

SYNTHESIS AND CHARACTERIZATION OF POLYAMIDES DERIVED FROM (4-(4-(2, 6-DIPHENYLPYRIDIN-4YL)PHENOXY)PHENYL)-3, 5- DIAMINOBEZAMIDE

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Abstract New types of polyamides containing pendent triaryl pyridine groups were successfully synthesized by direct polycondensation of a symmetry diamine, (4-(4-(2,6-diphenylpyridin-4yl)phenoxy)phenyl)-3,5-diaminobezamide (DPDAB), and various aromatic and aliphatic dicarboxylic diacids in NMP using triphenyl phosphate (TPP) and pyridine as catalyst. The diamine and all the prepared polyamides were fully characterized by using FT-IR, ¹H-NMR, UV-Vis spectroscopy, fluorimetry and elemental analysis. The inherent viscosity of polyamides ranged from 0.45 dL/g to 0.68 dL/g. All the polymers exhibited solubility in common polar aprotic solvents such as NMP, DMAc, DMF, DMSO, pyridine, HMPA, and even in less polar solvents such as THF and *m*-cresol at room temperature. Thermal properties of polyamides were evaluated by means of DSC, DMTA and TGA. These polymers showed glass transition temperatures (*T_g*) in the range of 138–210°C. Their initial decomposition temperature (*T_i*) varied from 265°C to 310°C under N₂. The dilute solution (0.2 g/dL) of polyamides in DMF exhibited fluorescence emission with λ_{max} in the range of 470–550 nm.

Keywords: Polyamides; Synthesis; Direct polycondensation; Solubility; Thermal stability.

INTRODUCTION

As high performance polymers, aromatic polyamides are characterized by their excellent chemical resistance, low flammability and strong mechanical and thermal properties. In general, they are insoluble in conventional solvents, and they also have the disadvantages of having high melting or softening temperatures because of the rigidity of the backbone and strong interchain interaction^[1–4]. These properties make them generally intractable or too expensive to process, thus limiting their application. The most successful approaches to enhancing solubility and lowering the glass-transition temperature (*T_g*) of polymers are replacing symmetrical aromatic rings by unsymmetrical ones^[5–9], introduction of flexible bridge groups in the main chain^[10, 11], bulky lateral or polar lateral substituents^[12–17], alicyclic^[18–20] and noncoplanar unit^[21–23] into the rigid polymer backbone. Another approach is based on the introduction of bulky pendent groups into the polymer chains^[24–30]. This modification performs by breaking the chain symmetry and by devastating hydrogen bonds and commonly causes to lower transition temperatures and enhance solubility. The present work afforded to synthesize and characterize a series of novel polyamides containing long bulky triaryl pendent groups derived from a new diamine (DPDAB) and various dicarboxylic acids. Thus, we expect to lower the inter- and intra-molecular interactions of the polymers and would generally disrupt the co-planarity of aromatic units to decrease the packing efficiency and the crystallinity. This should raise the solubility while maintaining a moderate to high *T_g* through qualified segmental mobility. Also, the effects of long, flexible and bulky side group on the inherent viscosity, solubility, thermal property, thermal stability, UV-Vis absorption and fluorescence characteristics of PAs were studied.

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EXPERIMENTAL

Materials and Measurements

All materials and solvents were purchased either from Merck or Fluka Chemical Co. 4-Hydroxybenzaldehyde, acetophenone, *p*-fluoronitrobenzene, hydrazine monohydrate, Pd/C, *N,N*-dimethyl acetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), pyridine and reagent-grade aromatic dicarboxylic acids such as pyridine-2,6-dicarboxylic acid (PDA), terephthalic acid (TPA), isophthalic acid (IPA), sebacic acid (SA), adipic acid (AD) were used without purification.

FT-IR spectra were recorded on a Bruker Tensor 27 using KBr pellets over the range of 400–4000 cm^{-1} . The ^1H and ^{13}C -NMR spectra were performed on a Bruker DRX 500 MHz Advance instrument, with DMSO- d_6 as solvent. Elemental analysis was performed with a CHN-600 Leco elemental analyzer. Inherent viscosities of polymers were measured by an Ubbelohde suspended-level viscometer at 25°C using 0.5 g/dL NMP solution. UV-Vis and fluorescence spectra were obtained by using a UV-2100 spectrophotometer and a Perkin-Elmer LS3 fluorescence spectrometer, respectively. The dynamic mechanical measurement was recorded on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA, Surrey, UK) over a temperature range of 25–300°C at 1 Hz and a heating rate of 10 K/min. Thermogravimetric analysis (TGA) was recorded on a Du Pont Instruments of TGA 951 analyzer in the temperature range of 30–600°C under N_2 (20 cm^3/min) at a heating rate of 10 K/min. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer Pyris 6 DSC under N_2 (20 cm^3/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 DPDAB was prepared according to the following steps, as shown in Scheme 1.

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

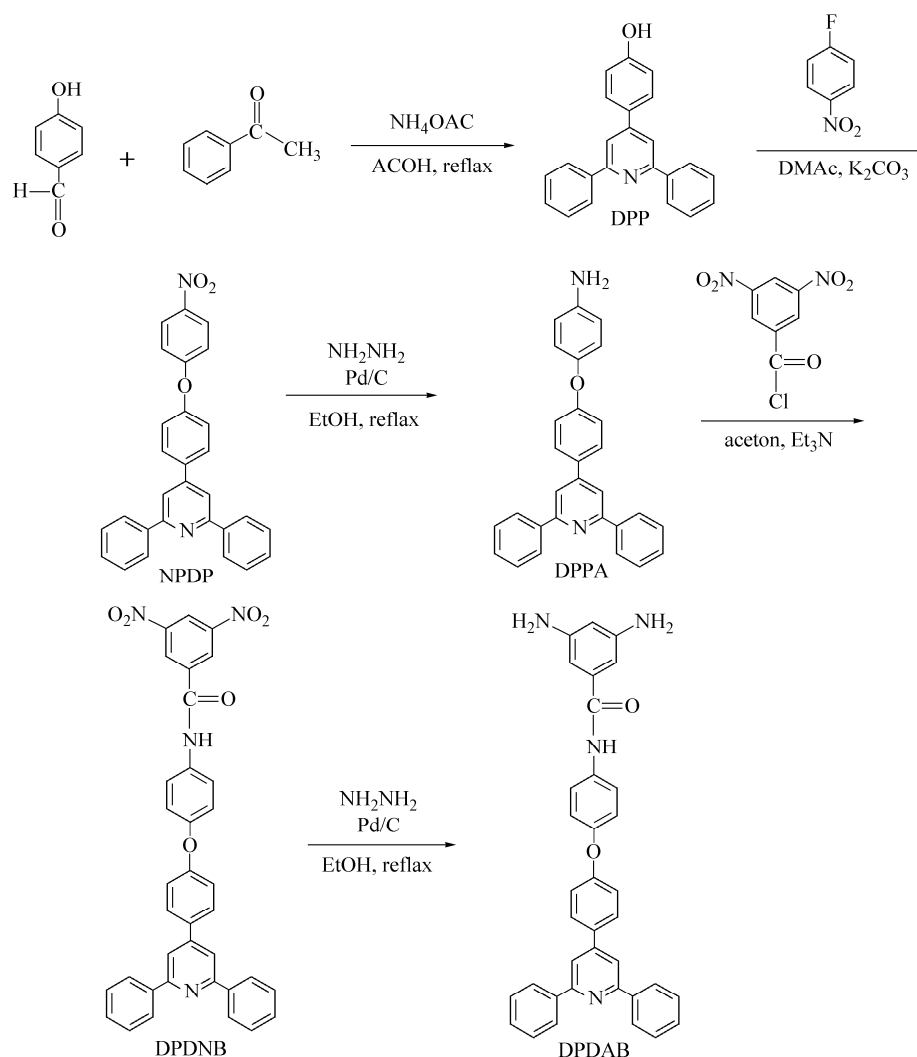
In a 250 mL round-bottomed, two-necked flask equipped with a condenser and a magnetic stirrer bar, a mixture of 5 g (0.4 mmol) 4-hydroxybenzaldehyde, 9.61 g (0.8 mmol) acetophenone, 17.0 g (2.8 mmol) ammonium acetate and 100 mL glacial acetic acid was refluxed at 120°C for 14 h. Upon cooling, the precipitated yellow solid was collected by filtration and washed with ethanol. The yield of the crude product was 84%. The crude product was recrystallized from ethanol giving white solid with yield 91% and mp = 196–198°C. FT-IR spectrum exhibited absorptions at 3010 (OH), 1623 (C=C), and 1556 (C=N) cm^{-1} . Anal. Calcd. for $\text{C}_{23}\text{H}_{17}\text{NO}$: C, 85.44%; H, 5.26%; N, 4.33%. Found: C, 85.39%; H, 5.20%; N, 4.40%.

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

In a 250 mL round-bottomed two-necked flask equipped with a condenser and a magnetic stirrer bar, a mixture of 19.46 g (0.6 mmol) DPP, 8.5 g (0.6 mmol) *p*-fluoronitrobenzene, and 8.28 g (0.6 mmol) potassium carbonate in 70 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 mp = 190–192°C. FT-IR spectrum exhibited absorptions at 1547–1345 (NO_2), 1244 (C—O—C), and 1603 (C=N) cm^{-1} . Anal. Calcd. for $\text{C}_{29}\text{H}_{20}\text{N}_2\text{O}_3$: C, 78.37%; H, 4.50%; N, 6.30%. Found: C, 78.45%; H, 4.56%; N, 6.22%.

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

In a 250 mL two necked round-bottomed flask equipped with a reflux condenser, a dropping funnel, a magnetic stirrer bar, a mixture of 10 g (0.22 mmol) of the purified nitro compound (NPP), 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 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, recrystallised from acetonitrile and dried in a vacuum oven at 70°C. The yield of the reaction was 88% and mp = 162–164°C. FT-IR spectrum exhibited absorptions at 3448–3378 (NH_2), 1239 (C—O—C), 1598 (C=N), and 1507 (C=C) cm^{-1} . Anal. Calcd. for $\text{C}_{29}\text{H}_{22}\text{N}_2\text{O}$: C, 84.03%; H, 5.31%; N, 6.76%. Found: C, 84.13% H, 5.45%; N, 6.82%.



Scheme 1 Synthesis of intermediates and diamine (DPDAB)

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

In a 250 mL two necked round-bottomed flask equipped with a reflux condenser, a dropping funnel, and a magnetic stirrer bar, 10 g (0.24 mmol) PBA was dissolved in 75 mL of acetone. 4 mL triethylamine (Et_3N) was added to the solution and 5.5 g (0.24 mmol) 3,5-dinitrobenzoylchloride 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 large volume of water. The yellow powder was collected by filtration, washed with water. The crude product was recrystallized from ethanol and then dried overnight under vacuum at 70°C . The yield was 87% and mp = $145\text{--}148^\circ\text{C}$. FT-IR spectrum showed characteristic absorptions at $1547\text{--}350$ (NO_2), 1694 ($\text{C}=\text{O}$), 1244 ($\text{C}-\text{O}-\text{C}$), 1603 ($\text{C}=\text{N}$), and 1502 ($\text{C}=\text{C}$) cm^{-1} . Anal. Calcd. for $\text{C}_{36}\text{H}_{24}\text{N}_4\text{O}_6$: C, 71.05%; H, 3.94%; N, 9.21%. Found: C, 71.11%; H, 3.87%; N, 9.17%.

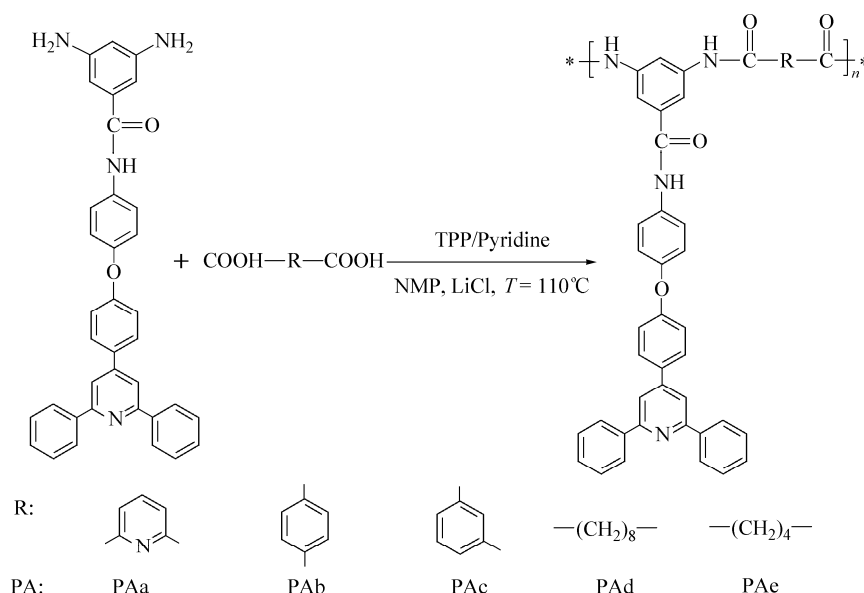
N-(4-(4-(2,6-diphenylpyridin-4-yl)phenoxy)phenyl)-3,5-diaminobenzamide (DPDAB)

In a 100 mL two necked round-bottomed flask equipped with a reflux condenser, a dropping funnel and a magnetic stirrer, 1 g (0.01 mmol) PPDN 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 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 (NH₂), 1653 (C=O), 1603 (C=N), 1542 (C=C), 1234 (C–O–C) cm⁻¹. ¹H-NMR (500 MHz, DMSO-d₆): δ 10.10 (s, 1H, NH), 8.30 (dd, 4H, Ar-Hn, *J* = 7 Hz), 8.18 (s, 2H, Ar-Hm), 8.07 (d, 2H, Ar-He, *J* = 8.5 Hz), 7.84 (d, 2H, Ar-Hh, *J* = 9 Hz), 7.48 (dd, 4H, Ar-Ho, *J* = 7 Hz), 7.18 (dd, 2H, Ar-Hp, *J* = 7 Hz), 7.13 (d, 2H, Ar-Hg, *J* = 9 Hz), 7.11 (d, 2H, Ar-Hf, *J* = 9 Hz), 6.30 (d, 2H, Ar-Hd, *J* = 2 Hz), 6.01 (t, 1H, Ar-Hc, *J* = 2 Hz), 4.98 (s, 4H, NH₂). ¹³C-NMR (500 MHz, DMSO-d₆): δ 167.24 (C, C=O), 158.81, 156.48, 150.99, 149.18, 148.86, 138.84, 136.82, 136.10, 132.09, 129.23, 129.13, 128.75, 126.96, 121.67, 119.84, 117.88, 116.22 and 102.27 (C, Ar). Anal. Calcd. for C₃₆H₂₈N₄O₂: C, 78.83%; H, 5.11%; N, 10.32%. Found: C, 78.88%; H, 5.16%; N, 10.26%.

Polymer Synthesis

The PAs were prepared by the following general procedure (Scheme 2).



Scheme 2 Reaction scheme for preparation of polyamides

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 1.5 mmol of a dicarboxylic acid, 0.4 g (1.5 mmol) diamine DPDAB, 1.2 mL triphenyl phosphite (TPP), 0.6 g lithium chloride (LiCl) and 0.5 mL NMP was refluxed at 110°C for 12 h under a stream of N₂. After cooling, the reaction mixture was poured into a large volume of methanol and the precipitate was washed thoroughly with hot water, collected on a filter paper and dried at 80°C in a vacuum oven for 24 h. The inherent viscosity of the polymers was in the range of 0.45–0.68 dL g⁻¹. The yields of reaction were in the range of 85%–92%.

PAa: FT-IR (KBr, cm⁻¹): 3350–3489 (N–H stretching), 1674 (C=O stretching), 1608 (C=N stretching), 1547–1502 (combined N–H bending and C–N stretching), 1234 (C–O–C). ¹H-NMR (500 MHz, DMSO-d₆): δ 10.73 (s, 2H, NH), 10.53 (s, 1H, NH), 7.05–8.99 (m, 26H, Ar-H). The yield of the reaction was 85%. Anal. Calcd. for (C₄₃H₂₉N₅O₄)_n: C, 75.99%; H, 4.27%; N, 10.30%. Found: C, 76.09%; H, 4.19%; N, 10.23%.

PAb: FT-IR (KBr, cm⁻¹): 3428–3339 (N–H stretching), 1664 (C=O stretching), 1603 (C=N stretching), 1552–1502 (combined N–H bending and C–N stretching), 1239 (C–O–C). ¹H-NMR (500 MHz, DMSO-

d_6): δ 10.73 (s, 2H, NH), 10.50 (s, 1H, NH), 7.14–8.66 (m, 27H, Ar-H). The yield of the reaction was 92%. Anal. Calcd. for $(C_{44}H_{30}N_4O_4)_n$: C, 77.87%; H, 4.42%; N, 8.26%. Found: C, 77.93%; H, 4.50%; N, 8.17%.

PAC: FT-IR (KBr, cm^{-1}): 3425–3335 (N–H stretching), 1674 (C=O stretching), 1603 (C=N stretching), 1542–1502 (combined N–H bending and C–N stretching), 1234 (C–O–C). ^1H -NMR (500 MHz, DMSO- d_6): δ 10.75 (s, 2H, NH), 10.49 (s, 1H, NH), 6.99–8.59 (m, 27H, Ar-H). The yield of the reaction was 70%. Anal. Calcd. for $(C_{44}H_{30}N_4O_4)_n$: C, 77.87%; H, 4.42%; N, 8.26%. Found: C, 77.80%; H, 4.35%; N, 8.32%.

PAD: FT-IR (KBr, cm^{-1}): 3420–3343 (N–H stretching), 2928–2852 (C–H stretching), 1689 (C=O stretching), 1603 (C=N stretching), 1542–1507 (combined N–H bending and C–N stretching), 1229 (C–O–C). The yield of the reaction was 87%. ^1H -NMR (500 MHz, DMSO- d_6): δ 10.36 (s, 1H, NH), 10.05 (s, 2H, NH), 7.10–8.29 (m, 23H, Ar-H) 2.48 (t, 4H, Aliphatic protons), 1.57–1.61 (m, 4H, Aliphatic protons), 1.27–1.30 (m, 8H, Aliphatic protons). Anal. Calcd. for $(C_{46}H_{42}N_4O_4)_n$: C, 77.31%; H, 5.88%; N, 7.84%. Found: C, 77.25%; H, 5.79%; N, 7.91%.

PAe: FT-IR (KBr, cm^{-1}): 3432 (N–H stretching), 3010, 2901 (C–H stretching), 1679 (C=O stretching), 1598 (C=N stretching), 1546–1501 (combined N–H bending and C–N stretching), 1229 (C–O–C). ^1H -NMR (500 MHz, DMSO- d_6): δ 10.39 (s, 1H, NH), 10.13 (s, 2H, NH), 7.10–8.29 (m, 23H, Ar-H), (1H, Aliphatic protons), 2.6 (t, 4H, Aliphatic protons), 1.17–1.60 (m, 4H, Aliphatic protons). The yield of the reaction was 72%. Anal. Calcd. for $(C_{42}H_{34}N_4O_4)_n$: C, 76.59%; H, 5.16%; N, 8.51%. Found: C, 77.65%; H, 5.11%; N, 8.60%.

RESULTS AND DISCUSSION

Monomer Synthesis and Characterization

A new diamine monomer containing long, flexible and bulky side group was synthesized according to the synthetic route shown in Scheme 1. First, condensation of 4-hydroxybenzaldehyde with acetophenone and ammonium acetate in glacial acetic acid afforded 4-(2,6-diphenylpyridine-4-yl)phenol (DPP). In the second step,

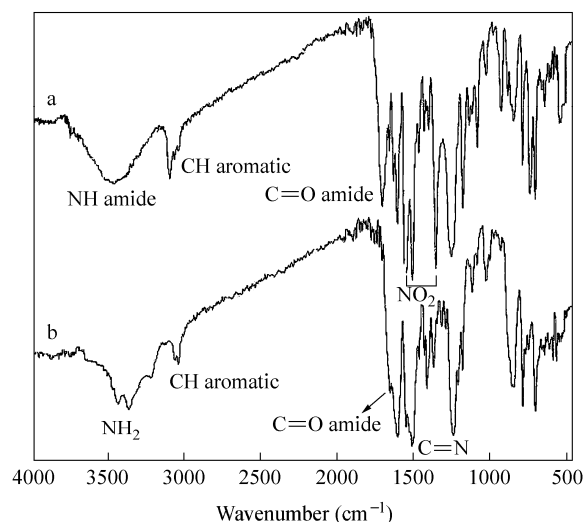


Fig. 1 FT-IR spectra of DPDNB (a) and DPDAB (b)

4-(4-nitrophenoxy)phenyl)-2,6-diphenylpyridine (NPDP) was prepared in DMAc and in the presence of K_2CO_3 from the nucleophilic aromatic substitution reaction between DPP and 4-fluoro nitrobenzene. Reduction of the nitro compound (NPDP) resulted in preparation of 4-(4-(2,6-diphenyl pyridine-4-yl)phenoxy)benzamine (DPPA). The dinitro compound, *N*-(4-(4-(2,6-diphenylpyridin-4-yl)phenoxy)phenyl)-3,5-dinitrobenzamide

(DPDNB), was synthesized by the nucleophilic aromatic substitution reaction of DPPA with 3,5-dinitrobenzoylchloride. In the final step, reduction of DPDNB in ethanol with hydrazine monohydrate in the presence of catalytic amount of palladium on activated carbon produced a new diamine (DPDAB). The structure of DPDAB was confirmed by elemental analysis, FT-IR, ^1H and ^{13}C -NMR techniques. The FT-IR spectra of DPDNB and DPDAB are shown in Fig. 1. DPDNB displayed the characteristic absorption bands corresponding to the symmetric and asymmetric NO_2 stretching at 1502 and 1350 cm^{-1} , respectively, which disappeared after reduction. FT-IR spectrum of DPDAB showed the characteristic absorption bands at 3357 and 3054 cm^{-1} due to N-H stretching. ^1H and ^{13}C -NMR spectra of the diamine compound are illustrated in Fig. 2. The signal at $\delta = 4.98$ in Fig. 2 is related to the protons of amino group. Assignments of each proton and carbon are also given in the figure, and these spectra clearly confirm that the diamine (DPDAB) prepared herein is consistent with the proposed structure.

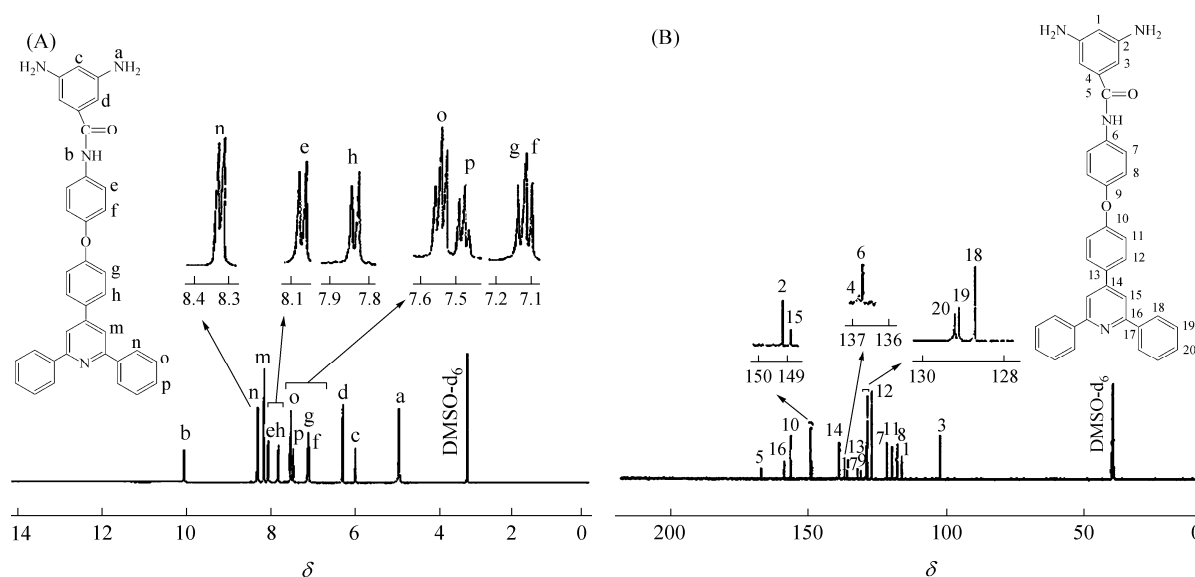
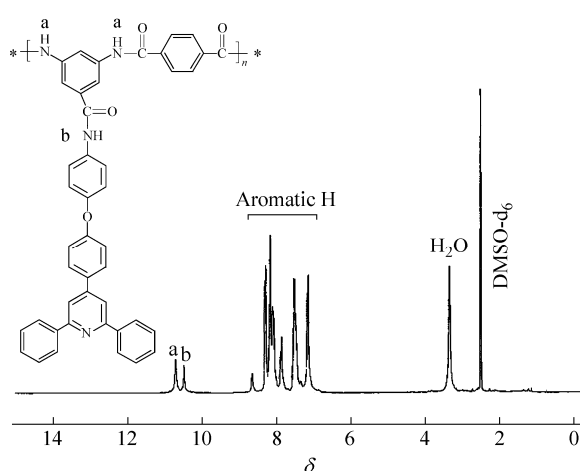
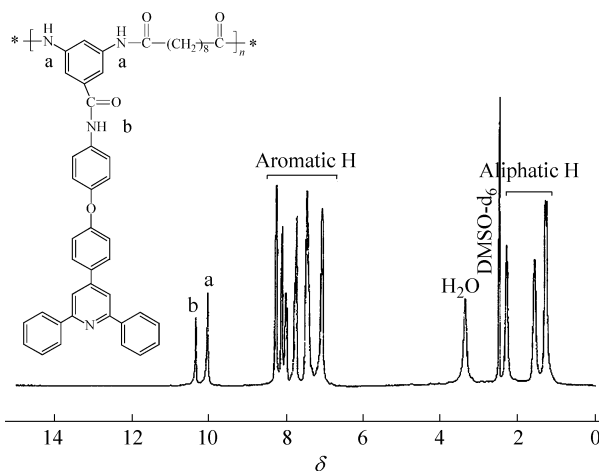


Fig. 2 ^1H -NMR (A) and ^{13}C -NMR (B) spectra of DPDAB

Polymer Synthesis and Characterization

A series of new polyamides having long, flexible and bulky triaryl pyridine pendent unit containing amide and ether linkages were prepared from the diamine monomer (DPDAB) with five aromatic and aliphatic dicarboxylic diacids by using Yamazaki phosphorylation method^[27]. The polymerization was carried out *via* solution polycondensation using triphenyl phosphite (TPP) and pyridine as catalyst (Scheme 2). Pyridine is employed invariably to activate TPP through a complex formation. Polymerization reaction was carried out homogeneously in NMP solution in the presence of LiCl. Addition of the inorganic salts increases both the solubility of the polymers in reaction media and viscosity of the resulting polymers, and, consequently, the yield and molecular weight of the polyamides. The polyamides were prepared in 70%–92% yields and they had moderate inherent viscosity values ranged between 0.45 dL g^{-1} and 0.68 dL g^{-1} (Table 1), indicating sufficient high molecular weights for casting thin and homogeneous films from NMP solution. The structures of polyamides were confirmed by elemental analysis, FT-IR and ^1H -NMR spectroscopic techniques. The elemental analysis values of the polyamides were in agreement with their respective structures. The FT-IR spectra of the polyamides exhibit characteristic absorption bands around 1689 – 1603 cm^{-1} due to the carbonyl group of amide, and a band around 3330 cm^{-1} related to $-\text{NH}-$ group. ^1H -NMR spectra of PAb and PAd are shown in Figs. 3 and 4, respectively. The signals at $\delta = 10.73$ and 10.50 in these figures are related to the protons of amide groups in the main chain and side chain, respectively. The signals of aromatic protons appeared in the range of $\delta = 7.14$ – 8.66 . These results agree well with the proposed polymer structure.

Fig. 3 ^1H -NMR spectrum of PAbFig. 4 ^1H -NMR spectrum of PAD

Solubility

The main aim of this study was to prepare novel polyamides with improved solubility without sacrificing their thermal stability. The solubility of the polyamides was investigated qualitatively in various solvents and the results are summarized in Table 1. The synthesized polyamides showed good solubility in common polar aprotic solvents such as DMF, NMP, DMAc, DMSO, pyridine, THF, *m*-cresol and HMPA at room temperature. In comparison with those reported by other researchers^[31–34], these polymers showed better solubility. The solubility of an aromatic polyamide with an all-meta aromatic ring substitution in the diacid residue can be different from an aromatic polyamide with an all-para aromatic ring substitution. However, the solubility of the synthesized polyamides was identical due to the presence of long and bulky pendent group in the diamine residue. This could be because the bulk of the pendent group in the diamine residue is sufficient to override the effect of the diacid residue in the polymer backbone. The increased solubility of these polymers is mainly due to their amorphous character, and can be explained by the presence of the long flexible and bulky pendent groups with polar amide and ether linkages which can interact with polar solvent molecules. Because of these flexible voluminous groups, the packing of the polymer chains in tight structures through hydrogen bonding between amid groups is prevented. It is evident that as a result of increased chain packing distances the solvent molecules can penetrate readily and interact with the polar groups in the pendant and to solubilize the polymer chain. However, the presence of bulky triaryl pyridine group with polar amide and ether linkages is especially effective for the high solubility of these PAs. The amorphous nature of the PAs was also reflecting their good organosolubility.

Table 1. Inherent viscosity and solubility of polyamides

Code	η_{inh}^a (dL/g)	DMAc	DMF	DMSO	NMP	PY	THF	HMPA	<i>m</i> -Cresol	Acetone
PAa	0.68	++	++	++	++	++	++	++	++	–
PAb	0.67	++	++	++	++	++	++	++	++	–
PAc	0.5	++	++	++	++	++	++	++	++	–
PAd	0.45	++	++	++	++	++	++	++	++	–
PAe	0.52	++	++	++	++	++	++	++	++	–

The solubility was determined by using 5 g sample in 100 mL of solvent;

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

++ soluble at room temperature; + soluble after heating at 60°C; +- partially soluble after heating at 60°C; – insoluble after heating at 60°C;

^a Viscosity, measured at a polymer concentration of 0.5 g/dL in NMP at 25°C

Optical Properties

The UV-Vis absorption studies were carried out on dilute (10^{-5} mol/L) solutions of DPDAB and polyamides (0.2 g/dL) in DMF. Generally the diamine and all of the polyamides show almost identical UV-Vis absorption spectra with maximum at 285 nm due to the $\pi \rightarrow \pi^*$ transition of aromatic chromophore. Their spectroscopy data were used to confirm the presence of the chromophore triaryl pyridine unit. The UV-Vis absorption spectra of the DPDAB and polyamides are exhibited in Fig. 5(a). The excitation wavelength of 285 nm was used for all the polyamides. The fluorescence emission wavelengths of the DPDAB and polyamides were in the range of 400–700 nm with the maximum in the range of 429–550 nm as can be seen in Fig. 5(b). These results confirm that triaryl pyridine unit in the side chain is responsible for the UV absorption and also for the fluorescence emission. The polyamides (PAd and PAb) and DPDAB have the same wide fluorescence spectral pattern with maximum in the region of 450–550 nm. The higher fluorescence intensity of aliphatic polyamide compared with the aromatic polyamide could be due to the efficiently diminished conjugation and capability of charge transfer complex formation by aliphatic diacids in comparison with the electron-donating amino moiety and the strongly electron-accepting aromatic diacid unit^[35].

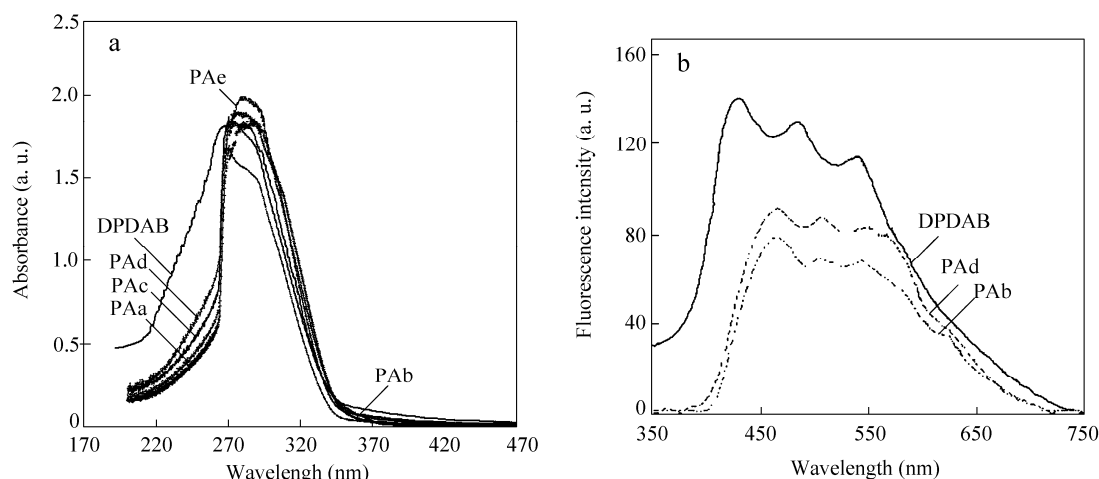


Fig. 5 UV-Vis absorption (a) and fluorescence emission (b) spectra of DPDAB and polyamides

Thermal Properties

Thermal behavior of all polymers was assessed by using differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA). DSC curves of the second scans of the polyamides are illustrated in Fig. 6, and the T_g s of polymers were taken as the midpoint of the change in slope of the baseline in DSC curve. Quenching from temperature of 350°C to room temperature yielded amorphous samples so that in most cases the glass transition temperatures (T_g s) could be easily observed in the second heating traces of DSC. The DSC traces showed T_g in the range of 138–210°C, as listed in Table 2, depending on the structure of dicarboxylic acid residue in the polymer backbone. The DSC curves did not exhibit endotherms until 350°C which can be associated to the amorphous nature of the polyamides. Regarding the peak temperature in the $\tan \delta$ curves, the polymer PAa demonstrates T_g at 220°C, PAb at 240°C and PAd at 160°C. As it is estimated, the T_g values of these polyamides pertained to the structure of the diacid component, and increased with increasing rigidity of the polyamides backbones. The polyamides PAd and PAe showed the lowest T_g due to aliphatic units in their main chains. The aromatic polyamides PAb, PAa, and PAc showed higher T_g s due to presence of rigid phenyl rings in their main chains. It could be clarified that the polyamides from aromatic diacid have more rigid chain structure and more limited rotation around the bond. DMTA curves of the representative polyamides are shown in Fig. 7, and the T_g s were taken as the maximum of $\tan \delta$ curves. Both DSC and DMTA data showed the highest T_g for the polymer prepared from terphthalic acid (PAb), and this can be due to symmetry in the diacid structure. Generally, polymers with bulky pendent groups have lower T_g s

than polymers without bulky side groups owing to the greater interchain distance, which lowers the force of the amide-amide hydrogen bonds that are to some extent responsible for the generally high T_g s of the aromatic polyamides. The reason for the relatively high T_g s of these polyamides can be due to the high barrier for segmental mobility as a result of side chain-side chain and side chain-main chain interactions through H-bonding.

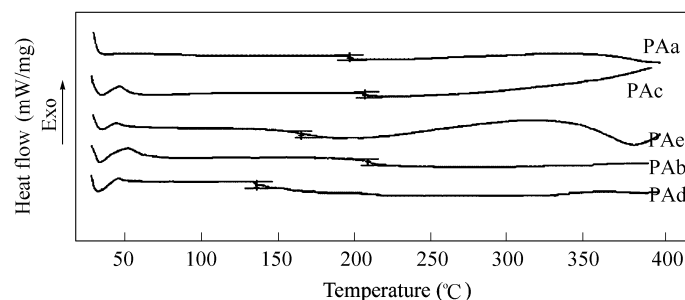


Fig. 6 DSC curves of polyamides

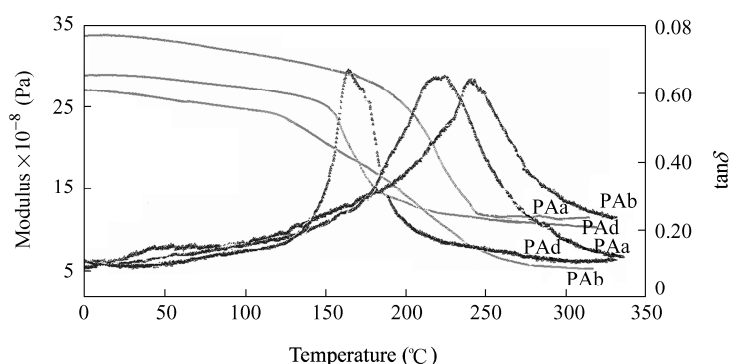


Fig. 7 DMTA curves of polyamides

Table 2. Thermal properties of PAs

Code	T_g (°C) ^a	T_g (°C) ^b	T_i (°C)	T_{10} (°C)	C. Y. (%) ^c
PAa	200	220	290	404	55
PAb	210	240	310	453	67
PAc	195	—	270	390	60
PAd	138	160	277	390	39
PAe	165	—	265	380	45

Decomposition temperature was recorded *via* TGA at a heating rate of 10 K/min in N₂;

T_i : initial decomposition temperature; T_{10} : temperature for 10% weight loss;

^a T_g was taken as midpoint temperature of baseline shift on the second DSC heating trace (10 K/min, in N₂) of the sample after quenching from 350°C; ^b T_g was taken as the maximum peak of tan δ curve, in N₂; ^c Char yield %, residual weight percentage at 600°C in N₂

Thermal stability of the polymers was evaluated by thermogravimetric analysis (TGA) in N₂ atmosphere at a heating rate of 10 K min⁻¹. TGA curves of the polyamides are illustrated in Fig. 8. The initial decomposition temperatures (T_i), the temperatures of 10% weight loss (T_{10}), and the residual weight values determined from the original TGA curves are tabulated in Table 2. Depending on the structure of dicarboxylic diacid residue in the polymer backbone, the T_i values were in the range of 265°C to 310°C. The aromatic polyamide (PAb) inclusive *p*-phenylene ring content in the main chain has the higher char yield and illustrates better thermal stability than the polyamide (PAc) with *m*-phenylene ring in the main chain. The temperatures for 10% weight loss (T_{10}), which is an important criterion to evaluate the thermal stability of polymers, were in range of 380–453°C, indicating their thermal stabilities. The PAe with longer aliphatic unit in the main chain showed higher thermal

stability than the PAd with shorter aliphatic unit, and this can be owing to better dissipation of thermal energy in the longer aliphatic chain as a result of additional free rotation. The values of residual weight of these polymers were in the range of 39%–68% at 600°C. The high char yields of these polymers could be attributed to incorporating pendent groups into the polymer backbone. There is a small weight loss at the beginning of the TGA curves of the polymers, in the temperature range of around 100°C, which is due to the hygroscopic moisture released (amide groups are involved in extensive hydrogen bonding with absorbed water molecules). A sharp weight loss is recorded for PAd and PAe on heating up to 400°C and corresponds to the degradation of methylene groups. The relatively high thermal stability of these polyamides can be attributed to the inter and intra molecular interactions between the side chains and also side chains with the main chain resulting in tight polymer chain packaging and aggregates.

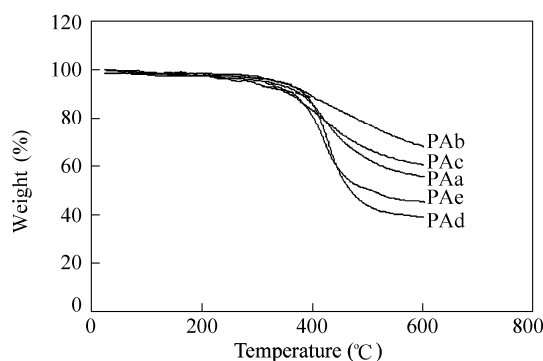


Fig. 8 TGA curves of polyamides

CONCLUSIONS

In this work we prepared a novel aromatic diamine containing long and bulky pendent group and used it to synthesize a series of polyamides by direct polycondensation of diamine with several dicarboxylic diacids using triphenyl phosphite and pyridine as catalyst. Polyamides with moderate inherent viscosities were obtained with excellent solubility in polar aprotic solvents and acceptable thermal stability. These polyamides demonstrated that incorporation of long flexible pendent unit containing polar linkage into the polymer backbone could remarkably enhance the solubility. These polymers could be considered as new processable high-performance polymeric materials.

REFERENCES

- 1 Yang, H.H., "Aromatic high-strength fibers", Wiley, New York, 1989, p. 10
- 2 Cassidy, P.E., "Thermally stable polymers", Marcel Dekker, New York Inc, 1980, p. 27
- 3 Frazer, A.H., "High temperature resistant polymers", Wiley, New York, 1968, p. 17
- 4 Culbertson, B.M. and Pittman, C.U., "New Monomers and Polymers", Plenum Press, New York, 1984, p. 22
- 5 Patil, P.S., Pal, R.R., Salunkhe, M.M., Maldar, N.N. and Wadgaonkar, P.P., Eur. Polym. J., 2007, 43: 5047
- 6 Shao, Y., Li, Y., Zhao, X., Ma, T., Gong C. and Yang, F., Eur. Polym. J. 2007, 43: 4389
- 7 Liaw, D.J., Wang, K.L., Pundlik Pujari, S., Huang, Y.C., Tao, B.C., Chen, M.H., Lee, K.R. and Lai, J.Y., Dyes Pigments, 2009, 82: 109
- 8 Ghaemy, M. and Alizadeh, R., Eur. Polym. J., 2009, 45: 1681
- 9 Ebadi, H. and Mehdipour-Ataei, S., Chinese J. Polym. Sci., 2010, 28(1): 29
- 10 Imai, Y., Malder, N.N. and Kakimoto, M., J. Polym. Sci. Part A: 1984, 22: 2189
- 11 Bruma, M., Mercer, F., Fitch, J. and Cassidy, P., J. Appl. Polym. Sci., 1995, 56: 527
- 12 Eastmond, G.C., Gibas, M. and Paprotny, J., Eur. Polym. J., 1999, 35: 2097

- 13 Hsiao, S.H. and Dai, L.R., *J. Polym. Sci. Part A*: 1999, 37: 665
- 14 Faghihi, K., Shabani, M. and Izadkhah, A., *Chinese J. Polym. Sci.*, 2010, 28(4): 589
- 15 Mallakpour, S. and Khani, M., *Chinese J. Polym. Sci.*, 2010, 28(6): 859
- 16 Mallakpour, S., and Dinari, M., *Chinese J. Polym. Sci.*, 2010, 28(5): 685
- 17 Kusama, M., Mastsumoto, T. and Kurosaki, T., *Macromolecules*, 1994, 27: 1117
- 18 Liaw, D.J., Chen, W.H., Hu, C.K., Lee, K.R. and Lai, J.Y., *Polymer*, 2007, 48: 6571
- 19 Liou, G.S., Fang, Y.K. and Yen, H.J., *J. Polym. Res.*, 2007, 14: 147
- 20 Ghaemy, M. and Barghamadi, M., *J. Appl. Polym. Sci.*, 2009, 114: 3464
- 21 Li, F., Fang, S., Ge, J.J., Honigfort, P.S., Chen, J.C., Harris, F.W. and Cheng, S.Z.D., *Polymer*, 1999, 40: 4571
- 22 Liaw, D.J., Chang, F.C., Leung, M.K., Chou, M.Y. and Muellen, K., *Macromolecules*, 2005, 38: 4024
- 23 Mallakpour, S. and Kolahdoozan, M., *React. Funct Polymers*, 2008, 68: 91
- 24 Liaw, D.J. and Liaw, B.Y., *Polymer*, 2001, 42: 839
- 25 Ghaemy, M. and Barghamadi, M., *J. Appl. Polym. Sci.*, 2009, 111: 1588
- 26 Myung, B.Y., Ahn, C.J. and Yoon, T.H., *Polymer*, 2004, 45: 3185
- 27 Yamazaki, N., Matsumoto, M. and Higashi, F., *J. Polym. Sci. Part A*, 1975, 13: 1373
- 28 Ghaemy, M. and Alizadeh, R., *Eur. Polym. J.*, 2009, 45: 3108
- 29 Ghaemy, M., Behmadi, H. and Alizadeh, R., *Chinese Chem. Lett.*, 2009, 20: 961
- 30 Mighani, H. and Ghaemy, M., *Chinese J. Polym. Sci.*, 2010, 28(2): 147
- 31 Liaw, D.J., Liaw, B.Y. and Jeng, M.Q., *Polymer*, 1998, 39: 1597
- 32 Mallakpour, S. and Taghavi, M., *Polymer*, 2008, 49: 3239
- 33 Yagci, H. and Mathias, L.J., *Polymer*, 1998, 39: 3779
- 34 San-José, N., Gómez-Valdemoro, A., Estevez, P., García, F.C., Serna, F. and José Miguel García J. M. *Eur. Polym. J.*, 2008, 44: 3578
- 35 Liou, G.S. and Chang, C.W., *Macromolecules*, 2008, 41: 1667