



## STUDY AND CHARACTERIZATION OF THERMALLY STABLE POLYAMIDES SYNTHESIZED FROM HETEROCYCLIC MOIETY IN THE MAIN CHAIN

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### ABSTRACT

Colored compounds were formed by polycondensation reaction of s-triazine consuming diamines with secondary amine morpholine. The diazotization coupling reaction with  $\alpha$ -Naphthol showed dark coloration property. Initially, secondary amines binded with s-triazine at lower temperature and then smoothly proceeded at room temperature and further compiled with coupling product to result out the required series. The inherent viscosities were obtained in between 0.21-0.42 g/dL which was measured by Ubbelohde viscometer. The colored series was identified by several techniques like NMR, IR, and UV spectroscopy. Furthermore, thermal degradation properties were determined by DSC and TGA techniques. The thermal stability was evaluated in the temperature range of 200°C-800°C. The DSC explained about increase in  $T_g$  value with an increase in the aromatic content in between 220-300°C. The obtained series showed excellent thermal stability with their temperature weight loss (10%) around 450°C and 480°C. Synthesized polyamides can be utilized as multipurpose roles in medicine, electronics, aerospace, and advanced structural composites. This paper will briefly review the role of obtained complex which involves processability, stability and performance of the materials.

**Keywords:** Polymer synthesis, Morpholine, Azo coupled molecule, Polycondensation, TGA.

### 1. INTRODUCTION

Academicians and industrialists have shown a great attention towards the macromolecular chemistry which is known as multidisciplinary science. It transacts with the chemical synthesis and chemical properties of polymers [1]. Due to their unique physical and thermomechanical property, the material shows emerging applications in numerous fields [2-5]. Polymeric materials are used to improve the thermal stability without decreasing the high thermal performance of various numbers of heterocyclic polymers such as polyamides, polyimides, polyesters, polyethers and more [6-8]. Aromatic polyamides and polyesters exhibit outstanding mechanical properties with excellent thermal and oxidative stability in heat resistant polymers [9-11]. Introduction of the heterocyclic unit to the polymeric chain of the aromatic polyamide is effective for improving the thermo-stability and solubility of the polymers [12-14]. Polymers containing s-triazine ring have become a subject of major interest because the thermal stability of the triazine ring makes an attractive monomer for use in

high performance material. The choice of this heterocyclic ring is based on its molecular symmetry and aromaticity [15, 16]. All these experimental facts lend support to present the work that involves the preparation and characterization of new kind of thermally stable polyamides bearing excellent high-performance properties due to the attachment of s-triazine ring as main moiety. Present investigation involves the synthesis and characterization of linear hetero-aromatic polyamides by using 6-(Morpholino)-2,4-bis-(4-(4-azobenzoyl chloride)-1-Naphthol)1,3,5-triazine [MANCT] and various commercial diamines.

### 2. MATERIAL AND METHODS

#### 2.1. Material

The diamines 4, 4'-diaminodiphenyl ether (4,4'-DADPE; 97%), 1, 3-diamino propane (1,3-DAP; 98.8%), 3, 4-diamino benzophenone (3,4-DABP; 98%), O-phenylene diamine (OPDA; 97%), M-phenylene diamines (MPDA; 96.7%), P-phenylene diamine (PPDA; 97.8%) were purchased from Aldrich and were utilized without further purification. The

secondary amine named as Morpholine (98%) was purchased from National Chemical Ltd. Baroda and used as received. Cyanuric chloride (National chemical Ltd. Baroda) was purified by crystallization from pure benzene (M.P.146°C). Chemicals such as Sodium hydroxide pellets, Sodium bicarbonate, Thionyl chloride, Cetramide were laboratory reagents and used as received. *N,N*-dimethylformamide (DMF; 99%), and tetrahydrofuran (THF; 99.5%) were purchased from Fluka. *N*-methyl pyrrolidone (NMP; 99%) and dimethylsulfoxide (DMSO; 99%) were provided by Merck.

## 2.2. Measurements

The recording of NMR spectra was done at room temperature using a BRUKER spectrometer operating at 300.13 MHz for <sup>1</sup>H NMR. Deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>) was used as solvent for analysis with tetramethylsilane as an internal reference. Attenuated total reflectance- Fourier transform infrared (ATR-FTIR) spectra (400cm<sup>-1</sup>-4000 cm<sup>-1</sup>) of monomers and polymers have been scanned in KBr pellets were recorded at room temperature on "IR affinity1, (DRS 8000A) Shimadzu Pvt. Ltd. (Japan) FT-IR Spectrometer Spectrum." For this, AR grade KBr was fused at red heat and was ground thoroughly. 1.0gm of KBr and 4.0mg of polymer sample were mixed intimately and ground in a ball mill. Melting points were recorded on an Electrothermal 1A9000 series digital melting point apparatus. Thermal stability of polymers has been obtained on the thermobalance "METTLER TOLEDO STAR SW 9.20" at a constant heating rate of 10°C/min. in the temperature range from 50-800°C in presence of air and METTLER TOLEDO STAR 8.10 under nitrogen atmosphere and differential scanning calorimetry (DSC) analyses were carried out with a Netzsch DSC-404C (Selb, Germany).

## 2.3. Synthesis of 4-(4-azobenzoic acid)-1 Naphthol [ABAN][17] (3)

A p-amino benzoic acid (compound 1) (13.71g, 0.1M) was dissolved in 20ml methanol in 250ml one neck round bottom flask and 50ml concentrated HCl was added. Obtained mixture was kept at 0-5°C temperature for 5-10 minutes. The solution of sodium nitrite (6.88 g, 0.1 M) in 25 ml of double distilled water at 0°C -5°C was added to the above cold mixture with good stirring. After 20 minutes, the diazotization was complete, which was verified by adding a small amount of 4-(*N,N*-dimethylamine) benzaldehyde solution

which generates color if undiazotized aromatic amine still present. When the diazotization was complete, a solution of  $\alpha$ -Naphthol (compound 2) (14.4g, 0.1M) in methanol was added to the paste-like diazonium salt, and the mixture was kept for a period of 10-20 min at 0-5°C temperature. The coupling process was started immediately. The azo dye 4-(4-azobenzoic acid)-1-Naphthol (compound 3) was formed which was filtered and washed with distilled water, dried and purified by recrystallization from hot carbon tetrachloride to give 67.1% yield. The dried product was used for the further reaction.

## 2.4. Synthesis of monomer [18-20]

### 2.4.1. Synthesis of 2, 4-dichloro-6-(Morpholino)-1, 3, 5-triazine [MT] (5)

A pure crystallized cyanuric chloride (compound 4) (18.44g, 0.1M) dissolved in a 60ml of acetone and mixture was kept at (0-5°C) for 5-10 minutes. A concentrated solution of sodium bicarbonate in 100ml of distilled water was prepared and at the same time a solution of morpholine (6.8g, 0.1M) in 10ml of acetone was also prepared, both the solutions were added simultaneously with good stirring to the above cold slurry of cyanuric chloride which was kept on a mechanical stirrer. After completing the addition, the mixture was stirred for 2 hour at 0-5°C. The white colored product was obtained and filtered. The product was recrystallized from ethanol and dried in vacuum desiccators. The yield was 80%.

### 2.4.2. Synthesis of 6-(Morpholino)-2,4-bis-(4-(4-azobenzoic acid)-1-Naphthol)1,3,5-triazine [MANT] (6)

A solution of 2,4-dichloro-6-(morpholino)-1,3,5-triazine [MT] (23.5g, 0.1M) in 40ml of acetone was mixed with dilute solution of NaOH and 4-(4-azobenzoic acid)-1-Naphthol (29.2g, 0.1M) in 80ml double distilled water. Reaction mixture was assembled with water condenser and stirred for 2 hours at room temperature and 2 hours at 80°C temperature. After completing the reaction, mixture was collected, filtered and washed with hot water. Product was dried in vacuum at 100°C. The yield was 90%. The product was recrystallized from acetone.

### 2.4.3. Synthesis of 6-(Morpholino)-2,4-bis-(4-(4-azobenzoyl chloride)-1-Naphthol)1,3,5-triazine [MANCT] (7)

A minimum quantity of thionyl chloride was added into

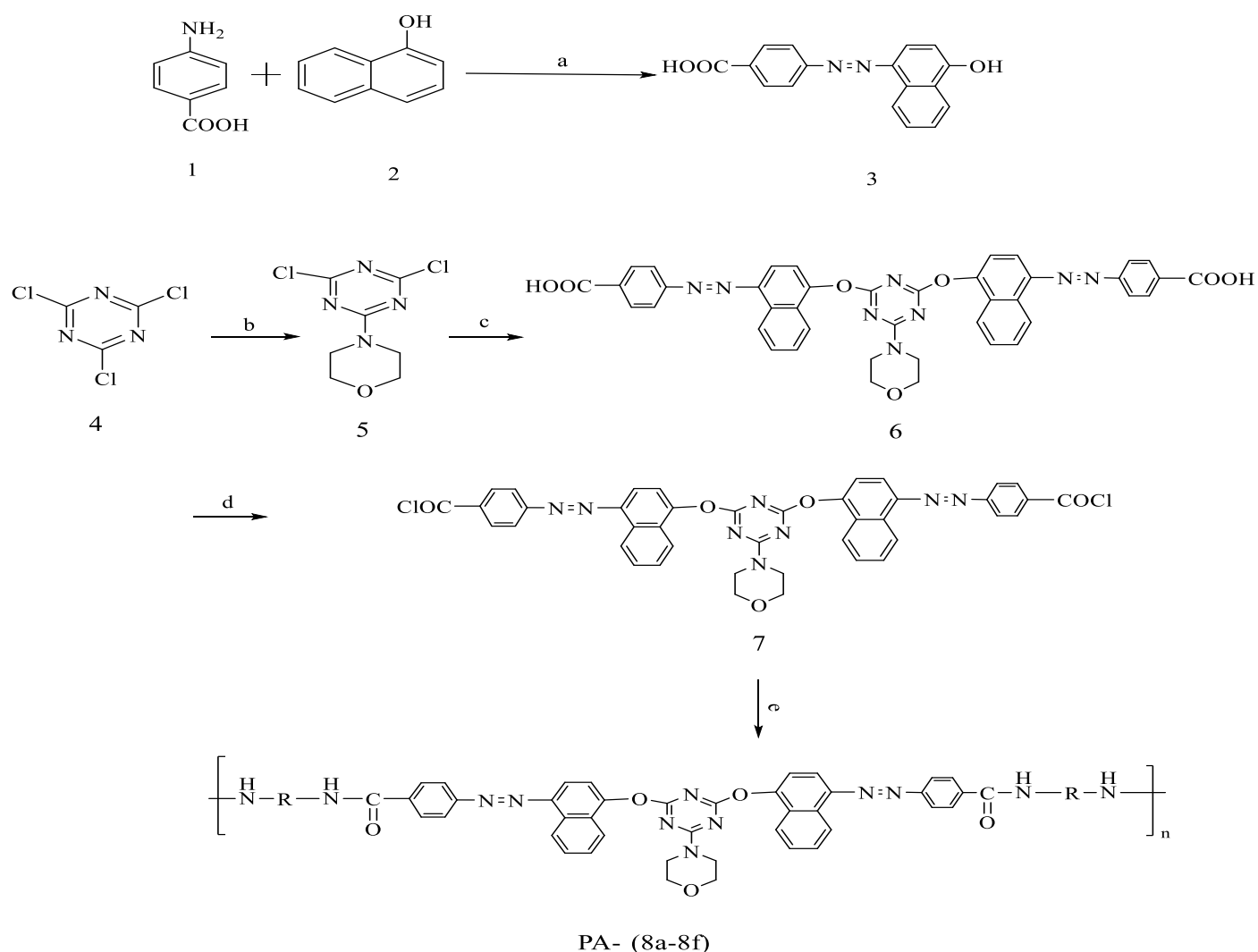
6-(Morpholino)-2,4-bis-(4-(4-azobenzoylchloride)-1-Naphthol) 1,3,5-triazine [MANCT] (7.46g 0.01M) in a dry round bottom flask. The reaction mixture was refluxed at 78°C for 2 hours. At the end of the reaction, excess thionyl chloride was distilled off and dry product was collected. The yield was about 72%. The product was recrystallized from dimethyl formamide.

## 2.5. General procedure for the synthesis of polyamides [21]

### 2.5.1. Synthesis of polyamides MANCTA (1-6) PA-(8a-8f) (Scheme 1)

6-(Morpholino)-2,4-bis-(4-(4-azobenzoyl chloride)-1-Naphthol)1,3,5-triazine [MANCT] (0.1M) and the

minimum quantity of DMF (approx. 10ml) was stirred in a two neck round bottom flask, then initiator cetrimide (0.25g) was added and heated up to 150°C. Then various diamines (0.2M) were added. The reaction temperature was raised to 160-180°C and heated for 8 hours. The reaction mixture was cooled and poured with constant stirring in 250ml of ice-cooled water. Solid was filtered, washed with hot water and dried. The other polyamides were synthesized by similar method as shown above using diamines named as o- phenylene diamine (7a), m-phenylene diamines (7b), p-phenylene diamine (7c), 4,4- diaminodiphenyl ether (7d), 3,4-diamino benzophenone (7e), 1, 3- diamino propane (7f).



R= Aliphatic/Aromatic diamines

Reagents: a)  $\text{NaNO}_2 + \text{HCl}$  at 0-5°C; b) Morpholine in acetone, 0-5°C, 2 hours; c) 5 in acetone, 3 in NaOH, 2 hours at RT then 2 hours at 60-70°C; d) 6 in  $\text{SOCl}_2$  2 hours at 80°C; e) 7 in DMF + diamine (a-f), cetrimide, 8 hours at 160-170°C.

## Reaction Scheme

PA-8a: IR (KBr)  $\text{cm}^{-1}$ : -C=N stretching 1580-1660  $\text{cm}^{-1}$ , C-O-C of morpholine ring 1119-1125  $\text{cm}^{-1}$ , C=O stretching 1573-1350  $\text{cm}^{-1}$ , N-H stretching 3350-3400  $\text{cm}^{-1}$ .

PA-8b: IR (KBr)  $\text{cm}^{-1}$ : -C=N stretching 1500-1620  $\text{cm}^{-1}$ , Ar-O-Ar 1203-1225  $\text{cm}^{-1}$ , C=O stretching 1545-1320  $\text{cm}^{-1}$ , N-H stretching 3255-3410  $\text{cm}^{-1}$ .

PA-8c: IR (KBr)  $\text{cm}^{-1}$ : -C=N- stretching 1520-1650  $\text{cm}^{-1}$ , C-O-C of morpholine ring 1011-1130  $\text{cm}^{-1}$ , C=O stretching 1550-1330  $\text{cm}^{-1}$ , N-H stretching 3217-3200  $\text{cm}^{-1}$ .

PA-8d: IR (KBr)  $\text{cm}^{-1}$ : -C=N stretching at 1410-1550  $\text{cm}^{-1}$ , Ar-O-Ar 1266  $\text{cm}^{-1}$ , >C=O stretching at 1637-1735  $\text{cm}^{-1}$ , N-H stretching 3311-3220  $\text{cm}^{-1}$ .

PA-8e: IR (KBr)  $\text{cm}^{-1}$ : -C=N- stretching 1550-1750  $\text{cm}^{-1}$ , C-O-C of morpholine ring 1119-1230  $\text{cm}^{-1}$ , >C=O stretching 1650-1700  $\text{cm}^{-1}$ , N-H stretching 3380-3400  $\text{cm}^{-1}$ .

PA-8f: IR (KBr)  $\text{cm}^{-1}$ : -C=N- stretching 1420-1550  $\text{cm}^{-1}$ , Ar-O-Ar 1535  $\text{cm}^{-1}$ , >C=O 1617-1734  $\text{cm}^{-1}$ , -CH<sub>2</sub> stretching 2900-3010  $\text{cm}^{-1}$ , N-H stretching 3447-3520  $\text{cm}^{-1}$ .

### 3. RESULTS AND DISCUSSION

#### 3.1. Color

The resultant polyamides showed different colours. Formed polyamides were mostly brown and coffee in

colour. The brief detail is shown in Table 1.

#### 3.2. Solubility

Generally, PAs possess poor solubilities and insoluble in organic solvents. Still, the amalgamation of polar groups into a PA inclines to improve the solubility. The 0.05 gm of compound to 1 ml of solvent was utilized to check the solubilities (Table 2). The results displayed that the series was soluble in polar aprotic solvents (DMSO, DMF, DMAc, and NMP) at room temperature. The improvement in solubility might be attributed to the presence of a bulky group, which increased the disorder in the chains, hindered the dense chain packing, and increased the free volume, reducing the inter chain interactions and causing better solvent molecule penetration into the polymer chain. However, they are soluble on heating in less polar solvents like n-butanol and are completely insoluble in common solvents such as halogenated, non-halogenated and aromatic compounds like CH<sub>3</sub>OH, CHCl<sub>3</sub>, CCl<sub>4</sub> and acetone. The PA 8d and 8e showed better solubility than the other polymers due to the presence of a bulkier unit. In general, the superior solubility of polyamides is due to the presence of ether linkage and azo coupling formation. Thus, it increases the polymer polar solvent interactions, results into better solubility in organic polar solvents.

**Table 1: Physical Data of Polyamides**

Diamine	Polyamide	Yield (%)	$\eta_{inh}^*$ (dL/g)	Color of polymer
7a	8a	87	0.34	Dark brown
7b	8b	91	0.32	Brown
7c	8c	94	0.35	Light brown
7d	8d	85	0.41	Black
7e	8e	82	0.38	Coffee
7f	8f	78	0.25	White

**Table 2: Solubilities of the PAs (8a-8f)**

Solvents	PA-8a	PA-8b	PA-8c	PA-8d	PA-8e	PA-8f
DMF	++	++	++	++	++	++
DMSO	++	++	++	++	++	++
Chloroform	--	--	--	--	--	--
CCl <sub>4</sub>	--	--	--	--	--	--
Acetone	±±	±±	±±	±±	±±	±±
Benzene	--	--	--	--	--	--
Chloro Benzene	--	--	--	--	--	--
Methanol	±±	±±	±±	±±	±±	±±
Ethanol	-±	±±	±±	±±	±±	-±
THF	++	++	++	++	++	++
n-Butanol	±±	±±	±±	±±	±±	±±
IPA	±±	±±	±±	±±	±±	±±
Ether	--	--	--	--	--	--
Ethyl Acetate	--	--	--	--	--	--

+ = Soluble, - = Insoluble, ± = partly soluble, The first and second symbol indicates the solubility of polyamides at room temperature and at 50°C respectively, DMF- dimethyl formamide, DMSO-dimethyl sulfoxide, THF- tetrahydrofuran, IPA- isopropyl alcohol

### 3.3. Viscosity measurement

Viscosity measurements were carried out using an Ubbelohde suspended level kinematic viscometer. The polymer solutions were prepared in DMSO and were filtered through G-3 sintered glass prior to flow time measurements. The viscosity for all polyamides at various concentrations were determined at  $25 \pm 0.1^\circ\text{C}$ . The series of PA (8a-8f) reveals that PA-8d which contains diamine DADPE showed the highest solution viscosity due to high molecular weight compound, whereas PA-8f displayed lowest viscosity due to the enrollment of aliphatic unit.

The viscosity of the polyamides obtained from the s-triazine holding azo compounds and different diamines follows the sequence given below:



### 3.4. $^1\text{H-NMR}$ study

High resolution (300 MHz) NMR spectra of solution of polyamides were measured in deuterated DMSO using TMS as an internal reference. All the spectra of the polyamides were consistent with their structure. As a representative, the assignments of the chemical shifts for the  $^1\text{H-NMR}$  spectrum of PA-8c is given in (Fig. 1).

The  $^1\text{H-NMR}$  spectrum of PA-8c shows a multiplet at  $\delta 5.58-7.65$  ppm (m) which was due to the presence of aromatic protons. Proton of methylene group  $\text{CH}_2\text{-O-CH}_2$  of morpholine ring produced at  $\delta 2.83-3.10$  ppm. Proton of methylene group  $\text{CH}_2\text{-N-CH}_2$  of morpholine ring produces multiplet at  $\delta 3.63-3.76$  ppm. Proton of amide N-H produced a singlet at  $\delta 9.5-9.7$  ppm.

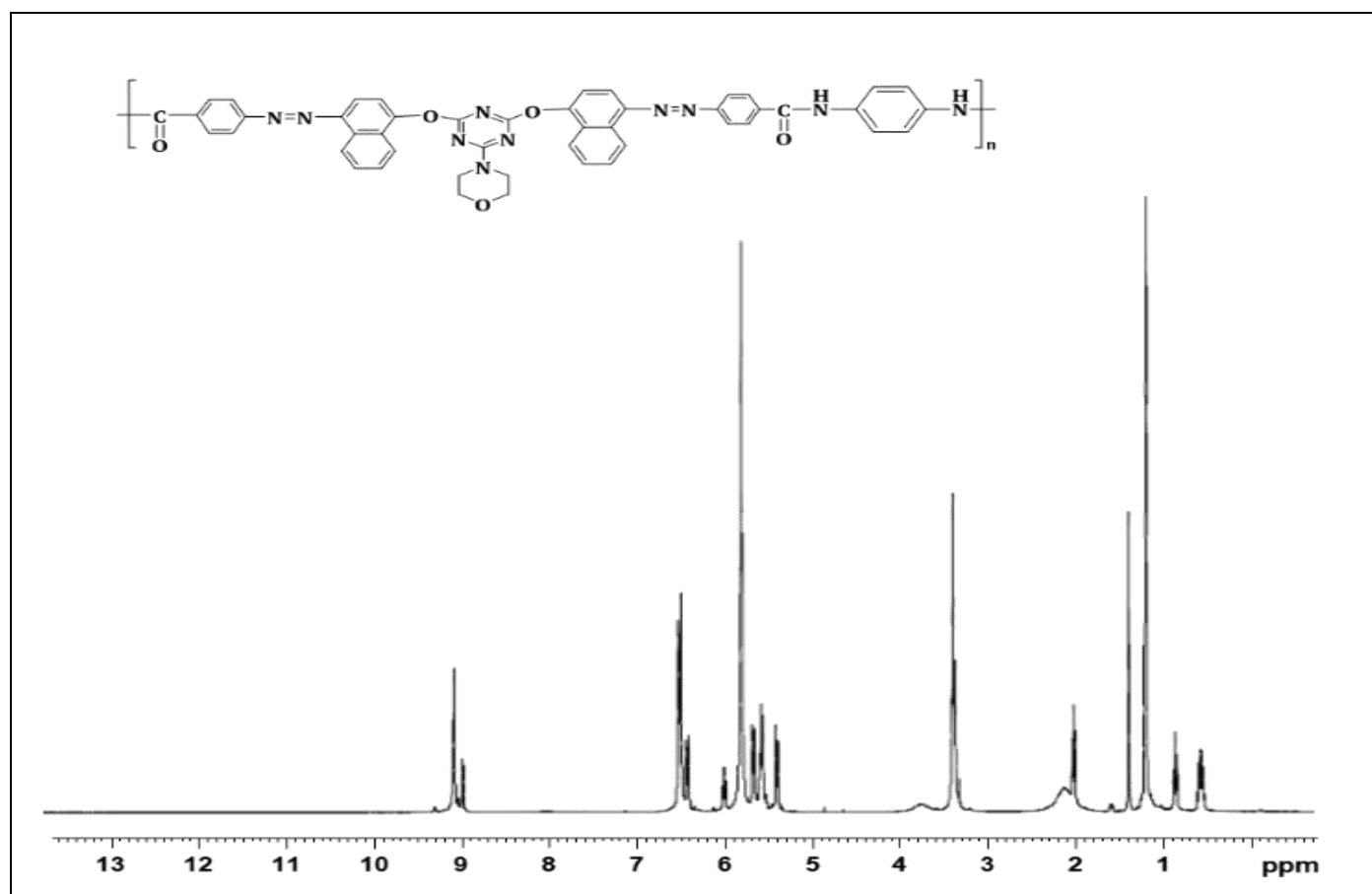


Fig. 1: Representative  $^1\text{H-NMR}$  of PA-8c

### 3.5. Thermal analysis

Methods used for the assessment of thermal stability of polymers from TG traces have been briefly reviewed by Reich and Levi [22]. The DSC and TGA was utilized to investigate thermal properties of the synthesized

polyamides under  $\text{N}_2$  atmosphere at a  $10^\circ\text{C}/\text{min}$  heating rate. All the polyamides showed almost similar pattern of decomposition. Results are summarized in Fig. 2. In DSC, the amorphous nature was highlighted as no endothermic melting peak was observed. The  $T_g$  was

taken as the midpoint of the change in slope of the DSC curve baseline. These polyamides exhibit  $T_g$  values in between 220°C to 300°C (Table 3 and Fig. 2). In general, the involvement of bulkier units in the backbone constrains the free rotation of the chain and give higher  $T_g$  values. Other side, the ether linkage unit reduces the rigidity due to flexible bond and so  $T_g$  value obtain low. Hence, bulkier pendent unit which inhibit the rotation and flexible unit which down the rigidity are two major factors in  $T_g$  values of the polyamide series.

The thermal properties of series were investigated by

TGA curves as shown in fig. 3, and table 3, including, the temperature at which a weight loss of 10% occurred ( $T_{10\%}$ ), and the residual weight at 900°C. All the synthesized polyamides displayed comparable thermal stabilities and upto 400°C no weight loss was observed. As presented in table 3,  $T_{10\%}$  values in between 450°C-500°C, respectively. At 480°C the thermal stability was exhibited highest by PA-8c, which is due to rigid aromatic backbone and p-substitution. The polyamide showed weight loss about 35-45%. The char yield can be further utilized for estimating LOI of each polyamide.

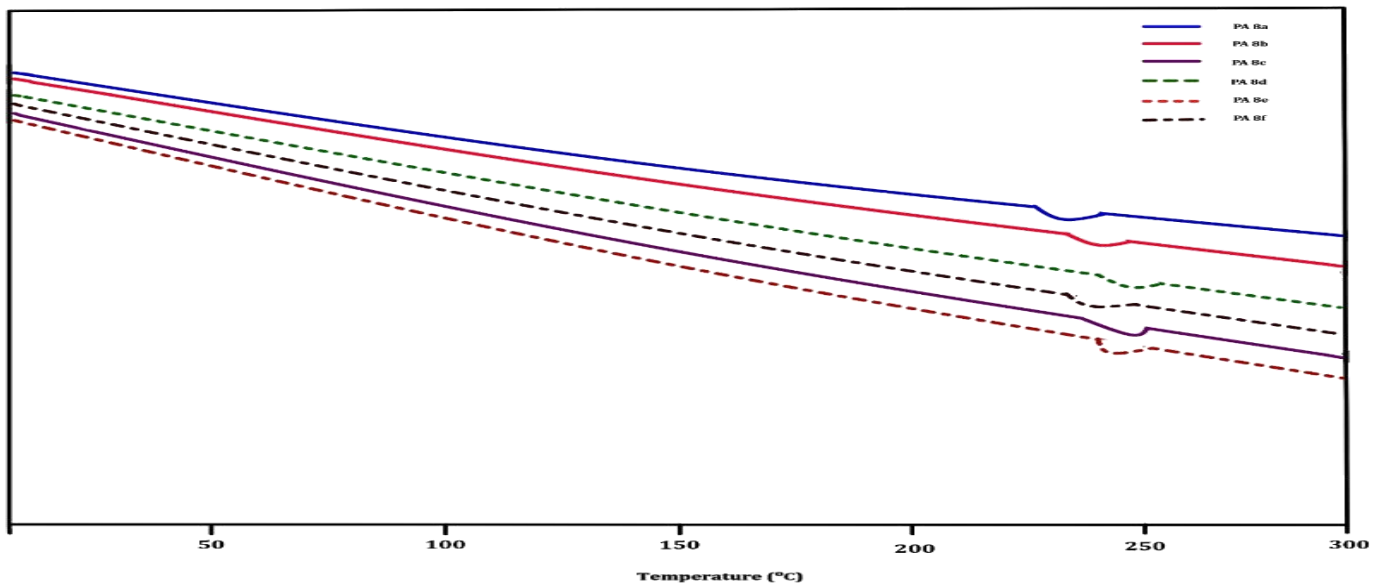


Fig. 2: DSC curve of PA (8a-8f) under  $N_2$ , heating rate 10°C/min

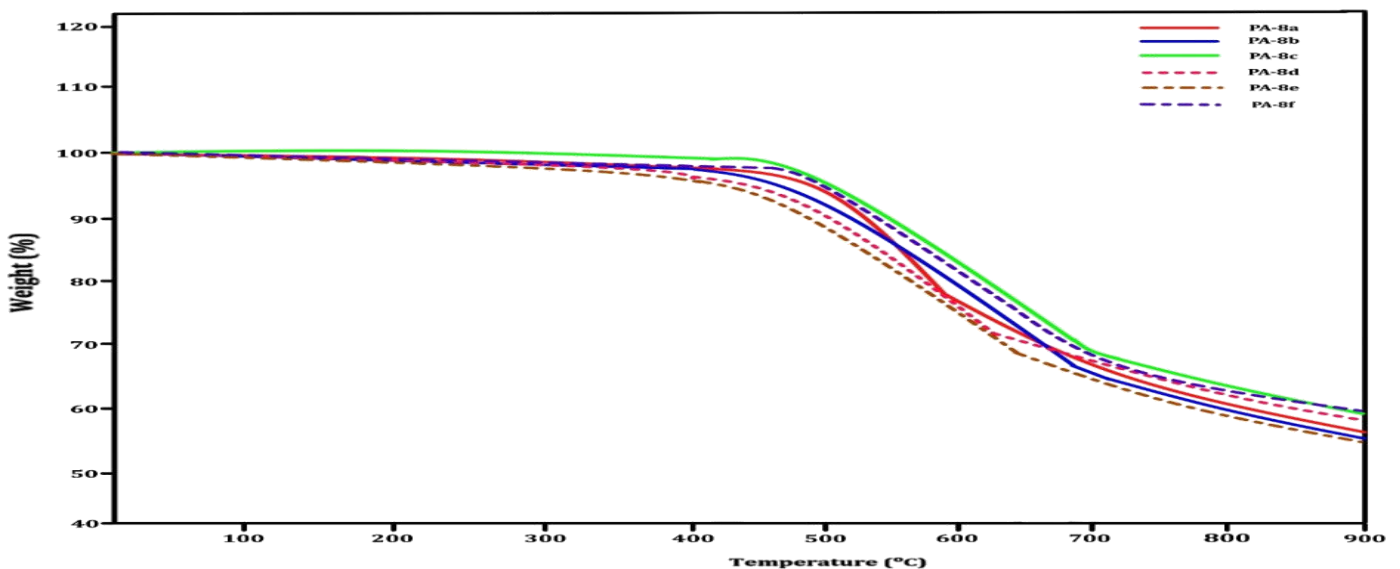


Fig. 3: TGA curve of s-triazine holding PA (8a-8f)

**Table 3: Thermal behaviour of s-triazine holding PAs (8a-8f)**

Polyamide	<sup>a</sup> T <sub>g</sub> (°C)	<sup>b</sup> T <sub>10</sub> (°C)	<sup>c</sup> Char Yield (%)
PA-8a	248	476	60
PA-8b	247	480	58
PA-8c	250	488	62
PA-8d	246	458	55
PA-8e	244	450	57
PA-8f	242	445	60

<sup>a</sup> Glass transition temperature was recorded at 10°C min<sup>-1</sup> under N<sub>2</sub> atmosphere.

<sup>b</sup> Temperatures at T<sub>10</sub> (°C) weight losses was recorded under N<sub>2</sub> at heating rate of 10°C/min.

<sup>c</sup> Residual char after TGA at the maximum temperature of 900°C.

#### 4. CONCLUSION

A series of polyamides MANCTA (1-6), i.e., PA (8a-8f) was synthesized via polycondensation chemical imidization utilizing aliphatic-aromatic diamine. s-triazine heterocyclic moiety was used as starting material for the synthesis of thermally stable and high molecular weight polyamide series. In general, an amorphous polyamide series showed excellent solubility, good thermal stability as well as higher molecular weight. A DSC curve showed the amount of energy absorbed or released by a sample and the thermal stability was obtained in the range of 200-800°C. The series showed to be admirable high-performance material which can be used in multilingual fields with huge application.

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#### Conflict of interest

There is no conflict of interest regarding the publication of this article.

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