

# Soluble Novel Optically Active Poly(amide–imide)s Derived from *N,N'*-(4,4'-Oxydiphthaloyl)-bis-L-leucine Diacid Chloride and Various Aromatic Diamines: Synthesis and Characterization

Shadpour Mallakpour,\* Elaheh Kowsari

*Organic Polymer Chemistry Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan, 84156–83111, I.R. Iran*

Received 10 September 2004; accepted 4 October 2004

DOI 10.1002/app.21462

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** 4,4'-Oxydiphthalic anhydride (**1**) was reacted with L-leucine (**2**) in acetic acid, and the resulting imide-acid (**3**) was obtained in high yield. The diacid chloride (**4**) was obtained from diacid derivative (**3**) by reaction with thionyl chloride. The polycondensation reaction of diacid chloride (**4**) with several aromatic diamines, such as 4,4'-sulfonyldianiline (**5a**), 4,4'-diaminodiphenyl methane (**5b**), 4,4'-diaminodiphenylether (**5c**), *p*-phenylenediamine (**5d**), *m*-phenylenediamine (**5e**), and 4,4'-diaminobiphenyl (**5f**), was performed by two conventional methods: low temperature solution polycondensation and short period reflux conditions. To compare conventional solution polycondensation reaction methods with microwave-assisted polycondensation, the reactions were also carried out under microwave conditions in the presence of a small amount of *o*-

cresol that acts as a primary microwave absorber. The reaction mixture was irradiated for 6 min with 100% of radiation power. Several new optically active poly(amide–imide)s with inherent viscosity ranging from 0.25–0.52 dL/g were obtained with high yield. All of the above polymers were fully characterized by IR, elemental analyses, and specific rotation techniques. Some structural characterizations and physical properties of these new optically active poly(amide–imide)s are reported. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 435–442, 2005

**Key words:** optically active polymers; poly(amide–imide)s; inherent viscosity; thermal stability; thermal gravimetric analysis (TGA); amino acid

## INTRODUCTION

Aromatic polyamides (PA) possess excellent mechanical properties and thermal stability, and are synthesized from aromatic diamines and aromatic dicarboxylic acids. For example, both Kevlar and Nomex have excellent thermal and mechanical properties. Because of their intermolecular hydrogen bonds, most PAs have good solubility in polar amide solvents and are widely used for a variety of applications.<sup>1–5</sup> Aromatic polyimides (PI) are certainly one of the most successful classes of high-performance polymers used in microelectronics. However, most PIs encounter processing difficulty due to their rigidity and poor solubility in organic solvents. To overcome this drawback, several copolymers have been developed,<sup>6,7</sup> among them poly(amide–imide)s (PAIs), whose amide groups can improve the solubility. PAIs can be synthesized by polycondensation from various mono-

mers containing anhydride, carboxylic acid, or aromatic amino groups.

Much attention has been paid in recent years to fabrication of chiral separation materials. Those polymers possess high chiral recognition ability as a chiral stationary phase in chromatography techniques to resolve a wide range of racemates or chiral media for asymmetric synthesis.<sup>8</sup> Recently, we synthesized novel optically active polymers by different methods.<sup>9–11</sup> In these polymers, we also used amino acids as chiral inducing agents. These materials are naturally occurring compounds; therefore, synthetic polymers based on amino acids are expected to be biodegradable and biocompatible.

On the other hand, microwave technology is becoming a more attractive alternative for scientists dealing with organic synthesis from both an environmental and economic angle. In the last few years there has been a growing interest in the use of microwave heating in organic synthesis. Recently, we have used microwave irradiation for the synthesis of organic compounds as well as macromolecules.<sup>12–14</sup>

Herein we wish to report the synthesis and characterization of new organosoluble and optically active PAIs containing 4,4'-oxydiphthalic anhydride and L-

Correspondence to: S. Mallakpour (mallak@cc.iut.ac.ir).

\* Previous name: Shadpour E. Mallakpour.

leucine moieties by conventional solution polymerization and compare this method with microwave-assisted polycondensation reaction.

## EXPERIMENTAL

### Materials

4,4'-Diaminodiphenylmethane (**5b**) and 4,4'-diaminobiphenyl (**5f**) were purified by recrystallization from water. 4,4'-Diaminodiphenylether (**5c**), 1,4-phenylenediamine (**5d**), and 1,3-phenylenediamine (**5e**) were purified by sublimation. 4,4'-Oxydiphthalic anhydride dianhydride was supplied from T.C.I Chemical Co (Japan). *N,N*-Dimethylacetamide (**DMAC**) was dried over BaO, then distilled in vacuum. The other chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), and Riedel-deHaen AG (Seelze, Germany), and were used as obtained without further purification.

### Apparatus

The apparatus used for the polycondensation was a Samsung microwave oven (2450MHz, 900W). All of the polymerization reactions were performed in a hood with strong ventilation.

### Measurements

Proton nuclear magnetic resonance  $^1\text{H-NMR}$  (500MHz) spectra were recorded on a Bruker, Avance 500 instrument (Rheinstetten, Germany). Tetramethylsilane (TMS) was used as an internal reference. Proton resonances are designated as singlet (s), doublet (d), doublet of doublet (dd), and multiplet (m). FT-IR spectra were recorded on (Jasco-680, Japan) spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber ( $\text{cm}^{-1}$ ). Band intensities are assigned as weak (w), medium (m), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fenske Routine Viscometer (Mianz, Germany). Specific Rotations were measured by a Jasco Polarimeter (Japan). Thermal Gravimetric Analysis (TGA) data for polymers were taken on a TGA 7 Perkin-Elmer (Jugeshein, Germany) in nitrogen atmosphere at a rate of  $40^\circ\text{C}/\text{min}$ . Elemental analyses were performed by Malek-Ashtar University of Technology, Tehran, I.R. Iran.

### Monomer synthesis

*N,N'*-(4,4'-oxydiphthaloyl)-bis-L-leucine diacid (**3**)

Into a 50-mL round-bottomed flask 1.00 g ( $3.22 \times 10^{-3}$  mol) of 4,4'-oxydiphthalic anhydride (**1**), 0.93 g (7.08

$\times 10^{-3}$  mol) of L-leucine (**2**), 30 mL of acetic acid, and a stirring bar were placed. The mixture was stirred at room temperature for 3 h and then was refluxed for 8 h. The solvent was removed under reduced pressure, and 5 mL of cold concentrated HCl was added to the residue. A white precipitate was formed, washed with cold water, and was added to it enough amount of ether that was converted to a clear solution. The ether was removed under reduced pressure to give 1.67 g (96.56%) of compound (**3**). mp:  $182\text{--}184^\circ\text{C}$ ,  $[\alpha]_{\text{D}}^{25}$ :  $-62.2^\circ$  (0.050 g in 10 mL DMF); FT-R (KBr): 3735–3073 (m, br), 2961 (m), 2874 (w), 1772 (m), 1719 (s), 1608 (m), 1474 (m), 1436 (w), 1382 (s), 1275 (s), 1240 (w), 1186 (w), 1166 (w), 1086 (m), 862 (w), 754 (m), 626 (m)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (DMSO- $d_6$ , TMS, 500 MHz):  $\delta$  0.30–0.70 (distorted, dd, 12H), 1.40–1.45 (m, 2H), 1.80–1.88 (m, 2H), 2.10–2.20 (m, 2H), 4.75–4.80 (dd, 2H,  $J_1 = 11.30$  Hz,  $J_2 = 4.60$  Hz), 7.58–7.62 (dd, 2H,  $J_1 = 8.14$  Hz,  $J_2 = 1.89$  Hz), 7.62–7.64 (d, distorted, 2H), 7.96–7.98 (d, 2H,  $J = 8.15$  Hz) ppm.

ELEM. ANAL. Calcd. for  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_9$ : C, 62.69%; H, 5.26%; N, 5.22%. Found: C, 62.79%; H, 5.26%; N, 5.83%.

*N,N'*-(4,4'-oxydiphthaloyl)-bis-L-leucine diacid chloride (**4**)

Into a 25-mL round-bottomed flask were placed 1.00 g ( $1.86 \times 10^{-3}$  mol) of compound **3** and 2.0 mL of thionyl chloride. The mixture was stirred at room temperature for 0.5 h until the suspension mixture was converted to a clear solution. Unreacted thionyl chloride was removed under reduced pressure and was washed with fresh dry ether three times, to leave 1.03 g (96.0%) of pale yellow solid. mp:  $114^\circ\text{C}$  (decomposed),  $[\alpha]_{\text{D}}^{25}$ :  $-136.2^\circ$  (0.050 g in 10 mL DMF); FT-IR (NaCl): 3430 (w), 2950 (m), 2900 (m), 2850 (m), 1800 (s), 1710 (s), 1460 (m), 1390 (s), 1300 (w), 1180 (s), 1125 (m), 1040 (w), 1020 (w), 960 (w), 900 (w), 840 (w), 755 (m), 660 (w)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (DMSO- $d_6$ , TMS, 500 MHz):  $\delta$  0.25–0.50 (distorted, dd, 12H), 1.35–1.40 (m, 2H), 1.75–2.00 (m, 2H), 2.00–2.25 (m, 2H), 4.50–5.00 (dd, 2H,  $J_1 = 11.42$  Hz,  $J_2 = 4.22$  Hz), 7.59–7.62 (dd, 2H,  $J_1 = 8.13$  Hz,  $J_2 = 2.1$  Hz), 7.63–7.66 (d, distorted, 2H), 7.96–7.80 (d, 2H,  $J = 8.15$ ) ppm.

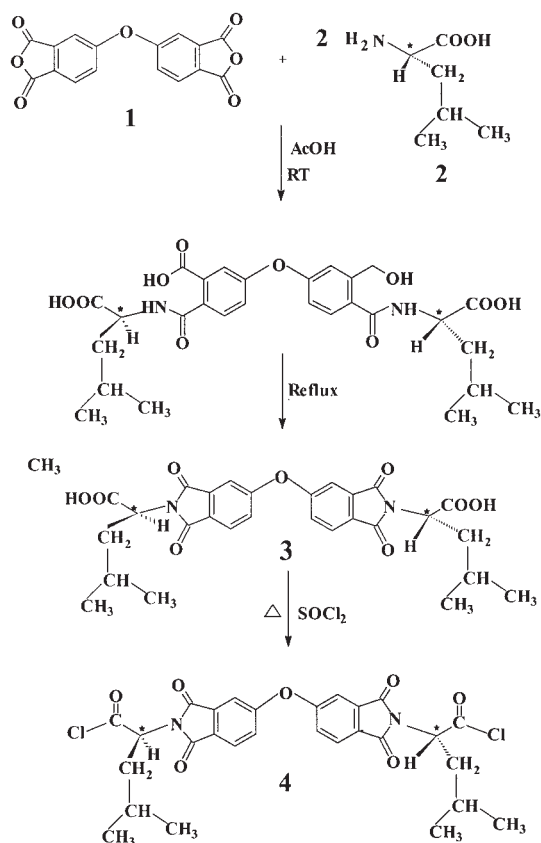
ELEM. ANAL. Calcd. for  $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_7\text{Cl}_2$ : C, 58.64%; H, 4.57%; N, 4.88%. Found: C, 58.18%; H, 4.37%; N, 5.01%.

### Polymer synthesis

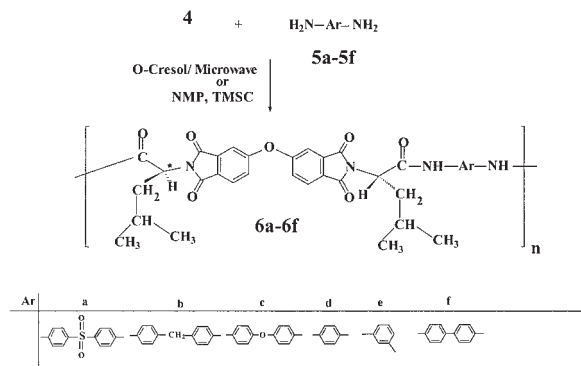
All of the polymers were synthesized with three different methods:

Method I: Low temperature solution polycondensation

Taking polymer **6aI** as an example, the general procedure consisted of adding 0.20 g ( $3.48 \times 10^{-4}$  mol) of

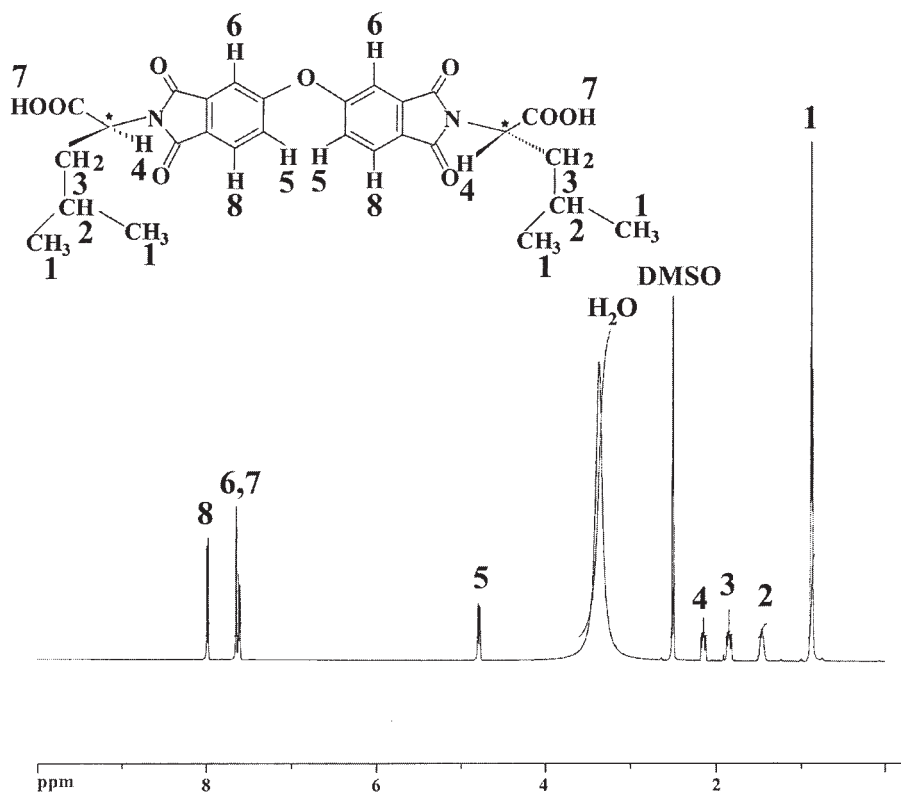


Scheme 1 Synthesis of monomer 4.



Scheme 2 Polycondensation reactions of monomer 4 with aromatic diamines.

diacid chloride 4 to a cooled ( $-5.0^{\circ}\text{C}$ ) and stirring solution of 0.0863 g ( $3.48 \times 10^{-4}$  mol) of diamine 5a in 0.25 mL of 1-methyl-2-pyrrolidone (NMP). After the reagents dissolved completely, 0.05 mL of TMSCl was added and the reaction was allowed to proceed for 2h under a blanket of nitrogen. Then the temperature was raised to room temperature. The reaction mixture was stirred for 5h. The viscous solution was poured into 40 mL of the mixture of methanol/H<sub>2</sub>O (70/30) and the precipitated solid was filtered off and dried at  $80^{\circ}\text{C}$  for 10 h under vacuum to leave 0.214 g (82.33%) of solid polymer 6aI. FT-IR (KBr): 3359 (m, br), 2958 (m, sh),

Figure 1 <sup>1</sup>H-NMR (500 MHz) spectrum of diacid (3) in DMSO, TMS at rt.

**TABLE I**  
Some Physical Properties of PAIs 6aI–6fI  
Prepared by Method I

Diamine	Polymer				
	Polymer	Yield (%)	$\eta_{inh}(dL/g)^a$	$[\alpha]_D^{25}$	$[\alpha]_{H_g}^{25}$
5a	6aI	82.3	0.39	-127.7	-130.2
5b	6bI	93.2	0.41	-100.2	-120.4
5c	6cI	87.3	0.28	-80.5	-94.3
5d	6dI	77.3	0.30	-72.4	-77.5
5e	6eI	68.7	0.28	-13.1	-18.3
5f	6fI	95.3	0.42	-78.3	-88.5

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

2871 (w), 1776 (s), 1719 (s), 1591 (s), 1524 (m), 1473 (m), 1439 (w), 1380 (s), 1232(s), 1152 (s), 1105 (m), 952 (w)  $cm^{-1}$ ; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, TMS, 500 MHz):  $\delta$  0.25–1.00 (distorted, dd), 1.20 (m), 1.80–2.00 (m), 2.10–2.25 (m), 4.80–5.00 (distorted, dd), 7. 65–7.70 (distorted, dd), 7.75 (d, *J* = 8.17), 7. 85 (d, 2H, *J* = 8.17), 8.00 (distorted, d), 10.4 (s), ppm.

The other PAIs (6bI–6fI) were prepared with similar procedures. All of the spectra were recorded with KBr pellets.

**Polymer 6bI.** FT-IR (KBr): 3376 (w, br), 3068 (w), 2957 (m), 2870 (w), 1776 (s), 1718 (s), 1607 (s), 1514 (s), 1473 (s), 1438 (w), 1381 (s), 1231 (m), 1155, 1086 (w), 954 (w), 1438 (w), 820 (m), 746 (m), 698 (w), 471  $cm^{-1}$  (w).

**Polymer 6cI.** FT-IR (KBr): 3372(w, br), 2958(w), 1776 (w), 1718 (s), 1609 (m), 1499 (m), 1473 (w), 1381 (s), 1230 (s), 1088 (w), 833 (w), 747 (w), 699  $cm^{-1}$  (w); <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, TMS, 500 MHz):  $\delta$  0.80–1.00 (distorted dd), 1.20 (m), 1.90–2.00 (m), 2.20–2.30 (m), 4.80–4.95 (distorted dd), 6.85–6.95 (d, *J* = 7.26), 7.50 (d, *J* = 8.08), 7.60–7.65 (m), 8.00 (distorted, dd), 9.80 (s) ppm.

**Polymer 6dI.** FT-IR (KBr): 3370 (w, br), 2958 (w), 1776 (m), 1718 (s), 1610 (w), 1515 (w), 1473 (w), 1438 (w), 1382 (s), 1273 (w), 1232 (w), 1175 (w), 1086 (w), 954 (w), 835 (w), 746 (w), 698 (w), 746 (w), 670  $cm^{-1}$  (w).

**TABLE II**  
Some Physical Properties of PAIs 6aII–6fII  
Prepared by Method II

Diamine	Polymer				
	Polymer	Yield (%)	$\eta_{inh}(dL/g)^a$	$[\alpha]_D^{25}$	$[\alpha]_{H_g}^{25}$
5a	6aII	87.6	0.40	-73.2	-75.2
5b	6bII	95.6	0.44	-49.7	-50.8
5c	6cII	76.4	0.26	-32.0	-33.4
5d	6dII	65.3	0.32	-33.5	-37.5
5e	6eII	75.9	0.25	-27.2	-30.4
5f	6fII	90.5	0.32	-20.6	-25.3

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

**TABLE III**  
Some Physical Properties of PAIs 6aIII–6fIII  
Prepared by Method III

Diamine	Polymer				
	Polymer	Yield (%)	$\eta_{inh}(dL/g)^a$	$[\alpha]_D^{25}$	$[\alpha]_{H_g}^{25}$
5a	6aIII	95.2	0.52	-73.1	-80.1
5b	6bIII	92.4	0.43	-57.4	-60.2
5c	6cIII	85.3	0.35	-29.3	-30.2
5d	6dIII	82.6	0.29	-3.1	-10.1
5e	6eIII	67.2	0.31	-1.6	-2.6
5f	6fIII	94.3	0.41	-33.1	-38.3

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

**Polymer 6eI.** FT-IR (KBr): 3375 (w, br), 2958 (m), 1777 (w), 1717 (s), 1609(m), 1540 (w), 1473 (m), 1381 (m), 1272 (m), 1231 (m), 1089 (m), 856 (w), 745 (m), 670  $cm^{-1}$  (w).

**Polymer 6fI.** FT-IR (KBr): 3366 (m, br), 2958 (m), 2871 (w), 2345 (w), 1776 (m), 1718 (s), 1608 (m), 1503 (m), 1473 (m), 1438 (m), 1381 (s), 1273 (s), 1232 (s), 1178 (w), 1086 (w), 953 (w), 820 (m), 746 (w), 698 (w), 670  $cm^{-1}$  (w).

#### Method II: High temperature solution polycondensation

Taking polymer 6aII as an example, into a 5-mL round-bottomed flask were placed 0.20 g ( $3.48 \times 10^{-4}$  mol) of diacid chloride 4, 0.0863 g ( $3.48 \times 10^{-4}$  mol) of diamine 5a, and 0.25 mL of DMAc, and 0.05 mL of TMSCl was added. The mixture was refluxed for 1 min. The viscous solution was poured into 40 mL of methanol/H<sub>2</sub>O (70/30) and the precipitated solid was filtered off and dried at 80°C for 10 h under vacuum to leave 0.228 g (87.54%) of polymer 6aII.

The other PAIs (6bII–6fII) were prepared with similar procedures.

#### Method III: Polymerization under microwave irradiation

The PAIs were prepared by the following general procedure (using polymer 6aIII as an example). Into a porcelain dish were placed 0.20 g ( $3.48 \times 10^{-4}$  mol) of diacid chloride 4 and 0.0863 g ( $3.79 \times 10^{-4}$  mol) of diamine 5a. After the reagents were completely ground, 0.25 mL of *o*-cresol was added as a solvent. The mixture was ground for 5 min. The reaction mixture was irradiated in the microwave oven for 4 min with 100% of the power of the microwave apparatus. The resulting product was isolated by adding methanol and triturating, followed by filtration, and was dried at 80°C for 10 h under vacuum to leave 0.248 g (95.23%) of solid 6aIII.

TABLE IV  
Elemental Analysis of PAIs 6aI–6fI

Polymer	Formula		Elemental analysis (%)			Moisture content (%) <sup>a</sup>
			C	H	N	
6aI	(C <sub>40</sub> H <sub>36</sub> N <sub>4</sub> O <sub>9</sub> S) <sub>n</sub> (748.8) <sub>n</sub>	Calcd	64.16	4.84	7.48	0.24
		Found	64.21	4.89	8.13	
		Corr <sup>b</sup>	64.36	4.87	8.14	
6bI	(C <sub>41</sub> H <sub>38</sub> N <sub>4</sub> O <sub>7</sub> ) <sub>n</sub> (698.7) <sub>n</sub>	Calcd	70.47	5.48	8.01	0.25
		Found	70.09	5.83	8.39	
		Corr <sup>b</sup>	70.26	5.84	8.40	
6cI	(C <sub>40</sub> H <sub>36</sub> N <sub>4</sub> O <sub>8</sub> ) <sub>n</sub> (700.6) <sub>n</sub>	Calcd	68.56	5.18	7.99	0.30
		Found	68.69	5.20	8.23	
		Corr <sup>b</sup>	68.89	5.18	8.25	
6dI	(C <sub>34</sub> H <sub>32</sub> N <sub>4</sub> O <sub>7</sub> ) <sub>n</sub> (608.6) <sub>n</sub>	Calcd	67.09	5.30	9.20	0.20
		Found	67.02	5.31	9.81	
		Corr <sup>b</sup>	67.15	5.29	9.82	
6eI	(C <sub>34</sub> H <sub>32</sub> N <sub>4</sub> O <sub>7</sub> ) <sub>n</sub> (608.6) <sub>n</sub>	Calcd	67.09	5.30	9.20	0.50
		Found	67.12	5.30	9.91	
		Corr <sup>b</sup>	67.45	5.20	9.95	
6fI	(C <sub>40</sub> H <sub>36</sub> N <sub>4</sub> O <sub>7</sub> ) <sub>n</sub> (684.6) <sub>n</sub>	Calcd	70.16	5.29	8.18	0.50
		Found	70.09	5.34	8.44	
		Corr <sup>b</sup>	70.44	5.31	8.48	

<sup>a</sup> Moisture content (%) =  $\times [(W - W_0)/W_0]100$ ,  $W$  = weight of polymer sample after standing at room temperature, and  $W_0$  = weight of polymer sample after being dried in vacuum at 100 °C for 10 h.

<sup>b</sup> Corrected value for C and N = Found value  $\times (100 + \text{moisture content})/100$ , and corrected value for H = found value  $\times (100 - \text{moisture content})/100$ .

## RESULTS AND DISCUSSION

### Monomer synthesis

The diacid **3** was synthesized by the condensation reaction of dianhydride **1** with two moles of L-leucine (**2**). In

this reaction the intermediate amic acid was not isolated, and ring closure for the formation of the imide ring was performed under refluxing conditions (Scheme 1).

The diacid **3** was converted to diacid chloride derivative **4** by reaction with thionyl chloride. The chem-

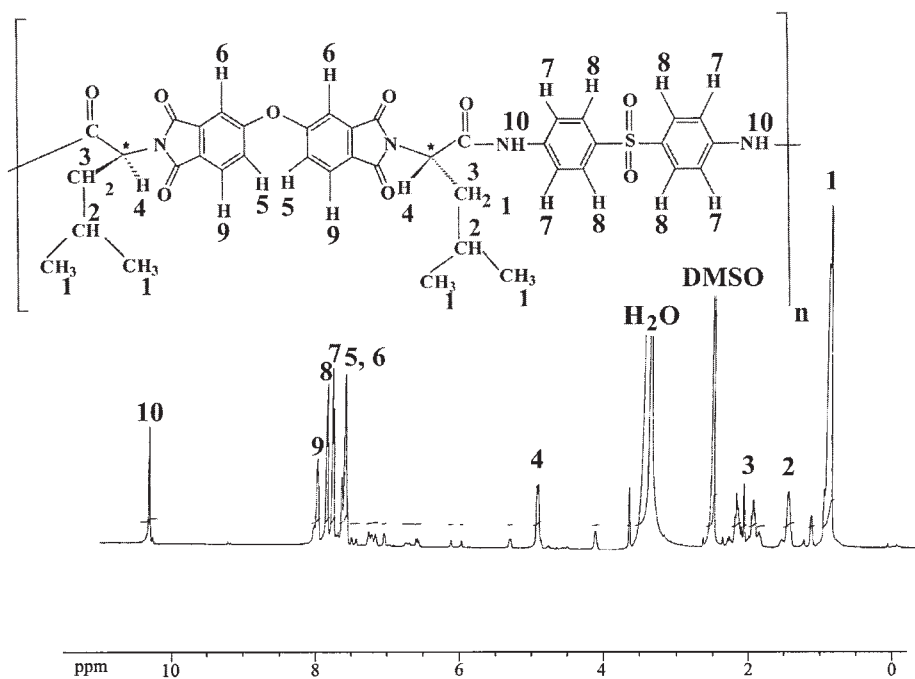
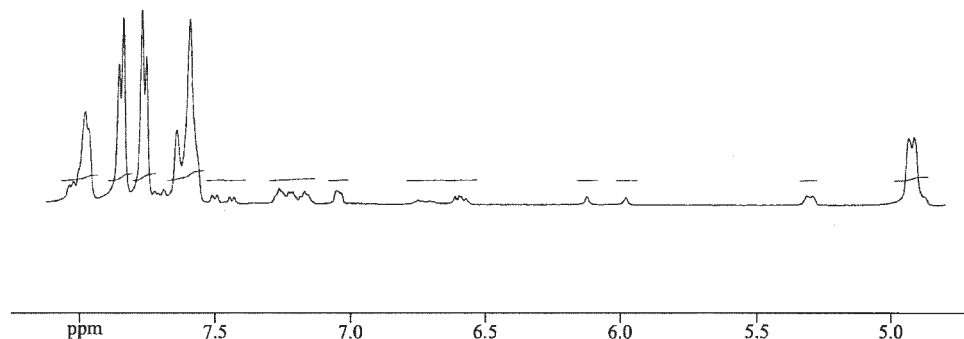


Figure 2 <sup>1</sup>H-NMR (500 MHz) spectrum of PAI-6aI in DMSO-*d*<sub>6</sub> at rt.



**Figure 3**  $^1\text{H-NMR}$  (500 MHz) spectrum of PAI-6aI in  $\text{DMSO-}d_6$  at rt. Expanded region for the aromatic protons ( $\delta = 4.50\text{--}8.00$  ppm).

ical structure and purity of the compounds **3** and **4** were proved using elemental analysis, IR, and  $^1\text{H-NMR}$  spectroscopic techniques. The IR spectrum of compound **3** showed a broad and strong peak at  $3500\text{--}2500\text{ cm}^{-1}$ , which was assigned to the COOH groups, and two absorption bands at  $1772$  and  $1719\text{ cm}^{-1}$ , which are characteristic peaks for imide rings. The disappearance of the strong acidic hydroxyl peak in the IR spectrum of compound **4** confirmed a complete conversion of diacid **3** to diacid chloride **4**. 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.

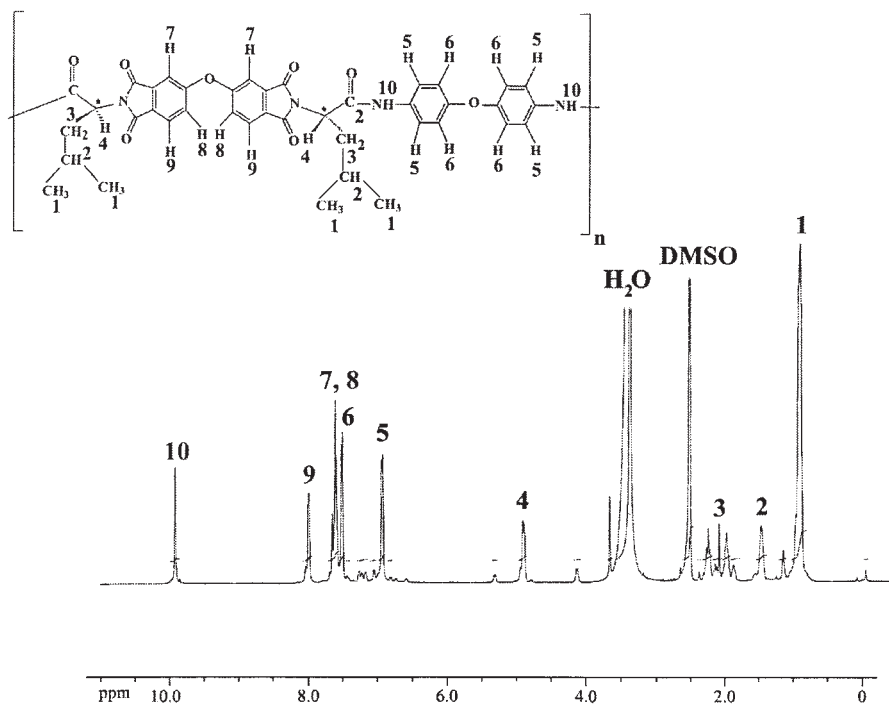
The  $^1\text{H-NMR}$  spectrum (500 MHz) of compound **3** is shown in Figure 1. The peaks at  $4.75\text{--}4.80$  ppm are

assigned to the protons of the chiral center, which appeared as doublet of doublet by the two-diastratopic protons.

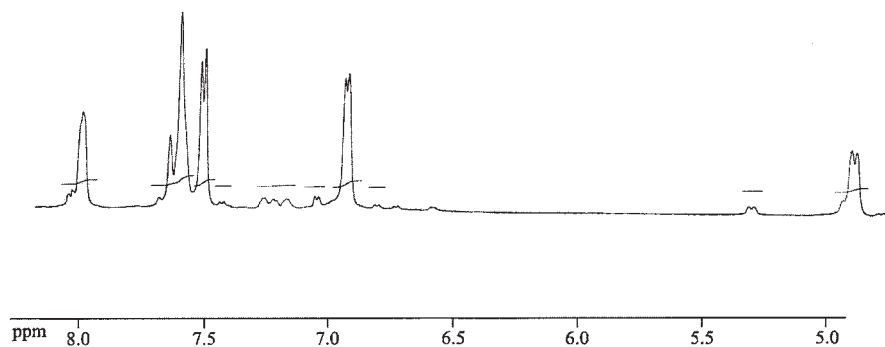
The  $^1\text{H-NMR}$  spectrum (500 MHz) of diacid chloride is similar to that of the diacid derivative.

### Polymer synthesis

The polymerization of diacid chloride **4** with aromatic diamines **5a–5f** was performed under low temperature (method I), reflux condition (method II), and microwave polycondensation reaction (method III) (Scheme 2). In method I, the polycondensation reaction was performed in cold NMP solution ( $-5^\circ\text{C}$ ) in the presence of a small amount of  $\text{TMSCl}$ . In this method, the polymerization reactions occurred at lower tem-



**Figure 4**  $^1\text{H-NMR}$  (500 MHz) spectrum of PAI-6cI in  $\text{DMSO-}d_6$  at rt.



**Figure 5**  $^1\text{H-NMR}$  (500 MHz) spectrum of PAI-6cI in  $\text{DMSO-}d_6$  at rt. Expanded region for the aromatic protons ( $\delta = 4.30\text{--}8.00$  ppm).

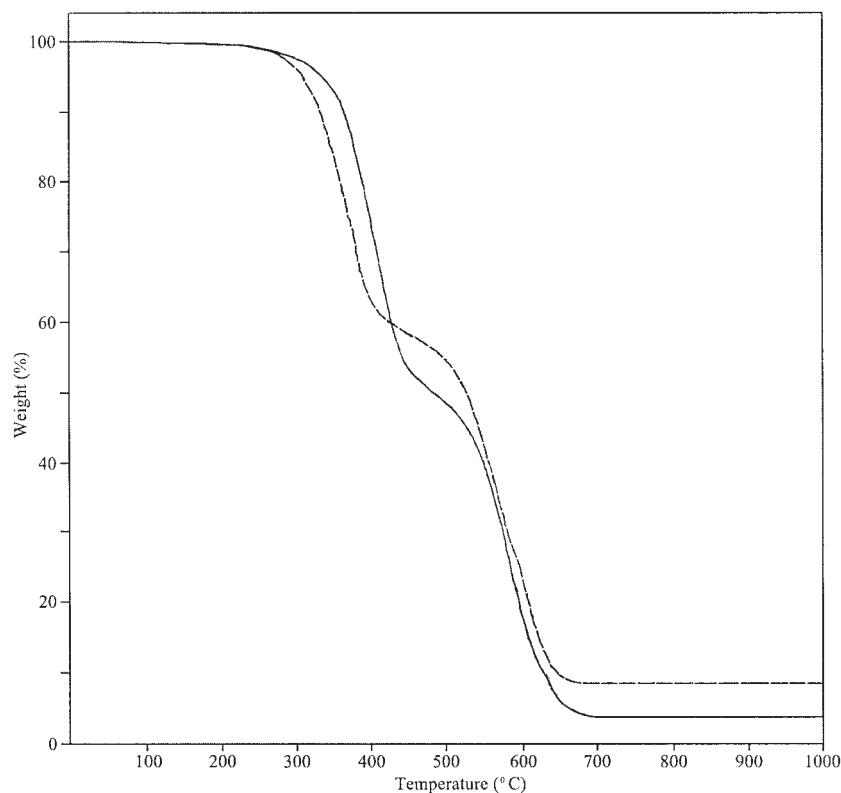
perature in a period of 2 h. In method II, polycondensation reactions proceeded rapidly at the reflux temperature of the solvent in 1 min. We obtained comparable yields and viscosity of PAIs **6a–6f** from methods I and II. The reaction yields and some physical data of the solution polycondensations are listed in Tables I and II.

To compare conventional solution polycondensation reaction methods with microwave-assisted polycondensation, the reactions were also carried out under microwave conditions in the presence of a small amount of *o*-cresol that acts as a primary microwave

absorber. The reaction mixture was irradiated for 6 min with 100% of radiation power. At higher radiation times, dark products were obtained, and on the other hand under low radiation times or power, reactions gave low yield and viscosity. The reaction yields and some physical data for PAIs **6aIII–6fIII** are listed in Table III.

#### Polymer characterization

The structures of these polymers were confirmed as PAIs by means of elemental analysis, IR, and  $^1\text{H-NMR}$



**Figure 6** TGA of PAI-6aI (—) and PAI-6dI (- - - -) with a heating rate of  $40^\circ\text{C}/\text{min}$  and chart speed  $10\text{ mm}/\text{min}$  in nitrogen atmosphere.

TABLE V  
Thermal Properties of PAIs

Polymer	$T_5$ (°C) <sup>a</sup>	$T_{10}$ (°C) <sup>b</sup>	Char Yield (%) <sup>c</sup>
<b>6aI</b>	347	382	18.1
<b>6dI</b>	300	347	23.1

<sup>a</sup> Temperature at which 5% weight loss was recorded by TGA at heating rate of 40°C/min in N<sub>2</sub>.

<sup>b</sup> Temperature at which 10% weight loss was recorded by TGA at heating rate of 40°C/min in N<sub>2</sub> and chart speed has been 20 mm/min.

<sup>c</sup> Percentage weight of material left undecomposed after TGA analysis at maximum temperature 550 °C in N<sub>2</sub>.

spectroscopy. Elemental analysis data of the resulting polymers are listed in Table IV.

The infrared (IR) spectra of all polymers show the characteristic absorption peaks for the imide ring at 1776 and 1719 cm<sup>-1</sup> due to the symmetrical and asymmetrical carbonyl stretching vibrations. Bands of amide N-H groups appeared around 3376 cm<sup>-1</sup> (hydrogen band) and 1504–1515 cm<sup>-1</sup> (amide II band). All of them exhibited strong absorptions at 1381 cm<sup>-1</sup> and 745 cm<sup>-1</sup> that show the presence of the imide heterocycle ring in these polymers.

The <sup>1</sup>H-NMR spectra of PAI **6aI** and PAI **6c** are shown in Figures 2–5. The pattern of spectra is similar to those of the monomer diacid chloride and corresponding diamine.

Most of the polymers are readily soluble in a variety of organic solvents, such as DMF, DMAc, and dimethyl sulfoxide(DMSO), and even in less polar solvents, such as *o*-cresol, *m*-cresol, and acetone. But these polymers are insoluble in solvents such as chloroform, acetonitril, cyclohexane, and water.

### Thermal properties

The thermal stability of some of the PAIs was investigated by thermogravimetric analysis (TGA) measurements. Typical TGA curves of representative polymers are shown in Figure 6. The temperatures of 5 and 10% weight loss together with char yield at 600°C for PAIs **6aI** and **6dI** have been calculated from their thermograms. From these data it is clear that the resulting polymers are thermally stable. The thermoanalyses data of PAIs **6aI** and **6dI** are summarized in Table V.

### CONCLUSIONS

Several new optically active aliphatic-aromatic PAIs having L-leucine and 3,3',4,4'-diphenylsulfonetetra-carboxylic dianhydride moieties were synthesized by three methods. The polycondensation lead to the formation of polymers having inherent viscosity ranging from 0.25–0.52 dL/g. These could indicate molecular weight ranging from 20,000–30,000 g/mol. We obtained results from these solution polycondensation methods comparable with the microwave assisted polymerization technique. TMSCl activates the diamine monomers.<sup>15</sup> The resulting PAIs are thermally stable and are readily soluble in common organic solvents. The synthetic polymers are expected to have potential as packing materials in chromatography technique. Furthermore, the resulting polymers due to the presence of amino acid moieties could have biodegradability and biocompatibility properties, so they could be environmentally friendly.

We wish to express our gratitude to the Management and Programming Organization of I.R. Iran for partial financial support. Further financial support from the Center of Excellency in Chemistry Research (IUT) is gratefully acknowledged.

### References

- Cassidy, P. E. *Thermally Stable Polymers*; Dekker: New York, 1980.
- Seymour, R. B.; Carraher, C. E. *Polymer Chemistry: An Introduction*; Dekker: New York, 1981.
- Yang, C. P.; Chen, W. T. *Makromol Chem* 1992, 193, 2323.
- Yang, C. P.; Hsiao, S. H.; Jang, C. C. *J Polym Sci Part A: Polym Chem* 1995, 33, 1095.
- Yang, C. P.; Lin, J. H. *J Polym Sci Part A Polym Chem* 1993, 31, 3081.
- Bell, V. L.; Stump, B. L.; Gager, H. J. *Polym Sci, Polym Chem Ed* 1976, 14, 2275.
- Takekoshi, T.; Wirth, J. G.; Heath, D. R.; Kochanocski, J. E.; Manello, J. S.; Webber, M. T. *J Polym Sci, Polym Chem Ed* 1980, 18, 3069.
- Subramanian, G. *Chiral Separation Techniques*; WILEY-VCH: New York, 2001.
- Mallakpour, S.; Shahmohammadi, M. H. *Polym Int* 2004, 53, 184.
- Mallakpour, S.; Kohee, S. *J Appl Polym Sci* 2004, 91, 2288.
- Mallakpour, S.; Zamanlou, M. R. *J Appl Polym Sci* 2004, 91, 3281.
- Mallakpour, S.; Kowsari, E. *J Appl Polym Sci* 2004, 91, 2991.
- Mallakpour, S. E.; Hajipour, A. R.; Taghizadeh, H. *Molecules* 2003, 8, 359.
- Mallakpour, S.; Kowsari, E. *J Polym Sci Part A* 2003, 41, 3974.
- Becker, K. H.; Schmidt, H. W. *Macromolecules* 1992, 25, 6784.