

ECO-FRIENDLY FAST SYNTHESIS AND THERMAL DEGRADATION OF OPTICALLY ACTIVE POLYAMIDES UNDER MICROWAVE ACCELERATING CONDITIONS*

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Abstract An optically active bulky aromatic diacid chiral monomer, (2*S*)-4-[(4-methyl-2-phthalimidyl)pentanoyl-amino]benzoylamino]isophthalic acid (**1**), containing a rigid phthalimide and flexible L-leucine pendent group was synthesized in five steps. A fast and clean method for direct polyamidation reaction of monomer **1** with various aromatic diamines under microwave irradiation and conventional heating was performed. The polymerization reactions provided optically active polyamides with high yields and inherent viscosities in the range of 0.36–0.74 dL/g. Their thermal properties were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry. TGA thermograms show that the polymers are thermally stable, 10% weight loss temperatures are in excess of 385°C, and char yields at 800°C are higher than 56%. The data obtained from TGA were used to study the kinetics of thermal decomposition of the resulting polymers. The interpretation of kinetic parameters (E , ΔH , ΔS and ΔG) of thermal decomposition stages was evaluated using Coats and Redfern equation.

Keywords: Optically active polyamides; Amino acid; Microwave irradiation; Kinetic study; Polycondensation.

INTRODUCTION

Aromatic polyamides (PA)s form an applicable family of polymers that in the past decades have attracted great interest of many research groups, at both the academic and industrial levels, not only as high performance materials but also for their peculiar conformational and physicochemical manners. The presence of both aromatic and amide groups, differently linked and oriented along the chain, allows for the preparation of a series of aramide structures, ranging from flexible to rigid ones. For example, *meta* structures provide flexible aramids, whereas all-*para* substitution leads to rigid chains^[1]. Processable engineering plastics possessing moderately high softening temperature and good solubility in some organic solvents are required for practical use^[2]. Novel, soluble PAs have been synthesized through delicate molecular design while maintaining their high-performance characteristics^[3]. Several approaches for the chemical structure improvement of aromatic PAs, such as the introduction of flexible or bulky aromatic units like naphthalene moiety, a nonsymmetric unit, a pendant group or a heterocycle moiety into the polymer backbone or incorporation of bent non-coplanar units in the polymer backbone, have been used to achieve good solubility in typical solvents while maintaining their other unique properties^[4–10].

A procedure for the preparation of aromatic PAs was reported by Yamazaki and co-workers in 1974, which

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implicated the complexation of a dicarboxylic acid with triphenyl or diphenyl phosphite and pyridine in a solvent consisting of NMP containing LiCl. Aromatic diamines are condensation monomers used in the preparation of aromatic polyimides and PAs, and among them, hinged diamines are preferred for the preparation of soluble polymers^[11, 12].

Due to the unique properties of high efficiency, low energy consumption, selectivity, homogeneity and enhancement in reaction rate, microwave-assisted heating has attracted wide attention and has been studied as energy source in almost all kinds of chemical reactions in recent years^[13–16]. Although many benefits of microwave irradiation have been fully recognized in organic chemistry, the use of microwave heating in polymer chemistry is still rather uncharted. However, the use of microwave irradiation in polymer science is a rapidly growing field of research leading to faster and cleaner polymerization procedures and can result in accelerated polymerizations and suppressed side reactions. Although many monomers have been polymerized under these conditions, the effect of microwave irradiation on the mechanism and the rate of chemical reactions is still under debate and many investigators have revealed the existence of a so-called nonthermal or specific microwave effect, responsible for the acceleration of the reaction rate and for which some theories have been proposed. It is well-known that the microwave heating has much more virtues than the normal heating for organic synthesis, such as time-saving, green processes and high yields^[17–20].

In the history of polymer science, both naturally occurring and synthetic, optically active polymers (OAPs) have gained much attention in conjunction with their stereochemistry, and detailed studies have been carried out on their syntheses, conformations and functions^[21, 22]. The preparation of OAPs and oligomers has been one of the most extensively studied fields in synthetic polymer chemistry and has been attracting considerable interest on several accounts^[23]. The simplest and the most versatile method of synthesizing OAPs involves the polymerization of optically active monomers^[24]. These polymers find enormous applications in the preparation of chromatographic supports as chiral stationary phases, in the production of synthetic biomaterials, as chiral catalysts or in the production of materials with nonlinear optical properties. In all of the aforementioned cases the optical activity is induced preferentially *via* polymerization of a chiral monomer. The synthesis of polymers containing amino acid and peptide moieties is a subject of much interest, since a high degree of amino acid functionality and chirality can lead to polymers with enhanced solubility and the ability to form regulated higher order structures. Recently we have synthesized various OAPs containing amino acid by different methods^[15, 19, 25–31].

Because of importance of chiral polymers and polymers with amino acid moieties, in continuation of our study to prepare optically active polymers, in this research a new series of thermally stable and optically active aromatic PAs were synthesized using chiral diacid **1** containing L-leucine moiety in pendent group and several aromatic diamines under microwave irradiation and conventional heating. The introduction of thermally stable side chain should disrupt interchain hydrogen bonding and reduce packing effectiveness and crystallinity, so all of the polymers are expected to show good solubility in many organic solvents. The TGA data have been applied in order to study thermal kinetic decomposition of the resulting PAs.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) were dried over BaO and then were distilled under reduced pressure. Benzidine (**2a**) was purified by recrystallization from ethanol. 4,4'-Diaminodiphenylmethane (**2c**) and 1,5-naphthalenediamine (**2e**) were purified by recrystallization from water. 4,4'-Diaminodiphenylether (**2d**), 2,5-diaminotoluene (**2f**), 1,3-phenylenediamine (**2g**) and 1,4-phenylenediamine (**2h**) were purified by sublimation.

Equipments

The microwave apparatus used for the polycondensation was a Samsung (South Korea) microwave oven (2450 MHz, 900 W). All of the polymerization reactions were performed in a hood with strong ventilation. Proton nuclear magnetic resonance ($^1\text{H-NMR}$, 500 MHz) spectra were recorded in DMSO- d_6 solution using a Bruker (Germany) Avance 500 instrument. Proton resonances are designated as singlet (s), doublet (d), doublet of doublet (dd) and multiplet (m). FTIR spectra were recorded on a Jasco-680 (Japan) spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wavenumbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Germany) at a concentration of 0.5 g/dL at 25°C. Specific rotations were measured by a Jasco Polarimeter (Japan). Thermal gravimetric analysis (TGA) data for polymers were taken on a Perkin Elmer (Pyris 1) instrument in a nitrogen atmosphere at a rate of 10 K/min, and differential scanning calorimetry (DSC) data were recorded at a rate of 20°C. Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity taken from the heating DSC traces. Elemental analyses were performed by the Iranian Polymer and Petrochemical Institute, Tehran, Iran.

Monomer Synthesis

An optically active diacid monomer (2*S*)-4-[(4-methyl-2-phthalimidylpentanoylamino)benzoylamino]isophthalic acid (**1**) was prepared according to our previous work^[32].

Polymer Synthesis

Method I: Polymerization of diacid **1** with aromatic diamines (**2a–2h**) under microwave irradiation

Synthesis of aromatic **PA3cI** is described as a typical procedure. A mixture of 0.06 g (0.24 mmol) of diamine **2c**, 0.10 g (0.24 mmol) of diacid **1**, 0.06 g of CaCl_2 , 0.15 mL of pyridine, 0.14 mL of triphenyl phosphite (TPP) and 0.5 mL of NMP was placed in a porcelain dish and the mixture was ground completely for 5 min. The whole reaction mixture was irradiated in a microwave oven for a period of 60 s at 100% (900 W) and 30 s at 80% (720 W) of its power level. At the end of the reaction, the obtained polymer was trickled into 20 mL of stirred methanol. The white polymer was washed thoroughly with hot water and methanol, collected by filtration and dried at 100°C under reduced pressure. A 92% yield was obtained and inherent viscosity of this polymer was 0.57 dL/g, measured with a polymer concentration of 0.5 g/dL in DMF at 25°C. Other PAs were synthesized in a similar method.

Method II: Polymerization of diacid **1** with diamines (**2a–2h**) under conventional heating

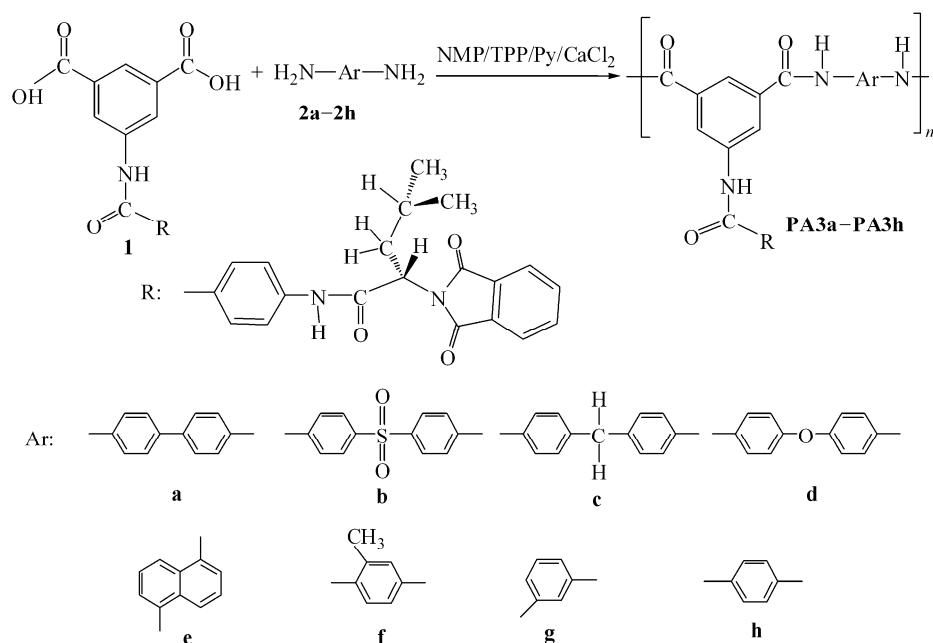
Synthesis of aromatic **PA3cII** is described as a typical procedure. A mixture of 0.06 g (0.24 mmol) of diamine **2c**, 0.10 g (0.24 mmol) of diacid **1**, 0.06 g of CaCl_2 , 0.15 mL of pyridine, 0.14 mL of TPP and 0.5 mL of NMP was placed into the flask equipped with a mechanical stirrer and a condenser. The mixture blanketed by nitrogen was stirred and refluxed for 5 h. At the end of the reaction, the obtained polymer solution was trickled into 20 mL of stirred methanol. The white-stringy polymer was washed thoroughly with hot water and methanol, collected by filtration and dried at 100°C under reduced pressure. A 84% yield was obtained and inherent viscosity of this polymer was 0.57 dL/g, measured with a polymer concentration of 0.5 g/dL in DMF at 25°C. Other PAs were synthesized in similar method.

RESULTS AND DISCUSSION

The bulky monomer **1** with chiral architecture was synthesized in five steps according to our previous work^[32].

Polymer Synthesis

Aromatic **PA3a–PA3h** containing bulky chiral were synthesized from the reaction of optically active dicarboxylic diacid **1** with aromatic diamines **2a–2h** by the direct polycondensation procedure using TPP/Py as condensing agents and NMP as a solvent under microwave irradiation (method I) and conventional heating (method II) as shown in Scheme 1.



Scheme 1 Polycondensation reactions of monomer **1** with different diamines

In method I polymerization reaction was carried out under microwave irradiation. The effect of microwave power levels and period of heating was examined to achieve the optimum reaction conditions. A series of experiments which were performed with different reaction times and power levels under this method revealed that the optimal results were obtained after 1 min at 100% (900 W) and 30 s at 80% (720 W) of its power level. At higher radiation times dark products were obtained, and on the other hand under low radiation times or power levels, low yields were achieved. Then the resulting viscose mixtures were precipitated in methanol, which gave **PA3aI–PA3hI** in high yields and the results are shown in Table 1. The inherent viscosities of the resulting polymers under chosen conditions were in the range of 0.36–0.73 dL/g and the yields were 78%–94%. All of the PAs show optical rotation, therefore are optically active.

Table 1. Physical properties of PAs synthesized by microwave irradiation (method I: 1 min at 100% and 30 s at 80% of its power levels, respectively)

Diamine	Polymer					
	Polymer	Yield (%)	η_{inh} (dL g ⁻¹) ^a	$[\alpha]_D^{25, a}$	$[\alpha]_{Hg}^{25, a}$	Color ^b
2a	PA3aI	90	0.37	−64.7	−54.2	W
2b	PA3bI	94	0.36	−50.3	−47.3	W
2c	PA3cI	92	0.57	−72.7	−74.2	LB
2d	PA3dI	93	0.47	−54.6	−52.2	DB
2e	PA3eI	78	0.51	+58.5	+53.9	B
2f	PA3fI	85	0.70	−63.6	−63.9	W
2g	PA3gI	82	0.63	−56.2	−70.9	B
2h	PA3hI	82	0.73	−51.4	−62.6	B

^a Measured at a concentration of 0.5 g dL⁻¹ in DMF at 25°C;

^b W = White, B = Brown, LB = Light Brown, DB = Dark Brown

To compare the microwave-assisted method with conventional heating, we also carried out the polymerization reactions under conventional heating (method II). When the same experiment was conducted by conventional heating, it took longer time (5 h under reflux) for completion of the reaction. Under this condition, yields and inherent viscosities of the polymers were ranging of 83%–94% and 0.37–0.74 dL/g, respectively. On

the other hand, a more homogeneous heating and exceptional rate acceleration were observed under microwave irradiation. This demonstrated the advantageous effect of microwave as the energy source. The yields and inherent viscosities of the resulting polymers obtained by microwave irradiation versus thermal heating are comparable. The optimum conditions which were obtained under microwave and conventional heating have been applied for the preparation of other PAs by the reaction of compound **1** with other diamines (Scheme 1) and the results are demonstrated in Tables 1 and 2. Most of the polymers precipitated in a fiber-like form when the resulting polymer solutions were slowly poured into methanol.

Table 2. Physical properties of PAs synthesized by conventional heating (method II: 5 h reflux)

Diamine	Polymer					
	Polymer	Yield (%)	η_{inh} (dL g ⁻¹) ^a	$[\alpha]_D^{25, a}$	$[\alpha]_{Hg}^{25, a}$	Color ^b
2a	PA3aII	89	0.37	+29.8	+40.9	W
2b	PA3bII	94	0.46	-32.3	-31.3	W
2c	PA3cII	84	0.57	-40.7	-32.2	LB
2d	PA3dII	86	0.43	-47.6	-53.6	LB
2e	PA3eII	88	0.54	-70.4	-85.5	B
2f	PA3fII	85	0.72	+38.6	-25.9	W
2g	PA3gII	83	0.67	-44.2	-35.9	B
2h	PA3hII	90	0.74	-72.4	-57.2	W

^a Measured at a concentration of 0.5 g dL⁻¹ in DMF at 25°C;

^b W = White, B = Brown, LB = Light Brown

Polymer Characterization

The resulting polymers were characterized by FTIR, ¹H-NMR spectroscopy techniques and elemental analyses. The results are shown in Tables 3 and 4. The FT-IR spectra of resulting PAs showed the presence of the characteristic peaks for amide and imide groups and the absence of the original peaks arising from the COOH and NH₂ groups in the corresponding diacid and diamines precursors. Absorption of amide N—H bonds appeared around 3310–3331 cm⁻¹ (hydrogen band) and the peak at 1650–1675 cm⁻¹ confirms the presence of amide group. All of these PAs exhibited absorption at 1370–1380 and 715–725 cm⁻¹ that show the presence of the imide heterocycle in these polymers (Table 3). For example the FTIR spectrum of **PA3dI** is shown in Fig. 1.

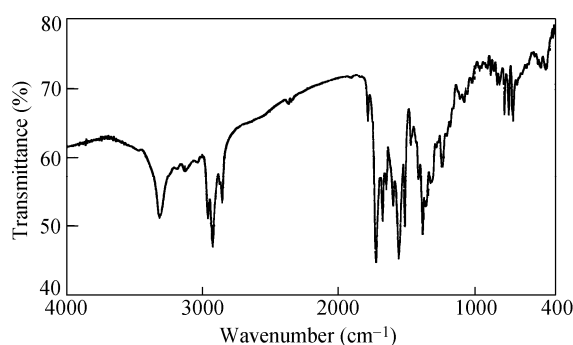


Fig. 1 FTIR spectrum of **PA3dI** in DMSO-d₆ at RT

In the ¹H-NMR spectrum of these polymers, appearances of the N—H protons of amides groups at δ = 10.30 and 10.45–10.51 as three peaks indicate the presence of amide group in the polymer's side chain, as well as main chain. The resonance of aromatic protons appeared in the range of δ = 6.93–8.45. The proton of the chiral center appeared as multiplets in the range of δ = 4.97–5.00. The resonance of the diastereotopic hydrogens bonded to neighbor carbon of chiral center appeared in the range of δ = 2.05–2.07 and 2.24–2.26 as two discrete multiplets peaks. The absorption of the diastereotopic CH₃ protons groups of L-leucine appeared as a broad multiplet peak at δ = 0.90–0.94 (Table 3). For example, ¹H-NMR spectrum of **PA3dI** is shown in Fig. 2.

Elemental analysis values of the resulting polymers are also in good agreement with calculated values of carbon, hydrogen and nitrogen in the polymers (Table 4).

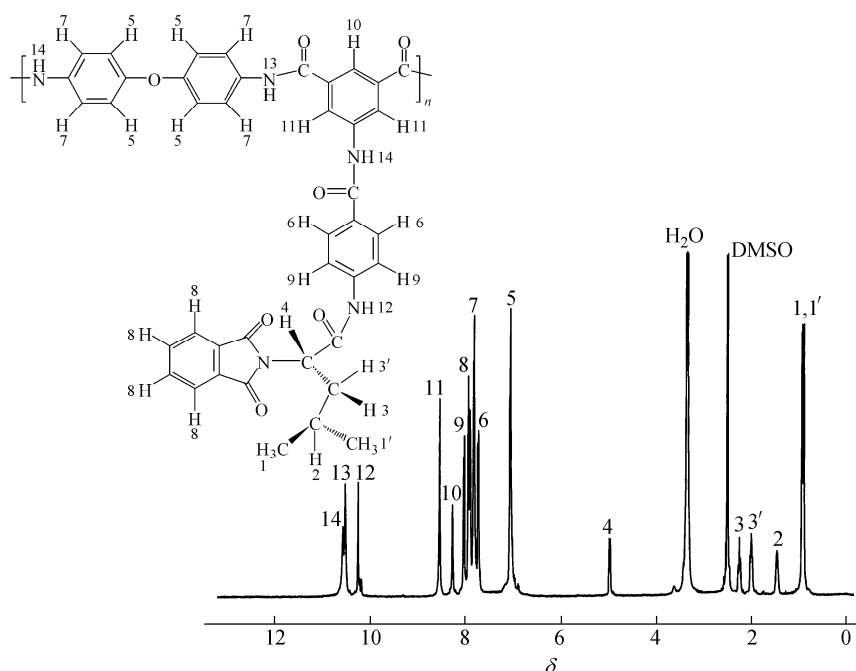


Fig. 2 ^1H -NMR spectrum of PA3dI in DMSO- d_6 at RT

Table 3. ^1H -NMR and FT-IR characterization of PAs

Polymer	Spectra data	
PA3c	FT-IR peaks (cm^{-1}): 3299 (s, br), 3041 (w), 2958 (s), 2890 (m), 1775 (w), 1719 (s), 1668 (m), 1594 (s), 1468 (w), 1409 (m), 1384 (s), 1254 (m, sh), 1246 (m), 1187 (m), 954 (w), 876 (m), 757 (s), 691 (w), 530 (m)	^1H -NMR peaks δ : 0.92 (d, 6H, CH_3 , $J = 7.21$ Hz), 1.36–1.38 (m, 1H, CH), 1.95–1.98 (m, 1H, CH_2), 2.10–2.12 (m, 1H, CH_2), 3.96 (s, 2H, CH_2), 4.87–4.89 (dd, 1H, CH, $J_1 = 6.64$, $J_2 = 6.92$ Hz), 6.90–7.20 (m, 4H, CH), 7.62–7.93 (m, 12H, CH), 8.01 (s, 1H, CH), 8.32 (s, 4H, CH), 10.21 (s, br, NH), 10.35 (s, br, NH).
PA3d	FT-IR peaks (cm^{-1}): 3315 (m), 2957 (m), 2870 (wm), 1774 (w), 1713 (s), 1662 (m), 1598 (m), 1522 (s), 1468 (w), 1385 (m), 1314 (w), 1246 (m), 1184 (w), 1077 (m), 958 (m), 853 (m), 759 (w), 721 (s), 529 (w)	^1H -NMR peaks δ : 0.87 (d, 6H, CH_3 , $J = 7.14$ Hz), 1.49–1.50 (m, CH), 2.01–2.08 (m, 1H, CH), 2.17–2.19 (m, 1H, CH), 4.93–4.96 (dd, 1H, CH, $J_1 = 6.57$, $J_2 = 6.85$ Hz), 7.01–7.12 (m, 4H, CH), 7.71–7.97 (m, 12H, CH), 8.10 (s, 1H, CH), 8.41 (s, 2H, CH), 10.01 (s, br, NH), 10.48 (s, br, NH).
PA3a	FT-IR peaks (cm^{-1}): 3413 (m), 3013 (w), 2957 (m), 2870 (w), 1774 (w), 1713 (s), 1662 (m), 1502 (s), 1462 (w), 1385 (s), 1314 (w), 1244 (m), 1184 (w), 1072 (m), 901 (w), 890 (w), 720 (m), 692 (w), 529 (m)	
PA3b	FT-IR peaks (cm^{-1}): 3369 (s), 3105 (w, sh), 2957 (w), 1774 (w), 1714 (s), 1668 (m), 1590 (s), 1525 (m), 1447 (w), 1404 (m), 1319 (m), 1249 (m), 1183 (m), 1015 (m), 962 (w, br), 879 (w), 857 (w), 822 (w), 757 (s), 692 (w)	
PA3e	FT-IR peaks (cm^{-1}): 3248 (m), 2957 (m), 2870 (w), 1774 (w), 1714 (s), 1661 (m), 1597 (s), 1494 (w), 1384 (s), 1334 (w), 1246 (s), 1075 (m), 940 (w), 890 (w), 780 (m), 660 (w), 530 (m)	
PA3f	FT-IR peaks (cm^{-1}): 3414 (m), 3034 (w), 2958 (m), 1774 (w), 1714 (s), 1661 (s), 1605 (s), 1536 (m), 1445 (w), 1384 (m), 1249 (m), 1185 (w), 1071 (w, br), 879 (w), 761 (w), 720 (w), 616 (w), 530 (m)	
PA3g	FT-IR peaks (cm^{-1}): 3297 (m), 3095 (w), 2957 (m), 1775 (w), 1713 (s), 1660 (s), 1596 (m), 1513 (w), 1468 (m), 1403 (s), 1315 (s), 1248 (m), 1180 (w), 1108 (m), 880 (w), 759 (w), 721 (w), 614 (w), 530 (m)	
PA3h	FT-IR peaks (cm^{-1}): 3422 (s), 3140 (w), 2957 (m), 2924 (m), 1775 (w), 1714 (s), 1665 (m), 1596 (w), 1445 (m), 1387 (m), 1316 (m), 1248 (m), 1222 (s), 1186 (w), 1073 (m), 878 (w), 761 (w), 721 (w), 692 (m), 529 (m)	

Table 4. Elemental analysis of typical PAs

Polymer	Formula		Elemental analysis (%)		
			C	H	N
PA3c	(C ₄₂ H ₃₅ N ₅ O ₆) _n	Calc.	68.31	5.03	10.12
	(705.31) _n	Found	67.51	5.16	9.94
PA3e	(C ₃₉ H ₃₁ N ₅ O ₆) _n	Calc.	69.36	4.98	9.92
	(665.51) _n	Found	68.14	4.96	9.62

Solubility of PAs

The solubility properties of PAs were studied in different solvents (Table 5). Polymers are readily soluble at room temperature in amide type solvents, such as NMP, DMAc and DMF. Differences in solubility of PAs were based on the polymer's structure. The good solubility of **PA3a–PA3h** is due to the fact that diacid monomer **1** contains a bulky phthalimidyl group that exhibits a strict hindrance, which prevents close chain packing and allows the solvent molecules to diffuse into the polymer (Table 5).

Table 5. Solubility properties of PAs^a

Polymer	Solvents					
	Amide type solvents NMP, DMAc, DMF	H ₂ SO ₄	DMSO	THF	CH ₂ Cl ₂	CH ₃ OH
PA3aI	+++	+++	++	±	–	–
PA3bI	+++	+++	++	±	–	–
PA3cI	+++	+++	++	±	–	–
PA3dI	+++	+++	++	±	–	–
PA3eI	+++	+++	++	±	–	–
PA3fI	++	+++	++	–	–	–
PA3gI	++	+++	+	–	–	–
PA3hI	++	+++	+	–	–	–

^a Solubility: measured at a polymer concentration of 5 mg/mL; +++ Soluble at RT; ++ Soluble at boiling temperature of water bath; + Soluble at boiling temperature of the solvent; ± Partially soluble at RT; – Insoluble

Thermal Properties

The thermal stability of some PAs was investigated by means of TGA and DSC techniques under a nitrogen atmosphere (Table 6). Samples were heated up to 300°C at the rate of 20 K/min in N₂, quenched to –50°C and reheated to obtain *T_g*. Thermal stability of the polymers was studied based on 5% and 10% weight loss (*T₅*, *T₁₀*) of the polymers and residue at 800°C (char yield). Figures 3 and 4 show the TGA curves for **PA3dI** and **PA3hI** as well as **PA3dII** and **PA3hII**, respectively. The results reveal that PAs are thermally stable up to 348°C. According to Table 6, it is clear that the **PA3hI** and **PA3hII** (based on 1,4-phenylenediamine) have higher thermal stability than the other PAs. It could be related to wholly aromatic, rigid structure of diamine **2h** for **PA3hI** and **PA3hII** compared to flexible structure of diamine **2d** for **PA3dI** and **PA3dII**, respectively. TGA data show that the thermal stability of the resulting polymers are rather high. The DSC analyses for PAs show *T_g* around 155–168°C (Table 6).

Char yield can be applied as decisive factor for estimated limiting oxygen index (LOI) of the polymers based on Van Krevelen and Hoftyzer equation^[33].

$$\text{LOI} = 17.5 + 0.4 \text{ CR}$$

Where CR = char yield

The **PA3dI**, **PA3dII**, **PA3hI** and **PA3hII** have LOI values around 40 which were calculated from their char yield at 800°C. On the basis of LOI values, all these PAs can be classified as self-extinguishing polymers (Table 6).

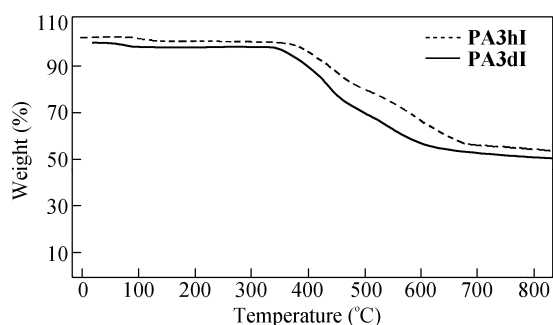


Fig. 3 TGA thermograms of (—) **PA3dI** and (---) **PA3hI** under N_2 atmosphere and a heating rate of 10 K/min

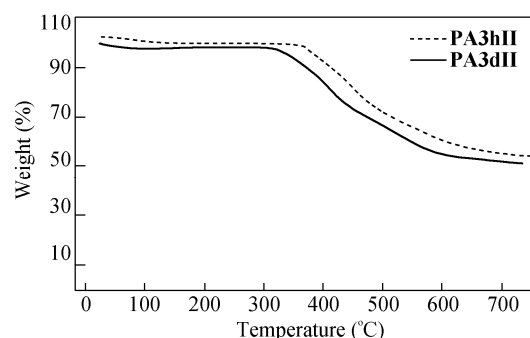


Fig. 4 TGA thermograms of (—) **PA3dII** and (---) **PA3hII** under N_2 atmosphere and a heating rate of 10 K/min

Table 6. Thermal properties of PAs

Polymer	Decomposition temperature (°C)		Char yield (%) ^c	T_g^d (°C)	LOI ^e
	T_5^a	T_{10}^b			
PA3dI	348	385	56	155	39.9
PA3dII	351	386	58	—	40.7
PA3hI	400	452	68	168	44.7
PA3hII	400	451	66	—	43.5

^a Temperature at which 5% weight loss was recorded by TGA at heating rate of 10 K/min in a N_2 atm;

^b Temperature at which 10% weight loss was recorded by TGA at heating rate of 10 K/min in a N_2 atm;

^c Weight percent of the material left undecomposed after TGA at maximum temperature 800°C in a N_2 atm;

^d Glass transition temperature was recorded at a heating rate of 20 K/min in a nitrogen atmosphere;

^e Limiting oxygen index (LOI) evaluating at char yield at 800°C

Kinetic Study

In order to study the effect of different existing functional groups in the obtained PAs on their thermal stability, the thermal kinetic investigation was carried out using the Coats-Redfern method equation (1)^[34–39]. The results are listed in Table 7. The calculating of thermodynamic data applied on the first decomposition peak in each of the four PAs.

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\phi} \int_{T_1}^{T_2} \exp\left(-\frac{E^*}{RT}\right) dT \quad (1)$$

For convenience of integration the lower limit T_1 is usually taken as zero. This Eq. (1) upon integration gives the Eq. (2):

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = -\frac{E^*}{RT} + \ln\left[\frac{AR}{\phi E^*}\right] \quad (2)$$

where α and ϕ are the fraction of the sample decomposed at time t and the linear heating rate, respectively. R is the gas constant and E is the activation energy in kJ mol^{-1} . A plot of $\ln[-\ln(1-\alpha)/T^2]$ verses $-1/T$ was found to be linear (Figs. 5 and 6), from the slope of this line E was calculated, and A (Arrhenius constant) can be deduced from the intercept. The entropy of activation ΔS in $\text{J mol}^{-1} \text{K}^{-1}$ was calculated by using Eq. (3), where K_B is the Boltzmann constant, h is the Plank's constant and T_S is the DTG peak temperature.

$$\Delta S = R \ln\left(\frac{Ah}{K_B T_S}\right) \quad (3)$$

The enthalpy of activation, ΔH , and the free enthalpy of activation, ΔG , can be calculated *via* the equations; $\Delta H = E - RT_m$ and $\Delta G = \Delta H - T_m \Delta S$ accordingly, and are shown in Table 7. The positive values of ΔH indicate

that the dissociation processes are endothermic in nature and enhanced with the rise of temperature. ΔG values for the dissociation constants are positive, thus dissociation processes are non-spontaneous. The overall activation energy and entropy for thermal decomposition of **PA3hI** and **PA3hII** based on 1,4-phenylenediamine are 60.25, 58.12, -0.208 and -0.202 kJ mol^{-1} , respectively, which are much higher than those of the other PAs. This reveals that there are more thermal stability and more ordering for these PAs. However, the existence of oxygen atom in the structure of **PA3dI** and **PA3dII** could lead to some difference in thermal degradation behaviors relative to **PA3hI** and **PA3hII** such as: flexibility of structure, stability of resulting radical, lower chain symmetry, packing efficiency and lower polymer lattice crystal order. A stiff and rigid activation complex (transition state) led to a lower degree of freedom of rotation and vibration and hence to a negative value of ΔS which meant the formation of a stiff and rigid activated complex with fewer degrees of freedom of rotation and vibration. It has been observed that the different approximations to the Arrhenius integral lead to systematic errors in the values of the activation energy determined by means of different integral methods. Although, the E values obtained by different methods show more than 8% error, but in this study by using the Coats and Redfern method, less than 1.5% error was achieved^[40].

Table 7. Kinetic parameters for the degradation of PAs determined using the Coats-Redfern equation

Polymer	Parameter					r
	E (kJ mol^{-1})	A (s^{-1})	ΔS (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	
PA3dI (360–483)	52.07	361.73	-0.198	47.93	135.02	0.998
PA3dII (375–490)	55.34	278.55	-0.201	49.03	138.52	0.996
PA3hI (383–552)	60.25	140.47	-0.208	56.84	159.56	0.999
PA3hII (405–575)	58.12	156.82	-0.202	54.03	156.47	0.999

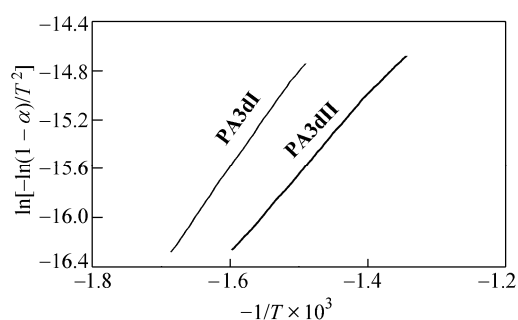


Fig. 5 Plot of $\ln[-\ln(1-\alpha)/T^2]$ against $-1/T$ for **PA3dI** and **PA3dII**

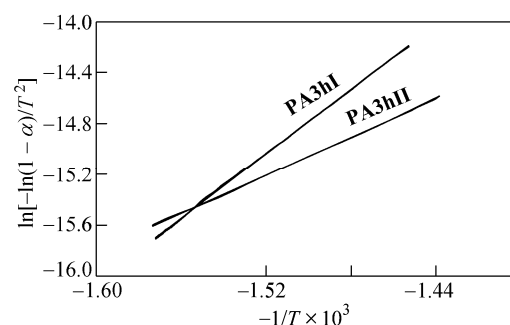


Fig. 6 Plot of $\ln[-\ln(1-\alpha)/T^2]$ against $-1/T$ for **PA3hI** and **PA3hII**

CONCLUSIONS

In this investigation, we have developed an efficient, convenient and practical approach for the synthesis of thermally stable and optically active PAs. At first we have successfully synthesized a novel chiral aromatic dicarboxylic acid **1**, containing a rigid phthalimide and flexible L-leucine pendent group in five steps. Then it was effectively applied as a condensation monomer in combination with diverse aromatic diamines for the synthesis of novel aromatic PAs by using microwave irradiation as well as conventional heating. A comparable result on the isolated yields and inherent viscosities was obtained by microwave irradiation verses thermal heating with remarkable reduction in reaction time. The resulting polymers have inherent viscosities in the range of 0.36–0.74 dL/g.

On the other hands, introducing pendent units into the chain of polymer backbone should disturb interchain hydrogen bonding, inherent macromolecular rigidity, and diminish packing efficiency and crystallinity that caused superior solubility. So these polymers are readily soluble in polar amidic solvents. Since, these optically active polymers have amino acids in the polymer architecture, they are expected to be biodegradable, and therefore are classified under environmentally friendly polymers. The polymers presented high thermal stability,

with the decomposition temperature being above 358°C, although slightly diminished compared with those of related aromatic PAs without any bulky units.

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