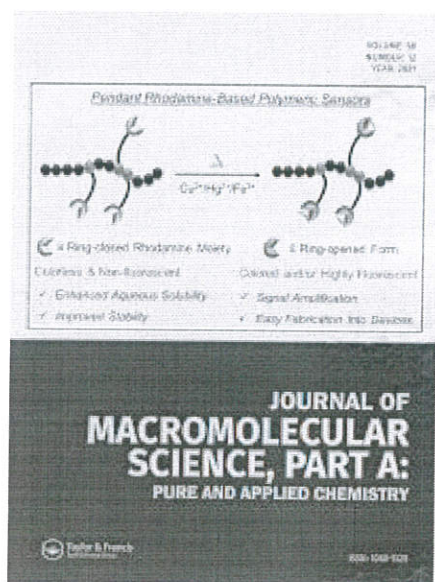


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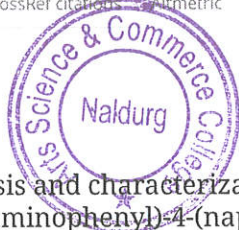
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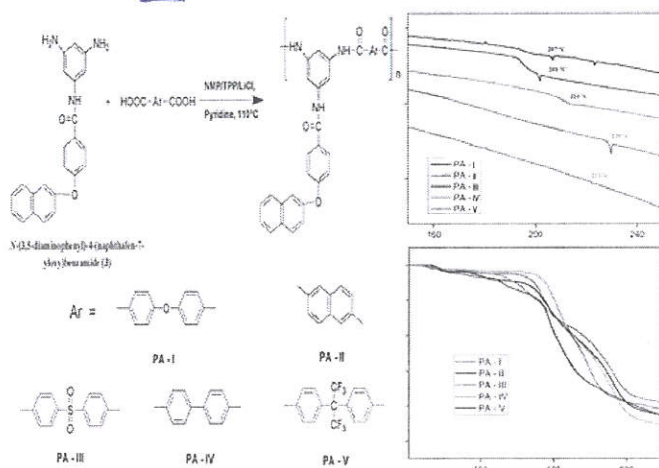
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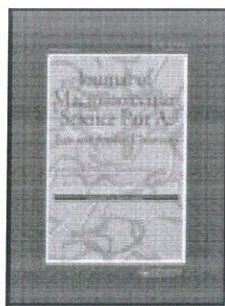
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Synthesis and characterization of soluble and heat-resistant aromatic polyamides derived from diamine; N-(3,5-diaminophenyl)-4-(naphthalen-7-yloxy)benzamide and various aromatic diacids

Shivaji. D. Ghodke^a, Aslam B. Tamboli^b, Arati V. Diwate^c, Mahesh B. Gurame^d, Vijay P. Ubale^e, Rajesh G. Bhorkade^d, and Noormahmad N. Maldar^d

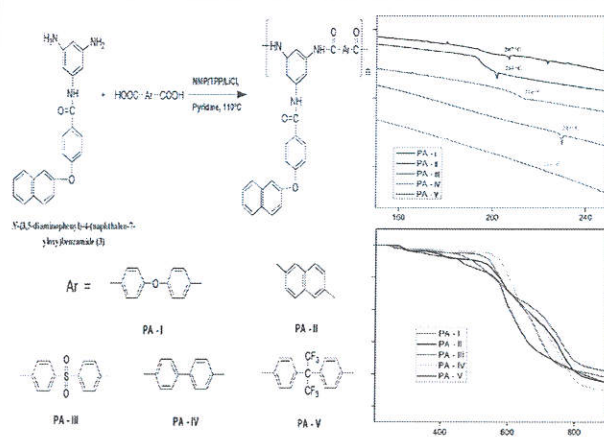
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ABSTRACT

The new aromatic m-catenated diamine, N-(3,5-diaminophenyl)-4-(naphthalen-7-yloxy)benzamide was synthesized from 2-naphthol and 4-fluoro benzonitrile as starting materials. A series of novel aromatic polyamides were synthesized from the diamine and several aromatic diacids such as 4,4'-Oxydibenzoic acid, Naphthalene-2, 6-dicarboxylic acid, 4,4'-Sulfonyldibenzoic acid, Biphenyl-4,4'-dicarboxylic acid and 4,4'-(perfluoropropane-2, 2-diyl) dibenzoic acid via direct Yamazaki's phosphorylative polycondensation method with triphenyl phosphite (TPP) as a condensing agent in pyridine (Py)/LiCl/1-methyl-2-pyrrolidone (NMP) solvent system. These new m-catenated/kink structured polyamides containing pendant naphthalene-oxy-benzamide units, were characterized by inherent viscosities, solubility in organic solvents, FTIR, DSC, TGA and XRD techniques. The polyamides were obtained in good yields and had inherent viscosities in range 0.35 and 0.55 dL/g. These polyamides were soluble in amide type aprotic solvents namely N, N' dimethyl formamide (DMF), N-methyl-2-pyrrolidone (NMP), N, N' dimethyl acetamide (DMAc), dimethyl sulfoxide (DMSO) and partly soluble in m-cresol, tetrahydrofuran (THF) and chloroform or dichloromethane. Polyamides showed glass-transition temperatures in the range 224 °C–262 °C indicating their processability at these temperatures. Thermogravimetric analysis in nitrogen atmosphere showed the 10% weight loss temperatures were more than 555 °C, indicating a good thermal stability. X-ray diffraction patterns of these polyamides indicated the amorphous nature, which is reflected in solubility characteristics.

GRAPHICAL ABSTRACT



ARTICLE HISTORY

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N-(3,5-diaminophenyl)-4-(naphthalen-7-yloxy)benzamide; aromatic diacids; polyamides; solubility; thermal stability

1. Introduction

Aromatic polyamides are class of high performance materials because of their excellent combination of good thermal

and mechanical properties, chemical resistance characteristic, low flammability, dielectrical properties and so on. Due to these properties aromatic polyamides have good impact in

various fields such as aerospace, military equipment, automotive industry, separation membranes, engineering plastics and electronic instruments.^[1–4] However, the rigid nature of these commercial aromatic polyamides (Kevlar and Nomex) leads to their poor solubility in organic solvents and limit their many potential applications. To overcome these limitations, incorporations of methylene spacers, ether linkages, bulky pendant group, sulfonyl linkages and non-coplanar moieties in-to the polymer chain were shown fruitful.^[5,6] Recently studies on such modifications were performed in our laboratory to demonstrate that these structural variations increased the inter-chain distance and decreased the packing efficiency; altering crystallinity in a way to promote the solubility and processability without sacrificing thermal properties to any great extent.^[7–14] Soluble optically active and photoactive aromatic polyesters containing naphthalimide groups^[15] and poly(amide-imide-ester)s from asymmetric diacids with diphenols containing silicon atoms^[16] have been reported. Many efforts have been made to synthesize structurally modified aromatic polyamides, PEEKs, polyimides, polybenzoxazoles having ether linkages in naphthalene derived diamine/diacid components which subsequently become part of main polymer chains.^[17–26] Studies indicated that the polyamides containing naphthalene ring or naphthalene-phenoxy moiety into the polyamide main-chains increased the thermal stability.^[27–29] Therefore, it was thought that incorporation of units viz. naphthaleneoxy, phenoxy and amide group as a side chain or pendant moiety to main polyamide chain would also increase the thermal stability of polyamides. Further pendant bulky units would result in to loose polyamide chains packing making polyamides less crystalline and subsequently soluble in organic solvents compared to commercial aromatic polyamides namely Kevlar or Nomex.

Thus in the present study we report the synthesis and characterization of a new kink structure aromatic diamine, *N*-(3,5-diaminophenyl)-4-(naphthalen-7-yloxy)benzamide derived from 2-naphthol and 4-fluorobenzonitrile. It was utilized as building block to obtain aromatic polyamides containing pendant naphthalene-oxy-benzamide moieties by polycondensation with various aromatic diacids. The structure of new diamine, *N*-(3,5-diaminophenyl)-4-(naphthalen-7-yloxy)benzamide was confirmed by spectroscopic techniques namely, FTIR, ¹H NMR and ¹³C NMR. The formation of novel aromatic polyamides was confirmed by FTIR spectroscopy and inherent viscosity. These polyamides were characterized by solubility in organic solvents, DSC, TGA and XRD to investigate effect of pendant naphthalene-oxy-benzamide moieties on aromatic polyamide properties.

2. Experimental

2.1. Materials

2-naphthol, 4-fluoro benzonitrile, pyridine, triphenyl phosphite, Palladium charcoal (10%), Hydrazine Hydrate (All Alfa-Aesar); anhydrous potassium carbonate, 3, 5-dinitroaniline, lithium chloride, *N*-Methyl-2-Pyrrolidone (All Sigma-Aldrich), were procured and used as received.

2.1.1. Measurements

Synthesized new aromatic diamine, intermediate organic compounds and polyamides were scanned for FTIR spectra on a Nicolet spectrometer using KBr pellets. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker Advance spectrometer at 25 °C using CDCl₃ and DMSO-d₆ as solvent and tetramethylsilane as reference. Inherent viscosities of polyamides were measured with a polyamide concentration of 0.5 g/dL in NMP solvent at 30 °C using an Ubbelohde suspended level viscometer. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC STARe instrument at heating rate of 20 °C/min under nitrogen. Thermogravimetric analysis (TGA) was recorded on a Mettler Toledo STARe instrument at a heating rate of 10 °C/min under nitrogen. Wide angle X-ray diffraction (WAXD) was performed with a Rigaku X-ray diffractometer using polyamide powder.

2.2. Synthesis of diamine; *N*-(3,5-diaminophenyl)-4-(naphthalen-7-yloxy)benzamide (3)

2.2.1. Synthesis of 4-(naphthalen-7-yloxy)benzoic acid (1).

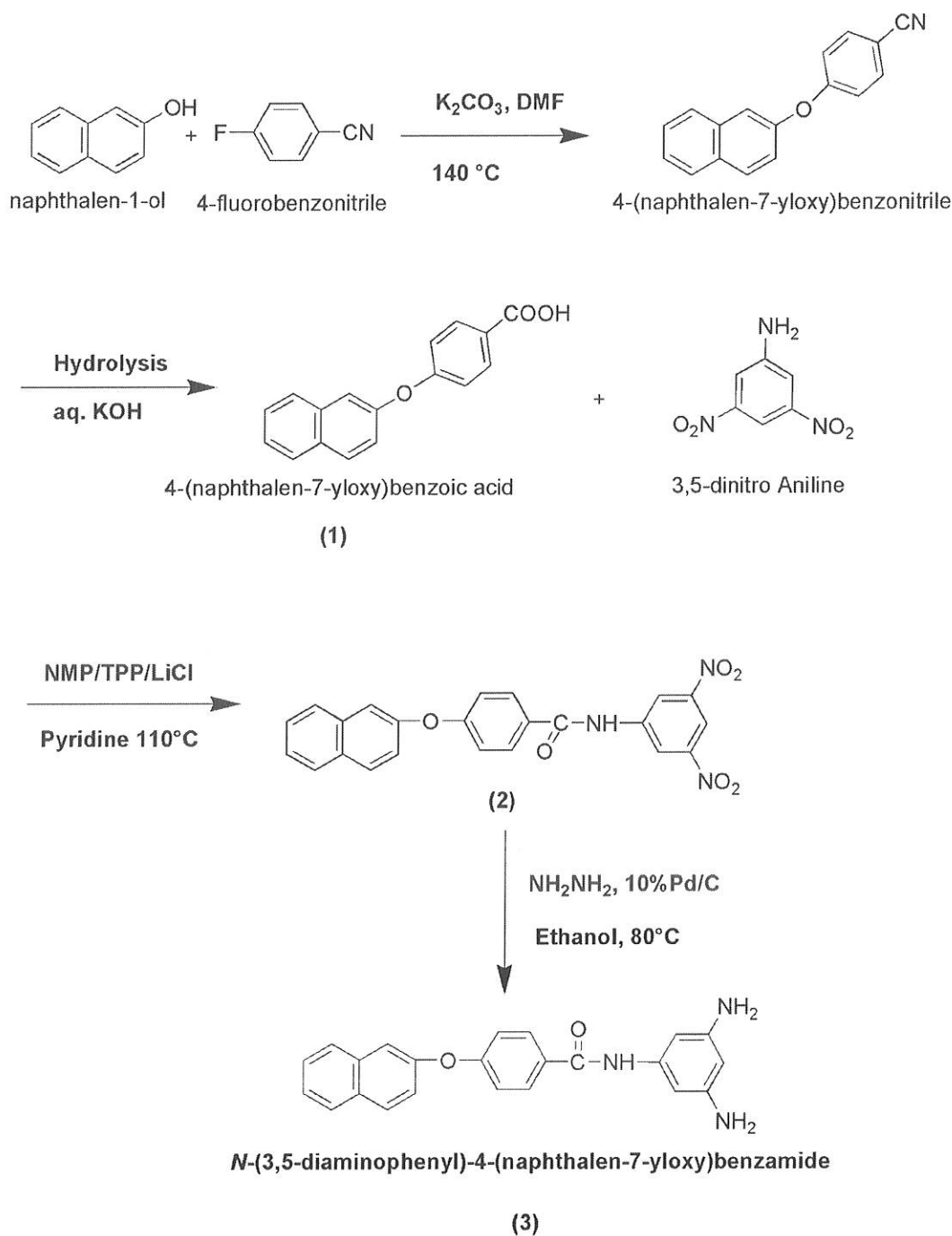
Synthesis of 4-(naphthalen-7-yloxy)benzonitrile was prepared as per reported procedure by using 2-naphthol and 4-fluoro benzonitrile as a starting material in presences of anhydrous potassium carbonate.^[30] Product was recrystallized from absolute ethanol to afford pure 4-(naphthalene-7-yloxy)benzonitrile in 91.06% yield. M. P. 146 °C.

A suspension of the intermediate 4-(naphthalene-7-yloxy)benzonitrile (12.74 g, 0.052 mol) was refluxed with KOH (14.5 g, 0.26 mol) in 500 mL distilled water and ethanol (1:1) for 48 h. The resulting solution was filtered hot, cooled and acidified with conc. HCl to pH 2–3. Light brown precipitate was filtered off, washed several time with hot water and dried. The crude mass was recrystallized in absolute ethanol to get 6.82 g. pure product (1) in 93.89% yield. M. P. 152 °C.

FTIR (KBr, cm⁻¹): 3028 cm⁻¹ (–OH stretch), 1720 cm⁻¹ (carbonyl stretch).

¹H NMR (CDCl₃, ppm): 6.9 ppm (d, 2H), 7.3 ppm (m, 3H), 7.5 ppm (s, 1H), 7.6 ppm (d, 1H), 7.7 ppm (d, 2H), 7.8 ppm (d, 1H), 8.08 ppm (d, 2H), 9.8 ppm (s, 1H).

2.2.2. Synthesis of 4-(naphthalene-7-yloxy)-*N*-(3,5-dinitrophenyl) benzamide (2): 3, 5-dinitroaniline (5 g. 0.027 mol), lithium chloride 3.10 g, pyridine (7.75 mL), NMP (31.03 mL) and triphenyl phosphite, TPP (11.54 g, 10.16 mL) were placed in round bottom flask fitted with a magnetic stir bar and a reflux condenser. To the clear solution 4-(naphthalene-7-yloxy)benzoic acid (6 g. 0.027 mol) (1) was added, and the reaction mixture was slowly heated to 110 °C; held at that temperature for 12 h with stirring under nitrogen flow. Reaction mixture was then allowed to cool to room temperature, and it was poured in to excess water. The precipitate was filtered, washed with sodium bicarbonate solution, then with hot water and dried. It was recrystallized from absolute alcohol to give 10.2 g. desired dinitro-amide compound. (2) in 88.07% yield. M. P. 288 °C.



Scheme 1. Synthesis of N-(3,5-diaminophenyl)-4-(naphthalene-7-yloxy)benzamide.

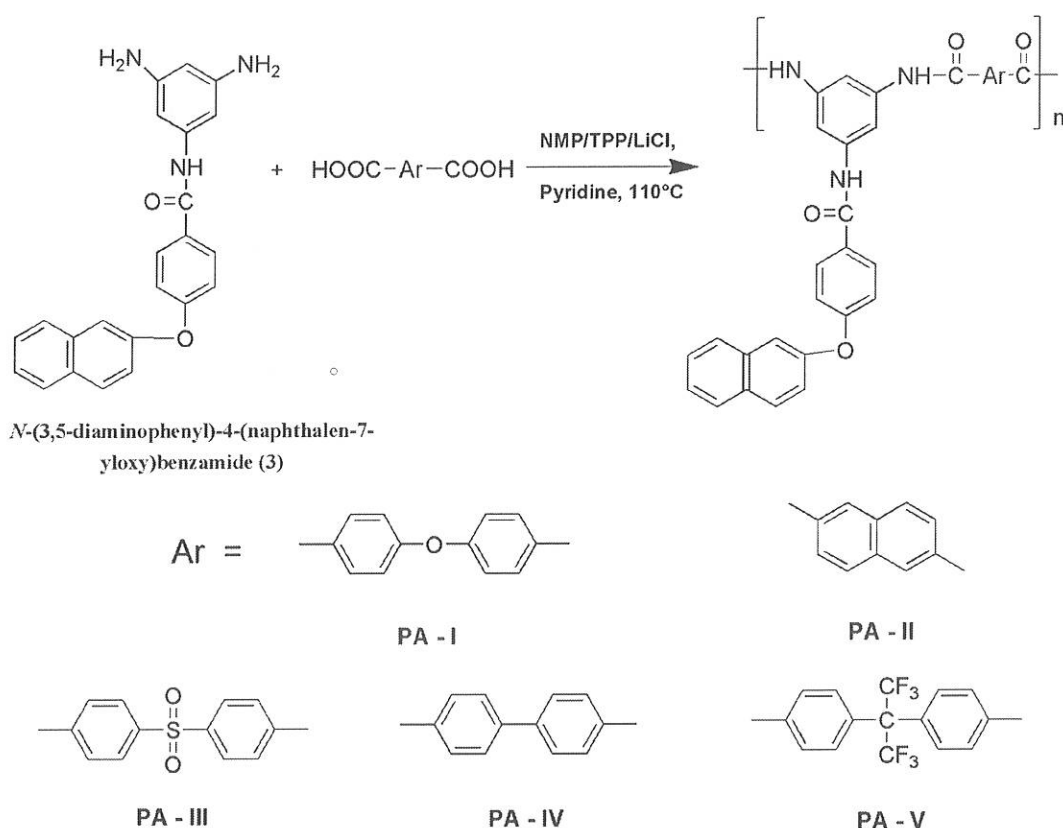
2.2.3. Synthesis of diamine: N-(3,5-diaminophenyl)-4-(naphthalene-7-yloxy)benzamide (3). In a 250 mL three neck round bottom flask equipped with a magnetic stirrer and a reflux condenser 4-(naphthalene-7-yloxy)-N-(3,5-dinitrophenyl) benzamide (2) (4.29 g, 0.01 mol), 10% Pd/C (0.29 g) and 110 mL ethanol were heated to reflux and hydrazine monohydrate 99% (20 mL) was added slowly through dropping funnel over 1 h. After additional 12 h of refluxing, the resultant clear, dark solution was filtered while hot to remove catalyst (Pd/C) and the filtrate was subjected to distillation to remove part of solvent. The concentrated solution was poured in to 300 mL water with stirring, giving off-white product, which was filtered,

washed with water till free from hydrazine hydrate. The mass was recrystallized from aqueous ethanol to produce 3.25 g pure diamine. (3) in 88.57% yield. M. P. 232–236 °C.

FTIR (KBr, cm^{-1}): 3315 cm^{-1} (-NH stretch amino group), 3200 cm^{-1} (-NH stretch of amide group) 1675 cm^{-1} (carbonyl stretch)

^1H NMR (DMSO- d_6 , ppm): 4.2 ppm (2H, s), 5.65 ppm (1H, s), 6.37 ppm (2H, s), 6.9 ppm (2H, d), 7.1 ppm (1H, s), 7.4 ppm (2H, d), 7.6 ppm (1H, d), 7.8–7.9 ppm (4H, m), 9.3 ppm (1H, s).

^{13}C NMR (DMSO- d_6 , ppm): 92.86, 99.79, 112.56, 113.80, 118.58, 121.50, 123.05, 123.43, 123.63, 123.83, 124.93, 126.92, 127.12, 131.75, 137.03, 147.48, 150.47, 159.84, 160.11 ppm.



Scheme 2. Synthesis of polyamides from N-(3,5-diaminophenyl)-4-(naphthalene-7-yloxy)benzamide and various aromatic diacid by Yamazaki's phosphorylation method.

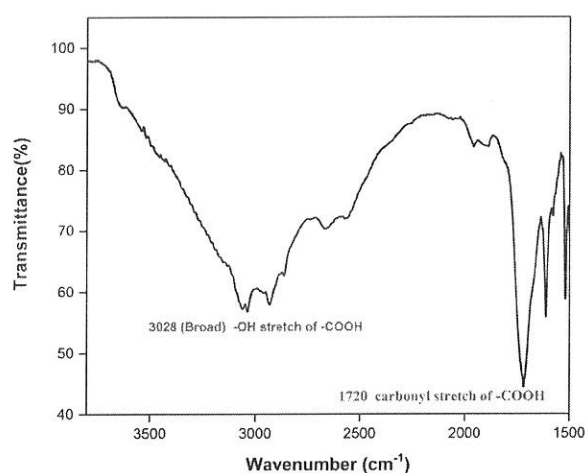


Figure 1. FTIR spectrum of 4-(naphthalen-7-yloxy)benzoic acid.

2.3. Polymerization

N-(3,5-diaminophenyl)-4-(naphthalene-7-yloxy)benzamide (3) 0.429 g. (1 mmol), biphenyl-4, 4'-dicarboxylic acid (1 mmol), 1 mL Triphenyl phosphite, 2 mL NMP and 0.5 mL pyridine containing 8 wt. % anhydrous lithium chloride (LiCl), were placed in three neck 100 mL R. B. flask and stirred under nitrogen atmosphere. Mixture was heated to 100 °C and stirred at this temperature for 3 h. The resultant viscous solution was poured into the 200 mL methanol. The precipitated polyamide was washed with methanol, hot

water, finally with methanol and the polyamide, PA-IV, was dried.

FTIR (KBr, cm^{-1}): 3272 cm^{-1} (–NH stretch amide group), 1675 cm^{-1} (carbonyl stretch).

The other polyamides (PA-I to PA-III, PA-V) were prepared in similar procedure using different diacids. The yields of all polyamides were in range 94–99%.

3. Result and discussion

3.1. Diamine synthesis and characterization

The new aromatic diamine with 1, 3-catenation (kink) and containing naphthyl ether and amide linkages was prepared in four steps as shown in Scheme 1. In the first step 2-naphthol was reacted with 4-fluoro benzonitrile in presences of anhydrous potassium carbonate to obtain nitrile compound; which was hydrolyzed using potassium hydroxide to get the corresponding carboxylic acid (1). In the third step carboxylic acid was condensed with 3, 5-dinitro aniline using TPP as condensing agent in pyridine/NMP solvent system to yield dinitro-amide derivative (2). This dinitro-amide derivative was then reduced by hydrazine hydrate and Pd/C catalyst in ethanol at reflux temperature to produce desired diamine, N-(3, 5-diaminophenyl)-4-(naphthalene-7-yloxy)-benzamide (3) in overall very good (66.60%) yields for four steps performed.

The chemical structure of the aromatic diamine (3) and all the intermediate compounds were confirmed by TLC,

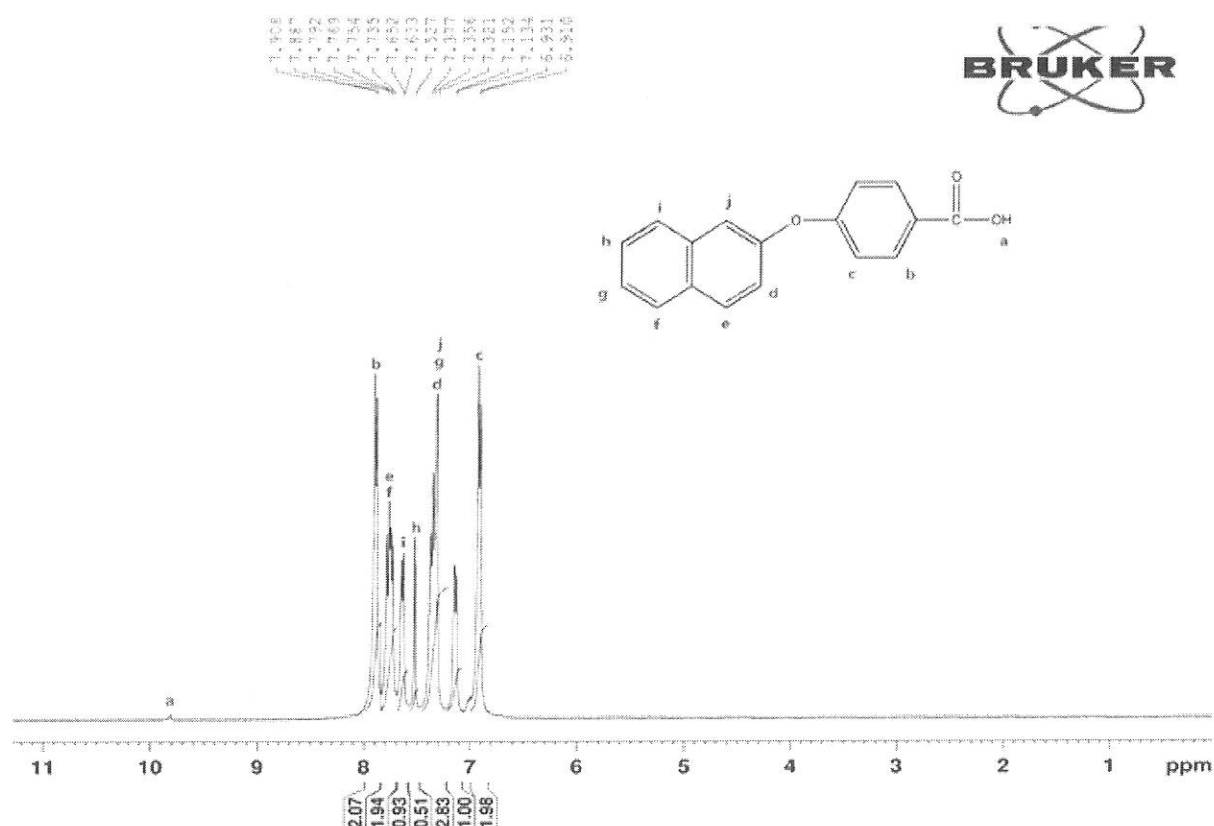


Figure 2. ^1H NMR spectrum of 4-(naphthalen-7-yloxy)benzoic acid.

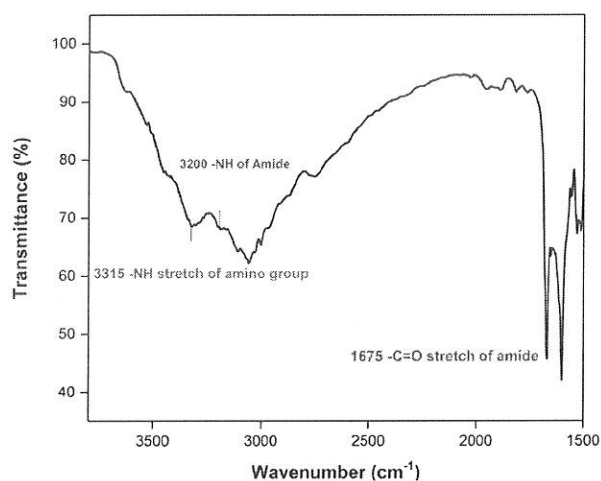


Figure 3. FTIR spectrum of N-(3,5-diaminophenyl)-4-(naphthalene-7-yloxy)benzamide.

FTIR, ^1H NMR and ^{13}C NMR spectroscopic techniques. The FTIR spectrum (Fig. 1) of 4-(naphthalene-7-yloxy)benzoic acid (**1**) showed the characteristic absorption bands at around 3028 cm^{-1} (due to $-\text{OH}$ stretch of carboxylic acid) and 1720 cm^{-1} (due to carbonyl stretch of carboxylic acid). ^1H NMR spectrum of (**1**), showed (Fig. 2) signals due to the aromatic protons at 6.9 to 7.9 ppm. However, the signal corresponding to carboxylic acid proton was not observed; probably due to the fast exchange of carboxylic acid proton with deuterium of the solvent used. FTIR spectrum (Fig. 3) of diamine, N-(3,5-diaminophenyl)-4-(naphthalene-7-

yloxy)benzamide (**3**) showed the characteristic absorption bands of amine groups at around 3315 cm^{-1} (due to $-\text{NH}$ stretch) and 1675 cm^{-1} is (due to carbonyl stretch of amide group). The ^1H NMR spectrum of diamine (Fig. 4) showed a signals at 9.3 ppm ($-\text{NH}$ proton of amide) and at 4.24 ppm ($-\text{NH}_2$ group protons). The signals in the range 5.66 ppm to 7.9 ppm were assigned to aromatic protons. The ^{13}C NMR spectrum (Fig. 5) of diamine, N-(3,5-diaminophenyl)-4-(naphthalene-7-yloxy)benzamide showed 19 different peaks corresponding to 19 different nonequivalent carbons present in the structure. The peak due to carbonyl carbon of amide group appeared at 160.11 ppm. Thus spectral data confirmed the structure of the synthesized diamine (**3**).

3.2. Polyamide synthesis

A series of new aromatic polyamides bearing pendant naphthalene-oxy-benzamide moiety was prepared by Yamazaki's direct phosphorylative polycondensation^[31] of new diamine, N-(3,5-diaminophenyl)-4-(naphthalene-7-yloxy) benzamide (**3**) with various aromatic dicarboxylic acids in NMP/pyridine solvent system containing LiCl using triphenyl phosphite (TPP) as condensing agent. (Scheme 2). The polymerization reaction proceeded homogeneously and afforded a clear, viscous polymer solution. Polyamides were precipitated by pouring the polymer reaction solutions into methanol with stirring. The prepared polyamides had

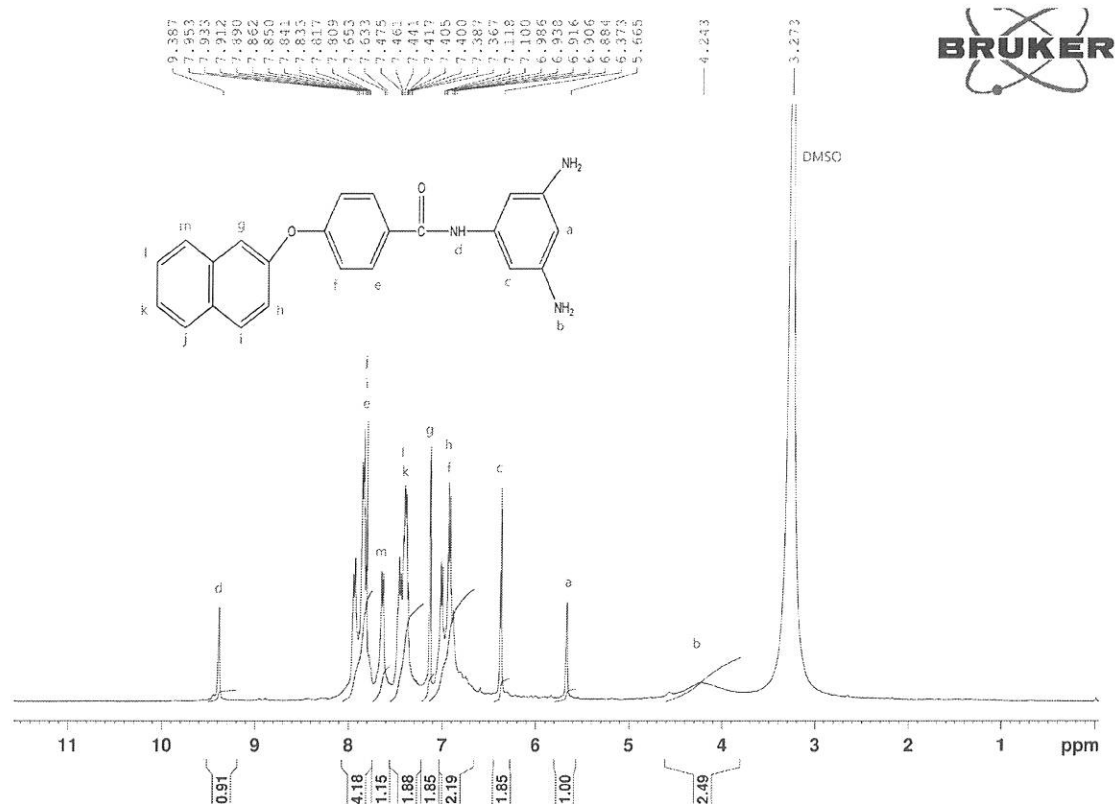
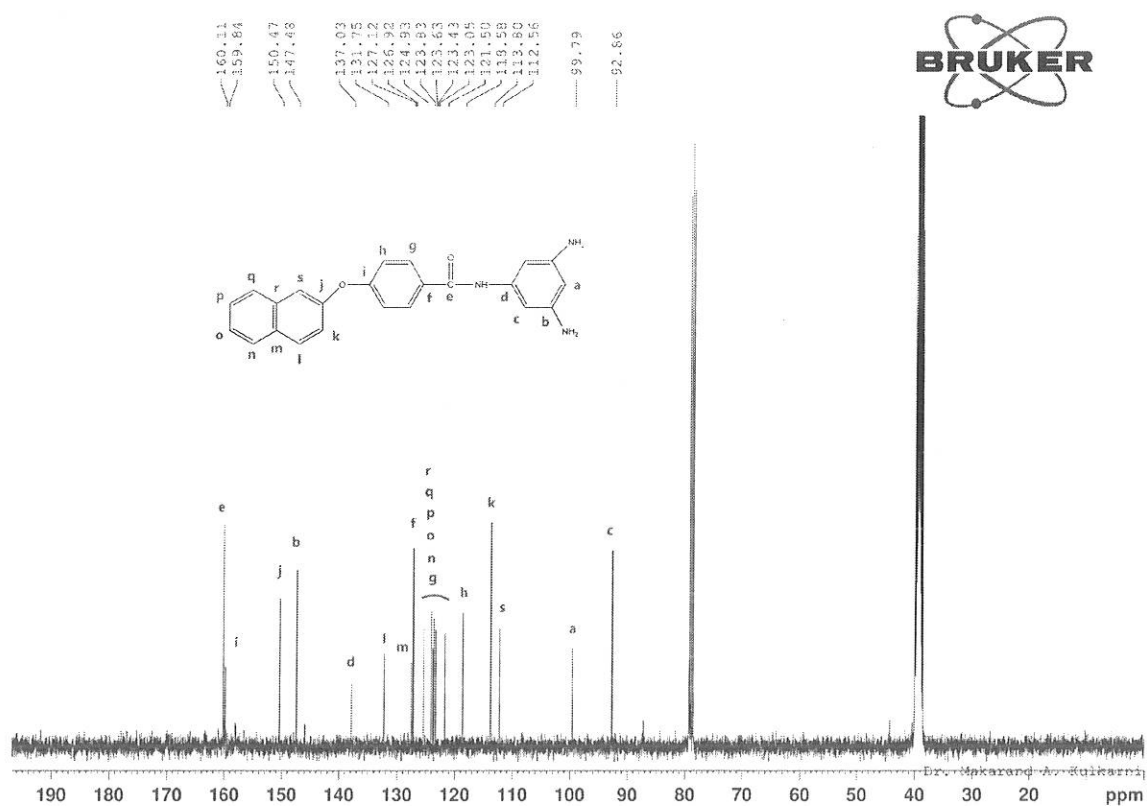
Figure 4. ^1H NMR spectrum of N-(3,5-diaminophenyl)-4-(naphthalene-7-yloxy)benzamide.Figure 5. ^{13}C NMR spectrum of N-(3,5-diaminophenyl)-4-(naphthalene-7-yloxy)benzamide.

Table 1. Yield and inherent viscosity of polyamides (PA-I to PA-V).

Sr. No.	Polyamide code	Diacid	Yield (%)	Inherent Viscosity η_{inh} (dL/g)
1.	PA-I	4,4'-Oxydibenzoic acid	99	0.55
2.	PA-II	Naphthalene-2, 6-dicarboxylic acid	97	0.41
3.	PA-III	4,4'-Sulfonyldibenzoic acid	98	0.35
4.	PA-IV	Biphenyl-4,4'-dicarboxylic acid	94	0.43
5.	PA-V	4,4'-(Perfluoropropane-2, 2-diyl) dibenzoic acid	99	0.45

a. Polymerization was carried out with 1 mmol each of N-(3,5-diaminophenyl)-4-(naphthalen-8-yloxy)Benzamide and various aromatic diacid.

b. N-(3,5-diaminophenyl)-4-(naphthalen-8-yloxy) benzamide.

c. Measured with 0.5% (w/v) polymer solution in NMP at $30 \pm 0.1^\circ\text{C}$.

inherent viscosities in the range of 0.35 to 0.55 dL/g with yields 94–99% as shown in Table 1.

The polyamides (PA-I to PA-V) formation was confirmed by FTIR spectroscopy. In FTIR spectrum of polyamide (PA-I) (Fig. 6) the characteristic absorption bands of the amide group at 3272 cm^{-1} (due to the $-\text{NH}$ stretching) and at around 1675 cm^{-1} (due to the carbonyl stretching of amide) appeared.

3.3. Solubility of polyamides

The solubility of these aromatic polyamides was tested qualitatively in various solvents and the results are summarized in Table 2. All these polyamides dissolved in common polar aprotic such as, N, N dimethyl formamide (DMF), N-Methyl-2-Pyrrolidone (NMP), N, N Dimethyl acetamide (DMAc) and Dimethylsulfoxide (DMSO). Most of the polyamides were partially soluble in solvents such as m-cresol, chlorinated hydrocarbons (Chloroform, Dichloromethane) and tetrahydrofuran (THF); however, polyamides PA-II and PA-IV, derived from naphthalene or biphenyl moiety containing diacids were not soluble in chloroform and dichloromethane. All these aromatic polyamides, PA-I to PA-V, were soluble in conc. Sulfuric acid. The good solubility of these aromatic polyamides may be due to the structural modification, that is, incorporation of pendant bulky (naphthalene-oxy-benzamide) units which decreased intermolecular interactions between polyamide chains, decreased the packing efficiency and thereby decreased crystallinity of these polyamides; creating amorphous morphology leading to solubility. Further m-catenation (1, 3 links) in the aromatic diamine helped for good solubility; as compared to, if it were p-catenated (1,4 link).

3.4. Thermal properties

These aromatic polyamides were investigated by DSC and TGA to evaluate their thermal behavior. Fig. 7 and Fig. 8 show DSC scans and the thermograms of these aromatic polyamides, respectively. The glass transition temperature (T_g); as obtained from the DSC curves, and initial decomposition temperature (T_i), the temperatures at 10% weight loss ($T_{10\%}$), char yields at 800°C in nitrogen of (PA-I to PA-V); as obtained from TGA curves are presented in Table 3. The glass transition temperatures of polyamides

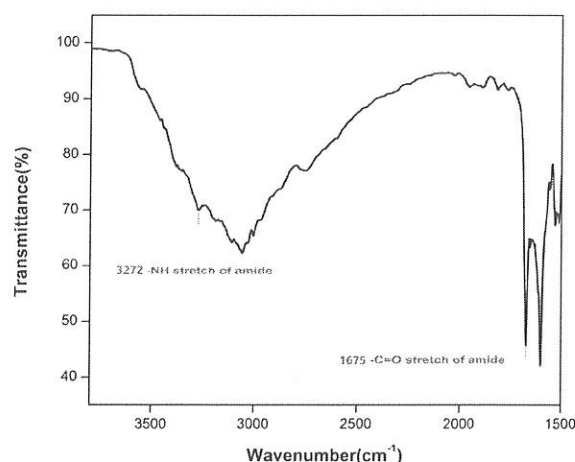


Figure 6. FTIR spectrum of PA-I.

Table 2. Solubility of polyamides.

Polyamide → Solvent ↓	PA-I	PA-II	PA-III	PA-IV	PA-V
DMF	++	++	++	++	++
DMSO	++	++	++	++	++
NMP	++	++	++	++	++
DMAc	++	++	++	++	++
m-Cresol	+-	+-	+-	--	+-
THF	+-	+-	+-	--	+-
CHCl ₃	+-	--	+-	--	+-
DCM	+-	--	+-	--	--
H ₂ SO ₄	++	++	++	++	++

++: Soluble; +-: Partially soluble; --: Insoluble.

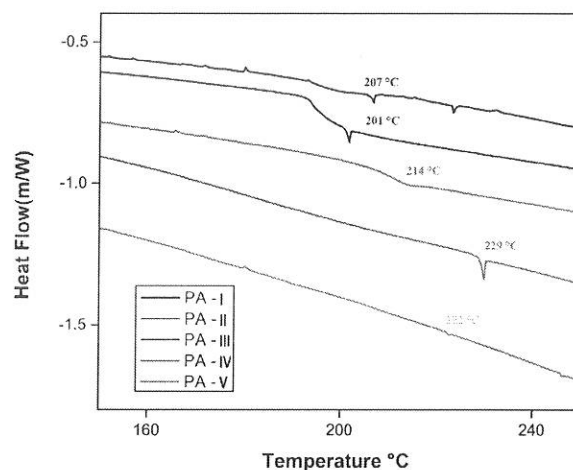


Figure 7. DSC curves of polyamides, PA-I to PA-V.

(PA-I to PA-V) were in the range of $224\text{--}262^\circ\text{C}$. It was observed that T_g values for PA-I and PA-III which contain flexible unit such as ether/sulphone were lower ($232/229^\circ\text{C}$) than the T_g value of the PA-II (262°C) which was derived from rigid naphthalene moiety containing diacid. The initial decomposition temperatures for aromatic polyamides, PA-I to PA-V were in the range of $234\text{--}267^\circ\text{C}$. The temperatures for 10% weight loss of these aromatic polyamides, PA-I to PA-V5 were in the range of $555\text{--}672^\circ\text{C}$; whereas the residual weights (%) at 800°C were in range 58–64%. The good thermal stability of these polyamides could be due to increased content of the

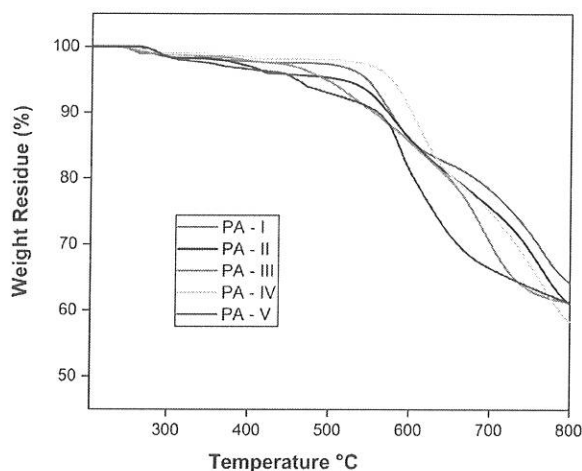


Figure 8. TGA curves of polyamides, PA-I to PA-V.

Table 3. Thermal properties^a of polyamides.

Polyamide Code	T _i (°C) ^b	T _{10%} (°C) ^c	T _g (°C) ^d	Residual wt. % at 800 °C
PA-I	234	575	232	64
PA-II	263	672	262	61
PA-III	243	555	229	61
PA-IV	253	602	224	58
PA-V	267	560	254	61

^aThermogravimetric analysis was conducted at a heating rate of 10 °C/min. under nitrogen atmosphere.

^bT_i: Temp at which weight loss initiated.

^cT_{10%}: Temp at which 10% weight loss was observed.

^dT_g: Determined by DSC measured at a heating rate 20 °C/min. under nitrogen atmosphere.

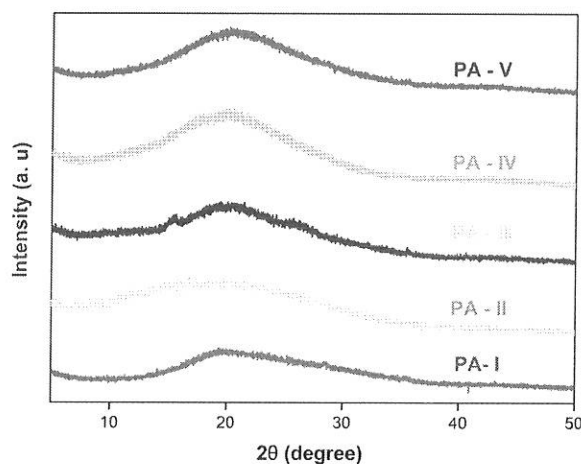


Figure 9. XRD curves of polyamides, PA-I to PA-V.

aromatic structures in main polyamide chain as well in pendant units. Further the links such as aryl ether and aryl amide were also thermally stable.


Wide angle X-ray Diffraction studies were conducted on these aromatic polyamides in the region $2\theta = 5\text{--}50^\circ$ at room temperature. Broad hallow peaks were observed in the range of $15\text{--}30^\circ$ in the XRD patterns (Fig. 9) of these aromatic polyamides and no sharp peaks were seen; indicating amorphous nature. The amorphous nature of these polyamides may be due to the bulky pendant moiety which did not allow close packing of polyamide chains and reduced considerably the intermolecular force of attraction between

them. This was reflected in good solubility of these aromatic polyamides in common organic solvents.

3.5. Conclusions

Aromatic polyamides with good thermally stability and good solubility in organic solvents were synthesized from new diamine, N-(3,5-diaminophenyl)-4-(naphthalene-7-yloxy)-benzamide with various aromatic dicarboxylic acids, by Yamazaki's direct phosphorylative polycondensation method. The polyamides had moderate to high molecular weights as indicated by their inherent viscosities, in the range 0.35 to 0.55 dL/g. All the prepared polyamides were soluble in aprotic polar organic solvents. These polyamides had glass transition temperatures in range 224 to 262 °C as determined from DSC curves. The thermogravimetric analysis of these polyamides showed no weight loss below 234–267 °C. Further these polyamides showed the 10% weight loss temperatures (T_{10%}) were in the range 555 to 672 °C; whereas char yields at 800 °C were in range 58 to 64%. All these data indicated good thermal stability. All these polyamides showed amorphous morphology when studied by WXR and it is reflected in good solubility of these polyamides. Solubility character of these polyamides may be due to incorporation of bulky pendant naphthalene-oxy-benzamide moieties in these aromatic polyamides which avoided close packing of the polyamide chains. Moderate T_g and solubility of these polyamides; without any significant loss in thermal stability; could be beneficial toward processability of these aromatic polyamides. These modified thermally stable and soluble aromatic polyamides may be useful as processable high performance polymeric materials.

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