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Fast Synthesis, Using Microwave Induction Heating in Ionic Liquid and Characterization of Optically Active Aromatic Polyamides

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A simple pathway for the preparation of optically active aromatic polyamides (PAs) is reported. A fairly inexpensive and readily accessible molten ionic liquid, tetrabutylammonium bromide (TBAB) was used for the synthesis of polymers. PAs were synthesized from polycondensation of (2S)-5-[4-(4-methyl-2-phthalimidyl pentanoylamino)benzoylamino]isophthalic acid with various commercially available diisocyanates in *N*-methylpyrrolidone (NMP) as common organic solvent and molten TBAB as a green medium with or without dibutyltin dilaurate as a catalyst under microwave irradiation. Polycondensation process in TBAB is safe and green since toxic and volatile organic solvent such as NMP was eliminated. Various PAs were obtained with high yields and moderate inherent viscosities in the ranging from 0.26 to 0.91 dL/g. The obtained polymers were characterized by FT IR, specific rotation measurements, ¹H NMR, elemental and thermogravimetric analysis techniques and differential scanning calorimetry.

Keywords: Optically active polymers, green chemistry, aromatic polyamide, ionic liquid, microwave irradiation, thermogravimetric analysis

1 Introduction

The field of microwave-assisted organic chemistry is rather young. In the recent years, numerous uses of the microwave (MW) technique have appeared, essentially drying different types of material such as paper, rubber, tobacco, leather, textile, treatment of elastomers and vulcanization, extraction, polymerization and food processing industries (1–5). MW energy in the chemical laboratory has proven to be a good power source to increase reaction rates and thereby decrease the reaction time. Moreover, it has also been an attractive tool for enhancing the selectivity in many processes (6–9). In the literature, many authors described the successful application of MW irradiation leading to accelerated synthesis of different classes of organic compounds, as well as macromolecules because of saving of energy, compared to traditional conductive heating (10–14).

Recently, the use of ionic liquids (ILs) as solvent and catalyst has attracted much attention in the field of green chemistry. They can be introduced as low melting organic

salts and consist of bulky organic cations in combination with organic or inorganic anions (15, 16). The physical and chemical properties of ILs, such as the melting point, density, solubility, viscosity, polarity, hydrophobic properties, and chemical affinity, can be specifically varied over a wide range through the careful design of cationic structures and the selection of suitable anions therefore, for this reason, they are called ‘green’ solvents, in contrast to traditional volatile organic compounds (17–20). Several chemical processes have been performed in ILs, such as electrochemical process, extraction, Diels-Alder, Wittig reactions, benzoin condensations, hydrogenation reactions, inorganic synthesis; enzyme catalyzed reactions, as well as polymerization reactions (21–25). Polymerization in ILs, in comparison with volatile organic solvents, may also improve the chemistry of synthesis and quality of the resulting polymers, such as higher reaction rate, yield, purity, molecular weight and easier recycling and recovering the reaction medium, ILs (26–28).

Tetraalkylammonium salts like tetrabutylammonium bromide (TBAB) are bulky in nature and are known to orient water molecules around them depending on their alkyl chain. They are extensively used for many applications, such as lubricating materials, cationic surfactants, fabric softeners, and electrostatics and adhesion promoters in asphalt, corrosion inhibitors, and many others. Recently, new

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applications for quaternary ammonium based **ILs**, derived from common, ammonium-based cations with a bromide anion as a reaction medium for step growth polymerization, have been presented (29–32).

In the past decades, with the extension of technology, more and more attention has been focused on optically active polymers, such as polypeptides and polynucleotides because of their large potential applications (33). Optically active polymers often play important roles as key basic materials for well-defined high-performance polymers (34, 35). They have found prosperous applications in chiral chromatographic separations and have shown potential use in chiral catalytic systems, liquid crystals, optical switches and biomedical devices. In a few synthetic methodologies for the preparation of optically active polymers, the simplest method is polymerization of optically active monomers (36, 37).

Aromatic polyamides (**PA**s) are a class of polymeric material with high temperature resistance, low flammability and excellent mechanical properties (38, 39). However some of difficulties of aromatic **PA**s are their poor solubility in common organic solvents and their extremely high transition temperatures (40). Bulky pendant groups in **PA**s restricts the formation of interchain hydrogen bonds, and prevents an efficient molecular packing, which are responsible of the **PA**s inflexibility and cause to removing the solubility and meltability problems (41, 42).

The purpose of the present work is utilization of **MW** energy for polycondensation of chiral diacid monomer with different diisocyanates for preparation of optically active **PA**s. In view of the emerging importance of the **IL**s as reaction media and our general interest in **MW**-assisted chemical processes, we decided to investigate a simple, rapid, green and efficient methodology for the synthesis of optically active **PA**s in **IL** under **MW** irradiation.

2 Experimental

2.1 Materials and Methods

Reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI) and Riedel-deHaen AG (Seelze, Germany). *N,N*-dimethylformamide (DMF) and 1-methyl-2-pyrrolidone (NMP) were dried over BaO and then were distilled under reduced pressure. TBAB (mp = 100–103°C) and dibutyltin dilaurate (DBTDL) were purchased from Merck Co. (Darmstadt, Germany) and were used without further purification.

The apparatus used for the polycondensation was a Samsung microwave oven (2450 MHz, 900 W). Proton nuclear magnetic resonance (¹H-NMR, 500 MHz) spectra were recorded in dimethyl sulfoxide-d₆ (DMSO-d₆) solution using a Bruker (Germany) Avance 500 instrument. Proton resonances are designated as singlet (s),

doublet (d), doublet of doublet (dd) and multiplet (m). FT IR spectra were recorded on Jasco-680 spectrophotometer (Japan). 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), strong (s) and broad (br). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Germany) at concentration of 0.5 g/dL at 25°C. Specific rotations were measured by a Jasco Polarimeter (Japan). All the polymerization reactions were carried out in a hood with strong ventilation. All melting points were taken with a melting-point apparatus (Gallenham, England). Quantitative solubility was determined with 0.05 g of the polymer in 1 mL of the solvent. 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. Elemental analyses were performed by Tarbit Moalem University, Tehran, Iran.

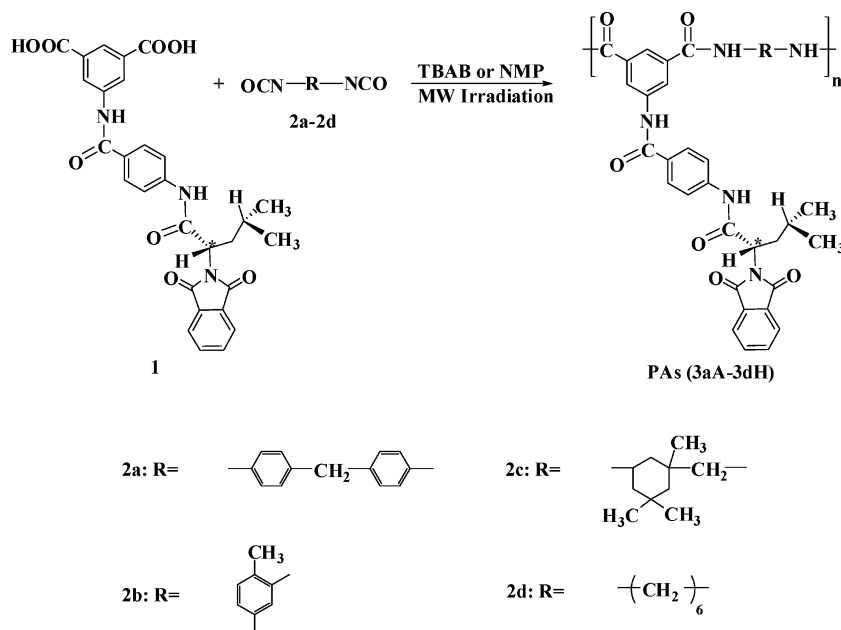
2.2 Monomer Synthesis

(2*S*)-5-[4-(4-Methyl-2-phthalimidylpentanoylamino)benzoylamino]isophthalic acid (**1**) was prepared according to our previous work (43).

2.3 Polymer Synthesis

2.3.1. Method I: Polymerization reaction in TBAB as an *IL* under *MW* irradiation

Into a porcelain dish was placed diacid **1** (0.10 g, 1.84 × 10⁻⁴ mol), and TBAB (0.23 g, 6.98 × 10⁻⁴ mol). After the mixture was completely ground, DBTDL (0.02 g, 3.01 × 10⁻⁴ mol) was added, and the mixture was ground for 5 min; then, 4,4'-methylene diphenyl diisocyanate (MDI) (**2a**) (0.05 g, 1.84 × 10⁻⁴ mol) was added, and the mixture was ground again for an additional 2 min. The reaction mixture was irradiated in the microwave oven for 4 min. at 100% (900 W) of its power level. The resulting product was isolated by the addition of 15 mL of methanol. It was then filtered and dried at 80°C for 8 h in vacuum; this yielded 0.14 g (96%) of white **PA3aIE**. The aforementioned polymerization was repeated, but the reaction mixture was irradiated in a microwave oven with TBAB without a catalyst. The optimized reaction conditions according to reaction time and power level were selected for the polymerization of diacid monomer **1** with other diisocyanates such as toluene diisocyanate (TDI) (**2b**), isophorone diisocyanate (IPDI) (**2c**) and hexamethylene-1,6-diisocyanate (HDI) (**2d**). The other **PA**s were prepared with an analogous procedure.



Sch 1. Polycondensation reactions of monomer **1** with aliphatic and aromatic diisocyanates.

Table 1. Synthesis and some physical properties of **PA3aIA-PA3dIH** prepared in TBAB under MW irradiation (method I)

Diisocyanate	Polymer	Catalyst	Yield (%)	Inherent Viscosity ^b (dL/g)	$[\alpha]_{Na,589}^{25,b}$	$[\alpha]_{Hg}^{25,b}$	Color
2a	PA3aIA ^c	No. Cat	85	0.91	-8.8	-19.0	Off-W ^e
2b	PA3bIB ^d	No. Cat	96	0.38	-10.0	-27.6	W
2c	PA3cIC ^d	No. Cat	87	0.49	-13.6	-26.1	Y ^f
2d	PA3dID ^d	No. Cat	86	0.31	-9.9	-32.5	Off-W
2a	PA3aIE ^c	DBTDL	96	0.87	-13.6	-11.2	W
2b	PA3bIF ^d	DBTDL	94	0.36	-8.8	-26.0	W
2c	PA3cIG ^d	DBTDL	95	0.45	-11.3	-14.9	Off-W
2d	PA3dIH ^d	DBTDL	94	0.38	-9.5	-10.8	Y

^a Measured at a concentration of 0.5 g/dL in DMF at 25°C.

^b Measured without filter.

^c This polymer was precipitated in MeOH.

^d These polymers were precipitated in MeOH/Water.

^e W = White; ^f Y = Yellow.

Table 2. Synthesis and some physical properties of **PA3aIA-PA3dIH** prepared in NMP under MW irradiation (method II)

Diisocyanate	Polymer	Catalyst	Yield (%)	Inherent Viscosity ^b (dL/g)	$[\alpha]_{Na,589}^{25,b}$	$[\alpha]_{Hg}^{25,b}$	Color
2a	PA3aIIA ^c	No. Cat	87	0.60	-12.3	-14.1	Y ^e
2b	PA3bIIB ^c	No. Cat	70	0.28	-9.4	-10.7	B ^f
2c	PA3cIIC ^d	No. Cat	62	0.26	-17.0	-28.8	W ^g
2d	PA3dIID ^c	No. Cat	75	0.31	-16.1	-35.4	W
2a	PA3aIIE ^c	DBTDL	89	0.68	-8.7	-12.3	Y
2b	PA3bIIF ^c	DBTDL	78	0.31	-11.4	-12.0	B
2c	PA3cIIG ^d	DBTDL	80	0.33	-7.5	-11.5	Off-W
2d	PA3dIIH ^c	DBTDL	88	0.36	-9.4	-10.3	Off-W

^a Measured at a concentration of 0.5 g/dL in DMF at 25°C.

^b Measured without filter.

^c These polymers were precipitated in MeOH/Water.

^d This polymer was precipitated in MeOH.

^e Y = Yellow.

^f B = Brown.

^g W = White.

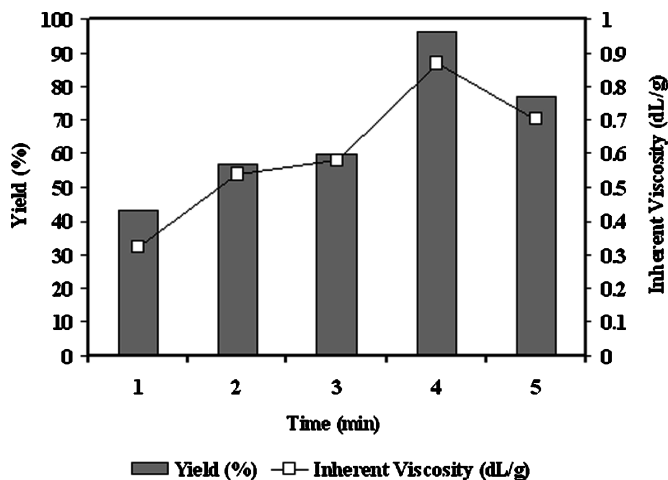


Fig 1. The effect of reaction time on the inherent viscosity and yield of PAs based on MDI by method I in the presence of DBTDL as a catalyst.

2.3.2. Method II: Polymerization reaction in NMP as solvent under MW irradiation

The PAs were prepared by the following general procedure (taking **PA3dIIIH** as an example): into a porcelain dish monomer **1** (0.10 g, 1.84×10^{-4} mol) and 0.20 mL of NMP were placed and was ground for two min. Then, DBTDL (0.02 g, 3.01×10^{-4} mol) and a solution of HDI (**2d**) (0.04 g, 1.84×10^{-4} mol) in 0.20 mL of dry NMP were added, and the mixture was pulverized again for an additional 2 min. The reaction mixture was irradiated in the microwave oven for 4 min at 100% of its power level (900 W). The resulting product was precipitated by the addition of 10 mL of methanol and 5 mL of water. It was then filtered and dried at 80°C for 8 h in vacuum; this yielded 0.12 g (88%) of off-white **PA3dIIIH**. The above polymerization was repeated, but the reaction mixture was irradiated in a microwave oven without catalyst. For each method, the

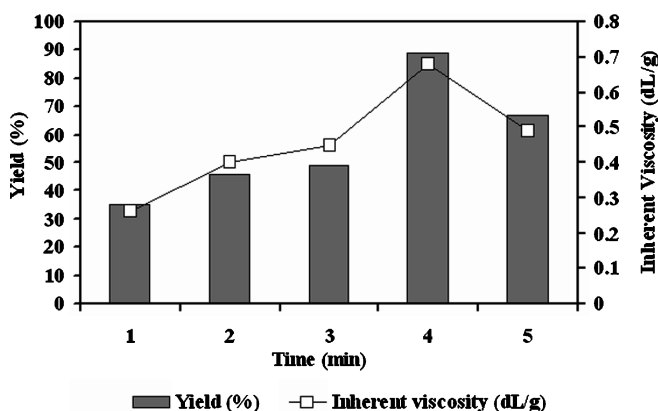


Fig 2. The effect of reaction time on the inherent viscosity and yield of PAs based on MDI by method II in the presence of DBTDL as a catalyst.

optimized reaction conditions according to reaction time and power of radiation were used for the polymerization of diacid monomer **1** with other diisocyanates such as MDI, TDI and IPDI.

PA3aIE: FT IR (KBr, cm^{-1}): 3307 (m, br), 2924 (w), 1900 (w), 1776 (w), 1715 (s), 1655 (m), 1594 (m), 1541 (m), 1410 (m), 1305 (s), 1233 (m), 1101 (w), 1017 (w), 761 (w). ^1H 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). Elemental analysis calculated for $(\text{C}_{42}\text{H}_{35}\text{N}_5\text{O}_6)_n$ (705.76 g/mol)_n: Calcd. C 71.48, H 5.00, N 9.92; Found C 71.65, H 5.31, N 11.32.

PA3bIF: FT IR (KBr, cm^{-1}): 3306 (m, br), 3116 (w), 2959 (m), 2593 (w), 1915 (w), 1776 (m), 1716 (s), 1644 (s), 1537 (s), 1384 (m), 1123 (w), 1078 (w), 760 (s), 719 (s), 670 (s).

PA3cIG: FT IR (KBr, cm^{-1}): 3372 (m, br), 3117 (w), 2955 (w), 1775 (w), 2607 (w), 2346 (w), 1777 (m), 1716 (s), 1557 (m), 1384 (s), 1245 (m), 761 (m), 619 (m).

PA3dIH: FT IR (KBr, cm^{-1}): 3324 (m, br), 3117 (w), 2933 (m), 2857 (w), 1776 (w), 1716 (s), 1615 (w), 1384 (s), 1248 (m), 1123 (w), 1077 (w), 1016 (s), 761 (m), 719 (m). ^1H 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). Elemental analysis calculated for $(\text{C}_{35}\text{H}_{37}\text{N}_5\text{O}_6)_n$ (623.70 g/mol)_n: Calcd. C 67.40, H 5.98, N 11.23; Found: C 65.66, H 5.20, N 10.89.

3 Results and Discussion

3.1 Monomer Synthesis

The diacid monomer **1** was prepared according to a previously reported five-step process (43).

3.2 Polymer Synthesis

The use of **ILs** in synthesis is very important in view of today's environment-conscious propensities. Beyond the fact that **ILs** have been considered to be green solvents, one of their other advantages is that, unlike organic solvents, they can be "tailored" by selecting the proper cation and anion species. Furthermore, **ILs** are inexpensive to

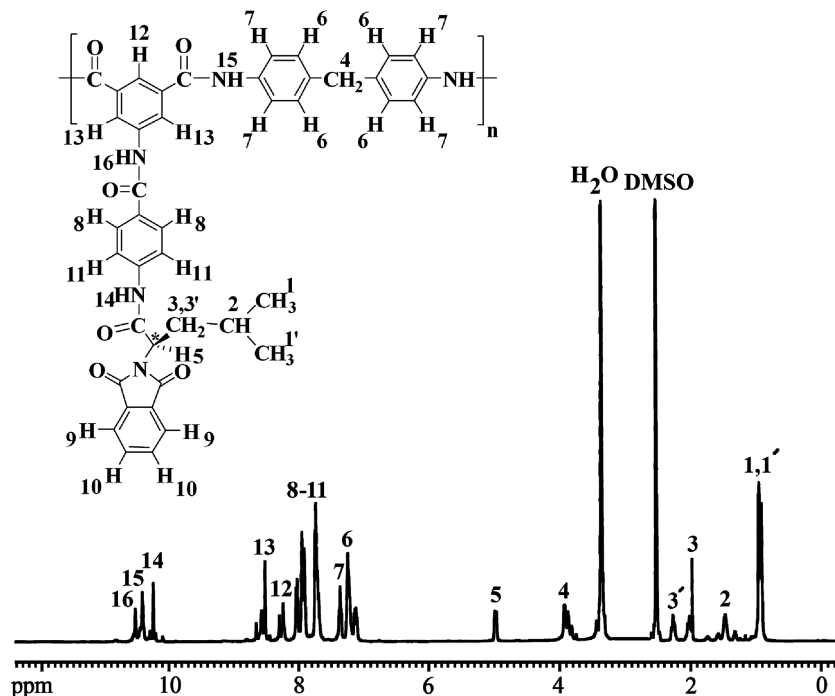


Fig 3. $^1\text{H-NMR}$ (500 MHz) spectrum of PA3aIE in DMSO- d_6 at RT.

prepare and easy to recycle. It is important to note that because of the highly polar nature of these solvents, polymers have higher solubility in them and they could absorb the microwave energy efficiently. Moreover, the risk of an explosion caused by rapid increase of vapor pressure of the solvent can be avoided since ionic liquids have no measurable vapor pressure, so we decided to synthesize optically active PAs bearing pendant (2S)-5-[4-(4-methyl-2-phthalimidylpentanoylamino)benzoylamino]benzoylamine via polycondensation of diacid **1** with diisocyanates **2a–2d** under microwave irradiation in TBAB as an IL and in NMP as a common organic solvent as presented in Scheme 1.

The obtained data from the polymerization reactions in TBAB and NMP under microwave irradiation are listed in Tables 1 and 2, respectively.

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 in the absence of DBTDL as a catalyst in TBAB and NMP as reaction media, was studied (Figs. 1 and 2).

These figures show that the optimum results under microwave irradiation were obtained after 240 s at 100% of power level (900 W) in both methods. 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 polymerization reactions of monomer **1** with TDI, IPDI and HDI were also carried out with the same procedure according to the optimized conditions. According to Tables 1 and 2 in the

presence of catalyst, obtain high yield or good inherent viscosity. It is clear that PAs including MDI provided higher viscosities than the viscosities of PAs-based on TDI, IPDI or HDI.

All of the PAs are optically active, because they have a chiral center in their pendant groups. They showed different specific rotations. Several factors effect on specific rotation such as monomer, catalyst, reaction time and temperature. As shown in Tables 1 and 2, it is interesting to mention that, the specific rotations of polymers based the same diacid prepared under different conditions were different. On the other hand, under the 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.

3.3 Polymer Characterization

3.3.1. FT IR and $^1\text{H-NMR}$ study

The structure of the PAs was confirmed by FT IR and $^1\text{H-NMR}$ spectroscopic techniques. All of these PAs exhibit

absorption around 1715 cm^{-1} which are commonly attributed to the stretches of carbonyl groups. The two absorption bands at 2900 and 2950 cm^{-1} are related to the corresponding C-H stretching vibration. Bands of amide N-H groups appeared at around $3300\text{--}3400\text{ cm}^{-1}$. Figure 3 shows the $^1\text{H-NMR}$ (500 MHz) spectrum of **PA3aIE**. In the $^1\text{H-NMR}$ spectrum of this polymer, appearances of the N-H protons of amide groups at 10.23, 10.39 and 10.51 ppm as three singlet peaks, respectively, indicate the presence of amide groups in the polymer's side chain as well as the main chain. The resonance of aromatic protons appeared in the range of 7.00–8.50 ppm. The proton of the chiral center appeared as doublet of doublet at 5.00 ppm. The resonance of the CH_2 protons of **PA3aIE** appeared as a singlet peak at 3.90 ppm.

3.3.2. 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, DMSO, *N,N*-Dimethylacetamide (DMAc), NMP, pyridine and in H_2SO_4 at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, acetone, cyclohexane, tetrahydrofuran and water. Some polymers were partially soluble in methanol and ethanol and precipitated in MeOH/ H_2O mixture. The good solubility of resulting **PAs** is due to the presence of bulky side group which prevent the packing of the macromolecules through hydrogen bonds between amide groups in the chain and thus facilitate the diffusion of solvent molecules among the polymer chains.

3.3.3. 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 $10^\circ\text{C}/\text{min}$. The temperature of 5% and 10% weight loss together with char yield at 800°C have been calculated by means of thermograms. Figure 4 shows the TGA thermograms of **PA3aIE** and **PA3dIH**.

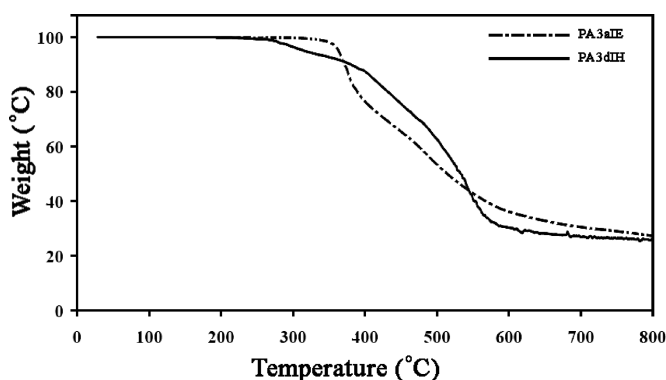


Fig 4. TGA thermograms of **PA3aIE** and **PA3dIH** under a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$.

Table 3. Thermal properties of **PA3aIE** and **PA3dIH**

Polymer	T_5^a ($^\circ\text{C}$)	T_{10}^b ($^\circ\text{C}$)	Char yield ^c (%)	T_g^d ($^\circ\text{C}$)	LOI ^e
PA3aIE	363	371	29	200	29
PA3dIH	315	380	27	180	28

^aTemperature at which 5% wt loss was recorded by TGA at a heating rate of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere.

^bTemperature at which 10% wt loss was recorded by TGA at a heating rate of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere.

^cPercentage weight of material left undecomposed after TGA analysis at maximum temperature 800°C in a nitrogen atmosphere.

^dGlass-transition temperature recorded at a heating rate of $20^\circ\text{C}/\text{min}$ in a nitrogen atmosphere.

^eLimiting oxygen index (LOI) evaluating at char yield at 800°C .

The thermoanalyses data of these polymers are summarized in Table 3. Results show that the obtained polymers with rigid aromatic spacer have higher thermal stability compared to other polymers without spacer (44, 45). Char yield can be used as criteria for evaluating limiting oxygen index (*LOI*) of the polymers in accordance with Van Krevelen and Hoftyzer equation (46). $LOI = 17.5 + 0.4 CR$ where $CR = \text{char yield}$. All of the polymers had *LOI* values calculated based on their char yield at 800°C were higher than 28. On the basis of *LOI* values, such macromolecules can be classified as self-extinguishing polymers. T_{10} ($^\circ\text{C}$), char yield and *LOI* of **PA3aIE** and **PA3dIH** are in the range of $371\text{--}380^\circ\text{C}$, 29–27 and, 29–28, respectively.

According to Table 3 it is clear that polymer based on MDI has better thermal stability and higher *LOI* as compared to **PA** based on HDI. It could be pertained to aromatic, rigid structure of diisocyanates compare to aliphatic, flexible structure of diisocyanates. The T_g s of the **PAs** were determined by DSC and the results are given in the Table 3. The DSC analyses for **PAs** show T_g around $180\text{--}200^\circ\text{C}$.

4 Conclusions

In summary, several optically active **PAs** were prepared from polycondensation reaction of chiral diacid **1** with several diisocyanates in the presence of small amount of molten TBAB as green medium (method I) under microwave irradiation and the results are comparable with polymerization in NMP as a solvent (method II). This methodology (method I) proffers significant improvements with consideration to yield of products, inherent viscosities, thermal stability, simplicity in operation, cost efficiency and green aspects eluding toxic catalysts and solvents. Incorporating of the bulky side chain in the **PAs** cause an increase in the solubility, while maintaining good thermal stability. In addition, because of the existence of chiral center and optical activity of these polymers, they have the potential to be used as a chiral stationary phase in

chromatography technique for the separation of racemic mixtures.

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