

Direct Polycondensation of *N*-Trimellitylimido-*L*-isoleucine with Aromatic Diamines

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ABSTRACT: *N*-Trimellitylimido-*L*-isoleucine (**3**) was prepared from the reaction of trimellitic anhydride with *L*-isoleucine [*L*-2-amino-3-methylvaleric acid or (2*S*,3*S*)-2-amino-3-methyl-*n*-valeric acid] in an *N,N*-dimethylformamide solution at the refluxing temperature. The direct polycondensation reaction of the monomer imide diacid (**3**) with 1,4-phenylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulfone, diaminodiphenylether, 1,5-naphthalendiamine, 2,4-diaminotoluene, and 1,3-phenylenediamine was performed in a medium consisting of triphenyl phosphite, *N*-methyl-2-pyrrolidone (NMP), pyridine, and calcium chloride. The polycondensation was performed under two different conditions: in one method, the reaction mixture was heated in an NMP solution at 60, 90, and then

130°C for different periods of time, and in the other method, the reaction mixture was refluxed only for 1 min in the same solvent. The resulting poly(amide imide)s (PAIs), with inherent viscosities of 0.21–0.37 dL/g, were obtained in high yields. All of these compounds were fully characterized by IR spectra, elemental analyses, and specific rotation measurements. Some structural characterizations and physical properties of these new optically active PAIs were examined. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 116–122, 2003

Key words: direct polycondensation; viscosity; thermogravimetric analysis (TGA)

INTRODUCTION

Aromatic polyimides, polyamides, and their copolymers are well recognized as commercially important thermostable polymers.^{1–4} However, most aromatic polyamides are intractable materials that do not melt before thermally decomposing and would, therefore, be difficult to process. Aromatic poly(amide imide)s (PAIs), however, are very useful high-performance materials that exhibit better processing characteristics than polyimides of analogous structures.⁵ A notable example is Torlon (Amoco Co.), a commercial PAI obtained from trimellitic anhydride chloride and 4,4'-diaminodiphenylmethane (**4b**).⁶

The syntheses and applications of optically active polymers have been paid more attention recently because polymers with chiral structures are biologically very important. Recently, we synthesized optically active polymers by different methods.^{7–10}

The triphenyl phosphite (TPP) activated polycondensation (phosphorylation reaction) technique for the synthesis of polyamides was reported by Yamazaki et al.¹¹ Recently, this technique was used for the preparation of high molecular weight polyamides and PAIs.^{12–14} In previous studies,^{15–19} we synthesized novel optically active PAIs containing amino acid moieties.

In this article, we report the synthesis and characterization of new optically active PAIs from aromatic diamines and *N*-trimellitylimido-*L*-isoleucine (**3**), a monomer containing preformed imide groups, by the direct polycondensation method.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), and Riedel-de Haen AG (Seelze, Germany). Trimellitic anhydride (**1**) was synthesized by the dehydration of 1,2,4-benzene tricarboxylic acid with acetic anhydride in boiling acetic acid. **4b** was purified by recrystallization from water. 4,4'-Diaminodiphenylsulfone (**4c**) was purified by recrystallization from water/ethanol. 1,4-Phenylenediamine (**4a**), 4,4'-diaminodiphenylether (**4d**), 2,4-diaminotoluene (**4f**), and

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1,3-phenylenediamine (**4g**) were purified by sublimation.

Apparatus

$^1\text{H-NMR}$ (90 MHz) spectra were recorded on a Varian EM-390 instrument (Palo Alto, CA). Tetramethylsilane (TMS) was used as an internal reference. IR spectra were recorded on a Shimadzu 435 IR spectrophotometer (Shimadzu, Japan). The spectra of solids were carried out with KBr pellets. Vibrational transition frequencies are reported as wave numbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosity (η_{inh}) values were measured by a standard procedure with a Cannon-Fenske routine viscometer (Hofheim, Germany). Specific rotations were measured with a PerkinElmer-241 polarimeter (Germany). Thermogravimetric analysis (TGA) data for the polymers were taken on a Mettler TGA-50 (England) under a nitrogen atmosphere at a rate of $10^\circ\text{C}/\text{min}$. Elemental analyses were performed at Tarbiat Modarres University (Tehran, Iran).

Monomer synthesis (3)

Into a 25-mL, round-bottom flask equipped with a magnetic stirrer, 0.150 g (7.806×10^{-4} mol) of **1**, 0.102 g (7.806×10^{-4} mol) of L-isoleucine (**2**), and 2 mL of *N,N*-dimethylformamide (DMF) were placed. The stirrer was started, and the mixture was refluxed for 4 h. The mixture was poured into 20 mL of a 10% HCl solution. A white precipitate was formed, filtered off, and dried *in vacuo*; this gave 0.181 g (76%) of diacid **3**. Recrystallization from methanol/water gave white crystals.

mp: $195\text{--}197^\circ\text{C}$. $[\alpha]_{\text{D}}^{25}$: +23 (0.050 g in 10 mL of DMF). IR (KBr): 3300 (s, sh), 2800 (s, br), 1780 (s, sh), 1700 (s, br), 1600 (m, sh), 1485 (m), 1460 (m), 1420 (m), 1380 (s), 1340 (s, sh), 1280 (s), 1260 (m, sh), 1200 (m), 1170 (m), 1150 (m, sh), 1090 (m), 1020 (w), 960 (w, sh), 930 (m), 880 (m), 800 (w), 760 (m), 730 (s), 705 (m), 650 (m), 570 (w), 530 cm^{-1} (w). $^1\text{H-NMR}$ [dimethyl sulfoxide- d_6 (DMSO- d_6), TMS, 90 MHz, δ]: 0.70–1.09 (disturbed triplet, 3H, $J = 6.0$ Hz), 1.10–1.30 (d, 3H, $J = 6.0$ Hz), 1.37–2.70 (m, 3H), 4.55–4.80 (d, 1H, $J = 6.9$ Hz), 8.05–8.25 (d, 1H, $J = 6.30$ Hz), 8.50–8.75 (m, 2H), 8.00–9.80 ppm (a broad peak for two acidic OH protons that overlapped with aromatic protons). ELEM. ANAL. Calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}_6$: C, 59.01%; H, 4.59%; N, 4.95%. Found: C, 59.22%; H, 4.59%; N, 5.04%.

Polymerization (5a)

The PAIs were prepared by direct polycondensation with the following general procedure, with **5a** given as

an example. Into a 10-mL round-bottom flask fitted with a water-cooled condenser and a magnetic stirrer were placed 0.100 g (3.27×10^{-4} mol) of diacid **3**, 0.1 g of calcium chloride, 0.327 mL (1.27×10^{-3} mol) of TPP, 0.29 mL of pyridine, 0.035 g (3.27×10^{-4} mol) of diamine **4a**, and 0.5 mL of *N*-methyl-2-pyrrolidone (NMP). The stirrer was started, and the mixture was heated under a nitrogen atmosphere in an oil bath at 60°C for 0.5 h, at 90°C for 2 h, and finally at 130°C for 8 h. The viscous reaction mixture was cooled and diluted with 2 mL of DMF and was poured into 50 mL of methanol. The precipitated polymer was collected by filtration and was dried at 100°C for 15 h *in vacuo*; this left 0.1143 g (92%) of solid **5a**.

mp: $>300^\circ\text{C}$. IR (KBr): 3300 (m, br), 3100 (m, sh), 2950 (m), 1770 (m), 1710 (s), 1650 (s), 1600 (m), 1540 (m, sh), 1505 (s), 1460 (m, sh), 1430 (w), 1400 (m), 1370 (s), 1330 (s), 1250 (m), 1170 (m), 1070 (m), 1020 (w), 940 (m), 900 (w), 830 (m), 760 (w), 720 cm^{-1} (s).

The other PAIs (**5b–5g**) were prepared with similar procedures.

Polymer 5b

IR (KBr): 3300 (m, br), 3050 (m, sh), 2950 (m), 1785 (m), 1710 (s), 1650 (s), 1600 (s), 1520 (s, br), 1510 (s), 1490 (m, sh), 1460 (m, sh), 1405 (m), 1370 (s), 1310 (s), 1250 (m), 1180 (m), 1070 (m), 1020 (w), 940 (m), 910 (w), 850 (w), 810 (m), 760 (m), 720 (s), 680 cm^{-1} (w).

Polymer 5c

IR (KBr): 3300 (m, br), 2900 (m), 1780 (m), 1710 (s), 1650 (s), 1580 (s), 1510 (s), 1495 (s), 1385 (s), 1300 (s), 1250 (s), 1170 (m, sh), 1140 (s), 1095 (s), 1070 (s, sh), 1020 (m, sh), 930 (m, sh), 830 (m), 720 (s), 680 (m), 550 cm^{-1} (m).

Polymer 5d

IR (KBr): 3300 (m, br), 3050 (m, sh), 2950 (m), 1770 (m), 1710 (s), 1670 (s, sh), 1600 (m), 1520 (m, sh), 1490 (s), 1400 (m, sh), 1360 (m), 1310 (m), 1210 (s), 1090 (m, sh), 1065 (m), 1005 (w), 940 (m), 870 (w, sh), 820 (m), 750 (m), 720 (s), 680 cm^{-1} (w).

Polymer 5e

IR (KBr): 3300 (m, br), 3070 (m), 2950 (m), 1770 (m), 1715 (s), 1670 (s), 1620 (m, sh), 1600 (m), 1520 (s), 1495 (s), 1485 (s, sh), 1410 (m), 1370 (s), 1330 (s), 1260 (m), 1250 (m), 1195 (m), 1070 (m), 940 (w), 900 (w), 860 (w), 790 (m), 720 (s), 680 cm^{-1} (w).

Polymer 5f

IR (KBr): 3300 (m, br), 2930 (m), 1775 (m), 1710 (m), 1650 (s), 1595 (s), 1520 (s), 1505 (s), 1365 (s), 1250 (m), 1190 (m, sh), 1180 (m), 1080 (m), 1020 (m), 1000 (w), 940 (m), 900 (m), 860 (w, sh), 820 (w), 760 (m), 720 (s), 680 cm^{-1} (m).

Polymer 5g

IR (KBr): 3300 (m, br), 3050 (m, sh), 2950 (m), 1770 (m), 1710 (s), 1660 (s, sh), 1600 (s), 1520 (s), 1500 (s), 1420 (s), 1370 (s), 1300 (s, sh), 1250 (m), 1160 (m), 1070 (m), 940 (w), 850 (w), 770 (m), 720 (s), 685 cm^{-1} (m).

The optically active PAIs **5a'–5g'** were prepared in NMP at the refluxing temperature for a period of 1 min, and they showed similar IR spectra patterns.

RESULTS AND DISCUSSION**Monomer synthesis**

The unsymmetrical diacid compound **3** was synthesized by the condensation reaction of one equimolar of anhydride **1** and one equimolar of **2** in refluxing DMF. The white diacids were obtained from a 10% HCl solution (Scheme 1).

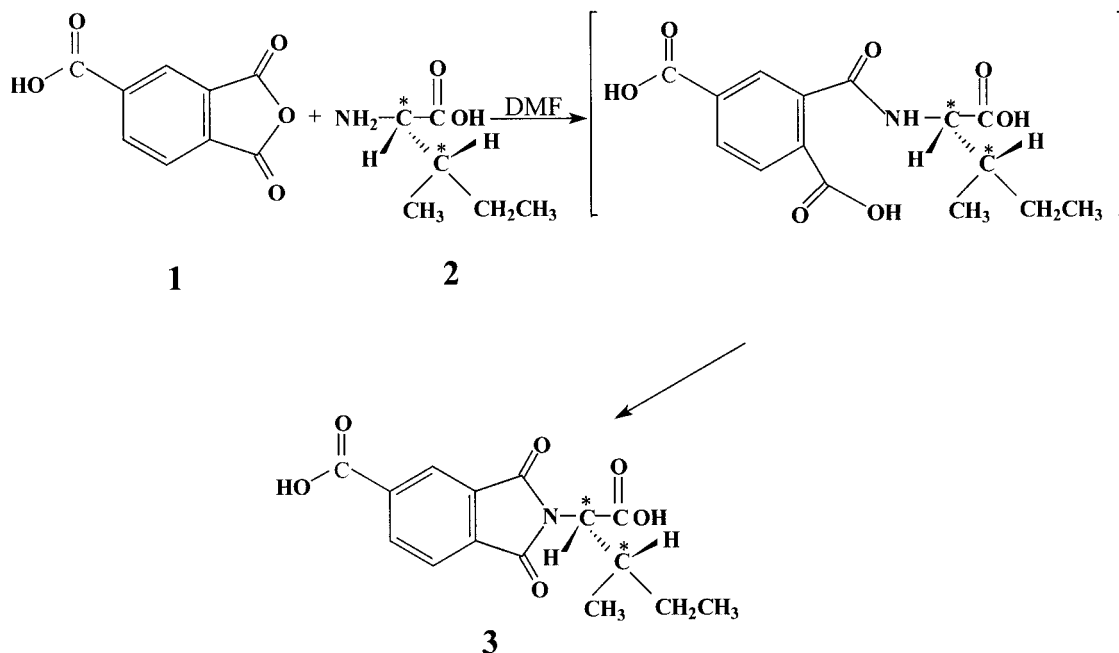
The resulting diacid **3** was obtained in a high yield. The chemical structure and purity of the optically active **3** were proved with thin-layer chromatography [$R_f = 0.84$ (20% cyclohexane and 80% ethyl acetate)], IR, $^1\text{H-NMR}$, and elemental analysis techniques. R_f is distance moved by substance/distance moved by the

solvent front. **3** was used for the formation of novel optically active PAIs via direct solution polycondensation reactions.

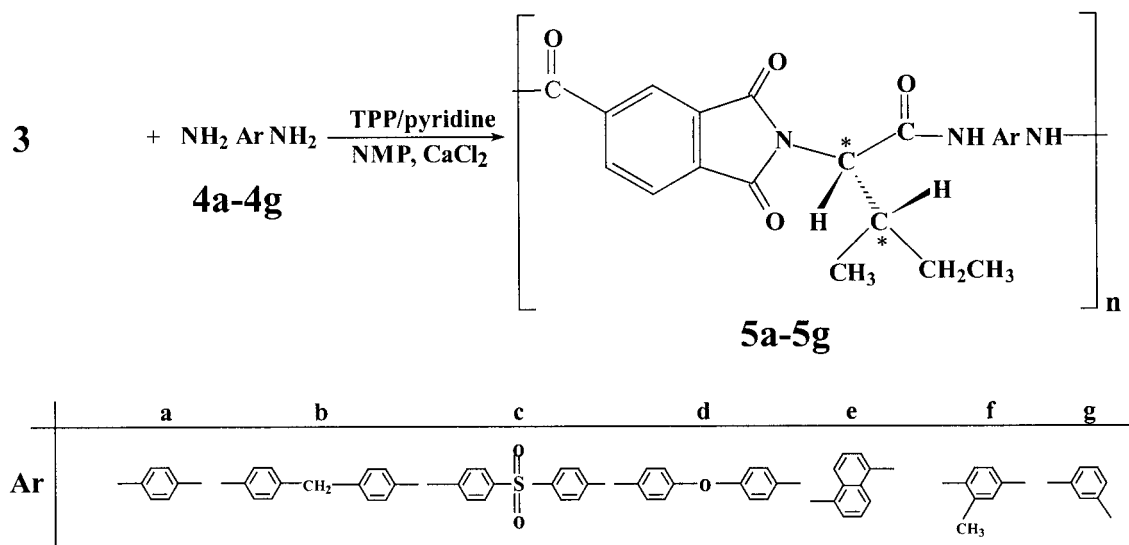
Polymer synthesis

PAIs **5a–5g** and **5a'–5g'** were synthesized by the direct solution polycondensation reactions of an equimolar mixture of monomer **3** and seven different aromatic diamines (**4a–4g**) with TPP, calcium chloride, and pyridine as condensing agents (Scheme 2).

PAIs **5a–5g** were prepared by the gradual heating of a mixture of two monomers and catalysts in NMP at different temperatures over a period of 10.5 h. PAIs **5a'–5g'** were prepared by the heating of a mixture of two monomers at the refluxing temperature in NMP for only 1 min and were obtained with better yields and viscosities. These results could be explained in terms of the stability of the monomers and oligomers at high temperatures. The high-temperature polymerization increased the rate of the polymerization reactions, and so a shorter period of time was needed for the polymerization reactions. The syntheses and some physical properties of the novel optically active PAIs **5a–5g** and **5a'–5g'** are given in Tables I and II. All of the polycondensation reactions readily proceeded in homogeneous solutions. In most cases, an additional amount of NMP had to be added to maintain a degree of agitation because the polymer solutions were too viscous to be stirred. Tough and stringy precipitates formed when the viscous PAIs solutions were trickled into



Scheme 1



Scheme 2

stirring methanol. All of the polymers were obtained in quantitative yields with moderate η_{inh} values of 0.21–0.37 dL g⁻¹, which corresponded to molecular weights of about 10,000–15,000 g/mol, and they showed optical rotations, which proved them to be optically active.

Polymer characterization

In this work, we selected seven aromatic diamines with different structures. The formation of PAIs was confirmed by means of IR spectroscopy and elemental analysis. For example, the IR spectrum of PAI **5e** (Fig. 1) showed the characteristic absorptions of amide and imide groups occurring around 3300, 1770–1780, 1710–1720, and 1650–1680 cm⁻¹, which are peculiar to N—H stretching and carbonyl stretching of imide and amide, respectively. All of these PAIs exhibited strong absorptions at 1360–1380 and 720–730 cm⁻¹, which showed the presence of the imide heterocycle in these

polymers. Polymer **5c** showed characteristic absorptions at 1300 and 1140 cm⁻¹ due to the sulfone moiety (SO₂ stretching). The elemental analysis values of the resulting polymers are listed in Table III. PAIs derived from monomer **3** ranged in color from white to yellow and formed films from DMF solutions. Because they had different structures than the diamine parts, they showed different IR patterns and different specific rotations.

The solubility of the PAIs was tested quantitatively in various solvents. All of the PAIs were soluble in organic solvents such as DMF, *N,N*-dimethylacetamide, DMSO, NMP, and H₂SO₄ at room temperature and were insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water.

Thermal properties

The thermal properties of PAIs **5b'**, **5e'**, and **5g** were evaluated with TGA/DTG (derivative thermogravimetric) under a nitrogen atmosphere (Table IV). All of

TABLE I
Synthesis and Some Physical Properties of PAIs 5a–5g

Diamine	Polymer				
	Code	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_D^{25b}$	Color ^c
4a	5a	92	0.34	+7.6	Y
4b	5b	83	0.31	+9.6	PY
4c	5c	100	0.22	+19.6	W
4d	5d	100	0.28	+16.6	Y
4e	5e	93	0.25	+13.0	G
4f	5f	98	0.22	+9.4	Off-white
4g	5g	97	0.30	+20.2	Off-white

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

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

^c W = white; PY = pale; yellow; Y = yellow; G = green.

TABLE II
Synthesis and Some Physical Properties of PAIs 5a'–5g'

Diamine	Polymer				
	Code	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_D^{25}$	Color ^b
4a	5a'	92	0.35	+8.6	Y
4b	5b'	96	0.35	+13.6	PY
4c	5c'	100	0.21	+19.0	W
4d	5d'	97	0.37	+19.0	Y
4e	5e'	100	0.32	+14.0	G
4f	5f'	90	0.21	+10.6	Off-white
4g	5g'	96	0.32	+20.4	Off-white

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

^b W = white; PY = pale yellow; Y = yellow; G = green.

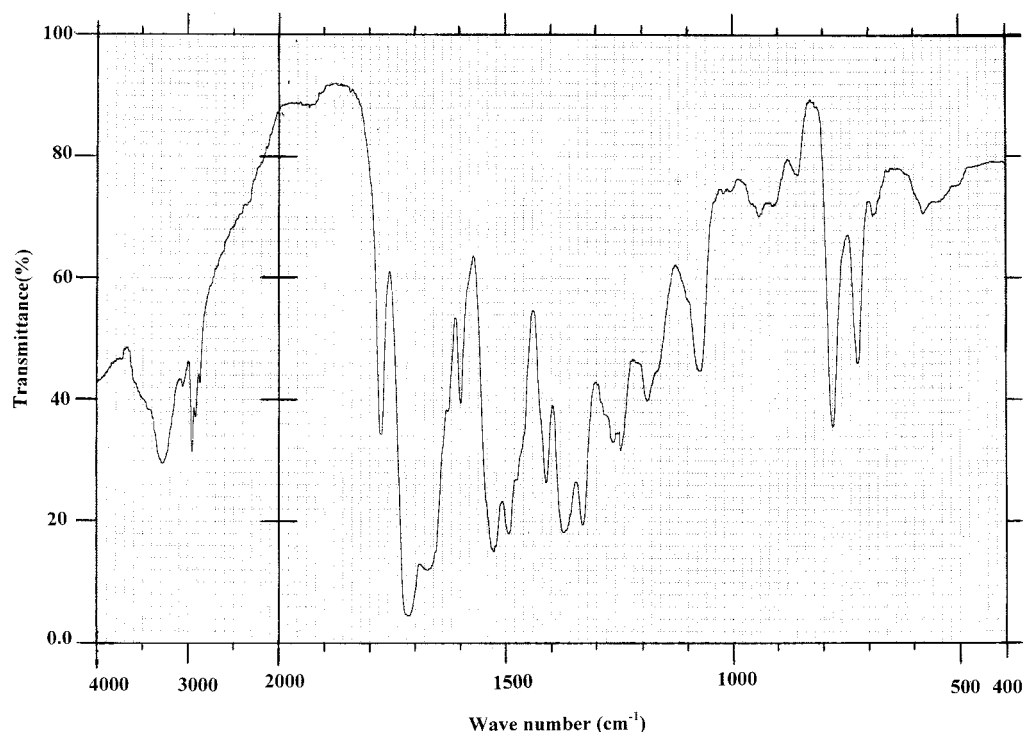


Figure 1 IR (KBr) spectrum of PAI 5e.

TABLE III
Elemental Analysis of PAIs 5a–5g

Polymer	Formula		Elemental analysis (%)			Moisture intake (%) ^a
			C	H	N	
5a	$(C_{21}H_{19}N_3O_4)_n$ (377.4) _n	Calcd.	66.83	5.07	11.13	2.46
		Found	64.46	5.21	9.87	
		Corr ^b	66.04	5.08	10.11	
5b	$(C_{28}H_{25}N_3O_4)_n$ (467.52) _n	Calcd.	71.93	5.39	8.98	3.73
		Found	69.67	5.43	8.22	
		Corr ^b	72.27	5.22	8.53	
5c	$(C_{27}H_{23}N_3O_6S)_n$ (517.56) _n	Calcd.	62.66	4.48	8.12	3.97
		Found	60.25	4.69	7.42	
		Corr ^b	62.64	4.41	7.71	
5d	$(C_{27}H_{23}N_3O_5)_n$ (469.49) _n	Calcd.	69.07	4.94	8.95	3.50
		Found	66.21	5.00	7.46	
		Corr ^b	68.5	4.83	7.72	
5e	$(C_{25}H_{21}N_3O_4)_n$ (427.46) _n	Calcd.	70.25	4.95	9.83	3.01
		Found	68.55	5.05	9.09	
		Corr ^b	70.61	4.90	9.36	
5f	$(C_{22}H_{21}N_3O_4)_n$ (391.43) _n	Calcd.	67.51	5.41	10.73	2.65
		Found	65.82	5.46	9.98	
		Corr ^b	67.56	5.31	10.24	
5g	$(C_{21}H_{17}N_3O_4)_n$ (377.4) _n	Calcd.	66.83	5.07	11.13	2.77
		Found	64.85	5.38	10.45	
		Corr ^b	66.64	5.23	10.73	

^a Moisture intake (%) = $(W - W_0)/W_0 \times 100$; W = weight of the polymer sample after standing at room temperature; W_0 = weight of the polymer sample after drying *in vacuo* at 100°C for 10 h.

^b Corrected value for C and N = Found value $\times (100 + \text{Moisture intake})/100$; and corrected value for H = Found value $\times (100 - \text{Moisture intake})/100$.

TABLE IV
Thermal Behavior of Aromatic PAIs 5b', 5e', and 5g

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield (%) ^c
5b'	150	290	32.16
5e'	193	307	30.32
5g	238	260	42.92

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

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

^c Percentage weight of material left undecomposed after TGA analysis at a maximum temperature of 996.3°C in N₂.

these polymers showed similar decomposition behaviors, but they showed three different decomposition maxima. PAIs **5b'**, **5e'**, and **5g** first showed decomposition with end temperatures of 202.3, 146.3, and 160.3°C with corresponding weight losses of 7.49, 4.17, and 3.68%, respectively. For **5e'** and **5g**, this could also be due to solvent or water exclusion. The second decomposition occurred with end temperatures of 785.5, 561.7, and 813.7°C with corresponding weight losses

of 48.26, 38.41, and 44.79%, respectively. The third decomposition occurred with an end temperature for all the polymers of 995.7°C with corresponding weight losses of 11.43, 25.57, and 7.70%, respectively. Figure 2 shows a typical TGA/DTG diagram.

CONCLUSIONS

A series of optically active PAIs with η_{inh} values of 0.21–0.37 dL/g were synthesized for the first time by the direct polycondensation of the optically active compound **3** (having a preformed imide ring) as an enlarged monomer containing one chiral **2** group with some aromatic diamines. The best method for the preparation of these polymers was heating a mixture of monomers and catalysts in NMP as a solvent under the refluxing temperature for 1 min; this saved a lot of energy and time. These aromatic PAIs showed optical rotations, were readily soluble in various organic solvents, and had moderate thermal stability. This could be due to the formation of some cyclic polymers instead of linear polymers. These resulting novel poly-

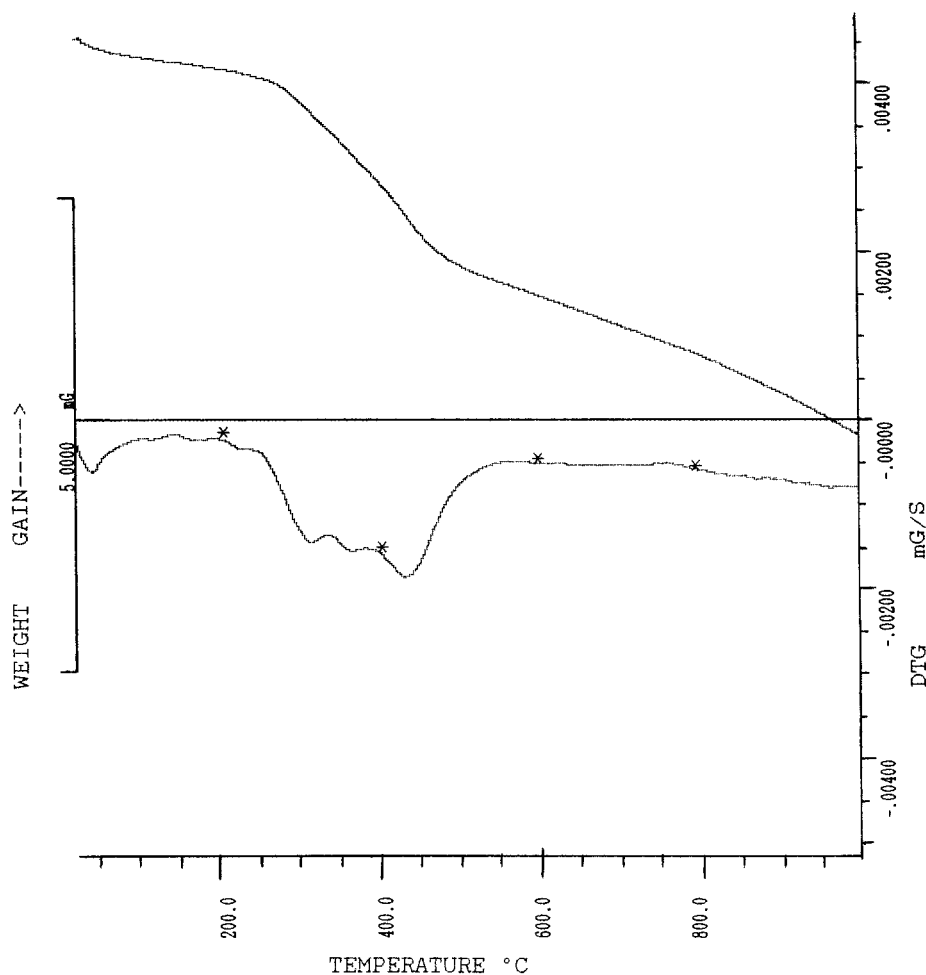


Figure 2 TGA/DTG thermogram of PAI **5b'** at a heating rate of 10°C/min under a nitrogen atmosphere.

mers have the potential to be used in a column chromatography technique for the separation of enantiomeric mixtures.

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