

# Preparation and Characterization of Novel Optically Active Poly(Amide-Ester-Imide)s Based on Bis(*p*-aminobenzoic acid)-*N*-trimellitylimido-*S*-valine via Direct Polyesterification

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## ABSTRACT

*N*-Trimellitylimido-*S*-valine was reacted with thionyl chloride, and *N*-trimellitylimido-*S*-valine diacid chloride was obtained in quantitative yield. The reaction of this diacid chloride with *p*-amino benzoic acid was performed in dry tetrahydrofuran, and bis(*p*-aminobenzoic acid)-*N*-trimellitylimido-*S*-valine (**6**) was obtained as a novel optically active aromatic amide-imide diacid monomer in high yield. The direct polycondensation reaction of the monomer amide-imide diacid (**6**) with bisphenol A, phenol phethalein, hydroquinone, 4,6-dihydroxypyrimidine, bis(4-hydroxyphenyl) sulphone, bis(4-hydroxyphenyl) sulphide, biphenyl-2,2'-diol, 1,5-naphthalene diol, 4,6-dihydroxytoluene, and 2,4-dihydroxyacetophenone was carried out, respectively in tosyl chloride (TsCl)/pyridine (Py)/dimethyl formamide (DMF) system. The effect of the amount of dimethyl formamide, aging time, reaction temperature, and reaction time was studied on the reaction yields and polymer viscosities. The resulting novel optically active poly(amide-ester-imide) with inherent viscosities ranging 0.36-0.71 dLg<sup>-1</sup> were obtained in high yield. All of these polymers were fully characterized with FTIR spectroscopy and specific rotation techniques. Some elemental analysis, thermal properties and <sup>1</sup>H NMR of these new optically active poly(amide-ester-imide)s are reported.

### Key Words:

poly(amide-ester-imide);  
direct polycondensation;  
condensing agent;  
optically active polymers.

## INTRODUCTION

Over the past decade, polyimides have become an important class of polymers that have found a wide range of application as high performance materials in aerospace and electronics industries [1]. It was the exceptionally high thermal stability,

which is the main characteristic of aromatic polyimides that clearly distinguished them from other known polymers [2]. Although aromatic polyimides are well recognized as a class of thermally stable engineering materials, their widespread use is

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limited due to poor handling and processing characteristics. To overcome these difficulties, various copolyimides such as poly (amide-ester-imide) **PAEIs** have been developed [3].

Chirality is a major concern in the modern pharmaceutical industry. This interest can be attributed largely to a heightened awareness that enantiomers of a racemic drug may have different pharmacological activities, as well as different pharmacokinetic and pharmacodynamic effects. The separation of chiral compounds has been of great interest because the majority of bioorganic molecules are chiral.

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 [4,5]. This situation will influence new methodologies for the preparation of optically active polymers (**OAPs**) in the coming century.

We now have a variety of tools for the synthesis of novel chiral monomers and polymers. Many chiral monomers will be prepared from these chiral chemicals. Recently, we have synthesized a variety of **OAPs** by different methods [6-10].

Various approaches have been carried out successfully in the synthesis of **PAEIs**. The polyesters are usually prepared by the solution or interfacial polymerization reaction between dicarboxylic-acid chlorides and diols, and an acid or phenyl ester exchange reaction of the acetate or ester of the acids under severe conditions (high temperature and reduced pressure). In these usual techniques, monomers such as acid chlorides, acetates and esters should be prepared before polymerization. The processes which are operative under mild conditions and adaptable to the direct polycondensations of free carboxylic acids and aromatic diols, can be more useful technique for polyesterification. This method produces polymers with lower energy consumptions, thus lower in cost. Several condensing agents suitable for the direct polycondensation reaction have been developed [11-14]. However, It was found that Vilsmeier adduct derived from arylsulphonyl chlorides and dimethyl formamide (DMF) in pyridine was successfully used as a suitable condensing agent for the synthesis of aromatic polyesters by the direct polycondensation of aromatic dicarboxylic acids and bisphenols and also of hydroxybenzoic acids [15,16].

In continuation of our study to develop new **OAPs**

via direct polycondensation [8-10,17,18] in this article we wish to report preparation of new optically active **PAEIs** containing (S)-(+)-valine moieties using  $\text{TsCl}/\text{DMF}/\text{Py}$  as a condensing agent.

## EXPERIMENTAL

### Materials

All chemicals were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck. Trimellitic anhydride (**1**) was purified with acetic anhydride in boiling acetic acid. Bisphenol A (**7a**) was purified by recrystallization from acetic acid-water. The other diols were used without further purification.

### Techniques

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR, 300 MHz) spectra were recorded on a Bruker (Germany) Avance 300 instrument. Tetramethylsilane (TMS) was used as an internal reference. 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 ( $\text{cm}^{-1}$ ). 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 Fensk routine viscometer. Specific rotations were measured by a Jasco Polarimeter (Japan). Thermal gravimetric analysis (TGA) data for polymers were taken on Mettler TG 50 in nitrogen atmosphere at a rate of  $20^\circ\text{C}/\text{min}$ . Elemental analyses were performed by the Research Institute of Petroleum Industry, Tehran, Iran.

### Monomer Synthesis

#### *N*-trimellitylimido-*S*-valine (**4**)

Into a 250 mL round-bottomed flask 3.00 g ( $1.56 \times 10^{-2}$  mol) of trimellitic anhydride (**1**), 1.83 g ( $1.56 \times 10^{-2}$  mol) of *S*-valine (**2**), 120 mL of acetic acid and a stirring bar were placed. The solution was stirred for 2 h at room temperature (RT) to yield amic acid (**3**) and then the mixture was refluxed for 4 h. The solvent was removed under reduced pressure and to the residue 100 mL of cold water was added. The solution was then decanted, and 5 mL of concentrated HCl was added. A

white precipitate was formed, filtered of and dried, to give 4.42 g (91.5%) of diacid (**4**). Recrystallization from methanol/water gave white crystals, mp: 186-188°C,  $[\alpha]_D^{25} = -23.2$  (0.050 g in 10 mL DMF); FTIR (KBr): 2970 (m, br), 1780 (m, sh), 1722 (s, sh), 1486 (w), 1422 (m), 1383 (s), 1289 (s), 1257 (m), 1173 (w), 1095 (w), 928(m), 878  $\text{cm}^{-1}$  (w).

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ): 0.82 (d, 3H,  $J = 6.7$  Hz), 1.05 (d, 3H,  $J = 6.6$  Hz), 2.55 (m, 1H), 4.48 (d, 1H,  $J = 7.7$  Hz), 8.01 (d, 1H,  $J = 7.7$  Hz), 8.25 (s, 1H), 8.37 (d, 1H,  $J = 7.7$  Hz), 13.39 (s, 2H) ppm.

#### *N*-trimellitylimido-*S*-valine Diacid Chloride (**5**)

Into a 50 mL round-bottom flask, 1.00 g ( $3.43 \times 10^{-3}$  mol) of *N*-trimellitylimido-*S*-valine (**4**), 10 mL (an excess amount) of thionyl chloride, and a stirring bar were placed. The stirrer was started and the mixture was refluxed for 1 h. Then the reaction mixture was stirred at room temperature for 2 h. The thionyl chloride was removed via distillation and 20 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 1.02 g (90%) of a white solid. mp: 42°C,  $[\alpha]_D^{25} = -25.6$  (0.050 g in 10 mL DMF); FTIR (KBr): 2959 (m), 1779 (m,sh), 1721 (s), 1431 (w), 1382 (m), 1289 (m), 1252 (m), 1203 (m), 1104 (w), 1074 (w), 1019 (w), 916 (w), 728  $\text{cm}^{-1}$  (m).

#### *N*-trimellitylimido-*S*-valine-bis(*p*-aminobenzoic acid)(**6**)

Into a 25 mL round-bottomed flask fitted with a magnetic stirrer was placed a solution of 1.00 g ( $3.05 \times 10^{-3}$  mol) diacid chloride (**5**) in 5 mL of tetrahydrofuran (THF). The reaction mixture was cooled in an ice water bath. To this solution 0.46 g ( $3.35 \times 10^{-3}$  mol) *p*-aminobenzoic acid in 7 mL THF 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 100 mL of water. The precipitate was collected by filtration and washed thoroughly with water and dried at 70°C for 10 h, to yield 1.36 g (84%) of diacid (**6**). mp >270°C (dec),  $[\alpha]_D^{25} = -19.6$  (0.050 g in 10 mL DMF); FTIR (KBr): 3316 (s, br), 2963 (m,br), 2666 (w, br), 1776 (m, sh), 1714 (s, br), 1599 (s), 1519 (s), 1422 (s, sh), 1377 (m), 1315 (m), 1248 (s, sh), 1179 (m), 1083 (m, sh), 1019 (w), 851 (m), 800 (m), 770  $\text{cm}^{-1}$  (m).

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  0.85 (d, 3H,  $J = 6.7$  Hz), 1.07 (d, 3H,  $J = 6.6$  Hz), 2.56 (m, 1H), 4.66

(d, 1H,  $J = 7.7$  Hz), 7.92-8.49 (m, 1H), 10.86 (s, 2H), 12.93 (s, 2H) ppm.

#### Polymer Synthesis

The PAEIs were prepared by the following procedure: For synthesis of polymer (**8a**), A pyridine (0.15 mL;  $1.9 \times 10^{-3}$  mol) solution of TsCl (0.180 g;  $9.5 \times 10^{-4}$  mol) after 30 min stirring at room temperature, was treated with DMF (0.07 mL;  $9.45 \times 10^{-4}$  mol) for 30 min and the solution was added dropwise to a solution of diacid (**6**) (0.100 g;  $1.89 \times 10^{-4}$  mol) in pyridine (0.15 mL). The mixture was maintained at room temperature for 30 min and then to this mixture, a solution of bisphenol A (**7a**) (0.043 g;  $1.89 \times 10^{-4}$  mol) in pyridine (0.15 mL) was added dropwise at room temperature and the whole solution was stirred at room temperature for 30 min and at 120°C for 2 h. As the reaction proceeded, the solution became viscous. Then the viscous liquid was precipitated in 30 mL of methanol to yield 0.127 g (89%) of the polymer (**8a**). IR (KBr): 3342 (m, sh), 3061 (w, sh), 2966 (m, sh), 1778 (w, sh), 1721 (s), 1597 (s), 1513(s, sh), 1407 (m), 1378 (m), 1319 (m), 1263 (m), 1206 (m), 1169 (s), 1066 (m), 1014 (m), 853 (m), 761 (w)  $\text{cm}^{-1}$ .

The other PEIs (**8b-8f**) were prepared with the similar procedure.

#### Polymer 8b

IR (KBr): 3370 (br), 3065 (w), 2965 (w), 1774 (w, sh), 1721 (s), 1597 (s), 1512 (s, sh), 1465 (w), 1408 (m), 1377 (m), 1319 (w), 1258 (m), 1207 (m), 1167 (m), 1068 (m), 1013 (m), 930 (m, sh), 853 (m), 758 (m), 725 (m), 691 (m)  $\text{cm}^{-1}$ .

#### Polymer 8c

IR (KBr): 3336 (br), 3066 (w, br), 2965 (m, sh), 1778 (w, sh), 1720 (s), 1597 (s, br), 1530 (s, sh), 1408 (w), 1378 (w), 1321 (w), 1260 (m), 1168 (m), 1069 (m), 1011 (m), 853 (m), 760 (m), 724 (w), 681 (s)  $\text{cm}^{-1}$ .

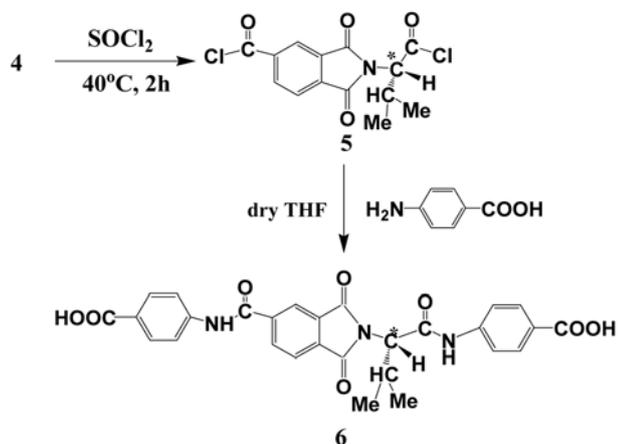
#### Polymer 8d

IR (KBr): 3400 (br), 3067 (w, br), 2966 (w), 1777 (m), 1719 (s, sh), 1596 (s), 1530 (s), 1408 (m), 1377 (m), 1248 (m, sh), 1168 (s), 1121 (w), 1036 (w, br), 1008 (w), 852 (w), 759 (w), 726 (w), 683 (w), 567 (w)  $\text{cm}^{-1}$ .

#### Polymer 8e

IR (KBr): 3346 (br), 3067 (w, br), 2965 (m), 1778 (w,





**Scheme II.** Synthesis of *N*-trimellitylimido-*S*-valine-bis(*p*-aminobenzoic acid) (**6**).

niques. The  $^1\text{H}$  NMR spectrum (300 MHz) of compound **4** is shown in Figure 1. The doublet in 4.48 ppm is assigned to the proton of chiral center.

The compound **4** was reacted with thionyl chloride,

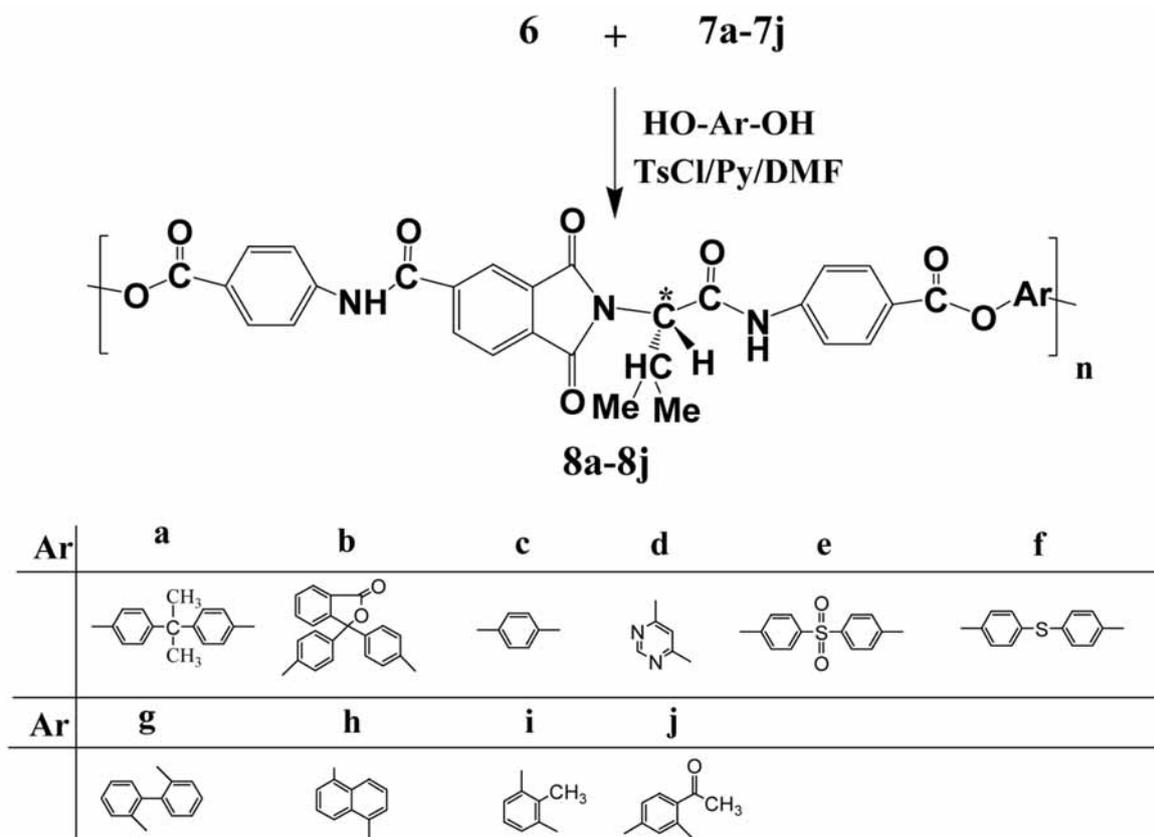
and the diacid chloride **5** was obtained in high yield (Scheme II). The chemical structure and purity of the optically active **5** were proven with FTIR spectroscopy techniques. The reaction of **5** with *p*-aminobenzoic acid was performed in dry THF at  $0^\circ\text{C}$ . The resulting novel optically active aromatic amide-imide diacid **6** was obtained in high yield (Scheme II), and its chemical structure and purity were proven with FTIR and  $^1\text{H}$  NMR spectroscopy techniques.

### Polymer Synthesis

**PAEIs (8a-8j)** were synthesized by the direct polycondensation reactions of an equimolar mixture of monomer (**6**) with several different aromatic diols (**7a-7j**) in a system of  $\text{TsCl}/\text{Py}/\text{DMF}$  (Scheme III).

In this work for the polycondensation of aliphatic-aromatic diacids and aromatic diols, a Vilsmeier adduct was prepared by dissolving tosyl chloride ( $\text{TsCl}$ ) in a mixed solvent of pyridine and DMF. The polycondensation was carried out in the following way:

$\text{TsCl}$  was dissolved in pyridine and after a certain



**Scheme III.** Polycondensation reactions of monomer **6** with aromatic diols.

**Table 1.** Effect of aging time of TsCl in pyridine on the  $\eta_{inh}$  and yield of **PAEI (8a)** prepared using TsCl/DMF/Py system.

Aging time (min)	$\eta_{inh}$ (dL/g)	Yield (%)
0	0.11	43
10	0.18	39
20	0.44	84
30	0.52	89
45	0.42	92

**Table 2.** Effect of the molar ratio of DMF to diacid added to TsCl/Py on the  $\eta_{inh}$  and yield of **PAEI (8a)** prepared using TsCl/DMF/Py.

DMF (mmol)/ diacid (mmol)	$\eta_{inh}$ (dL/g)	Yield (%)
0	No Polymer	-
1	0.35	83
2	0.40	88
5	0.52	89
10	0.33	63
15	0.16	38

period (aging time) the solution was treated with DMF for 30 min. The reaction mixture was added to a solution of diacid in pyridine. After a 30 min a solution of diol in pyridine was added and the whole solution was maintained at room temperature and elevated temperature for a period of time. Polycondensation was carried out by varying the aging time of the initial reaction of TsCl and pyridine, 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 (Tables 1-5).

The synthesis and some physical properties of these novel optically active **PAEIs** are listed in Table 6. The inherent viscosities of the resulting polymers under optimized condition were in the range of 0.36-0.71 dL/g and the yields were 78-95%. All of the **PAEIs** are optically active.

### Polymer Characterization

The formation of **PAEIs** was confirmed by IR spectroscopy analysis. As an example, the IR spectrum of **PAEIs (8g)** (Figure 2) showed the characteristic

**Table 3.** Effect of reaction time on the  $\eta_{inh}$  and yield of **PAEI (8a)** prepared using TsCl/DMF/Py at 120°C.

Reaction time (min)	$\eta_{inh}$ (dL/g)	Yield (%)
60	0.43	81
90	0.47	83
120	0.52	89
150	0.48	90

**Table 4.** Effect of reaction temperature on the  $\eta_{inh}$  and yield of **PAEI (8a)** prepared using TsCl/DMF/Py.

Reaction temperature (°C)	$\eta_{inh}$ (dL/g)	Yield (%)
120	0.52	89
100	0.46	86
80	0.35	84

absorptions of imide and ester groups occurred around 1778 and 1721  $\text{cm}^{-1}$ , peculiar to carbonyls stretching of imide and ester, respectively. All of these **PAEIs** exhibited absorption at about 1380  $\text{cm}^{-1}$  and 720  $\text{cm}^{-1}$  that show the presence of the imide heterocycle in these polymers.

The  $^1\text{H}$  NMR spectrum (300 MHz) of polymer (**8j**) is shown in Figure 3. In the  $^1\text{H}$  NMR spectrum of polymer (**8j**), appearance of the N-H proton of amide groups at 10.41 and 10.98 ppm indicates two amide groups in the polymer chain. The absorption of aromatic protons appeared at the range of 8.10-8.90 ppm. The proton of the chiral center appeared at 4.67 ppm. The peaks of C-H bonding to chiral center appeared as a multiple 2.49-2.95 ppm. The absorption of the  $\text{CH}_3$

**Table 5.** The optimum conditions for the preparation of **PAEIs**.

Optimum condition	
TsCl/Diacid (mol/mol)	5.0
Py/Diacid (mol/mol)	29.5
DMF (mmol)	0.95
Aging time (min)	30
Addition time of diol (min)	20
Reaction time (h)	2.0

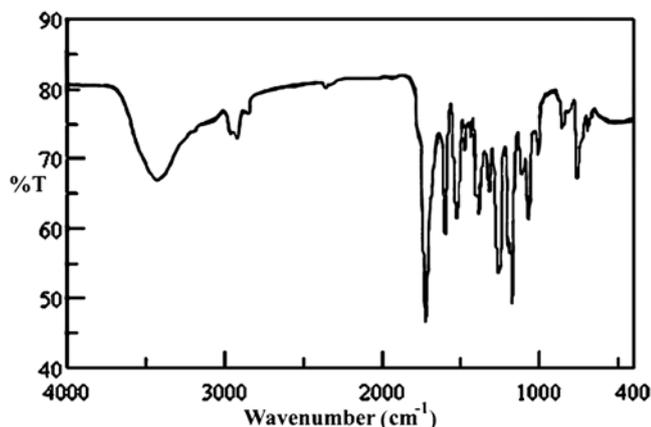


Figure 2. FTIR (KBr) Spectrum of PAEI-8g.

bonding to carbonyl group at 2.49 under the peak of DMSO and the CH<sub>3</sub> protons groups appeared at 0.89 and 1.07 ppm. Elemental analysis values of the resulting polymers are listed in Table 7.

The solubility of **PAEIs** was tested quantitatively in various solvents are listed in Table 8. All of the **PAEIs** are soluble in organic solvents such as DMF, DMAc, DMSO, NMP, and 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 **PAEI (8c)** was evaluated by

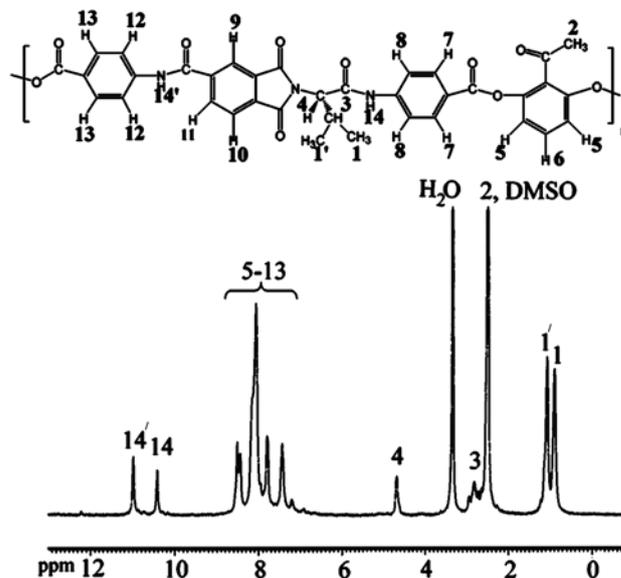


Figure 3. <sup>1</sup>H NMR (300MHz) Spectrum of PAEI-8j in DMSO-d<sub>6</sub> at room temperature.

means of TGA/DTG in nitrogen atmosphere. The **PAEI (8c)** showed 5% and 10% weight loss (T<sub>5</sub> and T<sub>10</sub>) around 285°C and 332°C under nitrogen atmosphere, respectively and the residual weight for this polymer at 588°C was 6.0%. The TGA/DTA curve of **PAEI (8c)** has been shown in Figure 4.

Table 6. Synthesis and some physical properties of PAEIs (**8a-8j**).

diol	Polymer	Physical properties						
		Yield (%)	$\eta_{inh}$ (dL/g) <sup>a</sup>	$[\alpha]_{Na,589}^{25^a}$	$[\alpha]_{Hg}^{25^a}$	$[\alpha]_{Hg,546}^{25^a}$	$[\alpha]_{Hg,577}^{25^a}$	Color <sup>c</sup>
7a	8a	89	0.52	-29.3	-27.34	.. <sup>b</sup>	.. <sup>b</sup>	C
7b	8b	83	0.43	-29.0	-24.22	.. <sup>b</sup>	.. <sup>b</sup>	OC
7c	8c	95	0.71	-30.9	-30.6	.. <sup>b</sup>	.. <sup>b</sup>	C
7d	8d	78	0.42	-44.4	-50.0	-11.0	-27.0	B
7e	8e	78	0.68	-50.0	-49.2	-45.0	-38.0	C
7f	8f	92	0.46	-32.4	-41.2	-34.4	-29.2	OC
7g	8g	82	0.36	-26.24	-6.8	-35.5	-31.0	Y
7h	8h	93	0.60	-68.3	-52.4	-39.6	-36.0	OC
7i	8i	81	0.52	-73.5	-42.0	-31.2	-27.6	OC
7j	8j	86	0.56	-86.5	-58.8	-48.0	-54.0	PB

(<sup>a</sup>) Measured at a concentration of 0.5 g/dL in DMF at 25°C; (<sup>b</sup>) Specific rotation could not be measured; (<sup>c</sup>) C= cream, OC= off cream, B= brown, Y= yellow, PB= pale brown.

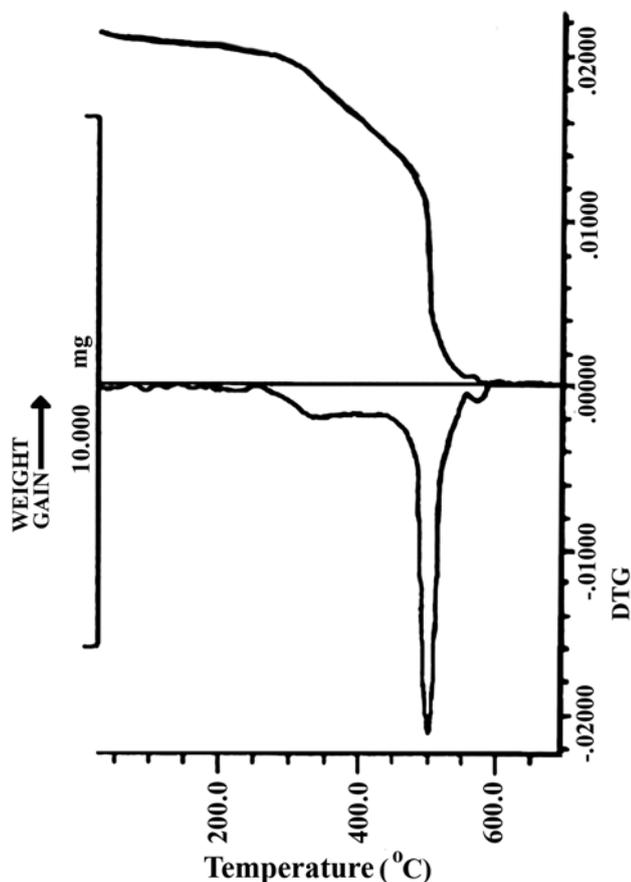


Figure 4. TGA/DTG Thermograms of PAEI-8c in a N<sub>2</sub> atmosphere.

Table 7. Elemental Analysis of PAEIs 8b and 8c.

Polymer No.	Formula		Elemental analysis (%)			Moisture intake (%) <sup>a</sup>
			C	H	N	
8b	(C <sub>48</sub> H <sub>33</sub> N <sub>3</sub> O <sub>10</sub> ) <sub>n</sub> (811.8) <sub>n</sub>	Calcd.	67.65	4.18	6.96	3.84
		Found	63.90	4.70	6.40	
		Corr. <sup>b</sup>	66.35	4.51	6.64	
8c	(C <sub>34</sub> H <sub>25</sub> N <sub>3</sub> O <sub>8</sub> ) <sub>n</sub> (603.5) <sub>n</sub>	Calcd.	71.01	4.10	5.18	3.92
		Found	67.00	4.60	4.90	
		Corr. <sup>b</sup>	69.62	4.41	5.09	

<sup>(a)</sup> Moisture intake(%)=(W-W<sub>0</sub>)/W<sub>0</sub> × 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; <sup>(b)</sup> Corrected value for C and N = Found value × (100 + moisture intake) / 100, and Corrected value for H= Found value temperature × (100 - moisture intake) / 100.

Table 8. Solubility of PAEIs 8a-8j<sup>a</sup>.

Solvent	6a	6b	6c	6d	6e	8f	8g	8h	8i	8j
DMAc	+	+	+	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+	+	+	+
NMP	+	+	+	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+	+	+	+
H <sub>2</sub> SO <sub>4</sub>	+	+	+	+	+	+	+	+	+	+
MeOH	-	-	-	-	-	-	-	-	-	-
EtOH	-	-	-	-	-	-	-	-	-	-
CHCl <sub>3</sub>	-	-	-	-	-	-	-	-	-	-
CH <sub>2</sub> Cl <sub>2</sub>	-	-	-	-	-	-	-	-	-	-
H <sub>2</sub> O	-	-	-	-	-	-	-	-	-	-

<sup>(a)</sup> Concentration: 5 mg ml<sup>-1</sup>; (+) Soluble at room temperature, (-) Insoluble at room temperature.

## CONCLUSION

From this study it is clear that the compound **6** as a new optically active monomer is an interesting diacid monomer for the synthesis of novel optically active polymers (OAPs) via direct polycondensation. Thus, polyesterification reaction of monomer **6** with several aromatic diols furnished new optically active PAEIs containing *S*-valine amino acid moiety using TsCl/DMF/Py as a condensing agent. In this polycondensation reaction we do not need to prepare diacid chloride, therefore saves time and energy. These OAPs are thermally stable and have good solubility. The influence of aging time, amount of DMF, reaction time, and temperature was investigated on the physical properties of the resulting PAEIs. Since the resulting polymers are optically active and have good thermal stability they have potential to be used as chiral stationary phase in GC for the separation of racemic mixtures.

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