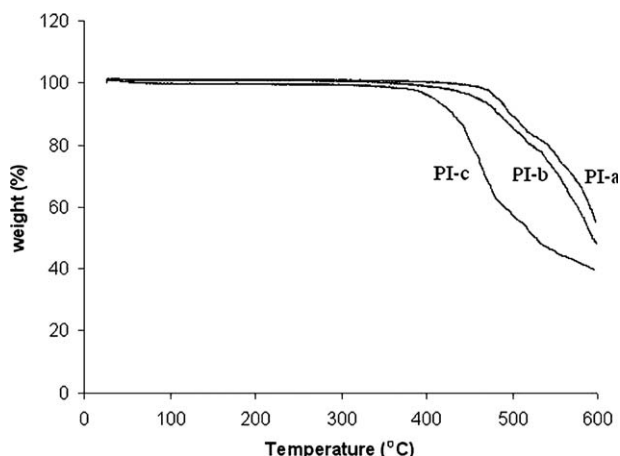


Figure 9 TGA thermograms of PIs.

TABLE II
Thermal Characteristic Data of Polyimides

PI code	T_g (°C)	T_i (°C)	T_5 (°C)	T_{10} (°C)	Char yield at 600°C (%)
PI-a	294	460	480	500	56
PI-b	278	400	453	478	51
PI-c	237	360	402	430	40

T_g , glass transition temperature; T_5 , temperature for 5% weight loss; T_{10} , temperature for 10% weight loss. Char yield: weight of polymer remained at 600°C.

that of the stronger electron-accepting aromatic diacids.²⁶

Polyimides thermal properties

The thermal properties of the PIs were investigated by TGA (in air) and DSC (under nitrogen atmosphere) at a heating rate of 10°C/min. DSC and TGA thermograms of the PIs are shown in Figures 8 and 9, respectively, and the data extracted from the original thermograms are summarized in Table II. As it is expected, the T_g values of these PIs, in the range of 237–294°C, showed dependence on the structure of polymer and decreased with increasing flexibility of the dianhydride unit in the polymer backbone. The PI-a derived from PMDA exhibited higher T_g (294°C) because of the rigid backbone which inhibits the molecular motion, and PI-c based on bicyclic aliphatic dianhydride (BCDA) showed the lowest T_g value (237°C) because of the absence of rigid phenyl groups which inhibit the molecular motion. It is evident that the bridging carbonyl group between two phenyl rings presents in BTDA, facilitated bond rotation and reduced T_g . No melting endothermic peak was observed in the DSC traces of the PIs. These observations and the results obtained from WAXD test confirm the amorphous nature of these PIs. The initial decomposition temperatures (T_i) of these polymers were in the range of 360–460°C depended on the dianhydride component in the

polyimide backbone. The TGA data indicated good thermal stability for the polyimides PI-a and PI-b up to 500°C in air with a weight loss of 10% in comparison with the polyimide PI-c containing cycloaliphatic unit in the backbone which lost almost 40% weight at this temperature. Also, char yields of the polyimides at 600°C were in the range of 40–56% implying that these PIs possess relatively good thermal stability.

CONCLUSIONS

A new unsymmetrical diamine (DAP) with bulky pendent of pyridine was successfully prepared in high purity and high yield and was polymerized with commercial available dianhydrides to obtain PIs. Using unsymmetrical diamine monomer and introduction of the bulky polar triaryl pyridine pendent group into the polymer backbone led to significantly improved solubility of the polymer in various organic solvents. The degradation temperatures of PIs for 10% weight loss are in the range of 430–500°C. The nice balance of properties (thermal stability vs. solubility) was observed in these polyimides. These polyimides could be considered as new processable high performance polymeric materials.

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