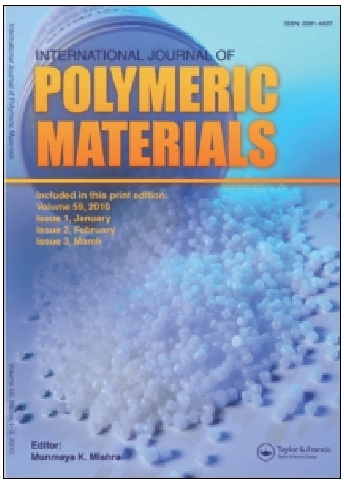

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Synthesis and Properties of Novel Polycyanurates Derived from 2-(N-piperidino)-4,6-bis (naphthoxy-2-carbonyl chloride)-s-triazine

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Synthesis and Properties of Novel Polycyanurates Derived from 2-(N-piperidino)-4,6-bis (naphthoxy-2-carbonyl chloride)-s-triazine

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Various polyamides containing s-triazine rings in the main chain were synthesized by high temperature polycondensation of 2-(N-piperidino)-4,6-bis(naphthoxy-2-carbonyl chloride)-s-triazine [PNCCT] with various aromatic diamines such as 4,4′-diaminodiphenyl [DADP], 4,4′-diaminodiphenylamide [DADPA], 4,4′-diaminodiphenylsulphone [DADPS], 4,4′-diaminodiphenylsulphonamide [DADPSA], 4,4′-diaminodiphenyl methane [DADPM], 2,4-diamino toluene [DAT] and p-phenylene diamine [PPDA]. All the polyamides were characterized by viscosity measurements, IR spectra, NMR spectra, and thermogravimetric analysis.

Keywords: high temperature polycondensation, IR spectra, polyamides, thermal analysis, viscosity measurements

INTRODUCTION

Aromatic polyamides (aramides) are well known as high-performance materials with useful properties, such as outstanding thermal stability, good chemical resistance, and excellent mechanical properties [1–3]. Due to increased demand of polymers with high performance characteristics in various fields including the aerospace, automobile, and microelectronic industries, the use of these aromatic polymers is

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growing steadily. However, these polymers are generally intractable and lack the properties essential for successful fabrication into useful forms. These inherent problems have been tackled by many researchers over the last few decades by modifying the monomers structures [4–5].The promising approach for modifying the properties of polyamides is the introduction of aromatic pendent groups [6–7] or heterocyclic rings [8–9] into the polyamide backbone, which imparts good solubility and thermal stability. As an approach to improve the stability and processibility of heterocyclic polymers while maintaining the thermal stability, a number of published reports have described the synthesis and properties of s-triazine ring containing polymers such as polyesters [10], polyimides [11], polyamides [12], polyureas [13], and so on. There are many reports describing the synthesis of polycyanurates [14–21].

In the present investigation, the authors describe the synthesis of 2-(N-piperidino)-4,6-bis(phenoxy-2-carbonyl chloride)-s-triazine (PNCCT) and its high temperature polycondensation with different types of diamines such as DADP, DADPA, DADPS, DADPSA, DADPM, DAT, and PPDA. A study of solubility, viscosity, IR spectra, and thermal behavior has been carried out in order to characterize these polymer samples.

MATERIALS

DADPA was synthesized by published methods [22] and purified by crystallization from hot water (mp 204°C). DADPS (MERCK), DADP (MERCK), and PPDA (MERCK) of purity better than 99% were used as received. DADPM and DADPSA of better purity were received from Atul Ltd. (Valsad, Gujarat) and purified by recrystallization from acetic acid (mp 92°C).

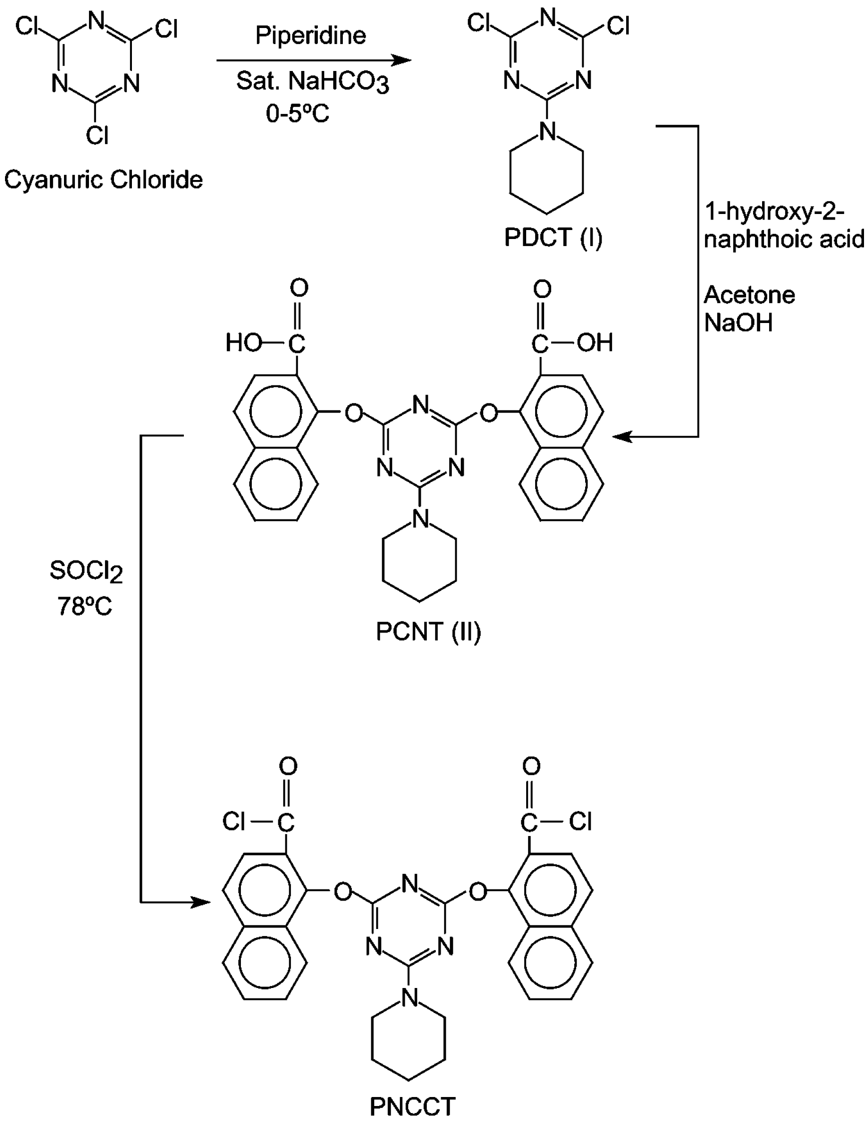
EXPERIMENTAL

Synthesis of Monomer [PNCCT]

The monomer (diacidchloride), 2-(N-piperidino)-4,6-bis(naphthoxy-2-carbonyl chloride)-s-triazine [PNCCT], was prepared as per scheme in Figure 1 by a reported procedure [23]. It was recrystallized from benzene. The yield was about 85%, M.P. 260°C.

Synthesis of Polyamides

A high temperature polycondensation is exemplified in what follows for the synthesis of polyamide from PNCCT and 4,4′ -diaminodiphenylamide(DADPA) for which the scheme is shown in Figure 2.



Scheme I

FIGURE 1 Scheme for synthesis of monomer 2-(N-piperidino)-4,6-bis (naphthoxy-2-carbonyl chloride)-s-triazine [PNCCT].

A mixture of PNCCT (5.09 gm, 0.01 mol), 0.02 mol of DADPA, Triethyl amine (5 ml), and minimum quantity of DMF (dimethyl formamide) was placed in a three-necked flask equipped with a

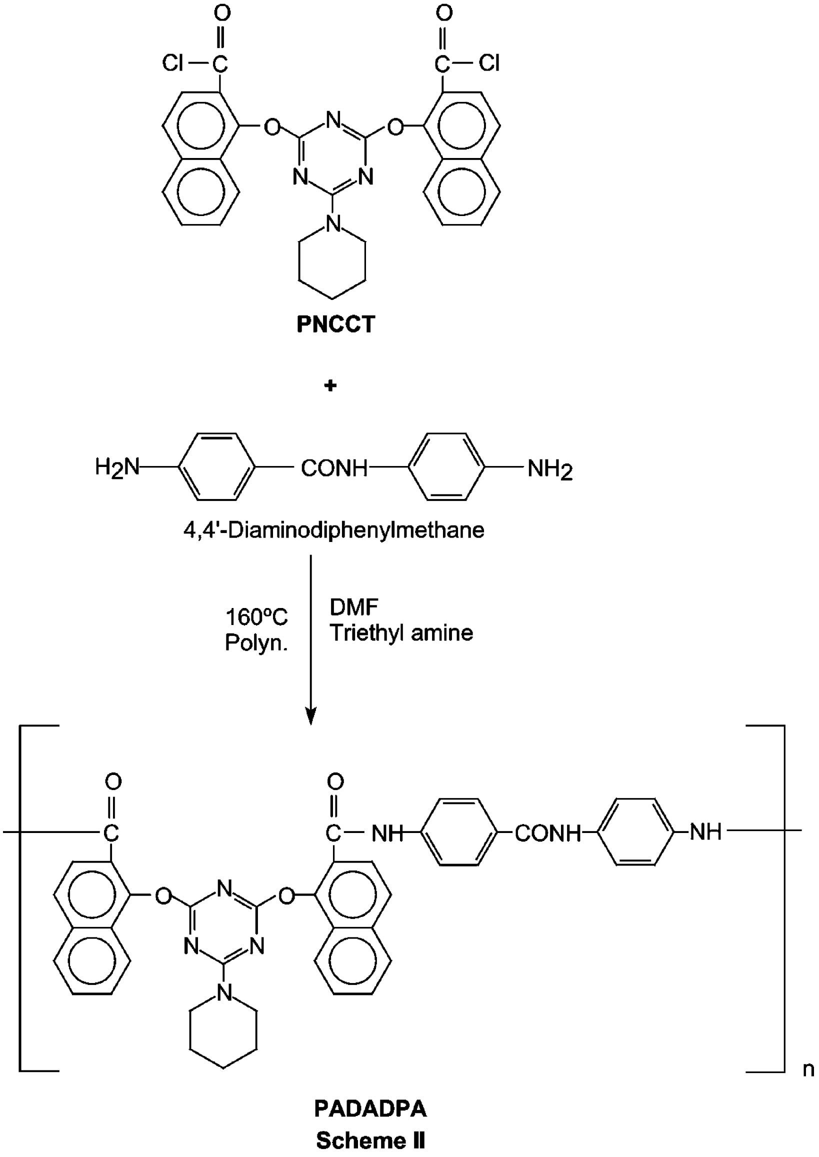


FIGURE 2 Scheme for synthesis of polyamides.

mechanical stirrer and a drying tube. The reaction mixture was heated with stirring at 160°C for 8 h. At the initial stage of reaction, the evolution of hydrogen chloride gas was rapid and later on it slowed down. The reaction mixture was cooled somewhat and poured with constant stirring into 250 ml of ice-cold water. The polymer obtained was filtered, thoroughly washed with hot methanol and hot acetone. Finally, the polymer was dried in a vacuum oven at 80°C over night. The yield of polymer was about 90%.

The other polyamides from PNCCT and various diamines such as DADP, DADPS, DADPSA, DADPM, DAT, and PPDA were synthesized by the same method.

Measurements

FTIR spectra of all the polyamides were recorded on "Perkin Elmer FTIR Paragon 1000 SPIR S. No. 42825" using KBr pellet technique. The thermograms were obtained on a thermobalance "Metler TA-4000 system" at a heating rate of 10°C/min. The NMR spectra were recorded on a Perkin-Elmer Model-32 ^{1}H NMR spectrometer (300 MHz). Reduced viscosities of polyamides were determined for 1 gm/dl solution in DMF using an Ubbelohde suspended level viscometer.

RESULTS AND DISCUSSION

The polyamides obtained from different aromatic diamines are highly soluble in polar aprotic solvents like N-methyl-2-pyrrolidone (NMP), N,N′-dimethyl formamide (DMF), N,N′-dimethyl acetamide (DMA), and dimethylsulphoxide (DMSO). All polyamides are a powdery substance (Table 1).

Viscosity Measurements

Typical Huggin's and Krammer's plots were used to obtain intrinsic viscosity for each of the polyamides. These data are presented in Table 1.

TABLE 1 Physical Characteristics of Polyamides

Polymer code	Product appearance	Yield (%)	$n_{sp/c}$ (dl/g)
PADADPA	Brown	85	0.8957
PADADPS	Black	90	0.7983
PADADPSA	Light gray	90	0.9391
PADADP	Reddish Brown	90	0.7217
PADAT	Black	90	0.7043
PADADPM	Reddish brown	90	0.8348
PAPPDA	Black	85	0.5478

The results reveal that among DMF soluble polyamides, PADADPSA has the highest whereas PAPPDA has the lowest solution viscosity. The trend of these values reflects the order of relative reactivity of diamines.

FTIR Measurements

The IR spectra of the polyamides (Figure 3) exhibited several common characteristic absorption frequencies (cm^{-1}).

All polymers exhibit strong or moderately strong absorption bands at frequencies around 1560–1410 cm^{-1} and 820–790 cm^{-1}, which may be assigned to in plane and out of plane vibrations of s-triazine ring, respectively [24]. The band observed around 3470–3440 cm^{-1} is attributed to N–H stretching vibration of secondary amide [25]. A broad band, maximum around 3390–3350 cm^{-1} is probably due to O–H stretching vibration (hydrogen bonded) of end –CONH group of polyamide. The bands at 3090–3040 cm^{-1} are attributed to aromatic C–H stretching [26–27]. The bands observed at 2850–2845 cm^{-1} and 2925–2910 cm^{-1} are assigned as symmetric and asymmetric C–H stretching vibration of $-CH_2$ group, respectively. Presence of amide carbonyl

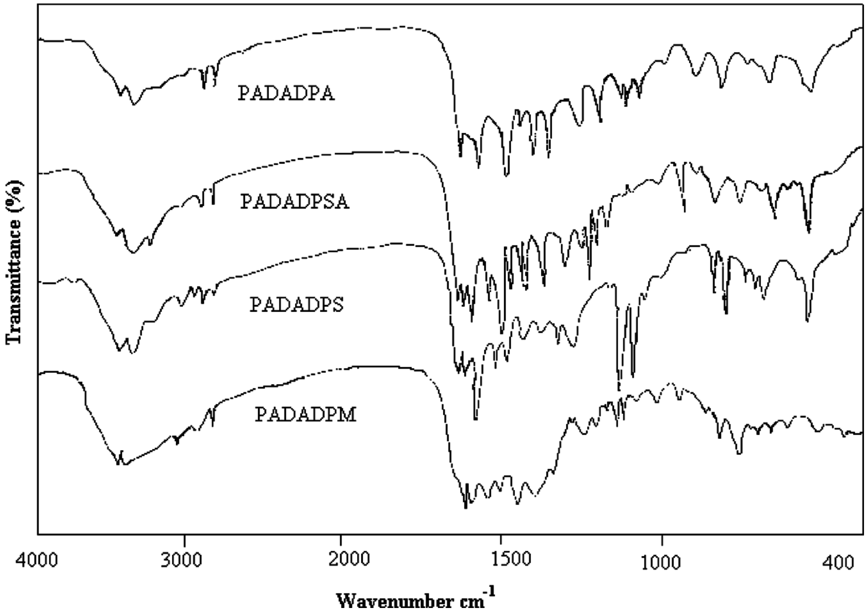


FIGURE 3 IR spectra of polyamides.

(−C=O) group (Amide-I band) is indicated by a strong band in the region of 1675–1620 cm^{-1}. The band at 1560–1520 cm^{-1} is attributed to N−H bending vibration (Amide-II band) [28]. The strong band in the region 1500–1400 cm^{-1} is attributed to skeletal ring stretching vibration of aromatic and hetero aromatic ring. The band in the region 1405–1390 cm^{-1} is attributed to C−N stretching vibration of amide.

In additon, the spectra exhibited several absorption frequencies that distinguish the polyamides from each other. In the spectrum of PADADPS and PADADPSA, bands observed at 1150 cm^{-1} and 1340–1320 cm^{-1} may be attributed to stretching vibration of $-SO_2$ linkage. In the spectrum of PAPPDA bands observed around 655 cm^{-1} may be attributed to vibration of p-disubstituted phenyl ring. The band appears at 1345 cm^{-1} in PADAT is attributed to the symmetrical bending vibration of $-CH_3$ group.

NMR ANALYSIS

High resolution (300 MHz) NMR spectras of solution of polyamides sample were measured in deuterated dimethyl sulphoxide (DMSO-d_6)

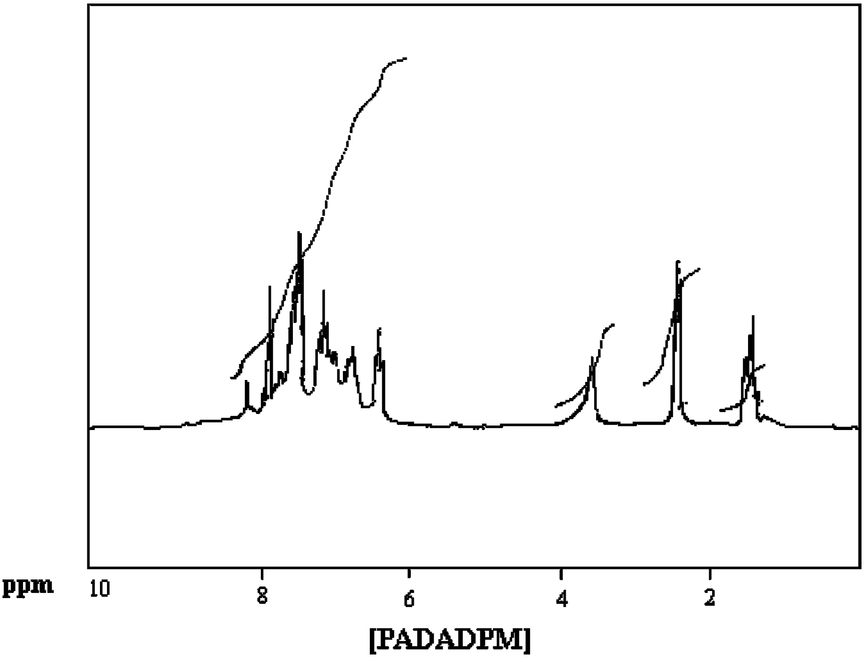


FIGURE 4 NMR spectra of polyamide PADADPM.

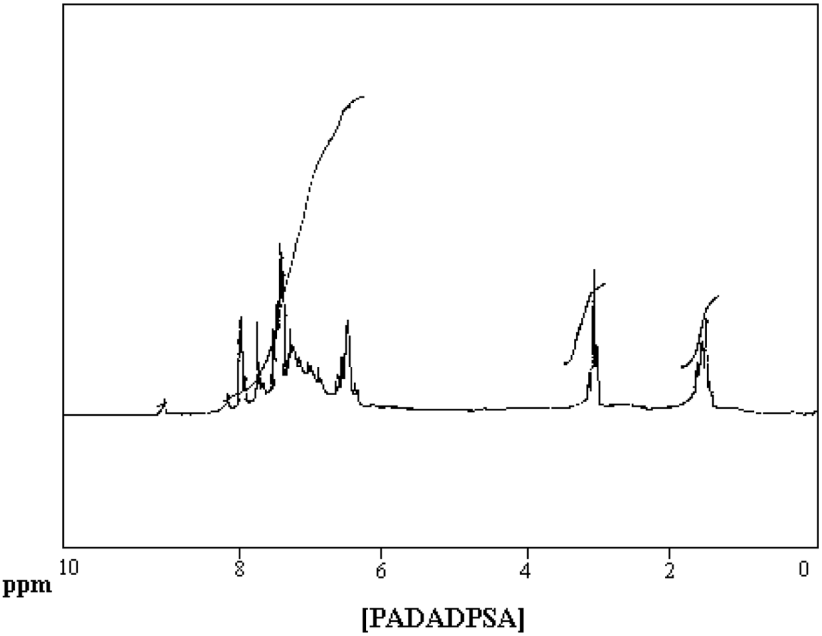


FIGURE 5 NMR spectra of polyamide DADPSA.

using TMS as an internal reference. NMR spectrum of PADADPM and PADADPSA, respectively, are shown in Figures 4 and 5.

PADADPM. The ^{1}H NMR spectrum of PADADPM (Figure 4) shows multiplet at chemical shift δ 6.438–8.217 ppm, which is due to the presence of aromatic protons. Piperidine ring protons show triplet at δ 2.501 ppm and multiplet at δ 1.460 ppm due to 4 H and 6 H, respectively. 2 H due to –CONH produces singlet at δ 8.280 ppm, whereas 2 H due to (–CH_2) produce triplet at δ 3.464 ppm.

PADADPSA. The ^{1}H NMR spectrum of PADADPSA (Figure 5) shows multiplet at δ 6.352–7.872 ppm, which is due to the presence of aromatic protons. Piperidine ring protons show triplet at δ 2.501 ppm and multiplet at δ 1.466 ppm due to 4 H and 6 H, respectively, and 2 H due to –CONH produces singlet at δ 7.950 ppm, whereas 1 H due to –SO_2NH shows singlet at 8.986 ppm.

Thermal Analysis

Thermograms of some polyamides are shown in Figure 6.

The thermogram of polyamide PADADPA follows single step thermal degradation whereas PADADP, PADADPSA, and PADADPM

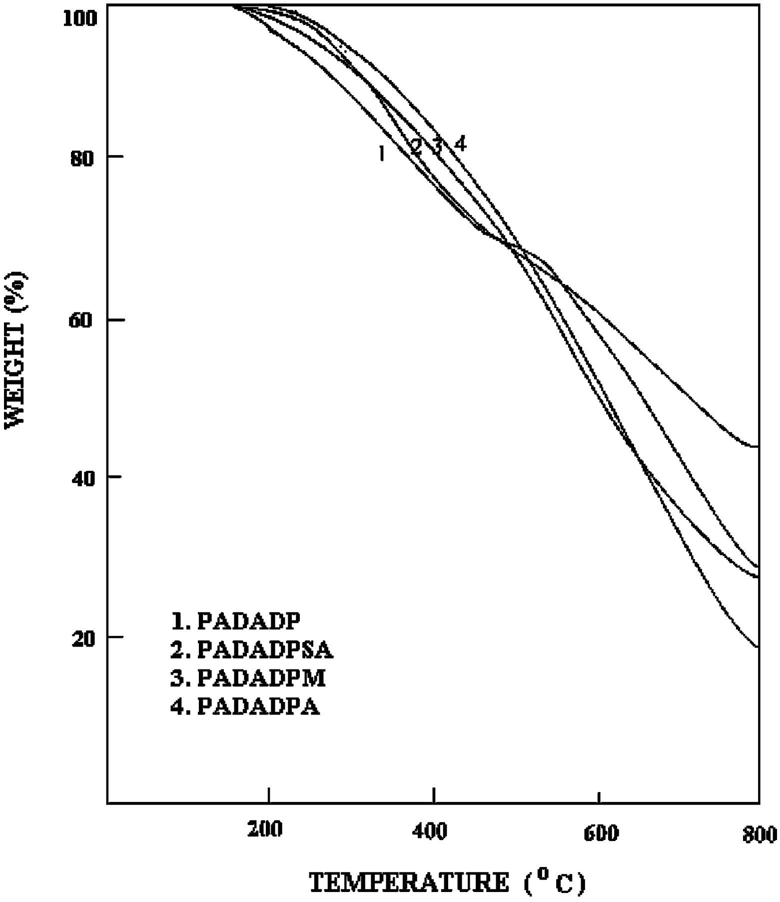


FIGURE 6 Thermograms of polyamides.

follow two-step thermal degradation. Methods used for the assessment of thermal stability of polymers from TG traces have been briefly reviewed by Reich and Levi [29]. These methods can broadly be classified as qualitative and semiquantitative. The relative thermal stability such as initial decomposition temperature T_0, temperature T_{10} for 10% weight loss, temperature T_{max} for maximum rate of decomposition, and temperature T_s for half volatilization, are presented in Table 2. The higher the value of T_{10}, the greater the thermal stability of the polymer. Comparison of T_{10} for polyamides indicates the following decreasing

TABLE 2 Temperature Characteristics of Polyamides

Polymer	T_0°C	T_{10}°C	T_{max}°C Step-I	T_{max}°C Step-II	T_s°C	Activation energy (kcal/mol) Step-I	Activation energy (kcal/mol) Step-II
PADADPA	200	305	620	—	610	11.21	—
PADADPS	170	275	490	—	630	11.88	—
PADADPSA	190	300	330	665	725	13.07	10.49
PADADPM	185	310	530	—	615	10.15	—
PADADP	165	260	290	665	670	8.95	10.09
PADAT	180	235	310	695	455	10.56	10.48
PAPPDA	180	245	275	—	485	11.26	12.80

order of thermal stability:

PADADPM > PADADPA > PADADPSA > PADADPS
> PADADP > PAPPDA > PADAT

A comparison of thermal stability based on T_{max} indicates the following order:

PADADPA > PADADPM > PADADPS > PADADPSA > PAPPDA
> PADADP > PADAT

A single heating rate method has been employed for the treatment of TGA data, to evaluate the activation energy (E_a) for each step of thermal decomposition of polyamides. Values of activation energy [E_a] were calculated according to the Broido method [30], which range between 8.95 and 13.07 KCal/mol for the thermal decomposition of the polyamides.

These studies reveal that the thermal stabilities of the polyamides are significantly related to the aromatic diamine component in the molecular chain. They are directly proportional to the molecular size of the diamine component.

CONCLUSION

A series of novel polyamides containing s-triazine rings in the main chain was successfully synthesized by high temperature polycondensation. The introduction of s-triazine ring into the wholly aromatic polyamides afforded soluble polymers with high thermal stability. Thus, these polyamides can be considered a promising, processable, high temperature–resistant polymer material.

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