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ORIGINAL PAPER

Synthesis and characterization of new heat-resistant polyamides bearing an *s*-triazine ring under green conditions

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Abstract In this work, cyanuric chloride was reacted with morpholine to obtain 2,4-dichloro-6-morpholino-1,3,5-triazine, which was then reacted with 4-aminobenzoic acid, yielding a new triazine monomer containing dicarboxylic acid. The chemical structure and purity of this monomer was confirmed by different techniques. Direct polycondensations of this diacid with several aromatic diamines were carried out in a molten ionic liquid, tetrabutylammonium bromide. Polyamides (PAs) with moderate inherent viscosities in the range 0.32–0.38 dL g^{-1} were obtained in high yields. These PAs were characterized by Fourier transform infrared spectroscopy, ^{1}H NMR spectroscopy, X-ray powder diffraction, inherent viscosity measurements, and elemental analysis. All of the PAs were found to be amorphous, to possess outstanding solubilities, and to be easily dissolved in amide-type polar aprotic solvents. The thermal properties of the PAs were evaluated by thermogravimetric analysis and differential scanning calorimetry. These polymers showed good thermal stability with glass transition temperatures (T_g) of 223–248°C, and their 10% weight loss temperatures were around 448°C and 460°C, confirming their good thermal stability. The char yields of these polymers were 53–59%, and, given their LOI values of 39–41, these polymers also show good flame retardancy.

Keywords *s*-Triazine · Aromatic polyamides · Tetrabutylammonium bromide · Heat-resistant · Solubility

Introduction

Polymers are extensively used in the modern world, and hundreds of millions of tons of synthetic polymers are created every year. They are important materials because of their numerous advantageous properties, such as their light weight, high performance and durability, design and processing flexibility, and high energy efficiency [1, 2]. They are used in the packaging, energy, communications, healthcare, construction, furniture, electronics, and transportation industries (among others). Common organic solvents that are volatile and often flammable, toxic, quite hazardous, and expensive are generally used in the synthesis of these materials [3]. It is important to decrease the amounts of volatile organic solvents used in chemical and industrial processes because these solvents are among the main contributors to air pollution [4, 5]. Such a goal could be achieved by developing new methods of polymer synthesis that reduce or eliminate the environmental problems associated with current polymer manufacturing processes [6, 7].

Chemists attempting to devise more efficient, and simultaneously more eco-friendly, polymer production processes have recently directed considerable attention to a new class of possible solvents: ionic liquids (IL)s, which are associated with so-called green chemistry [8]. ILs are salts that are composed of an organic cation and an organic or inorganic anion and typically have melting points below 100°C. They possess exceptional properties, such as high chemical and thermal stability, high ionic conductivity, negligible vapor pressure, nonflammability, a wide electrochemical window, and broad chemical diversity, owing to the large number of cations and anions that can be combined in an IL [8–11].

ILs can be applied as both solvents and catalysts in green polymerization processes [12]. The use of ILs as solvents in polymerization progressions yields some distinct advantages, such as increased molecular weight and narrower polydispersity,

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in comparison to when organic solvents are used [13, 14]. On the other hand, the high cost of most conventional room-temperature ILs and concern over their toxicity have led to the investigation of more benign and cheaper salts in the molten state as practical alternatives. Recently, molten tetrabutylammonium bromide (TBAB) was used as a cost-effective IL with low toxicity in a series of useful synthetic transformations [2, 15, 16].

Over the past few decades, increasing demand from the automotive, aerospace, microelectronics, and military industries for new high-performance polymers has provided the driving force for the development of such polymers for use in structural applications [17]. A great deal of effort has been directed into the development of aromatic heterocyclic polymers for use as advanced composite matrices, structural adhesives, or coatings in high-temperature applications [18–20]. Growth in the field of high-performance polymers (HPPs) began in the late 1950s, chiefly to satisfy the needs of the electronics and aerospace industries [20, 21]. Among the HPPs developed, wholly aromatic polyamides (aramids) have been widely used [20]. Aramids are a family of high-performance polymers with good chemical and thermal stability as well as useful mechanical properties [22–24]. They are used in aerospace and military applications, including bulletproof body armor fabric and ballistic composites. Aramids are fibers in which the chain molecules are highly oriented along the fiber axis, so the strength of the chemical bonds in the chains can be exploited [25]. However, aramids have high melt or glass transition temperatures (T_g) and their solubilities are limited in common organic solvents due to the rigidity of the aramid backbone and strong hydrogen bonding. Therefore, over the past decade, much research has been conducted into the chemical modification of semi-aromatic polyamides (PA)s in order to improve their processability. Many researchers have focused on developing structurally modified PAs by changing the structures of the bulky, packing-disruptive monomers through the introduction of flexible units and bulky side groups and by breaking the regularity and symmetry of the polymer chain [24–30]. Among the PAs in this category, *s*-triazine-containing polymers are attracting a great deal of interest due to their excellent thermal resistance and high tensile strengths and moduli at elevated temperatures compared to conventional polymers [28, 31–34].

In view of this interest in processable aromatic PAs, we investigated PAs generated through the reaction of a diacid-containing *s*-triazine with various aromatic diamines under green conditions. First, 4,4-((6-morpholino-1,3,5-triazine-2,4-diyl)bis(azanediyl) dibenzoic acid (**2**) was prepared through a nucleophilic aromatic substitution reaction between cyanuric chloride, morpholine, and 4-aminobenzoic acid. Then novel PAs with a good balance of thermal resistance and solubility were prepared in a green medium using tetrabutylammonium bromide (TBAB) as a molten IL. The properties of the obtained polymers, such as viscosity, solubility, thermal stability, and morphology, are discussed here.

Experimental

Materials

All materials and solvents were purchased from Merck Chemical Co. (Darmstadt, Germany) and Aldrich Chemical Co. (St. Louis, MO, USA). Cyanuric chloride, tetrahydrofuran (THF), glacial acetic acid, 4-aminobenzoic acid, morpholine, 1,3-phenylene diamine, 4,4′-diaminodiphenyl ether, and 4,4′-diaminodiphenyl sulfone were used as received.

Measurements

Fourier transform infrared (FT-IR; model 680, JASCO, Tokyo, Japan) spectra of the samples were recorded at room temperature in the range 4000–400 cm^{-1} at a resolution of 4 cm^{-1}. Spectra of solids were obtained using KBr pellets.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker (Karlsruhe, Germany) Avance DRX 500 or 125 MHz spectrometer, using solutions in deuterated dimethylsulfoxide (DMSO-d_6). The proton resonances were categorized into singlets (s) and multiplets (m).

Carbon, hydrogen, and nitrogen contents of the compounds were determined by pyrolysis using a Vario EL elemental analyzer (Elementar, Hanau, Germany).

X-ray diffraction (XRD) patterns were recorded using CuK_α radiation on a Bruker D8 Avance diffractometer operating at a current of 100 mA and a voltage of 45 kV. The diffractograms were measured for 2θ in the range 10–80° using the CuK_α incident beam ($\lambda = 1.51418$ Å).

Thermal stability was measured via thermogravimetry analysis (TGA, using a TGA instrument from TA Instruments, New Castle, DE, USA) from room temperature to 800°C at a heating rate of 10°C min^{-1} under a continuous flow of nitrogen. Differential scanning calorimetry (DSC) was conducted with a model 110 differential scanning calorimeter from Mettler (Greifensee, Switzerland) at a heating rate of 10°C min^{-1} under a nitrogen atmosphere.

Inherent viscosities were measured by a standard procedure using a Cannon-Fenske routine viscometer (Cannon, State College, PA, USA) with the sample at a concentration of 0.5 g/dL at 25°C.

Preparation of 2,4-dichloro-6-morpholino-1,3,5-triazine

To 100 mL of dry THF was added 10 mmol of cyanuric chloride and then a stoichiometric amount of morpholine. The reaction mixture was stirred for 3 h at 0°C, and 10 mmol of K_2CO_3 solution in water were added to the above mixture dropwise. The reaction was monitored by TLC. After product formation was detected, the product was filtered and washed with cold water. The product was a white solid (85%) with M.P. = 138–139°C.

FT-IR (KBr, cm^{-1}): 2983 (m), 2968 (m), 1584 (s), 1485 (m), 1278 (s), 847 (s), 817 (m).

Synthesis of the diacid monomer

4-Aminobenzoic acid (0.1260 g, 0.88 mmol) was added dropwise to the solution of 2,4-dichloro-6-morpholino-1,3,5-triazine (0.1 g, 0.4 mmol) in 5 mL of glacial acetic acid (AcOH). The mixture solution was refluxed for 1 h. The reaction was monitored by TLC. The product was filtered and washed with 100 mL of boiling water to remove solvent and excess *p*-aminobenzoic acid, yielding 4,4′-((6-morpholino-1,3,5-triazine-2,4-diyl)bis(azanediyl)dibenzoic acid (**2**) as a white powder with 92% yield and M.P. = 349–351°C.

FTIR (KBr, cm^{-1}): 2600–3300 (m, br), 1693 (s), 1602 (s), 1544 (m), 1513 (w), 1311 (m), 1241 (s), 794 (m).

^{1}H NMR (500 MHz, DMSO-d$_6$, ppm): 12.4–12.6 (2H, COOH), 9.81–9.83 (2H, NH), 7.81–7.94 (d, 4H, Ar–H, $J = 6.5$ Hz), 7.85–7.87 (d, 4H, Ar–H,), 3.81–3.82 (t, 2H, CH$_2$, $J = 3.6$), 3.70–3.72 (t, 2H, CH$_2$, $J = 3.5$).

^{13}C NMR (125 MHz, DMSO-d$_6$, ppm): 169 (1CH), 166 (2C=O amide), 164 (2CH), 120–150 (8CH, aromatic), 67 (2CH$_2$), 45 (2CH$_2$).

Anal. calcd. for $C_{21}H_{20}N_6O_5$ (436.43 g/mol): C, 57.79%; H, 4.62%; N, 19.26%. Found: C, 57.43%; H, 4.37%; N, 18.35%.

Preparation of aromatic PAs

The PAs were prepared by the following general procedure (using the preparation of PA **4a** as an example). A mixture of 0.100 g (0.458 mmol) of diacid **2** and 0.590 g (1.832 mmol) of TBAB was ground until a powder was formed, which was then transferred into a 25-mL round-bottom flask and 0.049 g (0.458 mmol) of 1,3-phenylene diamine were added to the mixture. This was heated until a homogeneous solution was formed and then 0.436 g (1.832 mmol) of triphenyl phosphate (TPP) were added. After that, the solution was stirred for 16 h at 130°C and the viscous solution was precipitated in 30 mL of methanol. The white solid was filtered off and dried to give 0.146 g (95%) of white polymer. The other polymers (PAs **4b–4d**) were prepared by a similar procedure.

PAa FT-IR peaks (KBr, cm^{-1}): 3420 (br), 3074 (w), 2987 (m), 2917 (w), 1678 (m), 1576 (w), 1439 (w), 1271 (m), 1158 (w) and 576 (w). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 10.20 (s, 2H, NH), 9.60 (s, 2H, NH), 7.92–7.97 (4H, Ar–H), 7.46–7.48 (2H, Ar–H), 7.22–7.24 (2H, Ar–H), 3.79 (t, 2H, CH$_2$), 3.70 (t, 2H, CH$_2$). Elemental analysis: calcd. for $C_{27}H_{24}N_8O_3$ (508.54 g/mol)$_n$: C, 63.77%; H, 4.76%; N, 22.03%. Found: C, 62.86%; H, 4.23%; N, 21.12%.

PAb FT-IR peaks (KBr, cm^{-1}): 3354 (br), 3090 (w), 2921 (m), 2851 (w), 1680 (m), 1583 (w), 1441 (w), 1307 (w), 1148 (w). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 10.50 (s, 2H, NH), 9.50 (s, 2H, NH), 7.7–8.3 (16H, Ar–H), 3.70 (t, 2H, CH$_2$), 3.80 (t, 2H, CH$_2$). Elemental analysis: calcd. for $C_{33}H_{28}N_8O_3S$ (648.70 g/mol)$_n$: C, 61.11%; H, 4.35%; N, 17.27%; S, 4.94%. Found: C, 60.40%; H, 3.88%; N, 16.67%; S, 4.05%.

PAc FT-IR peaks (KBr, cm^{-1}): 3372 (br), 3060 (w), 2963 (m), 2916 (w), 1673 (m), 1593 (w), 1217 (w). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 10.30 (s, 2H, NH), 9.65 (s, 2H, NH), 7.1–8.2 (16H, Ar–H), 3.90(t, 2H, CH$_2$), 4.10 (t, 2H, CH$_2$). Elemental analysis: calcd. for $C_{33}H_{28}N_8O_4$ (600.64 g/mol)$_n$: C, 65.99%; H, 4.70%; N, 18.66%. Found: C, 64.72%; H, 4.17%; N, 17.45%.

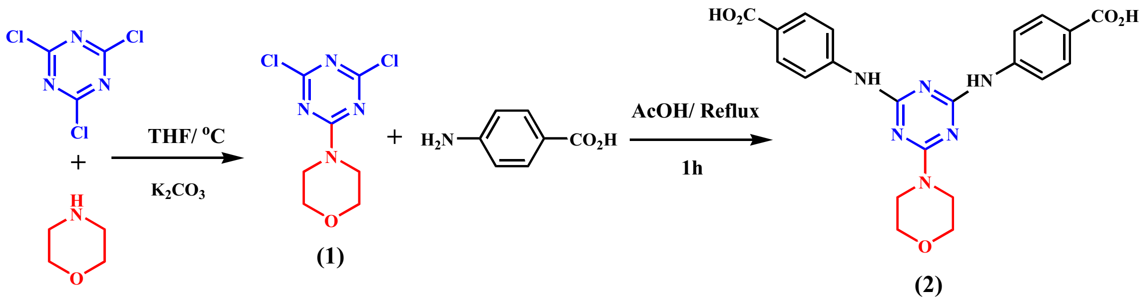
PAd FT-IR peaks (KBr, cm^{-1}): 3415 (br), 3030 (w), 2960 (m), 2930 (w), 1685 (m), 1593 (w), 14,998 (w), 1234 (w), 1112 (w). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 10.30 (s, 2H, NH), 9.80(s, 2H, NH), 7.0–8.2 (20H, Ar–H), 3.43 (t, 2H, CH$_2$), 3.92 (t, 2H, CH$_2$), 3.80 (s, 3H, CH$_3$). Elemental analysis: calcd. for $C_{40}H_{35}N_9O_4$ (705.78 g/mol)$_n$: C, 68.07%; H, 5.00%; N, 17.86%. Found: C, 66.76%; H, 5.24%; N, 16.38%.

Results and discussion

Preparation of the monomer and the organosoluble PAs

At low temperature (0°C), only one site on the triazine can be substituted, whereas two sites can participate in substitution reactions at room temperature (25°C), and all three sites on the triazine can react at elevated temperatures (>70°C). The first chlorine atom of cyanuric chloride was replaced with morpholine at low temperature to form 2,4-dichloro-6-morpholino-1,3,5-triazine [35]. The other two chlorine atoms of cyanuric chloride were then replaced via substitution reactions of 4-aminobenzoic acid with 2,4-dichloro-6-morpholino-1,3,5-triazine to give the *s*-triazine **2** in refluxed glacial acetic acid, as shown in Scheme 1. The purity of the *s*-triazine monomer was checked by different techniques.

Polycondensation is typically conducted at relatively high temperatures, so the nonvolatility and thermal stability of ILs make them suitable solvents for polycondensation processes [2, 11, 13]. In the current investigation, in order to extend the utilization of ILs in polymer synthesis, molten TBAB was used as the solvent in the formation of several novel organosoluble and thermally stable PAs by the direct polymerization of the diacid monomer with different aromatic diamines (Scheme 2). The combination of an ionic medium (TBAB) with an activating agent (TPP) allowed us to carry out polymer synthesis under relatively mild conditions. When the acid group of TPP is activated, it becomes a good leaving group, which is necessary for attack by the amino group. The



Scheme 1 Preparation of the diacid-containing *s*-triazine **2**

above polyamidation will not occur in the absence of either TPP or TBAB, as they act as catalyst and solvent.

The effect of duration of heating was examined to determine the optimum reaction conditions. In order to investigate the effect of duration of heating on the yield and inherent viscosities of each polymer, an initial polymerization reaction of diacid **2** with 1,3-phenylene diamine (**3a**) was carried out for different durations (Table 1). The best results were obtained for a duration of heating at 120°C of 16 h. With longer durations, lower yields of the dark yellow product were obtained; on the other hand, with short durations, low inherent polymer viscosities were achieved. So, a duration of heating at 120°C of 16 h was used in the preparation of other PAs. The results are summarized in Table 2. The inherent viscosities of the obtained PAs **4a**–**4d** under the optimized condensation conditions were 0.32–0.38 dL/g, and yields were 87–95%.

Characterization

FT-IR study

Figure 1 shows FT-IR spectra of 2,4-dichloro-6-morpholino-1,3,5-triazine (**1**) and the diacid monomer (**2**). As shown in Fig. 1a, a characteristic C=N stretching band was observed for *s*-triazine in the range 1590–1620 cm^{-1}. A strong absorption band due to C=N stretching in the triazine moiety also appeared in the range 1200–1400 cm^{-1}. Moreover, peaks at 1117–1121 cm^{-1} were attributed to C–O–C stretching in the morpholine ring. In the FTIR spectrum of diacid **2**, a broad and strong peak at 2600–3600 cm^{-1} was noted, which was assigned to the COOH groups (Fig. 1b). A strong peak from carbonyl in carboxylic acids occurred at 1693 cm^{-1}.

Figure 2 displays FT-IR spectra of the synthesized PAs. All of the polymers exhibited characteristic absorption bands of an amide group at around 3354–3425 cm^{-1} (N–H stretching) and 1673–1385 cm^{-1} (C=O stretching). Other characteristic bands originating from C=N, C=C, and C–O were also present in the FT-IR spectra of all the PAs. The PA **4b** showed absorption bands at 1251 and 1150 cm^{-1} arising from the sulfone moiety (SO_2 stretching). These FT-IR spectra thus confirm the formation of new aromatic PAs.

NMR study

The ^{1}H NMR spectrum of the new diacid-containing monomer is shown in Fig. 3. Two triplet peaks at 3.7–

Scheme 2 Synthesis of different *s*-triazines containing aromatic PAs

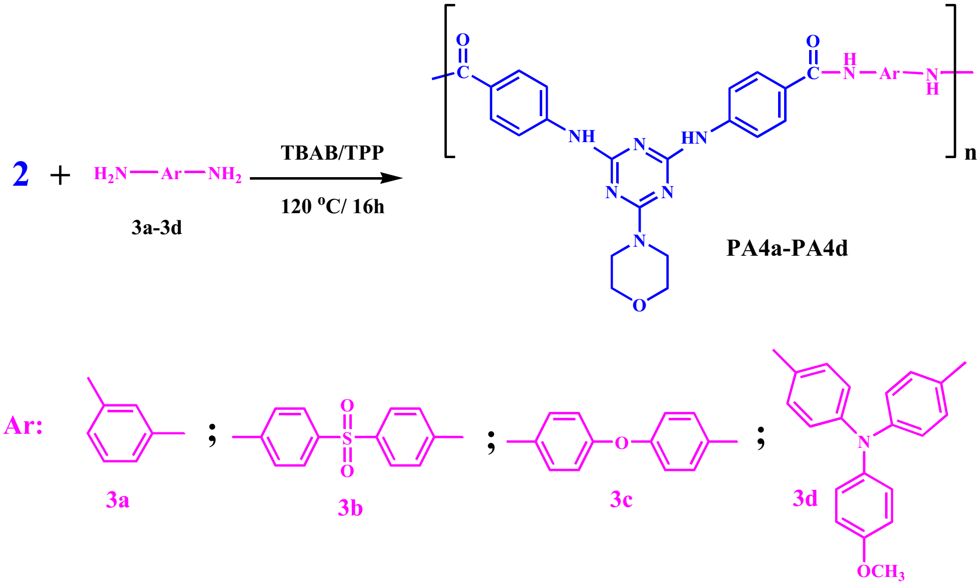


Table 1 Reaction conditions for the polymerization of monomer **2** with diamine **3a** at 120°C, and some physical properties of PA **4a**

Time (h)	TPP (mL)	η_{inh}* (dL/g)	Yield (%)	Color of polymer
8	0.436	0.21	92	Light yellow
12	0.436	0.29	93	Light yellow
16	0.436	0.38	95	Light yellow
24	0.436	0.32	80	Dark yellow
32	0.436	0.31	76	Dark yellow

3.8 ppm relate to the CH_2 protons on the morpholine ring. Aromatic protons appear in the range 7.6–7.9 ppm. A singlet peak at 9.81–9.83 ppm was assigned to the NH groups in this compound. A broad peak at around 12.6–12.8 ppm relates to carboxylic acid protons. The ^{13}C NMR spectrum of this dicarboxylic acid also shows features due to both aromatic and aliphatic carbon atoms (Fig. 4). The results of elemental analyses of this compound were close to the corresponding calculated values, demonstrating that the expected compound was obtained.

The structures of the synthesized PAs were clarified by ^1H NMR (the results of this are presented in the "Experimental" section). In the ^1H NMR spectra of these polymers, the appearance of signals due to amide N–H protons at around 10.20–10.5 ppm and due to amine N–H protons at 9.5–9.8 ppm indicate the presence of these groups in the polymer chain. Signals due to aromatic proton resonance appear in the range 7.0–8.3 ppm. Signals arising from aliphatic protons are seen in the range 3.4–4.1 ppm. ^1H NMR spectra of the PAs **4a** and **4d** are shown in Fig. 5. The results of elemental analysis of the PEs were also found to be in good agreement with the calculated percentages of carbon, hydrogen, and nitrogen in the polymers.

Solubilities of the polymers

In general, aromatic PAs possess poor solubilities and are generally insoluble in organic solvents. However, the incorporation of nonlinear chain segments or polar groups into a PA tends to significantly improve its solubility. Also, the solubility behavior of a PA depends on its chain-packing ability and intermolecular interactions [2, 13]. The solubilities of the PAs obtained in this work were tested in different solvents. The solubilities were determined by adding 0.05 g of each polymer to 1 mL of each solvent (Table 3). The results showed that the newly synthesized PAs were highly soluble in aprotic polar solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylacetamide

Table 2 Some physical properties of PAs **4a**–**4d**

Diamine	Polyamide	Yield (%)	η_{inh}* (dL/g)	Color of polymer
3a	**4a**	95	0.38	Light yellow
3b	**4b**	89	0.32	White
3c	**4c**	83	0.34	Light brown
3d	**4d**	90	0.37	Light green

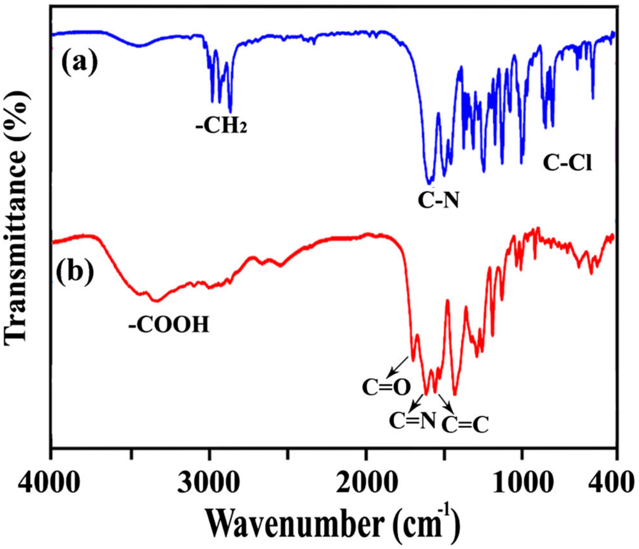


Fig. 1 FT-IR spectra of (*a*) 2,4-dichloro-6-morpholino-1,3,5-triazine and (*b*) the diacid-containing *s*-triazine monomer

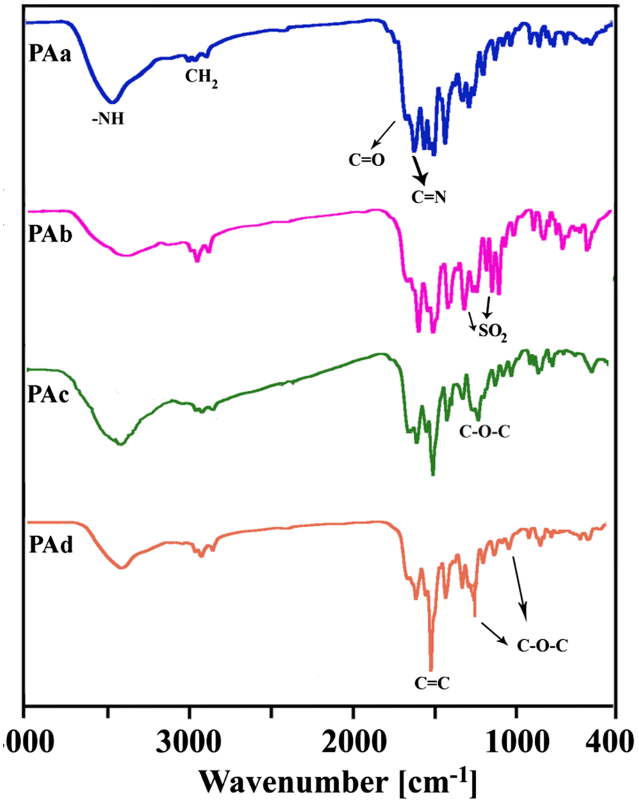


Fig. 2 FT-IR spectra of the *s*-triazine-containing aromatic PAs

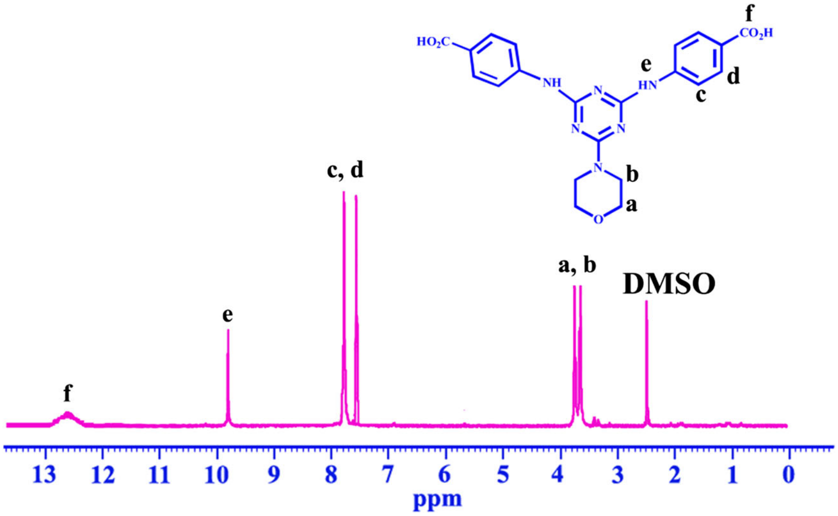


Fig. 3 ^{1}H NMR (500 MHz) spectrum of the diacid-containing *s*-triazine in DMSO-d$_6$ at room temperature

(DMAc), DMSO, and *N*,*N*-dimethylformamide (DMF) at room temperature. Their good solubilities and amorphous nature may be due to the presence of the pendent morpholinium groups, which disrupt interactions among polymer chains as they increase polymer chain separation, thereby leading to a decrease in crystallinity and an increase in solubility. However, the polymers were also found to be insoluble in general organic solvents such as CH_3OH, $CHCl_3$, and acetone, and to be partially soluble in THF. The PA **4d** showed better solubility than the other polymers due to the presence of a bulky pendant group.

X-ray diffraction

To investigate the crystallinity of the polymers, wide-angle X-ray powder diffractometry of the polymers was performed in the region 2θ = 10–80° at room temperature. As shown in Fig. 6, a set of broad diffraction peaks were observed, which indicated that the PAs had amorphous morphologies. This can be attributed to the presence of the morpholinium pendant groups as well as flexible linkages (–O– and $-SO_2-$) in the main chain of the polymer, which reduce interactions among chains and result in poorer chain packing, leading to amorphous PAs with improved solubility and processability. This agrees with the general rule that solubility decreases with increasing crystallinity.

Thermal properties

The thermal properties of the prepared polymers were investigated by means of DSC and TGA under a nitrogen atmosphere at a heating rate of 10°C/min. An endothermic melting peak was not observed in the DSC curves of the PAs, emphasizing the amorphous nature of these polymers. The glass-transition temperature (T_g) was taken as the midpoint of the change in slope of the DSC curve baseline. According to the results obtained, these polymers exhibit T_g values ranging from 223 to 248°C (Table 4 and Fig. 7). As a general rule,

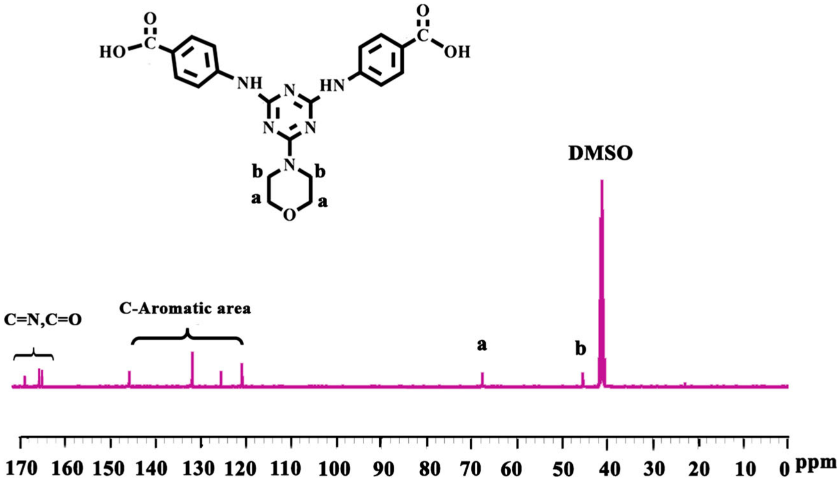


Fig. 4 ^{13}C NMR (125 MHz) spectrum of the diacid-containing *s*-triazine in DMSO-d$_6$ at room temperature

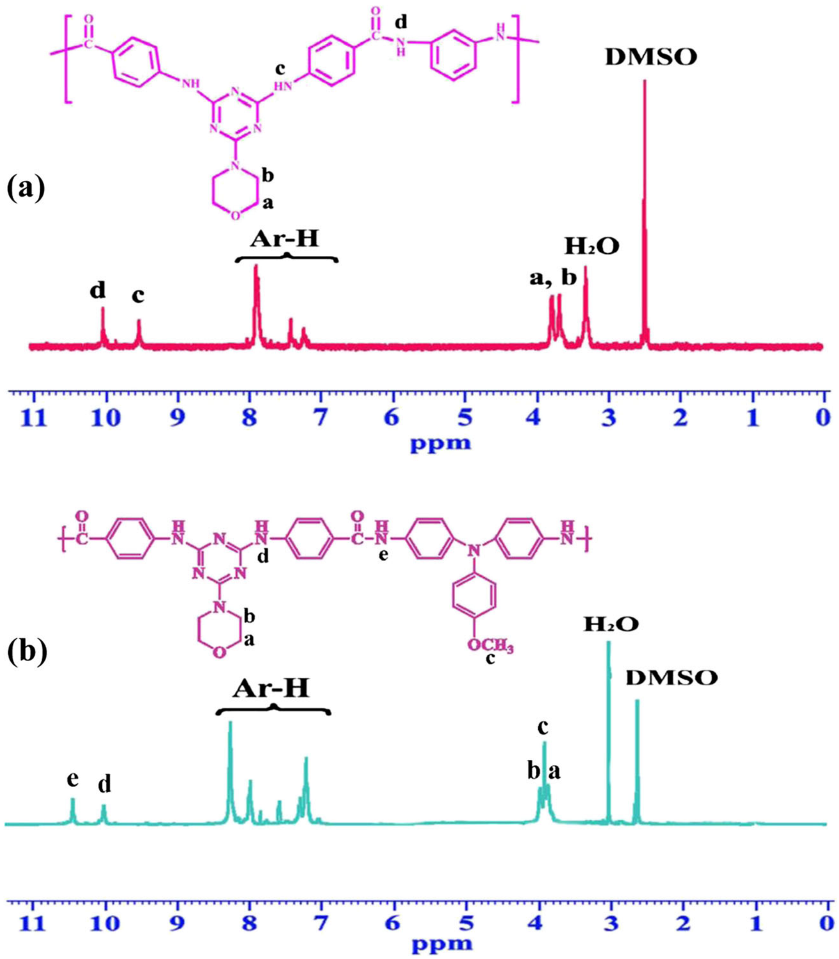


Fig. 5 **a–b** ^{1}H NMR (500 MHz) spectra of the PAs **a** **4a** and **b** **4d** in DMSO-d_6 at room temperature

the incorporation of bulky and rigid groups onto the polymer backbone restricts the free rotation of the macromolecular chain, leading to higher T_g values (see PAs **4a** and **4d**). On the other hand, the presence of flexible bonds such as ether and sulfone linkages in the main chain of the polymer reduces the rigidity of the backbone, and thus decreases T_g (see PAs **4b** and **4c**). Therefore, the T_g values of these polymers are affected by these two opposing factors: restricted bond rotation due to the presence of bulky pendant groups and increased flexibility of the main chain due to the inclusion of ether and sulfone linkages.

The TGA curves of the aromatic PAs are shown in Fig. 8, and Table 4 shows the thermal properties of the PAs, including the temperature at which a weight loss of 5% occurred ($T_{5\%}$), the temperature at which a weight loss of 10% occurred ($T_{10\%}$), and the residual weight at 800°C (char yield). All of the polymers presented similar thermal stabilities and exhibited no weight loss up to 370°C. As shown in Table 4, these polymers had $T_{5\%}$ and $T_{10\%}$ values of 418–496°C and 448–502°C, respectively. The highest thermal stability at 486°C was exhibited by **4a**, which is in accordance with its high molecular weight and rigid aromatic backbone.

Table 3 Solubilities of the aromatic PAs in various solvents

Polymer	Solvent								
	DMSO	NMP	DMAc	DMF	*n*-Hexane	THF	Chloroform	Acetone	Water
4a	+	++	+	++	−	−	−	−	−
4b	++	++	++	++	−	+−	−	−	−
4c	++	++	++	++	−	+−	−	−	−
4d	++	++	++	++	−	+−	−	−	−

++ Soluble at room temperature, + soluble at boiling point, +− partially soluble at room temperature, − insoluble

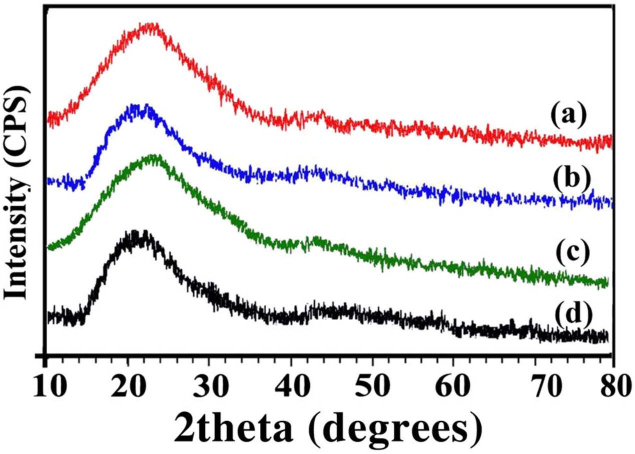


Fig. 6 XRD patterns of the various aromatic PAs

The amount of carbonized residues (the char yield) at 800°C under a nitrogen atmosphere was in the range 53–59 wt% for all the PAs. The high char yields of these PAs can be attributed to the high aromatic content in the main chain. The char yield is useful for estimating the limiting oxygen index (LOI) of each PA via the van Krevelen and Hoftyzer equation [36]:

$$\mathrm{LOI} = 17.5 + 0.4\,\mathrm{CR}.$$

Here, CR is the char yield. The LOI values of the PAs are in the range 39–41, indicating high flame retardancy. LOI values above a threshold value of 26 indicate that the polymer is self-extinguishing and can therefore be used in various applications requiring good flame resistance. The synthesized PAs show LOI values of greater than 26, confirming their good flame retardancy.

Table 4 Thermal properties of the *s*-triazine-containing PAs

Polymer	T_g [a]	Decomposition temperature (°C) T_5 [b]	 T_{10} [b]	Char yield (%) [c]	LOI [d]
4a	248	496	502	59	41.1
4b	223	418	448	53	38.7
4c	234	439	476	54	39.1
4d	240	465	492	56	39.9

[a] The glass transition temperature was recorded at a heating rate of 10°C min^{-1} under an N_2 atmosphere

[b] Temperatures at which 5 and 10% weight losses were recorded by TGA at a heating rate of 10°C min^{-1} under an N_2 atmosphere

[c] Weight percent of the material left undecomposed after TGA at the maximum temperature of 800°C under an N_2 atmosphere

[d] Limiting oxygen index (LOI) evaluated via the char yield at 800°C

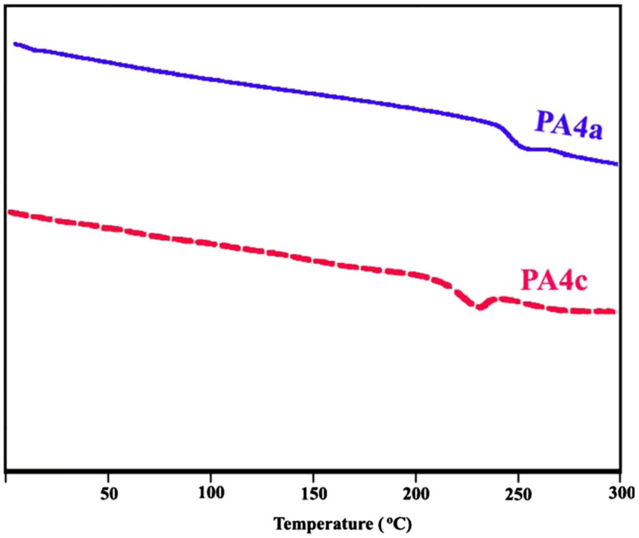


Fig. 7 DSC curves of PAs **4a** and **4c** under N_2, obtained at a heating rate of 10°C/min

Conclusions

Novel *s*-triazine-containing PAs were successfully synthesized via the direct polycondensation of 4,4-(6-morpholine-1,3,5-triazine-2,4-diyl)bis(azanediyl)dibenzoic acid with different aromatic diamines under green conditions, with molten TBAB employed to remove harmful materials from the reaction. The present one-pot synthesis of organosoluble PAs offers several advantages: it is safe, green, eco-friendly, and cost-effective. The structures of the monomer and the various polymers obtained were clarified by FT-IR, ^{1}H NMR, and elemental analysis. The polymers were found to be readily soluble in highly polar solvents and exhibited high thermal stability ($T_{10\%}$, 450–500°C) and good flame retardancy (LOI values of 39–41). These results suggest a new synthetic

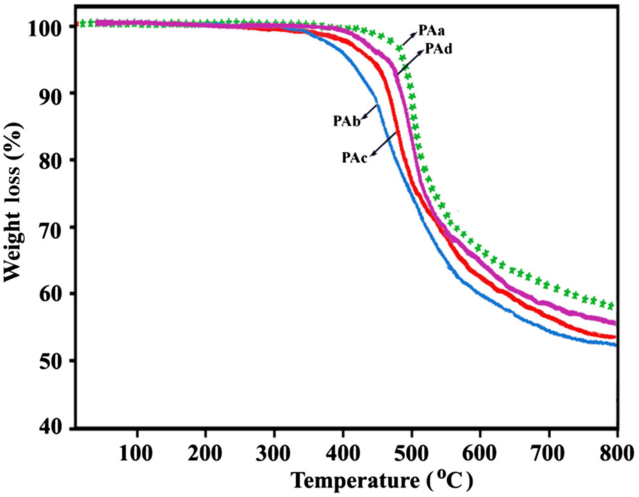


Fig. 8 TGA thermograms of *s*-triazine-containing aromatic PAs

pathway to novel PA-based materials, as it allows the synthesis of new polymers with well-defined molecular structures and advanced functional properties.

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Compliance with ethical standards

Conflict of interest The authors declare no competing financial interest.

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