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ORIGINAL ARTICLE

Microwave irradiation as a versatile tool for increasing reaction rates and yields in synthesis of optically active polyamides containing flexible L-leucine amino acid

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Abstract In this investigation, a series of thermally stable and optically active polyamides (PA)s containing bulky pendant chiral functionality from polymerization of a diacid monomer containing rigid phthalimide and flexible L-leucine groups, (2*S*)-5-[4-(4-methyl-2-phthalimidylpentanoylamino)benzoylamino]isophthalic acid with several aromatic and aliphatic diisocyanates such as 4,4′-methylenebis(phenyl isocyanate), toluylene-2,4-diisocyanate, isophorone diisocyanate, and hexamethylene diisocyanate under gradual heating method were prepared and compared with microwave-assisted polycondensation method. The polymerization reactions occurred rapidly under microwave irradiation and produced a series of PAs with good yields and moderate inherent viscosities of 0.26–0.68 dL/g. All of the new PAs showed good solubility and were readily dissolved in aprotic organic solvents. The resulting polymers were characterized by FT-IR, ^{1}H NMR spectroscopy, and elemental analysis technique. Thermal stability and thermal properties of PAs were evaluated by thermogravimetric analysis and differential scanning calorimetry. The interpretation of kinetic parameters (E, ΔH, ΔS, and ΔG) of thermal decomposition stages have been evaluated using Coats–Redfern equations.

Keywords Thermally stable polyamides · Microwave-assisted polycondensation · Green chemistry · L-leucine

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Introduction

The application of microwave heating in synthetic chemistry using a commercial domestic oven is a fast-growing area of research. Since the first report of microwave-assisted synthesis in 1986, the technique has been accepted as a method for reducing reaction times often by orders of magnitude and for increasing yields of product compared to conventional heating methods (Gedye et al. 1986; Glguere et al. 1986). It is well known that microwave irradiation is a special class of heating energy with important advantages (Li et al. 2008). Microwave, as a moderate source and nonionized electromagnetic of thermal energy, which supplies a clean and inexpensive alternative to conventional oil baths and reactions can be done in short time with more yield and also purity of products (Bogdal and Gorczyk 2004; Melo-Junior et al. 2009; Wiesbroc et al. 2005). Microwave irradiation, in organic synthesis, is used for optimization and acceleration of chemical reactions (Bogdal and Loupy 2008; Loupy 2002) and, in polymer chemistry, is used for developing different types of polymerizations containing addition polymerization, condensation polymerization, graft polymerization, free and controlled radical polymerization, ring-opening polymerization, polymer modification, and so on. One of the most important advantages of microwaves is selectivity in reactions, such it can, heat reactants, without exchange the concern energy of reactants and products or concern energy of reaction (Hoogenboom and Schubert 2007; Iwamura et al. 2009; Mallakpour and Rafiee 2008a, b, 2009).

Aromatic polyamides (PAs) are well known as high performance polymeric materials due to their excellent thermal stability, low flammability, electric insulation property, and chemical resistance (Frazer 1968; Marcos-Fernandez et al. 2001; Rogers and Long 2003). However,

the poor solubility in organic solvents and high softening temperatures or melting temperatures caused by their high crystallinity and the high tautness of the polymer backbone restrict their process ability. Approaches have been out lined to improve the solubility of PAs by means of chemical modification, such as the incorporation of flexible units in the polymer backbone and voluminous pendant groups to the main chain (Diakoumakos and Mikroyannidis 1994; Mikroyannidis 1996; Yang 1989).

A great number of studies on chiral materials, reported in literature, are devoted to amino acids and carbohydrates. The choice of amino acids is due to their availability with high optical purity and low price (Samui et al. 2002). Amino acids are among the simplest biomolecules that contain intramolecular hydrogen bonds, and they serve as building blocks of the most diverse biological compounds such as supplementary complex peptides and proteins. Several methods have been employed to prepare optically active polymers, including the polymerization of optically active monomers, asymmetric selective polymerization, and the introduction of a chiral group into an optically inactive polymer via direct polymerization reactions (Mallakpour and Seyedjamali 2008). Polymers prepared contain an asymmetric carbon in the side or main chain; have found successful uses in chromatographic separation of enantiomers, chiral liquid crystals, non-linear optical devices, optical switches, biodegradable and biomedical devices, and chiral media for asymmetric synthesis (Nakano 2001; Okamoto et al. 1984; Yoneyama et al. 2007), and also are used widely in the pharmaceutical manufacturing for enantio-selective separation of drugs (Feng et al. 2007).

The branched chain essential amino acids such as leucine have similar characteristics, properties, and physiological actions. These amino acids are unique metabolically; they are primarily catabolized by peripheral tissues and have similar catabolic pathways (Massey et al. 1998). The importance of leucine as the primary amino acid responsible for protein synthesis has been confirmed in many studies (Garlick 2005). Some of other significant roles of leucine are as follows: exert regulatory influences on carbohydrate and protein metabolism (Layman and Baum 2004; Nair et al. 1992), providing gluconeogenic precursors via the formation of alanine in muscle (Brooks 1987), stimulating muscle protein synthesis during caloric restriction or after endurance exercise (Norton and Layman 2006), regulating glucose homeostasis (Layman 2003), and decreasing protein breakdown (Frexes-Steed et al. 1992).

Because of importance of optically active materials and polymers with amino acid and phthalimide moieties, in continuation of our study in developing high performance polymers containing pendant units under microwave induction heating, herein we report the application of microwave radiation in direct synthesis of optically active PAs from the reaction of bulky aromatic chiral dicarboxylic acid with aromatic and aliphatic diisocyanates. Diacid monomer was synthesized by coupling reaction between L-leucine amino acid with bulky rigid phthalimide group and benzamide moiety. Different factors affecting the inherent viscosity (as a means of molecular weight) and yield of PAs, such as microwave power, time of irradiation, effect of catalyst and no catalyst, during the course of reaction have been studied and optimized.

Experimental

Materials and methods

Reagents were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI, USA), and Riedel-de Haen AG (Seelze, Germany). *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), and 1-methyl-2-pyrrolidone (NMP) were dried over barium oxide and then were distilled under reduced pressure. The apparatus used for the polycondensation was a Samsung microwave oven (2,450 MHz, 900 W). ^{1}H NMR (500 MHz) spectra were recorded on a Bruker (Ettlingen, Germany) Advance 500 instrument. Multiplicities of proton resonance were designated as singlet (s), doublet (d), doublet of doublet (dd) and multiplet (m). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Impact 400D IR spectrophotometer (Thunderdome, Germany). Spectra of solids were carried out with KBr pellets. Vibrational transition frequencies are reported as wave numbers (cm^{-1}). Band intensities are designated as weak (w), medium (m), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure with a Cannon-Fenske (Mainz, Germany) routine viscometer. Specific rotations were measured with a Jasco (Osaka, Japan) P-1030 polarimeter. All the polymerization reactions were carried out in a hood with strong ventilation. All melting points were taken with a melting-point apparatus (Gallenhamp, UK). Quantitative solubility was determined with 0.05 g of the polymer in 1 mL of the solvent. Elemental analyses were performed by Tarbit Moalem University, Tehran, Iran. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were recorded on a Setaram instrument (Caluire, France) at a heating rate of 10°C/min and 20°C/min under nitrogen atmosphere. Glass-transition temperatures (T_g's) were read at the middle of the transition in the heat capacity taken from the DSC heating traces.

Monomer synthesis

(2*S*)-5-[4-(4-Methyl-2-phthalimidylpentanoylamino)benzoylamino]isophthalic acid (**1**) was prepared according to our previous work (Mallakpour and Sepehri 2008).

Polymer synthesis

Polymers were synthesized with two different methods.

Method I: polymerization reaction under conventional heating in NMP as solvent

The synthesis of **PA3aIA** typically was carried out as follows: a mixture of 0.100 g (1.84×10^{-4} mol) of dicarboxylic acid **1**, 0.046 g (1.84×10^{-4} mol) of 4,4′-methylenebis(phenyl isocyanate) (MDI) (**2a**), and 0.50 mL of NMP was added and the reaction mixture was refluxed for 1 h at room temperature, 3 h at 60°C, 8 h at 80°C, 2 h 100°C, and finally 1 h 120°C by mechanical equipped stirrer. During of this synthesis, about 0.20 mL of NMP was added. **PA3aIA** was precipitated by pouring the flask content into methanol. Then it was filtered, washed with hot water and dried overnight under vacuum at 80°C to give 0.110 g (76%) of **PA3aIA**. The inherent viscosity of **PA3aIA** in DMF was 0.67 dL g^{-1}. This polymerization was also repeated using dibutyltin dilaurate (DBTDL) as catalyst.

All of the polymers were prepared using a similar procedure.

Method II: polymerization reaction under microwave energy in NMP as solvent

The PAs were prepared by the following general procedure (taking **PA3dIID** as an example) into a porcelain dish monomer **1** (0.100 g, 1.84×10^{-4} mol) and 0.20 mL of NMP was placed. A solution of hexamethylene diisocyanate (HDI) (**2d**) (0.040 g, 1.84×10^{-4} mol) in 0.20 mL of dry NMP was added, and the mixture was ground again for additional of 2 min. The reaction mixture was irradiated in the microwave oven for 240 s at 100% (900 W) of its power level. The resulting product was precipitated by the addition of 10 mL of methanol and 5 mL water. It was then filtered and dried at 80°C for 10 h in vacuum; this yielded 0.100 g (75%) of white **PA3dIID**. The above polymerization was repeated, but the reaction mixture was irradiated in a microwave oven with catalyst. For each method, the optimized reaction conditions according to reaction time and reaction catalysts were used for the polymerization of diacid monomer **1** with other diisocyanates such as MDI (**2a**), toluylene-2,4-diisocyanate (TDI) (**2b**), and isophorone diisocyanate (IPDI) (**2c**).

PA3aIA: FT-IR (KBr, cm^{-1}): 3,307 (m, br), 2,924 (w), 1,900 (w), 1,776 (w), 1,715 (s), 1,655 (m), 1,594 (m), 1,541 (m), 1,410 (m), 1,305 (s), 1,233 (m), 1,101 (w), 1,017 (w), 761 (w).^{1}H NMR (500 MHz, DMSO-d_6): δ: 0.89 (d, 3H, CH_3, $J = 5.80$ Hz), 0.93 (d, 3H, CH_3, $J = 3.90$ Hz), 1.46–1.48 (m, 1H, CH), 1.96–2.02 (m, 1H, CH_2), 2.23–2.28 (m, 1H, CH_2), 3.91 (s, 2H, CH_2), 4.98 (dd, 1H, CH, $J_1 = 4.10$, $J_2 = 7.05$ Hz), 7.35 (d, 8H, CH, $J = 8.25$ Hz), 7.71 (d, 2H, CH, $J = 7.95$ Hz), 7.92 (d, 4H, CH, $J = 8.50$ Hz), 8.02 (d, 2H, CH, $J = 6.95$ Hz), 8.23 (s, 1H, CH), 8.50 (s, 2H, CH), 10.23 (s, 1H, NH), 10.39 (s, 2H, NH), 10.51 (s, 1H, NH).
PA3bIB: FT-IR (KBr, cm^{-1}): 3,306 (m, br), 3,116 (w), 2,959 (m), 2,593 (w), 1,915 (w), 1,776 (m), 1,716 (s), 1,644 (s), 1,537 (s), 1,384 (m), 1,123 (w), 1,078 (w), 760 (s), 719 (s), 670 (s).
PA3cIC: FT-IR (KBr, cm^{-1}): 3,372 (m, br), 3,117 (w), 2,955 (w), 1,775 (w), 2,607 (w), 2,346 (w), 1,777 (m), 1,716 (s), 1,557 (m), 1,384 (s), 1,245 (m), 761 (m), 619 (m).
PA3dID: FT-IR (KBr, cm^{-1}): 3,324 (m, br), 3,117 (w), 2,933 (m), 2,857 (w), 1,776 (w), 1,716 (s), 1,615 (w), 1,384 (s), 1,248 (m), 1,123 (w), 1,077 (w), 1,016 (s), 761 (m), 719 (m). ^{1}H NMR (500 MHz, DMSO-d_6): δ: 0.88 (d, 3H, CH_3, $J = 6.00$ Hz), 0.93 (d, 3H, CH_3, $J = 6.05$ Hz), 1.22–1.31 (m, 8H, CH_2), 1.46–1.47 (m, 1H, CH), 2.00–2.02 (m, 1H, CH_2), 2.20–2.25 (m, 1H, CH_2), 2.94–3.01 (m, 4H, CH_2), 4.98 (dd, 1H, CH, $J_1 = 4.10$, $J_2 = 7.10$ Hz), 7.66 (d, 2H, CH, $J = 8.55$ Hz), 7.71 (d, 2H, CH, $J = 8.30$ Hz), 7.90 (d, 2H, CH, $J = 8.50$ Hz), 7.93 (s, 1H, CH), 7.99 (d, 2H, CH, $J = 6.05$ Hz), 8.21 (s, 2H, CH), 8.67 (s, 2H, NH), 10.22 (s, 1H, NH), 10.45 (s, 1H, NH).

Results and discussion

Synthesis of monomer

The diacid monomer **1** was prepared according to a previously reported five-step process (Mallakpour and Sepehri 2008).

Synthesis of polymers

In this study, we describe an efficient direct polycondensation of diacid **1** with diisocyanates **2a–d** both by thermal conventional heating (method I) and microwave technique (method II) in NMP as solvent (Scheme 1). In both methods, the polymerization reactions were repeated using DBTDL as a catalyst and no catalyst. The optimum conditions for the preparation of **PA3aA–PA3dH** and some

physical properties of this optically active PAs are listed in Tables 1 and 2. In order to find the best irradiation time at 100% of power level (900 W), the effect of time of irradiation on the inherent viscosities and yields of the polymers in the presence or absence of DBTDL as a catalyst in NMP as solvent was studied. Optimum results under microwave irradiation were obtained after 240 s at 100% of power level (900 W). At higher radiation times, dark products were obtained, and on the other hand, under low radiation times or power, reactions gave low yields and inherent viscosities. The microwave-assisted polycondensation method with conventional heating technique was compared. When the same experiment was conducted by conventional heating in the presence of NMP as a solvent, it took very long time (15 h) for completion of the reaction. Thus, noteworthy rate of acceleration was observed under microwave conditions. This confirmed the beneficial effect of microwave as the energy source. The optimum conditions which were obtained under microwave and conventional heating conditions have been applied for the preparation of other PAs by the reaction of monomer **1** with TDI (**2b**), IPDI (**2c**) and HDI (**2d**) (Scheme 1). The inherent viscosities of the resulting polymers under optimized condition were in the range of 0.26–0.68 dL g^{-1} and the yields were 60–89%. Because of, microwave to heat molecules directly through the interaction between microwave energy and molecular dipole moments of the monomers containing polar groups that favor the absorption of microwaves, the yields and inherent viscosities of the products obtained by microwave irradiation versus thermal heating are higher. According to Tables 1 and 2, PA, including MDI, provided higher inherent viscosity than the inherent viscosities of PAs-based on TDI, IPDI or HDI. It is due to the electron withdrawing effect of phenyl group which make the diisocyanate more reactive. The incorporation of amino acid as a chiral unit into the polymer side chains makes them as optically active materials, and it was confirmed by measuring their specific rotation (Tables 1, 2). The specific rotations of polymer based on different diisocyanates showed random changes. Several factors, such as monomer, catalyst, reaction time, and temperature, affect specific rotation. As shown in Tables 1 and 2, it is interesting to mention that, the specific rotations of polymers based on the same diacid prepared under different conditions were different. On the other hand, under same conditions, polymers based on the same diacid showed similar specific rotations. This is a normal behavior for all optically active compounds. Since optical rotation is highly dependent on the chemical structures of the resulting polymeric materials, any small changes in the chemical structures of any chiral molecules has substantial random effect on the optical rotations and is not predictable. Therefore, in this investigation during the polymerization under different conditions, different molecular structures could be formed. It is very important to mention that under different reaction conditions different inherent viscosities were also obtained, which could have substantial effects on optical rotations.

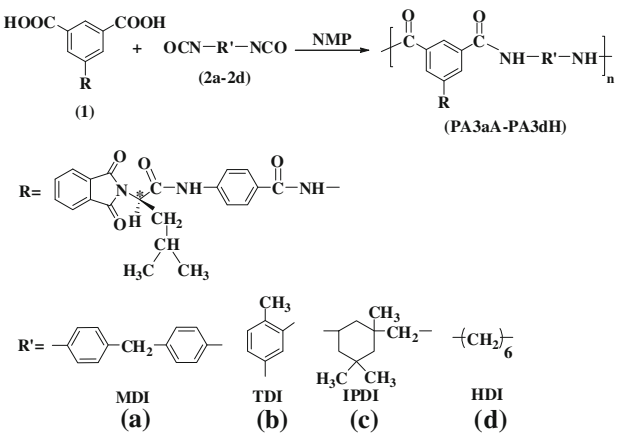
Polymer characterizations

FT-IR and ^{1}H NMR study

The structure of resulting polymers was characterized by FT-IR and some of them by ^{1}H NMR spectroscopy and elemental analyses. The FT-IR spectra of polymers show peak around 3,306–3,372 cm^{-1} for the N–H bond. Main absorption band at 1,716 cm^{-1} was attributed to the carbonyl group. The two absorption bands at 2,900 and 2,950 cm^{-1} are related to the corresponding C–H stretching vibration. The FT-IR spectrum of **PA3dID** is shown in Fig. 1. In the ^{1}H NMR spectrum of **PA3dID** (Fig. 2), appearance of the N–H proton of amide groups around 8.67, 10.22, and 10.45 ppm indicate three amide groups in the polymer's chain. The resonance of aromatic protons appeared at a range of 7.50–8.50 ppm. The proton of the chiral center appeared at 4.98 ppm. The peaks of C–H methylene bonding to chiral center appeared as a multiple around 2.00–2.30 ppm. The resonance of the CH_3 protons groups appeared at a range of 0.90–1.00 ppm. Some elemental analysis values of the resulting polymers are listed in Table 3.

Solubility of PAs

The solubility of PAs was tested quantitatively in various solvents. All of the PAs are soluble in organic solvents such as DMF, DMAc, dimethylsulfoxide (DMSO), NMP, pyridine and in H_2SO_4 at room temperature, and are



Scheme 1 Polycondensation reactions of monomer **1** with aliphatic and aromatic diisocyanates

Table 1 Polymerization reaction by method I

Diisocyanate	Polymer	Catalyst	Yield (%)	Inherent viscosity[a] (dL/g)	$[\alpha]^{25}_{Na,589}$ [a]	$[\alpha]^{25}_{Hg}$ [a]	Color
2a	**PA3aIA**[b]	No Cat	76	0.67	−14.3	−17.2	Yellow
2b	**PA3bIB**[c]	No Cat	68	0.26	−14.8	−16.5	Brown
2c	**PA3cIC**[c]	No Cat	60	0.26	−15.8	−13.9	White
2d	**PA3dID**[c]	No Cat	64	0.38	−10.7	−11.2	White
2a	**PA3aIE**[b]	DBTDL	80	0.58	−10.3	−16.2	Brown
2b	**PA3bIF**[c]	DBTDL	75	0.30	−9.3	−11.5	Brown
2c	**PA3cIG**[c]	DBTDL	88	0.32	−11.4	−12.1	White
2d	**PA3dIH**[c]	DBTDL	76	0.44	−11.0	−12.3	Brown

Reaction conditions: (1 h room temperature, 3 h 60°C, 8 h 80°C, 2 h 100°C, and 1 h 120°C)

[a] Measured at a concentration of 0.5 g/dL in DMF at 25°C

[b] This polymer was precipitated in MeOH

[c] These polymers were precipitated in MeOH/water

Table 2 Polymerization reaction by method II

Diisocyanate	Polymer	Catalyst	Yield (%)	Inherent viscosity[a] (dL/g)	$[\alpha]^{25}_{Na,589}$ [a]	$[\alpha]^{25}_{Hg}$ [a]	Color
2a	**PA3aIIA**[b]	No Cat	87	0.60	−12.3	−14.1	Yellow
2b	**PA3bIIB**[b]	No Cat	70	0.28	−9.4	−10.7	Brown
2c	**PA3cIIC**[c]	No Cat	62	0.26	−17.0	−28.8	White
2d	**PA3dIID**[b]	No Cat	75	0.31	−16.1	−35.4	White
2a	**PA3aIIE**[b]	DBTDL	89	0.68	−8.7	−12.3	Yellow
2b	**PA3bIIF**[b]	DBTDL	78	0.31	−11.4	−12.0	Brown
2c	**PA3cIIG**[c]	DBTDL	80	0.33	−7.5	−11.5	White
2d	**PA3dIIH**[b]	DBTDL	88	0.46	−9.4	−10.3	White

Reaction conditions: (240 s, power 100%)

[a] Measured at a concentration of 0.5 g/dL in DMF at 25°C

[b] These polymers were precipitated in MeOH/water

[c] This polymer was precipitated in MeOH

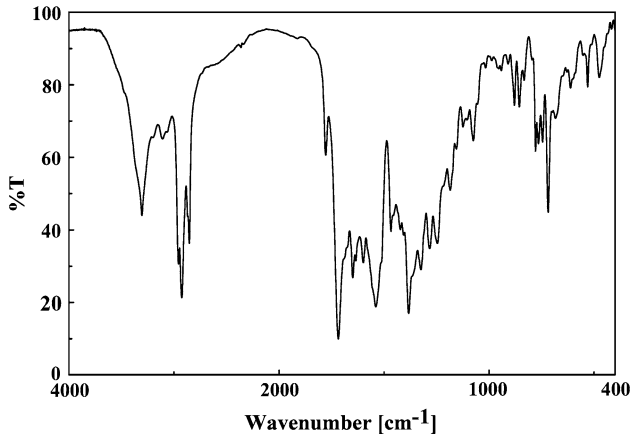


Fig. 1 FT-IR spectrum of **PA3dID**

insoluble in solvents such as chloroform, methylene chloride, methanol, acetone, cyclohexane, tetrahydrofuran, ethanol, and water. Some polymers were partially soluble in methanol and ethanol and precipitated in MeOH/H_2O mixture. Because of flexible side chain and two amide and imide group in polymer backbone, these polymers are expected to have higher solubility.

Thermal properties

The thermal properties of some PAs were evaluated by means of TGA/DTG and DSC techniques in a nitrogen atmosphere at a heating rate of 10 and 20°C/min, respectively. The temperature of 5 and 10% weight loss together with char yield at 800°C has been calculated by means of thermograms. Figure 3 shows the TGA thermogram of **PA3dID** prepared by method I. The thermoanalyses data of **PA3aIA** and **PA3dID** are summarized in Table 4. Char yield can be used as a criterion for evaluating limiting oxygen index (LOI) of the polymers in accordance with Van Krevelen and Hoftyzer equation (Van Krevelen and

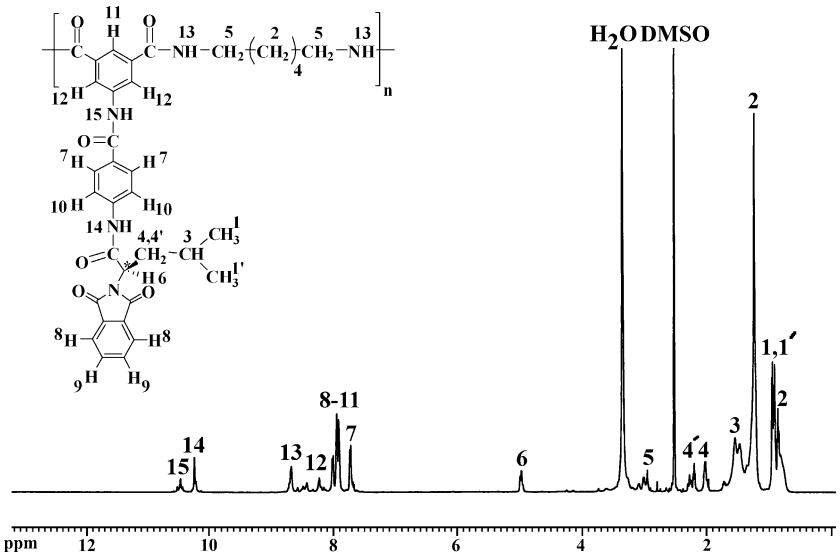


Fig. 2 ^{1}H NMR (500 MHz) spectrum of **PA3dID** in DMSO-d_6 at RT

Table 3 Elemental analysis of typical PAs

Polymer	Formula		Elemental analysis (%)		
			C	H	N
PA3aIA	$(C_{42}H_{35}N_5O_6)_n$	Calc.	71.48	5.00	9.92
	$(705.76)_n$	Found	71.65	5.31	11.32
PA3dID	$(C_{35}H_{37}N_5O_6)_n$	Calc.	67.40	5.98	11.23
	$(623.70)_n$	Found	65.66	5.20	10.89

The polymer sample was dried in vacuum at 80°C for 8 h

Hoftyzer 1976). LOI = 17.5 + 0.4CR where CR = char yield. All of the polymers had LOI values, calculated based on their char yield at 800°C, higher than 28. On the basis of LOI values, such macromolecules can be classified as self-extinguishing polymers. T_{10} (°C), char yield, and LOI of these polymers are in the range of 385–296, 35–27, and 31–28, respectively. According to Table 4, it is clear that polymers based on TDI and MDI have better thermal stability and higher LOI as compared to other PAs. It could be pertained to aromatic, rigid structure of diisocyanates compared to aliphatic, flexible structure of diisocyanates. The T_g's of the PAs were determined by DSC. The DSC analyses for PAs show T_g around 170–180°C.

Kinetic study of thermal decomposition of synthesized PAs

In polymer science thermal methods of analysis have found important applications, among them the determination of kinetic parameters. Analysis of the changes in thermogravimetic data, which are brought about by variation of heating rate, are the basis of the most powerful differential methods for the determination of kinetic parameters. Coats and Redfern method has been found to be the most versatile in calculating the kinetic parameters for the degradation process, which does not need a precise knowledge of the reaction mechanism, using the following equation:

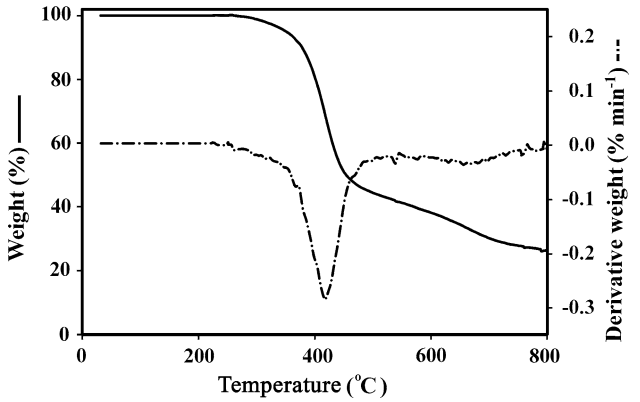


Fig. 3 TGA/DTG thermogram of **PA3dID** under a nitrogen atmosphere at a heating rate of 10°C/min

Table 4 Thermal properties of **PA3aIA** and **PA3dID**

Polymer	T_5[a] (°C)	T_{10}[b] (°C)	Char yield[c] (%)	T_g[d] (°C)	LOI[e]
PA3aIA	354	385	35	180	31
PA3dID	283	296	27	170	28

[a] Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10°C/min in a nitrogen atmosphere

[b] Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min in a nitrogen atmosphere

[c] Percentage weight of material left undecomposed after TGA analysis at maximum temperature 800°C in a nitrogen atmosphere

[d] Glass-transition temperature recorded at a heating rate of 20°C/min in a nitrogen atmosphere

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

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

According to the above equation, a plot of $\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]$ versus $-1/T$ should result in a straight line with slope equal to $-E/R$. In order to study the effect of different existing functional groups in the resulted PAs on their thermal stability, the thermal kinetic investigation was carried out using the Coats and Redfern method (Eq. 1) (Shih and Chieh 2007). The results are listed in Table 5.

The correlation coefficient, r, computed using least square method for n value which gave the best fit ($r \approx 1$) was chosen as the order parameter for the decomposition stage in all cases by plotting the left-hand side of Eq. 1 versus $-1/T$ (Fig. 4).

α and φ are the fractions of the sample decomposed at time t and the linear heating rate, respectively. R is the gas constant in cal mol^{-1} K^{-1} and E is the activation energy in kcal mol^{-1}. A plot of $\ln[-\ln(1-\alpha)/T^2]$ versus $-1/T$ was found to be linear; 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 kcal mol^{-1} K^{-1} was calculated by using Eq. 2 where K_B is the Boltzmann constant, h is the Plank's constant and T_S is the DTG peak temperature.

$$\Delta S = R\ln\left(\frac{Ah}{K_B T_S}\right) \quad (2)$$

The other kinetic parameters such as enthalpy of activation (ΔH), and Gibbs free energy (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 5.

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. A positive value of ΔS indicates a malleable activated compound that leads to a large number of degrees of freedom of rotation and vibration. On the other hand, a negative value of ΔS indicates a highly ordered activated complex, and the degrees of freedom of rotation as well as of vibration are less than that in the non-activated complex (Refat et al. 2007).

Table 5 Kinetic parameters for the degradation of PAs determined using the Coats and Redfern method

Polymer	Parameter					r
	E (kcal mol^{-1})	A (s^{-1})	ΔS (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔG (kcal mol^{-1})	
PA3aIA	27.3	8.98×10^5	−0.03	26.5	38.0	0.98
PA3dID	15.5	60.7	−0.05	14.7	34.4	0.99

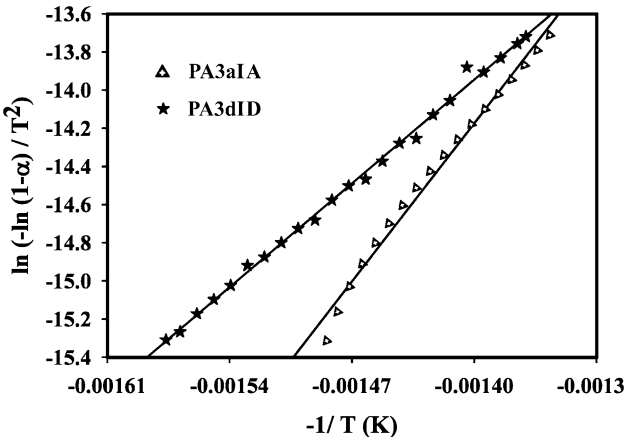


Fig. 4 Plot of $\ln[-\ln(1-\alpha)/T^2]$ against $-1/T$ for **PA3aIA** and **PA3dID**

Conclusion

Among the synthetic PAs, only those containing the naturally occurring (L)-α-amino acids, being structurally close to the natural polypeptides, possess potentially degradable linkages that make them suitable as biomaterials (Cianga 2003). In this work, we have effectively synthesized a series of novel biocompatible and optically active aromatic PAs via polycondensation reaction of chiral diacid and various diisocyanates under microwave irradiation which is comparable to conventional heating method. Microwave heating is an expedient and facile method (shorter reaction time and high efficiency of energy) for polycondensation reactions. Flexible pendant groups of the resulting polymers disturbed the strong interchain forces and inherent macromolecular rigidity. Since the resulting polymers showed good optical properties and thermal stability, they can be used as a chiral stationary phase in chromatography technique for the separation of enantiomers in racemic mixtures. Because of the existence of amino acid in the polymer structure, these polymers are predictable to be biodegradable, and therefore are eco-friendly polymers. Thermogravimetric studies on polymers determine the thermal stability of polymers, and have been extensively used for such studies. In this paper, we carried out a study of the temperature integral for the determination of the activation energy. For this purpose, we used Coats and Redfern method which has less error than other methods.

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