

ORGANOSOLUBLE AND THERMALLY STABLE POLYIMIDES DERIVED FROM A NEW DIAMINE CONTAINING BULKY-FLEXIBLE TRIARYL PYRIDINE PENDENT GROUP

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Abstract A novel kind of aromatic diamine, *N*-(4-(4-(2,6-diphenyl pyridine-4-yl) phenoxy) phenyl)-3,5-diaminobezamide (DPDAB), was synthesized *via* aromatic nucleophilic substitution of 3,5-dinitrobenzoylchloride with 4-(4-(2,6-diphenylpyridine-4-yl)phenoxy)aniline (DPPA), followed by palladium-catalyzed hydrazine reduction. This monomer was used to prepare polyimides (PIs) based on reaction with several commercially available tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA), benzophenone tetracarboxylic acid dianhydride (BTDA) and bicycle [2.2.2] oct-7-ene-2, 3,5,6-tetracarboxylic dianhydride (BCDA). These PIs had inherent viscosity in the range of 0.34–0.76 dL/g and showed good solubility in various aprotic polar solvents. The glass-transition temperatures (T_g s) of the PIs were in the range of 184–302°C, and showed high thermal stability with 10% weight loss in the temperature range of 360–500°C under nitrogen atmosphere.

Keywords: Polyimides; Inherent viscosity; Solubility; Thermal stability; DSC.

INTRODUCTION

Aromatic PIs are well recognized as high-performance polymeric materials for their excellent thermal, high heat resistance, electrical insulating and mechanical properties^[1, 2]. They are extensively employed as substrates for flexible printed circuits or semiconductor devices, adhesives and composite fiber in aerospace and automobile industries and film materials^[3, 4]. The major problem of aromatic PIs is insolubility in most organic solvents and infusibility in their fully imidized form, causing processing difficulties which limit their applications. To overcome these problems various efforts have been concentrated on the synthesis of soluble and tractable polyimides without sacrificing their outstanding properties. One of the approaches to rising solubility and lowering the glass-transition temperature (T_g) is the introduction of flexible segments such as linkages of $-O-$, $-S-$, $CO-$, $-SO_2-$, $-C(CF_3)_2-$, and meta-substituted phenylene moieties into the polymer-backbone which supply kinks between the stiffness phenyl rings in the main chain^[5–11]. Other conventional approaches are: Replacing *p*-terphenyls with the *o*-terphenyls which may result in polymers soluble in polar aprotic solvents with no significant influence on their thermal stability^[12]; incorporation of non-coplanar moieties in the main chain^[13–15], bulky lateral groups in the polymer backbone^[16–20] and alicyclic units^[21] which may decrease the packing density and lead to improved solubility of the polymer; introducing bulky pendent groups into the polymer main chain which may modify the properties, lower the melting temperature and fabricate amorphous and soluble polymer^[22–24].

In this paper, we describe synthesis and characterization of three novel polyimides from a new *m*-phenylene

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diamine monomer containing bulky-flexible polar side group, *N*-(4-(4-(2,6-diphenyl pyridine-4-yl) phenoxy) phenyl)-3,5-diaminobezamide (DPDAB), and commercially available dianhydrides *via* chemical imidization. The introduction of this pendent group meta-linked in the backbone of the polyimides is definitely responsible for lowering the interchain interactions connected to dissolution, and meanwhile, the chain stiffness of the polymer will also be improved due to limited free rotation of the polymer backbone. Therefore, it was anticipated that the obtained polymers would illustrate good thermal stability as well as solubility. The polyimides were characterized by FT-IR and ¹H-NMR spectroscopy, elemental analysis, viscosity measurement, solubility test, DSC and TGA analyses.

EXPERIMENTAL

Materials and Measurements

4-Hydroxybenzaldehyde, acetophenone, *p*-fluoronitrobenzene, hydrazine monohydrate and 10% palladium on activated carbon were purchased either from Merck or Fluka chemical Co. and used as received. *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 0.4 nm molecular sieves. 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*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), tetrahydrofuran (THF), *m*-cresol, ethanol and methanol were used without further purification.

FT-IR spectra were recorded on a Bruker Tensor 27 using KBr pellets over the range of 400–4000 cm⁻¹. ¹H-NMR and ¹³C-NMR spectra were performed in dimethyl sulfoxide-d₆ (DMSO-d₆) solution using a Bruker Advance 500 MHz instrument (Germany). Elemental analysis was performed with a CHN-600 Leco elemental analyzer. For measurements of the inherent viscosities at a concentration of 0.5 g/dL solution in NMP at 25°C, an Ubbelohde suspended-level viscometer was used. Thermogravimetric analysis (TGA) was recorded on a Du Pont Instruments (TGA 951) analyzer well equipped with a PC at a heating rate of 10 K/min under nitrogen atmosphere (20 cm³/min) in the temperature range of 30–600°C. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer pyris 6 DSC under nitrogen atmosphere (20 cm³/min) at a heating rate of 10 K/min. Melting point was measured with a Barnstead Electrothermal Engineering LTD 9200 apparatus.

Monomer Synthesis

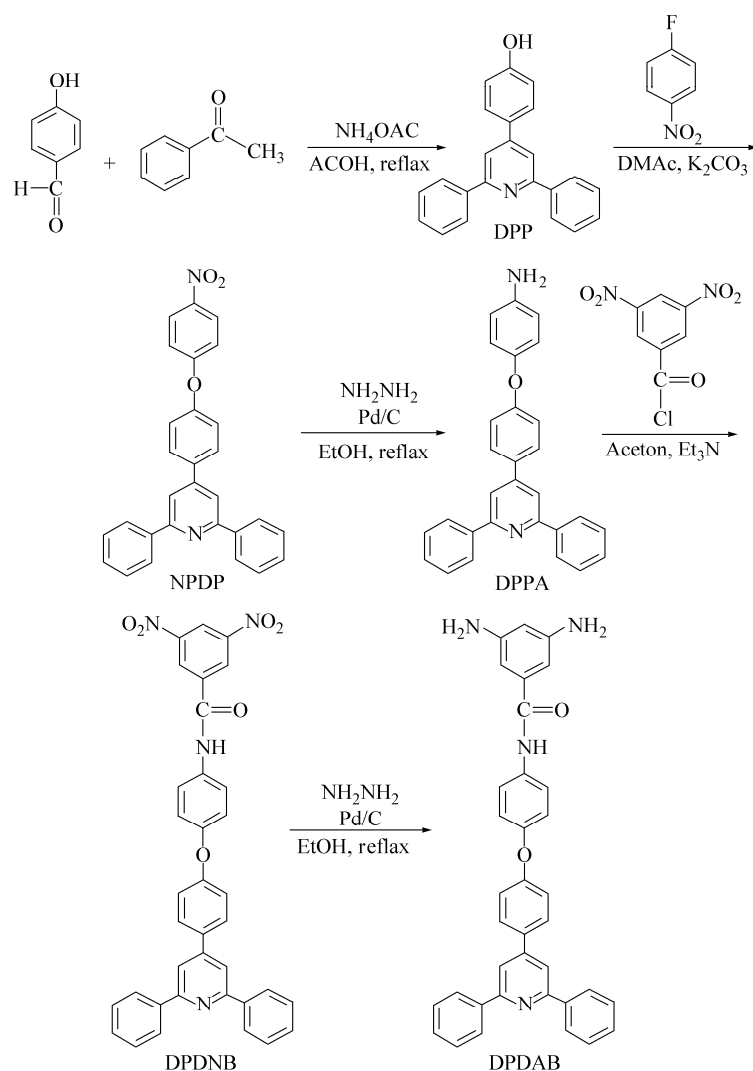
The diamine monomer was prepared according to the following steps, as shown in Scheme 1.

4-(2,6-Diphenylpyridine-4-yl) phenol (DPP)

The DPP was prepared by reacting 4-hydroxybenzaldehyde with acetophenone according to a reported procedure^[25,26]. The yield of the crude product was 84%.

4-(4-(4-Nitrophenoxy) phenyl)-2,6-diphenylpyridine (NPDP)

Into a 250 mL round-bottomed, two-necked flask equipped with a condenser and a magnetic stirrer bar, a mixture of 3.24 g (0.01 mol) DPP, 1.41 g (0.01 mol) *p*-fluoronitrobenzene and 1.50 g (0.01 mol) potassium carbonate in 40 mL DMAc was refluxed at 110°C for 12 h. During this time, the progress of the reaction was followed by thin layer chromatography. The mixture was then cooled and poured into 100 mL water and the yellow precipitate was filtered off, washed with water and dried in a vacuum oven. The yield of the reaction was 90%, and the melting point of the product was 190–192°C. FT-IR spectrum exhibited absorptions at 1547–1345 (NO₂), 1244 (C–O–C) and 1603 cm⁻¹ (C=N). Anal. Calcd. for C₂₉H₂₀N₂O₃: C, 78.37%; H, 4.50%; N, 6.30%. Found C 78.45%; H, 4.56%; N, 6.22%.



Scheme 1 Outline of synthesis procedure of diamine (DPDAB)

4-(4-(2,6-Diphenyl pyridine-4-yl) phenoxy) Aniline (DPPA)

Into a 250 mL two necked, round-bottomed flask equipped with a reflux condenser, a dropping funnel and a magnetic stirrer bar, a mixture of 10 g (0.022 mol) NPDP, 0.15 g of 10% Pd/C and 100 mL ethanol was charged. 10 mL hydrazine monohydrate was added drop-by-drop over a 30 min period through dropping funnel. The reaction mixture was refluxed at 85°C for 6 h. The mixture was filtered while hot to remove Pd/C and was heated to reduce the volume of the solvent. After cooling, the precipitated crystals were isolated by filtration and recrystallised from acetonitrile and dried in a vacuum oven at 70°C. The yield of the reaction was 88%, and the melting point of the product was 162–164°C. FT-IR spectrum exhibited absorptions at 3448–3378 (NH₂), 1239 (C–O–C), 1598 (C=N) and 1507 cm⁻¹ (C=C). Anal. Calcd. for C₂₉H₂₂N₂O: C, 84.03%; H, 5.31%; N, 6.76%. Found, C, 84.13%; H, 5.45%; N, 6.82%.

N-(4-(4-(2,6-diphenylpyridine-4-yl) phenoxy) phenyl)-3,5-dinitrobenzamide (DPDNB)

Into a 250 mL two necked round-bottomed flask equipped with a reflux condenser, a dropping funnel and a magnetic stirrer bar, 10 g (0.024 mol) DPPA was dissolved in 75 mL of acetone. 4 mL triethylamine (Et₃N) was added to the solution and 5.50 g (0.024 mmol) 3,5-dinitrobenzoyl chloride in 5 mL of acetone was charged into

the mixture through dropping funnel. Then the reaction mixture was refluxed at 70°C for 24 h. The progress of the reaction was followed by thin layer chromatography. After cooling to room temperature, the reaction mixture was poured into a large volume of water. The yellow powder was collected by filtration, washed and dried overnight under vacuum at 70°C. The yield was 87% and the melting point: 145–148°C. FT-IR spectrum exhibited absorptions at 1547–350 (NO₂), 1694 (C=O), 1244 (C–O–C), 1603 (C=N) and 1502 cm⁻¹ (C=C). Anal. Calcd. for C₃₆H₂₄N₄O₆: C, 71.05%; H, 3.94%; N, 9.21%. Found, C, 71.11%; H, 3.87%; N, 9.17%.

N-(4-(4-(2,6-diphenylpyridine-4-yl) phenoxy) phenyl)-3,5-diaminobezamide (DPDAB)

Into a 100 mL two necked round-bottomed flask equipped with a reflux condenser, a dropping funnel and a magnetic stirrer bar, 1 g (0.001 mol) DPDNB was refluxed in 10 mL of absolute ethanol in the presence of 0.01 g of 10% Pd/C catalyst. 1 mL hydrazine monohydrate was added drop-by-drop over a 30 min period through dropping funnel. The reaction mixture was refluxed at 85°C for 7 h. The mixture was filtered hot to remove the catalyst. Upon cooling, a pink powder precipitated, it was isolated by filtration and then recrystallized from ethanol and dried in a vacuum oven at 70°C overnight. The yield of the reaction was 86% and the melting point: 151–154°C. FT-IR spectrum exhibited absorptions at 3357–3054 (NH), 1653 (C=O), 1603 (C=N), 1542 (C=C) and 1234 cm⁻¹ (C–O–C). ¹H-NMR (500 MHz, DMSO-d₆) δ: 10.10 (s, 1H, NH^b), 8.30 (dd, 4H, Ar–Hⁿ, *J* = 7 Hz), 8.18 (s, 2H, Ar–H^m), 8.07 (d, 2H, Ar–H^c, *J* = 8.5 Hz), 7.84 (d, 2H, Ar–H^h, *J* = 9 Hz), 7.48 (dd, 4H, Ar–H^o, *J* = 7 Hz), 7.18 (dd, 2H, Ar–H^p, *J* = 7 Hz), 7.13 (d, 2H, Ar–H^g, *J* = 9 Hz), 7.11 (d, 2H, Ar–H^f, *J* = 9 Hz), 6.30 (d, 2H, Ar–H^d, *J* = 2 Hz), 6.01 (t, 1H, Ar–H^e, *J* = 2 Hz), 4.98 (s, 4H, NH₂^a). ¹³C-NMR (500 MHz, DMSO-d₆) δ: 167.24 (C⁵), 158.81 (C¹⁶), 156.48 (C¹⁰), 149.18 (C²), 148.86 (C¹⁵), 138.84 (C¹⁴), 136.82 (C⁴), 136.70 (C⁶), 136.10 (C¹⁷), 132.09 (C¹³), 131.1 (C⁹), 129.23 (C²⁰), 129.13 (C¹⁹), 128.67 (C¹⁸), 126.96 (C¹²), 121.67 (C⁷), 119.84 (C¹¹), 117.88 (C⁸), 116.22 (C¹), and 102.27 (C³). Anal. Calcd. for C₃₆H₂₈N₄O₂: C, 78.83%; H, 5.11%; N, 10.32%. Found, C, 78.88%; H, 5.16%; N, 10.26%.

Synthesis of Polyimides

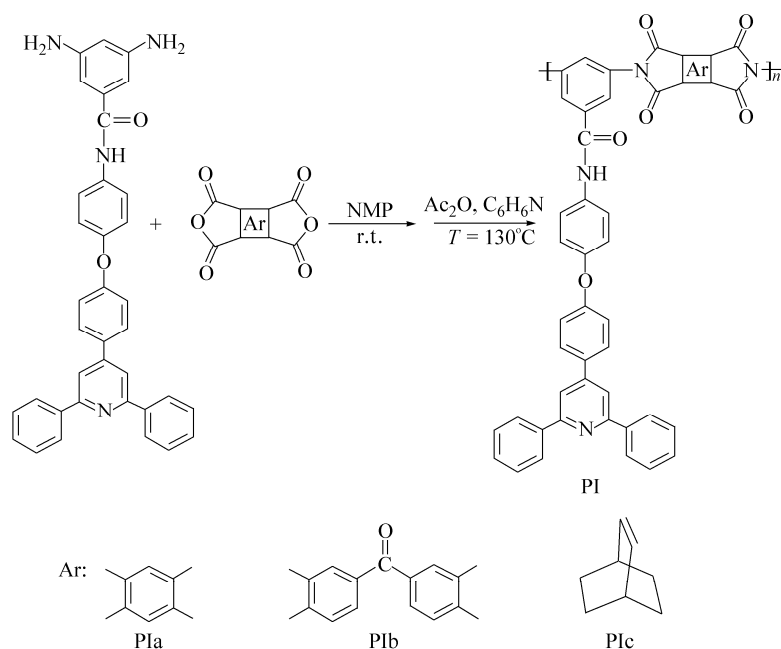
Into a 50 mL two-necked, round-bottomed flask equipped with a reflux condenser, a magnetic stirrer bar and a nitrogen gas inlet tube, a mixture of 0.72 mmol aromatic dianhydride and 0.4 g (0.72 mmol) DPDAB was dissolved in 5 mL of NMP and the mixture was stirred at room temperature for 24 h, forming a viscous solution of poly (amic acid) (PAA) precursor in NMP. The PAA was converted into polyimide by chemical imidization process. This process was performed by adding 5 mL acetic anhydride and 0.80 mL pyridine into the PAA solution with stirring at room temperature for 1 h. Then the mixture was stirred at 130°C for 10 h. The homogeneous polyimide solution was poured into methanol and the precipitate was collected by filtration, washed with hot water and dried at 80°C in a vacuum oven overnight. The other polymers were synthesized by an analogous procedure described above. General procedure for the synthesis of polyimides is also shown in Scheme 2.

PIa: Yield = 92%. FT-IR (KBr, cm⁻¹): 3570 (N–H stretching amide group), 3060 (C–H stretching aromatic) 1780, 1729 (imide carbonyl asymmetric and symmetric stretching), 1502 (C=N stretching), 1370 (C–N stretching), 1243 (C–O–C), 1107, 728 (imide ring deformation). ¹H-NMR (DMSO-d₆) δ: 10.52 (s, 1H, NH), 7.05–8.99 (m, 25H, Ar–H). Anal. Calcd. for [C₄₆H₂₆N₄O₆]_n: C, 75.61%; H, 3.56%; N, 7.67%. Found: C, 75.55%; H, 3.49%; N, 7.61%.

PIb: Yield = 89%. FT-IR (KBr, cm⁻¹): 3490 (N–H stretching amide group), 3100 (C–H stretching aromatic), 1775, 1737 (imide carbonyl asymmetric and symmetric stretching), 1501 (C=N stretching), 1357 (C–N stretching), 1229 (C–O–C), 1094, 714 (imide ring deformation). ¹H-NMR (DMSO-d₆) δ: 10.54 (s, 1H, NH), 6.67–8.55 (m, 29H, Ar–H). Anal. Calcd. for [C₅₃H₃₀N₄O₇]_n: C, 76.26%; H, 3.60 %; N, 6.71%. Found: C, 76.19%; H, 3.64%; N, 6.75%.

PIc: Yield = 86%. FT-IR (KBr, cm⁻¹): 3510 (N–H stretching amide group), 3150 (C–H stretching Aromatic), 2800 (C–H stretching Aliphatic), 1780, 1719 (imide carbonyl asymmetric and symmetric stretching), 1502 (C=N stretching), 1370 (C–N stretching), 1234 (C–O–C), 1173, 779 (imide ring deformation). ¹H-NMR (DMSO-d₆) δ: 10.54 (s, 1H, NH), 7.12–8.33 (m, 23H, Ar–H), 6.36–6.37 (m, 2H,

alkene protons), 3.27–3.31 (m, 4H, aliphatic porotons), 2.04–2.22 (m, 2H, bridge base protons). Anal. Calcd. for $[C_{48}H_{32}N_4O_6]_n$: C, 75.79%; H, 4.21%; N, 7.37%. Found: C, 75.82%; H, 4.26%; N, 7.32%.



Scheme 2 Outline of preparation of polyimides

RESULTS AND DISCUSSION

Monomer Synthesis and Characterization

In this work, we study the preparation of soluble polyimides without sacrificing their thermal stability from a diamine and three different tetracarboxylic dianhydrides. The monomer containing bulky and long pendent

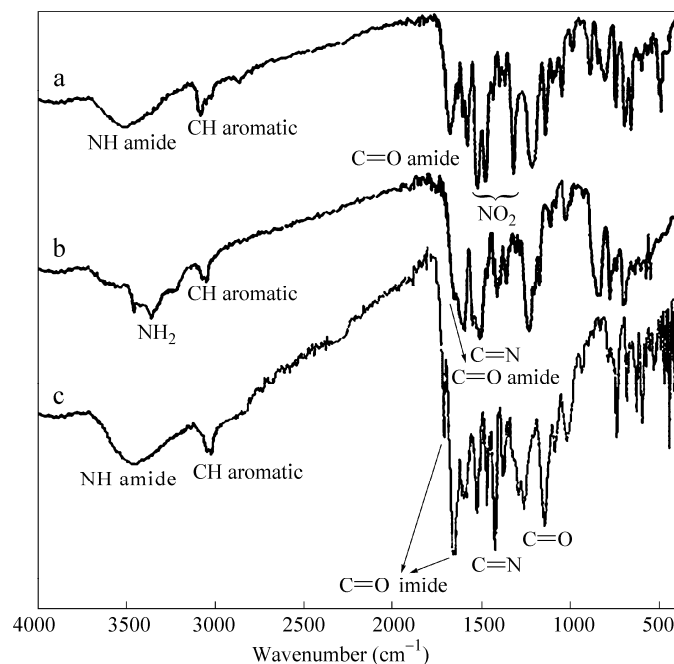


Fig. 1 FT-IR spectra of DPDNB (a), DPDAB (b) and polyimide PIa (c)

group was synthesized according to the synthetic route shown in Scheme 1. This diamine was prepared in five steps: starting from condensation of 4-hydroxybenzaldehyde with acetophenone and ammonium acetate in glacial acetic acid afforded 4-(2, 6-diphenylpyridine-4-yl) phenol (DPP)^[25, 26]. The reaction of DPP with 4-fluoro nitrobenzene in DMAc solvent and in the presence of K_2CO_3 gave 4-(4-nitrophenoxy) phenyl-2, 6-diphenylpyridine (NPDP). Reduction of nitro group of NPDP in the presence Pd/C in ethanol by using hydrazine monohydrate resulted in preparation of DPPA. The dinitro compound DPDNB was synthesized by the nucleophilic aromatic substitution reaction of DPPA with 3,5-dinitrobenzoyl chloride. Finally, the catalytic hydrogenation of DPDNB to the corresponding diamine (DPDAB) was accomplished by means of hydrazine monohydrate in ethanol. The structures of and intermediates were characterized by FT-IR spectra, and ^1H - and ^{13}C -NMR spectroscopies and elemental analysis. DPDNB displayed characteristic absorption bands at 1502 and 1350 cm^{-1} , corresponding to symmetric and asymmetric NO_2 stretching, respectively. These absorption bands disappeared after reduction and new absorption bands appeared at 3357, 3054 cm^{-1} due to N—H stretching and confirmed the formation of $-NH_2$ group. FT-IR spectra of DPDNB and PDPAB are exposed in Fig. 1. ^1H -NMR spectrum of PDPAB in Fig. 2 shows signals at: δ 10 (s, 1H), 4 (s, 4H) related to $-NH-$ and $-NH_2$, respectively. The signals of aromatic protons appeared at δ 10 (s, 1H), 8.3 (dd, 4H, $J = 7$ Hz), 8.18 (s, 2H), 8.07 (d, 2H, $J = 8.5$ Hz), 7.84 (d, 2H, $J = 9$ Hz), 7.5 (dd, 4H, $J = 7$ Hz), 7.4 (dd, 2H, $J = 7$ Hz), 7.13 (d, 2H, $J = 9$ Hz), 7.11 (d, 2H, $J = 9$ Hz), 6.3 (d, 2H, $J = 2$ Hz), 6.01 (t, 1H, $J = 2$ Hz), 4.98 (s, 4H) displayed the expected multiplicity and integration values. The ^{13}C -NMR of PDPAB is also illustrated in Fig. 3.

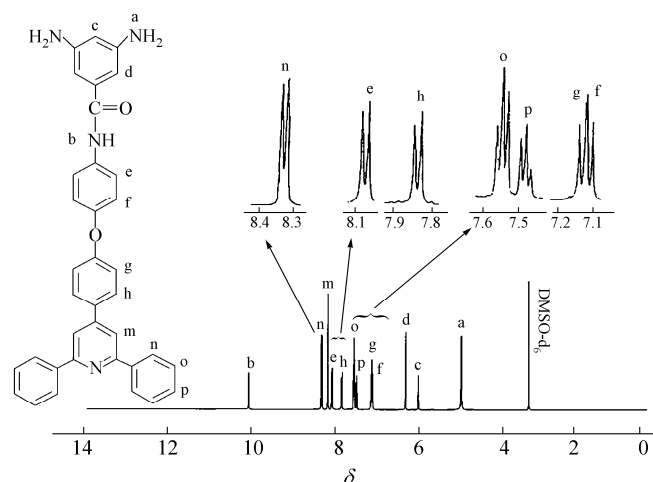


Fig. 2 ^1H -NMR spectrum of diamine (DPDAB)

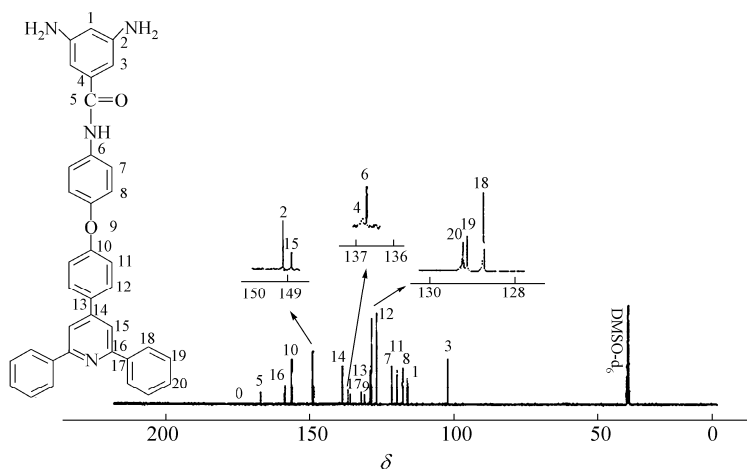


Fig. 3 ^{13}C -NMR spectrum of diamine (DPDAB)

Synthesis and Characterization of Polyimides

Three new polyimides containing pendent groups of bulky triaryl pyridine with ether and amide linkages were synthesized from a new diamine DPDAB and commercially available aromatic and cycloaliphatic dianhydrides (Scheme 2). Most conventional processing techniques involve the fabrication of poly(amic acid) precursors followed by thermal or chemical imidization. The new polyimides were synthesized using a two step method, which were carried out *via* poly(amic acid)s. First, the diamine was dissolved in NMP and the equimolar amount of a dianhydride was added to the solution. The solution was stirred for 24 h at room temperature, forming viscous poly(amic acid) solution. The chemical imidization with acetic anhydride and pyridine was employed forming polyimides with the yields ranging from 86% to 92%. The polyimides showed inherent viscosities varying from 0.34 dL/g to 0.76 dL/g which can be associated to the reactivity of the dianhydrides. All the polyimides gave colored and tough films from solution casting. The structures of polymers were confirmed by elemental analysis, FT-IR and $^1\text{H-NMR}$ spectroscopic techniques. The characteristic absorption bands of the five-membered imide ring appeared at 1780 and 1729 cm^{-1} , corresponding to asymmetric and symmetric C=O stretching, at 1095 and 765 cm^{-1} due to imide ring deformation, as shown in Fig. 1. The disappearance of the amide and carboxyl bands showed a virtually complete transfer of the poly(amic acid) precursor into polyimides. $^1\text{H-NMR}$ spectrum of polyimide PIa is illustrated in Fig. 4. Assignment of total protons in the spectrum is consistent with the proposed chemical structure of polymer. The characteristic resonance signals of aromatic protons appeared in the range of $\delta = 6.93\text{--}8.46$. The singlet peak at $\delta = 10.48$ indicates N-H amide group. The NH_2 protons in the monomer considered at $\delta = 4.96$ in Fig. 2, have been totally eliminated because of imidation reaction and this signal is not observed in the $^1\text{H-NMR}$ spectrum of the PIa.

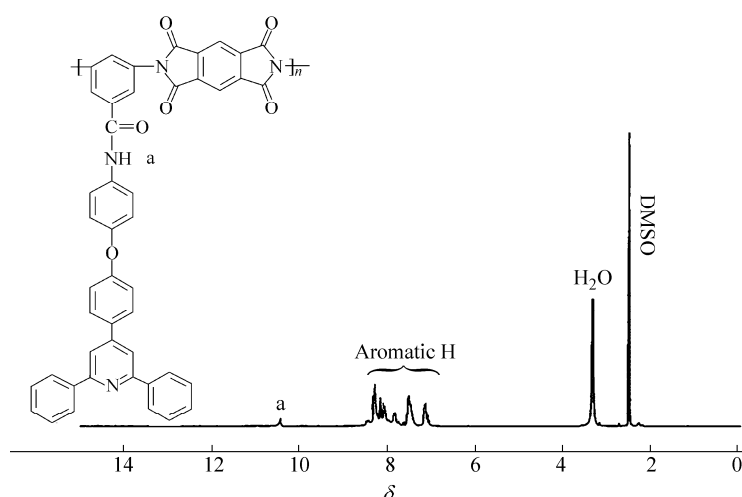


Fig. 4 $^1\text{H-NMR}$ spectrum of polyimide PIa

Solubility of Polyimides

The solubility of the polyimides was determined qualitatively at a concentration of 50 g/L in a number of solvents at room temperature or upon heating, and the results are tabulated in Table 1. The aromatic polyimides exhibited good solubility in polar aprotic solvents such as DMF, NMP, DMAc, DMSO, and even in less polar solvents like pyridine. Contrast to solubility of the formerly reported polyimides^[27–29], these polymers with triphenyl pyridine pendent group exhibit an enhanced solubility in organic solvents. The good solubility should be the result of the introduction of the bulky pendent triphenyl pyridine groups in polymer backbone which disturb a dense chain packing of the polymer chains and reduce packing force resulting in reduction of interchain interaction; consequently, the solvent molecules were able to penetrate easily to interact with the polar groups in the pendent. However, the polarizability resulting from the pyridine ring and the ether linkages would also improve their solubility in organic solvents. In addition, the solubility varies depending upon the

dianhydrides used. Polymers with flexible linkages are more soluble than those with rigid linkage. The polyimide PIb prepared from BTDA exhibited better solubility than polyimide PIa containing pyromellitic dianhydride (PMDA) in the backbone. Also, polyimide PIc which was synthesized from a cycloaliphatic dianhydride exhibited excellent solubility behavior even in less polar solvents such as THF and acetone. The introduction of bicyclic unit into the structure of polyimide PIc instead of rigid phenyl group improves solubility of this polyimide in comparison with the aromatic polyimides (PIa and PIb). Thus, all these polymers can be readily processed, and they could afford tough and flexible films *via* solution casting. The cast films of polyimides are transparent light yellowish. The obtained polyimides had inherent viscosities (η_{inh}) in the range of 0.34–0.76 dL/g in a concentration of 0.5 g/dL in NMP at 25°C, as shown in Table 1.

Table 1. Inherent viscosity and solubility data of the polyimides

PI	η_{inh} (dL/g)	DMAc	DMF	DMSO	NMP	PY	THF	AN	<i>m</i> -Cresol	Methanol
PIa	0.76	±	++	+	+	+	±	–	±	–
PIb	0.72	+	++	++	+	++	±	–	±	–
PIc	0.34	++	++	++	++	++	++	–	+	–

DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran; PY: pyridine; AN: acetonitrile;

++: soluble at room temperature; +: soluble after heating at 60°C; ±: partially soluble after heating at 60°C;

–: insoluble after heating at 60°C

Thermal Properties of Polyimides

DSC and TGA methods with a heating rate of 10 K/min under nitrogen atmosphere were applied to evaluate the thermal properties of the polyimides. DSC curves of the polyimides are shown in Fig. 5, and the T_g s obtained from the second heating trace of DSC are reported in Table 2. The T_g values of these polymers are in the range of 184–302°C, and as it is expected, the T_g values depended on the structure of the dianhydride component, and decreased with increasing flexibility of the polyimides backbones based on the applied structure of dianhydride. The polyimide PIa showed the highest T_g of 302°C due to the relatively rigid polymer chains which limit a free rotation. It is evident that the bridging carbonyl group between two phenyl rings presents in BTDA, facilitated bond rotation and reduced T_g of polyimide PIb in comparison with the T_g of polyimide PIa. The polyimide PIc based on bicyclic aliphatic dianhydride (BCDA) displayed the lowest T_g value of 184°C which is due to absence of rigid phenyl groups which inhibit the molecular motion. None of the polyimides showed clear melting endotherms in the DSC thermograms. This reveals amorphous nature of the polyimides which can be ascribed to their bulky pendent group which leads to an increase in steric hindrance for close chain packing and increase free volume and reduces the interchain interactions resulting in loose polymer chain packaging and aggregates. TGA curves for the polyimides are shown in Fig. 6. The initial decomposition temperatures (T_i), the temperatures of 10% weight loss (T_{10}) and the residual weight values were determined from original TGA

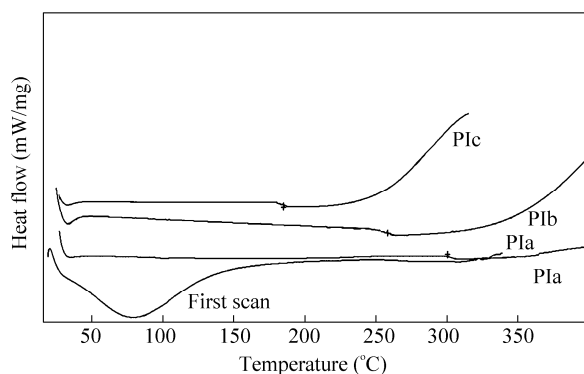


Fig. 5 DSC curves of polyimides at heating rate of 10 K/min in nitrogen

thermograms and included in Table 2. The polyimide PIa exhibited excellent thermal stability with insignificant weight loss up to 500°C. T_{10} values of the polyimides PIa, PIb, and PIc were recorded at 500°C, 400°C, and 360°C, respectively, indicating their different thermal stability. In addition, the residual weight retentions at 600°C for the resulting polyimides were in the range of 40%–68%. The polyimide PIc showed poor thermal stability which is related to introduction of bicyclic aliphatic unit in the backbone. The polyimide PIa has shown better thermal stability than polyimide PIb, because the carbonyl bridging group between two phenyl rings in the backbone of polyimide PIb increases flexibility of the polymer, therefore decreases the thermal stability.

Table 2. Data of thermal analysis of the resulting polyimides

PI	T_g (°C)	T_i (°C)	T_{10} (°C)	Char yield at 600 (%)
PIa	302	410	500	68
PIb	259	320	400	60
PIc	184	290	360	40

T_i : temperature for 0% weight loss; T_{10} : temperature for 10% weight loss;
 T_g : glass transition temperature

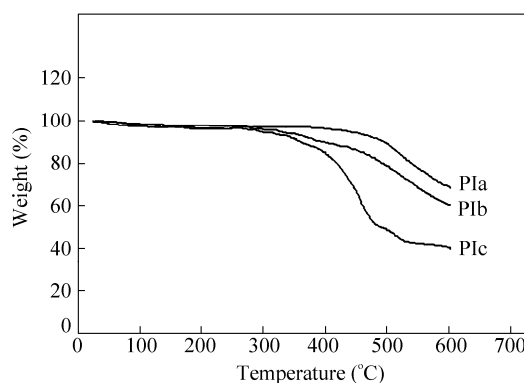


Fig. 6 TGA curves of polyimides at heating rate of 10 K/min in nitrogen

CONCLUSIONS

A new diamine containing a bulky-flexible triphenyl pyridine pendent group was prepared and used to synthesize a series of polyimides with various commercial dianhydrides by a two-step chemical imidization method. All of the polyimides demonstrated an amorphous nature. Experimental results showed that these polymers obtained satisfactorily balanced solubility and thermal stability because of introduction of large and flexible bulky pendant of 4-(4-(2,6-diphenyl pyridine-4-yl) phenoxy) benzenamine into the polymer backbone that cause reduction of interchain interactions and packing of polymer chains. In addition, the high T_g of these polymers is related to the decrease in the segmental mobility owing to side chain-side chain interaction through H-bonding. The polyimide PIa exhibited the highest thermal stability ($T_g = 302^\circ\text{C}$ and $T_{10} = 500^\circ\text{C}$) while the polyimide PIc exhibited highest solubility notwithstanding lowest thermal stability ($T_g = 184^\circ\text{C}$ and $T_{10} = 360^\circ\text{C}$) and char yield of 40%. The polyimides displayed desired combination of properties for high-performance materials that includes high thermal stability and excellent solubility.

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