

# Synthesis and Properties of Organosoluble and Optically Active Poly(amide-imide)s Based on Epiclon and (S)-(+)-Valine under Microwave Irradiation

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## ABSTRACT

**A**liphatic dianhydride, 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 (S)-(+)-valine **2** in acetic acid and the resulting imide-acid **3** was obtained in high yield. The diacid chloride **4** was obtained from the reaction of **3** with thionyl chloride. The polycondensation reaction of diacid chloride **4** with several aromatic diamines such as 4,4'-sulphonyldianiline **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 *o*-cresol. The polymerization reactions were also performed by two another methods: low temperature solution polycondensation and reflux conditions. A series of optically active poly(amide-imide)s with inherent viscosity of 0.13-0.32 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-imide)s are reported.

### Key Words:

microwave-assisted polycondensation;  
optically active polymers;  
poly(amide-imide)s;  
microwave oven;  
inherent viscosity.

## INTRODUCTION

Recently, a new technique that is set to revolutionize synthesis has come to the forefront of chemical research, microwave-assisted organic synthesis [1-7]. While fire is now rarely used in synthetic chemistry, it was not until Bunsen invented the burner

that the energy from this heat source could be applied to a reaction vessel in a focused manner. The Bunsen burner was later superseded by the isomantle, oil bath or hot plate as sources of applying heat to a chemical reaction. As of 2003 many of the

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top pharmaceutical, agrochemical and biotechnology companies are already heavily using microwave-assisted organic synthesis (MAOS) as a frontline methodology for library synthesis and lead optimization as they realize the ability of this enabling technology to speed chemical reactions. Not only are microwaves sometimes able to reduce chemical reaction times from hours to minutes, they are also known to reduce side reactions, often increase yields, and improve reproducibility. Almost any type of organic reaction requiring heating or thermal conditions can be performed using microwave radiation. Microwave dielectric heating is dependent on the ability of a solvent or matrix to absorb microwave energy and to convert it into heat. The matrix absorbs the radiation by two mechanisms, dipole polarization and conduction. When irradiated at microwave frequencies, the ions or dipole of the sample align in the applied electric field. As the applied field oscillates, the dipole or ion field attempts to realign itself with the alternating electric field and, in the process, energy is lost in the form of heat through molecular friction and dielectric loss. The amount of heat generated by this process is directly related to the ability of the matrix to align itself and the frequency of the applied field. If the dipole does not have time to realign, or reorients too quickly with the applied field, no heating occurs irradiation produces efficient internal heating (in-situ heating), resulting in even heating throughout the sample, as compared with the wall heat-transfer that occurs when an oil bath is applied as an energy source. Consequently, the tendency for the initiation of boiling is reduced, and superheating above the boiling point of the solvent is possible even at atmospheric pressure. Superheating can be rapidly generated in closed microwave-transparent vessels to temperatures as high as 100°C above the normal boiling point of a particular solvent. It is this combination of rapid microwave heating and sealed vessel technology that is responsible for most of the observed rate enhancements seen in MAOS, based on the well-known rule-of-thumb that for every 10°C increase in temperature, the rate of the reaction is approximately doubled.

Recently we have used microwave irradiation for the synthesis of organic compounds as well as macromolecules [8-10].

Much attention has been paid in recent years to fabrication of chiral separation materials. Those polymers

possesses 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]. Then the synthesis of optically active polymers is the newly considerable topics, which have been paid more attention. Recently, optically active polymers have been synthesized by different methods [12-14]. 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 inducing agents. These materials are naturally occurring compounds therefore synthetic polymers based on amino acids are expected to be biodegradable and biocompatible.

In this article we wish to report the microwave assisted synthesis of new optically active poly(amide-imide)s PAIs containing Epiclon and (S)-(+)-valine moieties by using a microwave oven and compares this method with conventional solution polymerization.

## EXPERIMENTAL

### Material

4,4'-Diaminodiphenylmethane **5b** and 4,4'-diaminobiphenyl **5g** was purified by recrystallization from water. 4,4'-diaminodiphenylether (**5c**), 1,4-phenylenediamine **5d**, 1,3-phenylenediamine **5e**, 2,4-diaminotoluene **5f** were purified by sublimation. Epiclon B-4400 [3a,4,5,7a-tetrahydro-7-methyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-1,3-isobenzofurandione] (IUPAC) or [5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexyl-1,2-dicarboxylic acid anhydride] (common name) was supplied from Merck Chemical Co (Germany). *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 as obtained without further purification.

### Apparatus

The apparatus used for the polycondensation was a

Samsung domestic microwave oven (2450MHz, 900W) without any modification, but all of the polymerization reactions were performed in a hood with strong ventilation.

Proton nuclear magnetic resonance  $^1\text{H-NMR}$  (90MHz) and (500MHz) 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) spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave number ( $\text{cm}^{-1}$ ). 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 TGA 7 Perkin Elmer (Germany) in nitrogen atmosphere at a rate of  $40^\circ\text{C}/\text{min}$ . Elemental analysis were performed by Malek-Ashtar University of Technology, Tehran, I. R. Iran.

### Monomer Synthesis

*5-[N-2-(2S-3-Methylbutanoic acid)succinimido]3-methyl-[N-2-(2S-4-methylpanthanoic acid)]-1,2,5,6-tetrahydrophthalimide (Diacid 3).*

Into a 50-mL round-bottomed flask 1.00 g ( $3.78 \times 10^{-3}$  mol) of Epiclone **1**, 0.97 g ( $8.31 \times 10^{-3}$  mol) of (S)-(+)-valine **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 gummy precipitate was formed, washed with cold water, and then ether was added to convert it to a clear solution. The ether was removed under reduced pressure to give 1.68 g (96.0 %) of compound (**3**).  $\text{Mp} = 98-100^\circ\text{C}$ ,  $[\alpha]_{\text{D}}^{25} = 134.6^\circ$  (0.050 g in 10 mL DMF); IR (KBr): 3300-2500 (s, br), 22995 (s), 1705 (s), 1540 (w), 1390 (s), 1190 (s), 1130 (w), 878 (w), 758 (w), 660 (w),  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 90 MHz):  $\delta$  0.30-3.70 (m, 25H), 4.30-4.80 (m, 2H) 5.50 (s, 1H), 8.15 (s, 2H) ppm; Elemental analysis. Calcd. for  $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_8$ : C,

59.73%; H, 6.54%; N, 6.05%; Found: C, 60.59%; H, 7.01%; N, 6.83%.

*5-[N-2-(2S-3-Methylbutanoylchloride)succinimido]2-ethyl-[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 ( $2.16 \times 10^{-3}$  mol) of compound **3**, 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 1.04 g (97.0%) of pale yellow solid.  $\text{mp} = 60^\circ\text{C}$  (decomposed),  $[\alpha]_{\text{D}}^{25} = 176.6^\circ$  (0.050 g in 10 mL DMF); IR (NaCl): 2995 (m), 2850 (m), 1818 (s), 1710 (s), 1460 (w), 1388 (s), 1295 (w), 1180 (s), 1138 (m), 1060 (w), 1010 (w), 964 (w), 920 (w), 840 (w), 755 (m), 660 (w)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 90 MHz):  $\delta$  0.30-3.80 (m, 25H), 4.50-4.90 (m, 2H) and 5.60 (d, 1H) ppm.

### Polymerization

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 ( $4.00 \times 10^{-4}$  mol) of diacid chloride **4** and 0.0866 g ( $4.00 \times 10^{-4}$  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 irradiated in the microwave oven for 6 min with 100% of the power of microwave apparatus. The resulting product was isolated by adding methanol/ $\text{H}_2\text{O}$  (70/30) and triturating, following by filtration and was dried at  $80^\circ\text{C}$  for 10 h under vacuum to leave 0.243 g (90.0%) of solid **6aI**; IR (KBr): 3350 (m, br), 2995 (m), 1778 (w), 1700 (s), 1590 (s), 1520 (s), 1460 (w), 1380 (s), 1310 (s), 1250 (w), 1142 (s), 1100 (s), 838 (w), 680 (w), 558 (w)  $\text{cm}^{-1}$ .

#### Method II: Low Temperature Solution Polycondensation

Using polymer **6aII** as an example, the general procedure consisted of adding 0.20 g ( $4.00 \times 10^{-4}$  mol) of diacid chloride **4** to a cooled ( $-5.0^\circ\text{C}$ ) and stirring solution of 0.0866 g ( $4.00 \times 10^{-4}$  mol) of diamine **5a** in 0.25

mL of NMP. After the reagents dissolved completely, 0.05 mL of TMSCl was added and 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°C for 10 h under vacuum to leave 0.189 g (70.3%) of solid polymer **6aII**.

The other **PAIs (6bII-6gII)** were prepared in a procedure similar to that of above.

#### Method III: High Temperature Solution Polycondensation

Polymer **6aIII** is used as an example. Into a 5 mL round-bottomed flask were placed 0.20 g ( $4.00 \times 10^{-4}$  mol) of diacid chloride (**4**), 0.0866 g ( $4.00 \times 10^{-4}$  mol) of diamine (**5a**), 0.25 mL of DMAc and 0.05 mL of TMSCl was added. The mixture was refluxed for one min. The viscous solution was poured into 40 mL the mixture 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 0.191 g (70.9 %) of polymer **6aIII**.

The other **PAIs (6bI-6gI)** were prepared in procedures similar to that described above.

#### Polymer **6bI**

IR (KBr): 3390 (m, br), 2990 (m), 1700 (s), 1600 (m), 1515 (s), 1460 (w), 1410 (w), 1380 (s), 1310 (w), 1180 (s), 1120 (w), 1018 (w), 920(w), 818 (m) cm<sup>-1</sup>.

#### Polymer **6cI**

IR (KBr): 3340 (m, br), 2950 (m), 1778 (w), 1700 (s), 1608 (w), 1500 (s), 1380 (m), 1315 (w), 1220 (m), 1130 (w), 1010 (w), 838 (w) cm<sup>-1</sup>.

#### Polymer **6dI**

IR (KBr): 3450 (m, br), 2950 (m), 1778 (m), 1705 (s), 1610 (w), 1520 (m), 1460 (w), 1380 (s), 1310 (m), 1170 (m), 1120 (w), 838 (w) cm<sup>-1</sup>.

#### Polymer **6eI**

IR (KBr): 3380 (m, br), 2980 (m), 1780 (w), 1700 (s), 1603 (w), 1520 (m), 1380 (s), 1130 (m), 1018 (w), 818 (w), 755 (w) cm<sup>-1</sup>.

#### Polymer **6fI**

IR (KBr): 3320 (m, br), 2955 (m), 1770 (m), 1700 (s),

1610 (w), 1530 (w), 1380 (s), 1180 (w), 1128 (m), 860 (w), 780 (w), 690 (w) cm<sup>-1</sup>.

#### Polymer **6gI**

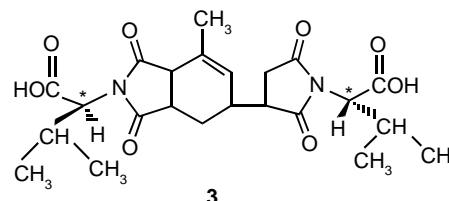
IR (KBr): 3400 (m), 3300 (m), 2850 (m), 2600 (m), 1760 (w), 1700 (s), 1638 (w), 1600 (w), 1495 (s), 1390 (s), 1295 (w), 1270 (w), 1220 (w), 1170 (w), 1120 (w), 810 (s), 755 (w) cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Monomer Synthesis

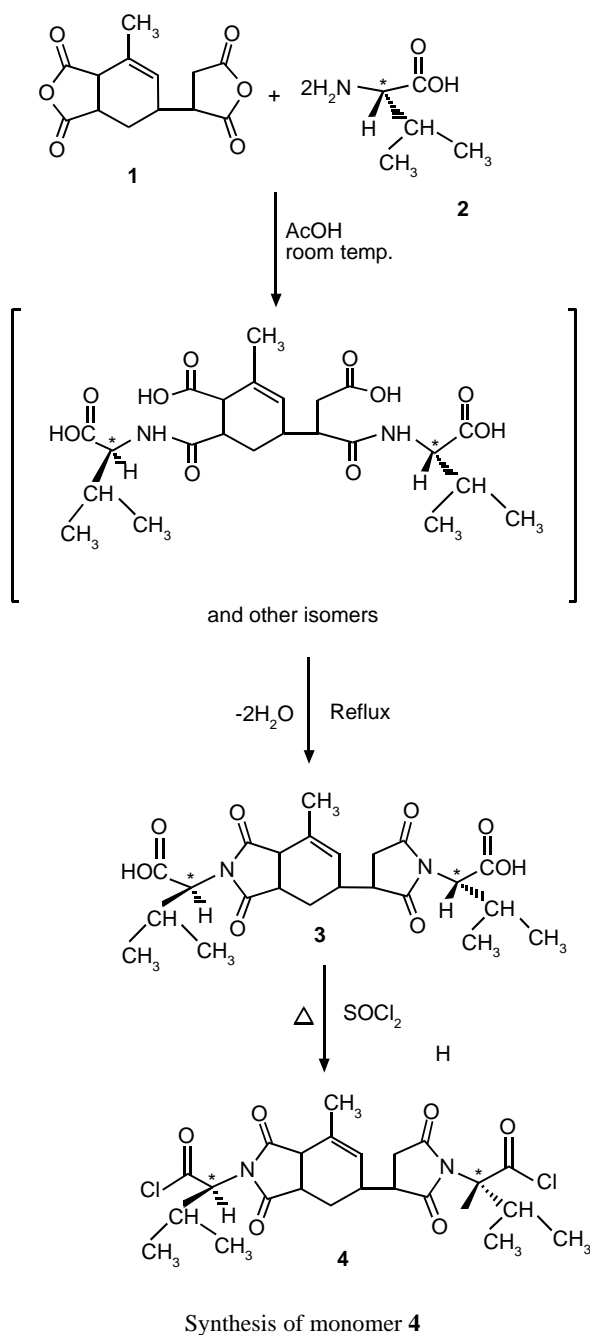
The new diacid chloride **4** was prepared, according to our earlier works [8-10] by the three-step process as shown in Scheme I.

The asymmetric diacid compound **3** was synthesized by the condensation reaction of dianhydride **1** with two moles (S)-(+)-valine **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 the compounds **3** and **4** were proved using elemental analysis, IR and <sup>1</sup>H NMR spectroscopic techniques. The IR spectrum of compound **3** showed a broad and strong peak at 3500-2500 cm<sup>-1</sup>, which was assigned to the COOH groups and two absorption bands at 1770 and 1705 cm<sup>-1</sup>, which are characteristic peaks for imide rings. Figure 1 shows the IR spectrum of diacid **3**.

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 2 shows the IR spectrum of diacid chloride **4**.



Scheme I

The  $^1\text{H}$  NMR spectrum (90 MHz) of compound 3 are shown in Figure 3. A singlet at 8.15 ppm is assigned to the carboxylic acid protons. A peak at 5.50 ppm is assigned to the vinylic proton. The distorted quartet in 4.30-4.80 ppm is assigned to the protons of the chiral center, which appeared as distorted doublet of doublet by the two-diastereotopic protons. The peaks of all of the other protons overlapped with each other and are reported as a multiplet from 0.3 to 3.70 ppm.

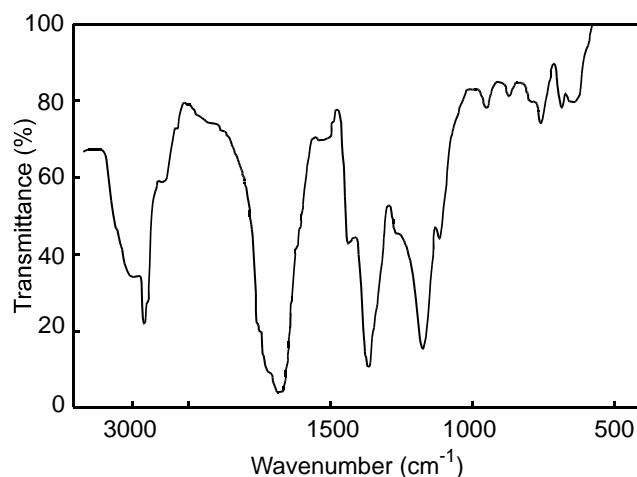


Figure 1. IR (KBr) Spectrum of diacid (3).

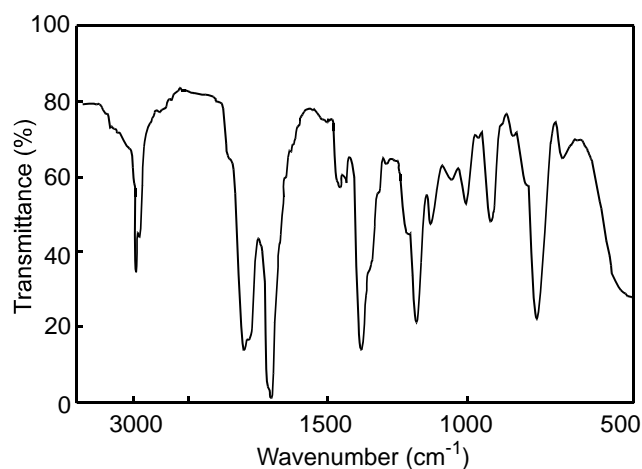
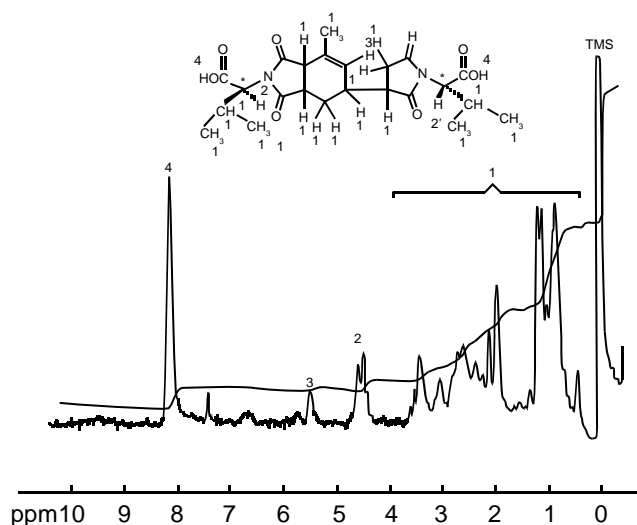


Figure 2. IR (KBr) Spectrum of diacid chloride (4).

Figure 3.  $^1\text{H}$  NMR (90 MHz) Spectrum of diacid (3) in  $\text{CDCl}_3$ , TMS at room temperature.

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 ( $\text{H}^3$ ) at 5.50 ppm, a peak as multiplet at 4.80 ppm, which is assigned to two nonequivalent hydrogens ( $\text{H}^{2'}$  and  $\text{H}^2$ ). These hydrogens are not equivalent because of the unsymmetrical structure of diacid chloride **4**. But, the doublet of doublet for each of hydrogens are overlapped and then their absorption appeared as multiplet. The other hydrogens are shown in the range of 0.30 to 3.70 ppm. Some small peaks which are due to acidic impurities, produced during NMR measurement.

### 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 II. The solution reactions were performed either under low temperature or at high temperature conditions.

The microwave-assisted polycondensation reactions were performed in the presence of 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 1.

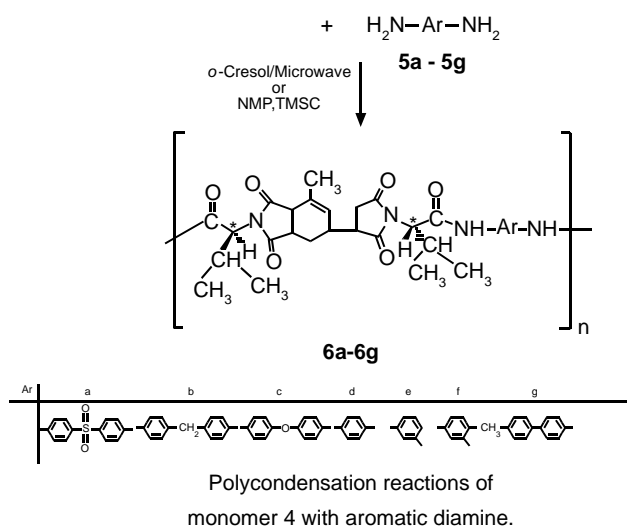
In order to compare microwave-assisted polycondensation method with conventional solution polycon-

**Table 1.** Some physical properties of PAIs (**6aI-6gI**) prepared by method I.

Diamine	Polymer			
	Polymer code	Yield (%)	$\eta_{\text{inh}}(\text{dL/g})^a$	$[\alpha]_{\text{D}}^{25}$
<b>5a</b>	<b>6aI</b>	90.0	0.32	- 76.6
<b>5b</b>	<b>6bI</b>	89.0	0.26	+9.8
<b>5c</b>	<b>6cI</b>	73.4	0.19	-23.8
<b>5d</b>	<b>6dI</b>	66.7	0.18	-51.2
<b>5e</b>	<b>6eI</b>	63.0	0.17	37.6
<b>5f</b>	<b>6fI</b>	76.0	0.20	-28.2
<b>5g</b>	<b>6gI</b>	93.0	0.24	81.2

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

densation methods, the polymerization of diacid chloride **5** with aromatic diamines **5a-5g** was performed under low temperature (Method II) and reflux condition (Method III). TMSCl activates the diamine monomers [15] 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 list-



**Scheme II**

**Table 2.** Some physical properties of PAIs (**6aII-6gII**) prepared by method II.

Diamine	Polymer			
	Polymer	Yield (%)	$\eta_{\text{inh}}(\text{dL/g})^a$	$[\alpha]_{\text{D}}^{25}$
<b>5a</b>	<b>6aII</b>	70.3	0.26	-46.2
<b>5b</b>	<b>6bII</b>	66.2	0.22	-27.0
<b>5c</b>	<b>6cII</b>	80.2	0.16	+0.6
<b>5d</b>	<b>6dII</b>	55.7	0.20	-31.4
<b>5e</b>	<b>6eII</b>	66.1	0.28	+6.0
<b>5f</b>	<b>6fII</b>	66.1	0.28	+1.6
<b>5g</b>	<b>6gII</b>	79.3	0.30	+12.2

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

**Table 3.** Some physical properties of PAIs (**6aIII-6gIII**) prepared by method III.

Diamine	Polymer			
	Polymer	Yield (%)	$\eta_{inh}(dL/g)^a$	$[\alpha]_D^{25}$
<b>5a</b>	<b>6aIII</b>	70.9	0.28	-56.6
<b>5b</b>	<b>6bIII</b>	65.3	0.23	-24.4
<b>5c</b>	<b>6cIII</b>	72.0	0.18	-14.4
<b>5d</b>	<b>6dIII</b>	69.0	0.14	+34.0
<b>5e</b>	<b>6eIII</b>	66.7	0.13	+5.4
<b>5f</b>	<b>6fIII</b>	78.5	0.21	+7.2
<b>5g</b>	<b>6gIII</b>	93.2	0.26	+5.8

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

**Table 4.** Elemental analysis of PAIs (**6aI-6gI**).

Polymer	Formula		Elemental analysis (%)			Moisture content (%) <sup>a</sup>
			C	H	N	
<b>6aI</b>	(C <sub>35</sub> H <sub>38</sub> N <sub>4</sub> O <sub>8</sub> S) <sub>n</sub> (675) <sub>n</sub>	Calcd	62.30	5.67	8.30	0.11
		Found	63.11	6.09	9.10	
		Corr <sup>b</sup>	63.17	6.08	9.12	
<b>6bI</b>	(C <sub>36</sub> H <sub>40</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> (625) <sub>n</sub>	Calcd	69.21	6.45	8.97	0.20
		Found	68.35	7.11	9.67	
		Corr <sup>b</sup>	68.50	7.09	9.68	
<b>6cI</b>	(C <sub>35</sub> H <sub>38</sub> N <sub>4</sub> O <sub>7</sub> ) <sub>n</sub> (627) <sub>n</sub>	Calcd	67.08	6.11	8.93	0.32
		Found	66.38	7.00	9.53	
		Corr <sup>b</sup>	66.60	6.97	9.56	
<b>6dI</b>	(C <sub>29</sub> H <sub>34</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> (535) <sub>n</sub>	Calcd	65.15	6.41	10.48	0.21
		Found	64.93	7.01	11.04	
		Corr <sup>b</sup>	65.06	6.99	11.06	
<b>6eI</b>	(C <sub>29</sub> H <sub>34</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> (535) <sub>n</sub>	Calcd	65.15	6.41	10.48	0.22
		Found	65.09	6.93	10.97	
		Corr <sup>b</sup>	65.23	6.91	10.99	
<b>6fI</b>	(C <sub>30</sub> H <sub>36</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> (549) <sub>n</sub>	Calcd	65.68	6.61	10.21	0.34
		Found	64.63	7.12	10.35	
		Corr <sup>b</sup>	64.84	7.09	10.38	
<b>6gI</b>	(C <sub>35</sub> H <sub>38</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> (611) <sub>n</sub>	Calcd	68.84	6.27	9.17	0.31
		Found	68.11	6.93	10.02	
		Corr <sup>b</sup>	68.32	6.90	10.05	

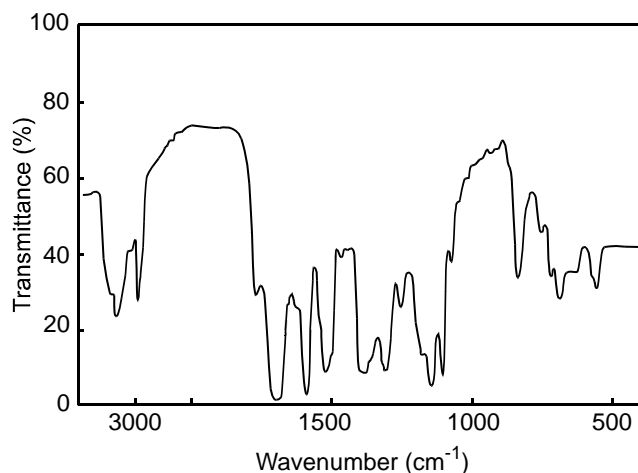
(a) Moisture content (%) =  $(W - W_0)/W_0 \times 100$ , W = weight of polymer sample after standing at room temperature and W<sub>0</sub> = weight of polymer sample after dried in vacuum at 100°C for 10 h.(b) Corrected value for C and N = found value  $\times (100 + \text{moisture content})/100$ , and corrected value for H = found value  $\times (100 - \text{moisture content})/100$ .

ed in Tables 2 and 3.

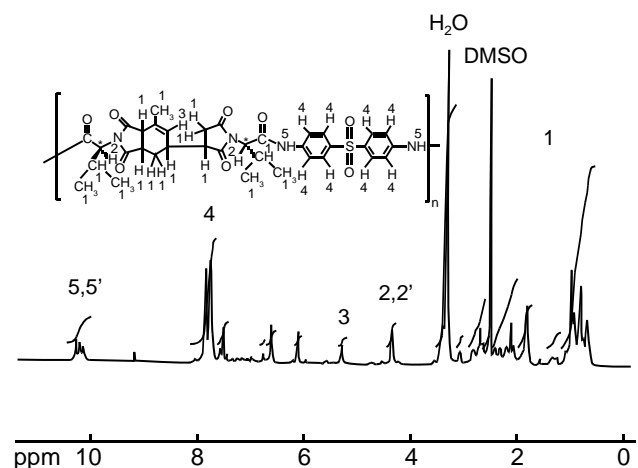
**Polymers Characterization**

The structures of these polymers were confirmed as **PAIs** by means of elemental analysis, IR and <sup>1</sup>HNMR spectroscopy. Elemental analysis data of the resulting polymers are listed in Table 4.

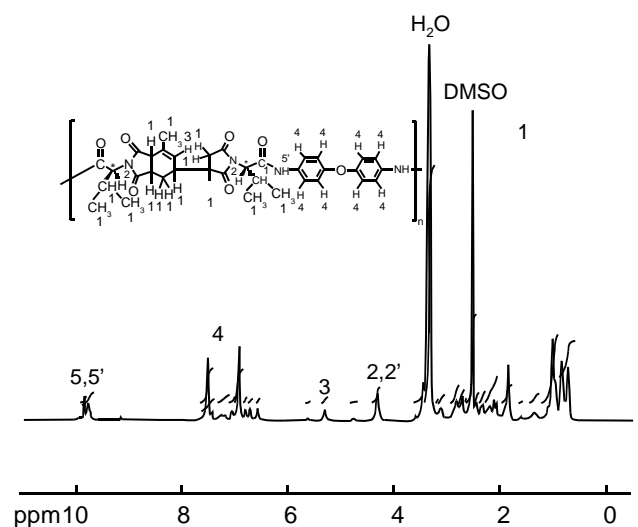
The infrared spectra of all polymers show the characteristic absorption peaks for the imide ring at 1700 and 1778 cm<sup>-1</sup> due to the symmetrical and asymmetrical carbonyl stretching vibrations. Bands of amide N-H groups appeared around 3300 cm<sup>-1</sup> (hydrogen band) and 1520 cm<sup>-1</sup> (amide II band). All of them exhibited strong absorptions at 1380 cm<sup>-1</sup> and 750-838 cm<sup>-1</sup> that show the presence of the imide heterocycle ring in these polymers. The polymer **6aI** showed characteristic



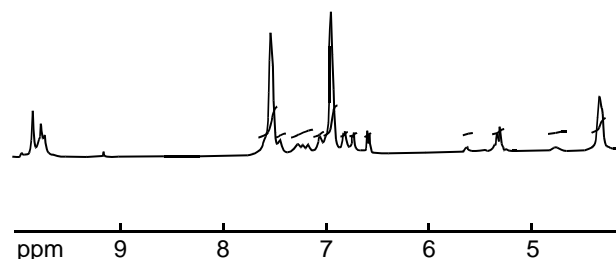
**Figure 4.** IR (KBr) Spectrum of PAI-6aI.



**Figure 5.**  $^1\text{H}$  NMR (500 MHz) Spectrum of PAI-6aI in DMSO- $\text{d}_6$  at room temperature.



**Figure 6.**  $^1\text{H}$  NMR (500 MHz) Spectrum of PAI-6cI in DMSO- $\text{d}_6$  at room temperature.



**Figure 7.**  $^1\text{H}$  NMR (500 MHz) Spectrum of PAI-6cI in DMSO- $\text{d}_6$  at room temperature. Expanded region for the aromatic protons ( $\delta = 4.20\text{--}10.00$  ppm).

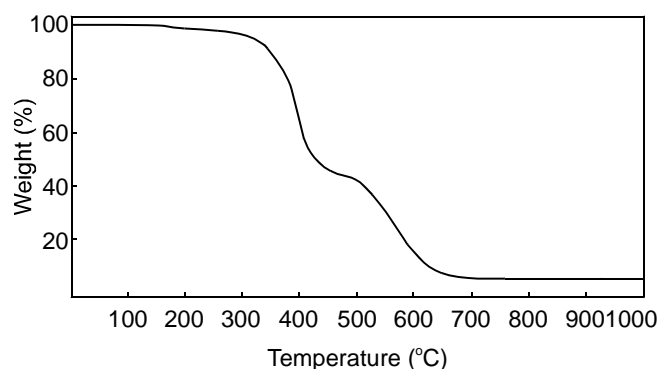
absorptions at  $1310$  and  $1100\text{ cm}^{-1}$  due to the sulfone moiety ( $\text{SO}_2$  stretching). Figure 4 shows a typical IR spectrum.

The  $^1\text{H}$  NMR spectra of PAI-6aI and PAI-6cI are shown in Figures 5-7. 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 shift. The absorption of aromatic hydrogens in PAI-6aI shows the AM pattern, which is the characteristic of two *para*-substituted benzene rings.

The solubility of PAIs is listed in Table 5. All polymers are soluble in organic polar solvents such as DMAc, DMF, DMSO and even in less polar solvents like *o*-cresol, *m*-cresol, acetone and THF. Most of PAIs show partial solubility in associated solvents such as ethanol or acetic acid. But, these polymers are insoluble in solvents such as chloroform, acetonitril, cyclohexane and water.

### Thermal Properties

The thermal stability of the some PAIs was investigat-



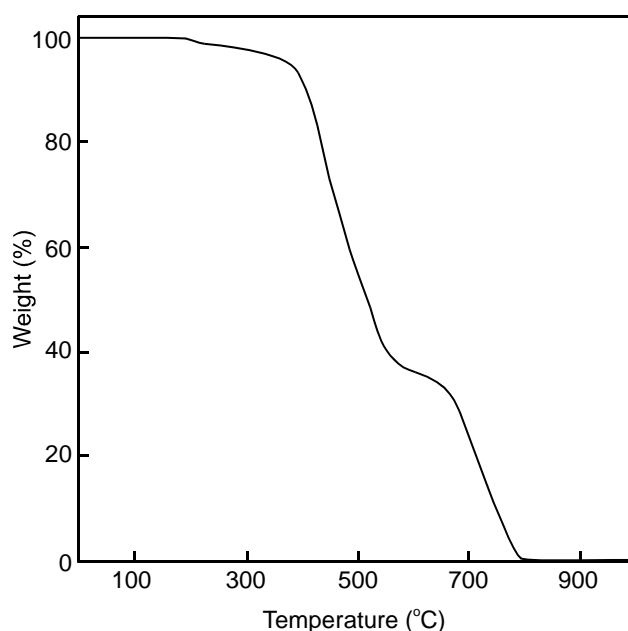
**Figure 8.** TGA of PAI-6aI with a heating rate of  $40^\circ\text{C}/\text{min}$  and chart speed  $20\text{ mm}/\text{min}$  in nitrogen atmosphere.



**Table 5.** Solubility of PAIs (**6aI-6gI**<sup>a</sup>).

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

(a) Concentration: 5 mg mL<sup>-1</sup>; (+): soluble at room temperature, (-): insoluble, (±): partially soluble.

**Figure 9.** TGA of PAI-**6fI** with a heating rate of 40°C/min and chart speed 10 mm/min in nitrogen atmosphere.**Table 6.** Thermal properties of PAIs (**6aI-6gI**).

Polymer	T <sub>5</sub> <sup>a</sup> (°C)	T <sub>10</sub> <sup>b</sup> (°C)	Char yield (%) <sup>c</sup>
<b>6aI</b> <sup>e</sup>	330.0	360.0	18
<b>6dI</b> <sup>d</sup>	383.3	441.6	38

(a) Temperature at which 5% weight loss was recorded by TGA at heating rate of 40°C/min in N<sub>2</sub>; (b) Temperature at which 10% weight loss was recorded by TGA at heating rate of 40°C/min in N<sub>2</sub>; (c) Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600°C in N<sub>2</sub>; (d) Chart speed has been 10 mm/min; (e) Chart speed has been 20 mm/min.

ed by thermogravimetric analysis (TGA) measurements. Typical TGA curves of representative polymers are shown in Figures 8-9. 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. The Figure of 8 and 9 show the TGA curve for PAI-**6aI** and **6fI**. The thermoanalyses data of PAIs **6aI** and **6dI** are summarized in Table 6.

## CONCLUSION

Several new optically active aliphatic-aromatic **PAIs** having (S)-(+)-valine and Epiclon moieties were synthesized by using a domestic microwave oven from polycondensation of optically active diacid chloride **4** with several diamines in the presence of small amount *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 0.13-0.32 dL/g. In order 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. Microwave-assisted heating has been shown to be an invaluable optimization method since it dramatically reduces reaction times, typically from days or hours to minutes.

The resulting polymers are soluble in many organic solvents. The synthetic polymers are expected to have potential to be used as packing materials in column chromatography.

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