

Synthesis of New Optically Active Poly(amide-imide)s Containing EPICLON and L-Phenylalanine in the Main Chain by Microwave Irradiation and Classical Heating

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ABSTRACT: EPICLON [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-phenylalanine (**2**) in acetic acid, and the resulting amic acid was refluxed under a Dean-Stark system with benzene, which produced diacid (**3**) in high yield. Compound (**3**) was converted to the diacid chloride (**4**) by reaction with oxalyl chloride in dry carbon tetrachloride. The polycondensation reaction of this diacid chloride (**4**) with several aromatic diamines such as 4,4'-sulfonyldianiline (**5a**), 4,4'-diaminodiphenylmethane (**5b**), 4,4'-diaminodiphenylether (**5c**), 1,4-phenylenediamine (**5d**), 1,3-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

N-methylpyrrolidone (NMP). The polymerization reactions were also performed under two different classical heating methods: low temperature solution polycondensation in the presence of trimethylsilyl chloride, and high temperature polymerization. A series of optically active poly(amide-imide)s with moderate yield and inherent viscosity of 0.14–0.22 dL/g were obtained. All of the above polymers were fully characterized by IR, elemental analyses, and specific rotation. Some structural characterization and physical properties of this optically active poly(amide-imide)s are reported. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3281–3291, 2004

Key words: polyamides; polyimides; microwave irradiation; L-phenylalanine; viscosity

INTRODUCTION

The energy of microwave radiation is a useful source for the synthesis of organic compounds. For this purpose, it is necessary to use a polar media to absorb energy from radiation and translate to the reacting system. This can create a new method for preparing of chemical compounds.^{1–5} In the field of polymers, the various types of processing or synthesis, such as crosslinking of bisamides,⁶ the synthesis of polyethers,⁷ polyurethanes,⁸ imidization of polyamic acids,⁹ and the direct polycondensation of aromatic diamines¹⁰ are from the interesting efforts of using of microwave radiation. Recently, we have also used microwave irradiation for the synthesis of organic compounds as well as macromolecules.^{11–16}

On the other hand, optically active polymers have found interesting applications because of their specific

properties. For example these polymers have the ability of molecular recognition, which cause to use them as a stationary phase in chromatographic methods for enantiomeric separations.^{17–22} they can also be used as chiral media for asymmetric synthesis and chiral liquid crystals in ferroelectric and nonlinear optical devices.^{23,24} Therefore, the synthesis and application of optically active polymers have been receiving more attention. In this area, recently, we have synthesized optically active polymers by different methods such as modification of polybutadiene with an optically active substituted urazole group,²⁵ Diels-Alder-Ene reactions,^{26,27} and the reaction of an optically active monomer with several diamines via solution polymerization.^{28–36} In the last case, we use amino acids as a chiral agent in the backbone of the polymers. Because the amino acids are naturally occurring compounds, synthetic polymers based on amino acids are expected to be nontoxic, biocompatible, and biodegradable. On the other hand, synthetic polymers containing amino acid residues in the main chain,^{37–41} or in the side chain⁴² can be used for biomedical applications.

In continuation of our previous works,^{28–36} here, we wish to report the synthesis and characterization of new optically active poly(amide-imide)s PAIs containing EPICLON moieties by using a microwave oven

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and comparing it with its conventional solution polymerization. EPICLON B-4400 is a unique tetracarboxylic dianhydride, which is useful, like other tetracarboxylic dianhydrides, as a raw material for polyimide resins, water-soluble polyester resins and plasticizers, or a curing agent for epoxy resins. Due to its flexible chemical structure, it is highly soluble in solvent or other materials, which makes it applicable to the production of solvent-soluble polyimide resins. On the other hand, this compound is highly soluble in epoxy resins, which makes it applicable to a wide range of uses.⁴³

EXPERIMENTAL

Materials

4,4'-Diaminodiphenylmethane (**5b**) was purified by recrystallization from water. 4,4'-Diaminodiphenylether (**5c**), 1,4-phenylenediamine (**5d**), 1,3-phenylenediamine (**5e**), 2,4-diaminotoluene (**5f**), and 1,5-diaminonaphthalene (**5g**) were purified by sublimation. *N,N*-Dimethylacetamide (**DMAc**) was dried over BaO, then distilled in vacuum. EPICLON 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 as the racemate mixture from Merck Chemical Co. (Darmstadt, Germany). The other chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), and Riedel-de Haen AG (Seelze, Germany), and were used as obtained without further purification.

Apparatus and measurements

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 ¹H-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. Multiplicities of proton resonance are designated as singlet (s), multiplet (m), and broad (br). IR spectra were recorded on Shimadzu 435 IR spectrophotometer (Japan). Spectra of solids were carried out using KBr pellets and as neat film on NaCl 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). Spe-

cific Rotations were measured by a Perkin-Elmer-241 Polarimeter (Germany). Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) data for polymers were taken on a Mettler TGA-50 (England) and a DSC-PL-1200 (England) instrument, respectively, under nitrogen atmosphere at a rate of 10°C/min by Isfahan University. Elemental analyses were performed by Malek-Ashtar University of Technology, Tehran, I.R. Iran.

Monomer synthesis

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

Into a 100-mL round-bottomed flask 1.00 g (3.78 × 10⁻³ mol) of dianhydride **1**, 1.28 g (7.75 × 10⁻³ mol) of *L*-phenylalanine **2**, 15 mL of acetic acid and a stirring bar were placed. The mixture was stirred at room temperature for 6 h, then 50 mL of benzene was added and the reaction was continued under refluxing in a Dean-Stark system for 24 h. The solvent was removed under reduced pressure and 50 mL of *n*-hexane was added to the residue. After stirring, a white precipitate was formed, filtered off, washed with *n*-hexane to give 1.84 g (87%) of compound **3**.

mp: 158–161°C. [α]_D²⁵: -147.4 (0.050 g in 10 mL DMF); IR (NaCl): 3700–2700 (s, br), 1770 (m, sh), 1740 (m, sh), 1700 (s), 1540 (w), 1500 (m), 1440 (m), 1390 (s), 1360 (m, sh), 1230 (s), 1160 (s), 1090 (w), 1030 (w), 940 (w), 830 (w), 790 (w), 750 (m), 700 cm⁻¹ (m); ¹H-NMR (CDCl₃, TMS, 90 MHz, δ): 0.80–3.70 (m, 15H), 4.60–5.40 (m, 3H), 7.00–7.50 (s, br, 10H), 10.1 ppm (s, 2H). Elem. anal. Calcd. for C₃₁H₃₀N₂O₈: C, 66.66%; H, 5.41%; N, 5.01%; Found: C, 65.93%; H, 6.04%; N, 5.00%.

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

Into a 100-mL round-bottomed flask were placed 1.00 g (1.79 × 10⁻³ mol) of compound **3** and 1.0 mL of oxalyl chloride in 80 mL carbon tetrachloride. After 10 min 0.35 mL pyridine was added to the reaction system. The mixture was stirred at room temperature for 5 h until the suspension mixture was converted to a clear solution. Then, the solvent was removed under reduced pressure, to leave 0.96 g (90.0%) of pale yellow solid.

mp: 94–96°C. [α]_D²⁵: -66.4 (0.050 g in 10 mL DMF); IR (NaCl): 3450 (w), 3050 (w), 3020 (m), 2900 (m), 1780 (s), 1710 (s), 1600 (w), 1495 (m), 1455 (m), 1440 (m), 1380 (s), 1355 (m, sh), 1300 (w), 1270 (w), 1220 (m), 1150 (m), 1040 (m), 1000 (w), 980 (w), 960 (w), 930 (w), 840 (w), 790 (m), 770 (m), 750 (m), 700 (m), 660 cm⁻¹ (w); ¹H-NMR (CDCl₃, TMS, 500 MHz, δ): 0.80–3.70 (m,

15H), 4.40–5.15 (m, 1H), 5.20–5.35 (m, 2H), 6.90–7.50 ppm (m, 10H).

Polymerization

All of polymers were synthesized by three different methods.

Method I: polymerization under microwave irradiation

The PAIs were prepared by the following general procedure: Taking polymer **6aI** as an example, into the porcelain dish 0.20 g (3.36×10^{-4} mol) of diacid chloride **4** and 0.0835 g (3.36×10^{-4} mol) of diamine **5a** were placed. After the reagents were completely ground, 0.25 mL of NMP as a solvent was added, and the mixture was ground for 5 min. Then the reaction mixture was irradiated in the microwave oven for 6 min with 50% of its power. The resulting polymer film was isolated by adding 20 mL of methanol and triturating, followed by filtration and was dried at 80°C for 10 h under vacuum to leave 0.22 g (85.0%) of solid **6aI**.

IR (KBr): 3450 (w), 3350 (m, br), 3050 (w), 3020 (w), 2900 (w), 1770 (m), 1710 (s), 1690 (s), 1590 (s), 1520 (s), 1495 (s), 1450 (m), 1430 (m), 1380 (s), 1310 (s), 1240 (s), 1145 (s), 1100 (s), 1070 (m), 1030 (w), 1010 (w), 970 (w), 930 (w), 890 (w), 830 (m), 740 (m), 690 (m), 570 cm^{-1} (m).

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

All of spectra were recorded with KBr pellets.

Polymer **6bI**

3300 (m, br), 3020 (m), 2900 (m), 1775 (m), 1700 (s), 1600 (s), 1520 (s), 1430 (m), 1410 (m, sh), 1380 (s), 1355 (m, sh), 1320 (m), 1250 (m), 1160 (s), 1110 (m, sh), 1020 (m), 970 (w), 930 (w), 820 (m), 740 (m), 700 cm^{-1} (m).

Polymer **6cI**

3300 (m, br), 3030 (w), 2900 (m), 1775 (m), 1700 (s), 1605 (m), 1530 (m, sh), 1495 (s), 1440 (m), 1385 (s), 1360 (m, sh), 1300 (m), 1220 (s), 1160 (m), 1100 (w), 1030 (w), 1010 (w), 930 (w), 830 (m), 790 (w), 740 (m), 700 cm^{-1} (m).

Polymer **6dI**

3300 (m, br), 3020 (w), 2900 (w), 1770 (m), 1700 (s), 1605 (m), 1540 (m, sh), 1510 (s), 1495 (m, sh), 1440 (m), 1380 (s), 1360 (m, sh), 1310 (m), 1230 (m), 1160 (s), 1030 (w), 970 (w), 930 (w), 890 (w), 830 (m), 790 (w), 740 (m), 700 (m), 660 cm^{-1} (w).

Polymer **6eI**

3350 (m, br), 3050 (w), 3020 (w), 2900 (w), 1775 (m), 1700 (s), 1610 (m), 1540 (m), 1490 (m), 1420 (m), 1385 (s), 1300 (w), 1250 (w), 1160 (m), 1030 (w), 1000 (w), 960 (w), 930 (w), 880 (w), 840 (w), 780 (m), 740 (m), 700 (m), 620 cm^{-1} (w).

Polymer **6fI**

3320 (m, br), 3050 (w), 3010 (m), 2900 (m), 1775 (m), 1700 (s), 1600 (s), 1530 (s), 1490 (s), 1450 (m), 1380 (s), 1360 (m, sh), 1310 (m), 1240 (m), 1160 (s), 1030 (w), 1000 (w), 970 (w), 930 (w), 890 (w), 820 (w), 750 (m), 700 (m), 670 (w), 620 cm^{-1} (w).

Polymer **6gI**

3350 (m, br), 3050 (w), 3020 (w), 2900 (w), 1770 (m), 1700 (s), 1600 (m), 1530 (s), 1490 (s), 1450 (m), 1385 (s), 1330 (w), 1250 (w), 1230 (w), 1210 (w), 1160 (s), 1030 (w), 970 (w), 930 (w), 840 (w), 780 (m), 740 (m), 700 (m), 670 cm^{-1} (w).

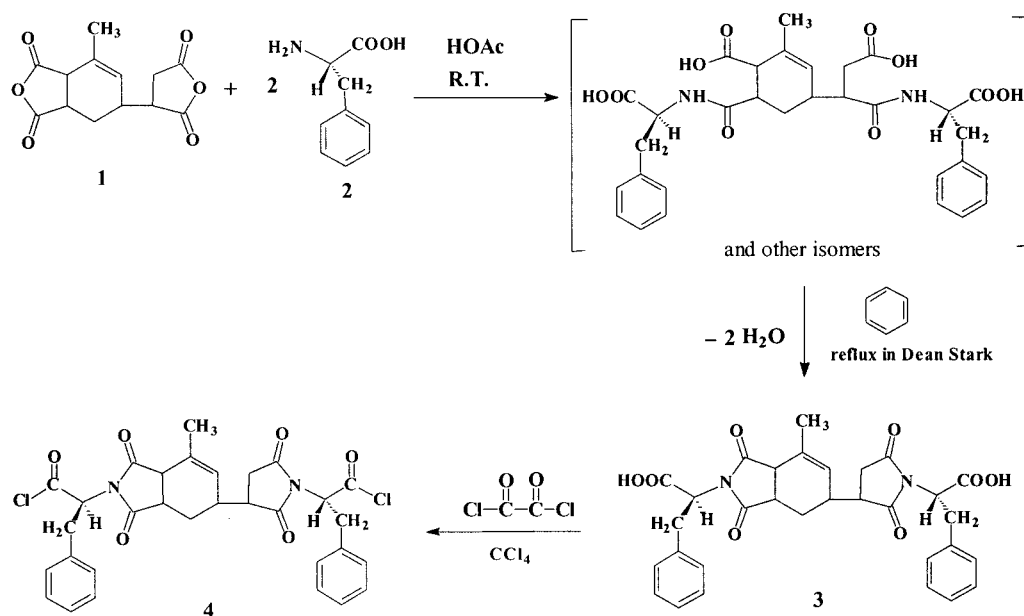
Method II: low temperature solution polycondensation with TMSCl

Taking polymer **6aII** as an example, the general procedure consisted of adding 0.20 g (3.36×10^{-4} mol) of diacid chloride **4** to a cooled (-5.0°C) and stirring solution of 0.0835 g (3.36×10^{-4} mol) of diamine **5a** in 0.30 mL of NMP. After the reagents were dissolved completely, 0.02 mL of trimethylchlorosilane 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 20 mL of methanol and the precipitated solid was filtered off and dried at 80°C for 10 h under vacuum to leave 0.181 g (70.0%) 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 were placed 0.20 g (3.36×10^{-4} mol) of diacid chloride **4**, 0.0835 g (3.36×10^{-4} mol) of diamine **5a** and 0.40 mL of DMAc. The mixture was refluxed for 1 min. Then it was allowed to stir for 5 h after the reaction temperature reached to room temperature. The viscous solution was poured into 20 mL of methanol and the precipitated solid was filtered off and dried at 80°C for 10 h under vacuum to leave 0.217 g (84.0%) 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 by the three-step process as shown in Scheme 1.

The asymmetric diacid compound 3 was synthesized by the condensation reaction of one equimolar of dianhydride 1 with two equimolar L-phenylalanine 2. According to our earlier works,¹¹ the reaction was performed in different solvents, such as HOAc/Py, Toluene/TEA, DMF, HOAc, and HOAc/benzene under heating, the best result obtained in the last solvent system. Therefore, after the reactants were converted

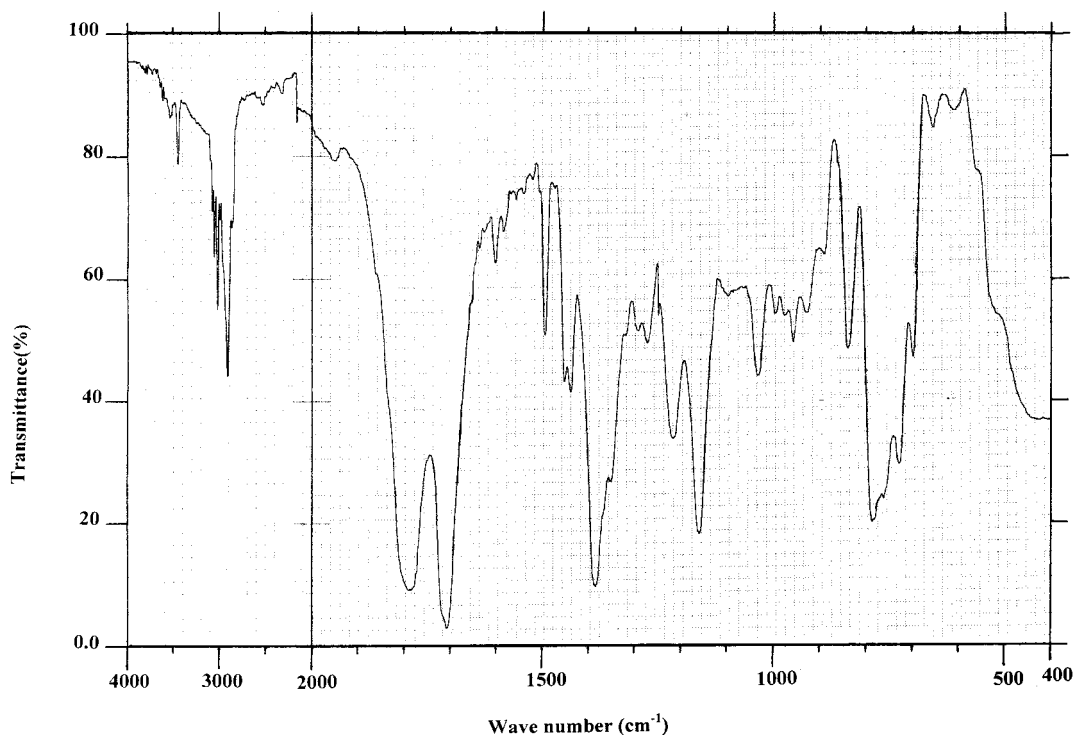


Figure 1 IR (NaCl) spectrum of diacid chloride 4.

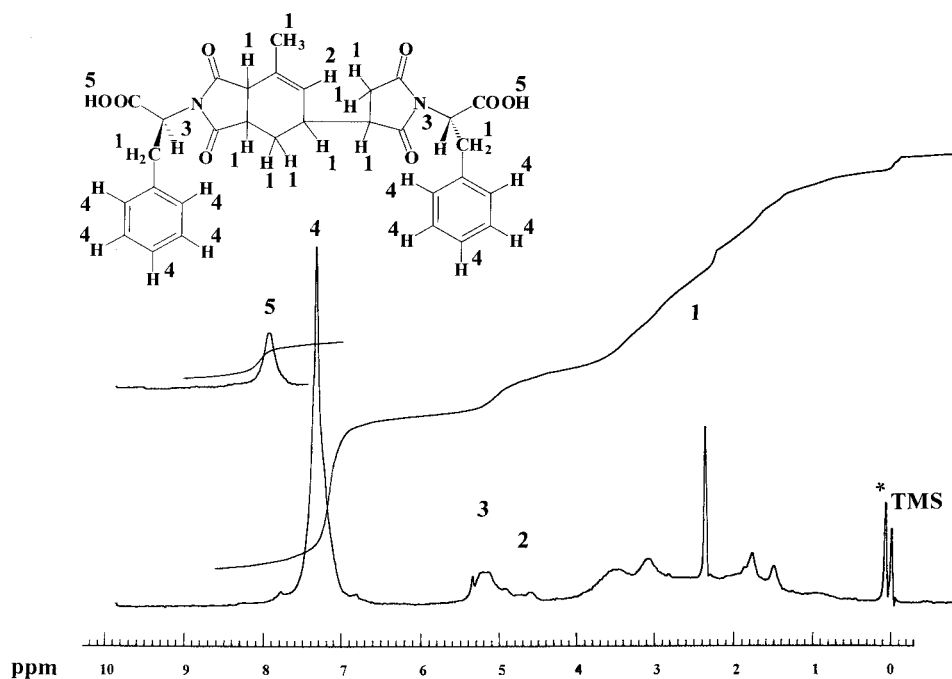


Figure 2 $^1\text{H-NMR}$ (90 MHz) Spectrum of diacid **3** in CDCl_3 at rt. Off-set 2 ppm. *Silicon grease.

to amic acid compound in acetic acid, without isolation of the product, dehydration was performed in the presence of benzene under reflux conditions in a Dean-Stark system. The reactant dianhydride **1**, EPICLON B-4400, has a four-chiral center; therefore, we can expect 16 stereoisomers, but the compound used, was a racemate mixture with specific rotation equal to

zero (EPICLON B-4400, Merck Chem. Co.). This is confirmed by TLC measurement, which showed only one spot for the dianhydride **1**, in dichloromethane/methanol at different ratios as eluting solvent. Therefore, it is expected that two diastereomeric isomers of diacid **3** are obtained, which we confirmed by TLC. Then its diacid chloride derivative **4** was prepared by

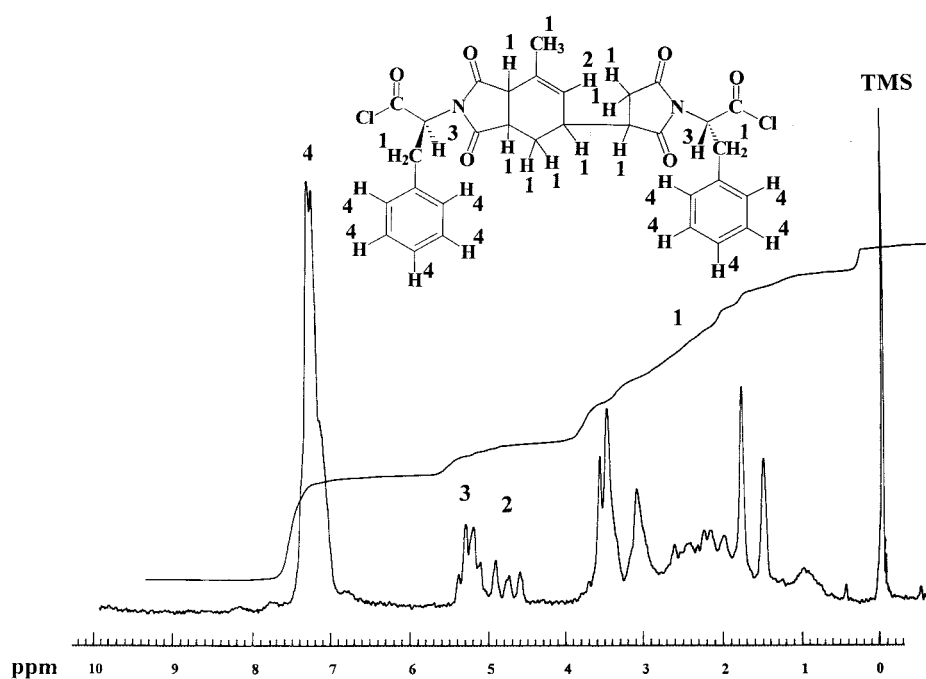
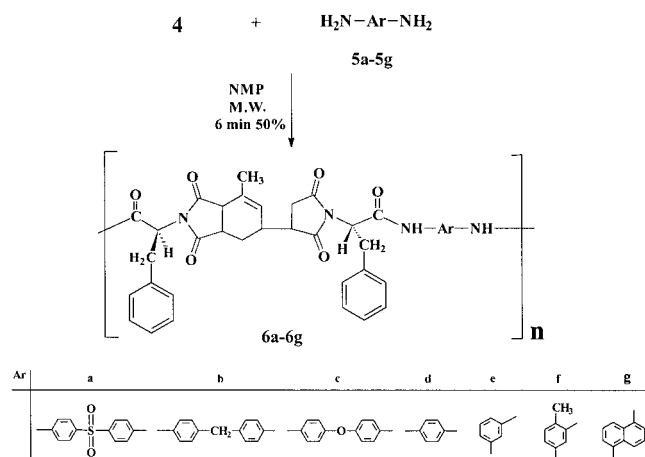


Figure 3 $^1\text{H-NMR}$ (500 MHz) Spectrum of diacid chloride **4** in CDCl_3 at rt.



Scheme 2

reaction with oxalyl chloride. This reagent has mild conditions for chlorinating relative to thionyl chloride. The chemical structure of the compounds 3 and 4 were proved using IR, $^1\text{H-NMR}$ spectroscopic techniques. The IR spectrum of compound 3 showed a broad and strong peak at $3700\text{--}2700\text{ cm}^{-1}$, which was assigned to the COOH groups and two absorption bands at 1770 and 1700 cm^{-1} , which are characteristic peaks for the carbonyl groups of the imide rings. The disappearance of strong acidic hydroxylic peak in IR spectrum of compound 4 (Fig. 1) 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 peak of diacid chloride in comparison with its starting diacid, was shifted to higher frequency.

The $^1\text{H-NMR}$ spectrum (90 MHz) of compound 3 in Figure 2 shows a slightly complex pattern, because of the existing two isomeric compounds. A singlet at 10.1 ppm is assigned to the carboxylic acid protons H_5 , and the absorption of aromatic protons H_4 has appeared as a broad singlet about 7.00–7.50 ppm. Absorption of protons on the α -carbon to carboxylic and imide groups H_3 has almost overlapped with that of vinylic

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

Diamine	Polymer			$[\alpha]_D^{25a}$
	Polymer code	Yield (%)	$\eta_{inh}(\text{dL/g})^a$	
5a	6aI	85.0	0.17	–43.8
5b	6bI	79.0	0.22	–35.0
5c	6cI	62.5	0.19	–41.4
5d	6dI	81.0	0.22	–37.2
5e	6eI	66.0	0.14	–31.8
5f	6fI	68.0	0.14	–31.6
5g	6gI	53.0	0.14	–40.0

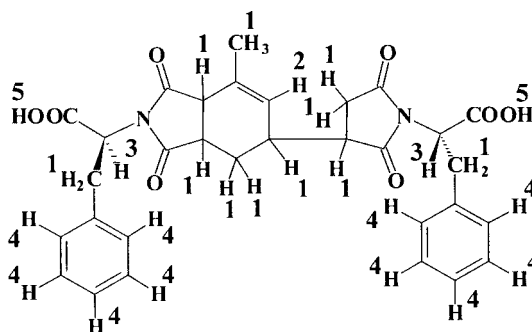
^a Measured at a concentration of 0.5 g/dL in DMF at 25°C.

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

Diamine	Polymer			$\eta_{inh}(\text{dL/g})^a$
	Polymer code	Yield (%)		
5a	6aII	70.0		0.15
5b	6bII	80.0		0.19
5c	6cII	75.0		0.17
5d	6dII	81.0		0.15
5e	6eII	70.0		0.12
5f	6fII	71.0		0.13
5g	6gII	60.0		0.12

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

proton H_2 at a range of 4.60–5.40 ppm, but it is interesting that, from the integration of peaks, the absorption of vinylic proton is in upper field with respect to protons H_3 . The peaks of all of the other protons H_1 overlapped with each other and are reported as a multiplet from 0.80 to 3.70 ppm.



(3)

The $^1\text{H-NMR}$ spectrum (500 MHz) of diacid chloride 4 has been shown in Figure 3. It has a similar pattern of the spectrum of the diacid derivative: A multiplet peak at 6.90–7.50 ppm for aromatic protons H_4 , another multiplet peak for proton H_3 at 5.20–5.35 ppm, and for the vinylic proton H_2 at 4.40–5.15 ppm

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

Diamine	Polymer			$[\alpha]_D^{25a}$
	Polymer code	Yield (%)	$\eta_{inh}(\text{dL/g})^a$	
5a	6aIII	84.0	0.15	–43.6
5b	6bIII	78.0	0.15	–35.6
5c	6cIII	67.0	0.16	–55.6
5d	6dIII	76.0	0.16	–39.8
5e	6eIII	66.0	0.13	–29.8
5f	6fIII	75.0	0.12	–31.8
5g	6gIII	64.0	0.12	–11.6

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

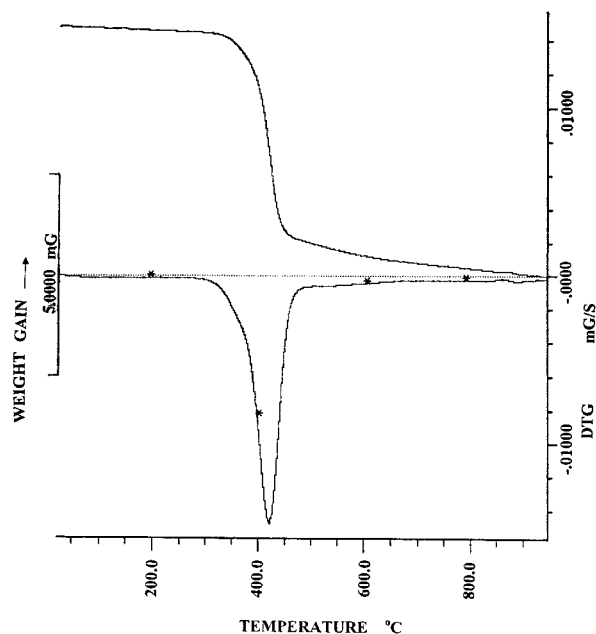


Figure 4 TGA/DTG thermograms of PAI-6aI with a heating rate of 10°C/min in nitrogen atmosphere.

and some multiplet peaks were shown for all aliphatic protons.

Polymer synthesis

PAIs 6a–6g were synthesized by microwave-assisted polycondensation as well as solution polycondensation reactions of an equimolar mixture of monomer 4 with seven different aromatic diamines 5a–5f as shown in Scheme 2.

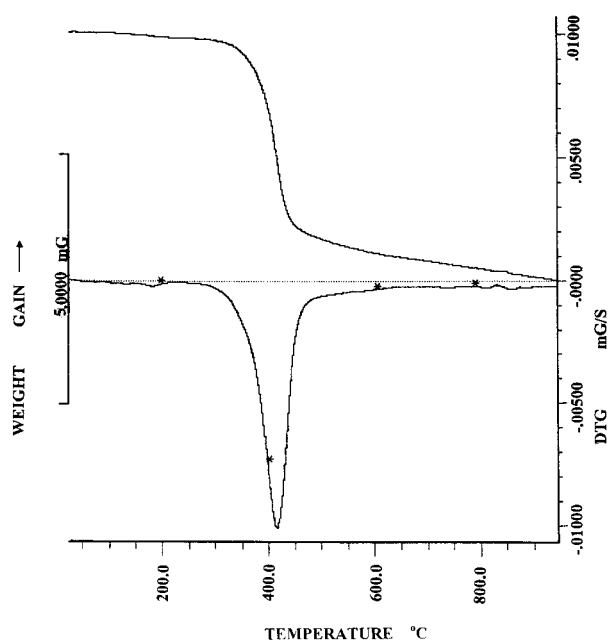


Figure 5 TGA/DTG thermograms of PAI-6bI with a heating rate of 10°C/min in nitrogen atmosphere.

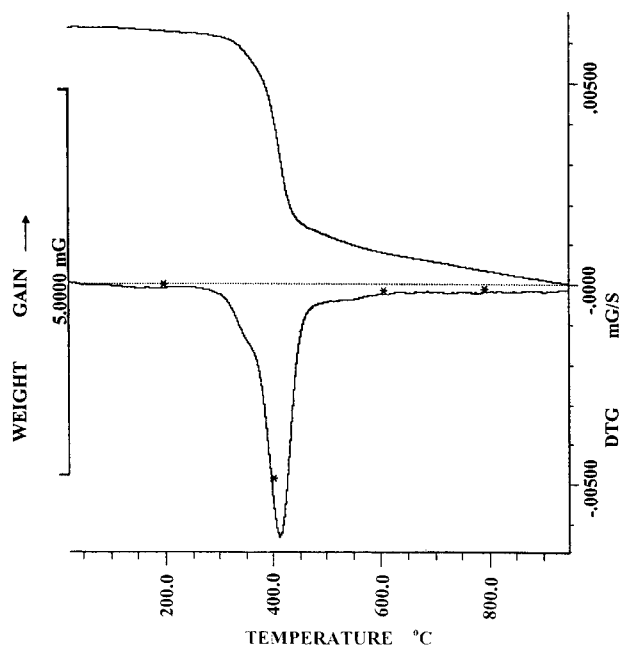


Figure 6 TGA/DTG thermograms of PAI-6cI with a heating rate of 10°C/min in nitrogen atmosphere.

The microwave-assisted polycondensation reactions were performed under different conditions of the power of irradiation to obtain the optimum conditions of polymerization. The best conditions were selected as 6-min irradiation with 50% of the power of the apparatus. At high powers, products were dark and the reaction had low yield. The reactions were performed in the presence of a small amount of a polar organic medium such as NMP, which acts as a primary microwave absorber. The reaction yields and some physical data are listed in Table I.

The resulting polymers show optical rotations, which indicate that in the presence of microwave irradiation the chiral centers do not change, and therefore the chirality are introduced into the backbone of the polymers.

To compare the microwave-assisted polycondensation method with conventional solution polyconden-

TABLE IV
Thermal properties of PAIs 6aI–6gI

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield (%) ^c	T_g (°C)
6aI	355	375	24.9	— ^d
6bI	350	374	3.02	200
6cI	337	370	28.4	— ^d

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

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

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

^d Were not measured.

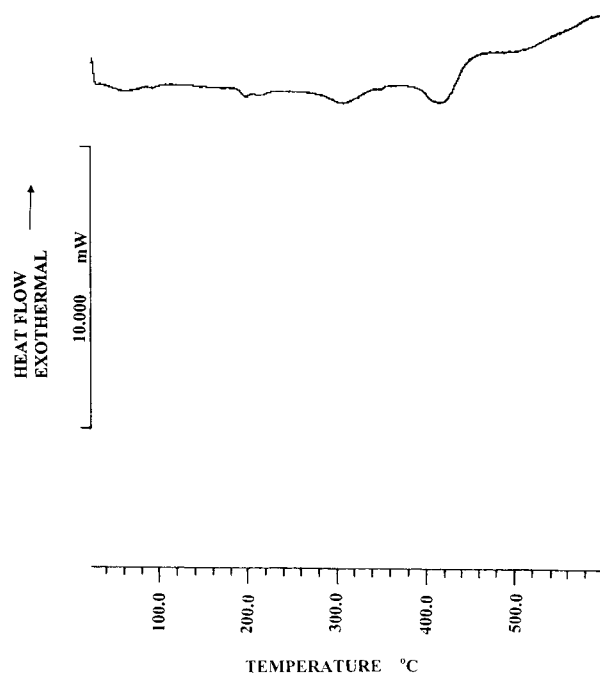


Figure 7 DSC curve of **PAI-6bI** with a heating rate of 10°C/min in nitrogen atmosphere.

sation reactions, the polymerizations were performed under two different methods: low-temperature (Method II) and high-temperature (Method III) poly-

condensation reactions. In method II, the reactions were performed in NMP solution in the presence of trimethylchlorosilane. In this method trimethylchlorosilane activates the diamine monomers,⁴⁴ and polymerization reactions occurred at lower temperature in a period of 2 h and then at room temperature for 3 h. We obtained comparable results from the point of yield and viscosity of the **PAIs**. Similar results were obtained from the method III. In this way, polycondensation reactions proceeded rapidly at the reflux temperature of solvent in 1 min, then 2 h at room temperature. Optical rotation measurements showed very similar rotation values for the polymers obtained from method III. The reaction yields and some physical data of the solution polycondensations are listed in Tables II and III.

Thermal properties

The thermoanalytical measurements of some of the **PAIs** were studied by TGA/DTG (derivative thermogravimetric) and DSC (differential scanning calorimetry). Typical TGA and DTG curves of representative polymers are shown in Figures 4–6. All of the polymers show similar pattern of decomposition. The temperatures of 5% and 10% weight loss for all of three **PAIs** are above 330 and 370°C, respectively, indicating the ther-

TABLE V
Elemental Analysis of **PAIs** 6aI–6gI

Polymer	Formula		Elemental analysis (%)			Moisture intake (%) ^a
			C	H	N	
6aI	(C ₄₃ H ₃₈ N ₄ O ₈ S) _n (771) _n	Calcd	67.00	4.97	7.27	1.4
		Found	64.39	5.44	6.85	
		Corr ^b	65.29	5.36	6.94	
6bI	(C ₄₄ H ₄₀ N ₄ O ₆) _n (721) _n	Calcd	73.32	5.59	7.77	0.9
		Found	71.66	5.72	7.36	
		Corr ^b	72.30	5.67	7.42	
6cI	(C ₄₃ H ₃₈ N ₄ O ₇) _n (723) _n	Calcd	71.45	5.30	7.75	1.7
		Found	68.70	5.41	6.78	
		Corr ^b	69.87	5.45	6.89	
6dI	(C ₃₇ H ₃₄ N ₄ O ₆) _n (631) _n	Calcd	70.46	5.43	8.88	1.8
		Found	67.94	5.69	8.19	
		Corr ^b	69.16	5.59	8.33	
6eI	(C ₃₇ H ₃₄ N ₄ O ₆) _n (631) _n	Calcd	70.46	5.43	8.88	0.8
		Found	69.24	6.03	8.53	
		Corr ^b	69.79	5.98	8.60	
6fI	(C ₃₈ H ₃₆ N ₄ O ₆) _n (645) _n	Calcd	70.79	5.63	8.69	1.1
		Found	68.86	5.94	7.98	
		Corr ^b	69.61	5.57	8.06	
6gI	(C ₄₁ H ₃₆ N ₄ O ₆) _n (681) _n	Calcd	72.34	5.33	8.23	1.5
		Found	68.72	5.67	7.83	
		Corr ^b	69.75	5.59	7.95	

^a Moisture Intake (%) = $\frac{(W - W_0)}{W_0} \times 100$, W = weight of polymer sample after standing at room temperature and W₀ = 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 intake)/100, and Corrected value for H = Found value × (100 - Moisture intake)/100.

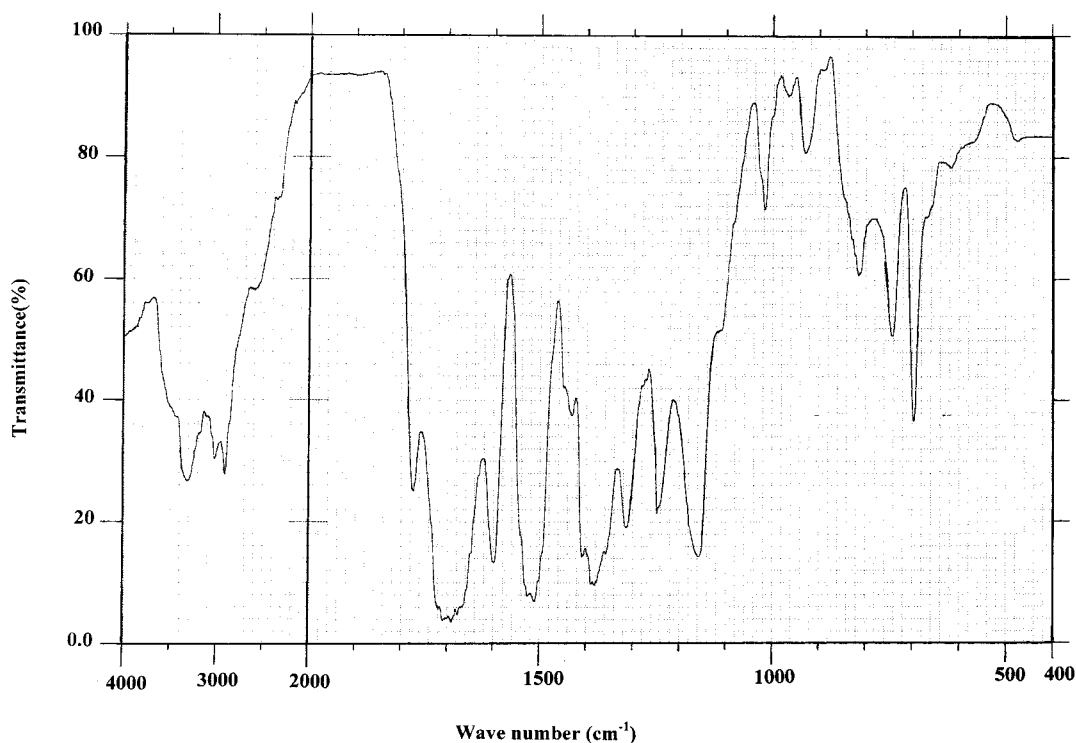


Figure 8 IR (KBr) Spectrum of PAI-6cI.

mal stability of polymers with aliphatic structures. The glass transition temperature (T_g) of PAI-6bI as an example was evaluated by means of DSC. Table IV summarizes the thermal transition data of PAI-6aI, 6bI, and 6cI. Figure 7 shows the typical DSC curve of PAI-6bI.

Polymer characterization

The structures of these polymers were confirmed as PAIs by means of elemental analysis, IR, and $^1\text{H-NMR}$ spectroscopy. Elemental analysis values of the resulting polymers are listed in Table V.

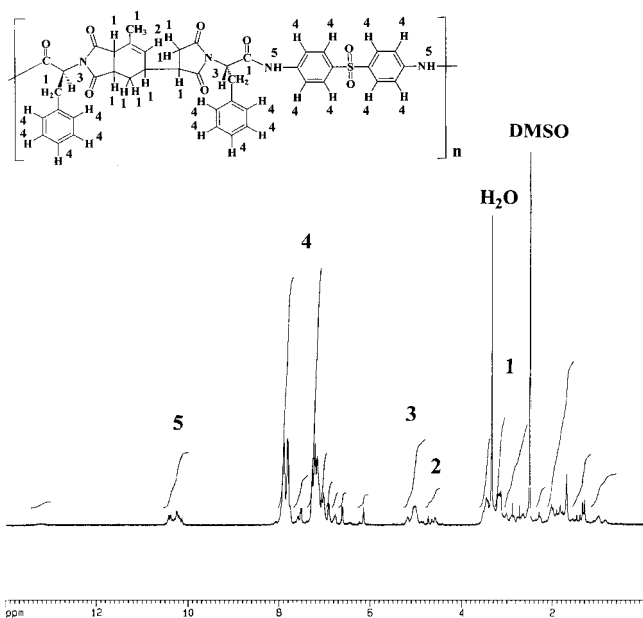
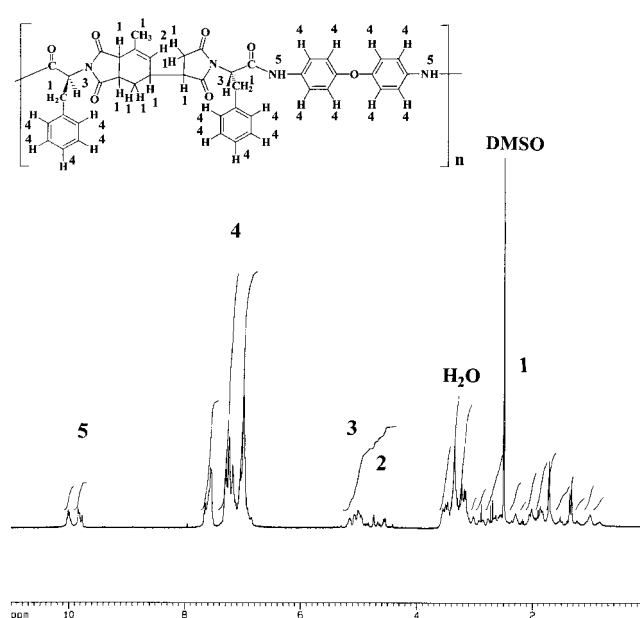
Figure 9 $^1\text{H-NMR}$ (500 MHz) Spectrum of PAI-6aI in $\text{DMSO-}d_6$ at rt.Figure 10 $^1\text{H-NMR}$ (500 MHz) Spectrum of PAI-6cI in $\text{DMSO-}d_6$ at rt.

TABLE VI
Solubility of PAIs 6aI–6gI

Solvents	6aI	6bI	6cI	6dI	6eI	6fI	6gI
DMAc	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+
<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.

The most distinctive feature of the infrared spectra of all polymers are the characteristic absorption peaks of the imide ring at 1770 and 1700 cm⁻¹ due to the symmetrical and asymmetrical carbonyl stretching vibrations. Bands of amide groups appeared around 3350 cm⁻¹ (N–H), an overlapped peak at 1700 cm⁻¹ (C=O stret.) and the peak of NH bending at 1590 cm⁻¹. All of them exhibited strong absorptions at 1370–1380 and 700–720 cm⁻¹, which show the presence of the imide heterocyclic ring in these polymers. Polymer **6aI** showed characteristic absorptions at 1310 and 1150 cm⁻¹ due to the sulfone moiety (SO₂ stretching). Figure 8 shows a typical IR spectrum.

The ¹H-NMR spectra of **PAI-6aI** and **PAI-6cI** are shown in Figures 9 and 10. The pattern of spectrum is similar to those of monomer diacid chloride and corresponding diamine. The two nonequivalent amidic hydrogens appeared at different chemical shift.

The solubility of **PAIs** is listed in Table VI. All of the **PEIs** are soluble in organic polar solvents such as DMF, DMAc, and DMSO at room temperature, but are insoluble in traditional organic solvents such as acetone, methanol, ethanol, and water except for **PAIs 6aI** and **6cI**, which show solubility in THF and acetone.

CONCLUSIONS

A series of novel optically active aliphatic-aromatic **PAIs** were synthesized by using a domestic microwave oven by the polycondensation of diacid chloride **4** with several diamines in the presence of a small amount of a polar organic medium such as NMP that acts as a primary microwave absorber. The use of such an organic medium was necessary to induce effective homogeneous heating of the monomers. Thereby, sub-

sequent polycondensation leads to the formation of optically active polymers, which show good solubility due to the flexible chemical structure of EPICLON moiety in the main chain and have inherent viscosity of 0.14–0.22 dL/g. According to the results, it can be concluded that the heat of microwave radiation can be used as a source for polymerization. As a comparison, **PAIs** were also synthesized by two different solution polymerizations at low temperature and high temperature. The results of these methods were comparable with the microwave method. But the microwave heating is a more efficient method (shorter reaction time and high efficiency of energy) for these polycondensation reactions. It is expected that the synthetic polymers with amino acid residues in the main chain have potential to be used as packing materials in column chromatography and have potential to be used as biodegrading and biocompatible materials.

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