

Rapid Formation of Optically Active and Organosoluble Polyamides Containing L-Alaninephthalimide Side Chain via Microwave Irradiation

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Abstract: Several aromatic optically active polyamides (PA)s were synthesized from 5-(2-phthalimidyl)propano-ylamino)isophthalic acid with various aromatic diamines via direct polycondensation with triphenyl phosphite and pyridine in the presence of calcium chloride and *N*-methyl-2-pyrrolidone under microwave irradiation and conventional heating conditions. Under the optimized conditions, the reaction mixture was irradiated for 2 min. with a 100% irradiation power (900 W). The resulting polymers were obtained in high yield and moderate inherent viscosity ranging from 0.35 to 0.60 dL/g. All synthesized polymers showed excellent solubility in amide-type solvents. Thermogravimetric analysis revealed a 10% weight loss temperature and char yield at 600 °C in a nitrogen atmosphere of > 350 °C and > 58%, respectively, which suggests that the resulting PAs have good thermal stability.

Keywords: chiral, direct polycondensation, inherent viscosity, microwave irradiation, green chemistry, optically active polymers, polyamides.

Introduction

Polyamides (PA)s are certainly one of the most successful classes of high-temperature polymers and have found extensive use in the aviation, automotive, and electronic industries. They have been well-known for their thermal stability, chemical resistance, and low flammability, along with excellent mechanical properties.¹⁻³ However, most of them have high melting or softening temperatures (T_g 's) and are insoluble in most organic solvents because of the rigidity of the backbone and strong interchain interactions. These properties generate them commonly intractable or difficult to process, thus limiting their applications.⁴ Attempts to increase the solubility and processability of PAs have been made through the introduction of some structural components such as flexible chains,^{5,6} noncoplaner units,^{7,8} bulky pendent groups,⁹⁻¹² heterocyclic rings¹³ and synthesis of cardo polymer,¹⁴ which this leads to a decrease of order along the chain and a reduced crystallinity.

The synthesis and properties of novel chiral polymers is of special attention from the point of view of material science, 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. A direct and efficient method for synthesizing chiral polymers is to intro-

duce chiral elements into the polymer backbone or side chains.¹⁵⁻²⁰ Amino acids are constituents of proteins, typical biological macromolecules, and their secondary and higher order structures are assembled through intra- and interchain associations by noncovalent forces, such as hydrogen-bonding, hydrophobic stacking, electrostatic, and dipolar interactions. Amino acid based synthetic polymers are of significance since these combinations make new nonbiological macromolecules with biomimetic structures and properties and therefore have many potential applications, including optical resolution, controlled drug release systems, and biologically active and degradable materials.²¹

Recently there has been increasing attention in applying microwave energy to polymerization reactions.²²⁻²⁶ Industrial employ of irradiation as an affordable alternative to thermal heating of the polymerization process has created interests because quick heating, improved efficiency, high temperature homogeneity, energy savings and trapped volatiles and material degradation with advantages of the eco-friendly approach, termed green chemistry.

In continuation of our study to synthesize and characterize variety of optically active polymers by incorporation of amino acid segments in polymer's main chain by different methods,¹⁵⁻¹⁸ the main objective of this work is to synthesize a new series of wholly aromatic PAs containing amino acid, L-alanine and phthalimide groups in the side chain of the polymers by using microwave irradiation and comparing it with conventional heating polymerization.

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Recently, we have also reported the synthesis of PAs from 5-(2-phthalimidylpropanoylamino)isophthalic acid and various diamines using 1,3-diisopropylimidazolium bromide under microwave irradiation as well as conventional heating.²⁷

Experimental

Materials. All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI, USA), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. *N*-Methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc) were dried over BaO, followed by fractional distillation. 1,5-Naphthalenediamine (6a), and 4,4'-diaminodiphenylmethane (6b) were purified by recrystallization from water. Benzidine (6c) was purified by recrystallization from ethanol. 4,4'-Diaminodiphenylether (6d), 2,5-diaminotoluene (6f), 1,3-phenylenediamine (6g), and 1,4-phenylenediamine (6h) were purified by sublimation.

Characterization. The apparatus used for the polycondensation was a Samsung (Seoul, South Korea) microwave oven (2,450 MHz, 900 W). Proton nuclear magnetic resonance (¹H NMR, 500 MHz) spectra were recorded in dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) solution using a Bruker (Ettlingen, Germany) Avance 500 instrument. FTIR spectra were recorded on (Jasco-680, Japan) spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wavenumbers (cm⁻¹). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Cannon, Mainz, Germany) at concentration of 0.5 g/dL at 25 °C. Specific rotations were measured by a Jasco Polarimeter (Toyonaka, Osaka, Japan). Thermal gravimetric analysis (TGA) data for polymers were taken on Perkin Elmer Thermal Gravimetric Analyzer (Karlsruhe, Germany) in nitrogen atmosphere at a rate of 10 °C/min by the Research Institute of Polymer and Petrochemical of Iran (IPPI). Differential scanning calorimetry (DSC) data were recorded on a DSC-PL-1200 instrument (London, UK) under nitrogen atmosphere by IPPI. 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 Iran Polymer and Petrochemical Research Institute, Tehran, Iran.

Monomer Synthesis. 5-(2-Phthalimidylpropanoylamino)-isophthalic acid (**5**) as an optically active diacid was prepared according to our previous published work.²⁸

Polymer Synthesis. All of the polymers were synthesized with two different methods.

Method I: Polymerization under Microwave Irradiation. The PAs were prepared by the following general procedure: as an example for the preparation of **PA7aI**, 0.100 g (2.61 × 10⁻⁴ mol) of diacid **5**, 0.041 g (2.61 × 10⁻⁴ mol) of diamine **6a**, 0.06 g of calcium chloride and 0.17 mL (6.54 × 10⁻⁴ mol) of

triphenyl phosphite (TPP) were placed in a porcelain dish and the mixture was ground completely, then 0.15 mL of pyridine (Py), and 0.25 mL of NMP was added and the mixture was ground for 3 min. The reaction mixture was irradiated in a microwave oven for 2 min. on 100% power level of microwave apparatus. The resulting viscous solution was poured into 30 mL of methanol, filtered, dried under vacuum to give 0.126 g (89%) of **PA7aI**.

Method II: Polymerization under Conventional Heating. A mixture of 0.100 g (2.61 × 10⁻⁴ mol) of diacid **5**, 0.041 g (2.61 × 10⁻⁴ mol) of diamine **6a**, 0.17 mL (6.54 × 10⁻⁴ mol) of TPP, 0.20 mL of Py, 0.06 g of calcium chloride and 0.5 mL of NMP was refluxed for 5 h. After cooling, the reaction mixture was poured into 30 mL of methanol with constant stirring, and the precipitate was washed thoroughly with methanol and hot water, filtered, and dried under vacuum to give 0.130 g (92%) of **PA7aII**.

FTIR (KBr): 3319 (N-H, amide), 2988 (C-H, alkyl), 1779 and 1714 (C=O, imide), 1653 (C=O, amide), 1598 and 1524 (C=C, aromatic) 1386 cm⁻¹ (C-N, imide).

The other PAs, **PA7b-PA7h** were prepared with an analogous procedure.

PA7b: FTIR (KBr): 3307 (N-H, amide), 2976 (C-H, alkyl), 1779 and 1715 (C=O, imide), 1665 (C=O, amide), 1594 and 1513 (C=C, aromatic), 1375 cm⁻¹ (C-N, imide). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 1.62-1.63 (d, br, 3H, CH₃, *J* = 7.13 Hz), 3.89 (s, 2H, CH₂), 4.98-5.02 (q, 1H, CH, *J* = 7.01 Hz), 7.21-7.22 (d, 4H, Ar-H, *J* = 8.4 Hz), 7.68-7.69 (d, 4H, Ar-H, *J* = 8.4 Hz), 7.86-7.88 (m, 2H, Ar-H), 7.91-7.95 (m, 2H, Ar-H), 8.21 (s, 1H, Ar-H), 8.29 (s, 2H, Ar-H), 10.25 (s, 1H, N-H), 10.39 (s, 2H, N-H).

PA7c: FTIR (KBr): 3329 (N-H, amide), 2976 (C-H, alkyl), 1779 and 1713 (C=O, imide), 1661 (C=O, amide), 1594 and 1501 (C=C, aromatic), 1386 cm⁻¹ (C-N, imide).

PA7d: FTIR (KBr): 3332 (N-H, amide), 2973 (C-H, alkyl), 1778 and 1714 (C=O, imide), 1668 (C=O, amide), 1593 and 1511 (C=C, aromatic), 1388 cm⁻¹ (C-N, imide). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 1.53-1.54 (d, br, 3H, CH₃, *J* = 7.13 Hz), 4.99-5.04 (q, 1H, CH, *J* = 7.03 Hz), 7.03-7.05 (d, 4H, Ar-H, *J* = 8.6 Hz), 7.80-7.82 (d, 4H, Ar-H, *J* = 8.6 Hz), 7.88-7.89 (m, 2H, Ar-H), 7.93 (m, 2H, Ar-H), 8.30 (s, 1H, Ar-H), 8.33 (s, 2H, Ar-H), 10.28 (s, 1H, N-H), 10.52 (s, 2H, N-H).

PA7e: FTIR (KBr): 3338 (N-H, amide), 2977 (C-H, alkyl), 1777 and 1714 (C=O, imide), 1664 (C=O, amide) 1591 and 1523 (C=C, aromatic), 1388 cm⁻¹ (C-N, imide).

PA7f: FTIR (KBr): 3308 (N-H, amide), 2974 (C-H, alkyl), 1778 and 1712 (C=O, imide), 1655 (C=O, amide), 1594 and 1512 (C=C, aromatic), 1388 cm⁻¹ (C-N, imide).

PA7g: FTIR (KBr): 3397 (N-H, amide), 2969 (C-H, alkyl), 1780 and 1712 (C=O, imide), 1655 (C=O, amide), 1597 and 1533 (C=C, aromatic), 1384 cm⁻¹ (C-N, imide).

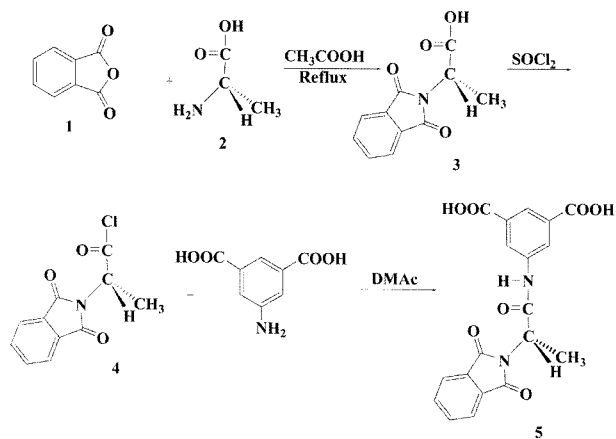
PA7h: FTIR (KBr): 3293 (N-H, amide), 2976 (C-H, alkyl), 1779 and 1711 (C=O, imide), 1656 (C=O, amide), 1597 and 1532 (C=C, aromatic), 1384 cm⁻¹ (C-N, imide).

Results and Discussion

Synthesis of Monomer. Dicarboxylic acid **5** was synthesized in three steps as reported previously (Scheme I).²⁸ In the first step the reaction of L-alanine with phthalic anhydride in acetic acid afforded the *N*-phthalimidylopropanoic acid (**3**). The acid chloride **4** was obtained in high yield by treatment of corresponding carboxylic acid with excess thionyl chloride, which was subsequently reacted with 5-aminoisophthalic acid in dry DMAc in the presence of triethylamine in a typical low-temperature condensation reaction.

The chemical structure of monomer and intermediate compounds was confirmed using ¹H NMR, ¹³C NMR, FTIR spectroscopy techniques and elemental analysis.

Synthesis of PAs. According to the Yamazaki-Higashi phosphorylation polyamidation technique, aromatic PAs containing optically active L-alaninephthalimide group were synthesized from diacid **5** with various aromatic diamines **6a-6h** by the direct polycondensation procedure in NMP solution containing dissolved CaCl₂, using TPP/Py as condensing agents by microwave heating (method I) and then this method was compared with the similar preparation

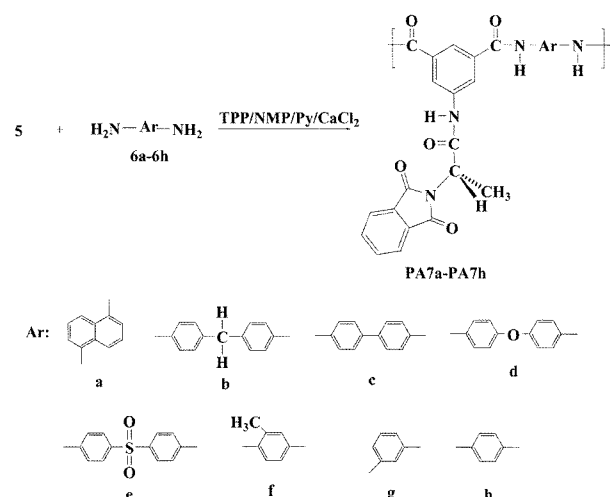


Scheme I. Synthesis of monomer **5**.

Table I. Synthesis and Some Physical Properties of PA7aI-PA7hI

Diamine	Polymer					
	Polymer	Yield (%)	η_{inh}^a (dL g ⁻¹)	$[\alpha]_{Na, 589}^{25, a}$	$[\alpha]_{Hg}^{25, b}$	Color
6a	PA7aI	89	0.52	+38.7	+80.2	Pale brown
6b	PA7bI	88	0.48	+50.8	+80.0	Off-White
6c	PA7cI	91	0.43	+31.2	+50.4	Off-White
6d	PA7dI	85	0.39	+21.9	+70.2	Off-White
6e	PA7eI	93	0.46	+20.5	+28.6	Off-White
6f	PA7fI	83	0.41	+22.8	+48.6	Off-White
6g	PA7gI	94	0.52	+34.2	+60.8	Pale brown
6h	PA7hI	85	0.48	+31.6	+56.2	Off-White

^aMeasured at a concentration of 0.5 g/dL in DMF at 25 °C. ^bWere measured without filter.



Scheme II. Polymerization reactions of monomer **5** with aromatic diamines.

using conventional heating (method II) (Scheme II). The microwave-assisted polycondensation reactions were performed under different conditions of the power of irradiation and reaction time to obtain the optimum conditions. The best conditions were selected as 2 min irradiation with 100% of the power level (900 W) of the apparatus. At high reaction time, products were dark and the reaction had low yield. When the reaction mixture was irradiated at 100% of power level (900 W) and duration times 3-6 min, PAs with brown color and yields below 60% were obtained. Overheating of the reaction mixture took place with evolution of vapor, leading to decomposition of the reaction mixture, which ultimately results in lower yields.

The results are summarized in Table I. Using microwave irradiation as the energy source is an efficient method for the preparation of aromatic PAs. This approach requires only a few minutes of reaction time in contrast to several hours (5 h) needed under traditional heating conditions which also uses the higher amount of Py and NMP. All

Table II. Synthesis and Some Physical Properties of PA7aII-PA7hII

Diamine	Polymer					
	Polymer	Yield (%)	η_{inh}^a (dL g ⁻¹)	$[\alpha]_{Na, 589}^{25, a}$	$[\alpha]_{Hg}^{25, b}$	Color
6a	PA7aII	92	0.58	+28.1	+55.5	Pale brown
6b	PA7bII	93	0.58	+30.2	+60.8	Off-White
6c	PA7cII	89	0.60	+18.2	+32.9	Pale brown
6d	PA7dII	86	0.36	+25.6	+60.1	Off-White
6e	PA7eII	91	0.58	+17.8	+24.9	Off-White
6f	PA7fII	85	0.49	+20.5	+42.1	Pale brown
6g	PA7gII	88	0.41	+22.1	+48.5	Pale brown
6h	PA7hII	80	0.35	+18.9	+44.3	Off-White

^aMeasured at a concentration of 0.5 g/dL in DMF at 25 °C. ^bWere measured without filter.

polyamidations proceeded in homogeneous, transparent and viscous solutions throughout the reaction, and the PAs were isolated in quantitative yields.

To compare the microwave-assisted polycondensation method with conventional heating technique, the polymerization reactions were also performed under classical heating method. In this method polymerization reactions occurred at high temperature for 5 h. The reaction yields and some physical data of this method are listed in Table II. We obtained comparable results from the point of view of yield and inherent viscosity of the PAs with reducing reaction time by several orders of magnitude under microwave conditions. These PAs had inherent viscosities between 0.35 and 0.60 dL/g. The structure of PAs was confirmed by FTIR and ¹H NMR spectroscopies and elemental analysis.

The incorporation of chiral unit into polymer backbone was confirmed by measuring their specific rotation (Tables I and II). The specific rotation of polymers based on different diamines and diverse methods showed random changes. These observations are the result of different polymers structure, inherent viscosities and reaction conditions. 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. All of the PAs show optical rotation and their specific rotations were in the range of +20.5 to +50.8 under sodium lamp.

Polymer Characterization. The structure of the PAs was confirmed by FTIR and ¹H NMR spectroscopy analysis. All of these PAs exhibited absorption around 1779-1653 cm⁻¹

are commonly attributed to the symmetric and asymmetric stretches of carbonyl groups. The presence of the imide heterocycle in these polymers was revealed by the absorption of 1380-1370 and 715-725 cm⁻¹ that belong to carbonyls bending of imide. Bands of amide N-H groups appeared around 3400-3300 cm⁻¹. The PA7e showed characteristic absorptions at 1317 and 1148 cm⁻¹ due to sulfone group of diamine 6e. Figures 1 and 2 show the ¹H NMR (500 MHz) spectra of polymers PA7b and PA7d, respectively. In the ¹H NMR spectrum of these two polymers, appearances of the N-H protons of amides groups at 10.25 and 10.39 ppm as two singlet peaks, respectively, which confirm the presence of amide group in the polymers side chain as well as main chain. The resonance of aromatic protons appeared in the range of 7.21-8.29 ppm. The proton of the chiral center appeared as quartet in the range of 4.98-5.02 ppm. The resonance of the CH₂ protons of PA7b appeared as a singlet peak at 3.89 ppm.

Elemental analysis data of PAs are listed in the Table III.

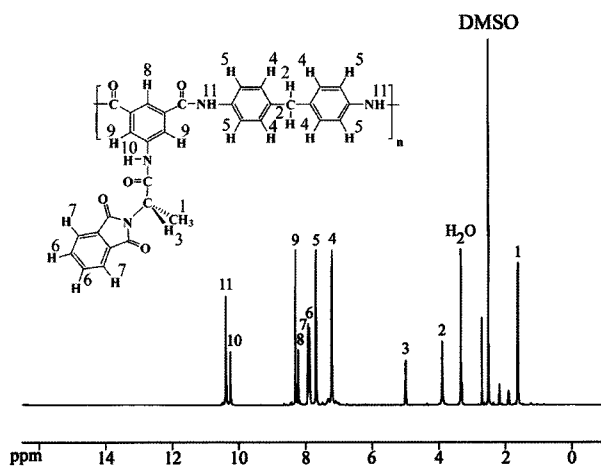


Figure 1. ¹H NMR (500 MHz) spectrum of PA7b in DMSO-*d*₆ at R.T.

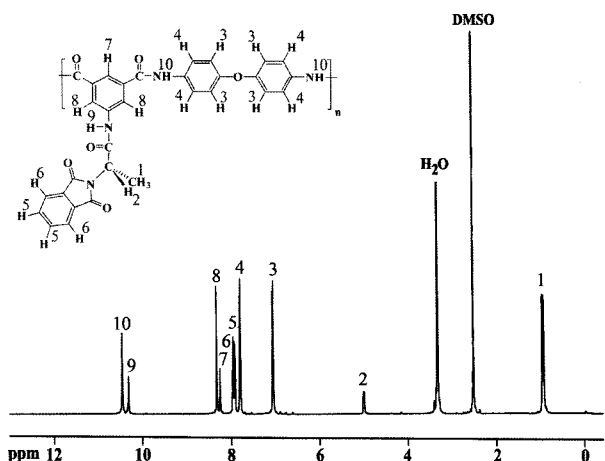


Figure 2. ^1H NMR (500 MHz) spectrum of PA7d in $\text{DMSO}-d_6$ at R.T.

Table III. Elemental Analysis of Typical PAs

Polymer	Formula		Elemental Analysis (%)		
			C	H	N
PA7a	$\text{C}_{29}\text{H}_{20}\text{N}_4\text{O}_5$	Calcd.	69.04	3.99	11.10
	$(504.5)_n$	Found	68.10	4.68	10.27
PA7f	$\text{C}_{26}\text{H}_{20}\text{N}_4\text{O}_5$	Calcd.	66.66	4.30	11.96
	$(468.5)_n$	Found	65.96	4.82	11.53

The chemical structures of these newly synthesized polymers were confirmed by the good agreement of the elemental analysis values with those of the calculated values.

Solubility of the PAs. All of the PAs showed excellent solubility in a variety of organic solvents such as *N,N*-dimethylformamide, DMAc, dimethyl sulfoxide, NMP, pyridine and in H_2SO_4 at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water. This can be attributed to the bulky substituent group in the side chain or backbone, which can reduce the interaction between polymer chains and allows the solvent molecules to diffuse into the polymer chains to enhance solubility.

Thermal Properties. The thermal properties of PA7cI and PA7eI were evaluated as representative polymers, by means of TGA, derivative of thermogravimetric (DTG) analysis and DSC analysis in a nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ and $20\text{ }^\circ\text{C}/\text{min}$, respectively. The thermal stability of the polymers were assessed based on temperature of 5% and 10% weight loss together with char yield at $600\text{ }^\circ\text{C}$. Figures 3 and 4 show the TGA/DTG thermograms of PA7cI and PA7eI, respectively. These polymers are stable up to $300\text{ }^\circ\text{C}$. The TGA measurement of the polymers revealed that these new polymers exhibited good thermal stability. The DSC analyses for PA7cI and PA7eI show T_g around $171\text{ }^\circ\text{C}$ and $113\text{ }^\circ\text{C}$, respectively. The thermoanalysis

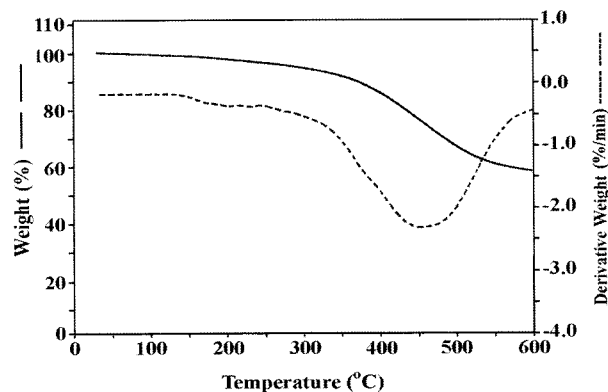


Figure 3. TGA/DTG of PA7cI at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under a nitrogen atmosphere.

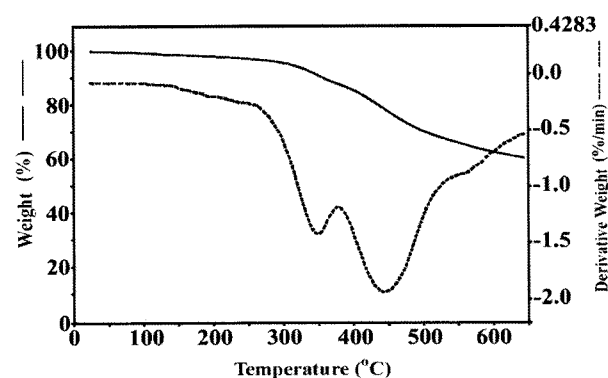


Figure 4. TGA/DTG of PA7eI at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under a nitrogen atmosphere.

Table IV. Thermal Properties of PA7cI and PA7eI

Polymer	Decomposition Temperature ($^\circ\text{C}$)		Char Yield ^c (%)	T_g^d ($^\circ\text{C}$)
	T_5^a	T_{10}^b		
PA7cI	300	373	58	171
PA7eI	304	355	62	113

^aTemperature at which 5% weight loss was recorded by TGA at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. ^bTemperature at which 10% weight loss was recorded by TGA at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. ^cPercentage weight of material left undecomposed after TGA analysis at maximum temperature $600\text{ }^\circ\text{C}$ in a nitrogen atmosphere. ^dGlass transition temperature was recorded at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$ in a nitrogen atmosphere.

data of these polymers are summarized in Table IV. Since, the inherent viscosities of polymers obtained by methods I and II are more or less close to each other, therefore, their thermal properties would be more or less similar.

The results demonstrate that the introducing of heat resistant phthalimide groups as well as the presence of imide and amide groups may compensate any loss of thermal stability that may cause due to the existence of amino acid flexible aliphatic group.

Conclusions

A series of highly organosoluble optically active aromatic PAs containing a rigid phthalimide and flexible L-alanine pendent group has been synthesized by direct polycondensation in the presence of TPP, CaCl₂ and Py in NMP under microwave irradiation and conventional heating conditions. The results of these methods were comparable, but the microwave heating is a more efficient method (shorter reaction time and high efficiency of energy) for these polycondensation reactions. The resulting PAs have L-alanine in polymer chain and are optically active. The introduction of pendent bulky groups along the polymer backbone results in a less ordered polymer matrix, therefore disturbed the strong interchain forces and inherent macromolecular rigidity, and consequently increasing the solubility characteristics without affecting thermal properties to any great extent. These PAs with good thermal stability could be considered as new processable high-performance polymeric materials. In addition because of the existence of amino acid in the polymer pendent group these polymers are expected to be bioactive and therefore are classified under environmentally friendly polymers. Since the resulting polymers are optically active, they have potential to be used as a chiral stationary phase in chromatography technique for the separation of racemic mixtures.

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