Synthesis of Soluble and Thermally Stable Polyamides from Diamine Containing (quinolin-8-yloxy) Aniline Pendant Group

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ABSTRACT: A novel diamine monomer having pendant 4-(quinolin-8-yloxy) aniline group was successfully synthesized via aromatic substitution reaction of 8-quinolinol with *p*-fluoronitrobenzene followed by Pd/C catalyzed hydrazine reduction, amidation reaction between 4-(quinolin-8-yloxy) aniline and 3,5-dinitrobenzoylcholoride followed by Pd/C catalyzed hydrazine reduction. The diamine monomer was fully characterized by using FTIR, ^{1}H-NMR, ^{13}C-NMR, and elemental analysis. The diamine monomer was polymerized with various aromatic and aliphatic dicarboxylic acids to obtain the corresponding polyamides. The polyamides had inherent viscosity in the range of 0.30–0.41 dL/g and exhibited excellent solubility in the polar aprotic solvents such as DMAc, NMP, *N,N*-dimethylformamide, Pyridine, and DMSO. The glass transition temperatures (T_g) of the polymers are high (up to 313°C) and the decomposition temperatures (T_i) range between 200 and 370°C, depending on the diacids residue in the polymers backbone. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 64–71, 2010

Key words: polyamides; polycondensation; synthesis; thermal properties

INTRODUCTION

Thermally stable polymers have received extensive interest due to the increasing demands for high temperature polymers as replacements for ceramics and metals in the automotive, aerospace, and microelectronics industries. Aromatic polyamides are one of the most important classes of high performance polymers, because they possess excellent mechanical properties, thermal stability, chemical resistance, and low flammability.[1,2] However, they encounter processing difficulties due to limited solubility in organic solvents and high glass transition or melting temperatures which is a result of chain stiffness and intermolecular hydrogen bonding between amide groups.[3] Modification of high performance materials by increasing the solubility and lowering the transition temperatures while maintaining thermal stability are of particular interest. The lower glass transition temperatures and also improved solubility in polyamides are attributed to the flexible linkages,[4,5] the use of meta-oriented monomers,[6,7] noncoplanar unit in the polymer chains,[8] mixed linkages of (ester-amide)s[9] and (amide-ester-imide)s,[10] introduction of bulky side groups into the polymer chains.[10–13] It is well-known that the solubility of polymers is often improved when flexible bonds, large pendent groups or polar substituents are included into the polymer backbone. If these groups are carefully chosen, they are likely to increase solubility without affecting thermal and mechanical properties to any great extent. These modifications work by breaking the chain symmetry and regularity and by destroying hydrogen bonds and generally lead to lower transition temperatures and better solubility.

The objective of the present work was to synthesize and characterize novel polyamides based on diamine monomer containing noncoplanar and bulky pendant group. Introduction of 4-(quinolin-8-yloxy) aniline unit in meta-linked polyamides was expected to provide molecular irregularity and good solubility. On the other hand, the presence of bulky pendant group of 4-(quinolin-8-yloxy) aniline in the backbone of a polyamide may decrease interchain interactions and the ability for polymer chains to pack while providing a barrier to segmental mobility due to intramolecular hydrogen bonding, thus resulting in an enhanced solubility and increased T_g for the polyamides.

EXPERIMENTAL

Materials and measurements

Commercially available 8-quinolinol, *p*-nitrofluorobenzene, pyridine, hydrazine monohydrate, 3,5-dinitrobenzoylchloride, Pd/C, triethylamine, all

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dicarboxylic acids, triphenyl phosphite (TPP) and all solvents were purchased either from Merck or Fluka chemical Co. N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc) were distilled over calcium hydride under reduced pressure.

Infrared measurements were performed on a Bruker-IFS 48 FTIR spectrometer (Ettlingen, Germany). ^{1}H-NMR and ^{13}C-NMR spectra were recorded in dimethyl sulfoxide-d6 (DMSO-d6) solution using a Bruker Advance 500 MHz instrument (Germany). Elemental analyzes were performed by a CHN-Rapid Heraeus elemental analyzer (Wellesley, MA). Differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK). Inherent viscosity was measured by using an Ubbelohde viscometer in a concentration of 0.5 dL/g in NMP at 25°C.

Synthesis of the monomer

A four-step reported strategy[14,15] was carried out for the preparation of diamine monomer, as shown in Scheme 1.

8-(4-nitrophenoxy) quinoline (I)

Into a 250-mL two-necked flask equipped with a magnetic stirrer bar, an efficient reflux condenser, and a thermometer, a mixture of 8-quinolinol (5 g, 0.034 mol), p-fluoronitrobenzene (3.65 mL, 0.034 mol), and K_2CO_3 (5 g, 0.036 mol) was added to 60 mL of DMAc. The content was heated at 180°C for 5 h with stirring. The progress of reaction was followed by TLC test in DMAc. The solution was cooled and poured into 500 mL of distilled water. The precipitate was collected by filtration and dried in vacuum oven at 80°C for 12 h. The product was used without further purification, yield = 97% and mp = 120 °C.

FTIR (KBr): 1511, 1354 cm^{-1} (NO_2), 1264 cm^{-1} (C—O—C stretching).

4-(8-quinolinoxy) aniline (II)

In a 250 mL flask equipped with a condenser and magnetic stirrer bar, 8-(4-nitrophenoxy) quinoline (I) (8 g, 0.031 mol) and palladium on activated carbon (0.4 g, 5 wt %) were added to 150 mL of ethanol. Hydrazine monohydrate (5 mL, 0.1 mol) was added dropwise to this mixture at 50°C for 1.5 h. After an additional reflux for 1.5 h, the catalyst was removed by hot filtration and the solvent was removed from the filtrate by rotary evaporation. The remaining mixture was added into 300 mL of distilled water and the resulting solid product was collected by filtration. Recrystallization from ethanol gave the white crystalline solid, yield = 95% and mp = 180°C.

FTIR (KBr): 3200, 3400 cm^{-1} (NH_2), 1267 cm^{-1} (C—O—C stretching).

3, 5-dinitro-N-[4-(8-quinolinoxy) phenyl] benzamide (III)

Into a two-necked flask equipped with a condenser and magnetic stirrer bar, monomer (II) (6 g, 0.025 mol) dissolved in 40 mL of dry acetone and 4 mL triethylamine were added. A solution of 3, 5-dinitro-benzoylcholoride (8 g, 0.034 mol) in dry acetone (10 mL) was added dropwise to the reaction flask. The mixture was stirred under nitrogen at reflux temperature for 2 h to yield the dinitro compound (III). The progress of the reaction was followed by TLC test in ethanol. The resulting solution was cooled to room temperature and poured into water to precipitate. The precipitate was collected by filtration and recrystallized from methanol to gain fine crystals, yield = 93% and mp = 120°C.

FTIR (KBr): 1511, 1354 cm^{-1} (NO_2), 1264 cm^{-1} (C—O—C stretching), 1643 cm^{-1} (O=C).

3, 5-diamino-N-(4-(8-quinolinoxy) phenyl) benzamide (IV)

In a 250 mL flask equipped with a condenser and magnetic stirrer bar, a suspension solution of the purified dinitro (III) (4 g, 0.009 mol) and Pd/C (0.4 g, 10 wt %) were added to 60 mL of ethanol. Hydrazine monohydrate (5.0 mL, 0.1 mol) was added drop-by-drop to the stirred mixture at 80°C. After complete addition, the mixture was heated at the reflux temperature. The progress of the reaction was followed by TLC test in ethanol. The reaction solution was hot filtered to remove Pd/C, and the filtrate was distilled to remove the partial solvent to obtain fine, white crystals, yield = 83% and mp = 200°C.

FTIR (KBr): 3464, 3423 cm^{-1} (NH_2), 3357, 3226, 3054 cm^{-1}(C—H), 1643 cm^{-1} (C=O). ^{1}H-NMR: 4.91 (s, 4H), 6.00 (s, 1H), 6.30 (d, J 1.7, 2H), 6.95 (d, J 8.2, 2H), 7.24 (d, J 7.6, 1H), 7.55 (d, J 8.0, 1H), 7.60 (q, J 7.53, 1H), 7.73 (d, J 7.7, 2H), 7.77 (d, J 8.18, 1H), 8.43 (dd, J 7.03, 1H), 8.89 (dd, J 8.0, 1H), 10.10 (s, 1H) ppm. ^{13}C-NMR: 103.0, 103.1, 118.0, 119.0, 122.5, 123.0, 124.1, 127.6, 130.4, 135.8, 137.0, 137.7, 141.4, 149.9, 150.8, 153.4, 153.9, 167.9.

Polymer synthesis

The following procedure was carried out for the preparation of all the polyamides. A 50-mL two-necked flask, equipped with magnetic stirrer bar, nitrogen inlet, and reflux condenser, was charged
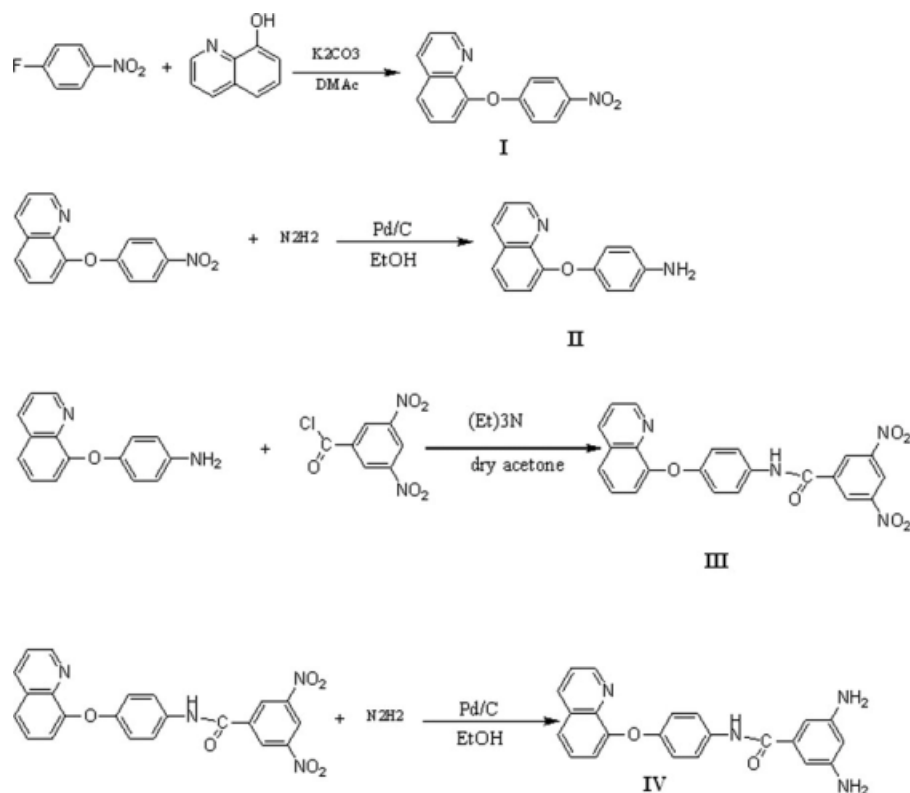
Scheme 1 Synthesis of the intermediates and the diamine monomer (IV).

with 1.3 mmol of diamine (IV) (0.5 g), 1.3 mmol of Pyridine dicarboxylic acid (0.23 g), 6.25 mmol of TPP (1.5 mL), 1.5 mmol of lithium chloride (0.063 g), 2 mL of pyridine, and 6 mL of NMP. The mixture was heated for 10 h in a thermostatically controlled oil bath at 120°C under stirring and mild nitrogen purging. The reaction mixture was then poured into a large amount of methanol to precipitate the polymer which was collected by filtration. The polymer was agitated in 12 mL of hot ethanol for 30 min and filtered. The washing treatment was repeated three times and the product was finally dried in a vacuum oven (80°C, 48h). The yields were in the range of 80–88%.

RESULTS AND DISCUSSION

Monomer synthesis and characterization

The asymmetric diamine monomer was synthesized by a four-step route, as shown in Scheme 1. In the first step, the aromatic substitution reaction of 8-quinolinol with *p*-fluoronitrobenzene in DMAc afforded the mononitro compound (I). FTIR spectra of the (I) showed characteristic absorptions at 1511 and 1354 cm^{-1} related to NO$_2$ and at 1264 cm^{-1} related to C—O—C stretching. The monoamine (II) was obtained in high yield (95%) by reduction of the corresponding mononitro (I) with Pd/C and hydrazine monohydrate and ethanol as solvent. FTIR spectra of the (II) showed characteristic absorptions at 3200 and 3400 cm^{-1} related to NH$_2$. In the third step, the nucleophilic substitution reaction of the monoamine (II) with 3,5-dinitrobenzoyl chloride was performed at 50°C in different solvents such as DMAc, NMP and acetone and different bases such as propylene oxide, pyridine and Et$_3$N. It has been found that dry acetone/Et$_3$N was the most effective mixture for obtaining high yield product. FTIR spectrum of the (III) showed the characteristic absorptions of NO$_2$ at 1511 and 1354 cm^{-1} and of C=O at 1643 cm^{-1}. In the final step, the reduction of the dinitro (III) was accomplished with Pd/C, hydrazine monohydrate and ethanol. The diamine monomer (IV) was characterized by FTIR, ^{1}H- and ^{13}C-NMR and the spectra are shown in Figures 1–3. FTIR spectrum of the (IV) showed the characteristic bands of the primary amine (NH$_2$) at 3464 and 3423 cm^{-1}, and of the C=O group at 1643 cm^{-1}. The assignments of each proton and carbon shown in Figures 2 and 3 agree well with the proposed molecular structure of the (IV). The ^{1}H-NMR spectrum confirms that the nitro groups have been completely transformed into the amino groups by the high field shift of the aromatic protons and by the signal at 4.91 ppm.
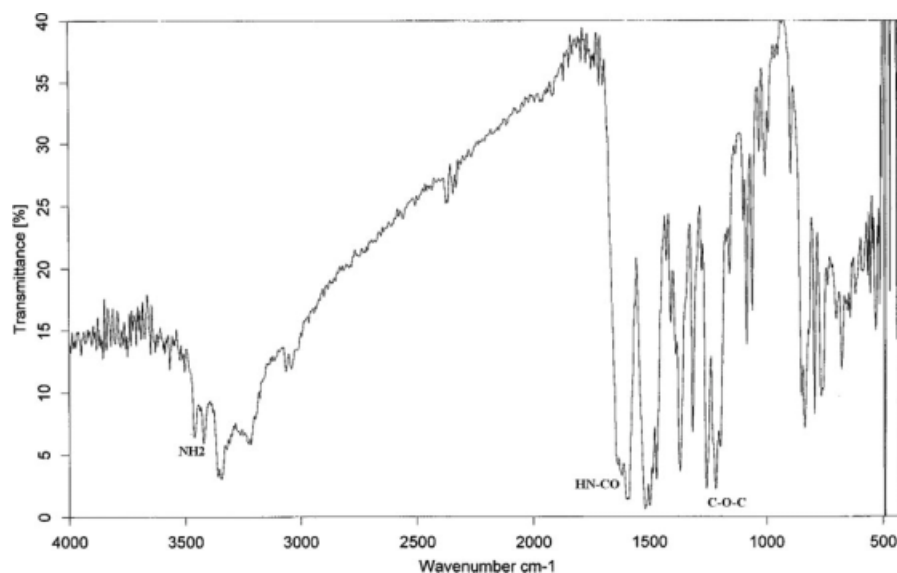
Figure 1 FTIR spectrum of the diamine (IV).

Polymerization and characterization

Among various methods for polyamidation reaction, direct polycondensation methods have been developed by several investigators and especially by Yamazaki and Higashi.[16–19] Direct polycondensation of diamine with dicarboxylic acid using TPP and pyridine as condensing agent to form amide bonds is an efficient way to obtain polyamides of moderate to high degree of polymerization on a laboratory scale. All of the polymerization reactions were carried out in NMP in the presence of LiCl and preceded homogeneously. The synthesis and designation of polyamides are shown in Scheme 2. The polyamides were obtained in good yields (>80%) and had inherent viscosity values ranging between 0.31 and 0. 4 dL/g. The structures of polyamides were confirmed by elemental analysis, FTIR and ^{1}H-NMR spectroscopy data. The FTIR spectra of the polyamides exhibited the characteristic absorption bands in the region at 3350–3340 cm^{-1} (N—H stretching), 1691–1670 cm^{-1} (C=O stretching) and 1545–1504 cm^{-1} (combined N—H bending and C—N stretching). ^{1}H-NMR signals of polyamide (PA-a) as the representative are shown in Figure 4. The signals
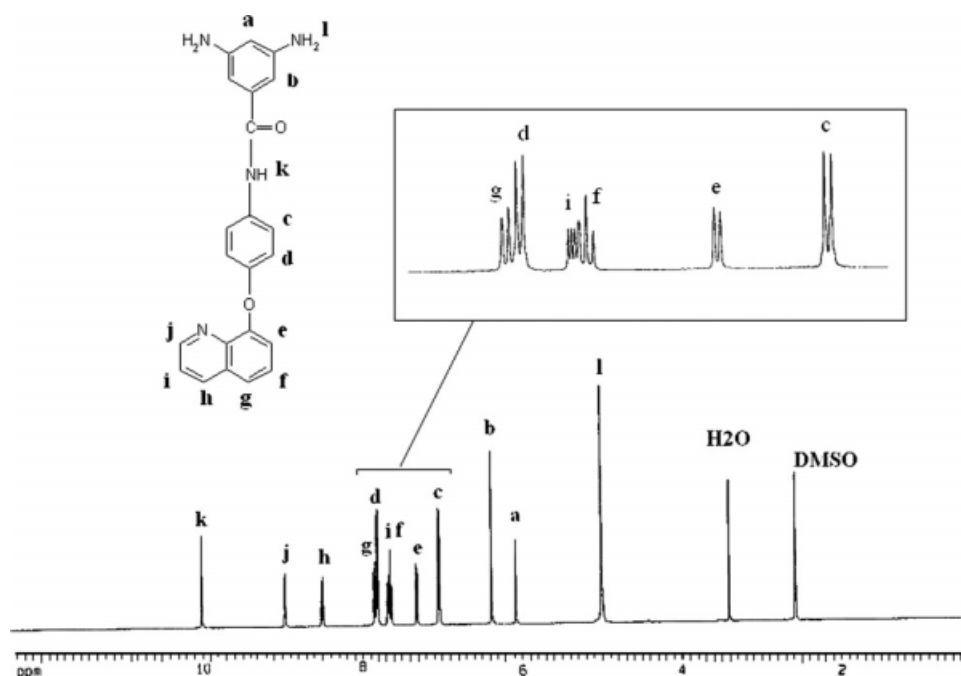

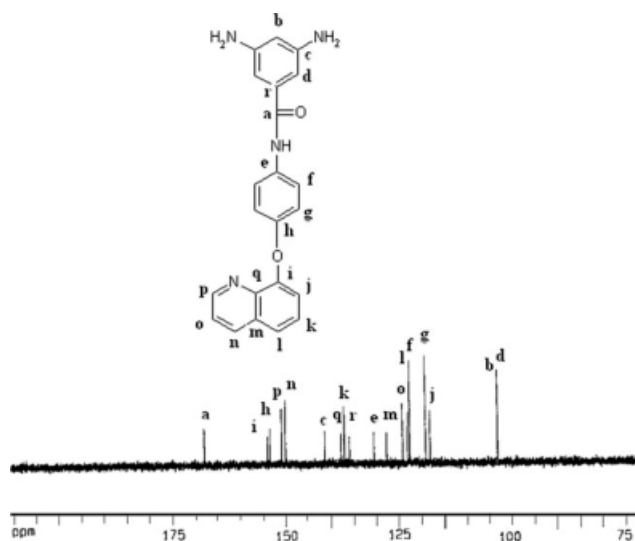**Figure 2** ^{1}H-NMR spectrum of the diamine (IV).

Figure 3 ^{13}C-NMR spectrum of the diamine (IV).

at 11.35 and 10.45 ppm were assigned to the N—H protons of two different amide groups in the polymer backbone and in the side chain. The signals of aromatic protons appeared in the range of 6.78–8.94 ppm. All the data are listed in Table I. The total protons in the spectra are consistent with the proposed chemical structures of the polymers.

Polymer solubility

The solubility behavior of the new polyamides was determined for the powdery samples in excess solvents. All the polyamides exhibited excellent solubility in the polar aprotic solvents such as NMP, DMAc, N,N-dimethylformamide, dimethyl sulfoxide (DMSO), and pyridine at room temperature, and were insoluble in THF and dioxane. All the polyamides were soluble in THF on heating. The solubil-

ity 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 bulky pendant group in the diamine residue. This could be because the bulk of the pendant group in the diamine residue is sufficient to override the effect of the interchain interactions superimposed by the backbone. We believe, however, that the presence of polar amide group in the pendant group can also contribute effectively in the solubility of these polyamides. Comparison of the solubility of the previously reported polyamides[11,12,16] with these polyamides indicates that the presence of flexible bulky pendent 4-(quinolin-8-yloxy) aniline group in polymer backbone display an enhanced solubility in organic solvents. A dense chain packing of the polymer chains was probably disturbed by the bulky pendant group; consequently, the solvents molecules were able to penetrate easily to soluble the polymer chains. Films were made by casting THF solution of polymer on a clean glass surface. In general, the films were hard and brittle at room temperature.

Thermal properties of polymers

The thermal behavior of the polyamides was evaluated by DSC and TGA. The DSC curves of the second scans of all the polyamides are shown in Figure 5. First DSC scan of all the polyamides showed a wide endothermic peak around 100°C which is related to the loss of moisture, as shown in Figure 5. The absence of the melting peak in the DSC thermograms supported the generally amorphous nature of the polyamides. The amorphous
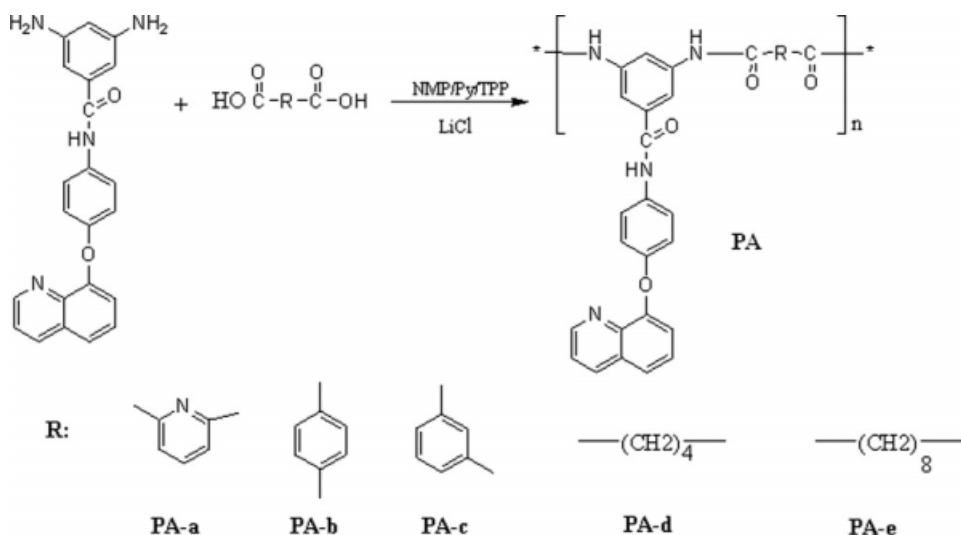
Scheme 2   Polycondensation reaction of diamine with different diacids.
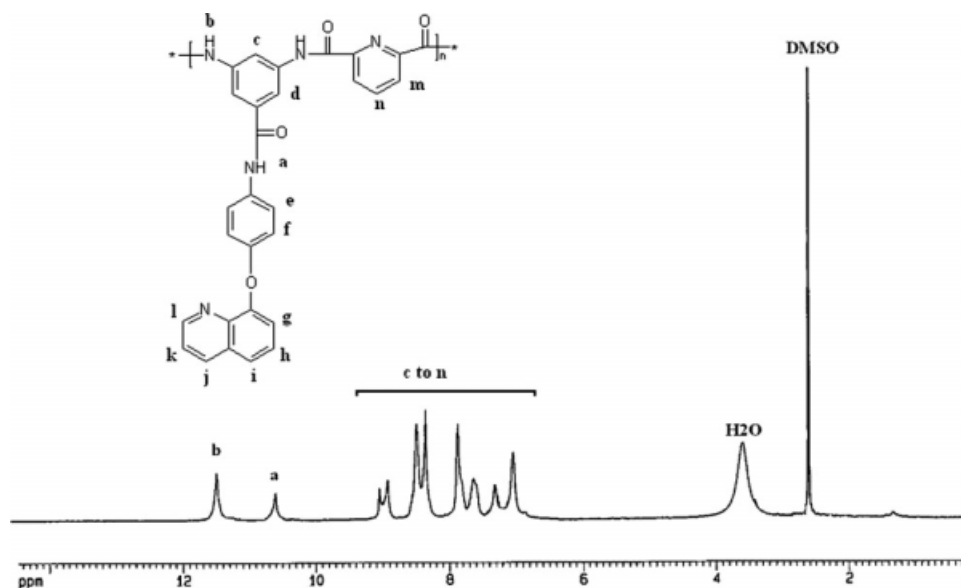
Figure 4 ^{1}H-NMR spectrum of the polyamide PA-a.

nature of the polyamides can be attributed to their bulky pendent group, which decreased the interchain interaction, resulting in loose polymer chain packaging and aggregates. The glass transition temperatures of the polyamides, as determined by DSC, are between 175 and 315°C as shown in Table II. Among all the synthesized polyamides, (PA-b) based on *p*-phenylene ring content in the main structural unit showed the highest T_g value because of the highest rigidity, which inhibited the molecular motion. In general, polymers with bulky side groups leads to lower T_g's than polymers without bulky side groups due to the greater interchain distance, which lowers the strength of the amide–amide hydrogen bonds that are partly responsible for the generally high T_g's of these aromatic polyamides. The high T_gs of the polyamides can be due to the high barrier for segmental mobility as a result of

TABLE I
Specification of Polymers

| Polymer	^{1}H-NMR (ppm)	Calc.			Found			Yield (%)	η (dL g^{-1})
		C	H	N	C	H	N		
Diamine (IV)		71.35	4.86	15.13	71.30	4.87	15.12	83	–
PA-a	8.94(1H), 8.90(1H), 8.82(1H) 8.46(2H), 8.39(1H), 8.25(2H) 7.77(1H),7.53(1H), 7.20(1H) 7.17(2H),6.93(1H), 6.76(2H)	69.46	3.79	13.90	69.50	3.81	14.00	80	0.4
PA-b	8.86(1H), 8.66(4H), 8.42(1H) 8.12(1H), 7.79(2H), 7.59(1H) 7.34(1H), 7.21(1H), 7.09(2H) 6.86(1H), 6.76(2H)	72.00	4.00	11.20	72.15	4.13	11.30	85	0.41
PA-c	8.86(1H), 8.78(1H), 8.66(2H) 8.40(1H), 8.22(1H), 8.10(1H) 7.76(2H), 7.56(1H), 7.33(1H) 7.27(1H), 7.16(2H), 6.97(1H) 6.76(2H)	72.00	4.00	11.20	73.00	4.12	11.24	81	0.35
PA-d	8.86(1H), 8.40(1H), 8.19(1H) 7.76(2H), 7.56(1H), 7.37(1H) 7.27(1H), 7.19(2H), 6.76(2H) 5.48(1H), 2.18(4H), 1.64(4H)	70.00	5.00	11.66	70.12	5.03	11.68	80	0.30
PA-e	8.86(1H), 8.42(1H), 8.16(1H) 7.74(2H), 7.57(1H), 7.37(1H) 7.25(1H), 7.17(2H), 6.76(2H) 6.09 (1H),1.59(4H), 1.15(**12**H)	71.64	5.97	10.44	71.78	6.00	10.53	88	0.35
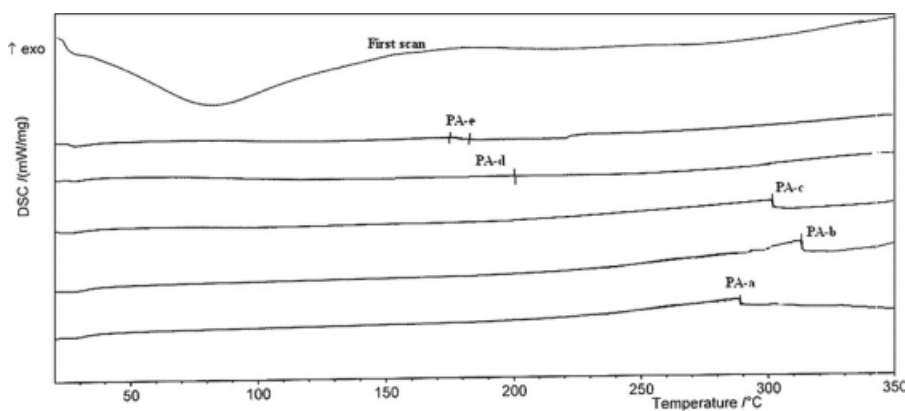
Figure 5 DSC thermograms of the polyamides.

side chain-side chain and side chain-main chain interaction through H-bonding. As we expected, T_g of the polyamides showed dependence on the structure of the dicarboxylic acid component, and decreased with increasing flexibility of the polyamides main chain. T_g,s of the aromatic polyamides PA-a, PA-b and PA-c are comparable with those of conventional aromatic polyamides and also those reported by other researchers.[6,11,12]

The thermal stability of polyamides was investigated by TGA in a heating program under N_2 to elucidate how the chemical structure influenced the value of initial decomposition temperature (T_i). TGA thermograms of the polyamides are shown in Figure 6, and the data extracted from the thermograms are listed in Table II. All polyamides showed a small weight loss (4–8 wt %) at a temperature range of 100–150°C which can be attributed to the loss of absorbed water (moisture) which is hydrogen-bounded with amide linkages and has not been removed in the precedent drying operation. The T_i of all polyamides range between 200 and 370°C, with the aromatic polyamide (PA-b) containing p-

phenylene ring content in the main chain has the highest T_i and showed better thermal stability than the polyamide (PA-c) with m-phenylene ring in the main chain. The temperature of 10% weight loss (T_{10}) range between 225 and 430°C. The breaking of a bond in a pendant structure gives rise to the elimination of a low molecular weight fragment, which is detected by TGA during thermal degradation of the aromatic polyamides. Thermal stability of these polyamides is comparable with those reported by the other researchers.[12,18] To compare thermal behavior, the breaking of a bond probably in the main chain of the aliphatic polyamides (PA-d and PA-e) caused these polymers to have lower thermal stability than the aromatic polyamides. The longer the aliphatic chain is, the higher the thermal stability is.[12] The (PA-e) with longer aliphatic unit in the backbone showed higher thermal stability than the (PA-d), and this can be due to better dissipation of thermal energy in the longer aliphatic chain as a result of more free rotation. In addition, the residual weight retentions for the resulting polyamides were in the range of 52–67 % at 600°C, implying that these polyamides possess reasonable thermal stability.

TABLE II
Thermal Properties of Polyamides

Polymer	$T_g(°C)^a$	$T_i(°C)^b$	$T_{10}(°C)^c$	Char yield (%)^d
PA-a	288	300	400	58
PA-b	313	370	430	67
PA-c	302	–	300	57
PA-d	∼ 200	∼ 205	225	55
PA-e	∼ 178	∼ 200	325	52

^{a} Midpoint of baseline shift in the second heating DSC trace with a heating rate of 10°C/min under nitrogen atmosphere.
^{b} Initial decomposition temperature were recorded by TGA at a heating rate of 10°C/min under nitrogen atmosphere.
^{c} Temperatures of 10% weight loss.
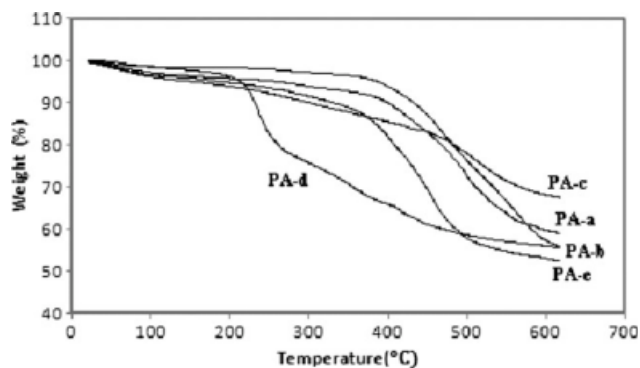^{d} Residual weight % at 600°C.

Figure 6 TGA thermograms of the polyamides.

CONCLUSION

A novel diamine containing flexible bulky pendent 4-(quinolin-8-yloxy) aniline group 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 and aliphatic dicarboxylic acides via the direct phosphorylation polycondensation. The introduction of flexible bulky pendent of 4-(quinolin-8-yloxy) aniline group into the polymer backbone led to significantly improvement in solubility of the polymer because of decrease in the ability for polymer chains to pack and reduction of interchain interactions, and this also increased T_g of the polymer as a result of decrease in the segmental mobility due to side chain-side chain and side chain-main chain interaction through H-bonding. Most of these polymers exhibited a desired combination of properties requiring high-performance materials that include high thermal stability, and excellent solubility in organic solvents for fabrication.

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