

# Microwave-Promoted Rapid Synthesis of New Optically Active Poly(amide imide)s Derived from *N,N'*-(Pyromellitoyl)-bis-*L*-isoleucine Diacid Chloride and Aromatic Diamines

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**ABSTRACT:** A pyromellitic dianhydride (benzene-1,2,4,5-tetracarboxylic dianhydride) was reacted with *L*-isoleucine in acetic acid, and the resulting imide acid [*N,N'*-(pyromellitoyl)-bis-*L*-isoleucine] (**4**) was obtained in a high yield. **4** was converted into *N,N'*-(pyromellitoyl)-bis-*L*-isoleucine diacid chloride by a reaction with thionyl chloride. The polycondensation reaction of this diacid chloride with several aromatic diamines, including 1,4-phenylenediamine, 4,4'-diaminodiphenyl methane, 4,4'-diaminodiphenylsulfone (4,4'-sulfonyldianiline), 4,4'-diaminodiphenylether, 2,4-diaminotoluene, and 1,3-phenylenediamine, was developed with two methods. The first method was polymerization under microwave irradiation, and the second method was low-temperature solution polymerization, with trimethyl-

silyl chloride used as an activating agent for the diamines. The polymerization reactions proceeded quickly and produced a series of optically active poly(amide imide)s with good yields and moderate inherent viscosities of 0.17–0.25 dL/g. All of the aforementioned polymers were fully characterized by IR, elemental analyses, and specific rotation. Some structural characterization and physical properties of these optically active poly(amide imide)s are reported. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 951–959, 2004

**Key words:** microwave-assisted polycondensation; optically active polymers; inherent viscosity; poly(amide-imide)s; thermogravimetric analysis (TGA); irradiation

## INTRODUCTION

Microwave irradiation is being used in an increasing number of applications in organic synthesis for optimizing and accelerating chemical reactions. These reactions are very fast and are completed within a short period of time.<sup>1–3</sup> Moreover, *N*-trimethylsilylated aromatic diamines have been found to be far more reactive than their parent diamines toward diacid chlorides, and so higher molecular weight polymers have readily been prepared by the low-temperature solution polycondensation of these monomers under milder reaction conditions, in comparison with poly(amide imide)s (PAIs) formed by the conventional diamine–diacid chloride route.<sup>4</sup>

Interesting applications have been found for optically active polymers because of their specific properties. For example, these polymers have molecular recognition, which allows them to be used as stationary

phases in chromatography methods for enantiomer separation.<sup>5–11</sup> They can also be used as chiral media for asymmetric synthesis and as chiral liquid crystals in ferroelectric and nonlinear optical devices.<sup>12–15</sup> Therefore, the syntheses and applications of optically active polymers have been paid more attention. Recently, we synthesized optically active polymers by different methods, such as the modification of polybutadiene with optically active substituted urazole groups,<sup>16</sup> Diels–Alder reactions,<sup>17,18</sup> and the reaction of an optically active monomer with several diamines via solution polymerization.<sup>19–23</sup> In the last case, we used amino acids as chiral agents in the backbone of the polymer.<sup>24–26</sup> Because amino acids are naturally occurring compounds, synthetic polymers based on amino acids are expected to be nontoxic, biodegradable, and biocompatible.

This article reports and compares two efficient methods for the synthesis of new optically active PAIs that contain amino acid *L*-isoleucine (**2**) moieties from the polycondensation reaction of *N,N'*-(pyromellitoyl)-bis-*L*-isoleucine diacid chloride (**5**) with aromatic diamines. The first method is polymerization under microwave irradiation, and the second method is low-temperature solution polymerization, with trimethyl-

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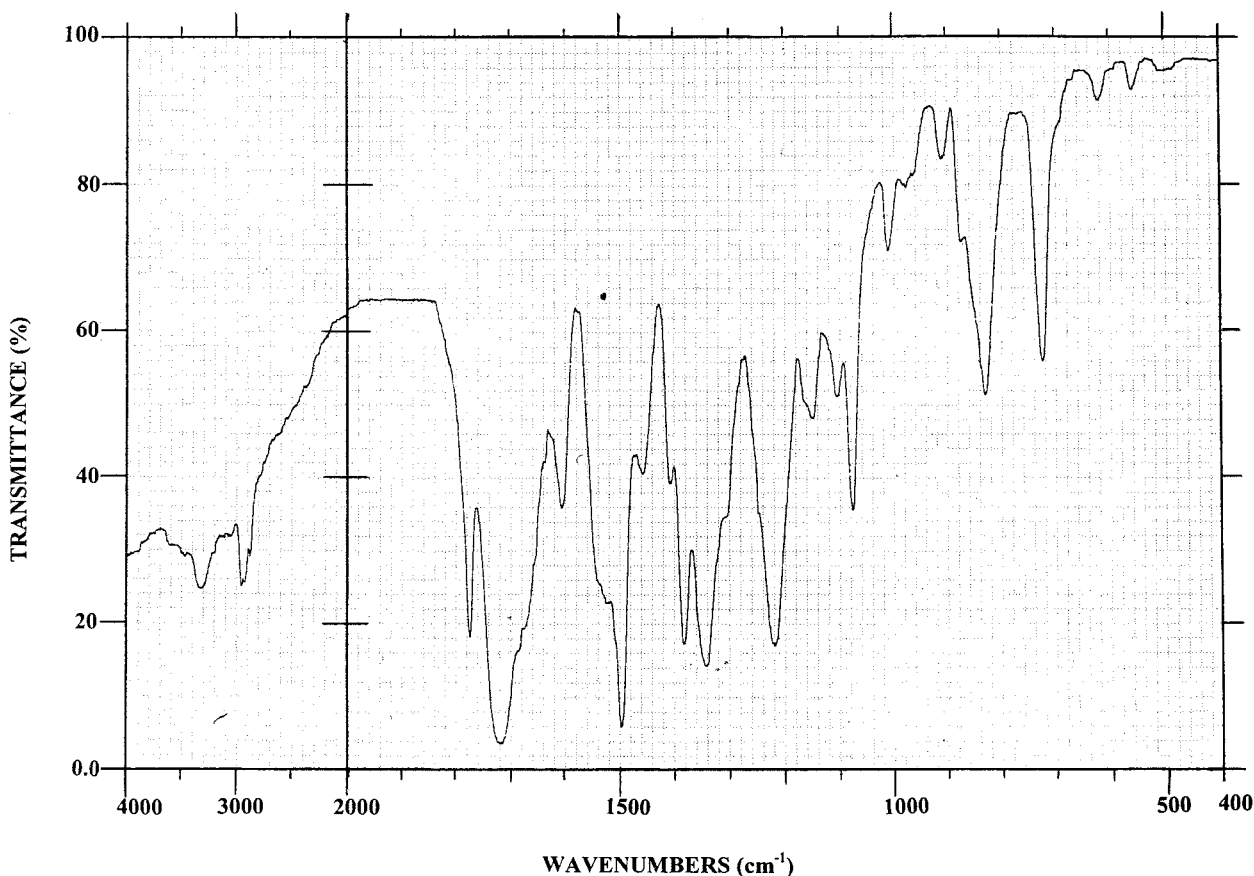


Figure 1 IR (KBr) spectrum of PAI 7d.

silyl chloride (TMSCl) used as an activating agent for the diamines.

all of the polymerization reactions were carried out in a hood with strong ventilation.

## EXPERIMENTAL

### Materials

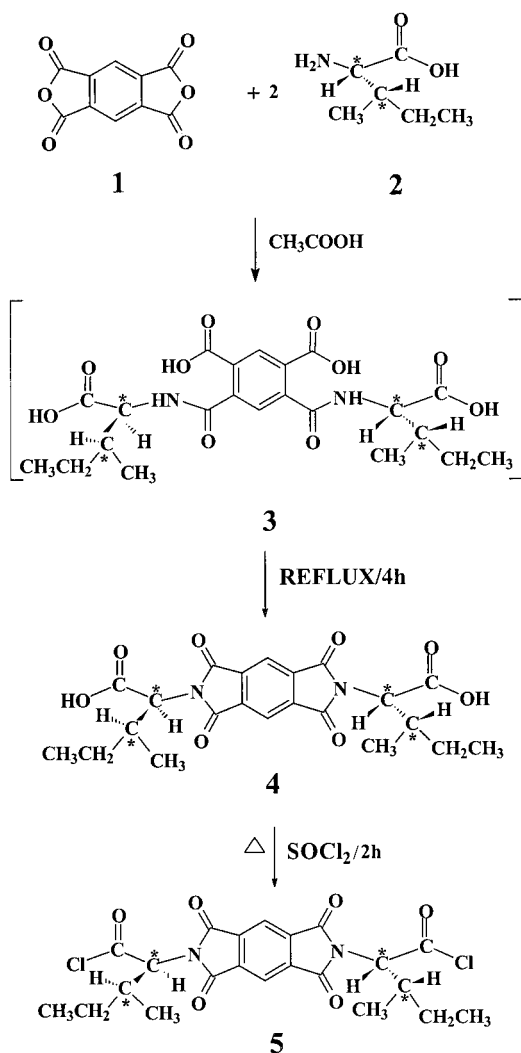
A pyromellitic dianhydride [benzene-1,2,4,5-tetracarboxylic dianhydride (**1**); Merck Chemical Co., Germany] was purified by recrystallization from a mixture of acetic anhydride and acetic acid (1:5). 1,4-Phenylenediamine (**6a**), 4,4'-diaminodiphenylmethane (**6b**), 4,4'-diaminodiphenylether (**6d**), 2,4-diaminotoluene (**6e**), and 1,3-phenylenediamine (**6f**) were purified by sublimation. 4,4'-Diaminodiphenylsulfone (**6c**) was used without purification. 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

The apparatus used for the polycondensation was a Samsung (South Korea) domestic microwave oven (2450 MHz and 900 W) without any modification, but

### Measurements

IR spectra were recorded on Shimadzu (Kyoto, Japan) 435 IR spectrophotometer. The spectra of the solids were determined with KBr pellets. Vibrational transition frequencies are reported as wave numbers ( $\text{cm}^{-1}$ ). The band intensities are categorized as weak (w), medium (m), shoulder (sh), strong (s), and broad (br).  $^1\text{H-NMR}$  (90 and 500 MHz) spectra were recorded on a Varian Associates (Palo Alto, CA) EM-390 and a Bruker (Rheinstetten, Germany) Avance 500 instrument, respectively. Tetramethylsilane (TMS) was used as an internal reference. The multiplicities of the proton resonance are designated singlet (s), doublet (d), doublet of doublet (dd), and multiplet (m). The inherent viscosities ( $\eta_{\text{inh}}$ ) were measured by a standard procedure with a Cannon (Mainz, Germany) Fenske routine viscometer. The specific rotations were measured with a PerkinElmer (Jügesheim, Germany) 241 polarimeter. Thermogravimetric analysis (TGA) data for the polymers were taken on a PerkinElmer 4 under a nitrogen atmosphere at a rate of  $40^\circ\text{C}/\text{min}$ .



Scheme 1 Synthesis of monomer 5.

Elemental analyses were performed at Malek-Ashtar University of Technology (Tehran, Iran).

### Monomer synthesis

#### *N,N'*-(Pyromellitoyl)-bis-L-isoleucine diacid (4)

Into a 25-mL, round-bottom flask, 0.10 g ( $4.58 \times 10^{-4}$  mol) of **1**, 0.12 g ( $9.17 \times 10^{-4}$  mol) of **2**, 4.0 mL of acetic acid, and a stirring bar were placed. The mixture was stirred at room temperature overnight and then was refluxed for 4 h. The solution was cooled, and the resulting crystal was filtered off, washed with water, and dried *in vacuo* at 80°C; this yielded 0.196 g (96%) of compound **4**.

mp: 266–268°C.  $R_f$  (the ratio of the distance moved by the substance to the distance moved by the solvent front): 0.80 (50:50 ethyl acetate/cyclohexane).  $[\alpha]_D^{25}$ : –88.2 [0.050 g in 10 mL of *N,N*-dimethylformamide (DMF)]. IR (KBr): 3000 (s, br), 1775 (s), 1720 (s, br),

1460 (m), 1430 (m), 1380 (s), 1360 (s), 1280 (s), 1170 (m), 1110 (m), 1080 (s), 1010 (m), 925 (m, sh), 890 (m), 820 (w), 810 (w), 775 (m), 740 (m), 700 (m), 630 (m), 580  $\text{cm}^{-1}$  (w).  $^1\text{H-NMR}$  [dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ), TMS, 90 MHz,  $\delta$ ]: 0.7–1.8 (m, 16H), 2.5 (m, 2H), 4.7 (dd, 2H,  $J = 9$  Hz), 8.6 (s, 2H), 10.9 ppm (broad, 2H). ELEM. ANAL. Calcd. for  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8$ : C, 59.45%; H, 5.44%; N, 6.30%. Found: C, 59.52%; H, 5.49%; N, 5.84%.

#### *N,N'*-(Pyromellitoyl)-bis-L-isoleucine diacid chloride (5)

Into a 25-mL, round-bottom flask were placed 0.10 g ( $2.25 \times 10^{-4}$  mol) of compound **4** and 2.5 mL (an excess amount) of thionyl chloride. The mixture was refluxed for 2 h. Unreacted thionyl chloride was removed under reduced pressure, and the residue was washed with *n*-hexane; this yielded 0.105 g (97.0%) of diacid chloride **5**.

mp: 243–244°C.  $[\alpha]_D^{25}$ : –91.2 (0.05 g in 10 mL of DMF). IR (KBr): 2950 (m), 2900 (m), 1815 (s), 1795 (s), 1775 (s), 1455 (m), 1380 (s), 1360 (s), 1150 (m), 1120 (m), 1080 (s), 1015 (m), 895 (m), 800 (w), 760 (w), 730 (s), 630 (w), 600  $\text{cm}^{-1}$  (m). ELEM. ANAL. Calcd. for  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_6\text{Cl}_2$ : C, 54.89%; H, 4.61%; N, 5.82%. Found: C, 55.14%; H, 4.87%; N, 5.55%.

### Polymer synthesis

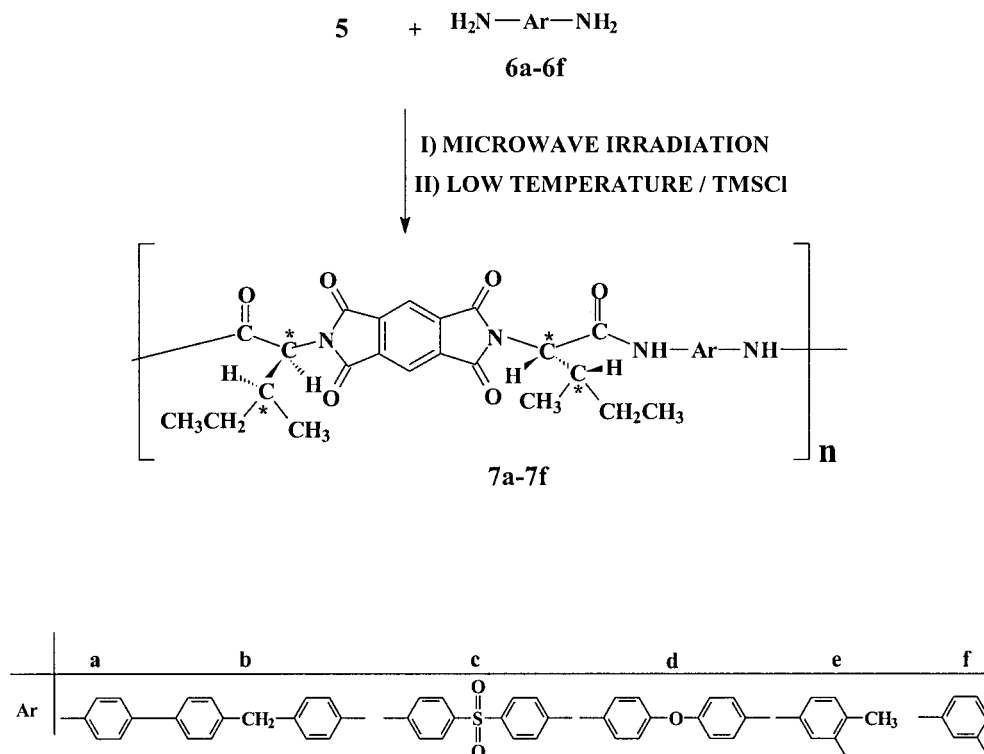
All of the polymers were synthesized by two different methods.

#### Method I: polymerization under microwave irradiation

The PAIs were prepared by the following general procedure (polymer **7aI** is described as an example). Into a porcelain dish were placed 0.10 g ( $2.07 \times 10^{-4}$  mol) of diacid chloride **5** and 0.0225 g ( $2.07 \times 10^{-4}$  mol) of diamine **6a**. After the reagents were completely ground with a pestle for 5 min, 0.10 mL of *N*-methyl-2-pyrrolidone (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 5 min at 50% power. The resulting polymer film was isolated by the addition of 20 mL of methanol and trituration; it was then filtered and dried at 80°C for 10 h *in vacuo*. This yielded 0.20 g (80.0%) of solid **7aI**.

IR (KBr): 3300 (m, br), 2950 (s), 1770 (s), 1720 (s, br), 1605 (m), 1520 (m, sh), 1500 (s), 1460 (m), 1410 (m), 1380 (s), 1340 (s), 1220 (s), 1150 (m), 1100 (m), 1070 (m), 1010 (w), 910 (w), 855 (m), 830 (s), 720 (s), 620 (w), 560  $\text{cm}^{-1}$  (w).

$^1\text{H-NMR}$  (DMSO- $d_6$ , TMS, 500 MHz,  $\delta$ ) of PAI **7c**: 0.82 (s, br,  $\text{CH}_3$ ), 0.99 (m,  $\text{CH}_3$ ), 1.50 (s, br,  $\text{CH}_2$ ), 2.63 (s, br, CH), 4.71–4.73 (d, CH,  $J = 7.60$  Hz), 7.74–7.76 (d,



Scheme 2 Polycondensation reactions of monomer 5 with aromatic diamines.

CH,  $J = 7.75$  Hz), 7.82–7.84 (d, CH,  $J = 7.85$  Hz), 8.29–8.31 (s, CH), 10.45–10.50 ppm (s, NH).

The other PAIs (**7bI–7fI**) were prepared with a similar procedure.

Method II: low-temperature solution polycondensation with TMSCI

The general procedure (polymer **7dII** is described as an example) consisted of adding 0.10 g ( $2.07 \times 10^{-4}$  mol) of diacid chloride **5** to a cooled ( $-5.0^\circ\text{C}$ ) and stirred solution of 0.041 g ( $2.07 \times 10^{-4}$  mol) of diamine **6d** in 0.50 mL of NMP. After the reagents dissolved completely, 0.03 mL of TMSCI was added, and the

reaction was allowed to proceed for 4 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 25 mL of methanol, and the precipitated solid was filtered off and dried at  $80^\circ\text{C}$  for 10 h *in vacuo*; this yielded 0.114 g (90.0%) of solid polymer **7dII**. The IR spectrum of this polymer is shown in Figure 1.

$^1\text{H-NMR}$  (DMSO- $d_6$ , TMS, 500 MHz,  $\delta$ ) of PAI **7d**: 0.83 (s, br,  $\text{CH}_3$ ), 1.02 (s, br,  $\text{CH}_3$ ), 1.50 (m,  $\text{CH}_2$ ), 2.69 (m, CH), 4.66–4.68 (d, CH,  $J = 7.90$  Hz), 6.90–6.92 (d, CH,  $J = 7.60$  Hz), 7.51–7.52 (d, CH,  $J = 7.85$  Hz), 8.29 (s, CH), 10.12 ppm (s, NH).

**Polymer 7b**. IR (KBr): 3300 (m, br), 2950 (s, br), 1720 (s, br), 1670 (s, sh), 1600 (m), 1510 (s), 1460 (m), 1410 (m),

**TABLE I**  
Some Physical Properties of PAIs 7aI–7fI

Diamine	Polymer			
	Polymer code	Yield (%)	$\eta_{\text{inh}}$ (dL/g) <sup>a</sup>	$[\alpha]_D^{25b}$
<b>6a</b>	<b>7aI</b>	80	0.22	–32.0
<b>6b</b>	<b>7bI</b>	73	0.20	–3.2
<b>6c</b>	<b>7cI</b>	84	0.22	–73.6
<b>6d</b>	<b>7dI</b>	71	0.25	–14.6
<b>6e</b>	<b>7eI</b>	78	0.22	25.4
<b>6f</b>	<b>7fI</b>	73	0.20	14.5

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMF at  $25^\circ\text{C}$ .

<sup>b</sup> Measured at a concentration of 0.50 g/dL in DMF at  $25^\circ\text{C}$ .

**TABLE II**  
Some Physical Properties of PAIs 7aII–7fII

Diamine	Polymer			
	Polymer code	Yield (%)	$\eta_{\text{inh}}$ (dL/g) <sup>a</sup>	$[\alpha]_D^{25b}$
<b>6a</b>	<b>7aII</b>	80	0.22	–29.2
<b>6b</b>	<b>7bII</b>	73	0.24	–2.0
<b>6c</b>	<b>7cII</b>	84	0.18	–45.0
<b>6d</b>	<b>7dII</b>	90	0.21	–13.0
<b>6e</b>	<b>7eII</b>	70	0.17	+27.2
<b>6f</b>	<b>7fII</b>	87	0.24	+31.6

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMF at  $25^\circ\text{C}$ .

<sup>b</sup> Measured at a concentration of 0.5 g/dL in DMF at  $25^\circ\text{C}$ .

1380 (s), 1340 (s), 1250 (m), 1180 (m), 1150 (m), 1100 (m), 1070 (s), 1010 (w), 910 (w), 810 (m), 720 (s), 620 (w), 560 cm<sup>-1</sup> (w).

**Polymer 7c.** IR (KBr): 3300 (m, br), 2950 (s), 1770 (s), 1720 (s, br), 1590 (s), 1520 (s), 1460 (m), 1400 (s, sh), 1380 (s), 1340 (s), 1310 (s, sh), 1245 (m), 1180 (m), 1150 (s), 1070 (s), 1100 (s), 1075 (s), 1010 (w), 900 (w), 830 (m), 720 (s), 680 (m), 620 (m), 550 cm<sup>-1</sup> (m).

**Polymer 7e.** IR (KBr): 3300 (m, br), 2900 (s), 1770 (s), 1720 (s, br), 1660 (s), 1600 (m), 1520 (m), 1490 (m), 1450 (m), 1380 (s), 1340 (s), 1315 (m), 1140 (m), 1100 (m, sh), 1070 (s), 1000 (w), 910 (w), 860 (m), 820 (m), 720 (s), 650 (w), 620 (w), 560 cm<sup>-1</sup> (w).

**Polymer 7f.** IR (KBr): 3300 (m, br), 2950 (s), 1770 (s), 1720 (s, br), 1605 (s), 1530 (s), 1480 (s), 1420 (s), 1380 (s), 1340 (s), 1210 (m), 1150 (m), 1100 (m, sh), 1080 (s), 1000 (w), 910 (w), 860 (m), 760 (m), 720 (s), 680 (m), 620 (w), 560 cm<sup>-1</sup> (w).

## RESULTS AND DISCUSSION

### Monomer synthesis

**5** was prepared by the three-step procedure shown in Scheme 1. The symmetric diacid compound (**4**) was synthesized by the condensation reaction of dianhydride **1** with 2 mol of **2** in acetic acid. The intermediate amic acid **3** was not isolated, and dehydration was performed under refluxing conditions. The resulting symmetric diacid **4** was converted into its diacid chloride derivative **5** by a reaction with thionyl chloride. **5**

was purified via washing with *n*-hexane. The chemical structure and purity of the optically active monomers **4** and **5** were proved with elemental analysis and IR spectroscopy.

The IR spectrum of **4** showed a broad and strong peak at 2400–3500 cm<sup>-1</sup>, which was assigned to the COOH groups, and two absorption bands at 1720 and 1775 cm<sup>-1</sup>, which were characteristic peaks for imide rings. The disappearance of a strong acidic hydroxyl peak in the IR spectrum of compound **5** confirmed the complete conversion of diacid **4** into diacid chloride **5**. However, because of the electron-withdrawing character of the Cl group, the two carbonyl peaks of diacid chloride, in comparison with its starting diacid, were shifted to a higher frequency.

### Polymer synthesis

PAIs **7a–7f** were synthesized by microwave-assisted polycondensation and solution polycondensation reactions of an equimolar mixture of monomer **5** with six different aromatic diamines (**6a–6f**), as shown in Scheme 2.

The microwave-assisted polycondensation reactions were performed at different irradiation power levels to obtain the optimum conditions of polymerization: 5 min of irradiation at 50% power. The reactions were performed in the presence of a small amount of a polar organic medium, such as NMP, that acted as a primary microwave absorber. The reaction yields and some physical data are listed in Table I.

TABLE III  
Elemental Analysis of PAIs 7a–7f

Polymer	Formula		Elemental analysis (%)			Moisture intake (%) <sup>a</sup>
			C	H	N	
7a	(C <sub>28</sub> H <sub>28</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> (517) <sub>n</sub>	Calcd.	65.11	5.46	10.85	4.16
		Found	62.63	5.84	11.00	
		Corrected <sup>b</sup>	65.23	5.64	11.45	
7b	(C <sub>35</sub> H <sub>34</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> (607) <sub>n</sub>	Calcd.	69.29	5.65	9.23	3.47
		Found	69.64	6.00	9.62	
		Corrected <sup>b</sup>	67.93	5.79	9.95	
7c	(C <sub>34</sub> H <sub>31</sub> N <sub>4</sub> SO <sub>8</sub> ) <sub>n</sub> (657) <sub>n</sub>	Calcd.	62.18	4.91	8.53	1.76
		Found	59.98	5.34	9.19	
		Corrected <sup>b</sup>	61.03	5.24	9.35	
7d	(C <sub>34</sub> H <sub>32</sub> N <sub>4</sub> O <sub>7</sub> ) <sub>n</sub> (609) <sub>n</sub>	Calcd.	67.09	5.30	9.20	1.62
		Found	65.13	5.76	9.81	
		Corrected <sup>b</sup>	67.14	5.66	9.97	
7e	(C <sub>29</sub> H <sub>30</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> (531) <sub>n</sub>	Calcd.	65.65	5.69	10.56	1.24
		Found	63.82	6.09	11.06	
		Corrected <sup>b</sup>	64.61	6.01	11.19	
7f	(C <sub>28</sub> H <sub>28</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> (517) <sub>n</sub>	Calcd.	65.11	5.46	10.85	3.02
		Found	62.49	6.00	11.24	
		Corrected <sup>b</sup>	64.38	5.82	11.58	

<sup>a</sup> Moisture intake (%) = (W - W<sub>0</sub>)/W<sub>0</sub> × 100, where W is weight of the polymer sample after standing at room temperature and W<sub>0</sub> is the weight of the polymer sample after drying *in vacuo* at 100°C for 10 h.

<sup>b</sup> Corrected value for C and N = Found value × (100 + Moisture intake)/100; corrected value for H = Found value × (100 - Moisture intake)/100.



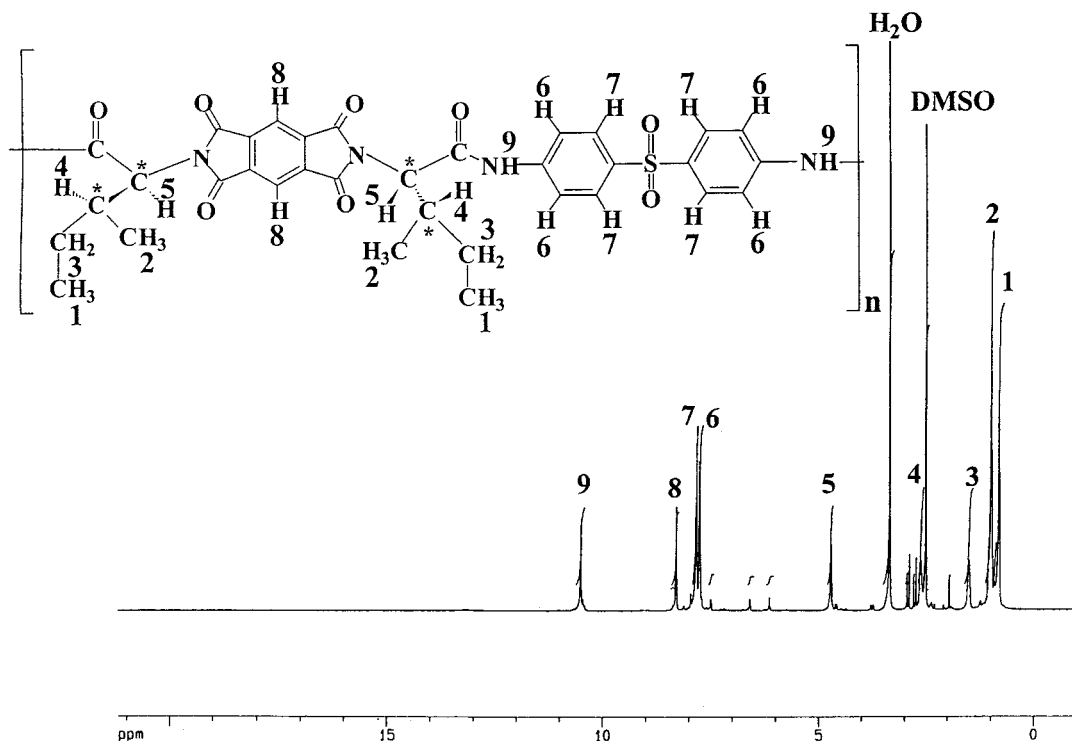


Figure 2  $^1\text{H-NMR}$  (500 MHz) spectrum of PAI 7c in  $\text{DMSO-}d_6$  at room temperature.

The resulting polymers showed optical rotations, which indicated that they were optically active.

To compare the microwave-assisted polycondensa-

tion method with conventional solution polycondensation reactions, we performed the polymerization reactions with low-temperature solution polymerization

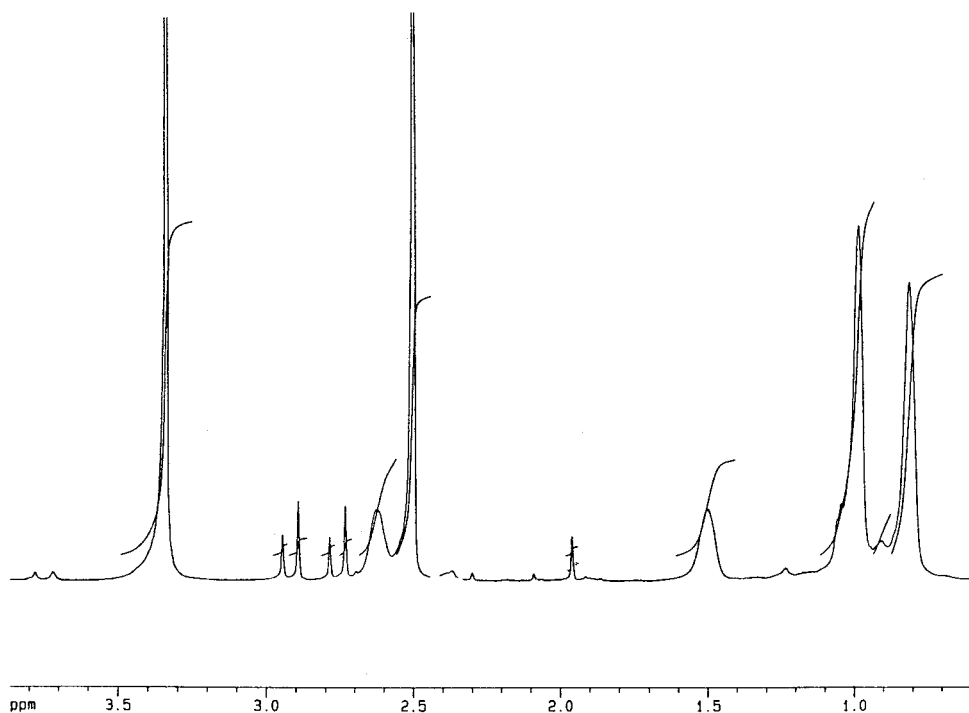
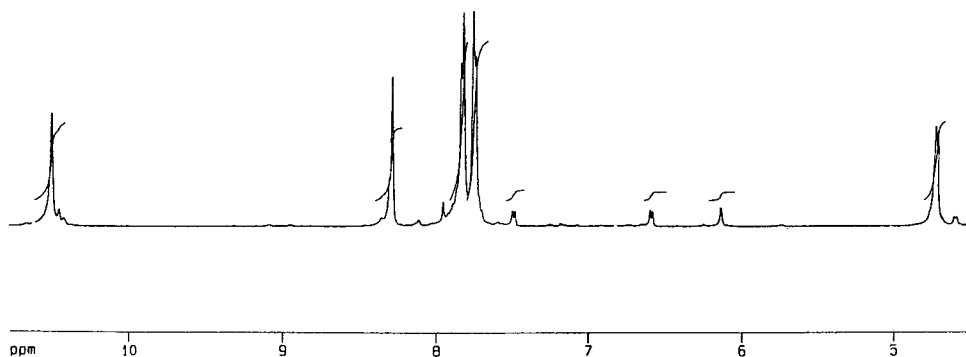


Figure 3  $^1\text{H-NMR}$  (500 MHz) spectrum of PAI 7c in  $\text{DMSO-}d_6$  at room temperature. An expanded region is shown for the aliphatic protons ( $\delta = 0.6\text{--}3.8$  ppm).



**Figure 4**  $^1\text{H-NMR}$  (500 MHz) spectrum of PAI 7c in  $\text{DMSO-}d_6$  at room temperature. An expanded region is shown for the aromatic protons ( $\delta = 4.5\text{--}11.0$  ppm).

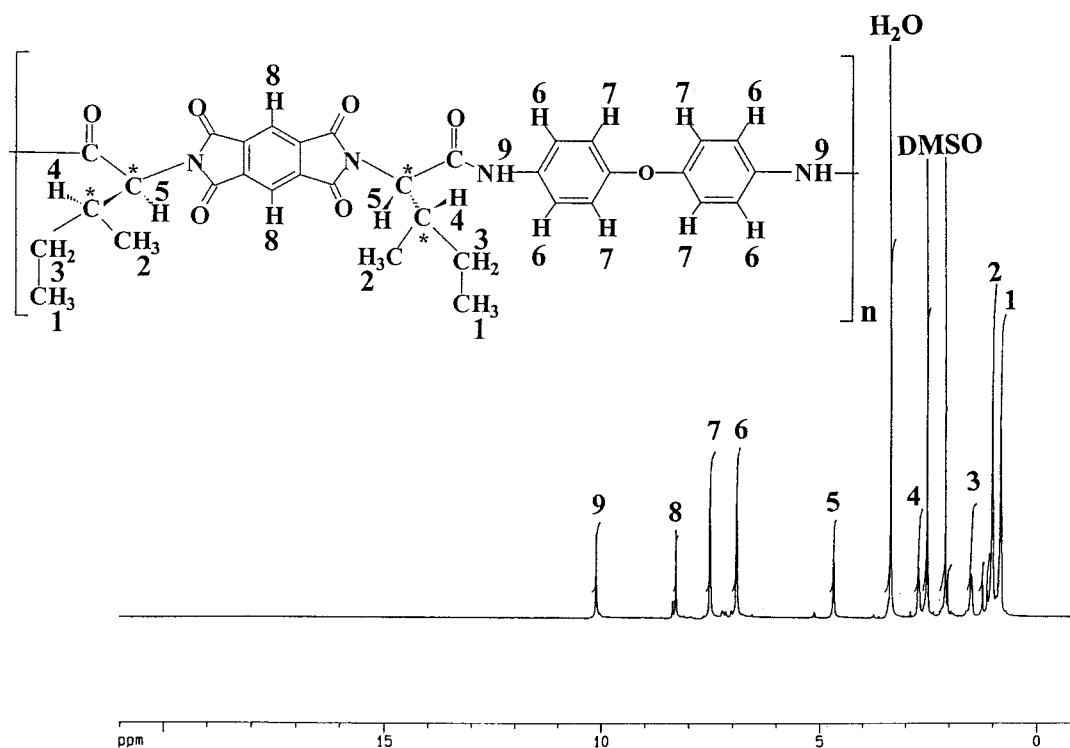
(method II). In this method, the reactions were performed in NMP solutions in the presence of  $\text{TMSCl}$ , which acted as a diamine activator. The polymerization reactions occurred at a low temperature for 4 h and then at room temperature for 5 h. We obtained comparable yields and viscosities of PAIs from method II with respect to microwave-assisted polymerizations. The reaction yields and some physical data of the solution polycondensations are listed in Table II.

#### Structural characterization of the polymers

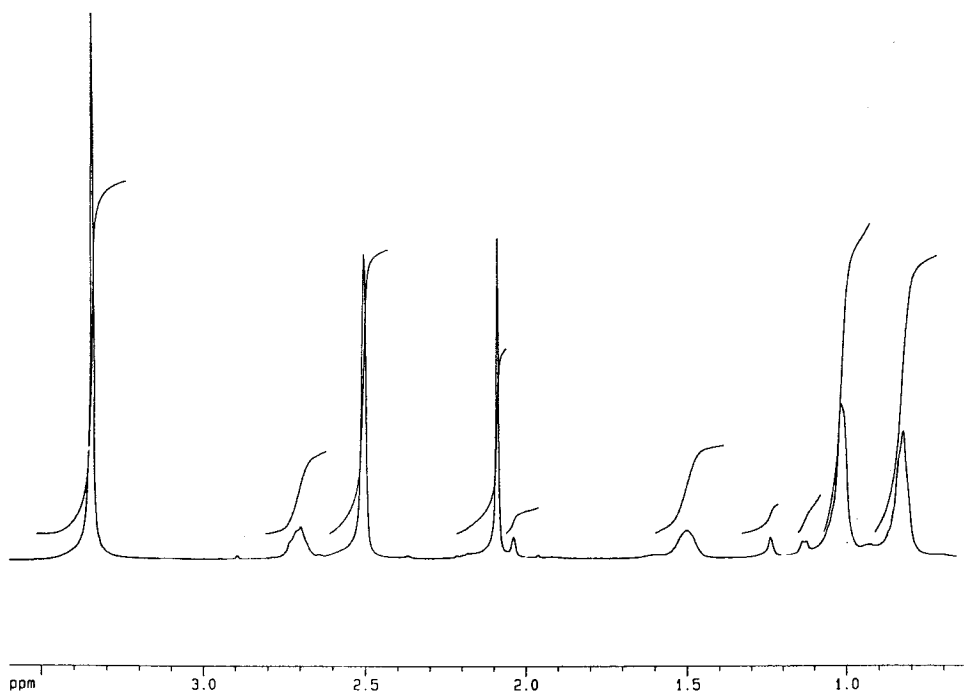
The structures of the polymers were confirmed as PAIs by means of elemental analysis, IR, and  $^1\text{H-NMR}$

spectroscopy. The elemental analysis values of the resulting polymers are listed in Table III.

The IR spectra of all the polymers exhibited characteristic absorptions for the imide ring at 1680, 1720, and 1775  $\text{cm}^{-1}$  due to the symmetrical and asymmetrical carbonyl stretching vibrations. Bands of amide groups appeared around 3300  $\text{cm}^{-1}$  (N—H), and an overlapped peak (shoulderlike) appeared around 1650  $\text{cm}^{-1}$  (C=O). All of them exhibited strong absorbance at 1340–1380 and 680–720  $\text{cm}^{-1}$ , which showed the presence of the imide heterocycle in these polymers. Polymer 7c showed characteristic absorptions at 1310 and 1070  $\text{cm}^{-1}$  due to the sulfone moiety ( $\text{SO}_2$  stretching). Figure 1 shows a typical IR spectrum of a PAI (7d).



**Figure 5**  $^1\text{H-NMR}$  (500 MHz) spectrum of PAI 7d in  $\text{DMSO-}d_6$  at room temperature.



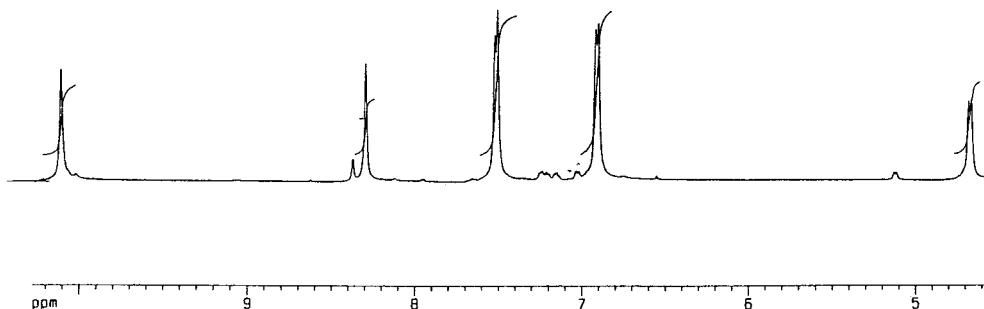
**Figure 6**  $^1\text{H-NMR}$  (500 MHz) spectrum of PAI **7d** in  $\text{DMSO-}d_6$  at room temperature. An expanded region is shown for the aliphatic protons ( $\delta = 0.7\text{--}4.0$  ppm).

The  $^1\text{H-NMR}$  spectra of PAI **7c** and PAI **7d** are shown in Figures 2–4 and 5–7. The patterns of the spectra are similar to those of the monomer diacid chloride and corresponding diamine. Two equivalent amidic hydrogens can be seen in a similar chemical shift. Figure 3 shows an expanded region for the aliphatic protons, and Figure 4 shows an expanded region for the aromatic protons. Figure 6 also shows an expanded region for the aliphatic protons, and Figure 7 shows an expanded region for the aromatic protons.

All the polymers were soluble in aprotic polar solvents such as *N,N*-dimethylacetamide, DMF, NMP, and DMSO and in protic solvents such as sulfuric acid and were insoluble in organic solvents such as tetrahydrofuran, chloroform, acetone, and benzene.

### Thermal properties

The thermal decomposition temperatures of two PAIs, **7b** and **7d**, were evaluated with TGA under a nitrogen atmosphere at a rate of heating of  $40^\circ\text{C}/\text{min}$ . **7b** and **7d** exhibited good resistance to thermal decomposition up to about  $310^\circ\text{C}$  in nitrogen with minimum decomposition, but above this temperature, the decomposition was faster. The temperatures of 5% weight loss were  $330$  and  $310^\circ\text{C}$ , and the temperatures of 10% weight loss were  $350$  and  $340^\circ\text{C}$ , respectively. The residual weight for these polymers at  $600^\circ\text{C}$  ranged from 10 to 9%. Figure 8 shows the TGA curves for these polymers.



**Figure 7**  $^1\text{H-NMR}$  (500 MHz) spectrum of PAI **7d** in  $\text{DMSO-}d_6$  at room temperature. An expanded region is shown for the aromatic protons ( $\delta = 4.6\text{--}10.3$  ppm).



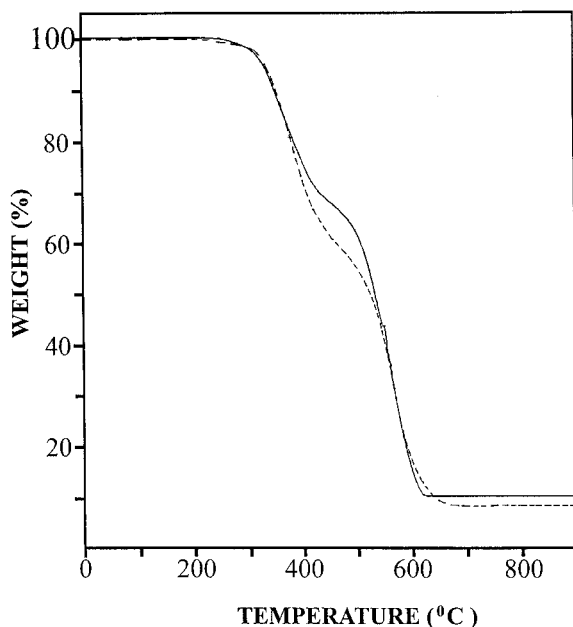


Figure 8 TGA of (---) PAI 7b and (—) PAI 7d at a heating rate of 40°C/min under a nitrogen atmosphere.

### CONCLUSIONS

This work has shown that **5** is an interesting monomer that contains both a pyromellitimide group and chiral **2** groups. A series of new optically active PAIs with  $\eta_{inh}$  values of 0.17–0.25 dL/g have been synthesized by two different methods through the polycondensation reaction of the optically active monomer **5** with six different aromatic diamines (**6a–6f**). These aromatic PAIs are optically active and soluble in various organic solvents and have good thermal stability. The resulting novel polymers have the potential to be used in column chromatography techniques for the separation of enantiomeric mixtures. Furthermore, the results of this study demonstrate that both two methods are efficient for the synthesis of PAIs, but microwave heating is more efficient (shorter reaction time and high energy efficiency) for the polycondensation reactions. We are currently using these methods for the

synthesis of novel polymers and the modification of polymers.

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### References

- Gedye, R.; Smith, F.; Westaway, H. A.; Baldisera, L.; Laberge, L.; Rousell, J. *Tetrahedron Lett* 1986, 27, 279.
- Abramovich, R. A. *Org Prep Proc Int* 1991, 23, 683.
- Caddick, S. *Tetrahedron* 1995, 51, 10403.
- Oishi, Y.; Kakimoto, M.; Imai, Y. *Macromolecules* 1988, 21, 547.
- Akekah, A.; Sherrington, D. C. *Chem Rev* 1981, 81, 557.
- Aglietto, M.; Chiellini, E.; Antone, S. D.; Ruggeri, G.; Solaro, R. *Pure Appl Chem* 1988, 60, 415.
- Yuki, H.; Okamoto, Y.; Okamoto, I. *J Am Chem Soc* 1980, 102, 6358.
- Okamoto, Y.; Yashima, E. *Angew Chem Int Ed Engl* 1999, 37, 1020.
- Soai, K.; Niwa, S. *Chem Rev* 1992, 92, 833.
- Noyori, K.; Kitamura, M. *Angew Chem Int Ed Engl* 1991, 30, 49.
- Pu, L.; Yu, B. *Chem Rev* 2001, 101, 757.
- Okamoto, Y.; Nakano, T. *Chem Rev* 1994, 94, 349.
- Farina, M. *Top Stereochem* 1987, 17, 1.
- Ciardelli, F. *Encycl Polym Sci Eng* 1987, 10, 463.
- Wulff, G. *Angew Chem Int Ed Engl* 1989, 28, 21.
- Mallakpour, S. E.; Hajipour, A. R.; Khoee, S.; Sheikholeslami, B. *Polym Int* 1998, 47, 193.
- Mallakpour, S. E.; Hajipour, A. R.; Mahdavian, A. R.; Khoee, S. *J Polym Sci Part A: Polym Chem* 1999, 37, 1211.
- Mallakpour, S. E.; Hajipour, A. R.; Mahdavian, A. R.; Rafiemanzelat, F. *Polym Int* 1999, 48, 109.
- Mallakpour, S. E.; Hajipour, A. R.; Khoee, S. *J Polym Sci Part A: Polym Chem* 2000, 38, 1154.
- Mallakpour, S. E.; Hajipour, A. R.; Roohipour-Fard, R. *Eur Polym J* 2000, 36, 2455.
- Mallakpour, S. E.; Hajipour, A. R.; Zamanlou, M. R. *J Polym Sci Part A: Polym Chem* 2001, 39, 177.
- Mallakpour, S. E.; Hajipour, A. R.; Zamanlou, M. R. *Eur Polym J* 2002, 38, 475.
- Mallakpour, S. E.; Hajipour, A. R.; Zamanlou, M. R. *Polym Sci Ser A* 2002, 44, 443.
- Mallakpour, S.; Hajipour, A. R.; Shahmohammadi, M. H. *J Appl Polym Sci* 2003, 89, 116.
- Mallakpour, S.; Hajipour, A. R.; Shahmohammadi, M. H. *Iran Polym J* 2002, 11, 425.
- Mallakpour, S. E.; Hajipour, A. R.; Habibi, S. *Eur Polym J* 2003, 39, 1823.