

Synthesis and Characterization of New Soluble Polyamides from an Unsymmetrical Diamine Bearing a Bulky Triaryl Pyridine Pendent Group

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ABSTRACT: New unsymmetrical diamine monomer containing triaryl pyridine pendent group, 2,4-diaminophenyl [4-(2, 6-diphenyl-4-pyridyl) phenyl]ether, was synthesized via aromatic substitution reaction of 1-chloro-2,4-dinitrobenzene with 4-(2,6-diphenyl-4-pyridyl) phenol, followed by Pd/C-catalyzed hydrazine reduction. Five Polyamides (PA) were prepared by the phosphorylation polycondensation of different dicarboxylic diacids with the diamine. Inherent viscosities of PAs were in the range 0.51–0.59 g/dL indicating formation of medium molecular weight polymers. The weight and number average molecular weights of a PA, (PA-d), determined by GPC were

6944 g/mol and 17,369 g/mol, respectively. PAs exhibited glass-transition temperatures (T_g) in the range 140–235°C. These polymers, essentially amorphous, were soluble in polar aprotic solvents such as DMF, NMP, DMAc, DMSO, pyridine, *m*-cresol, and THF. The initial decomposition temperatures (T_i) of PAs, determined by TGA in air, were in the range 300–380°C indicating their good thermal stability. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3725–3731, 2010

Key words: Polyamides; polycondensation; bulky pendent group; thermal properties

INTRODUCTION

Wholly aromatic polyamides exhibit high thermal stability, good chemical resistance, and excellent mechanical properties that make them find applications in many areas.^{1–4} However, all of these polymers have the common problem of being difficult to process because of their infusibility and poor solubility in organic solvents. The reasons are strong interchain forces, inherent macromolecular rigidity, or semicrystallinity. There has been, therefore, an increased interest in the preparation of polyamides with different substituents or structural irregularities to improve their processability without compromising their other desired properties. These studies include introducing flexible segments into the polymer chain,^{5–9} replacing symmetrical aromatic rings by unsymmetrical ones,^{10–14} introducing bulky pendent groups to minimize crystallization,^{15–19} and forming a non-coplanar structure.^{20–23} Generally, one of the successful approaches to increase the solubility and processability of polyamides without sacrificing high thermal stability is the introduction of bulky pendent groups into polymer backbone. On the other hand, some reports have concerned the incorporation of pyridine and its deriva-

tives into polymeric frameworks.^{24–29} The rigidity based on the symmetry and aromaticity of the pyridine ring would contribute to the thermal and chemical stability, retention of mechanical property of the resulting polymer at elevated temperature, and the polarizability resulting from the nitrogen atom in pyridine ring would be suitable to improve their solubility in organic solvents.³⁰ Most of aromatic polyamides are prepared by reaction between two different bifunctional symmetric monomers, whereas polyamides from asymmetrically substituted *m*-phenylene diamine monomers have been relatively less explored. The meta-catenation is one of the aspects of improvement in processability and solubility. The introduction of these kinds of monomers, so that monomeric units become symmetrically nonequivalent, leads to constitutional isomerism due to the unequal reactivities of monomer unit functional groups, and the sequence distribution influences the final polyamide properties.³¹ The objective of this work was to synthesize new aromatic and aromatic–aliphatic polyamides containing triaryl pyridine pendent group based on asymmetrically substituted *m*-phenylene diamine monomer namely, 2,4-diaminophenyl[4-(2,6-diphenyl-4-pyridyl)phenyl]ether by direct polycondensation of diamine with dicarboxylic acids by means of triphenyl phosphite and pyridine. The resulting polyamides were fully characterized by inherent viscosity measurements, solubility tests, FTIR, ¹H-NMR spectroscopy, DSC and TGA analysis.

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EXPERIMENTAL

Materials and measurements

All chemicals were purchased either from Merck or Fluka Co. *N*-Methyl-2-pyrrolidinone (NMP) and pyridine (Py) were purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves 4 Å. LiCl was dried for 10 h at 180°C under vacuum. All other reagents and solvents were used as received from commercial sources. 4-(2,6-Diphenyl-4-pyridyl)phenol (1) was prepared as formerly described.³⁰

¹H-NMR and ¹³C-NMR spectra were recorded on a 500 MHz Bruker Advance DRX instrument using DMSO-*d*₆ as solvent and tetramethyl silane as an internal standard. FTIR spectra were recorded using a Bruker Tensor 27 spectrometer on KBr pellets. Elemental analysis was 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 in air. Differential scanning calorimetry (DSC) thermograms were recorded with a PerkinElmer Pyris 6 differential scanning calorimeter under nitrogen atmosphere (20 cm³/min) at a heating rate of 10°C/min. The inherent viscosity of the polymers was determined for the solutions of 0.5 g/dL in NMP at 25°C using an ubbelohde viscometer.

Monomer synthesis

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

4-(2,6-Diphenyl-4-pyridyl)phenol (1) (6.43 g, 0.02 mol) and 1-chloro-2,4-dinitrobenzene (4.1 g, 0.02 mol) were dissolved in 50 mL of DMAc in a 250 mL flask, and potassium carbonate (4.14 g, 0.03 mol) was added to the solution. After 30 min of 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 precipitated yellow solid was filtered off, washed with water, and dried. The crude product was recrystallized from methanol. The yield of the reaction was about 93% (8.9 g), and the melting point was 215–217°C. Anal. calcd. for C₂₉H₁₉N₃O₅: C, 71.16%; H, 3.91%; N, 8.58%. Found: C, 71.69%; H, 3.56%; N, 8.45%. ¹H-NMR (500 MHz, DMSO-*d*₆, ppm): δ = 8.94 (s, 1H), 8.51 (d, 1H, *J* = 9.25 Hz), 8.36 (d, 4H, *J* = 7.27 Hz), 8.25(m, 4H), 7.57 (t, 4H, *J* = 7.24 Hz), 7.52 (d, 2H, *J* = 8.75 Hz), 7.48 (d, 2H, *J* = 8.75Hz), 7.33 (d, 1H, *J* = 9.25 Hz).

2,4-Diaminophenyl[4-(2,6-diphenyl-4-pyridyl)phenyl]ether (3)

In a 250-mL round-bottom flask equipped with stirring bar, a mixture of 4.89 g (0.01 mol) of dinitro

compound (2) and 0.1 g of palladium on activated carbon (Pd/C, 10%) were dispersed in 100 mL of ethanol. The suspension was heated to reflux, and 8 mL of hydrazine monohydrate was added slowly to the mixture. After a further 5 h of reflux, the solution was filtered hot to remove Pd/C, and the filtrate was cooled to precipitate white crystals. The product was collected by filtration and dried in vacuum at 80°C. The yield of the reaction was 72% (3.10 g), and the melting point was 168–170°C.

Anal. calcd for C₂₉H₂₃N₃O: C, 81.09%; H, 5.40%; N, 9.78%. Found: C, 81.34%; H, 5.56%; N, 9.45%. ¹H-NMR (500 MHz, DMSO-*d*₆, ppm): δ = 8.32(d, 2H, *J* = 7.13 Hz), 8.14 (s, 2H), 7.99 (d, 2H, *J* = 8.80 Hz), 7.55(t, 4H, *J* = 7.70), 7.49 (t, 2H, *J* = 7.14 Hz), 6/61 (d, 1H, *J* = 8.36 Hz), 6.09 (s, 1H), 5.88 (d, 1H, *J* = 8.36 Hz), 4.76 (s, 2H), 4.62 (s, 2H); ¹³C-NMR (500 MHz, DMSO-*d*₆, ppm): δ = 102.13, 103.99, 116.78, 116.92, 122.77, 127.78, 129.52, 129.58, 130.03, 131.53, 132.59, 139.78, 141.85, 147.50, 150.01, 157.30, 161.00.

Polyamide synthesis

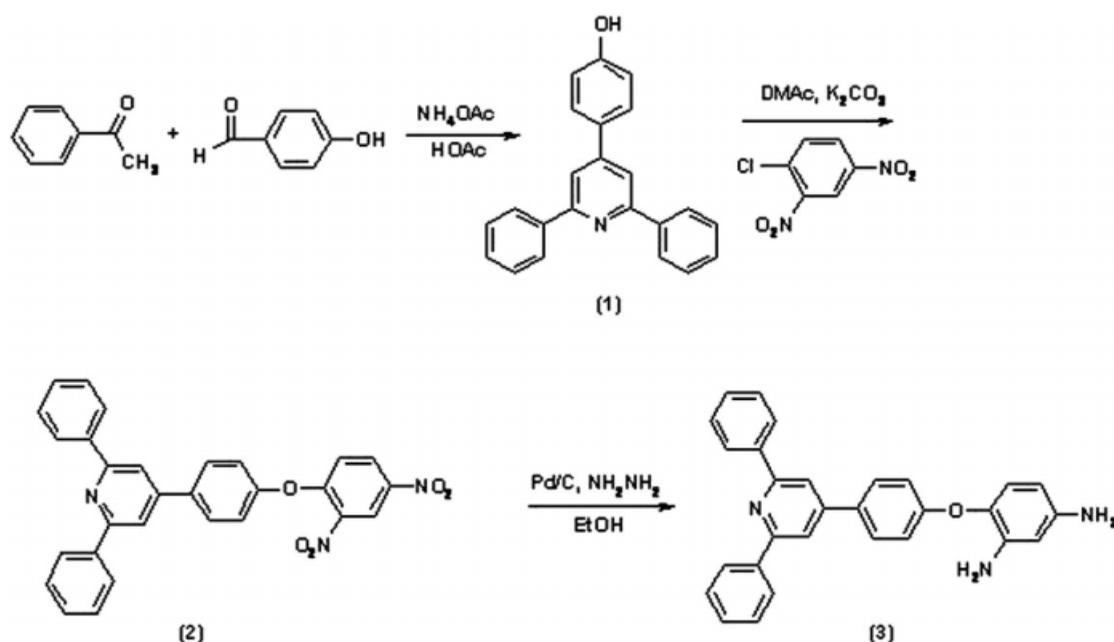
A typical polymerization reaction is as follows. The diamine (1 mmol), dicarboxylic acid (1 mmol), and lithium chloride (0.6 g) were dissolved in a mixture of pyridine (1 mL), triphenyl phosphite (1.2 mmol), and NMP (8 mL) in a 50-mL three-necked flask fitted with a mechanical stirrer, and the resulting solution stirred and heated at 110°C under dry nitrogen for 8 h. The system was then cooled to room temperature, and the solution precipitated in 300 mL of methanol to give a white precipitate. The polymer obtained was filtered off and washed with hot water. For purification, the polyamides obtained from pyridine-2,6-dicarboxylic acid (PA-a), terephthalic acid (PA-b), and isophthalic acid (PA-c) were refluxed for 1 h in methanol, and the polyamides obtained from adipic acid (PA-d) and sebacic acid (PA-e) were refluxed for 1 h in water. The extracted polyamides were then filtered and vacuum-dried at 100°C.

PA-a

The yield 90%, η_{inh} (dL/g) = 0.51. FTIR (KBr, cm⁻¹): 3348 (NH amide), 3035 (C–H aromatic), 1691 (C=O amide), 1604 (C=N), 1525 (N–H bending), 1222 (C–O). ¹H-NMR (DMSO-*d*₆): δ 10.98 (s-1H), 10.68 (s-1H), 6.99–8.75 (m-22H). Anal. Calcd. C, 77.14; H, 4.28; N, 10.0. Found C, 77.76; H, 4.26; N, 9.57.

PA-b

The yield 88%, η_{inh} (dL/g) = 0.53. FTIR (KBr, cm⁻¹): 3420 (NH amide), 3035 (C–H aromatic), 1671 (C=O amide), 1605 (C=N), 1504 (N–H bending),



Scheme 1 Synthetic procedure for preparation of new diamine, 2,4-diaminophenyl[4-(2,6-diphenyl-4-pyridyl)phenyl]ether(3).

1221(C—O). $^1\text{H-NMR}$ (DMSO-d_6): δ 10.56 (s-1H), 10.14 (s-1H), 7.11–8.28 (m-23H). Anal. Calcd. C, 79.42; H, 4.47; N, 7.51. Found C, 79.58; H, 4.26; N, 7.18.

PA-c

The yield 93%, η_{inh} (dL/g) = 0.59. FTIR (KBr, cm^{-1}): 3422 (NH amide), 3060 (C—H aromatic), 1675 (C=O amide), 1605 (C=N), 1508 (N—H bending), 1223 (C—O). $^1\text{H-NMR}$ (DMSO-d_6): δ 10.60 (s-1H), 10.13 (s-1H), 7.15–8.61 (m-23H). Anal. Calcd. C, 79.42; H, 4.47; N, 7.51. Found C, 79.31; H, 4.33; N, 7.88.

PA-d

The yield 91%, η_{inh} (dL/g) = 0.55. FTIR (KBr, cm^{-1}): 3423 (NH amide), 3035 (C—H aromatic), 2933 (C—H aliphatic), 1670 (C=O amide), 1604 (C=N), 1507 (N—H bending), 1211(C—O). $^1\text{H-NMR}$ (DMSO-d_6): δ 9.95 (s-1H), 9.37 (s-1H), 6.93–9.38(m-19H), 2.26 (t-4H), 1.55 (m-4H). Anal. Calcd. C, 77.92; H, 5.38; N, 7.79. Found C, 77.23; H, 5.82; N, 7.15.

PA-e

The yield 91%, η_{inh} (dL/g) = 0.51. FTIR (KBr, cm^{-1}): 3425 (NH amide), 3036 (C—H aromatic), 2923 (C—H aliphatic), 1669 (C=O amide), 1604 (C=N), 1507 (N—H bending), 1217(C—O). $^1\text{H-NMR}$ (DMSO-d_6): δ 9.92 (s-1H), 9.32 (s-1H), 6.99–8.27(m-19H), 2.08 (t-4H), 1.28 (m-12H). Anal. Calcd. C, 78.65; H, 6.21; N, 7.05. Found C, 78.29; H, 6.42; N, 7.36.

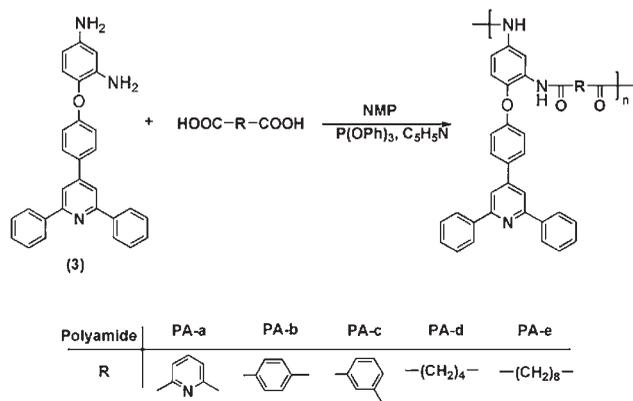
RESULTS AND DISCUSSION

Monomer synthesis and characterization

A new diamine was synthesized according to the synthetic route shown in Scheme 1. Condensation of acetophenone with aromatic aldehyde and ammonium acetate is well known as a classical but convenient synthetic method for preparation of triaryl pyridine.³² This reaction was applied for the synthesis of 4-(2,6-diphenyl-4-pyridyl) phenol (1). The dinitro compound (2) was synthesized by nucleophilic aromatic substitution reaction of (1) with 1-chloro-2,4-dinitrobenzene. The reaction was performed in DMAC solvent and in the presence of K_2CO_3 . The catalytic hydrogenation of (2) to the corresponding diamine (3) was accomplished by means of hydrazine hydrate in ethanol.

The structure of diamine monomer was confirmed by IR spectrum, ^1H and ^{13}C -NMR spectroscopy. The FTIR spectrum of dinitro compound (2), in Figure 1(a), shows absorption bands at 1540 and 1344 cm^{-1} due to asymmetric and symmetric $-\text{NO}_2$ stretching vibration, whereas bands at 1268 and 1200 cm^{-1} are assigned to C—O—C asymmetric and symmetric stretching. Band at 870 cm^{-1} corresponds to aromatic C—N stretching vibration of C— NO_2 group. After reduction, nitro peaks at 1540 and 1344 cm^{-1} disappeared and characteristic absorption bands of primary amine due to N—H stretching appeared at 3442 and 3357 cm^{-1} , as can be seen in Figure 1(b).

The $^1\text{H-NMR}$ spectrum of dinitro compound (2), in Figure 2, shows aromatic proton at δ : 8.94 (s, 1H), 8.51 (d, 1H, $J = 9.25$ Hz), 8.36 (d, 4H, $J = 7.27$ Hz),



Scheme 2 Synthetic procedure for preparation of polyamides.

optimize the reaction conditions of this new diamine with dicarboxylic acids, the polyamidation reaction with terephthalic acid was investigated by measuring the viscosity of polymer solution at different times. The inherent viscosity of PA-b was measured during polyamidation in a concentration of 0.5 g/dL in NMP at 25°C, and the results are shown in Figure 5. The viscosity increased with the time of polymerization to 0.48 dL/g after 4 h and changed to 0.53 dL/g when the reaction time increased up to 8 h. The inherent viscosities of the polyamides were very close and in the range of 0.51–0.59 dL/g. As the inherent viscosity is a good criterion for estimation of molecular weight, the prepared polyamides should have medium molecular weights. The number and weight average molecular weights (M_n and M_w) of one of the polymer, PA-d, which had acceptable solubility in THF for GPC measurements were determined and the values are 6.9445×10^3 g/mol and 1.7369×10^4 g/mol, respectively. This medium molecular weight and relatively wide molecular weight distribution ($M_w/M_n = 2.50$) can be due to unsymmetrical structure of diamine monomer and formation of constitutional isomerism as a result of the unequal reactivities of

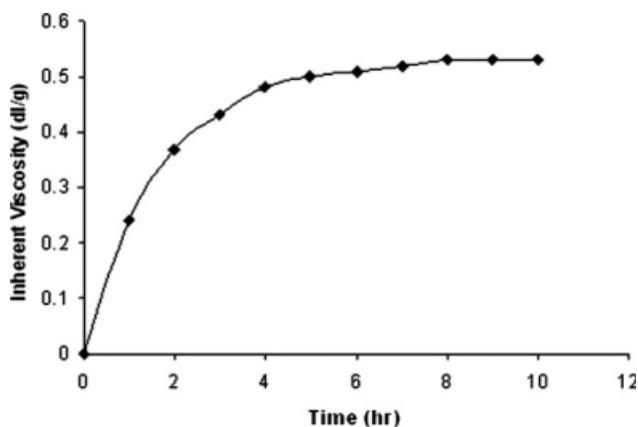


Figure 5 Change in the viscosity of PA, PA-b, with time.

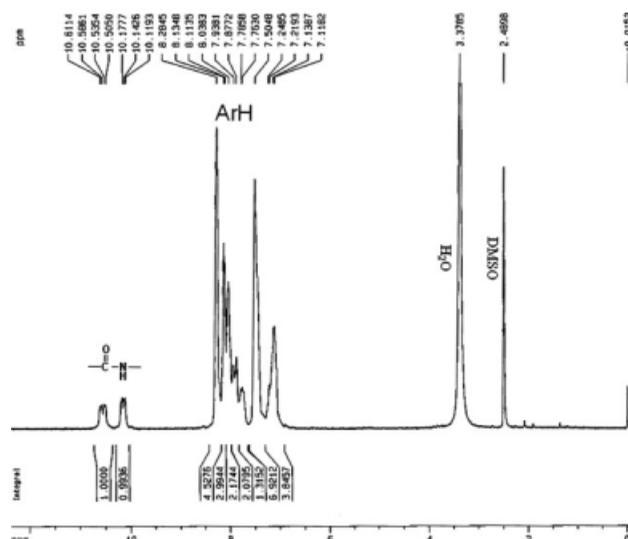


Figure 6 $^1\text{H-NMR}$ spectrum of PA-b.

functional groups in monomer units. The molecular weights of these polymers are similar to the molecular weights of PAs prepared by using unsymmetrical diamines in polycondensation with dicarboxylic acids reported by Hsiao et al.¹³ However, the molecular weights of these PAs are lower than the molecular weights of PAs that have been prepared by using an unsymmetrical diamine in an interfacial polycondensation with dicarboxylic dichlorides.¹⁴

FTIR spectrum of a representative polymer, PA-b, is shown in Figure 1(c). The FTIR spectra of PAs exhibited the characteristic absorption bands in the region of $3350\text{--}3340\text{ cm}^{-1}$ (N–H stretching), $1691\text{--}1670\text{ cm}^{-1}$ (C=O stretching), and $1545\text{--}1504\text{ cm}^{-1}$ (combined N–H bending and C–N stretching) with strong absorptions of aryl ether group in the region of $1250\text{--}1100\text{ cm}^{-1}$. The elemental analysis values were in good agreement with the calculated ones. The results further demonstrated that the polyamides have the expected chemical structures. $^1\text{H-NMR}$ signals at 10.1 and 10.5 ppm, as shown in Figure 6 for the representative polyamide (PA-b), were assigned to the N–H protons. Meanwhile, no signals were detected in the range greater than 10.5 ppm, and this indicated the completely polymerization. The total protons in the spectrum are consistent with the proposed chemical structure of polymer.

Solubility

The solubility behavior of the new polyamides was determined at concentration of 5% (W/V) in a number of solvents, and the results are tabulated in Table I. Almost all prepared polyamides exhibited excellent solubility in polar aprotic solvents such as NMP, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO)

TABLE I
Solubility Behavior of Polyamides

Polyamide	NMP	DMSO	DMAC	DMF	<i>m</i> -cresol	THF	Dioxane	Pyridine	TCE
PA-a	++	++	++	++	++	±	±	++	–
PA-b	++	++	++	++	++	++	±	++	–
PA-c	++	++	++	++	++	++	±	++	–
PA-d	++	++	++	++	++	++	+	++	±
PA-e	++	++	++	++	++	++	+	++	±

DMAC, *N,N*-dimethyl acetamide; DMF, *N,N*-dimethyl formamide; NMP, *N*-methyl pyrrolidone; DMSO, dimethyl sulfoxide; TCE, tetrachloroethane; ++, Soluble at room temperature; +, Soluble on heating at 60°C; ±, partially soluble on heating at 60°C; –, Insoluble on heating at 60°C.

and even in less polar solvents like pyridine, THF, and *m*-cresol but showed poorer solubility in dioxane and tetrachloroethane because of the low value of dielectric constants of these solvents. The good solubility should be the result of the introduction of the bulky pendent triphenyl pyridine group in polymer backbone and unsymmetrical structure coming from diamine monomer. The bulky pendent groups increase the chain distance, inhibit the chain packing, and decrease the interaction of the polymer chains; consequently, the solvents molecules are able to penetrate easily and interact with the polar groups and to solubilize the polymer chains. The amorphous nature of the PAs was also reflecting their good organosolubility. We believe, however, that the presence of pyridine and ether groups in the pendent unit can also contribute effectively in the solubility of these polyamides by interacting with the polar molecules of solvents. In addition, the solubility varies depending upon the dicarboxylic acid used. Polyamides were synthesized from aliphatic dicarboxylic acids (PA-d and PA-e) exhibited better solubility behavior in less polar solvents such as THF and *m*-cresol. The methylene units instead of rigid phenyl improve the solubility of these polyamides.

Thermal properties

DSC and TGA methods applied to evaluate the thermal properties of the polyamides. Thermal analysis

TABLE II
Thermal Characteristic Data of Polyimides

Polymer	T_g (°C)	T_i (°C)	T_5 (°C)	T_{10} (°C)	Char yield (%)
PA-a	233	310	376	409	28
PA-b	235	380	421	472	68
PA-c	223	346	409	456	69
PA-d	164	300	371	396	32
PA-e	140	305	350	377	38

T_g , glass-transition temperature; T_i , initial decomposition temperature; T_5 , temperature for 5% weight loss; T_{10} , temperature for 10% weight loss.

Char yield, weight of polymer remained at 600°C.

data from the TGA and DSC curves of the polyamides are summarized in Table II. The absence of melting peak in DSC thermograms supported the generally amorphous nature of the polyamides. The polyamides showed T_g in the range of 140–235°C. The amorphous nature of the polyamides could be attributed to their asymmetric structural units and bulky pendent group, which decreased the intra and interchain interaction, resulting in loose polymer chain packaging and aggregates. As we expected, the T_g values of the polyamides showed dependence on the structure of the dicarboxylic acid component and decreased with increasing flexibility of the polyamides backbones.

It is evident that the methylene groups between two diamine component present in PA-d and PA-e, facilitating bond rotation, reduced T_g . Among all the synthesized polyamides, PA-b based on terephthalic acid showed the highest T_g value because of the highest rigidity, which inhibited the molecular motion. The DSC curves of polyamides are shown in Figure 7.

Thermal stability of polyamides was evaluated by TGA in air atmosphere at a heating rate 10°C/min. Because the polyamides are hygroscopic materials, a small weight loss (1–3%) is recorded between 90 and 200°C due to loss of moisture. The T_i values were in the range of 300–380°C, and the temperatures of 10%

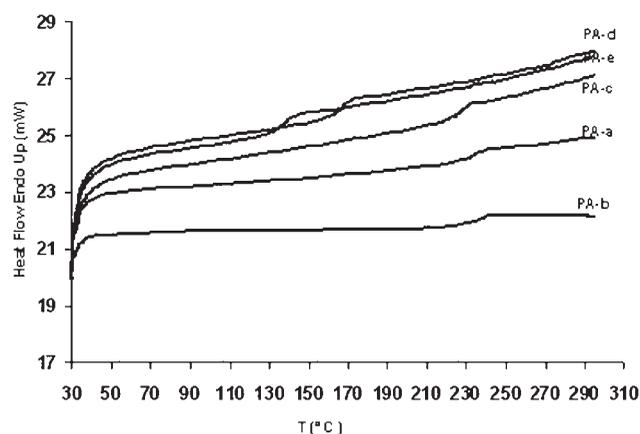


Figure 7 The DSC curves of polyamides.

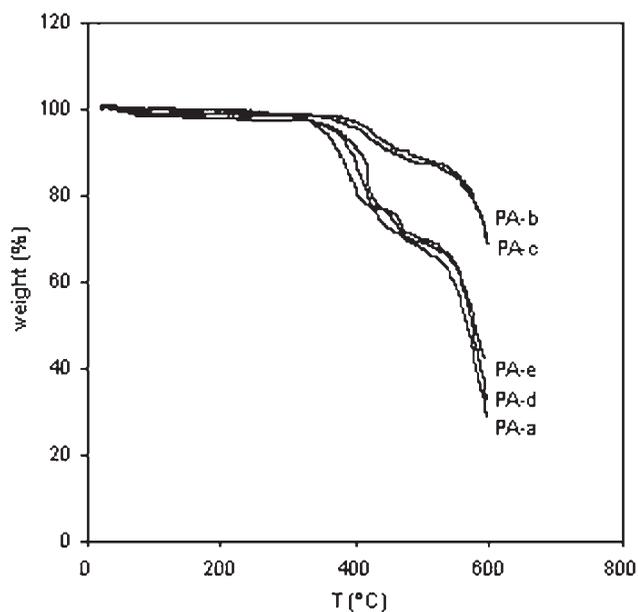


Figure 8 The TGA curves of polyamides.

weight loss were in the range of 377–472°C. In addition, the residual weight retentions at 600°C for the resulting polyamides were in the range of 28–69%, implying that these polyamides possess good thermal stability. The TGA curves are shown in Figure 8. The relatively wide molecular weight distribution, measured by GPC, may be the reason for showing different decomposition temperatures in TGA traces. The other possibility for different decomposition temperatures may be due to presence of traces of NMP, which were not entirely removed during washing the polymers. To compare thermal behavior, the polyamides PA-b and PA-e have the highest and the lowest thermal stability, which is due to presence of rigid phenyl and flexible aliphatic units, respectively, in the polyamides backbone.

CONCLUSIONS

A novel unsymmetrical diamine has been synthesized in good yields and high purity from readily available reagents. Series of polyamides have been prepared from this diamine and various aromatic dicarboxylic acids via the direct phosphorylation polycondensation. The introduction of the bulky triaryl pyridine pendent group into the polymer backbone leads to significantly improved solubility of the polymer in various organic solvents. However, the molecular weight of the polymers, as measured by GPC for one of the polyamides, is not very high. This has been explained and may be due to unequal reactivity of functional groups in the unsymmetrical structure of diamine monomer which leads to formation of constitutional isomerism. Most of these polymers exhibited a desired combination of proper-

ties, such as high thermal stability and excellent solubility in organic solvents, required for high-performance materials.

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