Microwave-Assisted and Conventional Polycondensation Reaction of Optically Active *N,N′*-(4,4′-Sulphonediphthaloyl)-bis-*L*-Leucine Diacid Chloride with Aromatic Diamines

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ABSTRACT: 3,3′,4,4′-Diphenylsulfonetetracarboxylic dianhydride (**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 prepared 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**), 2,4-diaminotoluene (**5f**), and 1,5-diaminonaphthalene (**5g**) 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 were also performed under two conventional methods: low temperature solution polycondensation in the presence of trimethylsilyl chloride, and a short period reflux conditions. A series of optically active poly(amide-imide)s with inherent viscosity of 0.25–0.42 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 optically active poly (amide-imide) s are reported. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2992–3000, 2004

Key words: polyamides; polyimides; polycondensation

INTRODUCTION

In the last 2 decades, there has been a considerable interest in the development of microwave-assisted synthesis of small and macromolecular organic compounds. The reactions are very fast, and are completed within 10 min.[1] It was recently shown that microwave (MW) activation for polymers syntheses allows enhancements in the reactivity and selectivity.[2] We have used microwave irradiation for syntheses of organic compounds as well as macromolecules with safe and clean procedure in the so-called green chemistry.[3–6]

Incorporation of amino acid moieties in biopolymers are of interest due to their inherent biological compatibility and degradability, making them ideal candidates for a variety of biomaterial application. On the other hand, optically active polymers containing amino acids can induce crystallinity with the ability to form higher ordered structures that exhibit enhanced solubility characteristics.[7] Polymers with optically active properties have found interesting applications such as chiral phase for enantiomeric separations in chromatography or chiral media for asymmetric synthesis.[8–12] Recently, we have synthesized optically active polymers by different methods,[13–19] such as modification of polybutadiene with an optically active substituted urazole group,[13] Diels-Alder-ene reactions,[14,15] and reaction of an optically active monomer with several diamines via solution polymerization.[16–21] In polycondensation reactions, we use amino acids as chiral inducting agents. These materials are a naturally occurring compound; therefore, synthetic polymers based on amino acids are expected to be biodegradable and biocompatible.

This article reports the microwave-assisted synthesis of optically active poly(amide-imide)s (**PAI**s) containing 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride and *L*-leucine moieties by using a microwave oven, and compares this method with conventional solution polymerization.

EXPERIMENTAL

Materials

4,4′-Diaminodiphenylmethane (**5b**) and Benzidine (**5g)** was purified by recrystallization from water. 4,4′-

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Diaminodiphenylether (**5c**) was purified by acetone and water. 1,4-Phenylenediamine (**5d**), 1,3-phenylenediamine (**5e**), 2,4-diaminotoluene (**5f**), and (**5g**) were purified by sublimation. 3,3′4,4′-Diphenylsulfonetetracarboxylic 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) were used without further purification.

Apparatus

The apparatus used for the polycondensation was a Samsung 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.

Measurements

Proton nuclear magnetic resonance ^{1}H-NMR (90 MHz) and (500 MHz) spectra were recorded on a Varian EM-390 (Varian Associates, Palo Alto, CA) and Bruker, Avance 500 instrument (Germany), respectively. Tetramethylsilane (TMS) was used as an internal reference. Proton resonances are designated as singlet (s), doublet (d), doublet of doublet (dd), and multiplet (m). IR spectra were recorded on Shimadzu 435 IR (Shimadzu, Japan) and FTIR Unicom Mattson 1000 (England) spectrophotometers. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave number (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 Fenske Routine Viscometer (Germany). Specific Rotations were measured by a Perkin-Elmer-241 Polarimeter (Germany). Thermal Gravimetric Analysis (TGA) data for polymers were taken on a TGA 7 Perkin-Elmer (Germany) in nitrogen atmosphere at a rate of 40°C/min. Elemental analysis were performed by Malek-Ashtar University of Technology, Tehran, I.R. Iran.

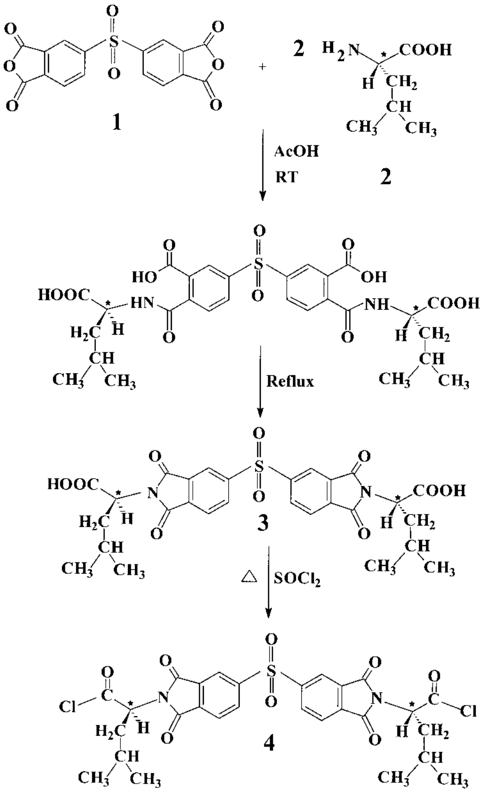
Monomer synthesis

N,N′-(4,4′-sulphonediphthaloyl)-bis-L-leucine diacid (Diacid 2)

Into a 50-mL round-bottomed flask 1.00 g (2.79×10^{-3} mol) of 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (**1**), 0.80 g (6.14×10^{-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 pale yellow precipitate was formed, filtered off, and washed with cold concentrated HCl, to give 1.52 g (93.2%) of compound (**3**). mp: 132–134°C, $[\alpha]_D^{25}$: −54.2 (0.050 g in 10 mL of DMF); IR (KBr): 3500–2400 (s, br), 3020 (m), 2950 (m,), 2550 (m), 1780 (m), 1720 (s), 1460 (w), 1420 (m), 1380 (s), 1320 (m), 1275 (m), 1150 (m), 1060 (w), 930 (w), 860 (w), 740 (m) ,665 (w), 615 (w), 560 cm^{-1} (w). ^{1}H-NMR [(CDCl$_3$, TMS), 90 MHz, δ]: 0.50–1.2 (d, 12H, J = 7.5 Hz), 4.80–5.10 (dd, 2H, J_1 = 12.0 Hz, J_2 = 4.5 Hz), 7.35 (s, 2H), 8.4 (d, 2H, J = 9.0 Hz), 8.90 (d, overlapped with singlet, 2H), 9.0 ppm (s, overlapped with doublet, 2H). Elem. Anal. Calcd. for $C_{28}H_{28}N_2O_{10}S$: C, 57.53%; H, 4.83%; N, 4.80%. Found: C, 56.90%; H, 4.74%; N, 5.74 %.

N,N′-(4,4′-sulphonediphthaloyl)bis-L-leucine diacid chloride (Diacid chloride 4)

Into a 25-mL round-bottomed flask were placed 1.00 g (1.71×10^{-3} mol) of compound **3** and 6 mL (an excess amount) of thionyl chloride. The mixture was heated on an oil bath up to 50°C until the suspension mixture was converted to a clear solution, then the heating was continued for additional of 2 h. Unreacted thionyl chloride was removed under reduced pressure and the residue was washed with dry ether three times, to leave 0.99 g (93.3%) of pale yellow solid. mp: 120°C



Scheme 1

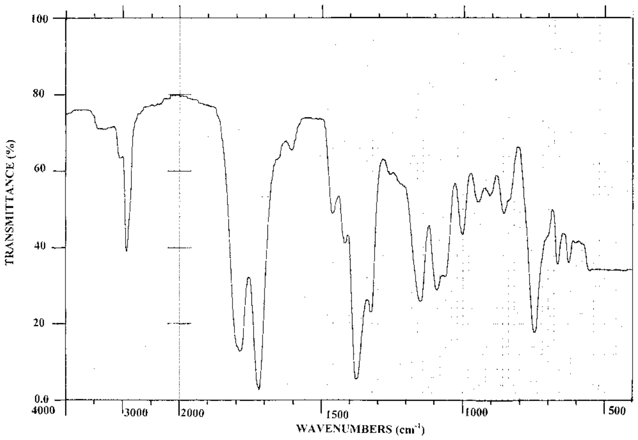


Figure 1 IR (KBr) spectrum of diacid chloride (**4**).

(decomposed), $[\alpha]^{25}_{D}$: −67.0 (0.050 g in 10 mL DMF); IR (KBr): 2990 (m), 1790 (s), 1720 (s), 1460 (m), 1420 (m), 1380 (s), 1330 (m), 1150 (w), 1090 (w), 1060 (w), 1000 (w), 850 (w), 630 (w), 665 cm^{-1} (w). ^{1}H-NMR [($CDCl_3$, TMS), 500 MHz, δ]: 0.90–1.10 (d, 12H), 5.10–5.20 (dd, 2H, J_1 = 11.3 Hz, J_2 = 4.2 Hz) 8.40–8.50 ppm (m, 6H).

Polymer synthesis

All polymers were synthesized with three different methods.

Method I: polymerization under microwave irradiation

The **PAI**s were prepared by the following general procedure (using polymer **6aI** as an example). Into a porcelain dish were placed 0.100 g (1.61×10^{-4} mol) of diacid chloride (**4**) and 0.0396 g (1.61×10^{-4} mol) of diamine (**5a**). After the reagents were completely ground, 0.10 ml of *o*-cresol as a solvent was added, and the mixture was ground for 5 min, then 0.03 mL of trimethylsilyl chloride (TMSCl) was added and the reaction mixture was irradiated in the microwave oven for 6 min with 100% of the power. The resulting product was isolated by adding methanol and triturating, following by filtration, and was dried at 80°C for 10 h under vacuum to leave 0.122 g (95.0%) of solid **6aI**.

FTIR (KBr): 3361.5 (w), 2961.5 (w), 1784.6 (w), 1723.0 (s), 1592.3 (m), 1530.7 (m), 1384.6 (m), 1323.0 (m), 1153 (m), 1107.0 (w), 746.1 (w), 675.9 (w), 669.2 cm^{-1} (w) ^{1}H-NMR [(DMSO-d_6), TMS, 500 MHz, δ]: 0.85 (dd, distorted) 1.40–2.25 (m), 5.30–5.40 (dd, distorted), 7.75 (s), 8.15 (d, J = 8.0 Hz), 8.60 (d, overlapped with singlet), 8.65 (s, overlapped with doublet), 10.20–10.40 ppm (s,br).

The other **PAI**s **6bI–6gI** were prepared in procedures similar to that above.

Polymer **6bI**

FTIR (KBr): 3723.0 (m), 3000 (w), 1723.1 (s), 1607.7 (w), 1523.1 (m), 1384.6 (m), 1153.8 (m), 623.1 cm^{-1} (w). ^{1}H-NMR [(DMSO-d_6), TMS, 500 MHz, δ]: 0.80 (dd, distorted), 1.40–3.80 (m), 4.90 (dd, distorted), 7.10 (d, J = 6.6), 7.35 (d, J = 7.7 Hz), 8.15 (d, J = 7.2 Hz), 8.60 (d, overlapped with singlet), 8.65 (s, overlapped with doublet), 9.80 ppm (s,br).

Polymer **6cI**

FTIR (KBr): 3700 (s), 2961.5 (w), 1723.1 (s), 1507.6 (m), 384.6 (m), 1223.1(w), 676.9cm^{-1}(w). ^{1}H-NMR [(DMSO-d_6), TMS, 500 MHz, δ]: 0.70–0.90 (dd, J_1 = 19.2 Hz, J_2 = 5.30 Hz), 1.40–2.20 (m), 4.90 (dd, distorted), 6.90 (d, J = 8.23Hz), 7.45 (d, J = 7.12 Hz), 8.15 (m), 8.60 (d, overlapped with singlet), 8.65 (s, overlapped with doublet), 9.90 ppm (s, br).

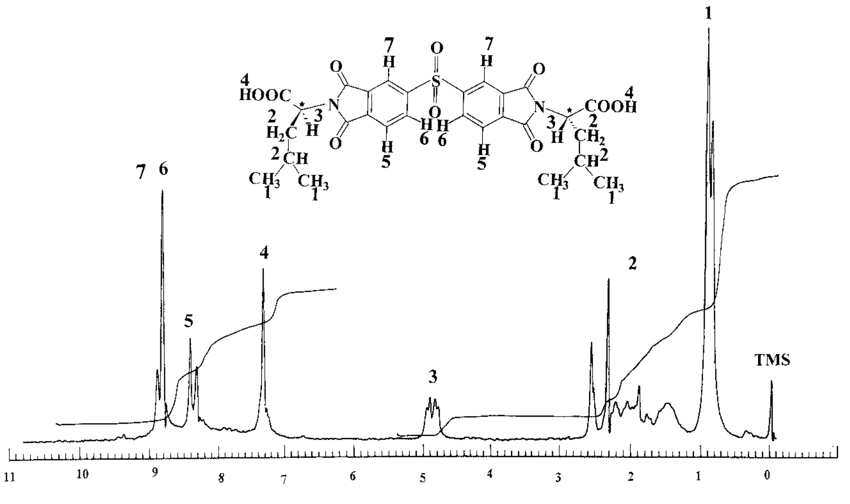
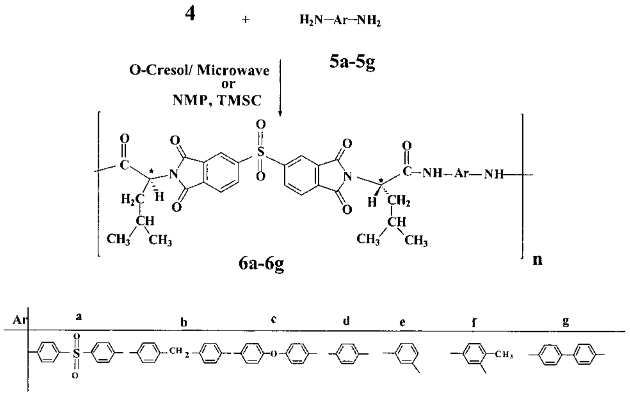


Figure 2 ^{1}H-NMR (90 MHz) spectrum of diacid (**3**) in $CDCl_3$ at rt. Off-set 2 ppm.



Scheme 2

Polymer **6dI**

FTIR (KBr): 3359.2 (w), 2951.5 (w), 1784.6 (w), 1723.1 (s), 1523.1 w), 1384.6 (m), 1153.8 (m), 538.5 (w), 569.2 cm^{-1} (w).

Polymer **6eI**

FTIR (KBr): 3376.9 (w), 2961.5 (w), 1784.6 (w), 1723.1 (s), 1615.4 (w), 1545.2 (w), 1384.6 (m), 1153.8 (m), 676.9 (w), 569.2 cm^{-1} (w).

Polymer **6fI**

FTIR (KBr): 3361.5 (w), 2961.5 (w), 1784.6 (w), 1723.1 (s), 1607.6 (w), 1530.75 (w), 1384.6 (m), 1153.8 (m), 676.9 (w), 569.2 cm^{-1} (w).

Polymer **6gI**

FTIR (KBr): 3615.4 (s), 1723.1 (m), 1507.7 (w), 1384.6 (m), 1153.8 (w), 753.8 cm^{-1} (s).

Method II: low temperature solution polycondensation reaction

Using polymer **6aII** as an example, the general procedure consisted of adding 0.100 g (1.61 × 10^{-4} mol) of diacid chloride (**4**) to a cooled (−5.0°C) and stirred solution of 0.0396 g (1.61 × 10^{-4} mol) of diamine (**5a**) in 0.20 mL of NMP. After the reagents dissolved completely, 0.03 mL of trimethylsilyl chloride (TMSCl) was added and reaction was allowed to proceed for 2 h under a blanket of nitrogen. Then the temperature was raised to room temperature. The reaction mixture was stirred for 8 h. The viscous solution was poured into 40 mL of methanol and the precipitated solid was filtered off and dried at 80°C for 10 h under vacuum to leave 0.1198 g (93.5%) of solid polymer **6aII**.

TABLE II
Some Physical Properties of PAIs 6aIII–6gIII **Prepared by Method II**

	Polymer			
Diamine	Polymer code	Yield (%)	η_{inh}(dL/g)[a]	$[\alpha]_D^{25}$ [a]
5a	**6aII**	93.4	0.27	−45.2
5b	**6bII**	80.2	0.40	−13.2
5c	**6cII**	78.0	0.32	−1.0
5d	**6dII**	68.0	0.35	−31.0
5e	**6eII**	93.0	0.30	−31.2
5f	**6fII**	90.0	0.35	−61.6
5g	**6gII**	70.0	0.38	−21.6

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

The other **PAIs 6bII–6gII** were prepared in procedures similar to that above.

Method III: high temperature solution polycondensation reaction

Polymer **6aIII** is used as an example. Into a 5-mL round-bottomed flask were placed 0.100 g (1.61 × 10^{-4} mol) of diacid chloride (**4**), 0.0396 g (1.61 × 10^{-4} mol) of diamine (**5a**) 0.10 mL of DMAc and 0.03 mL of trimethylsilyl chloride (TMSCl). The mixture was refluxed for 1 min then the reaction temperature allowed to reach to room temperature. The viscous solution was poured into 40 mL of methanol and the precipitated solid was filtered off and dried at 80°C for 10 h under vacuum to leave 0.1178 g (92.0%) of polymer **6aIII**.

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

	Polymer			
Diamine	Polymer code	Yield (%)	η_{inh}(dL/g)[a]	$[\alpha]_D^{25}$ [a]
5a	**6aI**	95.0	0.28	−56.4
5b	**6bI**	94.3	0.35	−30.2
5c	**6cI**	70.0	0.36	−1.0
5d	**6dI**	68.6	0.28	−22.8
5e	**6eI**	70.0	0.30	−12.0
5f	**6fI**	92.4	0.39	−0.6
5g	**6gI**	65.0	0.42	−41.4

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

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

	Polymer			
Diamine	Polymer code	Yield (%)	η_{inh}(dL/g)[a]	$[\alpha]_D^{25}$ [a]
5a	**6aIII**	92.0	0.25	−41.2
5b	**6bIII**	91.8	0.4	−17.2
5c	**6cIII**	85.0	0.37	−1.0
5d	**6dIII**	86.2	0.32	−20.4
5e	**6eIII**	90.0	0.35	−26.0
5f	**6fIII**	80.0	0.32	−36.0
5g	**6gIII**	68.2	0.42	−43.0

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

TABLE IV
Elemental Analysis of PAIs 6aI–6gI

			Elemental analysis (%)			Moisture content
Polymer	Formula		C	H	N	(%)[a]
6aI	$(C_{40}H_{36}N_4O_{10}S_2)_n$	Calcd	60.30	4.50	7.03	2.1
	$(796)_n$	Found	59.23	5.00	6.28	
		Corr[b]	60.47	4.90	6.41	
6bI	$(C_{41}H_{38}N_4O_8S)_n$	Calcd	65.95	5.09	7.50	1.2
	$(714)_n$	Found	65.00	5.21	7.53	
		Corr[b]	65.71	5.15	7.62	
6cI	$(C_{40}H_{36}N_4O_9S)_n$	Calcd	64.17	4.85	7.48	2.8
	$(748)_n$	Found	61.90	5.45	6.75	
		Corr[b]	63.62	5.30	7.00	
6dI	$(C_{34}H_{34}N_4O_8S)_n$	Calcd	62.00	5.16	8.50	3.8
	$(658)_n$	Found	60.09	5.28	7.08	
		Corr[b]	62.37	5.10	7.30	
6eI	$(C_{34}H_{34}N_4O_8S)_n$	Calcd	62.00	5.16	8.53	4.2
	$(658)_n$	Found	59.80	5.51	7.65	
		Corr[b]	62.00	5.27	8.00	
6fI	$(C_{35}H_{36}N_4O_8S)_n$	Calcd	62.70	5.10	8.35	2.5
	$(669)_n$	Found	61.13	5.40	7.60	
		Corr[b]	62.70	5.25	7.80	
6gI	$(C_{40}H_{36}N_4O_8S)_n$	Calcd	65.57	4.95	7.60	4.85
	$(681)_n$	Found	63.00	5.31	6.80	
		Corr[b]	65.50	5.18	6.33	

[a] Moisture content (%) = × $[(W - W0)/W0]$ 100, W = weight of polymer sample after standing at room temperature and W_0 = weight of polymer sample after dried in vacuum at 100°C for 10 h.
[b] Corrected value for C and N = Found value × (100 + moisture content)/100, and corrected value for H = Found value × (100 − moisture content)/100.

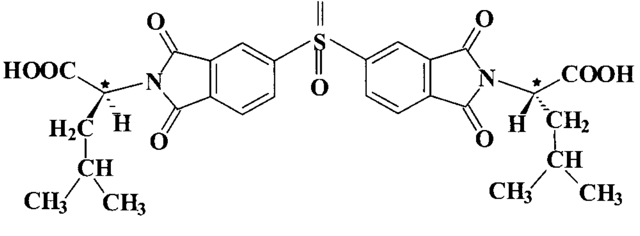
The other **PAI**s **6bIII–6gIII** were prepared in procedures similar to that above.

RESULTS AND DISCUSSION

Monomer synthesis

The new diacid chloride (**4**) was prepared, according to our earlier method[17–20] by the three-step process as shown in Scheme 1.

The asymmetric diacid compound (**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 imide ring was performed under refluxing conditions.



(3)

The diacid (**3**) was converted to diacid chloride derivative (**4**) by reaction with thionyl chloride. The chemical structure and purity of the compounds **3** and **4** were proved using elemental analysis, IR, and ^{1}H-NMR spectroscopic techniques. The IR spectrum of compound **3** showed a broad and strong peak at 3500–2400 cm^{-1}, which was assigned to the COOH groups and two absorption bands at 1720 and 1780 cm^{-1}, which are characteristic peaks for imide rings. The disappearance of strong acidic hydroxyl peak in 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, was shifted to a higher frequency. Figure 1 shows the IR spectrum of diacid chloride (**4**).

The ^{1}H-NMR spectrum (90 MHz) of compound (**3**) is shown in Figure 2. A singlet at 7.35 ppm is assigned to the carboxylic acid protons. The quartet at 4.80–5.10 ppm is assigned to the protons of the chiral center, which appeared as doublet of doublet by the two-diastreotopic protons with the two coupling constants J_1 = 12.0 Hz and J_2 = 4.50 Hz.

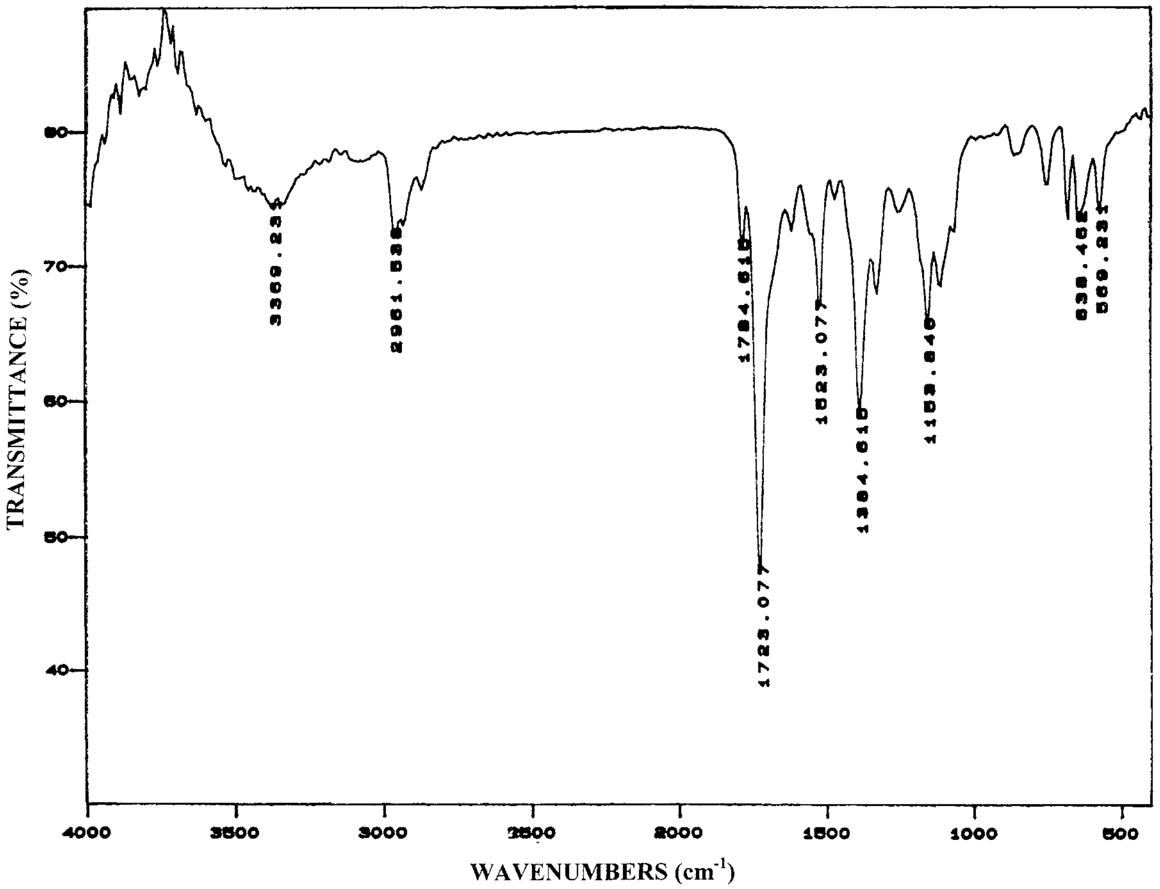


Figure 3 IR (KBr) spectrum of **PAI-6eI**.

Polymer synthesis

Microwave-assisted polycondensation as well as solution polycondensation reactions of an equimolar mixture of monomer **4** with seven different aromatic diamines **5a–5g** in the presence of TMSCl were used to produce **PAIs 6a–6g**, as shown in Scheme 2. The solution reactions were performed under low temperature and high temperature conditions.

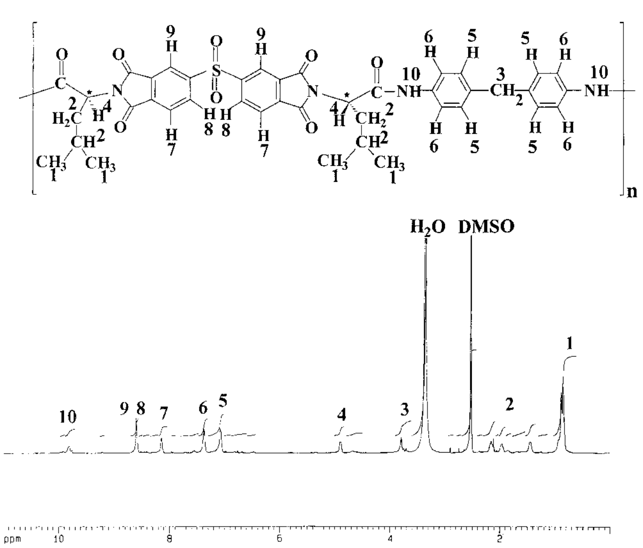


Figure 4 ^{1}H-NMR (500 MHz) spectrum of **PAI-6bI** in DMSO-d_6 at rt.

The microwave-assisted polycondensation reactions were performed in the presence of a 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 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. The reaction yields and some physical data for **PAIs 6aI–6gI** are listed in Table I.

To compare microwave-assisted polycondensation method with conventional solution polycondensation methods, the polymerization of diacid chloride (**4**) with aromatic diamines **5a–5g** was performed under low temperature (Method II) and reflux condition (Method III). In method II, polycondensation reactions were performed in cold NMP solution (−5°C). In this method the polymerization reactions occurred at lower temperature in a period of 2 h. In method III, polycondensation reactions proceeded rapidly at the reflux temperature of solvent in 1 min. We obtained

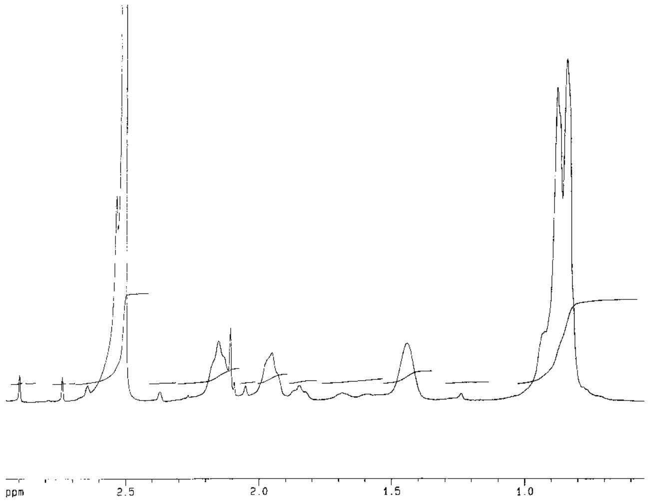


Figure 5 ^{1}H-NMR (500 MHz) spectrum of **PAI-6bI** in DMSO-d_6 at rt. Expanded region for the aliphatic protons (δ = 0.0–2.9 ppm).

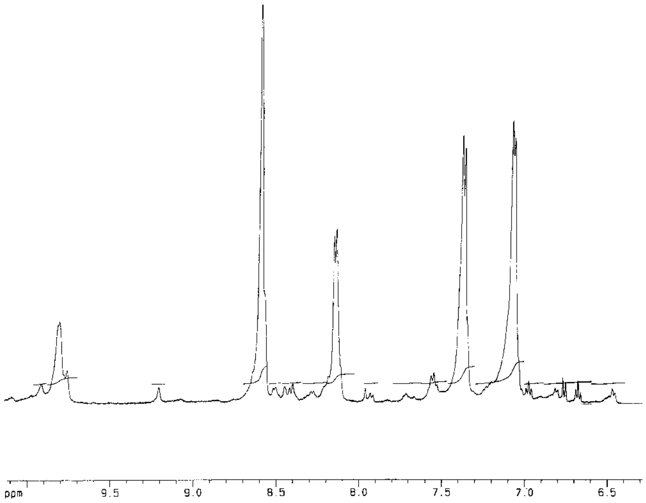


Figure 7 ^{1}H-NMR (500 MHz) spectrum of **PAI-6bI** in DMSO-d_6 at rt. Expanded region for the aromatic protons (δ = 6.3–10.0 ppm).

comparable yields and viscosity of **PAI**s **6aII–6gII** from methods II and III compared with microwave-assisted polymerizations. The reaction yields and some physical data of the solution polycondensations are listed in Tables II and III.

Polymers characterization

The structures of these polymers were confirmed as **PAI**s by means of elemental analysis, IR, and ^{1}H-NMR spectroscopy. Elemental analysis data of the resulting polymers are listed in Table IV.

The infrared (FTIR) spectra of all polymers show the characteristic absorption peaks for the imide ring at 1723 and 1785 cm^{-1} due to the symmetrical and asymmetrical carbonyl stretching vibrations. Bands of amide N—H groups appeared around 3360–3723 cm^{-1} (hydrogen band) and 1507–1523 cm^{-1} (amide II band). All of them exhibited strong absorptions at 1384 cm^{-1} and 638–753 cm^{-1} that show the presence of the imide heterocycle ring in these polymers. All polymers showed characteristic absorptions at 1323 and 1153 cm^{-1} due to the sulfone moiety (SO_2 stretching). Figure 3 shows a typical IR spectrum.

The ^{1}H-NMR spectra of **PAI–6bI** and **PAI–6cI** are shown in Figures 4–7and 8–11. The pattern of spectra is similar to those of monomer diacid chloride and corresponding diamine. The two equivalent amidic hydrogens are seen in a similar chemical shift. Figures 5 and 6 show an expanded region for aliphatic pro-

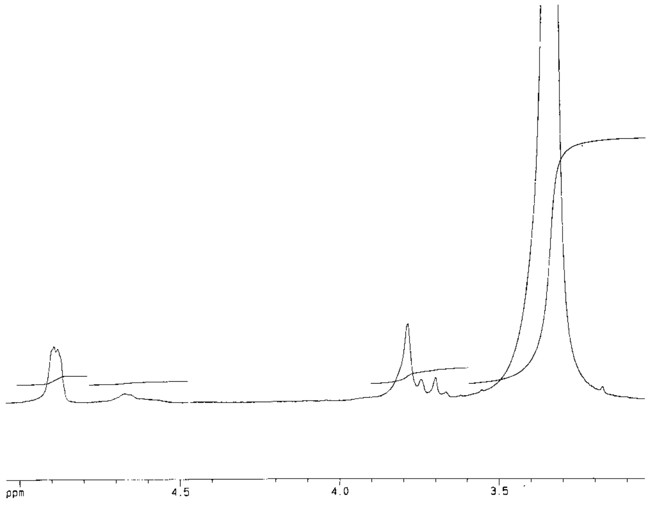


Figure 6 ^{1}H-NMR (500 MHz) spectrum of **PAI-6bI** in DMSO-d_6 at rt. Expanded region for the aliphatic protons (δ = 3.1–5.0 ppm).

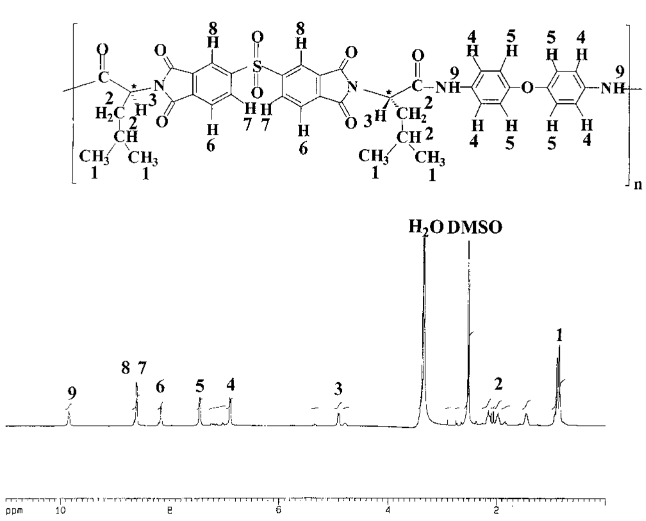


Figure 8 ^{1}H-NMR (500 MHz) spectrum of **PAI-6cI** in DMSO-d_6 at rt.

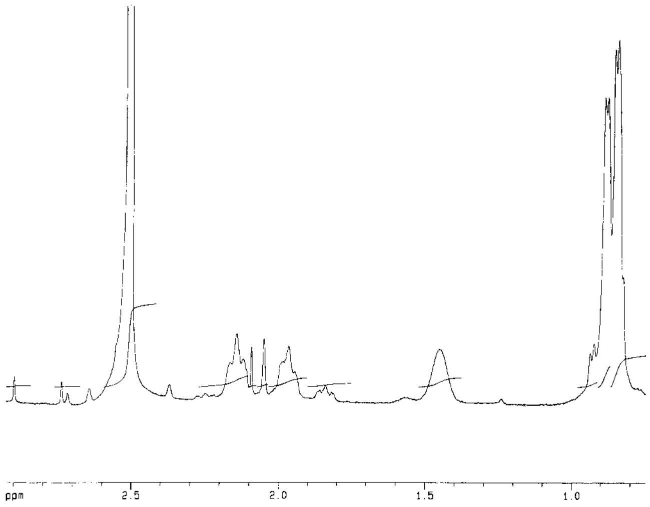


Figure 9 ^{1}H-NMR (500 MHz) spectrum of **PAI-6cI** in DMSO-d_6 at rt. Expanded region for the aliphatic protons (δ = 0.0–2.9 ppm).

tons, and Figure 7 shows an expanded region for aromatic protons. Figures 9 and 10 show also an expanded region for aliphatic protons, and Figure 11 shows an expanded region for aromatic protons.

All polymers are soluble in organic polar solvents such as DMAc, DMF, NMP, and even in less polar solvents like *o*-cresol, *m*-cresol, acetone, and THF. Most of **PAI**s show partial solubility in associated solvents such as acetic acid or ethanol. But these polymers are insoluble in solvents such as chloroform, acetonitrile, cyclohexane, and water.

Thermal properties

The thermal stability of some **PAI**s was investigated by thermogravimetric analysis (TGA) measurements.

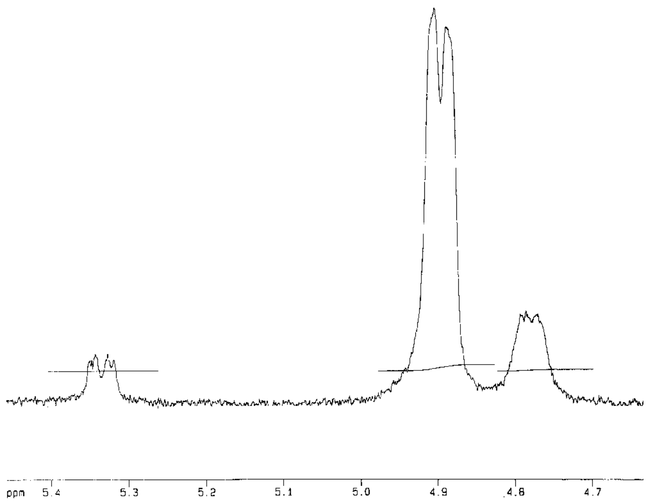


Figure 10 ^{1}H-NMR (500 MHz) spectrum of **PAI-6cI** in DMSO-d_6 at rt. Expanded region for the aliphatic protons (δ = 4.7–5.4 ppm).

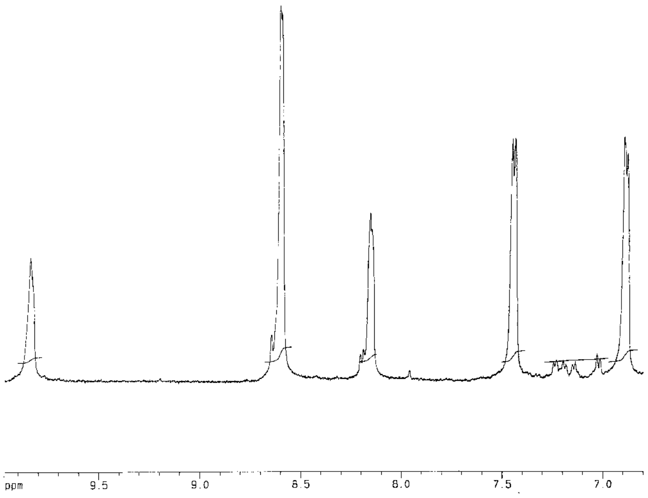


Figure 11 ^{1}H-NMR (500 MHz) spectrum of **PAI-6cI** in DMSO-d_6 at rt. Expanded region for the aromatic protons (δ = 6.8–9.9 ppm).

Typical TGA curves of two representative polymers are shown in Figure 12. The temperatures of 5% and 10% weight loss together with char yield at 600°C for **PAIs 6bI** and **6fI** are 286.5°C, 313.5°C, 14% and 347.0°C, 360.5°C, 16.5%, respectively. From this information it is interesting to note that the resulting polymers are rather thermally stable.

CONCLUSIONS

New optically active aliphatic-aromatic **PAI**s having *L*–leucine and 3,3′,4,4′- diphenylsulfonetetracarboxy-

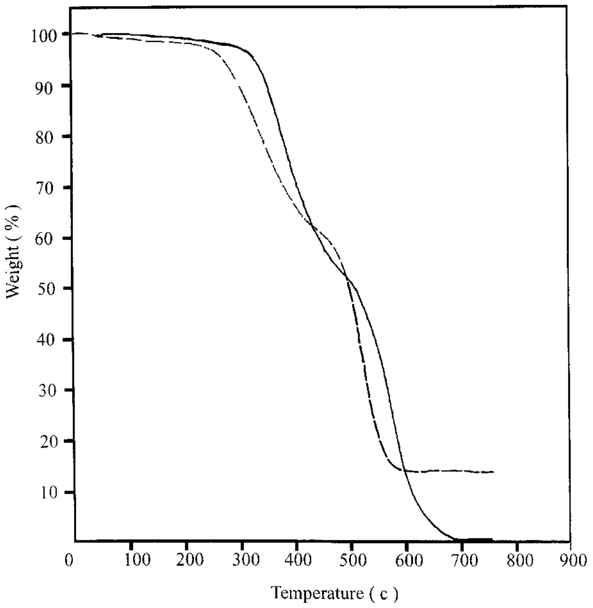


Figure 12 TGA of **PAI-6bI** (- - -) and **6fI** (—) with a heating rate of 40°C/min in nitrogen atmosphere.

lic dianhydride moieties were synthesized by using a domestic microwave oven from polycondensation of optically active diacid chloride (**4**) with several diamines in the presence of a small amount of a polar organic medium such as *o*-cresol. The use of such an organic medium was necessary to induce effective homogeneous heating of the monomers the polycondensation lead to the formation of polymers having inherent viscosity of 0.24–0.42 dL/g. To compare this method with solution polymerization methods, **PAI**s were also synthesized by both low-temperature and high-temperature solution polycondensation. Although we obtained comparable results from these methods with microwave-assisted polymerization, but the above results demonstrate that microwave heating is an efficient method (shorter reaction time and high efficiency of energy) for the polycondensation reactions. In all three methods trimethylchlorosilane activates the diamine monomers.[22] The resulting **PAI**s are thermally stable, and are readily soluble in common organic solvents. The synthetic polymers are expected to have a potential as packing materials in column chromatography.

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