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Synthesis and Characterization of Novel Copolyamides Based on *s*-Triazine Derivatives

Shahrukh T. Asundaria and Keshav C. Patel

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Various copolyamides have been synthesized from 2-(*N*- β -naphthylamine)-4,6-bis-(naphthoxy-3-carbonylchloride)-*s*-triazine [NANCCT] with each of the mixture of diols: 4,4'-diaminodiphenyl (DADP)+4,4'-diaminodiphenyl methane (DADPM), DADP + 4,4'-diaminodiphenyl amide (DADPA), DADP+4,4'-diaminodiphenylsulfonamide (DADPSA), DADP+4,4'-diaminodiphenyl sulfone (DADPS), DADP+2,4-diaminotoluene (DAT), DADP+p-phenylenediamine (PPDA), DADP+ethylene diamine (EDA), EDA+DADPM, EDA+DADPA, EDA+DADPSA, EDA+DADPS, EDA+DAT, EDA+PPDA. All polyamides were characterized by various physicochemical properties such as yield, color, solubility, density, viscosity, temperature characteristics, activation energy of thermal decomposition, IR spectra and NMR spectra.

Keywords copolyamides, *s*-triazine, synthesis

INTRODUCTION

Recently, much attention has been paid to the synthesis of thermally stable high-performance polymers, as they are important materials for various applications. Demands on polymeric materials in scientific and technological applications is such that they should withstand high temperature and possess

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high mechanical strength and easy processability. The choice of heterocyclic rings in the main chain of the synthetic polymer is to impart certain properties like resistance to heat and chemical attack, good mechanical and dielectrical properties and ease of processability to the polymer [1].

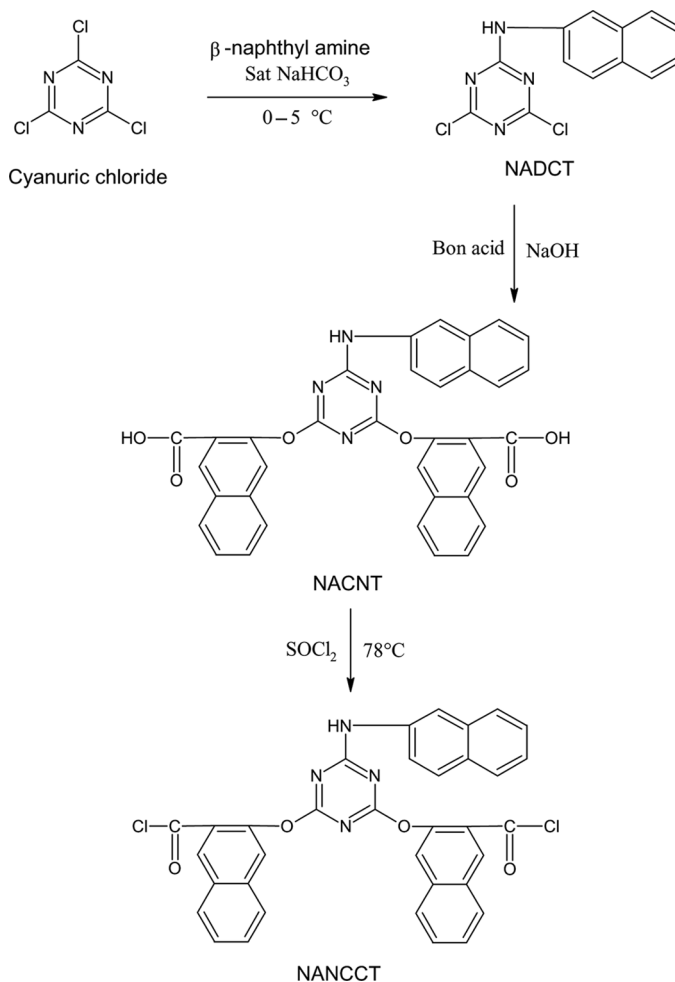
Perusal of the literature shows that polymers containing *s*-triazine in the main chain are noted for their high transition temperature and thermal stability [2–4]. Historically and commercially, polyamides occupy an important place in the polymer world. Polyamides are well-established as high performance materials with excellent thermal stability and mechanical properties [5–9]. Some of the main uses of polyamides are for synthetic fibers for the tire, carpet, stocking, and upholstery industries [10–12]. Polyamide polymers are used for electrical grommets, bearings, gears, pipe, film, monofilaments, wire straps, wire covering, electrical connectors, sport equipment and many other functional components [13]. The linear polyamides of high molecular weight afford synthetic fibers of excellent properties. Wholly aromatic polyamides are characterized as high temperature-resistant materials with a favorable balance of other physical and chemical properties [14]. The presence of the amide group provides a focal point for hydrogen bonding, which results in the formation of crystalline structures that are characterized by toughness, resistance to oils and solvents, superior physical strength, a degree of sensitivity to moisture and high melting points. Because of these versatile properties and applications, many research activities have been undertaken to synthesize new polyamides and to modify them for desired properties.

In our previous work [15], we have studied various homopolyamides based on 2-(*N*- β -naphthylamine)-4,6-bis-(naphthoxy-3-carbonylchloride)-*s*-triazine [NANCCT] which were found to have high performance properties. To go on with our work, the present investigation describes systematic study of the synthesis and characterization of novel copolyamides based on *s*-triazine.

MATERIALS

The monomer, 2-(β -naphthylamino)-4,6-bis(naphthoxy-3-carbonyl chloride)-*s*-triazine [NANCCT] was synthesized as per the reaction scheme shown in Scheme 1. Water was distilled in the presence of alkaline potassium permanganate twice. The dissolved carbon dioxide was boiled off. Always fresh double-distilled water was used for the preparation of solutions.

Benzene, acetone, dimethyl formamide and other solvents, like triethylamine, ethanol, *N*-methyl-2-pyrrolidone, *N,N'*-dimethylacetamide, dimethyl sulphoxide, *m*-cresol, and sulphuric acid were all laboratory reagents and were used as received from Merck. β -naphthyl amine (Sigma), and cyanuric



Scheme 1: Synthesis of monomer 2-(N-β-naphthylamine)-4,6-bis-(naphthoxy-3-carbonylchloride)-s-triazine [NANCCT].

chloride (Fluka) were used as received. 4,4'-diaminodiphenylamide (DADPA) [16], 4,4'-diaminodiphenyl sulphonamide (DADPSA) [17] were synthesized as per the reported procedures. The other diamines, such as 4,4'-diaminodiphenyl (Merck), 4,4'-diaminodiphenylsulphone (Cibatul, Atul), 2,4-diaminotoluene (Merck), o-phenylene diamine (Merck), m-phenylene diamine (Merck), p-phenylene diamine (Merck), ethylene diamine (Merck), 4,4'-diaminodiphenylmethane (Cibatul, Atul), 2,4-diamino toluene (Merck), all of purity better than 99%, were used as received.

Chemicals such as thionyl chloride, sodium bicarbonate, sodium hydroxide were used as received.

EXPERIMENTAL

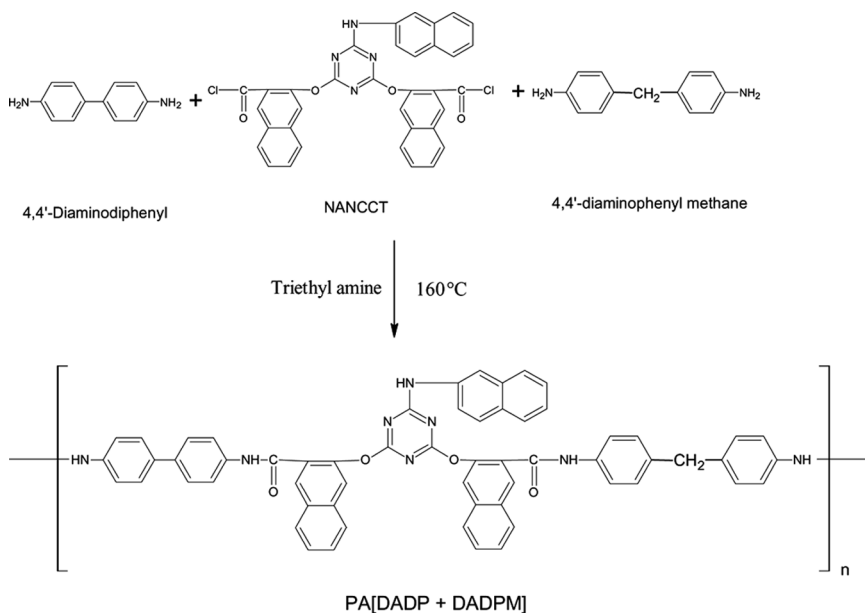
Synthesis of Monomer

The monomer, 2-(*N*- β -naphthylamino)-4,6-bis(naphthoxy-3-carbonylchloride)-*s*-triazine [NANCCT] was synthesized by the reported procedure [18] as per the reaction scheme shown in Scheme 1. The yield was 90%. It was recrystallized from acetone, m.p. 200°C.

Synthesis of Aromatic Polyamides

A high temperature solution polycondensation is exemplified for the synthesis of aromatic copolyamides from NANCCT with 4,4'-diaminodiphenyl and 4,4'-diaminodiphenylmethane and is described as a model reaction.

A mixture of 2-(*N*- β -naphthylamino)-4,6-bis(naphthoxy-3-carbonylchloride)-*s*-triazine (6.62 gm, 0.01 mol), 4,4'-diaminodiphenyl (1.84 gm, 0.01 mol), 4,4'-diaminodiphenylmethane (1.98 gm, 0.01 mol), triethyl amine (2 mL) and dimethylformamide (15 mL) was placed in a three-necked flask equipped with a mechanical stirrer, and a dry tube. The reaction mixture was heated with stirring at 155–160°C for 8 h. At the initial stage of the reaction, the evolution of hydrogen chloride was rapid and later on it slowed down. The polymer obtained was filtered, and thoroughly washed with hot distilled water. Finally the polymer was dried in a vacuum oven at 80°C overnight. The yield of polymer was 75%.



Scheme 2: Synthesis of copolyamide of diaminodiphenyl and diaminodiphenyl methane.

The other copolyamides from 2-(N- β -naphthylamine)-4,6-bis-(naphthoxy-3-carbonylchloride)-s-triazine and various diamine mixtures such as (4,4'-diaminodiphenyl and 4,4'-diaminodiphenylamide), (4,4'-diaminodiphenyl and 4,4'-diaminodiphenylsulfonamide), (4,4'-diaminodiphenyl and 4,4'-diaminodiphenylsulfone), (4,4'-diaminodiphenyl and 2,4-diaminotoluene), (4,4'-diaminodiphenyl and p-phenylenediamine), (ethylenediamine and 4,4'-diaminodiphenyl amide), (ethylene diamine and 4,4'-diaminodiphenyl sulfonamide), (ethylenediamine and 4,4'-diaminodiphenyl sulfone), (ethylenediamine and 2,4-diaminotoluene), (ethylenediamine and 4,4'-diaminodiphenyl methane) and (ethylenediamine and p-phenylenediamine) were synthesized by a similar method as shown in Scheme 2.

MEASUREMENTS

The solubility test was conducted as follows: 30 to 50 mg sample of finely ground polymer was placed in a small test tube and 1 mL of solvent was added to each. The mixtures were stored at 25°C for some time with occasional shaking. Formation of streaks while shaking indicated dissolution. Polymer samples that swelled without dissolving at 25°C were heated to 50°C in order to affect the process of dissolution. Several solvents were tested for this purpose.

Density of polymers has been determined at $25 \pm 3^\circ\text{C}$ by the use of powdered samples [19]. The method is as follows: The powdered polymer sample was placed in a liquid of lower density held in a test tube. To this a liquid of higher density was added dropwise with constant stirring from a micro burette. The addition of higher density liquid was continued until a state of suspension was reached. In the state of suspension, the density of the liquid mixture was then determined with the aid of a pycnometer. The liquid system is selected in such a way that the polymer sample remained in a state of suspension even for a prolonged time. Estimated accuracy of density is $\pm 0.001 \text{ gm cm}^{-3}$. Solution viscosity measurements have been carried out for the copolyamides. Viscosities of dilute polymer solution are conveniently measured using the Ubbelohde type of capillary viscometers [20]. Intrinsic viscosity is obtained from the plot of reduced viscosity versus concentration, and inherent viscosity versus concentration according to the Huggins [21] and Kraemer [22] equation. Infrared spectra of the synthesized polymers have been scanned using KBr pellets on a Perkin-Elmer FTIR Spectrometer Paragon-500. The study of nuclear magnetic resonance (NMR) spectroscopy of polymers has been carried out using DMSO as a solvent and TMS as a reference compound. NMR spectra were recorded on a Perkin-Elmer Model-32 ^1H -NMR Spectrometer (300 MHz) for the structure elucidation. All the thermograms of polymers have been obtained on the thermo balance Universal

V1-12E TA instrument with a constant heating rate of 10°C/min in the temperature range from ambient temperature to 800°C. All the thermograms have been analyzed as per the graphical method proposed by Broido [23] and Horowitz and Metzger [24].

RESULTS AND DISCUSSION

Yield and Color

The yield of copolyamides varies from 68 to 90% depending upon the reactivity of the diamine component. The highest yield 90% was obtained for PA[DADP+DADPS], while the lowest 68% for PA[EDA+DADPA]. Most of the copolyamides are light yellow to dark brown in color. The color of the copolyamides involving 4,4'-diaminodiphenyl are darker than the copolyamides involving ethylenediamine. All the copolyamides were obtained as powder. The yield and color of copolyamides depends upon the color, nature and structure of the diamine component. The color, yield and density are presented in Table 1.

Solubility

Examination of information presented therein reveals that copolyamides are soluble in polar aprotic solvents like N-methyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, m-cresol, sulfuric acid and formic acid. It was also found that copolyamides are insoluble in halogenated aliphatic and aromatic compounds like chloroform, carbon tetrachloride, chlorobenzene and bromobenzene and also in common organic solvents like benzene, cyclohexane, methanol, acetone, tetrahydrofuran and

Table 1: Yield and density of copolyamides

Polymer	Yield (%)	Color	Density gm/cm ³
PA(DADP+DADPM)	75	Gray	1.202
PA(DADP+DADPA)	70	light brown	1.198
PA(DADP+DADPSA)	83	dark yellow	1.225
PA(DADP+DADPS)	90	Brown	1.222
PA(DADP+DAT)	74	dark brown	1.162
PA(DADP+PPDA)	79	Brown	1.193
PA(DADP+EDA)	88	Brown	1.180
PA(EDA+DADPM)	71	dark yellow	1.172
PA(EDA+DADPA)	68	Green	1.178
PA(EDA+DADPSA)	72	dark brown	1.860
PA(EDA+DADPS)	86	Yellow	1.192
PA(EDA+DAT)	75	dark green	1.155
PA(EDA+PPDA)	80	Gray	1.167

diethyl ether. It is also observed that the solubility of the copolyamides increases with an increase in temperature. The polymers, which are partly soluble at room temperature, get soluble at higher temperature (50°C).

The solubility of various copolyamides in various solvent is presented in Table 2.

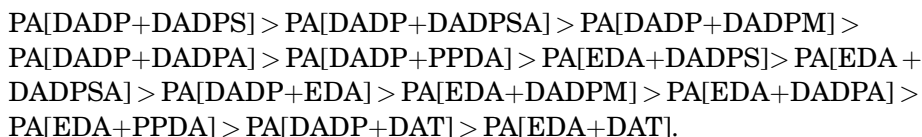
Density

Density and specific volumes are very important characteristics of polymers, giving an idea of the average distance between their macromolecules and extent of crystallinity in polymer [25–28].

The liquid system of carbontetrachloride and petroleum ether was found to be inert to all the copolyamides. The sample remains in a state of suspension even after long time. Estimated accuracy of density is $\pm 0.001 \text{ gm cm}^{-3}$. The results are shown in Table 1.

Density of all the copolyamides varies from $1.222\text{--}1.155 \text{ gm cm}^{-1}$. The highest density is displayed by PA[DADP+DADPS], while the lowest by PA[EDA+DAT]. The density of copolyamides varies with the different chemical properties of the diamine used. PA[DADP+DADPS] shows highest density value than other copolyamides but this value is less than the value for the homopolyamide of DADPS. This may be due to the fact that in the copolyamide, the structure is not as compact as in PA[DADPS].

The density of the copolyamides obtained from NANCCT and various diamines decreases in the following order:



Viscosity

Intrinsic, reduced and inherent viscosities for all the copolyamides at various concentrations were determined at $25 \pm 1^\circ\text{C}$. The relative (η_{rel}) and specific (η_{sp}) viscosities were calculated. Reduced and inherent viscosities were then calculated from experimental data. Typical Huggins and Kraemer's plots were used to obtain intrinsic viscosity for each copolyamide. Flow time (t_0) for DMF solvent was found 125 sec. Solution viscosity of PA[DADP+DADPM] and PA[EDA+DADPS] at different concentration is shown in Tables 3 and 4, respectively. Intrinsic, reduced and inherent viscosity along with Huggins and Kraemer's constants for 1% solution for all the copolyamides reveals that PA[DADP+DADPM] has the highest solution viscosity and hence the

Table 2: Solubility of copolyamides in various solvents.

Solvent	PA(DADP + DADPA)	PA(DADP + DADPSA)	PA(DADP + DADPS)	PA(DADP + DAT)	PA(DADP + PPDA)	PA(DADP + EDA)	PA(DADP + DAT) + (DAT)	PA(EDA + PPDA)	PA(EDA + DADPM)	PA(EDA + DADPA)	PA(EDA + DADPSA)	PA(DADP + DADPS)
H ₂ SO ₄	++	++	++	++	++	++	++	++	++	++	++	++
m-cresol	++	++	++	++	++	++	++	++	++	++	++	++
DMF	++	++	++	++	++	++	++	++	++	++	++	++
DMSO	++	++	±±	±±	++	++	++	++	++	++	++	++
DMAc	++	++	++	++	++	++	++	++	++	++	++	++
N-methyl-2-pyrrolidon	++	++	++	++	++	++	++	++	++	++	++	++
HCOOH	++	++	++	++	++	++	++	++	++	++	++	++
Pyridine	±±	±±	±±	±±	±±	±±	±±	±±	±±	±±	±±	±±
CHCl ₃	--	--	--	--	--	--	--	--	--	--	--	--
THF	--	--	--	--	--	--	--	--	--	--	--	--
Cl-C ₆ H ₅	--	--	--	--	--	--	--	--	--	--	--	--
ethanol	--	--	--	--	--	--	--	--	--	--	--	--
(CH ₃) ₂ CO	--	--	--	--	--	--	--	--	--	--	--	--
Benzene	--	--	--	--	--	--	--	--	--	--	--	--
cyclohexane	--	--	--	--	--	--	--	--	--	--	--	--

The first and second symbol indicates the solubility of polymer at room temperature and 50°C, respectively.

+ = Soluble, -- = Insoluble, ± = Partly soluble.

Table 3: Solution viscosity of copolyamides of PA(DADP+DADPM).

Conc. (C) g/dl	Flow time t sec	$\eta_{rel} = t/t_0$	$\eta_{sp} = \eta_{rel} - 1$	η_{sp}/C	$\ln \eta_{rel}/C$
0.2	141.1	1.128	0.128	0.640	0.6022
0.4	158.0	1.264	0.264	0.660	0.5857
0.6	175.9	1.408	0.408	0.675	0.5702
0.8	194.1	1.552	0.552	0.690	0.5494
1.0	213.0	1.704	0.704	0.704	0.5329

highest molecular weight amongst all the copolyamides, where as the PA[EDA+DADPS] has the lowest.

The intrinsic viscosity of the copolyamides obtained from NANCCT and various diamine mixture follows the sequence given below:

PA[DADP+DADPM] > PA[DADP+DAT] > PA[DADP+DADPA] >
 PA[DADP+DADPA] > PA[DADP+DADPSA] > PA[DADP+DADPS] >
 PA[EDA+DADP] > PA[EDA+DADPM] > PA[EDA+DAT] > PA[EDA +
 DADPA] > PA[EDA+PPDA] > PA[EDA+DADPSA] > PA[EDA+DADPS].

Intrinsic, reduced and inherent viscosities of the copolyamides and constants of Huggins and Kraemer's equation are shown in Table 5.

Infrared Spectra

Examination of IR absorption frequencies reveals that all the copolyamides exhibit bands at 630 cm^{-1} , $700\text{--}650\text{ cm}^{-1}$ and $790\text{--}750\text{ cm}^{-1}$ that may be attributed to the out-of-plane bending vibration of C–H bonds of aromatic ring.

The entire copolyamides exhibit several bands at $820\text{--}800\text{ cm}^{-1}$ due to out-of-plane vibration of the *s*-triazine ring. The presence of the *s*-triazine ring is further supported by the appearance of a band at $1510\text{--}1450\text{ cm}^{-1}$, which is due to the in-plane bending vibration of *s*-triazine ring. The band observed around $850\text{--}875\text{ cm}^{-1}$ may be due to the C–H banding vibration of the aromatic ring.

The bands observed around $1010\text{--}1020\text{ cm}^{-1}$ and $1050\text{--}1090\text{ cm}^{-1}$ are attributed to the vibration of aryl-ester linkage and in-plane bending vibration of aromatic C–H bonds. The presence of aryl-ester linkage is further supported by the appearance of a band at $1240\text{--}1260\text{ cm}^{-1}$.

Table 4: Solution viscosity of copolyamides of PA(EDA+DADPS).

Conc. (C) g/dl	Flow time t sec	$\eta_{rel} = t/t_0$	$\eta_{sp} = \eta_{rel} - 1$	η_{sp}/C	$\ln \eta_{rel}/C$
0.2	135.7	1.085	0.085	0.428	0.4078
0.4	147.0	1.176	0.176	0.440	0.4052
0.6	158.7	1.270	0.270	0.450	0.3983
0.8	147.0	1.368	0.368	0.460	0.3916
1.0	135.7	1.475	0.475	0.475	0.3886

Table 5: Intrinsic, reduced and inherent viscosities and constants of Huggins and Kraemer equation for copolyamides.

Polymer*	Intrinsic viscosity η	Reduced viscosity η_{sp}/C (dl/g)	Inherent viscosity $\ln \eta_{rel}/C$	Huggins constant K	Kraemer constant β
PA(DADP+DADPM)	0.625	0.704	0.533	0.2522	0.2357
PA(DADP+DADPA)	0.580	0.648	0.499	0.2221	0.2675
PA(DADP+DADPSA)	0.521	0.600	0.470	0.2980	0.1879
PA(DADP+DADPS)	0.513	0.590	0.464	0.2926	0.1873
PA(DADP+DAT)	0.595	0.696	0.528	0.2853	0.2087
PA(DADP+PPDA)	0.574	0.640	0.495	0.2483	0.2550
PA(DADP+EDA)	0.493	0.584	0.456	0.3744	0.1362
PA(EDA+DADPM)	0.475	0.552	0.439	0.3413	0.1573
PA(EDA+DADPA)	0.450	0.530	0.425	0.3950	0.1224
PA(EDA+DADPSA)	0.420	0.490	0.399	0.3968	0.1207
PA(EDA+DADPS)	0.415	0.475	0.389	0.3484	0.1533
PA(EDA+DAT)	0.463	0.540	0.432	0.3593	0.1460
PA(EDA+PPDA)	0.425	0.500	0.405	0.3952	0.1085

*Concentration of solution is 1 g/dl for all polymers.

Two bands at 1585–1600 cm^{-1} and 1440–1420 cm^{-1} are attributed to aromatic stretching linkage. The bands at 1410–1450 cm^{-1} , which are due to skeletal and ring-stretching vibrations of the aromatic and heteroaromatic ring. The bands observed around 1590 cm^{-1} , 1530–1510 cm^{-1} and 1470 cm^{-1} may be attributed to C-H stretching vibration of the aromatic nucleus.

The presence of a band due to stretching of the amide carbonyl group is anticipated in the region 1640–1670 cm^{-1} , depending upon the structure. The presence of two bands due to stretching and bending vibrations of the NH system of amide is anticipated in the region 3450–3250 cm^{-1} and 1580–1530 cm^{-1} , respectively. IR spectra of copolyamides of PA[DADP+DAT] and PA[EDA+DAT] exhibit a band at 1370–1375 cm^{-1} confirming the presence of CH_3 group due to 2,4-diaminotoluene. IR spectra of copolyamides of PA[DADP + DADPSA] and PA[EDA+DADPSA] exhibit two distinct bands at 1350–1380 cm^{-1} and 1210–1240 cm^{-1} confirming the presence of SO_2NH group due to DADPSA. IR spectra of PA[DADP+DADPS] and PA[EDA+DADPS] exhibit distinct bands at 1175–1185 cm^{-1} and 1320–1330 cm^{-1} , confirming the presence of SO_2 group due to DADPS. IR spectra of copolyamides containing EDA, exhibit bands at 535 cm^{-1} , 557 cm^{-1} and 584 cm^{-1} confirming the presence of aliphatic chain due to EDA. IR spectral characteristics of all copolymer samples are in good agreement with the expected IR frequencies of proposed structures.

NMR Spectra

High resolution (300 MHz) NMR spectra of solution of copolyamides sample were measured in deuterated dimethyl sulfoxide (DMSO-d_6) using TMS as

an internal reference. The $^1\text{H-NMR}$ spectra of PA[DADP+DADPA] show chemical shift δ at 6.48–8.00 ppm due to the presence of aromatic protons. Signal for $-\text{NH}$ group appears around δ 8.22 ppm and CONH produce a singlet at δ 7.84 ppm. The ^1H spectrum of PA[DADP+EDA] shows a multiplet at δ 6.63–8.04 ppm due to the presence of aromatic protons. $-\text{NH}$ group shows chemical shift around 8.30 ppm. CONH group produced a singlet at δ 7.78 ppm and CH_2 group shows a triplet at δ 3.13 ppm.

Thermogravimetric Analysis

Thermal stability of a polymer provides an important guideline of its usefulness, practically as well as scientifically. The studies of the thermal behavior, not only explain the behavior at high temperature but also assists in establishing criteria for the selection of materials of specific uses [29–33].

Within a sample of specific copolyamides, 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 absorbed in the sample or other occluded impurities, the initiator used and the mechanism of termination in the original preparation of the polymer, extraneous units polymerized in to polymer and many other factors. In order to identify the generalized mechanisms, thermal decomposition is therefore carried out under inert atmosphere with carefully purified polymers in the form of powder.

The thermogram of PA[DADP+DADPA] shows a single step of thermal degradation. The polymer begins to decompose at about 260°C. The maximum rate of decomposition occurs at 372°C involving about 56% of weight loss.

The thermogram of PA[DADP+DADPM] involves two distinct steps. The first decomposition step involving a loss of 45% weight starts at 275°C and proceeds up to 435°C. The maximum rate of weight loss occurs at 390°C. The second decomposition step begins at 435°C and ends at 800°C involving a weight loss of 49%. The maximum rate of weight loss in this step occurs at 510°C.

The thermogram of PA[DADP+DADPS] involves two distinct steps. The first decomposition step, involving a loss of 46% weight, starts at 250°C and proceeds up to 460°C. The maximum rate of weight loss occurs at 390°C. The second decomposition step begins at 465°C and ends at 800°C involving a weight loss of 48%. The maximum rate of weight loss in this step occurs at 530°C. The thermogram of PA[EDA+DADPA] reveals that the polymer begins to decompose at about 220°C, and extends to about 600°C involving about 51% weight loss with a maximum rate at 370°C.

The thermogram of PA[EDA+DADPS] reveals that the polymer begins to decompose at about 215°C, and extends to about 700°C, involving about 89% weight loss with a maximum rate at 410°C.

The thermogram of PA[EDA+DAT] involves two distinct steps. The first decomposition step involving a loss of 42% weight, starts at 230°C and proceeds up to 465°C. The maximum rate of weight loss occurs at 400°C. The second decomposition step begins at 465°C and ends at 750°C involving a weight loss of 54%. The maximum rate of weight loss in this step occurs at 530°C.

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). These characteristics are presented in Table 6.

Thermal stability of the copolyamides is established on the basis of T_{\max} for the first step of decomposition. The thermal stability of copolyamides derived from NANCCT decreased in the following order:



The thermal stability behavior for the 10% decomposition temperature is as follows;



The thermal stability based on half volatilization point temperature (T_s) follows somewhat different sequence. The thermal stability decreases as follows.



Table 6: Temperature (°C) characteristics of copolyamides of NANCCT and various diamine mixtures.

Polymer	T_0	T_{10}	T_{\max}		T_s
			Step I	Step II	
PA(DADP+DADPA)	260	285	372	–	745
PA(DADP+DADPM)	275	310	390	510	490
PA(DADP+DADPS)	250	315	390	530	505
PA(EDA+DADPA)	220	260	370	–	526
PA(EDA+DADPS)	215	280	410	–	490
PA(EDA+DAT)	230	308	400	530	495

Table 7: Application of Broido method of TGA thermogram of PA(DADP+DADPA) obtained at 10°C/min.

Temp. °C	% Wt.	$y = \frac{W_t - W_x}{W_t - W_0}$	1/y	ln ln 1/y	T°K	1/T × 10 ³ K ⁻¹
350	83.30	0.4930	2.0279	-0.3466	623	1.6051
360	81.83	0.4455	2.2446	-0.2125	633	1.5797
370	79.75	0.3836	2.6066	-0.0428	643	1.5552
372	79.50	0.3712	2.6935	-0.0091	645	1.5503
380	77.78	0.3141	3.1833	0.1466	653	1.5313
390	75.84	0.2503	3.9942	0.3256	663	1.5082
400	74.62	0.2075	4.8188	0.4526	673	1.4858

The observation of above thermal stability trends shows that the copolyamides containing DADP are more stable than copolyamides containing EDA.

Evaluation of Kinetic Parameters

Dynamic TGA thermograms obtained at heating rate 10°C/min have been analyzed as per the graphical methods proposed by Broido [23] and Horowitz-Metzger [24].

A typical application of Broido's methods is exemplified for PA[DADP + DADPA] in Tables 7 and 8. The Horowitz-Metzger method is exemplified for PA[DADP+DADPA] and PA[EDA+DADPA] in Tables 9 and 10.

Since the magnitude of an apparent activation energy for degradation reaction reflects the ease with which it can proceed, it may be used to approximate relative ease of thermal degradation of copolyamides and hence, their relative thermal stability.

The thermograms of other copolyamides were also analyzed in the same graphical method. The values of apparent activation energy corresponding to different decomposition steps involved are evaluated from the slope of the least squares plots of the relevant data and are presented in Table 11. Examination of data presented therein reveals that both methods yield comparable values for E. The experimental points corresponding to initial stage (10% loss)

Table 8: Application of Broido method of TGA thermogram of PA(EDA+DADPA) obtained at 10°C/min.

Temp. °C	% Wt.	$y = \frac{W_t - W_x}{W_t - W_0}$	1/y	ln ln 1/y	T°K	1/T × 10 ³ K ⁻¹
340	78.09	0.6138	1.6290	-0.7174	613	1.6313
350	75.79	0.5704	1.7530	-0.5774	623	1.6051
360	73.03	0.5183	1.9292	-0.4198	633	1.5797
370	70.16	0.4510	2.2170	-0.2279	643	1.5552
380	66.42	0.3935	2.5410	-0.0697	653	1.5313
390	64.06	0.3522	2.8385	0.0423	663	1.5082
400	62.45	0.3186	3.1382	0.1342	673	1.4858

Table 9: Application of Horowitz and Metzger's method to TGA thermogram of PA(DADP+DADPA).

T°C	%wt	1 - α	1/1 - α	ln ln (1/1 - α)	θ
350	83.30	0.4930	2.0279	-0.3466	-22
360	81.83	0.4455	2.2446	-0.2125	-12
370	79.75	0.3836	2.6066	-0.0428	-2
372	79.50	0.3712	2.6935	-0.0091	0
380	77.78	0.3141	3.1833	0.1466	8
390	75.84	0.2503	3.9942	0.3256	18
400	74.62	0.2075	4.8188	0.4526	28

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. Between the two methods, the Broido method is expected to provide reliable estimates of E, since no other temperature characteristics are involved.

The value of activation energy (E) for the first step vary from 10.68 to 18.66 Kcal/mol according to Broido method. The values for E calculated according to the Horowitz and Metzger's method are in good agreement with these values. The activation energy of PA[DADP+DADPM] is higher than the other copolyamides.

In view of higher aromaticity, the copolyamides having 4,4'-diaminodiphenyl are expected to be most thermally stable amongst copolyamides having ethylenediamine. Further, this trend of relative stability indicates that site of initial degradation may lie in the nature of the bridge 'X' in the diamine component of the molecular chain. Thus, results based on qualitative and semi-qualitative treatment of dynamic thermogravimetric data on copolyamides point out that inclusion of 4,4'-diaminodiphenyl and 4,4'-diaminodiphenyl amide moiety in a copolyamide backbone is advantageous, so far as thermal stability requirement is concerned. Moreover, such an inclusion does not adversely affect the solubility of the resultant copolyamide.

Table 10: Application of Horowitz and Metzger's method to TGA thermogram of PA(EDA+DADPA).

T°C	%wt	1 - α	1/1 - α	ln ln (1/1 - α)	θ
340	78.09	0.6138	1.6290	-0.7174	-30
350	75.79	0.5704	1.7530	-0.5774	-20
360	73.03	0.5183	1.9292	-0.4198	-10
370	70.16	0.4510	2.2170	-0.2279	0
380	66.42	0.3935	2.5410	-0.0697	10
390	64.06	0.3522	2.8385	0.0423	20
400	62.45	0.3186	3.1382	0.1342	30

Table 11: Kinetic parameters for the thermal decomposition of copolyamides.

Polyamide	Energy of activation E (Kcal/mol)			
	Broido method		Horowitz-Metzger method	
	Step I	Step II	Step I	Step II
PA(DADP+DADPA)	13.67	–	13.77	–
PA(DADP+DADPM)	18.66	24.78	19.49	24.88
PA(DADP+DADPS)	17.53	31.27	17.58	31.40
PA(EDA+DADPA)	11.31	–	11.46	–
PA(EDA+DADPS)	10.68	–	10.34	–
PA(EDA+DAT)	11.94	13.51	11.92	13.57

CONCLUSION

The properties of copolyamides largely depend upon the structure and mode of their preparation. These properties are influenced by the nature of substituents on the *s*-triazine nucleus and also by the nature of diamine components of polymer chain. These aromatic polyamides are promising as materials of high thermal stability and processibility.

SYMBOLS AND 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
NADCT	2-(N- β -naphthylamine)-4,6-dichloro- <i>s</i> -triazine
NACNT	2-(N- β -naphthylamine)-4,6-bis-(3-carboxynaphthoxy)- <i>s</i> -triazine
NANCCT	2-(N- β -naphthylamine)-4,6-bis-(naphthoxy-3-carbonyl-chloride)- <i>s</i> -triazine
PA(DADP+DADPM)	Copolyamide of 4,4'-diaminodiphenyl and 4,4'-diaminodiphenylmethane
PA(DADP+DADPA)	Copolyamide of 4,4'-diaminodiphenyl and 4,4'-diaminodiphenylamide
PA(DADP+DADPSA)	Copolyamide of 4,4'-diaminodiphenyl and 4,4'-diaminodiphenyl sulfonamide
PA(DADP+DADPS)	Copolyamide of 4,4'-diaminodiphenyl and 4,4'-diaminodiphenyl sulfone

PA(DADP+DAT)	Copolyamide of 4,4'-diaminodiphenyl and 2,4-diaminotoluene
PA(DADP+PPDA)	Copolyamide of 4,4'-diaminodiphenyl and p-phenylenediamine
PA(DADP+EDA)	Copolyamide of 4,4'-diaminodiphenyl and ethylene diamine
PA(EDA+DADPM)	Copolyamide of ethylene diamine and 4,4'-diaminodiphenylmethane
PA(EDA+DADPA)	Copolyamide of ethylene diamine and 4,4'-diaminodiphenylamide
PA(EDA+DADPSA)	Copolyamide of ethylene diamine and 4,4'-diaminodiphenyl sulfonamide
PA(EDA+DADPS)	Copolyamide of ethylene diamine and 4,4'-diaminodiphenyl sulfone
PA(EDA+DAT)	Copolyamide of ethylene diamine and 2,4-diaminotoluene
PA(EDA+PPDA)	Copolyamide of ethylene diamine and p-phenylenediamine

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