

Microwave-Assisted Synthesis of New Optically Active Poly(ester-imide)s Containing *N,N'*-(pyromellitoyl)-bis-*L*-phenylalanine moieties

Shadpour E. Mallakpour, Abdol-Reza Hajipour, Sakineh Habibi

Organic Polymer Chemistry Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan, 84156, I.R. Iran

Received 5 December 2001; accepted 7 March 2002

ABSTRACT: Pyromellitic dianhydride (benzene-1,2,4,5-tetracarboxylic dianhydride) (**1**) was reacted with *L*-phenylalanine (**2**) in a mixture of acetic acid and pyridine (3 : 2) and the resulting imide-acid [*N,N'*-(pyromellitoyl)-bis-*L*-phenylalanine diacid] (**4**) was obtained in quantitative yield. The compound (**4**) was converted to the *N,N'*-(pyromellitoyl)-bis-*L*-phenylalanine diacid chloride (**5**) by reaction with thionyl chloride. A new facile and rapid polycondensation reaction of this diacid chloride (**5**) with several aromatic diols such as phenol phthalein (**6a**), bisphenol-A (**6b**), 4,4'-hydroquinone (**6c**), 1,8-dihydroxyanthraquinone (**6d**), 4,4'-dihydroxy biphenyl (**6e**), and 2,4-dihydroxyacetophenone (**6f**) was developed by using a domestic microwave oven in the

presence of a small amount of a polar organic medium such as *o*-cresol. The polymerization reactions proceeded rapidly and are completed within 20 min, producing a series of optically active poly(ester-imide)s with good yield and moderate inherent viscosity of 0.10–0.26 dL/g. All of the above polymers were fully characterized by IR, elemental analyses, and specific rotation. Some structural characterization and physical properties of these optically active poly(ester-imide)s are reported. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2211–2216, 2002

Key words: optically active poly(ester-imide)s; polycondensation; thermal properties; thermogravimetric analysis (TGA)

INTRODUCTION

Aromatic polyimides and their copolymers are very important commercial materials possessing outstanding mechanical behavior combined with excellent thermal properties and good solvent resistance.^{1,2} However, most aromatic polyimides are intractable materials that do not melt before thermally decomposing, therefore, would be difficult for processing. One way to decrease the melting point of polyimides is introducing a flexible spacer that has been reported in the synthesis of poly(ester-imide)s.³

The synthesis and application of optically active polymers are the newly considerable topics, which have been paid more attention recently. Because polymers with chiral structures are biologically very important. Most of the natural polymers are optically active, and have special chemical activities such as catalytic properties that exist in genes, proteins, and enzymes. Recently, we have synthesized optically active polymers by different methods including micro-

wave irradiation techniques.^{4–17} Polymers having both optically active and thermally stable properties are required for the column chromatography at high temperature for the separation of enantiomeric mixtures.

In previous articles^{18,19} we synthesized a series of novel optically active poly(ester-imides) PEIs. The resulting polymers are optically active and have an inherent viscosities in a range of 0.35–1.12 dLg⁻¹.

In this article we wish to report the synthesis and characterization of new optically active PEIs from aromatic diols and *N,N'*-(pyromellitoyl)-bis-*L*-phenylalanine diacid chloride (**5**), a monomer containing preformed imide group under microwave irradiation.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (benzene-1,2,4,5-tetracarboxylic dianhydride) (**1**) (from Merck Chemical CO., Germany) was purified by recrystallization from acetic anhydride followed by sublimation; 1,8-dihydroxyanthraquinone (**6e**) and Bisphenol A (**6b**) were purified by recrystallization from acetic acid and acetic acid–water, respectively. The other diols were used as obtained without further purification. 1,4-Diazabicyclo [2.2.2]octane (DABCO) was purified by sublimation.

Correspondence to: S. E. Mallakpour (MALLAK@CC.IUT.AC.IR).

Contract sponsors: the Research Affairs Division Isfahan University of Technology (IUT), Isfahan, and Center of Excellency in Chemistry Research (IUT).

Techniques

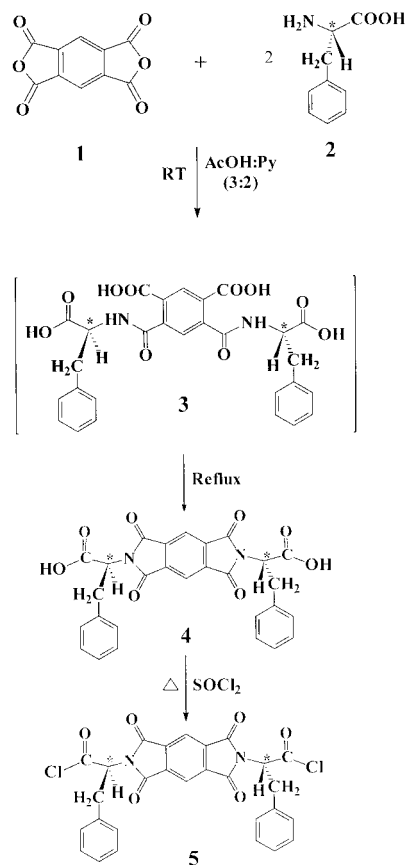
The apparatus used for the polycondensation was a Samsung (South Korea) domestic microwave oven (2450 MHz, 900 W) without any modification, but all of the polymerization reactions were carried out in a hood with strong ventilation. Proton nuclear magnetic resonance ($^1\text{H-NMR}$, 90 MHz) spectra was recorded on a Varian (Varian Associates, Palo Alto, CA) EM-390 instrument. Tetramethylsilane (TMS) was used as an internal reference. IR spectra were recorded on Shimadzu 435 IR spectrophotometer (Shimadzu, Japan). Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave numbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fensk Routine Viscometer. Specific Rotations were measured by a Perkin-Elmer-241 Polarimeter (Germany). Thermal Gravimetric Analysis (TGA) data for polymers were taken on a Mettler TGA-50 (England) in N_2 atmosphere at a rate of $10^\circ\text{C}/\text{min}$. Elemental analyses were performed by Tarbiet Moderres University, Tehran, I.R. Iran.

Monomer synthesis *N,N'*-(pyromellitoyl)-bis-*L*-phenylalanine diacid (4)

Into a 25-mL round-bottomed flask 1.716 g (7.83×10^{-3} mol) of pyromellitic dianhydride (benzene-1,2,4,5-tetracarboxylic dianhydride) (**1**), 2.600 g (1.574×10^{-2} mol) of *L*-phenylalanine (**2**), 10 mL of mixture of acetic acid and pyridine (3 : 2), and a stirring bar were placed. The mixture was stirred and refluxed for 15 h. The solvents were removed under reduced pressure and 5 mL of cold concentrated HCl was added. A white precipitate was formed, filtered off, washed with water and dried, then was recrystallized from DMF-water mixture to give 4.00 g (99.2%) of compound (**4**). m.p. $292\text{--}294^\circ\text{C}$, $[\alpha]_{\text{D}}^{25} = +0.2^\circ$ (0.050 g in 10 mL DMF); IR (KBr): 3650–3000 (m,br), 2950 (m), 1760 (s,br), 1710 (s,br), 1680 (s,br), 1600 (m), 1490 (m), 1450 (m), 1390 (s), 1370 (s), 1250 (m), 1220 (s), 1170 (s), 1110 (s), 1040 (m), 1030 (m), 990 (m), 940 (m), 920 (m), 880 (m), 850 (w), 820 (m), 750 (m), 730 (m), 700 (m), 670 (m), 630 (m), 560 (m), 490 (w) cm^{-1} ; Anal. calc. For $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_8$ (%): C, 65.62; H, 3.93; N, 5.47. Found: C, 65.73; H, 4.00; N, 5.58.

N,N'-(pyromellitoyl)-bis-*L*-phenylalanine diacid chloride (5)

Into a 25-mL round-bottomed flask were placed 1.50 g (2.93×10^{-3} mol) of compound **4** and 7 mL (an excess amount) of thionyl chloride. The mixture was refluxed for overnight. Unreacted thionyl chloride was re-

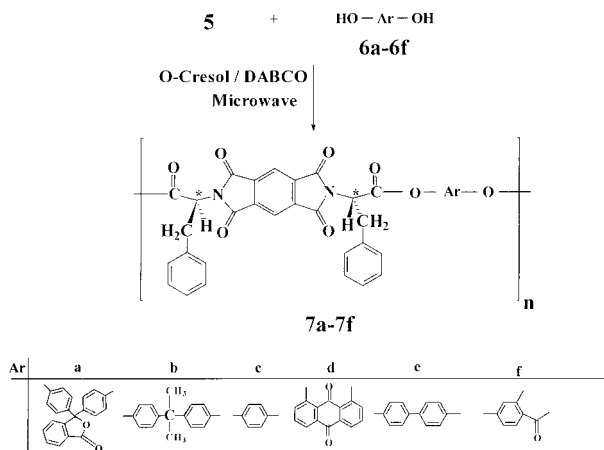


Scheme 1 Synthesis of *N,N'*-(pyromellitoyl)-bis-*L*-phenylalanine diacid chloride (**5**).

moved under reduced pressure and the residue was washed with *n*-hexane, to leave 1.37 g (85.0%) of white crystals. m.p. = $189\text{--}191^\circ\text{C}$ $[\alpha]_{\text{D}}^{25} = +0.2^\circ$ (0.050 g in 10 mL DMF); IR (KBr): 3550 (m), 3480 (m), 3400 (m), 3100 (m), 3050 (m), 3000 (m), 2940 (m), 1790 (s), 1770 (s), 1730 (s,br), 1650 (m), 1630 (m), 1620 (m), 1600 (m), 1490 (m), 1460 (m), 1440 (m), 1380 (s), 1360 (s), 1290 (w), 1270 (w), 1250 (w), 1200 (m), 1150 (m), 1130 (m), 1110 (m), 1070 (w), 1040 (m), 1030 (m), 1000 (m), 960 (m), 920 (m), 890 (w), 840 (m), 820 (m), 770 (m), 740 (m), 700 (m), 670 (w), 610 (m), 560 (m), 520 (w), 480 (w), cm^{-1} ; Anal. calc. for $\text{C}_{28}\text{H}_{18}\text{N}_2\text{O}_6\text{Cl}_2$ (%): C, 61.22; H, 3.30; N, 5.10; Found: C, 61.36; H, 3.36; N, 5.16.

Polymerization: synthesis of polymer **7c**

The PEIs were prepared by the following procedure (using polymer **7c** as an example). Into a porcelain dish was placed 0.10 g (1.82×10^{-4} mol) of diacid chloride (**5**) and 0.040 g (3.64×10^{-4} mol) of DABCO as a catalyst. After the reagents were completely ground, for 5 min, 0.020 g hydroquinone (**6c**) was added and the mixture was ground for 5 min then 0.20 mL of *o*-cresol as a solvent was added, and the mixture was ground for 10 min and the reaction mixture was irradiated in the microwave oven for 20 min. The



Scheme 2 Preparation of PEIs 7a-7f.

resulting homogenous glassy polymer film was isolated by adding methanol and triturating, followed by filtration. Powdered polymer was dried at 80°C for 15 h under vacuum to leave 0.099 g (82.8%) of off-white solid **7c**. IR (KBr): 3450 (m, br), 3050 (m), 3000 (m), 1780 (s), 1720 (s, br), 1640 (m), 1610 (m), 1590 (m), 1500 (m), 1490 (m), 1460 (m), 1450 (m), 1390 (m), 1370 (s), 1320 (m), 1300 (m), 1250 (s), 1210 (s), 1170 (s), 1110 (s), 1080 (m), 1040 (m), 1000 (m), 970 (m), 930 (m), 900 (m), 840 (m), 800 (m), 750 (m), 720 (m), 690 (m), 620 (w), 580 (w), 520 (m), cm^{-1} .

The other PEIs **7a-7b** and **7d-7f** were prepared in a procedure similar to that above.

Polymer 7a

White solid; IR (KBr): 3450 (m, br), 3050 (m), 3000 (m), 1780 (s), 1720 (s, br), 1640 (m), 1610 (m), 1590 (m), 1490 (m), 1370 (s, br), 1320 (s, br), 1240 (s), 1200 (s, sh), 1160 (s, br), 1150 (s), 1040 (m), 1010 (m), 1000 (m), 930 (m), 900 (m), 840 (m), 790 (m), 750 (m), 720 (m), 690 (m), 650 (m), 620 (w), 560 (w), 520 (m), cm^{-1} .

TABLE I
Synthesis and Some Physical Properties of PEIs 7a-7

		Polymer			
Diol	Polymer	Yield (%)	$\eta_{\text{inh}}(\text{dL/g})^a$	$[\alpha]_{\text{D}}^{25b}$	Color ^c
6a	7a	66.0	0.10	+0.2	PY
6b	7b	87.8	0.15	+0.4	PY
6c	7c	82.8	0.26	+0.4	OW
6d	7d	93.0	0.10	+0.6	P-O
6e	7e	87.8	0.15	+0.4	Y
6f	7f	85.3	0.16	+0.6	OW

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

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

^c OW = off-white, PY = pale yellow, P-O = pale-orange Y = yellow.

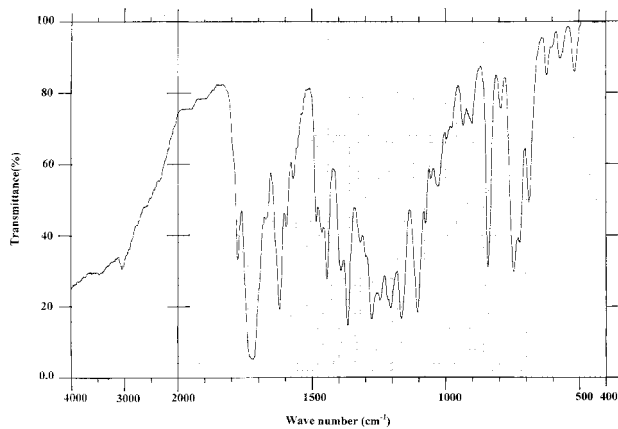


Figure 1 IR (KBr) spectrum of PEIs 7d.

Polymer 7b

Pale yellow solid; IR (KBr): 3450 (m, br), 3050 (m), 3000 (m), 2900 (m), 2780 (m), 2700 (m), 2550 (m), 2500 (m), 2450 (m), 1780 (m), 1720 (s, br), 1630 (m), 1610 (m), 1490 (m), 1440 (m), 1370 (s), 1320 (m), 1240 (m), 1200 (s), 1160 (s), 1110 (s), 1050 (m), 1000 (m), 940 (w), 900 (m), 840 (m), 750 (m), 720 (m), 690 (m), 620 (w), 600 (w), 560 (w), 520 (w), cm^{-1} .

Polymer 7d

Yellow solid; IR (KBr): 3050 (m), 1780 (m), 1720 (s, br), 1670 (m), 1620 (m), 1600 (m), 1570 (m), 1490 (m), 1460 (m), 1440 (m), 1390 (m), 1370 (s), 1320 (m), 1280 (s), 1250 (s), 1200 (s), 1170 (s), 1100 (s), 1070 (m), 1050 (m), 1030 (m), 990 (m), 980 (w), 930 (m), 900 (m), 840 (m), 790 (m), 740 (m), 720 (m), 690 (m), 620 (w), 570 (w), 520 (m), cm^{-1} .

Polymer 7e

Off white solid; IR (KBr): 3450 (m, br), 3050 (m), 3000 (m), 2950 (m), 2850 (m), 2750 (m), 2700 (m), 2550 (m), 2500 (m), 2450 (m), 2350 (m), 1780 (s), 1720 (s, br), 1630 (m), 1600 (m), 1490 (m), 1440 (m), 1390 (s, sh), 1370 (s), 1320 (s), 1300 (s), 1250 (m), 1200 (s), 1170 (s), 1100 (s), 1070 (m), 1050 (m), 1010 (m), 990 (m), 970 (m), 930 (m), 900 (m), 840 (s), 790 (m), 750 (m), 720 (m), 690 (m), 620 (m), 600 (w), 560 (m), 520 (m), cm^{-1} .

Polymer 7f

Off white solid; IR (KBr): 3450 (m, br), 3050 (m), 3090 (m), 1780 (m), 1730 (s), 1635 (m), 1490 (m), 1450 (m), 1390 (m), 1370 (s), 1320 (m), 1300 (m, sh), 1250 (m), 1240 (s), 1210 (m), 1170 (m), 1130 (m), 1110 (m), 1070 (w), 1030 (m), 1000 (w), 980 (m), 940 (w), 900 (w), 840 (m), 780 (w), 750 (m), 720 (m), 690 (m), 620 (w), 580 (w), 520 (m), cm^{-1} .

TABLE II
Elemental Analysis of PEIs 7a–7f

Polymer	Formula	Elemental Analysis (%)			
		C	H	N	
7a	(C ₄₈ H ₃₀ N ₂ O ₁₀) _n (795) _n	Calcd	72.54	3.80	3.52
		Found	71.12	3.90	3.79
7b	(C ₄₃ H ₃₂ N ₂ O ₈) _n (704) _n	Calcd	73.29	4.58	3.98
		Found	71.57	4.02	4.34
7c	(C ₃₄ H ₂₂ N ₂ O ₈) _n (586) _n	Calcd	69.62	3.78	4.78
		Found	68.47	3.72	4.68
7d	(C ₄₂ H ₂₄ N ₂ O ₁₀) _n (717) _n	Calcd	70.39	3.38	3.91
		Found	70.17	3.83	3.82
7e	(C ₄₀ H ₂₆ N ₂ O ₈) _n (663) _n	Calcd	72.50	3.95	4.23
		Found	71.11	4.12	4.14
7f	(C ₃₆ H ₂₄ N ₂ O ₉) _n (628) _n	Calcd	68.79	3.85	4.46
		Found	68.58	3.77	4.17

RESULTS AND DISCUSSION

Monomer synthesis

N,N'-(pyromellitoyl)-bis-*L*-phenylalanine diacid chloride (**5**) was prepared by the three-step procedure as shown in Scheme 1. The asymmetric diacid compound **4** was synthesized by the condensation reaction of dianhydride **1** with 2 mol of *L*-phenylalanine (**2**) in a mixture of acetic acid and pyridine (3 : 2). The intermediate amic-acid **3** was not isolated and dehydration was performed under reflux conditions. The resulting symmetric diacid **4** was converted to its diacid chloride derivative **5** by reaction with thionyl chloride. The monomer **5** was purified by washing with *n*-hexane. Chemical structure and purity of the optically active monomers **4** and **5** were proved using elemental analysis and IR spectra.

The IR spectrum of compound **4** showed a broad and strong peak at 3650–3000 cm⁻¹, which was assigned to the COOH groups and two absorption bands at 1760 and 1710 cm⁻¹, which are characteristic peaks for imide rings.

Disappearance of strong acidic hydroxyl peak in IR spectrum of compound **5** confirmed a complete conversion of diacid **4** to diacid chloride **5**. On the other hand, because of the electron withdrawing character of the Cl group, the two carbonyl peaks of diacid chloride in comparison with its starting diacid, were shifted to higher frequency. It is interesting to mention that the monomer **5** has a C₂ axis, when enters in backbone of the polymer, it will cause stereoregularity in polymer structure.

Polymer synthesis

PEIs **7a–7f** were synthesized by the microwave-assisted polycondensation reactions of an equimolar mixture of monomer **5** with six different aromatic

diols **6a–6f** using DABCO as catalyst as shown in Scheme 2.

Recently we have used microwave irradiation technique and synthesized novel poly(amide-imide)s^{9,12,13} as well as poly(ester-imide)s.^{17,18} Microwave-assisted polycondensation proceeds rapidly compared to conventional solution polycondensation, and is almost completed within a short period of time. This method should become more and more important due to its high-efficiency utilization of heat energy. In this work the microwave-assisted polycondensation reactions were performed in a porcelain dish in the presence of small amount of a polar organic medium such as *o*-cresol, which acts as a primary microwave absorber, then the reaction mixture was irradiated for 20 min. The resulting PEIs (**7a–7f**) were obtained in good yield. The reaction yields and some physical data are listed in Table I.

All of the polymers were obtained in good yields with moderate inherent viscosities of 0.10–0.26 dL g⁻¹ and show optical rotation; therefore, they are optically active. We also tried the polymerization of diacid chloride **5** with diol **6c** under solution conditions; thus, the monomer **5** was allowed to react with diol **6c** in *N*-methyl pyrrolidone (NMP) at low temperature and then was heated up to 120°C under nitrogen atmosphere, but the resulting product was soluble in methanol and no polymeric material was obtained. Similarly, the above reaction was repeated under phase transfer catalysis technique, but no polymeric material was obtained.

Polymer characterization

The formation of PEIs was confirmed by IR spectroscopy analysis. As an example, the IR spectrum of PEIs **7d** (Fig. 1) showed the characteristic absorptions of the imide group occurred around 1780, 1720, and 1660 cm⁻¹, peculiar to carbonyls stretching of imide and ester, respectively. All of these PEIs exhibited absorptions at 1390 cm⁻¹ and 710–720 cm⁻¹, which show the

TABLE III
Solubility of PEIs 7a–7f^a

Solvents	6a	6b	6c	6d	6e	6f
DMAc	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
H ₂ SO ₄	+	+	+	+	+	+
MeOH	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
CHCl ₃	–	–	–	–	–	–
CH ₂ Cl ₂	–	–	–	–	–	–
H ₂ O	–	–	–	–	–	–

^a Concentration: 5 mg ml⁻¹; +; Soluble at room temperature, –; Insoluble.

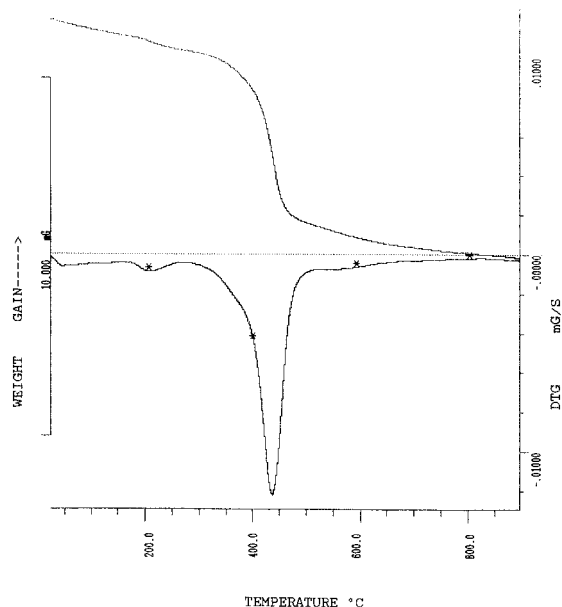


Figure 2 TGA/DTG thermograms of PEIs 7c in N₂ atmosphere.

presence of the imide heterocycle in these polymers. Elemental analysis values of the resulting polymers are listed in Table II. PEIs derived from monomer 5 may range in color from white to yellow.

As mentioned before, polymers obtained from monomer 5 and aromatic diamines have a special arrangement. This is due to arrangement of alkyl groups on optically active center that are syndiotactic arrangement. Therefore, this situation produced stereoregular PEIs with syndiotactic arrangement.

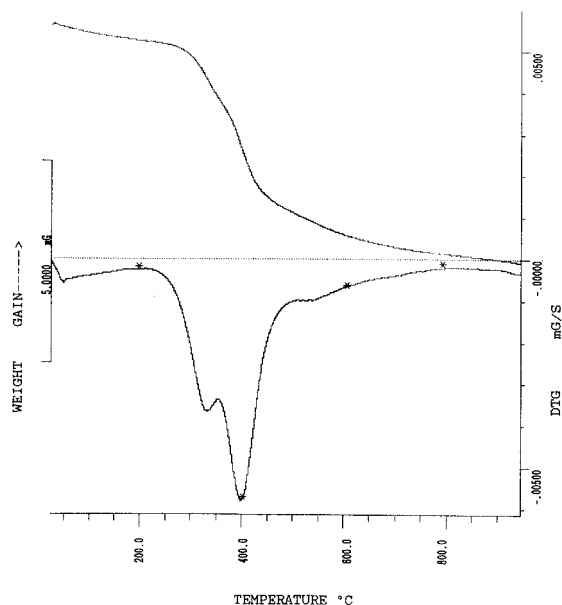


Figure 3 TGA/DTG thermograms of PAEIs 7f in N₂ atmosphere.

TABLE IV
Thermal Behavior of Aromatic PEIs 7c, 7f

Polymer	Decomposition Temperature(°C) T ₅ ^a	Char Yield (%) ^b
7c	237.5	20.32
7f	206.0	34.40

^a Temperature at which 5% weight loss was recorded by TGA at heating rate of 10°C/min in N₂.

^b Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600°C in N₂.

The solubility of PEIs was tested quantitatively in various solvents and are listed in Table III. All of the PAIs are soluble in organic solvents such as DMF, DMAc, DMSO, NMP, and H₂SO₄ at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water.

Thermal properties

The thermal properties of PEIs 7c and 7f were evaluated by means of TGA/DTG in nitrogen atmosphere. All of these polymers show similar decomposition behavior (Figs. 2 and 3). Table IV summarizes the thermal properties of some of the PEIs. The PEIs exhibited good resistance to thermal decomposition around 300°C in nitrogen and began to decompose gradually above that temperature. The temperature of 5% weight loss for these polymers was 237.5 and 206°C, the temperature of 10% weight loss was 368.8 and 300°C and the residual weight for these polymers at 600°C in nitrogen was 20.32 and 34.40%, respectively.

CONCLUSION

A series of stereoregular optically active PEIs having inherent viscosities of 0.10–0.26 dL/g was synthesized for the first time by microwave assisted polycondensation of the optically active *N,N'*-(pyromellitoyl)-bis-*L*-phenylalanine diacid chloride (5) as a diacid chloride having a preformed imide ring as an “enlarged” monomer containing one chiral *L*-phenylalanine group with some aromatic diol. These aromatic PEIs show optical rotation and are readily soluble in various organic solvents and have good thermal stability.

We wish to express our gratitude to the Research Affairs Division Isfahan University of Technology (IUT), Isfahan, for financial support. Further financial support from Center of Excellency in Chemistry Research (IUT) is gratefully acknowledged. We thank Amine Pharmaceutical center, Isfahan, I.R, Iran for recording optical rotations.

References

- Mittal, K. L., Ed. In *Polyimides, Synthesis, Characterization and Application*; Plenum Press: New York, 1984.

2. Abade, M. J. M.; Sillion, B. In *Polyimides and Other High-Temperature Polymers*; Elsevier: New York, 1991.
3. Hus, T. F.; Lin, Y. L.; Lee, Y. D. *J Polym Sci Polym Chem Ed* 1998, 36, 1791.
4. Mallakpour, S. E.; Hajipour, A. R.; Khoee, S.; Sheikholeslami, B. *Polym Int* 1998, 47, 193.
5. Mallakpour, S. E.; Hajipour, A. R.; Mahdavian, A. R.; Khoee, S. *J Polym Sci Polym Chem Ed* 1999, 37, 1211.
6. Mallakpour, S. E.; Hajipour, A. R.; Mahdavian, A. R.; Rafiemanzelat, F. *Polym Int* 1999, 48, 109.
7. Mallakpour, S. E.; Hajipour, A. R.; Khoee, S. *Polym Int* 1999, 48, 1133.
8. Mallakpour, S. E.; Dabbagh, A. H.; Faghihi, Kh. *Iranian Polym* 2000, 9, 41.
9. Mallakpour, S. E.; Hajipour, A. R.; Khoee, S. *J Polym Sci Polym Chem Ed* 2000, 38, 1154.
10. Mallakpour, S. E.; Hajipour, A. R.; Mahdavian, A. R.; Khoee, S. *J Appl Polym Sci* 2000, 76, 240.
11. Mallakpour, S. E.; Hajipour, A. R.; Roohipour-fard, R. *Eur Polym J* 2000, 36, 2455.
12. Mallakpour, S. E.; Hajipour, A. R.; Faghihi, Kh. *Eur Polym J* 2001, 37, 119.
13. Mallakpour, S. E.; Hajipour, A. R.; Zamanlou, R. *J Polym Sci Polym Chem Ed* 2001, 39, 177/
14. Mallakpour, S. E.; Hajipour, A. R.; Habibi, S. *Polym Int* 2001, 50, 331.
15. Mallakpour, S. E.; Hajipour, A. R.; Roohipour-fard, R. *Polym Sci Ser B* 2001, 43, 11.
16. Mallakpour, S. E.; Hajipour, A. R.; Habibi, S. *J Appl Polym Sci* 2001, 80, 1312.
17. Mallakpour, S. E.; Hajipour, A. R.; Roohipour-fard, R. *Eur Polym J* 2000, 36, 2455.
18. Mallakpour, S. E.; Hajipour, A. R.; Khoee, S. *J Appl Polym Sci* 2000, 77, 3003.
19. Mallakpour, S. E.; Hajipour, A. R.; Faghihi, Kh. *Polym Int* 2000, 49, 1383.