

Application of Microwave Irradiation for Synthesis of Novel Optically Active Poly(Amide Imides) Derived from Diacid Chloride Containing Epiclone and L-Isoleucine with Aromatic Diamines

Shadpor Mallakpour,* Elaheh Kowsari

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

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ABSTRACT: Epiclone [3a,4,5,7a-tetrahydro-7-methyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-1,3-isobenzofurandione] or [5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexyl-1,2-dicarboxylic acid anhydride] (**1**) was reacted with L-isoleucine (**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**), 2,4-diaminotoluene (**5f**), and 4,4'-diaminobiphenyl (**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 in two other different methods: low-temperature solution polycondensation and reflux conditions. A series of optically active poly(amide imides) with inherent viscosity of 0.12–0.30 dL/g were obtained. 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 imides) are reported. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2218–2229, 2004

Key words: microwave-assisted polycondensation; optically active polymers; poly(amide imides); microwave oven; inherent viscosity

INTRODUCTION

The short reaction times and expanded reaction range that are offered by microwave-assisted organic synthesis are suited to the increased demands in industry. In microwave-assisted synthesis, a homogeneous mixture is preferred to obtain a uniform heating pattern. The reactions are very fast and are completed within 10 min.¹ Recently, we used microwave irradiation for the synthesis of organic compounds as well as macromolecules.^{2–10}

Much attention was paid in recent years to the fabrication of chiral separation materials. Those polymers possess a high chiral recognition ability as a chiral stationary phase in high-performance liquid chromatography (HPLC) to resolve a wide range of racemates or chiral media for asymmetric synthesis.^{11–15} Then, the synthesis of optically active polymers is the newly con-

sidered topics, which have been paid more attention. Recently, we have synthesized optically active polymers by different methods,^{16–23} such as modification of polybutadiene with an optically active substituted urazole group,¹⁶ Diels–Alder-ene reactions,^{17–18} and reaction of an optically active monomer with several diamines via solution polymerization.^{19–23} Degradable polymer will not only be of interest to polymer scientists in academia and industry alike, but also to environmental scientists and biomedical scientists working on controlled drug release. In polycondensation reactions, we use amino acids as chiral inducting agents. These materials are naturally occurring compounds; therefore, synthetic polymers based on amino acids are expected to be biodegradable and biocompatible.

This article reports on the microwave-assisted synthesis of optically active poly(amide imides) (PAIs) containing Epiclone and L-isoleucine moieties by using a microwave oven and compares this method with conventional solution polymerization.

EXPERIMENTAL

Materials

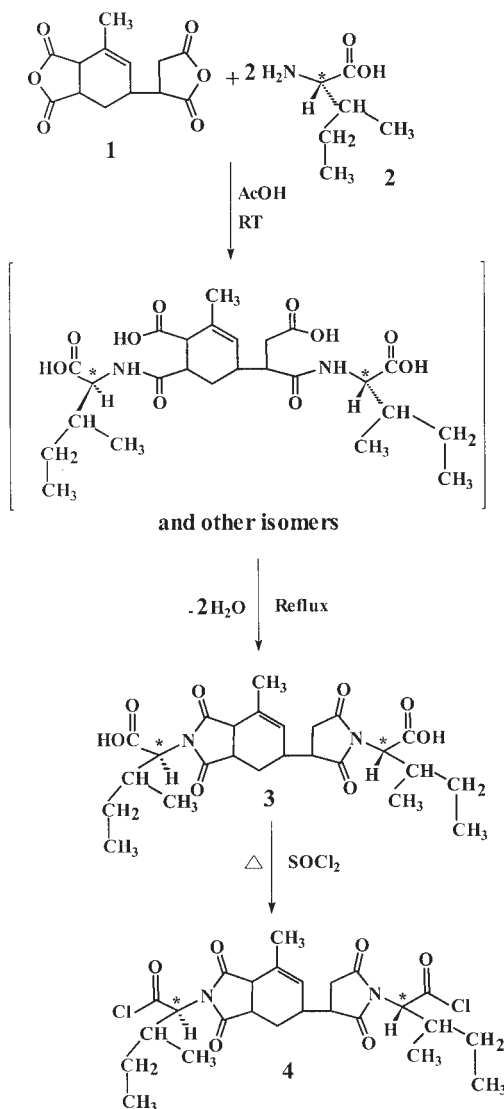
4,4'-Diaminodiphenylmethane (**5b**) and 4,4'-diaminobiphenyl (**5g**) was purified by recrystallization from

* Previous name: Shadpour E. Mallakpour.

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

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water. 4,4'-Diaminodiphenylether (**5c**), 1,4-phenylenediamine (**5d**), 1,3-phenylenediamine (**5e**), and 2,4-diaminotoluene (**5f**) were purified by sublimation. Epiclone B-4400 [3a,4,5,7a-tetrahydro-7-methyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-1,3-isobenzofurandione] or [5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexyl-1,2-dicarboxylic acid anhydride] was supplied from Merck Chemical Co. (Darmstadt, Germany). *N,N*-dimethylacetamide (DMAc) was dried over BaO and 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 domestic microwave oven (2450 MHz, 900

W) without any modification, but all of the polymerization reactions were performed in a hood with strong ventilation.

Measurements

Proton nuclear magnetic resonance $^1\text{H-NMR}$ (90 and 500 MHz) spectra were recorded on a Varian EM-390 (Varian Associates, Palo Alto, CA) and Bruker, Avance 500 instrument (Rheinstetten, 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, Kyoto, Japan) spectrophotometer. Spectra of solids were carried out by using KBr pellets. Vibrational transition frequencies are reported in wavenumbers (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 by using a Cannon Fenske Routine Viscometer (Mainz, Germany). Specific rotations were measured by a Perkin-Elmer 241 Polarimeter (Jugeshein, Germany). Thermal gravimetric analysis (TGA) data for polymers were taken on TGA 7 (Perkin-Elmer) in nitrogen atmosphere at a rate of $40^\circ\text{C}/\text{min}$. Elemental analysis was performed by Malek-Ashtar University of Technology (Tehran, I.R. Iran).

Monomer synthesis

5-[*N*-2-(2*S*-4-methylpanthanoicacid)succinimido]3-methyl-[*N*-2-(2*S*-4-methylpanthanoicacid)]-1,2,5,6-tetrahydrophthalimide (Diacid **3**)

Into a 50-mL round-bottomed flask, 1.00 g (3.78×10^{-3} mol) Epiclone (**1**), 1.02 g (7.77×10^{-3} mol) L-isoleucine (**2**), 30 mL acetic acid, and a stirring bar were placed. The mixture was stirred at room temperature for 3 h and was then refluxed for 8 h. The solvent was removed under reduced pressure and 5 mL cold concentrated HCl was added to the residue. A white gummy precipitate formed and was washed with cold water, and enough amount of ether was added to it to convert it to a clear solution. The ether was removed under reduced pressure to give 1.76 g (95.0%) of compound (**3**).

Melting point (mp): $102\text{--}104^\circ\text{C}$, $[\alpha_D^{25}]$: -99.8° (0.050 g in 10 mL DMF); IR (KB): 3300–2500 (s, br), 1700 (s), 1540 (w), 1380 (s), 1190 (s), 960 (w), 885 (w), 770 (w), 660 (w) cm^{-1} . $^1\text{H-NMR}$ (90 MHz, CDCl_3 , TMS): δ 0.60–3.90 (m, 29H), 4.40–4.80 (m, 2H), 5.50 (s, 1H), 9.20 (s, 2H) ppm. ELEM. ANAL. calcd. for $\text{C}_{25}\text{H}_{34}\text{N}_2\text{O}_8$: C, 61.22%; H, 6.93%; N, 5.71%. Found: C, 60.36%; H, 7.21%; N, 6.21%.

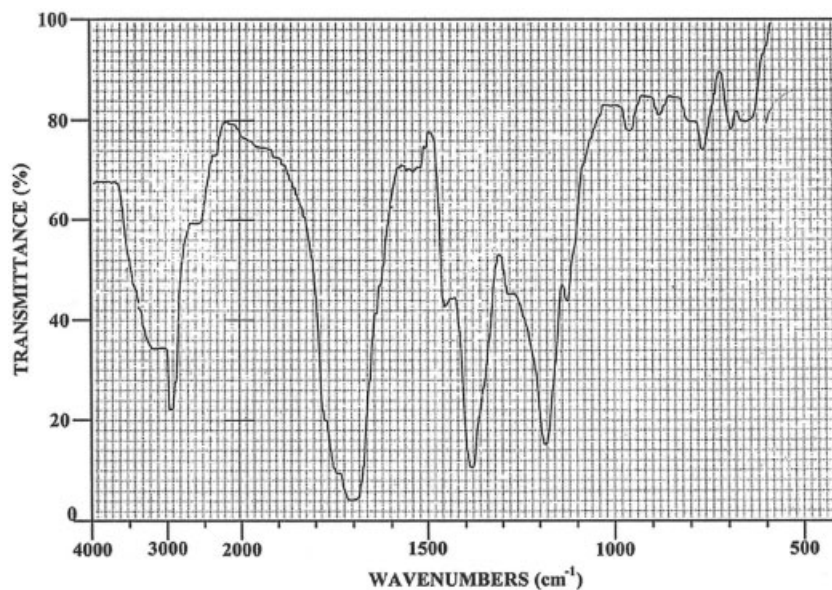


Figure 1 IR (KBr) Spectrum of diacid (3).

5-[N2-(2S-4-methylpanthanoylchloride)succinimido]-
2-methyl-[N-2-(2S-4-methylpanthanoylchloride)]-
1,2,5,6-tetrahydrophthalimide (Diacid chloride 4)

Into a 25-mL round-bottomed flask were placed 1.00 g (2.04×10^{-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 washed with fresh dry ether three times, to leave 1.03 g (96.0%) of pale yellow solid.

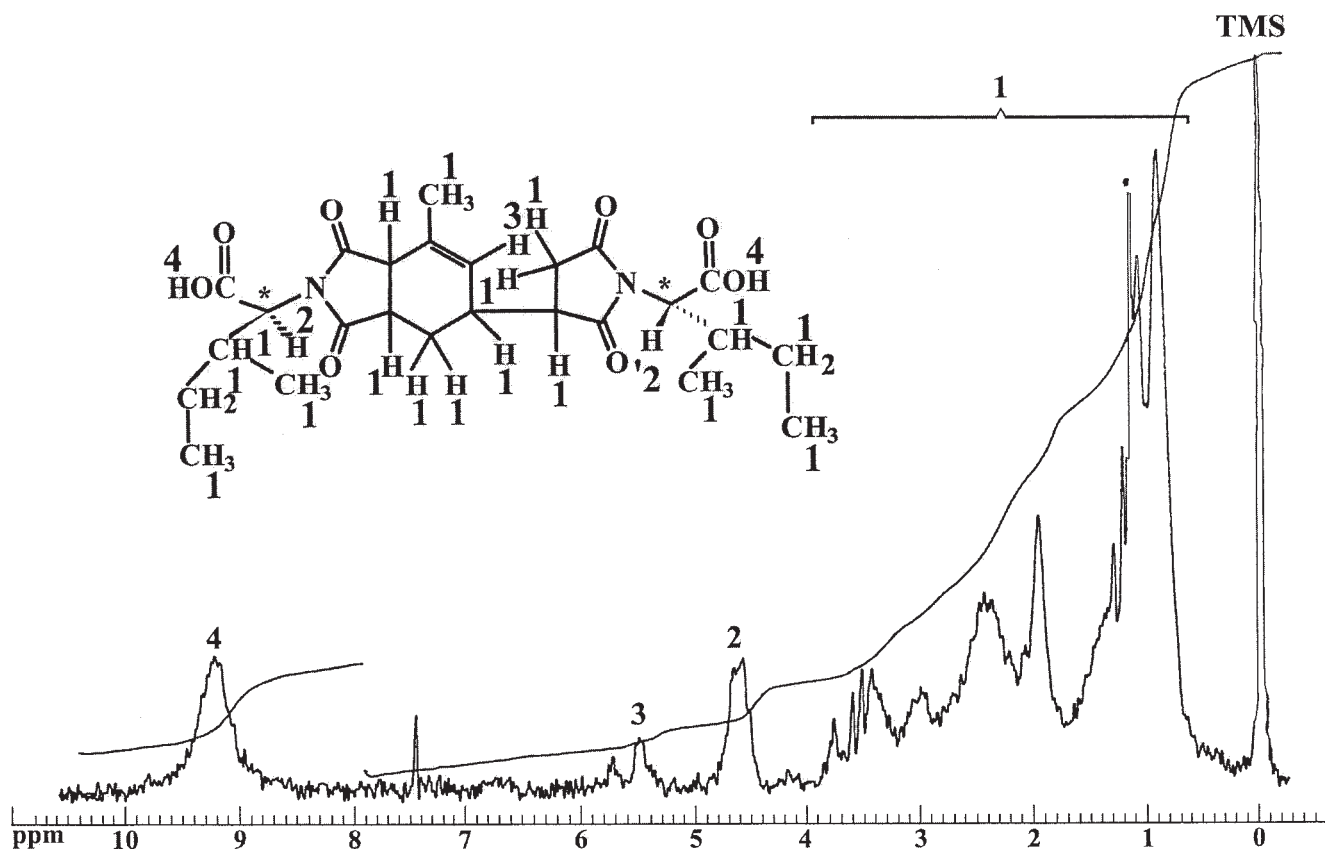
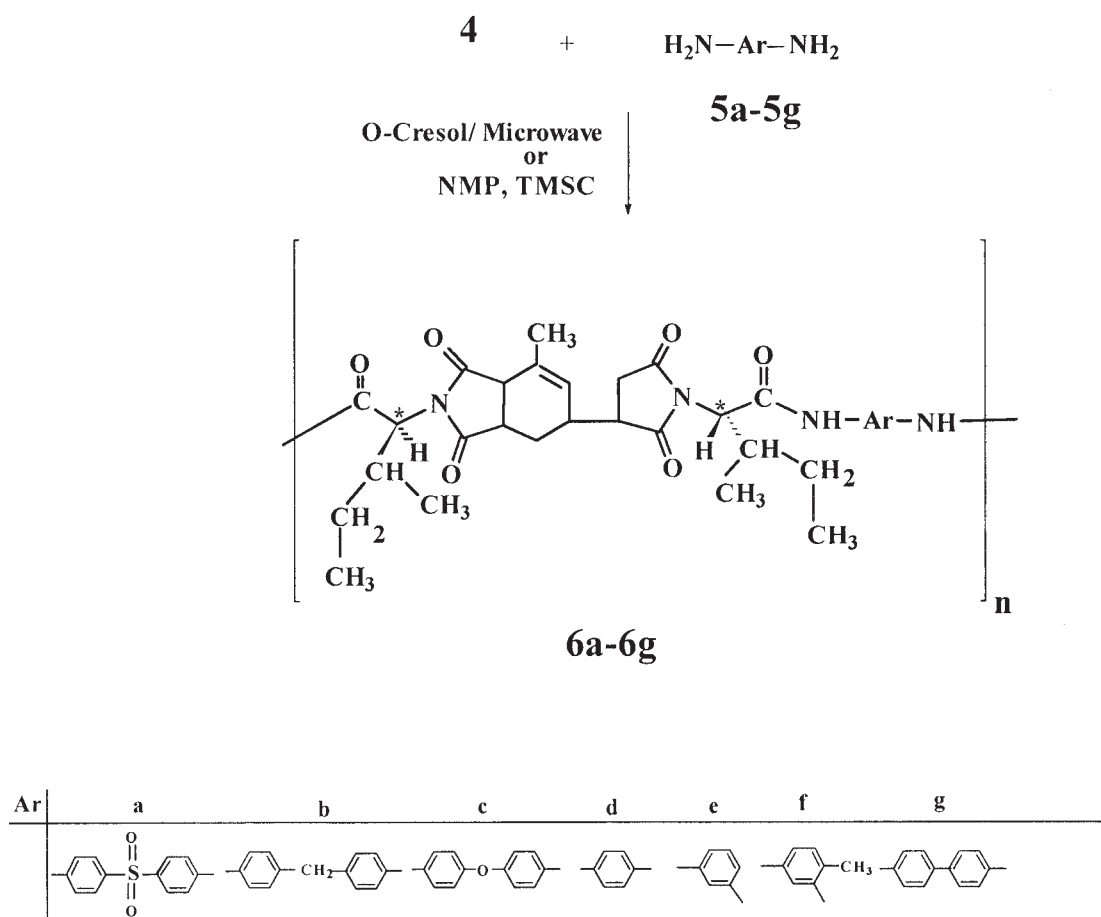


Figure 2 $^1\text{H-NMR}$ (90 MHz) Spectrum of diacid (3) in CDCl_3 , TMS at RT.



Scheme 2

mp: 63°C (decomposed), $[\alpha_D^{25}]$: -124.2° (0.050 g in 10 mL DMF); 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) cm^{-1} ; $^1\text{H-NMR}$ (90 MHz, CDCl_3 , TMS): δ 0.50–3.90 (m, 29H), 4.50–5.00 (m, 2H), and 5.55 (d, 1H) ppm.

Polymer synthesis

All of the polymers were synthesized with three different methods.

Method I: Polymerization under microwave irradiation

The PAIs were prepared by the following general procedure (using polymer **6aI** as an example). Into a porcelain dish were placed 0.20 g (3.79×10^{-4} mol) of diacid chloride (**4**) and 0.0942 g (3.79×10^{-4} mol) of diamine (**5a**). After the reagents were completely ground, 0.25 mL of *o*-cresol as a solvent and 0.05 mL of trimethylsilyl chloride TMSCl was added. The mixture was ground for 5 min. The reaction mixture was

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	90.0	0.30	−93.2
5b	6bI	90.0	0.30	−56.4
5c	6cI	62.0	0.18	+4.4
5d	6dI	67.3	0.20	+5.0
5e	6eI	75.0	0.22	+5.4
5f	6fI	76.0	0.23	−98.0
5g	6gI	78.0	0.24	−124.2

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

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

		Polymer		
Diamine	Polymer	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_D^{25}$ ^a
5a	6aII	73.8	0.21	−40.0
5b	6bII	82.0	0.19	−71.0
5c	6cII	56.4	0.17	+6.2
5d	6dII	67.3	0.18	+10.6
5e	6eII	79.9	0.20	−1.6
5f	6fII	63.5	0.20	−92.0
5g	6gII	76.0	0.25	−86.6

^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

Diamine	Polymer			$[\alpha]_D^{25a}$
	Polymer	Yield (%)	η_{inh} (dL/g) ^a	
5a	6aIII	87.4	0.25	-43.6
5b	6bIII	62.0	0.22	-42.0
5c	6cIII	60.3	0.14	-38.2
5d	6dIII	55.5	0.12	+11.2
5e	6eIII	68.7	0.18	+4.7
5f	6fIII	73.5	0.23	-75.8
5g	6gIII	78.4	0.23	+43.6

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

irradiated in the microwave oven for 6 min on 100% power of microwave apparatus. The resulting product was isolated by adding methanol/H₂O (70/30) and triturating, followed by filtration, and was dried at 80°C for 10 h under vacuum to leave 0.249 g (90.0%) of solid **6aI**.

IR (KBr): 3300 (m, br), 2950 (m), 2920 (m, sh), 2850 (w), 1700 (s), 1590 (s), 1520 (s), 1450 (w), 1380 (s), 1310 (s), 1240 (w), 1150 (s), 1100 (s), 830 (w), 720 (w) cm⁻¹.

The other PAIs (**6bI–6gI**) were prepared with similar procedures.

All of spectra were recorded with KBr pellets.

Polymer **6bI**

3300 (m, br), 2950 (m), 1700 (s), 1600 (m), 1515 (s), 1460 (w), 1380 (s), 1315 (w), 1170 (s), 1120 (w), 1020 (w), 960 (w), 878 (m), 748 cm⁻¹ (m).

Polymer **3cI**

3300 (m, br), 2950 (m), 1700 (s), 1600 (w), 1500 (s), 1460 (w), 1380 (m), 1300 (w), 1220 (m), 1180 (w), 1120 (w), 1100 (w), 830 cm⁻¹ (w).

Polymer **3dI**

3400 (m, br), 2950 (m), 1760 (m), 1700 (s), 1490 (m), 1450 (w), 1380 (s), 1220 (m), 1170 (m), 1100 (w), 750 cm⁻¹ (w).

Polymer **3eI**

3400 (m, br), 2950 (m), 1770 (w), 1700 (s), 1610 (w), 1510 (m), 1380 (s), 1170 (m), 1150 (w), 820 (w), 740 cm⁻¹ (w).

Polymer **3fI**

3300 (m, br), 2950 (m), 1700 (s), 1600 (w), 1520 (w), 1490 (w), 1380 (s), 1220 (w), 1180 (m), 1130 (w), 810 (w), 750 cm⁻¹ (w).

TABLE IV
Elemental Analysis of PAIs 6aI–6gI

Polymer	Formula		Elemental analysis (%)			Moisture content (%) ^a
			C	H	N	
6aI	(C ₃₇ H ₄₂ N ₄ O ₈ S) _n (703) _n	Calcd	63.23	6.03	7.97	0.35
		Found	63.13	6.33	8.10	
		Corr ^b	63.45	6.00	8.00	
6bI	(C ₃₈ H ₄₄ N ₄ O ₆) _n (653) _n	Calcd	69.92	6.79	8.58	0.20
		Found	69.21	7.23	9.37	
		Corr ^b	69.34	7.21	9.38	
6cI	(C ₃₇ H ₄₂ N ₄ O ₇) _n (655) _n	Calcd	67.87	6.46	8.56	0.37
		Found	67.05	6.71	9.01	
		Corr ^b	67.32	6.48	9.04	
6dI	(C ₃₁ H ₃₈ N ₄ O ₆) _n (563) _n	Calcd	66.17	6.81	9.96	0.20
		Found	65.23	7.11	10.61	
		Corr ^b	65.36	7.09	10.63	
6eI	(C ₃₁ H ₃₈ N ₄ O ₆) _n (563) _n	Calcd	66.17	6.81	9.96	0.21
		Found	65.52	7.03	10.55	
		Corr ^b	65.65	7.01	10.57	
6fI	(C ₃₂ H ₄₀ N ₄ O ₆) _n (577) _n	Calcd	66.65	6.99	9.71	0.32
		Found	66.03	7.29	10.11	
		Corr ^b	66.24	7.20	10.14	
6gI	(C ₃₇ H ₄₂ N ₄ O ₆) _n (638) _n	Calcd	69.57	6.62	8.77	0.33
		Found	68.43	7.10	9.81	
		Corr ^b	68.65	7.07	9.84	

^a Moisture content (%) = $(W - W_0)W_0 / 100$, 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 $\times (100 + \text{moisture content}) / 100$, and corrected value for H = Found value $\times (100 - \text{moisture content}) / 100$.

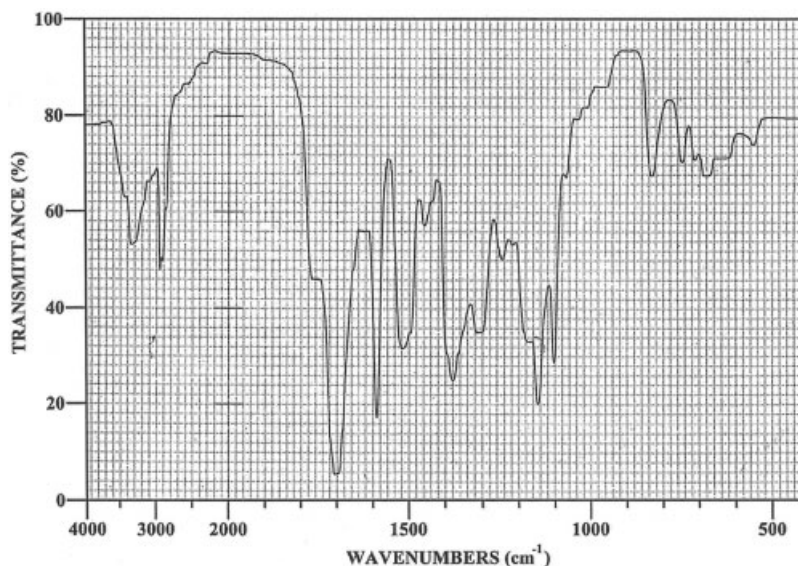


Figure 3 IR (KBr) spectrum of PAI 6aI.

Polymer 3gI

3350 (m, br), 2950 (m), 1760 (m), 1710 (s), 1485 (w), 1455 (w), 1380 (s), 1210 (w), 1160 (m), 1100 (w), 960 (w), 810 (w), 745 cm^{-1} (w).

Method II: Low-temperature solution polycondensation

Taking polymer 6aII as an example, the general procedure consisted of adding 0.20 g (3.79×10^{-4}

mol) of diacid chloride (4) to a cooled (-5.0°C) and stirring solution of 0.0942 g (3.79×10^{-4} mol) of diamine (5a) in 0.25 mL NMP. After the reagents dissolved completely, 0.05 mL 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 5 h. The viscous solution was poured into 40 mL of the mixture of methanol/ H_2O (70/30)

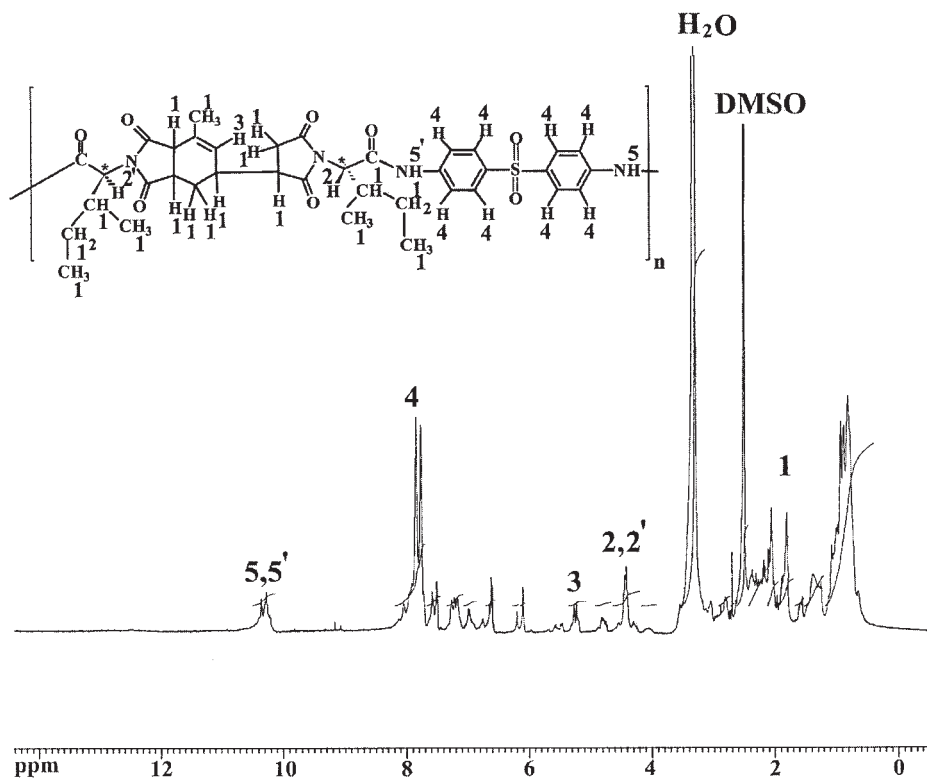


Figure 4 $^1\text{H-NMR}$ (500 MHz) spectrum of PAI 6aI in DMSO-d_6 at RT.

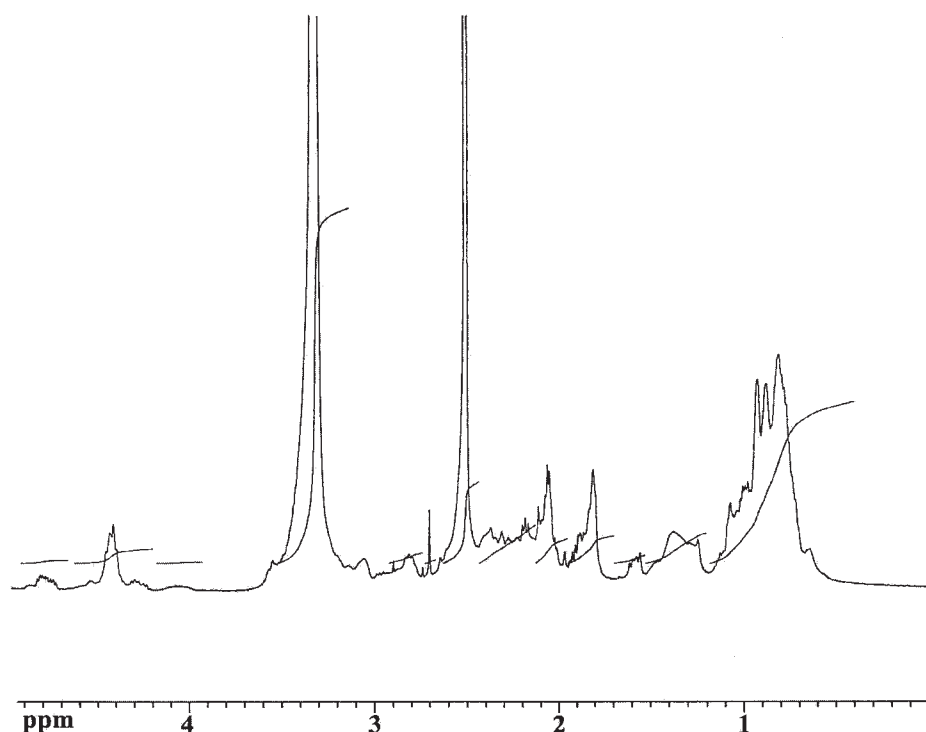


Figure 5 $^1\text{H-NMR}$ (500 MHz) Spectrum of PAI **6aI** in $\text{DMSO-}d_6$ at RT. Expanded region for the aliphatic protons ($\delta = 0.00\text{--}4.90$ ppm).

and the precipitated solid was filtered off and dried at 80°C for 10 h under vacuum to leave 0.198 g (73.8%) of solid polymer **6aII**.

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

Method III: High temperature solution polycondensation

Taking polymer **6aIII** as an example, into a 5-mL round-bottomed flask 0.20 g (3.49×10^{-4} mol) of diacid chloride (**4**), 0.0942 g (3.49×10^{-4} mol) of diamine (**5a**), 0.25

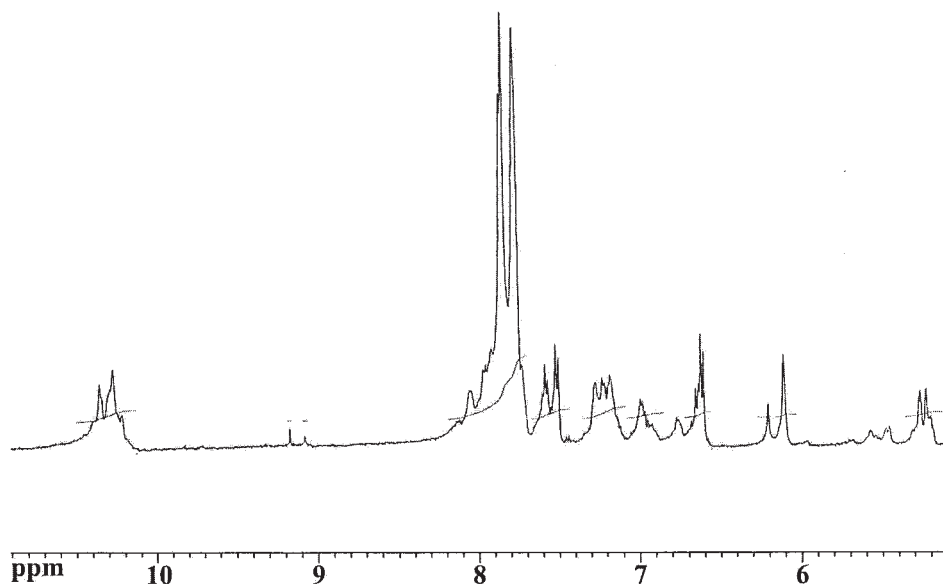


Figure 6 $^1\text{H-NMR}$ (500 MHz) Spectrum of PAI **6aI** in $\text{DMSO-}d_6$ at RT. Expanded region for the aromatic protons ($\delta = 5.00\text{--}10.9$ ppm).

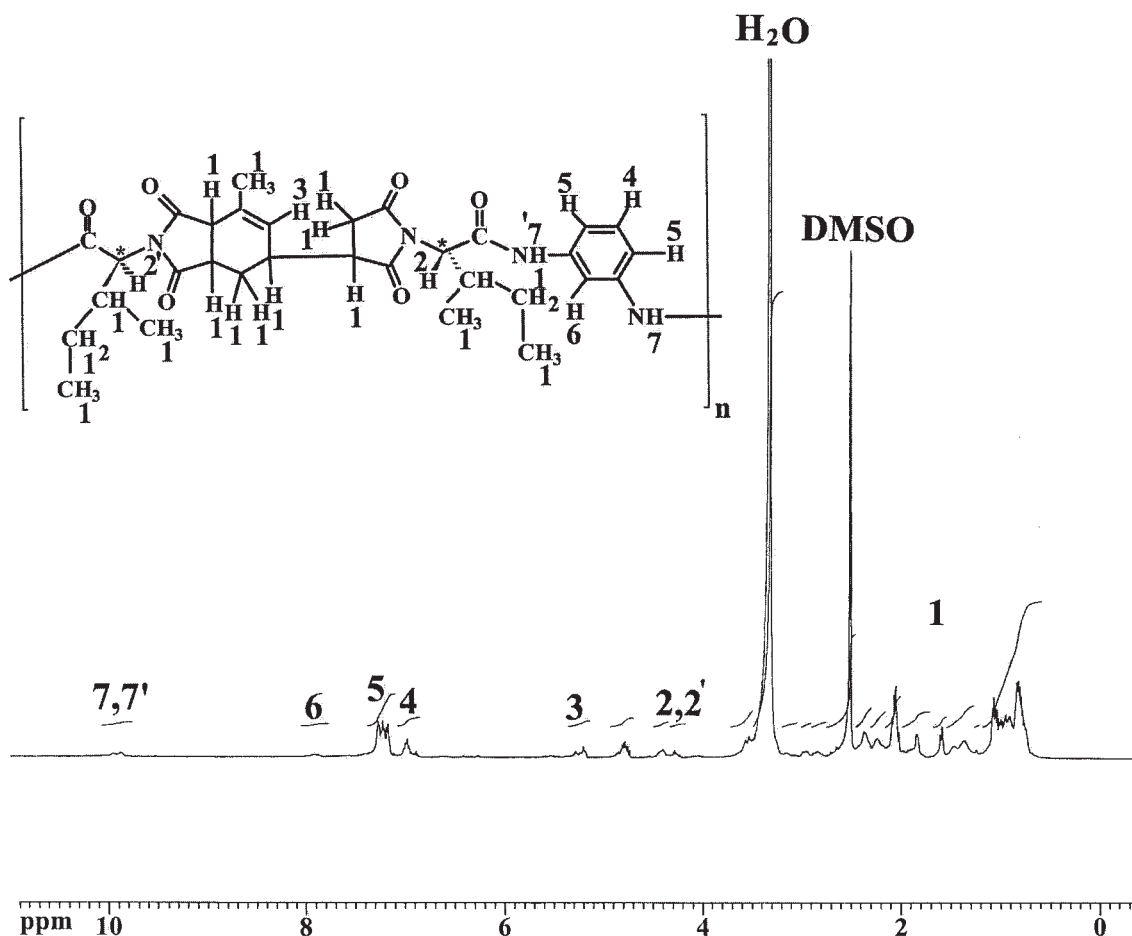


Figure 7 $^1\text{H-NMR}$ (500 MHz) Spectrum of PAI **6eI** in $\text{DMSO-}d_6$ at RT.

mL DMAc, and 0.05 mL TMSCl were added. The mixture was refluxed for 1 min. The viscous solution was poured into 40 mL of the mixture of methanol/ H_2O (70/30) and the precipitated solid was filtered off and dried at 80°C for 10 h under vacuum to leave 0.234 g (87.4%) of polymer **6aIII**.

The other PAIs (**6bIII**–**6gIII**) were prepared with similar procedures.

RESULTS AND DISCUSSION

Monomer synthesis

The new diacid chloride (**4**) was prepared, according to our earlier works,^{20–23} by the three-step process shown in Scheme 1.

The asymmetric diacid compound (**3**) was synthesized by the condensation reaction of dianhydride (**1**) with 2 mol L-isoleucine (**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:

The diacid (**3**) was converted to diacid chloride derivative (**4**) by reaction with thionyl chloride. The chemical

structure and purity of compounds **3** and **4** were proved by 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 1770 and 1705 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 higher frequency. Figure 1 shows the IR spectrum of diacid (**3**).

The $^1\text{H-NMR}$ spectra (90 MHz) of compound (**3**) are shown in Figure 2. A singlet at 9.20 ppm is assigned to the carboxylic acid protons. A peak at 5.50 ppm is assigned to the vinylic proton. The distorted quartet in 4.40–4.80 ppm is assigned to the protons of the chiral center, which appeared as distorted dd by the two diastrotopic protons. The peaks of all of the other protons overlapped each other and are reported as a multiplet from 0.6 to 3.80 ppm.

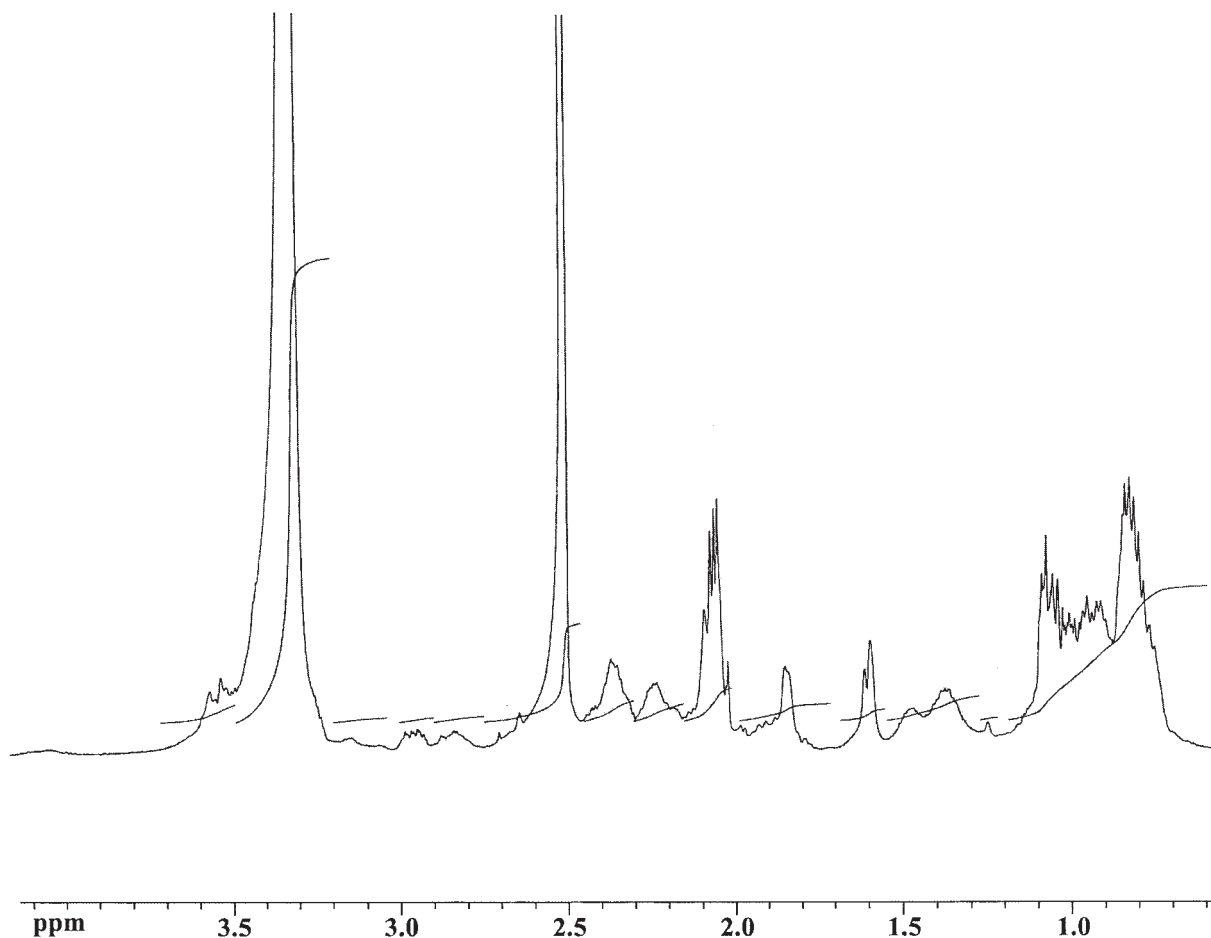


Figure 8 $^1\text{H-NMR}$ (500 MHz) Spectrum of PAI **6eI** in $\text{DMSO-}d_6$ at RT. Expanded region for the aromatic protons ($\delta = 0.60\text{--}4.10$ ppm).

The $^1\text{H-NMR}$ spectrum (90 MHz) of diacid chloride is similar to that of diacid derivative: a distorted doublet peak for vinylic hydrogen (H^3) at 5.55 ppm, a peak as multiplet at 4.80 ppm, which is assigned to two nonequivalent hydrogens ($\text{H}^{2'}$ and H^2). These hydrogens are not equivalent because of the unsymmetrical

structure of diacid chloride (**4**). However, the dd for the hydrogens are overlapped and then their absorption appeared as multiplet. The other hydrogens are shown in the range of 0.60–3.80 ppm. Some small peaks, which are due to acidic impurities, were produced during NMR measurement.

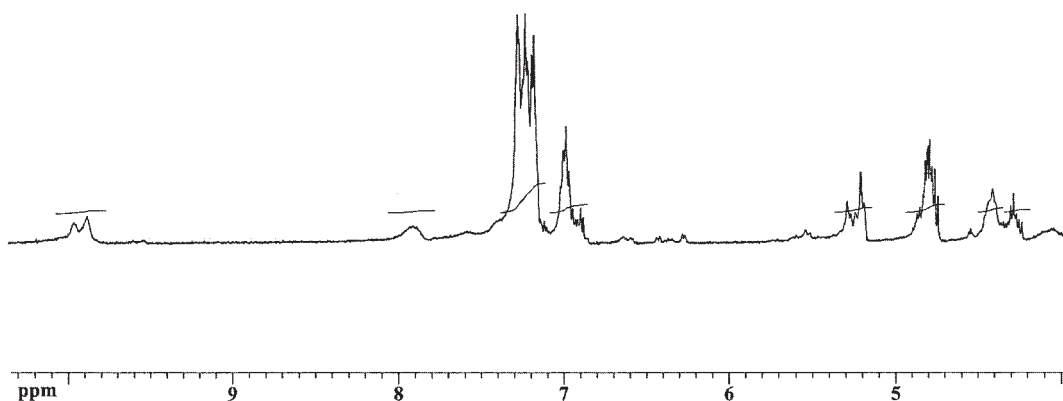


Figure 9 $^1\text{H-NMR}$ (500 MHz) Spectrum of PAI **6eI** in $\text{DMSO-}d_6$ at RT. Expanded region for the aromatic protons ($\delta = 4.0\text{--}10.3$ ppm).

TABLE V
Solubility of PAIs 6aI–6gI^a

Solvents	6aI	6bI	6cI	6dI	6eI	6fI	6gI
DMAc	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+
<i>o</i> -Cresol	+	+	+	+	+	+	+
<i>m</i> -Cresol	+	+	+	+	+	+	+
H ₂ SO ₄	+	+	+	+	+	+	+
NO ₂ -Ph	–	–	–	–	–	–	–
THF	+	+	+	+	+	+	+
Acetone	+	+	+	+	+	+	+
CHCl ₃	–	–	–	–	–	–	–
CH ₂ Cl ₂	–	–	–	–	–	–	–
HOAc	–	–	±	±	±	±	±
EtOAc	–	–	–	–	–	–	–
CH ₃ CN	–	–	–	–	–	–	–
Toluene	–	–	–	–	–	–	–
MeOH	±	±	±	±	±	±	±
EtOH	±	±	±	±	±	±	±
H ₂ O	–	–	–	–	–	–	–

^a Concentration: 5 mg ml^{–1}; +: soluble at room temperature, –: insoluble, ±: partially soluble.

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** were used to produce PAIs **6a–6g** as shown in Scheme 2. The solution reactions were performed under low-temperature and high-temperature conditions.

The microwave-assisted polycondensation reactions were performed in the presence of a small amount of a polar organic medium such as *o*-cresol that acts as a primary microwave absorber; the reaction mixture was irradiated for 6 min with 100% of radiation power. 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 conditions (Method III). TMSCl activates the diamine monomers²⁴ and 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 comparable yield and viscosity of the PAIs (**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 PAIs by means of elemental analysis, IR, and ¹H-NMR 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 1700 and 1770 cm^{–1} due to the symmetrical and asymmetrical carbonyl stretching vibrations. Bands of amide N–H groups appeared around 3300 cm^{–1} (hydrogen band) and 1520 cm^{–1} (amide II band). All of them exhibited strong absorptions at 1380 and 745–750 cm^{–1} that show the presence of the imide heterocycle ring in these polymers. The polymer **6aI** showed characteristic absorptions at 1310 and 1100 cm^{–1} due to the sulfone moiety (SO₂ stretching). Figure 3 shows a typical IR spectrum.

The ¹H-NMR spectra of PAI-**6aI** and PAI-**6eI** are shown in Figures 4–6 and 7–9. The pattern of spectra is similar to those of monomer diacid chloride and corresponding diamine. The two nonequivalent amidic hydrogens are seen in different chemical shifts. The absorption of aromatic hydrogens in PAI **6aI** shows the AM pattern, which is characteristic of two *para*-substituted benzene rings.

The solubility of PAIs is listed in Table V. All polymers are soluble in organic polar solvents such as DMAc, DMF, DMSO, and even in less polar solvents such as *o*-cresol, *m*-cresol, acetone, and THF. Most of the PAIs show partial solubility in associated solvents such as acetic acid or ethanol. However, these polymers are insoluble in solvents such as chloroform, acetonitrile, cyclohexane, and water.

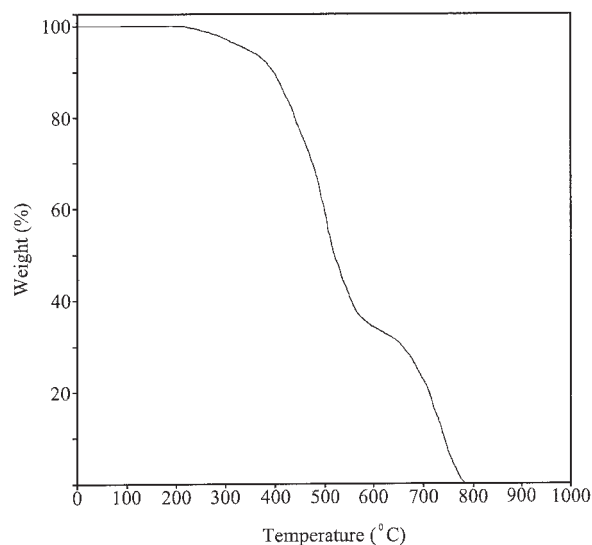


Figure 10 TGA of PAI **6aI** with a heating rate of 40°C/min and chart speed 10 mm/min in nitrogen atmosphere.

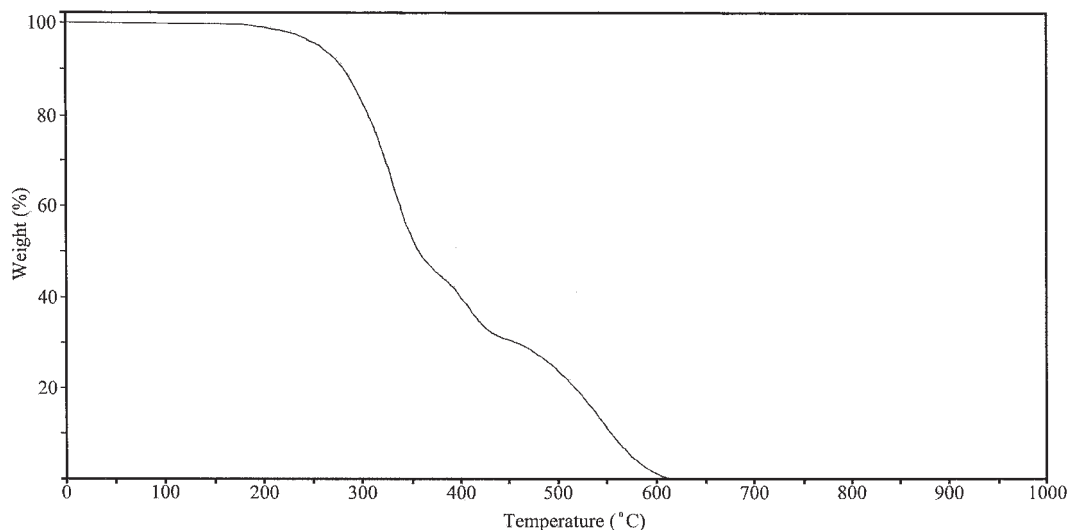


Figure 11 TGA of PAI **6fi** with a heating rate of 40°C/min and chart speed 20 mm/min in nitrogen atmosphere.

Thermal properties

The thermal stability of the some PAIs was investigated by thermogravimetric analysis (TGA) measurements. Typical TGA curves of representative polymers are shown in Figures 10 and 11. The temperatures of 5 and 10% weight loss together with char yield at 600°C for PAIs **6aI** and **6fi** were calculated from their thermograms. Figures 10 and 11 show the TGA curve for PAI **6aI** and **6fi**. The thermoanalyses data of PAIs **6aI** and **6fi** are summarized in Table VI.

CONCLUSION

New optically active aliphatic-aromatic PAIs having L-isoleucine and Epiclou 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 and

thereby subsequent polycondensation leading to the formation of the polymers having inherent viscosity of 0.12–0.30 dL/g. To compare this method with solution polymerization methods, PAIs were also synthesized by both low-temperature and high-temperature solution polycondensation. We obtained comparable results from these methods with microwave-assisted polymerization. The synthetic polymers are expected to have the potential to be used as packing materials in column chromatography.

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TABLE VI
Thermal Properties of PAIs **6aI**–**6gI**

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield (%) ^c
6aI	340 ^d	400 ^d	43
6fi	255 ^e	285 ^e	17

^a Temperature at which 5% weight loss was recorded by TGA at heating rate of 40 °C/min in N₂.

^b Temperature at which 10% weight loss was recorded by TGA at heat rate of 40°C/min in N₂.

^c Percentage weight of material left undecomposed after TGA analysis at maximum temperature 550 °C in N₂.

^d Chart speed was 10 mm/min.

^e Chart speed was 20 mm/min.

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