

# Preparation of New Poly(amide–imide)s with Chiral Architectures Via Direct Polyamidation Reaction

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**ABSTRACT:** *N*-trimellitylimido-*L*-methionine (**3**) was prepared by reaction of trimellitic anhydride (**1**) with *L*-methionine (**2**) in acetic acid solution at refluxing temperature. This diacid was reacted with thionyl chloride, and *N*-trimellitylimido-*L*-methionine diacid chloride (**4**) was obtained in quantitative yield. The resulting diacid chloride was reacted with *p*-aminobenzoic acid in dry acetone and bis(*p*-aminobenzoic acid)-*N*-trimellitylimido-*L*-methionine (**5**) was obtained as a novel optically active amide–imide diacid monomer in high yield. The direct polycondensation of amide–imide diacid

monomer **5** with several aromatic diamines was carried out with tosyl chloride (TsCl)/pyridine (Py)/dimethylformamide (DMF) system. The resulting thermally stable poly(amide–imide)s (PAIs) were obtained in good yields and inherent viscosities ranging between 0.24 and 0.46 dL g<sup>-1</sup> and were characterized with FTIR, <sup>1</sup>H NMR, CHN, and TGA techniques. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1248–1254, 2007

**Key words:** polycondensation; chiral; thermogravimetric analysis; poly(amide–imide)s; inherent viscosity

## INTRODUCTION

Organic polymers are one of the most versatile groups of materials that combine light weight, cost-effectiveness, and processability. Aromatic polyimides are the most useful super engineering plastics, which display excellent mechanical, electrical, and thermal properties, and have been used widely in electronics, aerospace, and other industries over the past three decades.<sup>1,2</sup> However, because of some inherent deficiencies, such as limited heat- and flame-resistance and low solubility, these materials are inappropriate for many important applications. Therefore, further research is needed to develop new polymeric systems, as well as to modify existing systems, to enhance the wanted properties and applications. Several approaches have been proposed, based on the incorporation of flexible segments bearing ester, sulfone, amide, and ether moieties in the polymer backbone, without sacrificing the heat resistance.<sup>3–8</sup> Thus, several type of copolyimides such as poly(amide–imide)s (PAIs) possess desirable characteristics between polyamides and polyimides such as high thermal stability

and good mechanical properties as well as better processability have been developed.

We are undoubtedly living in a chiral world. Most naturally occurring macromolecules, such as polysaccharides, proteins, and nucleic acids are chiral and optically active. In the history of polymer science, both naturally occurring and synthetic, optically active polymers (OAPs) have received much attention in conjunction with their stereochemistry, and extensive studies have been conducted on their syntheses, conformations, and functions. Recent advances in asymmetric reactions and catalysis as well as in chiral separations have afforded a rapid increase in the number of commercially available optically active compounds and reagents.<sup>9,10</sup> This situation will influence new methodologies for the preparation of OAPs in the coming century. Many chiral monomers will be prepared from these chiral chemicals. The simplest method for synthesizing OAPs involves the polymerization of optically active monomers.

Methionine is particularly important because it supplies sulfur, a mineral, that helps to maintain healthy skin tone, well-conditioned hair, and strong nails. In addition, it is thought to keep fat from building up in liver, and it is often included in liver-detoxifying products called lipotropic combinations. These formulations are believed to accelerate the flow of bile and cell-damaging toxins away from the liver. Because body cannot produce this essential amino acid on its own, mostly one get it from methionine rich foods, such as cheddar cheese, eggs, chicken, and beef. Supplements are also a source.<sup>11</sup>

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Recently, we have synthesized a variety of OAPs by incorporation of optically active segments in polymer's backbone. In addition of optical properties of these polymers, the solubility of them was improved without significant loss of mechanical and thermal properties.<sup>12–14</sup>

Higashi et al. have developed new condensing agents for direct polyesterification.<sup>15–18</sup> Because of importance of methionine and the existence of flexible group in this amino acid, to induce the chirality and improve the solubility of the polymers, in continuation of our study to develop new OAPs via direct polycondensation,<sup>19–22</sup> here, we report the application of the Vilsmeier adduct derived from TsCl/DMF/Py for direct polyamidation of new optically active bis(*p*-aminobenzoic acid)-*N*-trimellitylimido-*L*-methionine (**5**) monomer with different aromatic diamines.

## EXPERIMENTAL

### Materials

All chemicals were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany), and Merck Chemical Trimellitic anhydride (**1**) was purified with acetic anhydride in boiling acetic acid. *p*-Aminobenzoic acid was recrystallized from water. 4,4'-Diaminodiphenylsulfone (**6a**) was used as obtained without further purification. Benzidine (**6c**) and 4,4'-diaminodiphenyl methane (**6d**) was purified by recrystallization from ethanol and water, respectively. 4,4'-Diaminodiphenylether (**6b**), *p*-phenylenediamine (**6e**), and 2,5-diaminotoluene (**6f**) were purified by sublimation.

### Techniques

Proton nuclear magnetic resonance (<sup>1</sup>H NMR, 300 MHz) spectra were recorded in DMSO-*d*<sub>6</sub> solution using a Bruker (Germany) Avance 300 instrument at Shahid Beheshti University, Tehran, Iran. FTIR spectra were recorded on (Jasco-680, Japan) spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wave numbers (cm<sup>-1</sup>). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Germany) at concentration of 0.5 g/dL at 25°C. Specific rotations were measured by a Jasco Polarimeter (Japan). Thermal gravimetric analysis (TGA) data for polymers were taken on PerkinElmer under nitrogen atmosphere at a rate of 10°C/min. Elemental analyses were performed by the Iran Polymer and Petrochemical Research Institute, Tehran, Iran.

### Monomer synthesis

#### *N*-trimellitylimido-*L*-methionine (**3**)

Into a 250-mL round-bottomed flask, 3.00 g (1.56 × 10<sup>-2</sup> mol) of trimellitic anhydride (**1**), 2.33 g (1.56 × 10<sup>-2</sup> mol) of *L*-methionine (**2**), 40 mL of acetic acid, and a stirring bar were placed. The solution was stirred for 2 h to yield amic acid and then the mixture was refluxed for 8 h. The solvent was removed under reduced pressure and to the residue 50 mL of HCl solution (0.5M) was added. A white precipitate was formed, filtered off, washed with water, and dried, to give 4.58 g (86%) of diacid **3**. Recrystallization from methanol/water gave white crystals, mp 195–197°C, [α]<sub>D</sub><sup>20</sup> = -5.8 (0.050 g in 10 mL DMF).

FTIR (KBr): 2400–3400 (br), 1779 (m, sh), 1725 (s), 1487 (m), 1418 (m), 1381 (s), 1279 (s), 1203 (m), 1169 (m), 1121 (m), 1103 (s), 953 (m), 898 (w), 804 (s), 756 (w, sh), 731 (s), 568 cm<sup>-1</sup> (m).

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 1.99 (s, 3H), 2.25 (m, 2H), 2.53 (m, 2H), 4.96 (distorted dd, 1H, *J* = 7.2 Hz), 8.01 (d, 1H, *J* = 7.7 Hz), 8.25 (s, 1H), 8.38 (d, 1H, *J* = 7.7 Hz), 13.54 (s, 2H) ppm.

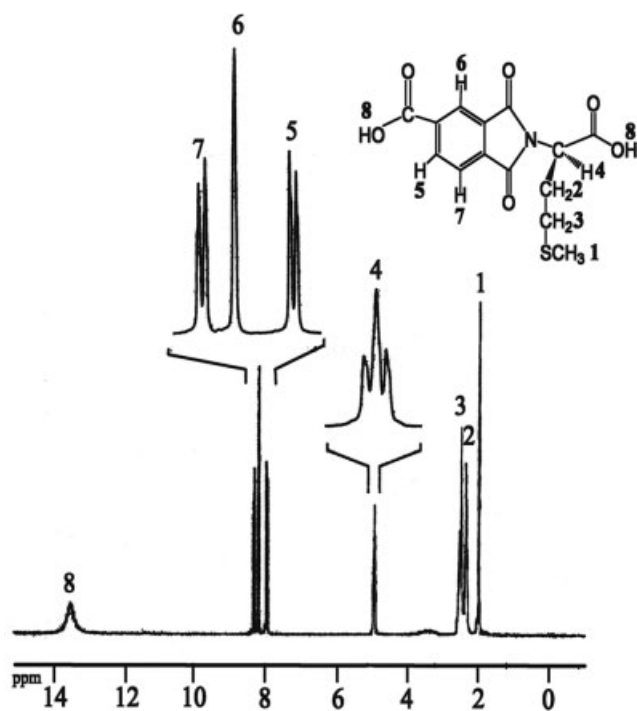
Mass (EI): 323 (M<sup>+</sup>), 249, 231(base peak), 176, 174, 148, 75, 61.

#### *N*-trimellitylimido-*L*-methionine diacid chloride (**4**)

Into a 50-mL round-bottomed flask, 1.00 g (3.01 × 10<sup>-3</sup> mol) of *N*-trimellitylimido-*L*-methionine (**3**), 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, 0.5 mL of thionyl chloride, and a stirring bar were placed. The stirrer was started and the mixture was refluxed for 2 h. The excess thionyl chloride was removed via distillation and 10 mL of *n*-hexane was added, the mixture was heated, *n*-hexane was distilled off, and the solid was collected, and dried *in vacuo* to give 1.00 g (90%) of a white solid. FTIR (KBr): 2919 (w), 1783 (m, sh), 1725 (s), 1622 (w), 1428 (m), 1380 (s), 1262 (m), 1218 (m), 1183 (m), 1142 (m), 1105 (m, sh), 1015 (w), 842 (w), 800 (w), 458 (w), 691 cm<sup>-1</sup> (m).

#### *N*-trimellitylimido-*L*-methionine-bis(*p*-aminobenzoic acid) (**5**)

Into a 25-mL round-bottomed flask fitted with a magnetic stirrer was placed a solution of 1.00 g (2.77 × 10<sup>-3</sup> mol) diacid chloride **4** in 5 mL of dry acetone. The reaction mixture was cooled in an ice water bath. To this solution, 0.83 g (6.11 × 10<sup>-3</sup> mol) *p*-aminobenzoic acid in 5 mL of acetone was added dropwise. The mixture was stirred in ice bath for 2 h and at room temperature for an overnight. The mixture was poured into 50 mL of HCl (0.05M). The precipitate was collected by filtration and washed thoroughly



**Figure 1**  $^1\text{H}$  NMR (300 MHz) spectrum of compound 3 in  $\text{DMSO}-d_6$  at rt.

with hot water and dried at  $70^\circ\text{C}$  for 10 h to yield 1.36 g (87%) of diacid 5, mp  $209\text{--}212^\circ\text{C}$  (dec),  $[\alpha]_D^{20} = -3.28$  (0.050 g in 10 mL DMF).

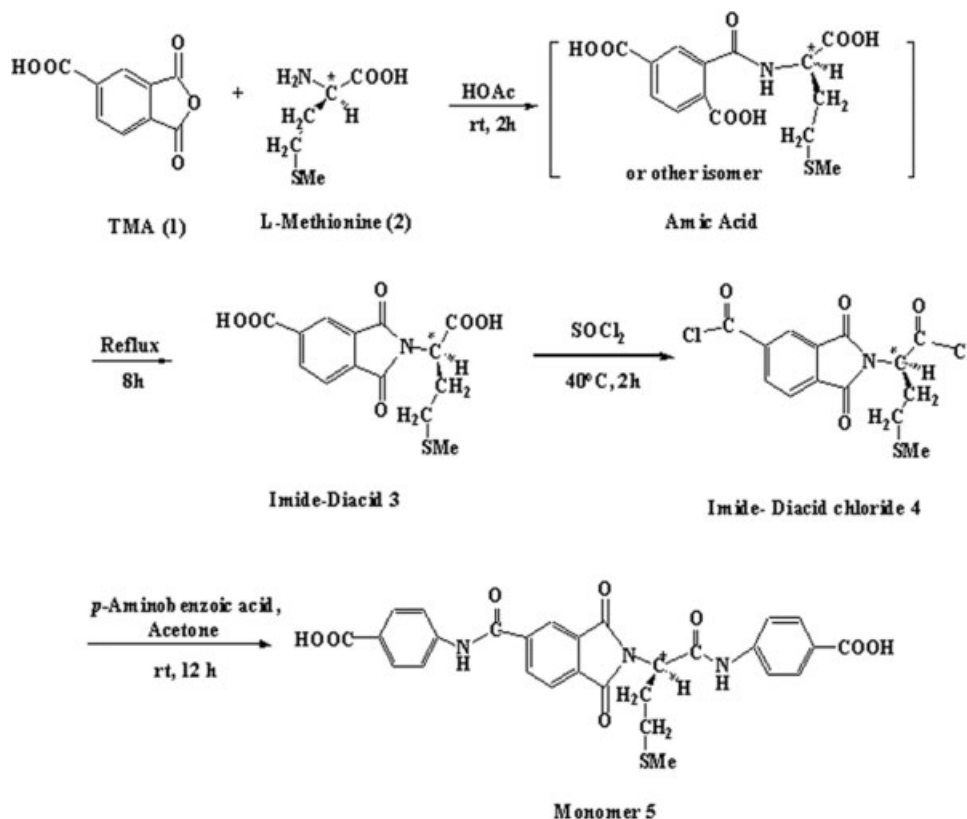
FTIR (KBr): 2500–3400 (br), 1776 (m, sh), 1716 (s), 1599 (s), 1683 (s), 1599 (s), 1532 (s), 1409 (m), 1378 (m), 1317 (m), 1252 (m), 1175 (s), 1102 (s), 856 (m), 771 (m),  $724\text{ cm}^{-1}$  (m).

$^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.04 (s, 3H), 2.37 (m, 2H), 2.57 (m, 2H), 5.07 (distorted dd, 1H,  $J = 4.2$  Hz), 7.67 (d, 2H,  $J = 8.7$  Hz), 7.88 (d, 2H,  $J = 8.6$  Hz), 7.96 (m, 4H), 8.09 (d, 1H,  $J = 7.8$  Hz), 8.42 (d, 1H,  $J = 7.9$  Hz), 8.48 (s, 1H), 10.27 (s, 1H), 10.86 (s, 1H), 12.80 (s, 1H) ppm.

Elemental analysis: calcd. for  $\text{C}_{28}\text{H}_{23}\text{N}_3\text{O}_8\text{S}$ : C, 59.89%; H, 4.13%; N, 7.48%. Found: C, 59.62%; H, 4.19%; N, 7.38%.

### Polymer synthesis

Polymer 7a, for an example of synthesis of poly (amide-imide)s (PAIs), was prepared by the following procedure: A pyridine (0.20 mL) solution of TsCl (0.18 g;  $9.5 \times 10^{-4}$  mol) after 30 min stirring at room temperature was treated with DMF (0.07 mL;  $9.0 \times 10^{-4}$  mol) for additional 30 min. The reaction mixture was added dropwise to a solution of monomer 5 (0.100 g;  $1.78 \times 10^{-4}$  mol) in Py (0.15 mL). The mixture was maintained at room temperature for 30 min, and then to this mixture, a solution of 4,4'-diaminophenylsulfone (6a) (0.044 g;  $1.78 \times 10^{-4}$  mol) in Py (0.15 mL) was added dropwise and the whole solution was



**Scheme 1** Synthesis of *N*-trimellitylimido-*L*-methionine (3) and *N*-trimellitylimido-*L*-methionine-bis(*p*-aminobenzoic acid) (5).

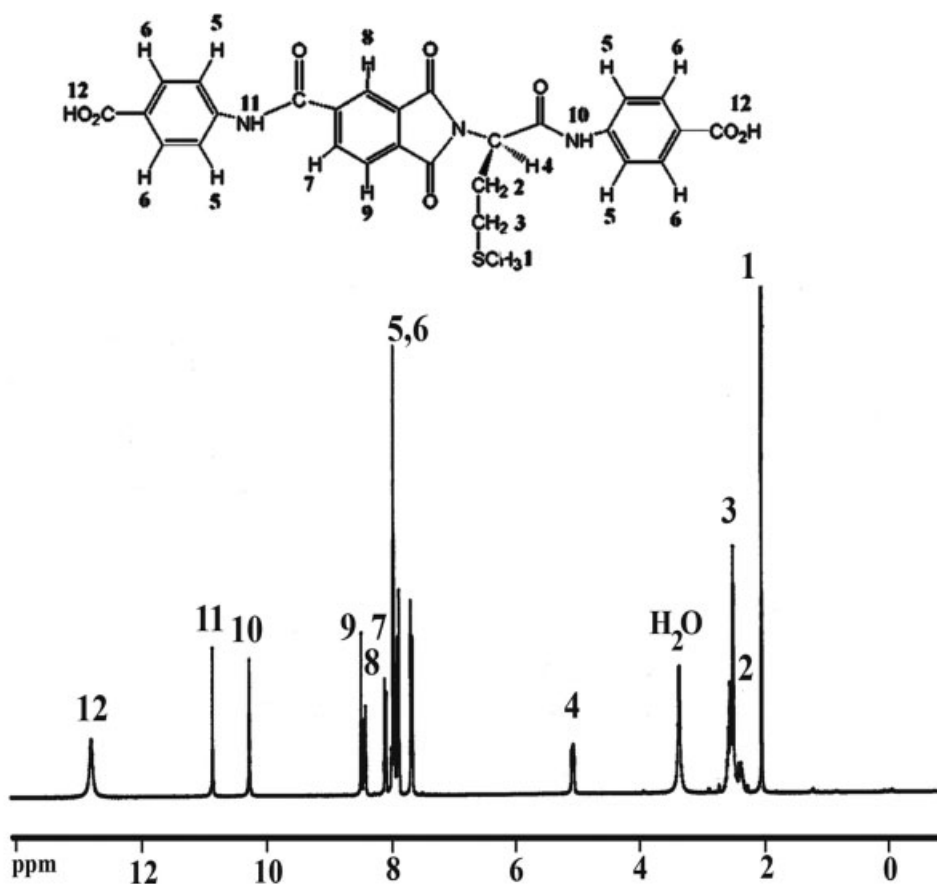


Figure 2  $^1\text{H}$  NMR (300 MHz) spectrum of monomer 5 in  $\text{DMSO-}d_6$  at rt.

stirred at room temperature for 30 min and at  $100^\circ\text{C}$  for 2 h. As the reaction proceeded, the solution became viscous, then was precipitated in 20 mL of methanol and filtered off, dried *in vacuo* to yield 0.134 g (93%) of the polymer 7a.

IR (KBr): 3364 (br), 2920 (w), 1776 (m), 1719 (s, sh), 1594 (s), 1529 (s), 1407 (m, sh), 1380 (m), 1317 (m), 1250 (m), 1174 (m), 1144 (m), 1105 (m), 1072 (w, sh), 1013 (w), 855 (m), 832 (m), 773 (m), 723 (m)  $\text{cm}^{-1}$ .

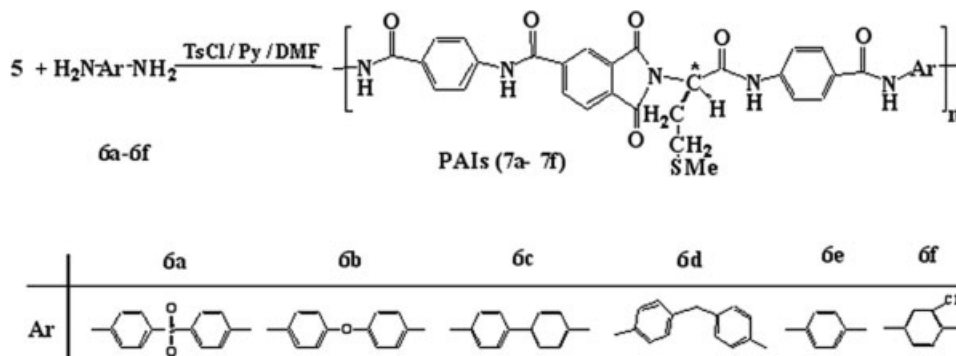
$^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  2.04 (s, 3H), 2.41–2.56 (m), 5.07 (distorted dd, chiral center hydrogen),

6.94–8.50 (m, aromatic hydrogens), 10.20 (s, amide hydrogen), 10.88 (s, amide hydrogen) ppm.

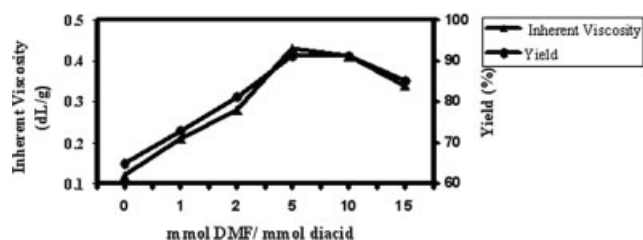
The other PAIs (7b–7f) were prepared with a similar procedure.

#### Polymer 7b

IR (KBr): 3311 (br), 2920 (w), 1776 (m), 1717 (s, sh), 1599 (s), 1499 (s, sh), 1379 (m), 1319 (m), 1251 (m), 1174 (m), 1104 (m), 1011 (w), 854 (m, sh), 772 (m), 725 (m)  $\text{cm}^{-1}$ .



Scheme 2 Polyamidation reactions of monomer 5 with aromatic diamines.



**Figure 3** Effect of the molar ratio of DMF to diacid added to TsCl/Py on the  $\eta_{inh}$  and yield of PAI-7a prepared using TsCl/DMF/Py.

$^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.04 (s, 3H), 2.41–2.57 (m), 5.08 (distorted dd, chiral center hydrogen), 6.59–8.49 (m, aromatic hydrogens), 10.27 (s, amide hydrogen), 10.87 (s, amide hydrogen), 12.79 (s, acidic hydrogen) ppm.

#### Polymer 7c

IR (KBr): 3316 (br), 2915 (w), 1776 (w), 1717 (s), 1597 (s), 1504 (s,sh), 1378 (m), 1317 (m), 1245 (m), 1101 (m), 816 (m), 768 (w), 724 (w, sh)  $\text{cm}^{-1}$ .

#### Polymer 7d

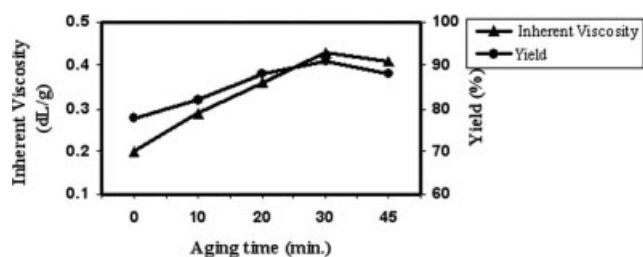
IR (KBr): 3316 (br), 2917 (w), 1776 (m), 1718 (s), 1597 (s), 1512 (s, sh), 1409 (m), 1377 (m), 1317 (s), 1249 (s), 1175 (m), 1100 (m), 1009 (w), 853 (m), 760 (m), 725 (m)  $\text{cm}^{-1}$ .

#### Polymer 7e

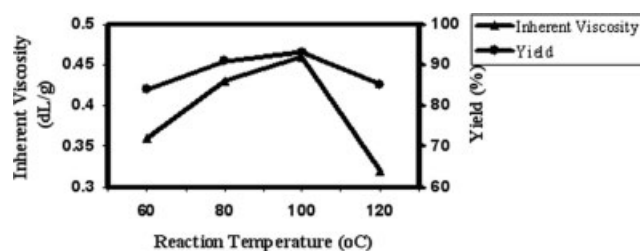
IR (KBr): 3313 (br), 2924 (w), 1777 (m), 1716 (s), 1597 (s), 1515 (s, sh), 1406 (m), 1379 (m), 1316 (m), 1249 (m), 1181 (w), 1089 (w, sh), 1010 (w), 827 (m), 760 (m), 723 (m)  $\text{cm}^{-1}$ .

#### Polymer 7f

IR (KBr): 3357 (br), 2915 (m), 1777 (w), 1720 (s), 1596 (s), 1509 (s, sh), 1382 (m), 1315 (m), 1245 (m), 1178 (w), 1099 (m), 848 (w), 759 (w), 718 (w)  $\text{cm}^{-1}$ .



**Figure 4** Effect of aging time of TsCl in pyridine on the  $\eta_{inh}$  and yield of PAI-7a prepared using TsCl/DMF/Py.



**Figure 5** Effect of reaction temperature on the  $\eta_{inh}$  and yield of PAI-7a prepared using TsCl/DMF/Py.

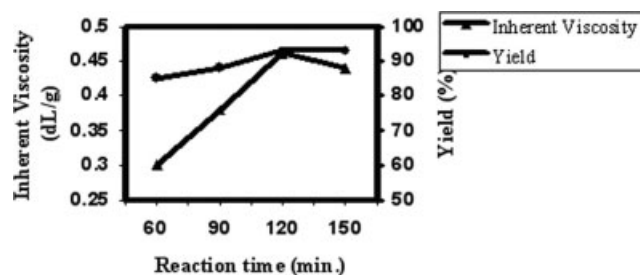
## RESULTS AND DISCUSSION

### Monomer synthesis

The unsymmetrical diacid compound **3** was synthesized by the condensation reaction of equimolar amounts of **1** and **2** in acetic acid. Chemical structure and purity of the monomer **3** were proved using FTIR, mass, and  $^1\text{H}$  NMR spectroscopy techniques. The  $^1\text{H}$  NMR spectrum (300 MHz) of compound **3** is shown in Figure 1. The distorted doublet of doublet in 4.96 ppm is assigned to the proton of chiral center. The mass spectrum of compound **3** shows the  $M^+$  peak at 323 and base peak at 231. The compound **3** was reacted with thionyl chloride, and the diacid chloride **4** was obtained in high yield. FTIR spectrum of this compound does not show broad peak at 2400–3400, and so confirms that the acidic hydroxy group is completely converted to acid chloride. The reaction of **4** with *p*-aminobenzoic acid was performed in dry acetone at  $0^\circ\text{C}$ . The resulting novel optically active aromatic amide–imide diacid **5** was obtained in high yield (Scheme 1), and its chemical structure and purity were confirmed with elemental analysis, FTIR, and  $^1\text{H}$  NMR spectroscopy (Fig. 2) techniques.

### Polymer synthesis

PAIs **7a–7f** were synthesized by the direct polycondensation reactions of an equimolar mixture of monomer **5** with several different aromatic diamines **6a–6f** in TsCl/Py/DMF system as condensing agent (Scheme 2).



**Figure 6** Effect of reaction time on the  $\eta_{inh}$  and yield of PAI-7a prepared using TsCl/DMF/Py.

**TABLE I**  
The Optimum Conditions for the Preparation of PAI-7a

Optimum condition	
TsCl/diacid (mol/mol)	5.3
Py/diacid (mL/g)	5.0
DMF/diacid (mol/mol)	5.0
Aging time (min)	30.0
Reaction temperature (°C)	80.0
Reaction time (h)	2.0

In this work for the polycondensation of aliphatic-aromatic diacids and aromatic diamines, a Vilsmeier adduct was prepared by dissolving TsCl in a mixed solvent of Py and DMF. The polycondensation was carried out as the following way: TsCl was dissolved in Py and after a certain period of time (aging time), the solution was treated with DMF for 30 min. The reaction mixture was added to a solution of diacid in Py. After 30 min, a solution of diamine in Py was added and the whole solution was maintained at room temperature, and then elevated temperature for a period of time. Polycondensation was carried out by varying the aging time of the initial reaction of TsCl and Py, the molar ratio of DMF to diacid, the reaction time, and reaction temperature. All of these parameters had critical effect on the polymer chain growth (Figs. 3–6). The outcome of Figures 3–6 is in Table I that show the optimum condition for polymerization reaction.

The synthesis and some physical properties of these novel optically active PAIs are listed in Table II. The inherent viscosities of the resulting polymers under optimized condition were in a range of 0.24–0.46 dL/g and the yields were 72–93%. All of the PAIs are optically active.

### Polymer characterization

#### FTIR study

The structures of these polymers were confirmed as PAIs by means of FTIR spectroscopy. The FTIR spec-

**TABLE II**  
Synthesis and Some Physical Properties of PAIs (7a–7f)

Polymer code	Polymer			
	Yield (%)	$\eta_{inh}$ (dL/g) <sup>a</sup>	$[\alpha]_D^{20b}$	Color <sup>c</sup>
7a	93	0.46	+8.4	OW
7b	85	0.42	+7.1	PY
7c	84	0.46	+3.3	PY
7d	78	0.36	+4.7	PY
7e	72	0.24	+5.2	Y
7f	76	0.28	+3.7	PY

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMF at 25°C.

<sup>b</sup> Measured at a concentration of 0.5 g/dL in DMF at 25°C with 589 nm filter.

<sup>c</sup> OW, off-white; Y, yellow; PY, pale yellow.

**TABLE III**  
Elemental Analysis of PAIs (7a, 7d)

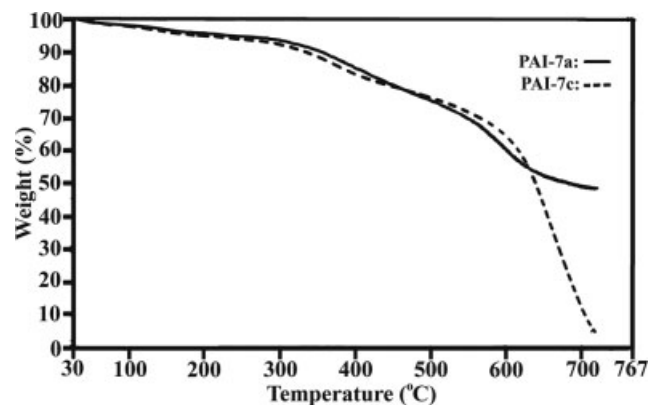
Polymer	Formula		Elemental analysis (%)			
			C	H	N	S
7a	$(C_{40}H_{31}N_5O_8S_2)_n$ (773.83) <sub>n</sub>	Calcd.	62.09	4.03	9.05	8.28
		Found	60.87	4.18	8.76	8.05
7d	$(C_{41}H_{33}N_5O_6S)_n$ (723.80) <sub>n</sub>	Calcd.	68.03	4.59	9.67	4.43
		Found	67.37	4.88	9.48	4.38

tra of all polymers showed absorptions around 3335  $cm^{-1}$  (N–H) and two overlapped carbonyl (amide and imide C=O) absorptions at 1777, 1719, and 1675  $cm^{-1}$  respectively. All of these PAIs exhibited absorption at 1370–1380 and 715–725  $cm^{-1}$  that show the presence of the imide heterocycle in these polymers. The polymer 7a showed characteristic absorptions at 1250 and 1144  $cm^{-1}$  because of the sulfone moiety (SO<sub>2</sub> stretching).

#### <sup>1</sup>H NMR Study and elemental analysis

The <sup>1</sup>H NMR spectrum (300 MHz) data of polymer PAI-7a, PAI-7b are reported in Experimental Part. In the <sup>1</sup>H NMR spectrum of these two polymers, appearance of the N–H proton of amide groups around 10.25, 10.85 ppm indicate two amide groups in the polymer's chain. The absorption of aromatic protons appeared at a range of 6.90–8.50 ppm. The proton of the chiral center appeared at 5.07 ppm. The peaks of C–H methylene bonding to chiral center and methylene bonding to sulfone atom appeared as a multiple around 2.40–2.57 ppm. The absorption of the CH<sub>3</sub> protons groups appeared at 2.04 ppm as a single peak. Some elemental analysis values of the resulting polymers are listed in Table III.

Because of flexible side chain and two amide and imide group in polymer backbone, these polymers are expected to have higher solubility. The solubility of PAIs was tested quantitatively in various solvents. All



**Figure 7** TGA thermograms of PAI-7a and PAI-7c under N<sub>2</sub> atmosphere and a heating rate of 10°C/min.

**TABLE IV**  
**Thermal Properties of Some Aromatic PAIs**

Polymer	$T_5^a$ (°C)	$T_{10}^b$ (°C)	Char yield (%) <sup>c</sup>
7a	217	352	61
7c	213	345	64

<sup>a</sup> Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10°C/min under N<sub>2</sub> atmosphere.

<sup>b</sup> Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min under N<sub>2</sub> atmosphere.

<sup>c</sup> Weight percent of the material left undecomposed after TGA at maximum temperature 600°C under N<sub>2</sub> atmosphere.

of the PAIs are soluble in organic polar aprotic solvents such as DMF, *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidone (NMP), and polar protic solvent such as H<sub>2</sub>SO<sub>4</sub> at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water.

#### Thermal properties

The thermal properties of PAI-7a and PAI-7c were evaluated by means of TGA under nitrogen atmosphere at a heating rate of 10°C/min. The temperature of 5 and 10% weight loss together with char yield at 600°C have been calculated by means of thermograms. Figure 7 shows the TGA thermogram of PAI-7a and PAI-7c. These polymers are stable up to 200°C. However, the char yield of PAI-7a is considerably higher than of it for PAI-7c, this could be because of the existence of sulfone group in the polymer backbone. The thermoanalysis data of these polymers are summarized in Table IV. The TGA measurement of the polymers revealed that these polymers exhibited moderate to good thermal stability.

#### CONCLUSIONS

Direct polyamidation reaction of monomer **5** with several aromatic diamines furnished new optically active PAIs containing L-methionine amino acid moiety using TsCl/DMF/Py as a condensing agent. The influences of aging time, amount of DMF, reaction time, and temperature on the physical properties of the resulting PAIs were investigated. The main

advantage of this polycondensation reaction is that in this procedure we do not need to prepare diacid chloride, therefore saves time and energy. Because of combination of aromatic backbone and aliphatic side chain in the presence of several functional groups, the solubility of these OAPs was improved without significant loss in their thermal properties. In addition, because of the existence of amino acid in the polymer backbone, these polymers are expected to be biodegradable and therefore are classified under environmentally friendly polymers. Since the resulting polymers are optically active and have good thermal stability, they have potential to be used as a chiral stationary phase in chromatography technique for the separation of racemic mixtures.

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