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Synthesis, Characterization and Thermal Properties of New Polyamides from N-(3’, 5’-Diaminophenyl)-2-(Naphthalene-1”-Yl) Acetamide

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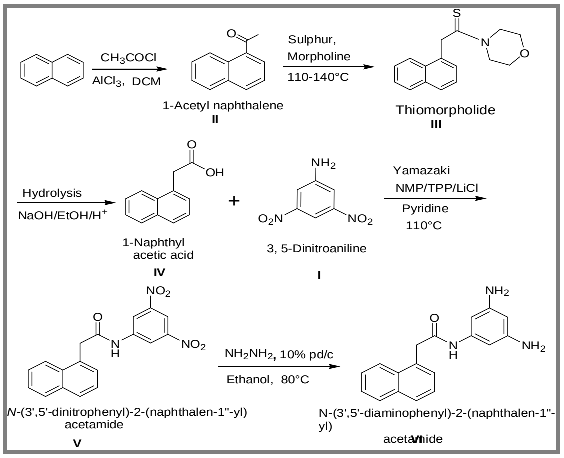
ABSTRACT

A new diamine containing a pendant naphthalene moiety via a amide linkage; N-(3’, 5’-diaminophenyl)-2-(naphthalene-1”-yl) acetamide (1-DAPNA), was prepared in four steps starting from naphthalene and characterized by spectroscopic technique. The diamine 1-DAPNA was polycondensed directly with various aromatic dicarboxylic acids to produce novel polyamides using pyridine and triphenyl phosphite as condensing agent. The resulting polyamides were characterized by inherent viscosity measurement, solubility, FT- IR, ^{1}H-NMR spectroscopy, thermal properties and XRD. The polyamides had inherent viscosities in the range between 0.37-0.59 dLg^{-1} in N-methyl-2-pyrrolidone (NMP) at 30°C. All these polyamides were soluble at room temperature in polar aprotic solvents such as N-methyl-2-pyrrolidone (NMP), N, N- dimethylacetamide (DMAc), dimethyl-sulphoxide (DMSO), N, N-dimethylformamide (DMF), pyridine and m-cresol. Transparent and tough films of these new polyamides could be cast from NMP solution. Thermogravimetric analysis of all these polyamides showed no weight loss below 303°C with a char yield of above 20% at 900°C under nitrogen atmosphere. All polyamides are amorphous in nature and have glass transition temperatures (Tg) in the range 252-268°C.

Graphical Abstract



Synthesis of N-(3’, 5’-diaminophenyl)-2-(naphthalene-1”-yl) acetamide (1-DAPNA).

Keywords: Naphthalene, Polyamides. Solubility, Amorphous, Thermal Properties.

INTRODUCTION

Aromatic polyamides constantly attract much interest because of their high temperature resistant and mechanical strength and have excellent thermal and oxidative stability [1, 2]. However, the application of polyamides is limited due to processing difficulties, insolubility in organic solvent and their high glass transition temperature or melting temperature. A number of successful approaches to increase solubility and processability of polyamides without sacrificing their high thermal stability employ the introduction of flexible or non-symmetrical linkages in the polymer backbone or the incorporation of bulky substituent as pendant groups in to the polymer backbone [3-6]. The syntheses of new polyamides with good solubility by introduction of new diamines containing bulky pendent groups were reported [7, 8]. The incorporation of bulky substituent [9] or bulky pendant groups [10-12] in rigid polymer backbones has led to the most success. From the results of these works, it was observed that introduction of pendent loops along the polymer backbone has been shown to impart greater solubility and enhanced rigidity as well as thermal properties. The resulting “cardo” polymer is of particular importance in aromatic polymers with rigid chains [13]. The previous studies reported that incorporating cardo groups such as cyclododecylidene, adamantane, [14, 15] and tert-butylcyclohexylidene [16] groups into the backbones of polyamides result in polymers with enhanced solubility, processability and good thermal stability [14-16]. It was observed that the polymers containing tert-butylcyclohexylidene exhibited better solubility than the cardo group-containing other polymers. The better solubility behaviour is due to the presence of the bulkier tert-butylcyclohexylidene as compared with the other cardo groups [16]. Because of these properties they are of major commercial and industrial importance. Aromatic diamines are valuable building block for the preparation of polyamides. The present work was undertaken to synthesize novel diamine containing a pendent 1-naphthalenyl acetamide group N-(3’, 5’-diaminophenyl)-2-(naphthalene-1”-yl) acetamide (1-DAPNA). Therefore, the polyamides prepared from 1-DAPNA were expected to exhibit good thermal stability, moldability and an enhanced solubility owing to the presence of the 1-naphthalenyl acetamide as pendant group. This article deals with the synthesis and characterization of new polyamides by direct polycondensation of 1-DAPNA with conventional aromatic dicarboxylic acids. In addition, the effect of the bulky pendent 1-naphthalenyl acetamide group based on a new diamine, N-(3’, 5’-diaminophenyl)-2 (naphthalene-1”-yl) acetamide (1-DAPNA) on the general properties such as viscosity, solubility, thermal properties, crystallinity and optical properties of the polyamides are also discussed herein.

MATERIALS AND METHODS

All chemicals were purchased either Merck or S D Fine (naphthalene, acetyl chloride, aluminium chloride, sulphur, morpholine, triphenyl phosphate, 3, 5-dinitro benzoic acid, sodium azide). 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 8 h at 150°C and 2 h at 180°C under vacuum.

Synthesis of monomer and intermediate

3, 5-dinitro aniline (DNA): A flask with charged a mixture of 3, 5- dinitro benzoic acid (12.5g 0.063 mol), oleum (22 mL), conc. H_2SO_4 (5 mL) and chloroform (25 mL). Heat was applied and when reaction mixture reaches to 45°C, sodium azide (4.38g 0.067 mol.) was introduced in small portion, by maintaining the temperature 35-45°C. The reaction mixture is accompanied by foaming, afterwards 0.75g of sodium azide was introduced and stirring was continued at 62°C and this temperature was maintained for 3 h. Then the reaction mixture was cooled and poured on a 250 g of crushed ice and diluted it with 1 L of water. The yellow solid residue was collected by filtration and then recrystallized to obtain 3, 5- dinitro aniline (DNA) in 86% yield; M.P.162-164°C.

N-(3’, 5’-dinitrophenyl)-2-(naphthalene-1”-yl) acetamide (1-DNPNA): A 250 mL three neck round bottom flask was equipped with a water condenser, a calcium chloride guard tube, a magnetic stirrer. A mixture of pyridine (in the ratio of 4:1, containing 8 wt % LiCl, 2.83 mL), NMP (11.35 mL), TPP (3.71 mL), 3, 5-dinitroaniline (DNA) (1.83 g, 10 mmol), 1-naphthyl acetic acid (1.86 g, 10 mmol) was heated to 110°C under stirring and maintained reaction mixture for 12 h in inert condition. The reaction mixture was then allowed to cool to room temperature and poured in to excess of water to precipitate the product, which was washed with sodium bicarbonate solution and with hot water, dried under vacuum at 80°C. The crude product was recrystallized from acetone and water mixture to get pure product in 87.3% yield; M. P. 270-272°C.

FT-IR: 1537 and 1344 cm^{-1} (NO_2), 1650 cm^{-1} (amide C=O stretching) and 2853 cm^{-1} (aliphatic –CH).

N-(3’, 5’-diaminophenyl)-2-(naphthalene-1”-yl) acetamide (1-DAPNA): A mixture of 1-DNPNA (3.51 g 0.01 mol), ethanol (110 mL), and a catalytic amount of 10% palladium on activated carbon (Pd/C, 0.297 g) was heated till it becomes homogeneous and was refluxed for 1 h. Hydrazine monohydrate (15 mL 99%) was added drop wise through dropping funnel over an hour, and reaction mixture was refluxed for 8 h. The resulting clear and dark solution was then filtered to remove Pd/C and the filtrate was subjected to distillation to remove part of solvent. The precipitated white crystals were isolated, filtered and washed with water till free from hydrazine hydrate. The product was recrystallized from ethanol in 79% yield; M. P. 210-212°C.

FT-IR: 3431 cm^{-1}(amide N-H stretching), 1606 cm^{-1} (amide N-H bending), 3284 (–NH_2 stretching), 1655 (-C=O stretching), 1339 cm^{-1} (C-N stretching), 729 cm^{-1} (monosubstituted benzene).

^{1}H NMR (400 MHz, d_6 DMSO), δ (ppm): 8.73(s, 1H), 4.02 (s, 2H), 5.7 (s, 1H), 6.24 (s, 2H), 7.35 & 7.38 (m 2H), 7.40 & 7.46 (m, 2H), 7.72 (d, 1H), 7.79 (d, 1H) and 8.00 (d, 1H) aromatic protons).

^{13}C NMR (400 MHz, d_6 DMSO), δ (ppm): 169.35 (-C=O), 148.35, 140.21, 133.76, 132.26, 132.10, 128.62, 127.90, 127.74, 126.35, 125.84, 125.63, 124.16, 97.67, 97.13, 41.82 (-CH_2-).

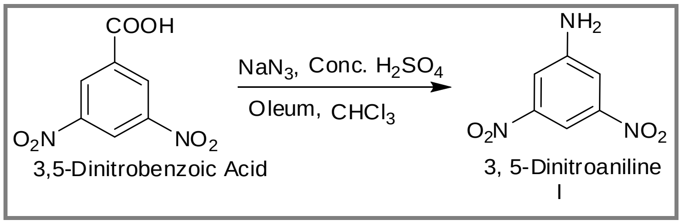
Synthesis of polymers: The general procedure is illustrated by the synthesis of polymer PA-1. A flask equipped with a mechanical stirrer and a condenser was charged with a mixture of diamine, 1-DAPNA (0.291g, 1 mmol), biphenyl-4, 4’-dicarboxylic acid (0.242 g, 1 mmol), pyridine (0.5 mL), lithium chloride (0.2 g), and NMP (3 mL). The reaction mixture, blanketed by nitrogen, stirred and heated to 110°C. TPP (0.63 mL, 2.4 mmol) was then added to the solution, and the reaction proceeded for 3 hours. After cooling, the viscous polymer solution was poured into 200 mL of stirring methanol, giving rise to a stringy, fiber-like precipitate that was collected by filtration, washed thoroughly with methanol and hot water. The polymer was collected and dried in a vacuum oven at 110°C overnight. All other polymers were prepared with a similar procedure. FT-IR spectra: 1661 cm^{-1} (amide C=O stretch), 3054 cm^{-1} (Ar-C-H stretch) and 3054 cm^{-1} (aliphatic C-H stretch). The disappearance of absorption bands at 3352 and 3321 cm^{-1} due to primary amine group confirms the completion of formation of the polyamide from amine.

Preparation of the polyamide films: A solution of the polymer was made by dissolving about 0.5 g of the polyamide sample in 10 mL of NMP. The homogeneous solution was poured on a 9 cm glass plate, which was placed in a 90°C oven for 5 h to remove most of the solvent; then the semi-dried film was further dried in vacuum at 170°C for 8 h. The obtained films were about 40–60 mm thick and were used for X-ray diffraction measurements and thermal analysis.

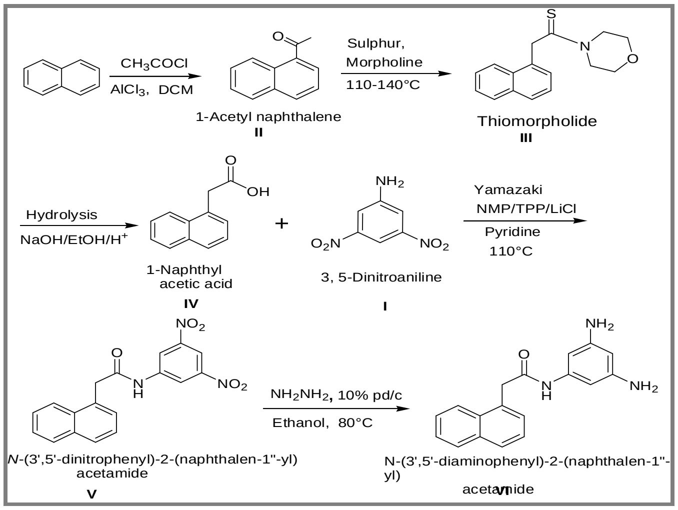
Measurements: Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer DSC-7 analyzer at the rate of heating 20°Cmin^{-1} under nitrogen. Thermogravimetric analyses (TGA) were performed on a PerkinElmer TGA-7 analyzer at the rate of heating 10°Cmin^{-1} on 2-3 mg samples under nitrogen. Fourier transform infrared (FT-IR) spectra of monomers and intermediate were recorded on a Nicolet 520 FT-IR spectrometer technique. ^1H and ^{13}C NMR spectra of monomers and polymers were recorded on a 400MHz Bruker instrument using deuterated N, N-dimethylsulphoxide (DMSO-d_6) as a solvent and tetramethyl silane (TMS) as an internal solvent. Inherent viscosities (at a polymer concentration of 0.5 g dL^{-1}) were measured with a Ubbelohde Suspended-level viscometer at 30°C using N-methyl-2- pyrrolidone (NMP) as a solvent. Qualitative solubility was determined using 20 mg of polyamide in 1 mL of solvent.

RESULTS AND DISCUSSION

Monomer synthesis: The synthetic route applied for the new 1-naphthalenyl acetamide containing diamine monomer, 1-DAPNA, was four-steps route depicted in scheme 1 and 2 from the corresponding 3,5-dinitrobenzoic acid and naphthalene. In the first step, the 1-acetyl naphthalene **IV** was obtained from the reaction of the naphthalene and acetyl chloride in dichloromethane with a practically quantitative yield. The reaction of 1-acetyl naphthalene with sulphur and morpholine was used to obtain the intermediate thiomorpholide which was subsequently acid hydrolyzed with glacial acetic acid in a reflux condition with high yields (84%) **IV** **[17-18]**. The intermediate 3, 5-dinitro aniline (DNA) **I** was obtained from the reaction of 3, 5-dinitro benzoic acid, sodium azide, oleum, conc. H_2SO_4 in chloroform with a practically quantitative yield. The compound **IV** was reacted with **I** in the presence of triphenyl phosphite and pyridine in NMP and afforded the dinitro compound 1-DNPNA **V.** The IR spectrum (Fig. 1) of dinitro compound **V** gave a characteristic



Scheme 1. Synthesis of 3, 5-dinitroaniline (DNA).



Scheme 2. Synthesis of N-(3’, 5’-diaminophenyl)-2-(naphthalene-1”-yl) acetamide (1-DAPNA).

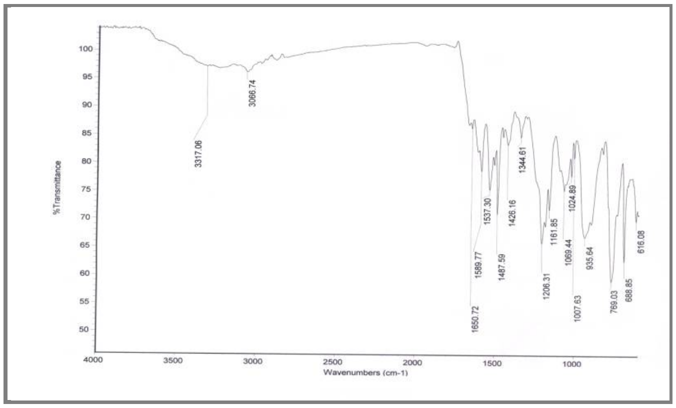


Figure 1. FT-IR spectrum of 1-DNPNA (V).

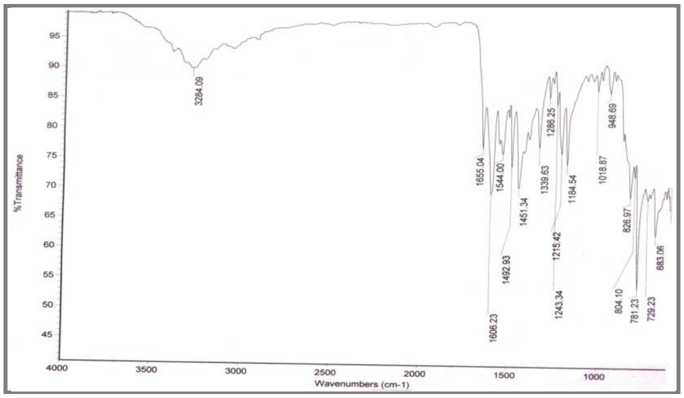


Figure 2. FT-IR spectrum of 1-DAPNA (VI).

absorption peak at 1344 and 1537 cm^{-1} (-NO_2 stretching). It was obtained in high yield (84%) and purified by recrystallizing in ethanol. The catalytic hydrogenation of dinitro compound **V** to the diamine 1-DAPNA **VI** was accomplished by using hydrazine monohydrate and catalytic amount of Pd/C as a reducing agent. After hydrolysis, the characteristic absorption of the nitro group disappeared, and the amine group showed a absorption band at 3284 and 3398 cm^{-1} (N-H stretching) and 1606 cm^{-1} (N-H deformation) (Fig 2). The structure **VI** was also confirmed by high resolution NMR spectra. The ^{1}H and ^{13}C NMR spectra of these compounds are illustrated in figure 3-5 respectively. The assignment of each proton and carbon are also given in the figures, and these spectra are in good agreement with the molecular structures.

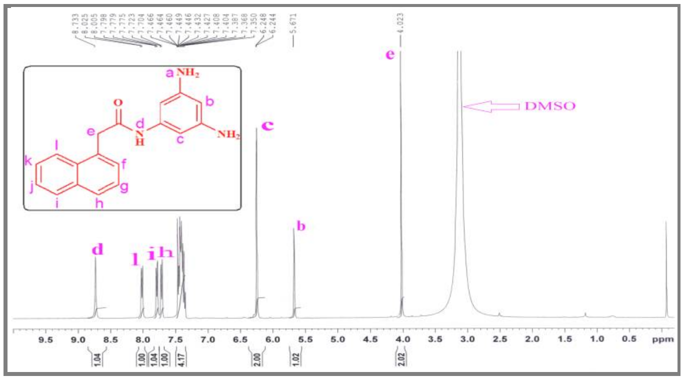


Figure 3. ^{1}H NMR spectrum of 1-DAPNA in DMSO-d_6.

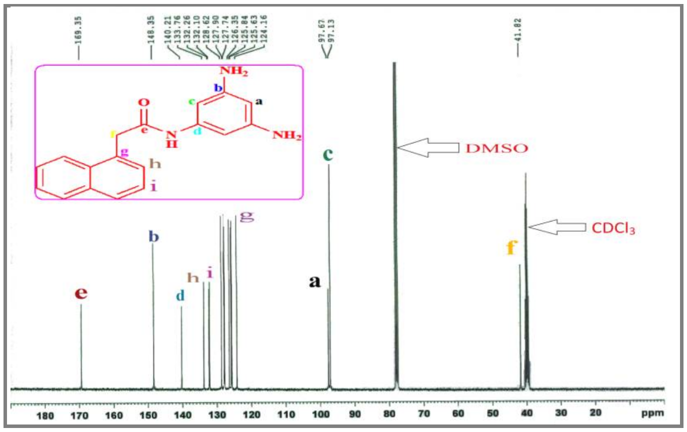


Figure 4. ^{13}C NMR spectrum of 1-DAPNA in DMSO-d_6.

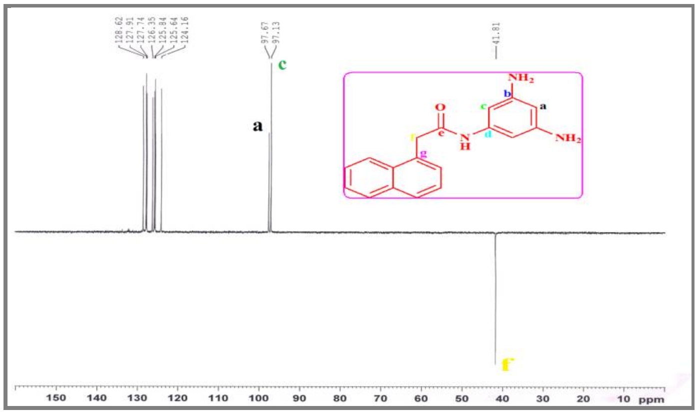
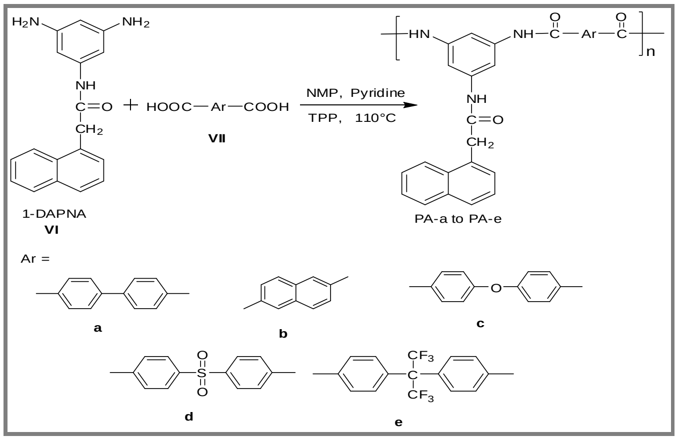


Figure 5. ^{13}C NMR (DEPT) spectrum of 1-DAPNA in DMSO-d_6.

Polymer synthesis: The direct polycondensation of aromatic diamines and diacids in a typical Yamazaki-Higashi reaction was adopted for the preparation of the polyamides [19-22] (Scheme-2). A series of new aromatic polyamides was synthesized from diamine **VI** and five aromatic diacids (**VIIa-VIIe**), by the Yamazaki-Higashi method (phosphorylation method) using TPP and pyridine as condensing agent (Scheme 3). All the polymerizations proceeded homogeneously throughout the



Scheme 3. Synthesis of polyamides PA-a to PA-e from 1-DAPNA and various diacids by direct Yamazaki's phosphorylation method.

reaction and afforded clear and highly viscous polymer solutions, which precipitated in a tough, fiber like form when the resulting polymer solutions were slowly poured into methanol with stirring. The inherent viscosities and molecular weights depend on the reactivity of the diacids moiety. The obtained polyamides had inherent viscosities in the range of 0.37–0.59 dLg^{-1} (Table 1) and could be solution-cast into flexible and strong films, indicating the formation of high molecular weight polymers. The formation of polyamides was also confirmed by IR and ^1H NMR spectroscopy. The representative IR spectrum for polyamide PA-a is given (Fig. 6), which shows the characteristic absorption bands of the amide group at around 1662 cm^{-1} (amide carbonyl) and 3100 cm^{-1} (N–H stretching). Absorption bands at 3352 and 3321 cm^{-1} were completely absent confirming all NH_2 groups reacted to form polyamide. Figure 7 shows the ^1H NMR of polyamide PA-c in DMSO-d_6. All the peaks could be readily assigned to the hydrogen atoms in the repeating unit. The resonance peak appearing at 10.35 ppm in the ^1H NMR spectrum also supports the formation of amide linkages.

Table 1. Yield, inherent viscosity of polyamides[a] from DAPNA[b] and different diacid.

S. No.	Polyamide Code	Diacid	Yield (%	Inherent Viscosity[c] η_{inh}, ($dL\ g^{-1}$)
1.	PA-a	Biphenyl-4,4’-dicarboxylic acid	98.39	0.59
2.	PA-b	Naphthalene-2, 6-dicarboxylic acid	99.46	0.46
3.	PA-c	4,4’-Oxydibenzoic acid	99.24	0.44
4.	PA-d	4,4’-Sulfonyldibenzoic acid	97.98	0.37
5.	PA-e	4,4’-(Perfluoropropane-2, 2-diyl) dibenzoic acid	99.73	0.51

a) Polymerization was carried out with 1 mmol each of 1-DAPNA and diacid.
b) 1-DAPNA, N-(3’, 5’-diaminophenyl)-2-(naphthalene-1”-yl) acetamide.
c) Measured with a 0.5 % (w/v) polymer solution in NMP at 30 °C.

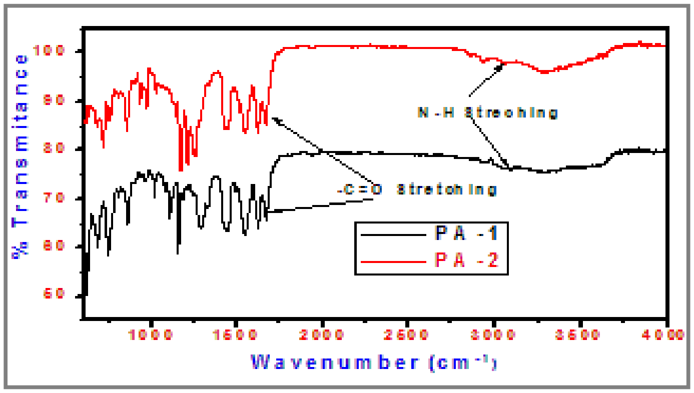


Figure 6. FT-IR spectra of polyamides PA-a and PA-b

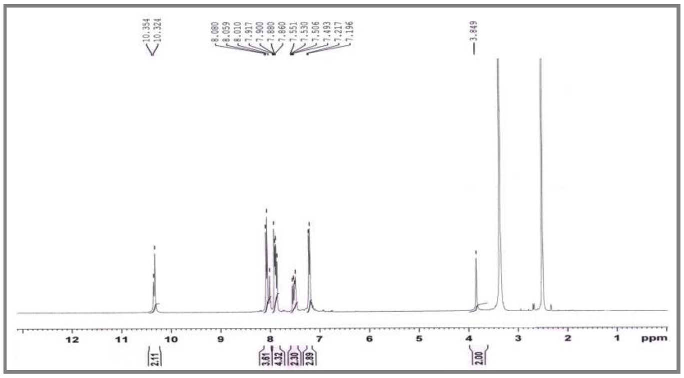


Figure 7. ^1H NMR spectrum of PA-c in DMSO-d_6

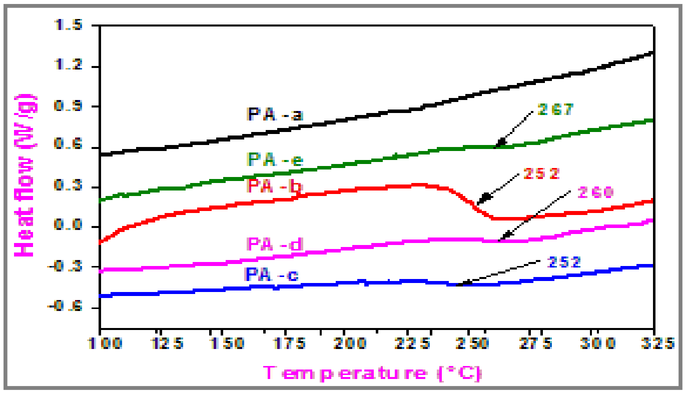


Figure 8. DSC curves of polyamides, PA-a to PA-e

Polymer properties

Basic characterization: The solubility behaviors of these polyamides were tested qualitatively in various organic solvents, and the results are summarized in table 2. The polyamides were readily soluble in polar aprotic organic solvents such as NMP, DMAc, DMSO and DMF at room temperature. The good solubility associated with these polymers could be attributed to the presence of bulky pendent 1-naphthalenyl acetamide group, and amide linkage sequences in the repeating unit. These factors decrease the interaction of the polymer chains and increase the chain distance; consequently, the solvents molecules are able to penetrate easily and interact with the polar groups and to solubilize the polymer chains. The solubility also depends upon the various dicarboxylic acids used. The polyamides (PA-c and PA-d) synthesized from 4, 4'-oxy dibenzoic acid and 4, 4'-sulphonyl dibenzoic acid exhibited better solubility behavior in less polar solvents such as m-cresol and pyridine. Polyamide PA-a and PA-b showed a relatively less solubility due to the presence of the para catenation of the biphenylene and rigid naphthalene unit in its backbone. The polyamides here in showed a slightly higher solubility compared to the other cardo polymers containing cyclododecylidene, adamantane, [14, 15] and benzo-15-crown-5 groups, indicating that the 1-naphthalenyl acetamide group is more effective on enhancing solubility of the polymers than the other cardo groups. The higher bulkiness and/or stiffness of the 1-naphthalenyl acetamide group compared to the other cardo groups should be responsible for this result. It was also observed that polyamides bearing pendant 1-naphthalenyl acetamide groups showed quite similar solubility behavior to those containing benzo-15-crown-5-pendant groups, implying that 1-naphthalenyl acetamide and benzo-15-crown-5-pendant groups exhibited similar bulkiness and stiffness.

Table 2. Solubility of polyamides, PA-a to PA-e from 1-DAPNA by Yamazaki's phosphorylation methods

Polyamide→ Solvent↓	PA-a	PA-b	PA-c	PA-d	PA-e
NMP	+ +	+ +	+ +	+ +	+ +
DMAc	+ +	+ +	+ +	+ +	+ +
DMSO	+ +	+ +	+ +	+ +	+ +
DMF	+ +	+ +	+ +	+ +	+ +
Pyridine	- -	- -	+ +	+ +	+ -
m-Cresol	- -	+ -	+ +	+ +	+ -
$CHCl_3$	- -	- -	- -	- -	- -
DCM	- -	- -	- -	- -	- -
THF	- -	- -	- -	- -	- -
Conc. H_2SO_4	+ +	+ +	+ +	+ +	+ +

+ + : Soluble + - : Partly soluble - - : Insoluble

Polymers were synthesized by high temperature solution polycondensation method and inherent viscosities, except PA-d, were in the range of 0.44-0.59 dLg^{-1} in NMP, with good yield in the range

98-99% (Table-1), indicating that the polymers had moderate to high molecular weights. Polyamide, PA-d has inherent viscosity 0.37 dL g^{-1}.

The morphology of the polyamides was estimated by means of wide-angle X-ray diffractograms. It was observed that all of these polymers are amorphous in nature. The amorphous behavior of these polymers is attributed to the bulky substituent groups which significantly increased disorder in the chains and therefore, caused less chain packing [19]. In addition, the pendant 1-naphthalenyl acetamide group also decreases the intermolecular force such as hydrogen bonding between the polymer chains, subsequently causing a decrease in crystallinity. The wide-angle X-ray diffraction diagrams of polymers are given in figure 9.

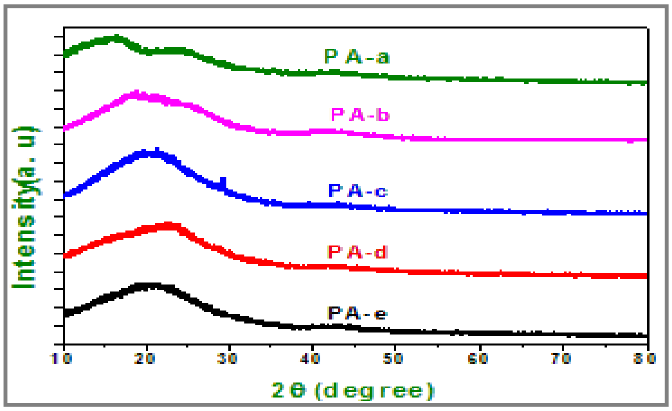


Figure 9. X-ray diffractograms of polyamides, PA-a to PA-e

Thermal Properties: The thermal properties of the polyamides were evaluated by differential scanning calorimetry (DSC) as well as thermogravimetric analysis (TGA) and are tabulated in table 3. The DSC thermograms of polyamides obtained from the second heating traces except PA-a showed glass transition temperature (Tg) in the range of 252-268°C. The Tg order was comparable to the decreasing order of stiffness and polarity of the polymers backbone. One master plot of the DSC Tg scans of PA-a to PA-e is provided as figure 10. As expected, polymer PA-c containing flexible ether linkage biphenylene showed relatively lower Tg value while PA-b bearing rigid 2, 5- naphthalene linkage didn't show the highest Tg value while PA-a bearing rigid para biphenylene linkage not showed the Tg value. In general, the chain rigidity was increased due to the pendent groups, which restricted the free rotation of the polymer backbone. Hence, the polymers could show high glass transition temperatures.

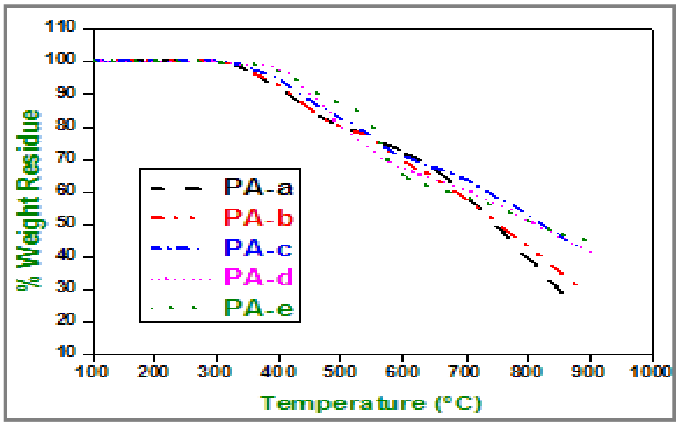


Figure 10. TG Curves of polyamides, PA-a to PA-e

Table 3. Thermal Properties[a] of polyamides PA-a to PA-e from 1-DAPNA by Yamazaki's phosphorylation methods.

S. No.	Polyamide code	^bT_i (°C)	$^cT_{10}$ (°C)	$^dT_{max}$ (°C)	Char Yield (Yc) (%) at 900°C	^eT_g (°C)
1.	PA-a	310	411	457	20	-
2.	PA-b	317	416	448	28	268
3.	PA-c	314	430	538	41	252
4.	PA-d	304	447	528	41	260
5.	PA-e	303	459	560	44	267

a) Thermogravimetric analyses were conducted at a heating rate of 10 °C min^{-1} under nitrogen
b) Temperature at which initial weight loss was observed.
c) Temperature at which 10% weight loss was observed.
d) Temperature at which maximum rate of weight loss was observed; determined from DTG curve
e) Determined from DSC curve obtained at a heating rate 20 °C min^{-1}

The 10% weight loss temperatures (T10) as well as the anaerobic char yield (Yc) at 900°C in nitrogen, measured by TGA of polyamides are also summarized in table 3. They were stable up to 303°C and 10% weight loss was observed between 411-459°C in nitrogen. All of the polymers exhibited excellent thermal stability. They started to decompose around or above 303°C. All of the polymers afforded high anaerobic char yield in the range of 20-44% at 900°C in a nitrogen atmosphere. It implied that these polymers showed good thermal stability irrespective of introducing 1-naphthalenyl acetamide groups in the polymer backbone.

APPLICATION

The novel polyamides were prepared by the direct phosphorylation polycondensation from the diamine and various dicarboxylic acids. The introduction of the bulky 1-naphthalene acetamide pendant group in to polymer backbone makes it easily soluble at room temperature in polar aprotic solvents. These polymers showed excellent thermal stability, up to 303°C, and displayed glass transition in the range of 252-268°C, with a large interval between decomposition and glass transition temperatures that make these polyamides appropriate for processing by a thermoforming technique, as well.

CONCLUSIONS

Design and synthesis of a new diamine monomer, 1-DAPNA, containing a rigid and bulky 1-naphthalene acetamide as a pendent group was carried out. New amorphous and thermally stable polyamides show improved solubility. A novel diamine namely, N-(3', 5'-diaminophenyl)-2-(naphthalene-1"-yl) acetamide was successfully prepared by four steps starting from the naphthalene. This compound was characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. A series of novel polyamides was prepared by the direct phosphorylation polycondensation from the diamine and various dicarboxylic acids. The introduction of the bulky 1-naphthalene acetamide pendant group in to polymer backbone makes it easily soluble at room temperature in polar aprotic solvents. PA-a and PA-b, were soluble even in less polar solvents such as pyridine and m-cresol. The polymers showed excellent thermal stability, up to 303°C, and displayed glass transition in the range of 252-268°C, with a large interval between decomposition and glass transition temperatures that make these polyamides appropriate for processing by a thermoforming technique, as well.

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