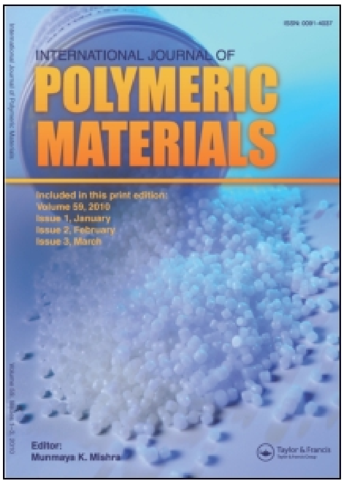

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Novel Copolyamides Based on s-Triazine Derivatives

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Ten copolyamides have been synthesized by polycondensation of 2-(N-methylpiperazine)-4,6-bis(2-naphthoxy-6-carbonyl chloride)-s-triazine [MPNCCT] and different mixtures of diamines such as; 4,4′-diamino diphenylamide [DADPA] + 4,4′-diamino diphenyl sulphone [DADPS]; 4,4′-diamino diphenylamide [DADPA] + 4,4′-diamino diphenylmethane [DADPM]; 4,4′-diaminodiphenylamide [DADPA] + p-phenylene diamine [PPDA]; 4,4′-diaminodiphenylamide [DADPA] + ethylene diamine [EDA]; 4,4′-diaminodiphenylamide [DADPA] + 2,4-diamino toluene [DAT]; 2,4-diamino toluene [DAT] + 4,4′-diaminodiphenyl sulphone [DADPS]; 2,4-diamino toluene [DAT] + 4,4′-diaminodiphenyl sulphonamide [DADPSA]; 2,4-diamino toluene [DAT] + 4,4′-diamino-diphenyl methane [DADPM]; 2,4-diamino toluene [DAT] + o-phenylene diamine [OPDA] and p-phenylene diamine [PPDA] + 4,4′-diaminodiphenyl sulphonamide [DADPSA]. All the copolyamides have been characterized by IR spectra, NMR spectra, solubility, density, viscosity measurements and thermogravimetric analysis [TGA]. The obtained products, have high thermal stability along with good solubility in organic solvents.

Keywords copolyamide, density, s-triazine, synthesis, thermogravimetric analysis, viscosity

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INTRODUCTION

A literature survey of polymers containing s-triazine moiety in their backbone reveals that they are unique in the sense that they exhibit an unusual combination of properties such as high softening temperature, high glass transition point and thermal stability along with fair processibility [1–6]. A major part of the synthetic polymers used in various fields nowadays are copolymers, and so, a lot of research work in this field is going on. Historically and commercially, polyamides [7,8] occupy an important place in the world of polymers. Aromatic polyamides [9–11] are well-known as high-performance polymers as they possess high melting points, good thermal stability and excellent mechanical properties. Because of these properties they are of major commercial and industrial importance [12,13]. This has become possible because of the particular characteristics of polyamides and availability of polyamides of varied structures. Some of the main uses [14] of polyamides are for synthetic fibers for the tire, carpet, stocking, adhesives and upholstery industries. Use of polyamides as molding and extrusion resins for the plastics industry is also of increasing importance [15]. Various polyamides and copolyamides based on 2-(N-piperidino)-4,6-bis (naphthoxy-2-carbonyl chloride)-s-triazine [16], 2-(N-ethyl anilino)-4,6-bis(phenoxy-2-carbonyl chloride)-s-triazine [17] and 2-(β-naphthylamino)-4,6-bis(naphthoxy-3-carbonyl chloride)-s-triazine [18] derivatives have been synthesized and characterized in our laboratory. They possess good thermal stability, which is dependent on the type and structure of the polymer.

In the present work, we have synthesized and characterized various copolyamides based on 2-(N-methyl piperazine)-4,6-bis(2-naphthoxy-6-carbonyl chloride)-s-triazine [MPNCCT]. A study of solubility, viscosity, IR spectra, and thermal behavior has been carried out in order to characterize these polymer samples.

MATERIALS

Fresh double-distilled water was used for the preparation of solutions. Solvents, like benzene, N,N-dimethyl formamide, triethylamine, petroleum-ether, carbon tetrachloride, methanol, ethanol, N-methyl-2-pyrrolidone, N,N′-dimethylacetamide, dimethyl sulphoxide, m-cresol, sulphuric acid, and hexane were all laboratory reagents, obtained from Merck and used as received. Cyanuric chloride (Fluka) was purified by repeated crystallization from pure benzene (M.P. 146°C). N-methyl piperazine of purity greater than 99% was received from Enzal Chemicals Ltd., Panoli, Ankleshwar. 6-hydroxy-2-naphthoic acid of purity greater than 99% was received from Atul Ltd., Atul, Valsad.

4,4′-diaminodiphenylamide (DADPA) [19], 4,4′-diaminodiphenyl sulphonamide (DADPSA) [20] was synthesized as per the reported procedure. The other diamines, such as: 4,4′-diaminodiphenylsulphone (Cibatul, Atul), 4,4′-diaminodiphenylmethane (Cibatul, Atul), 2,4-diamino toluene (Merck), p-phenylene diamine (Merck), o-phenylene diamine (Merck) and ethylene diamine (Merck) of purity better than 99% were used as received.

EXPERIMENTAL

Synthesis of Monomer (MPNCCT)

The monomer, 2-(N-methyl piperazine)-4,6-bis(2-naphthoxy-6-carbonyl chloride)-s-triazine [MPNCCT], was synthesized as per the reaction in Figure 1. The procedure adopted for synthesis is described below.

(1) 2-(N-methyl piperazine)-4,6-dichloro-S-triazine (MPDCT)

A solution of cyanuric chloride (18.44 gm, 0.1 mol) in 60 mL acetone was added with stirring to a cold solution (0–5°C) of sodium bicarbonate (9.4 gm, 0.1 mol) in 100 mL distilled water, in a three-necked flask (250 mL). This resulted in the formation of slurry of cyanuric chloride. A solution of N-methyl piperazine (11.1 mL, 0.1 mol) in 10 mL acetone was added to the cold slurry of cyanuric chloride with continuous stirring. After the addition was completed, the reaction mixture was stirred for 2 h at 0–5°C. The white-colored product was filtered and recrystallized from ethanol and dried in a vacuum desiccator (yield 90% and m.p. 125°C).

If the reaction is carried out in water, the reaction is left incomplete with low yield. But the yield is improved considerably if the cyanuric chloride is freshly precipitated by pouring an acetone or dioxane solution into ice-cold water. The use of aqueous system allows the product to be isolated easily in higher yield [21].

(2) 2-(N-methyl piperazine)-4,6-bis(2-naphthoxy-6-carboxy)-s-triazine (MPNCT)

There was dissolved 2-(N-methyl piperazine)-4,6-dichloro-s-triazine (MPDCT) (24.8 gm, 0.1 mol) in 40 mL of acetone. A mixture of NaOH (16.0 gm, 0.4 mol) and 6-hydroxy-2-naphthoic acid (37.6 gm, 0.2 mol) in 80 mL double-distilled water was then added slowly at room temperature to the solution of MPDCT with constant stirring. Reaction was continued for 4 h. The first 2 h at room temperature and then another 2 h at 80°C. At the end

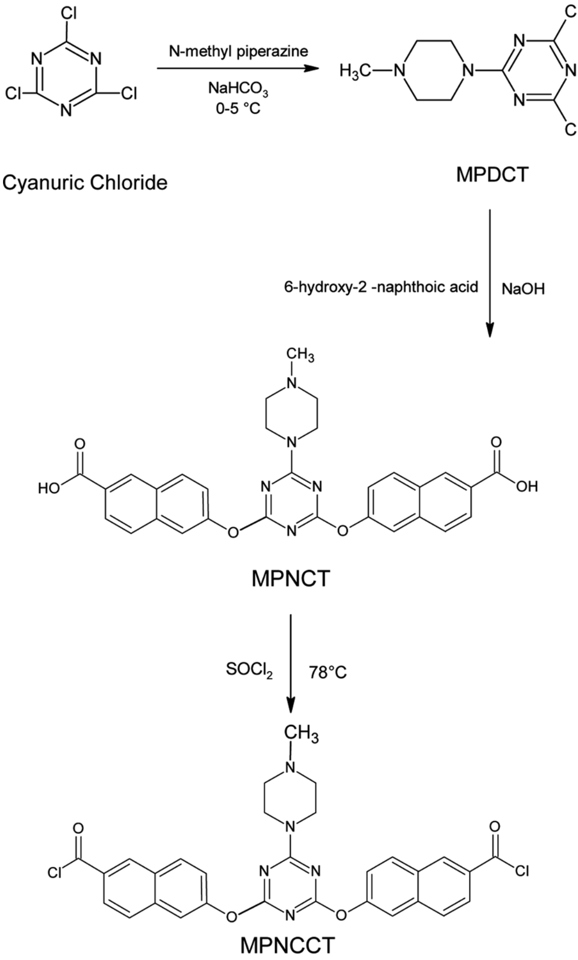

Figure 1: Scheme for the synthesis of monomer 2-(N-methyl piperazine)-4,6-bis(2-naphthoxy-6-carbonyl chloride)-s-triazine (MPNCCT).

of the reaction, the white solid separated from the reaction mixture was filtered and washed several times with hot water, and dried in vacuum at 100°C. The product was recrystallized from acetone. The yield was 85% with m.p. 220°C.

(3) 2-(N-methyl piperazine)-4,6-bis(2-naphthoxy-6-carbonyl chloride)-s-triazine (MPNCCT)

Thionyl chloride (11.9 mL, 0.1 mol) was added to 2-(N-methyl piperazine)-4,6-bis(6-naphthoxy-2-carboxy)-s-triazine (MPNCT) (5.51 gm, 0.01 mol) and the reaction mixture was refluxed at 78°C for 2 h. At the end of the reaction the excess thionyl chloride was distilled off and a dry product was recovered. The yield was about 65% and recrystallized from dimethylformamide (m.p. 180°C).

Synthesis of Polymers

A method for synthesis of copolyamides from MPNCCT and mixture of diamine (DADPM + DADPA) using high temperature solution polycondensation technique is described as a model reaction. Reaction scheme for the same is given in Figure 2.

A mixture of MPNCCT (5.88 g, 0.01 mol), 4,4′-diamino diphenylamide (1.14 g, 0.005 mol), 4,4′-diaminodiphenyl methane (0.99 g, 0.005 mol), triethylamine (~5 mL) and minimum quantity of DMF (~10 mL) was placed in a three-necked flask equipped with a drying tube. The reaction mixture was heated with stirring at 165°C for 8 h. At the initial stage of the reaction, the evolution of hydrogen chloride gas was rapid and later it slowed down. The polymer obtained was filtered, thoroughly washed with hot distilled water, then with hot methanol, and hot acetone. Finally, the polymer was dried in a vacuum oven at 80°C overnight. The yield of polymer was 85%.

The other copolyamides from MPNCCT and various diamine mixtures such as [DADPA + EDA], [DADPA + DADPS], [DADPA + PPDA], [PPDA + DADPSA], [DAT + DADPSA], [DAT + DADPS], [DAT + DADPM],

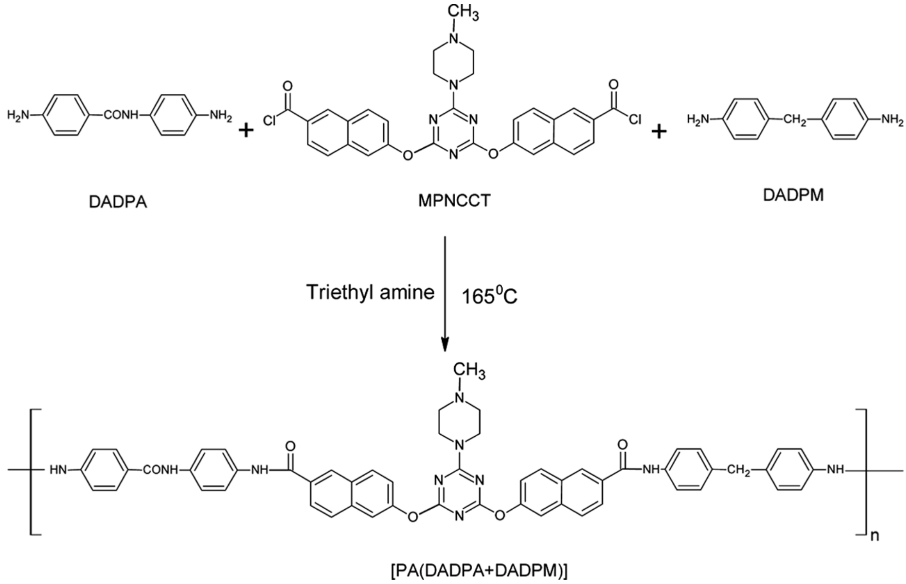

Figure 2: Synthesis of copolyamides.

[DAT + DADPA], [DAT + OPDA], [DAT + EDA], were synthesized by the same method as shown above.

MEASUREMENTS

Infrared spectra of the synthesized polymers have been measured using KBr pellets on a Perkin-Elmer FTIR Spectrometer Paragon-500. The Nuclear magnetic resonance (NMR) spectroscopy of the polymers has been carried out using DMSO as solvent and TMS as reference compound. NMR spectra were recorded on Perkin-Elmer Model-32 ^{1}H-NMR Spectrometer (300 MHz) for the structure elucidation. Density of the polymers has been determined pyknometrically at 25°C using the suspension method. Solution viscosity measurements have been carried out for the copolyamides. Intrinsic viscosity was obtained from the plot of reduced viscosity vs. concentration and inherent viscosity vs. concentration according to Huggins [22] and Kraemer [23] equations. Thermogravimetric analysis of some of the polymers has been carried out on the thermobalance Metter TA4000 system with constant heating rate of 10°C/min. in the temperature range from ambient to 800°C. All the thermograms have been analyzed as per the graphical methods proposed by Broido [24] and Horowitz and Metzger [25].

RESULTS AND DISCUSSION

Various copolyamides synthesized from MPNCCT and various mixtures of diamines have been evaluated for various physicochemical properties such as yield, color, solubility, density, viscosity, temperature characteristics, activation energy of thermal decomposition, IR and NMR spectroscopy.

Yield and Color

The yield of copolyamides varies from 65 to 90% depending upon the reactivity of the diamine components. Most of the copolyamides are reddish brown to black in color. All the copolyamides were obtained as solid powder. The yield and color of the copolyamides depend upon the color, nature and structure of the diamine components. The composition, color and yield are presented in Table 1.

Density

Density of each of the ten copolyamides was measured at 25 ± 1°C by suspension method. The liquid system of carbon tetrachloride and petroleum

Table 1: Yield and density of copolyamides.

Polymer	Yield (%)	Color	Density gm/cm^3
PA(DADPA + DADPS)	65	black	1.187
PA(DADPA + DADPM)	75	light yellow	1.031
PA(DADPA + PPDA)	80	light yellow	1.145
PA(DADPA + EDA)	75	brown	1.165
PA(DAT + DADPSA)	65	light brown	1.025
PA(DAT + DADPS)	70	light green	1.150
PA(DAT + DADPM)	85	black	1.135
PA(DAT + DADPA)	75	brown	1.174
PA(DAT + OPDA)	90	light red	1.157
PA(PPDA + DADPSA)	75	black	1.116

ether was found to be inert to all the copolyamides. The sample remains in a state of suspension even after a long time. The results are shown in Table 1. Density of all the copolyamides varies from 1.245–1.169 g/cm^3. The highest density is displayed by PA(DADPA + DADPS), while the lowest by PA(DAT + DADPSA). The density of copolyamides varies with the different chemical properties of the diamines used. PA(DADPA + DADPS) shows the highest density value compared to other copolyamides, but this value is less than the value for the homopolyamide of PADADPS. This may be due to the fact that in the copolyamides, the structure is not as compact as in PADADPSA due to the introduction of other diamines. The density of the copolyamides obtained from MPNCCT and various diamine mixtures decreases in following order:

$$\mathrm{PA(DADPA + DADPS) > PA(DAT + DADPA) > PA(DADPA + EDA) > PA(DAT + OPDA) > PA(DAT + DADPS) > PA(DADPA + PPDA) > PA(DAT + DADPM) > PA(PPDA + DADPSA) > PA(DADPA + DADPM) > PA(DAT + DADPSA).}$$

Solubility

The solubilities of various copolyamides were determined for powdery specimens in different solvents at room temperature with concentration approximately 1% (w/v), and are summarized in Table 2. The copolyamides are soluble in polar aprotic solvents like N-methyl-2-pyrrolidone, dimethylsulphoxide, N,N′-dimethylformamide, N,N′-dimethylacetamide, and m-cresol, as well as soluble in concentrate sulphuric acid and formic acid. The reason for this may be that the presence of the side bulky groups brings about an increase in solubility. It was also found that the copolyamides are insoluble in halogenated aliphatic and aromatic solvents like chlorobenzene, chloroform, and carbon tetrachloride. They are also insoluble in common organic solvents such as benzene, toluene, cyclohexane, tetrahydrofuran, acetone,

Table 2: Solubility of copolyamides in various solvents.

Solvent	PA(DADPA + DADPM)	PA(DADPA + PPDA)	PA(PPDA + EDA)	PA(DADPA + DADPSA)	PA(DADPA + DADPS)	PA(DAT + DADPM	PA(DAT + DADPS)	PA(DAT + DADPM	PA(DAT + DADPA)	PA(DAT + OPDA)	PA(DAT + DADPSA
DMF	++	++	++	++	++	++	++	++	++	++	++
DMSO	++	++	++	++	++	++	++	++	++	++	++
DMAc	++	++	++	++	++	++	++	++	++	++	++
NMP	++	++	++	++	++	++	++	++	++	++	++
m-cresol	±+	++	−±	++	++	++	++	++	++	++	±+
H_2SO_4	++	++	++	++	++	++	++	++	++	++	++
$Cl-C_6H_5$	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−
$CHCl_3$	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−
CCl_4	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−
Benzene	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−
THF	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−
$(CH_3)_2CO$	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−	−−

The first and second symbol indicates the solubility of polymer at room temperature and 50°C, respectively.
+ = Soluble, − = Insoluble, ± = Partly soluble.

methanol and diethyl ether. The solubility of the copolyamides markedly decreases with an increase in the content in the phenyl moiety in the polymer.

Viscosity

Dilute solution viscosity measurements were carried out using Ubbelohde suspended level kinemetic viscometer by a standard method. Intrinsic, reduced and inherent viscosities for all the copolyamides at various concentrations were determined at 25 ± 0.1°C. Reduced and inherent viscosities were then calculated from experimental data. Typical Huggins and Kraemer plots were used to obtain intrinsic viscosity for each of the copolyamides. Solution viscosity of PA(DADPA + PPDA) at different concentrations is shown in Table 3. Flow time (t_0) for DMF solvent was found 127 sec. Intrinsic, reduced and inherent viscosity along with Huggins and Kraemer constants for 1% solution for all the copolyamides reveals that PA(DADPA + PPDA) has the highest solution viscosity and hence the highest molecular weight amongst all the copolyamides, whereas the PA(DAT + DADPSA) has the lowest.

The intrinsic viscosity of the copolyamides follows the sequence given below. PA(DADPA + PPDA) > PA(DAT + OPDA) > PA(DADPA + DADPM) > PA(DAT + DADPM) > PA(DADPA + EDA) > PA(DAT + DADPA) > PA(DADPA + DADPS) > PA(DAT + DADPSA) > PA(PPDA + DADPSA) > PA(DAT + DADPS).

Intrinsic, reduced and inherent viscosities of all the copolyamides and constants of Huggins and Kraemer equations are shown in Table 4.

Infrared Spectroscopy

The expected spectral features of the synthesized copolyamides were assigned. The position of all the easily discernible bands was noted. The band observed around 3250–3350 cm^{-1} is attributed to N-H stretching vibration of secondary amide. The bands at 3060–3090 cm^{-1} are attributed to aromatic C-H stretching. Bands at about 2790–2810 cm^{-1} are attributed to C-H stretching vibration of –N-CH$_3$ group. The bands observed at 2850–2855 cm^{-1} and

Table 3: Solution viscosity of PA(DADPA + PPDA).

Conc. (gm/dl)	**Flow time T sec.**	$\eta_{rel} = t/t_o$	$\eta_{sp} = \eta_{rel}-1$	η_{sp}/C **(dl/g)**	$\ln \eta_{rel}/C$ **(dl/g)**
0.2	143.4	1.129	0.129	0.646	0.607
0.4	161.0	1.268	0.268	0.670	0.594
0.6	180.1	1.418	0.418	0.696	0.582
0.8	200.5	1.579	0.579	0.724	0.571
1.0	222.0	1.748	0.748	0.748	0.558

Table 4: Intrinsic, reduced and inherent viscosity values and constants of Huggins and Kraemer for copolyamides.

Polyamides*	**Intrinsic viscosity** η	**Reduced viscosity** η**sp/C**	**Inherent viscosity ln** η**rel/C**	**Huggins constant K**	**Kraemer constant** β
PA(DADPA + PPDA)	0.619	0.748	0.558	0.337	0.159
PA(DAT + OPDA)	0.582	0.710	0.536	0.375	0.136
PA(DADPA + DADPM)	0.552	0.668	0.512	0.381	0.131
PA(DAT + DADPM)	0.537	0.641	0.495	0.368	0.146
PA(DAT + DADPS)	0.436	0.503	0.407	0.352	0.152
PA(DADPA + EDA)	0.522	0.621	0.483	0.362	0.143
PA(DADPA + DADPS)	0.511	0.593	0.466	0.314	0.172
PA(DAT + DADPSA)	0.492	0.584	0.460	0.380	0.132
PA(PPDA + DADPSA)	0.470	0.551	0.439	0.379	0.131
PA(DAT + DADPA)	0.515	0.609	0.476	0.354	0.143

*Conc. for all the polymer solution is 1.0 gm/dl.

2925 cm^{-1} are assigned as symmetric and asymmetric C-H stretching vibrations of –CH_2 group, respectively. The presence of two bands due to stretching and bending vibration of amide bands is anticipated in the region of 1640–1660 cm^{-1} and 1540–1560 cm^{-1} respectively, depends upon the structure. Strong band in the region 1400–1500 cm^{-1} was attributed to skeletal and ring stretching vibrations of aromatic and heteroaromatic ring. The strong band observed around 800–840 cm^{-1} is due to out-of-plane vibrations of s-triazine ring. The presence of s-triazine ring is further supported by the appearance of band at 1445–1515 cm^{-1}, which is due to in-plane bending vibrations of s-triazine ring. The band at 1400 cm^{-1} is attributed to C-N stretching vibrations of amide group. The bands appearing at 1020 cm^{-1} and 1240–1260 cm^{-1} may be attributed to symmetric and asymmetric vibrations of aryl-ether linkage. The band observed around 860–900 cm^{-1} might be due to C-H bending vibrations of aromatic ring. IR spectra of copolyamides containing DAT exhibit bands at around 1340–1360 cm^{-1} confirming the presence of –CH_3 group. IR spectra of copolyamides exhibit two distinct bands at 1180 cm^{-1} (symmetric) and 1370 cm^{-1} (asymmetric) for PA(PPDA + DADPSA) and PA(DAT + DADPSA), confirming the presence of –SO_2NH group due to DADPSA. IR spectra of copolyamides exhibit two distinct bands at 1145 cm^{-1} (symmetric) and 1315 cm^{-1} (asymmetric) for PA(DADPA + DADPS) and bands at 1150 cm^{-1} (symmetric) and 1340 cm^{-1} (asymmetric) for PA(DAT + DADPS), confirming the presence of –SO_2 group due to DADPS. IR spectra of copolyamide containing EDA, exhibit a bands at 520 cm^{-1} and 560 cm^{-1} confirming the presence of aliphatic chain due to EDA.

All the IR spectral characteristics of the different copolyamide samples are in good agreement with the proposed structure.

NMR Spectroscopy

High-resolution (300 MHz) ^{1}H-NMR spectra of solutions of representative copolyamides were scanned in deuterated dimethylsulphoxide (DMSO-d_6) using TMS as an internal reference. The chemical shift in δ ppm for the copolyamides is presented below. ^{1}H-NMR spectrum of PA(PPDA + DADPSA) shows a multiplet at δ 6.80–8.60 ppm that may be due to the presence of aromatic protons. 3H of methyl of –N-CH_3 of piperazine ring produce a singlet at 2.40 ppm. Piperazine ring protons show a multiplet for 8H of methylene of piperazine ring $[(CH_2)_4]_2$ at δ 2.70–3.60 ppm. Hydrogen of –CONH produces a singlet at δ 10.20 ppm. 1H of –SO_2NH produces a singlet at δ 11.0 ppm. ^{1}H-NMR spectrum of PA(DAT + DADPSA) shows a multiplet at δ 6.60–8.70 ppm due to the presence of aromatic protons. 3 H of methyl of toluene ring produce a singlet at δ 1.70 ppm. 3 H of methyl of –N-CH_3 of piperazine ring produce a singlet at 2.65 ppm. Piperazine ring protons show a multiplet for 8 H of methylene of piperazine ring $[(CH_2)_4]_2$ at δ 2.80–3.70 ppm. 1H of –CONH produces a singlet at δ 10.15 ppm. 1 H of –SO_2NH produces a singlet at δ 10.90 ppm.

Thermogravimetric Analysis

Polymers with high thermal stabilities are constantly required for special applications in industries as well as for high-speed aircraft and missiles. Because the resonance along the polymer chain should greatly enhance the thermal stability of the polymer, the aromatic or heterocyclic rings in the backbone are advantageous to achieve thermally stable polymers. Examples of such heterocycles are imide, imidazole, s-triazine etc. Within a sample of specific polyamides, the thermal degradation reaction depends upon a large number of variables and can become complex. Important variables include decomposition temperature, heating rate, rate of removal of volatile products from the reaction zone, softening and melting points of the polymer, sample size and dimensions, presence of oxygen in the atmosphere or absorbed in the sample or other occluded impurities, the initiators used and the mechanism of termination in the original preparation of the polymer, extraneous units copolymerized into the polymer and many other factors. In order to identify the generalized mechanism, therefore, thermal decomposition is carried out under inert atmosphere with carefully purified polymers in the form of finely divided powder. Thermogravimetric curves for some representative copolyamide samples were obtained at a heating rate of 10°C/min in nitrogen (30 ml/min.) atmosphere.

Qualitative Estimation of Thermal Stability

Several temperature characteristics used for the qualitative assessment of relative thermal stability of polymers, are initial decomposition temperature (T_0), temperature for 10% weight loss (T_{10}), temperature for maximum rate of decomposition (T_{max}) and half volatilization temperature (T_s) in nitrogen atmosphere. The characteristics are presented in Table 5.

The thermogram of PA(PPDA + DADPSA) indicates that the decomposition occurs in a single step. The polymer begins to decompose at 220°C. The rapid weight loss step commences at 300°C and proceeds up to about 550°C, involving the weight loss of 60–65% of original weight. The maximum rate of weight loss occurs at 380°C. After 650°C, the sample degrades slowly up to the end temperature and leaves about 28.00% residue. The thermogram of PA(DADPA + DADPS) reveals a single step degradation. The polymer begins to decompose at 215°C. Marked decomposition with a rapid weight loss occurs in the temperature range 350–550°C, with a maximum rate at 390°C, involving about 30–35% weight loss. At the end, residue left is about 42%. The copolyamide of DADPA and EDA shows a single step thermal degradation. The polymer, involving a weight loss of 33.32%, starts to decompose at 150°C. The maximum rate of weight loss occurs at 250°C, involving about 25.00% weight loss. The residue left at the end is about 20%. The thermogram of PA(DAT + OPDA) reveals that decomposition occurs in two distinct steps. The polymer begins to decompose at 165°C. The first degradation step is marked with a rapid weight loss in the temperature range 320–480°C, involving about 35% weight loss. The maximum rate of decomposition occurs at 350°C. The second decomposition step is marked with a rapid weight loss in the temperature range 485–720°C, with the maximum rate of weight loss occuring at 520°C, involving a loss of 38% weight. After 720°C, the sample degrades slowly up to the end temperature and leaves about 45% residue.

The thermal stability of the copolyamides was established on the basis of 10% decomposition temperature T_{10}. The thermal stability of the copolyamides decreased in the following order:

PA(DADPA + DADPM) > PA(PPDA + DADPSA) > PA(DAT + OPDA) > PA (DADPA + EDA).

The thermal stability behavior for maximum decomposition temperature (T_{max}) for the first step is as follow:

PA(PPDA + DADPSA) > PA(DADPA + DADPM) > PA(DAT + OPDA) > PA (DADPA + EDA).

Table 5: Temperature characteristics of copolyamides.

			T_{max}		
Polymer	**T_0**	**T_{10}**	**Step I**	**Step II**	**Ts**
PA(PPDA + DADPSA)	220	310	380	–	485
PA(DADPA + DADPM)	215	300	360	–	610
PA(DADPA + EDA)	150	230	260	–	305
PA(DAT + OPDA)	165	295	350	520	650

Table 6: Application of Broido method of TGA thermogram of PA(PPDA + DADPSA).

Temp.°C	% Wt.	$y = \frac{W_t - W_\alpha}{W_t - W_0}$	1/y	ln ln 1/y	T °K	$1/T \times 10^3 \,°K^{-1}$
360	85.90	0.804	1.244	−1.522	633	1.686
370	81.85	0.748	1.337	−1.236	643	1.631
380	77.60	0.689	1.451	−0.988	653	1.580
390	73.20	0.628	1.592	−0.766	663	1.531
400	68.85	0.567	1.764	−0.566	673	1.486
410	64.80	0.511	1.957	−0.398	683	1.443
420	61.30	0.462	2.164	−0.259	693	1.402

Evaluation of Kinetic Parameters

Dynamic TGA thermograms obtained at a heating rate of 10°C/min have been analyzed as per the graphical methods, proposed by Broido [24] and Horowitz-Metzger [25]. A typical application of Broido's method is exemplified for PA(PPDA + DADPSA) in Table 6. The Horowitz-Metzger method is exemplified for the PA(PPDA + DADPSA) in Table 7.

The thermograms of other copolyamides were also analyzed in the same manner using both the graphical methods. The values of apparent activation energy corresponding to different decomposition steps involved were evaluated from the slope of the least square plots of the relevant data and are presented in Table 8.

Examination of the data reveals that both methods yield comparable values for activation energy. The experimental points corresponding to initial stage (10% loss) of thermal degradation tended to deviate from linearity. This deviation may be due to the fact that the decomposition of solids does not obey first-order kinetics in the initial stages. The Broido method is expected to provide more reliable estimates of energy E than the Horowitz-Metzger method, as no other temperature characteristics are involved. The values of activation energy (E_a) for the first step vary from 8.03 to 12.14 KCal/mole according to Broido's method. Thus, results based on qualitative and semiquantitative

Table 7: Application of Horowitz and Metzger's method to TGA thermogram of PA(PPDA + DADPSA).

T°C	%wt	$1-\alpha$	$1/1-\alpha$	$\ln\ln(1/1-\alpha)$	θ
320	85.90	0.804	1.244	−1.522	−60
340	81.85	0.748	1.337	−1.236	−40
360	77.60	0.689	1.451	−0.988	−20
380	73.20	0.628	1.592	−0.766	0
400	68.85	0.567	1.764	−0.566	20
420	64.80	0.511	1.957	−0.398	40
440	61.30	0.462	2.164	−0.259	60

Table 8: Kinetic parameters for the thermal decomposition of copolyamides.

	Activation energy E (Kcal/mol)			
	Broido		Horowitz-Metzger	
Polyamide	**Step I**	**Step II**	**Step I**	**Step II**
PA(PPDA + DADPSA)	8.89	–	8.90	–
PA(DADPA + DADPM)	8.03	–	7.95	–
PA(DADPA + EDA)	12.14	–	13.19	–
PA(DAT + OPDA)	10.27	11.46	10.56	10.80

treatment of thermogravimetric data on copolyamides, point out that 4,4′-diminodiphenylamide and 4,4′-diaminodiphphenylsulphonamide yield highly thermally stable polyamides. Moreover, such an inclusion does not adversely affect the solubility of the resultant copolyamides.

CONCLUSION

A series of novel copolyamides containing s-triazine rings in the main chain was synthesized by high temperature polycondensation. Wholly aromatic copolyamides containing 1,3,5-triazine rings possess excellent thermal stability along with good solubility in organic solvents. Therefore, they might be used as new processable thermally stable polymers.

ABBREVIATIONS

η_{sp}/c	Reduced viscosity
D	Density
E_A	Activation energy
T_0	Initial decomposition temperature
T_{10}	Temperature for 10% weight loss
T_{max}	Maximum rate of decomposition temperature
T_s	Temperature for 50% weight loss
K	Huggins constant
β	Kraemer constant
MPNCCT	2-(N-methylpiperazine)-4,6-bis(2-naphthoxy-6-carbonyl chloride)-s-triazine
PA(DADPA + PPDS)	Polyamide of 4,4′-diamino diphenylamide and 4,4′-diamino diphenyl sulphone
PA(DADPA + DADPM)	Polyamide of 4,4′-diaminodiphenylamide and 4,4′-diamino diphenylmethane
PA(DADPA + PPDA)	Polyamide of 4,4′-diaminodiphenylamide and p-phenylene diamine

PA(DADPA + EDA)	Polyamide of 4,4′-diaminodiphenylamide and ethylene diamine
PA(DAT + DADPSA)	Polyamide of 2,4-diamino toluene and 4,4′-diaminodiphenyl sulphonamide
PA(DAT + DADPS)	Polyamide of 2,4-diamino toluene and 4,4′-diaminodiphenyl sulphone
PA(DAT + DADPM)	Polyamide of 2,4-diamino toluene and 4,4′-diaminodiphenyl methane
PA(DAT + DADPA)	Polyamide of 2,4-diamino toluene and 4,4′-diaminodiphenylamide
PA(DAT + OPDA)	Polyamide of 2,4-diamino toluene and o-phenylene diamine
PA(PPDA + DADPSA)	Polyamide of p-phenylene diamine and 4,4′-diaminodiphenyl sulphonamide

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