

Synthesis of Novel Poly(amide-imide)s Containing Trimellitylimido-DL/L-Alanine Moieties via Direct Polycondensation

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ABSTRACT: *N*-Trimellitylimido-DL and L-alanine (**3**) were prepared from the reaction of trimellitic anhydride (**1**) with DL and L-alanine (**2**) in *N,N*-dimethyl formamide (DMF) solution at refluxing temperature. The direct polycondensation reaction of the monomers imide-diacid (**3**) with 4,4'-diaminodiphenylsulfone (**4a**), 4,4'-diaminodiphenylmethane (**4b**), 1,4-phenylenediamine (**4c**), 1,3-phenylenediamine (**4d**), 2,4-diaminotoluene (**4e**), and 4,4'-diaminodiphenylether (**4f**) was carried out in a medium consisting of triphenyl phosphite, *N*-methyl-2-pyrrolidone (NMP), pyridine, and calcium chloride. The resulting poly(amide-imide)s **PAIs**, with inherent viscosities 0.32–0.66 dL/g, were obtained in high yield. All of the above-mentioned compounds were fully characterized by IR, elemental analyses, and specific rotation. Some structural characterization and physical properties of these new optically active **PAIs** are reported. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1312–1318, 2001

Key words: *N*-trimellitylimido-DL/L-alanine; poly(amide-imide)s; optically active polymers; direct polycondensation; inherent viscosities; thermally stable polymers

INTRODUCTION

Thermally stable polymers such as aromatic polyimides, polyamides, and their copolymers have received much interest over the past decade because of increasing demands for high-performance polymers as replacement for ceramics or metals in the microelectronic, aerospace, and automotive industries.^{1–4} However, most aromatic polyamides are intractable materials that do not melt before thermally decomposing, thus making it difficult to process. Aromatic poly(amide-imide)s

(**PAIs**), however, are very useful high-performance materials that exhibit better processing characteristics than those of polyimides of analogous structures.⁵ A notable example is Torlon (Amoco Co., USA), a commercial **PAI** obtained from trimellitic anhydride chloride and 4,4'-diaminodiphenylmethane.⁶

The synthesis and application of optically active polymers have recently become the focus of greater attention because polymers with chiral structures are biologically very important. Most of the natural polymers are optically active and have special chemical activities such as catalytic properties that exist in genes, proteins, and enzymes. Recently, we synthesized optically active polymers by different methods.^{7–10}

The triphenyl phosphite-activated polycondensation (phosphorylation reaction) technique for

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the synthesis of polyamides was reported by Yamazaki and coworkers.¹¹ Recently, this technique was used for the preparation of high molecular weight polyamides as well as PAIs and are reported in the literature.^{12–14} In previous studies,^{15–18} we synthesized a series of novel optically active poly(amide-imide)s containing amino acid moieties.

In this study we report the synthesis and characterization of new optically active PAIs from aromatic diamines and *N*-trimellitylimido-DL/L-alanine (**3a**, **3b**), a monomer containing performed imide groups, by the direct polycondensation method.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical (Milwaukee, WI), Aldrich Chemical (Milwaukee, WI), and Riedel-de Haën 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. 4,4'-Diaminodiphenylsulfone (**4a**) was purified by recrystallization from water/ethanol. 4,4'-Diaminodiphenylmethane (**4b**) was purified by recrystallization from water. 1,4-Phenylenediamine (**4c**), 1,3-phenylenediamine (**4d**), 2,4-diaminotoluene (**4e**), and 4,4'-diaminodiphenylether (**4f**) were purified by sublimation.

Apparatus

Proton nuclear magnetic resonance (¹H-NMR, 90 MHz) spectra were recorded on a Varian EM-390 instrument (Varian Associates, Palo Alto, CA). Tetramethylsilane (TMS) was used as an internal reference. IR spectra were recorded on a Shimadzu 435 IR spectrophotometer (Japan). Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wave number (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 (Germany). Specific rotations were measured by a Perkin-Elmer 241 Polarimeter (Germany). Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TGA-50 in nitrogen atmosphere at a rate of 10°C/min. Elemental anal-

yses were performed by Research Institute of Petroleum Industry, Tehran, I.R. Iran.

Monomer Synthesis

N-Trimellitylimido-L-alanine (**3a**)

Into a 25-ml round-bottom flask, equipped with a magnetic stirrer, 1.50 g (7.81×10^{-3} mol) of trimellitic anhydride (**1**), 0.695 g (7.81×10^{-3} mol) of L-alanine (**2**), and 10 ml of DMF were placed. The stirrer was started and the mixture was refluxed for 6 h. The mixture was poured into 100 ml of 5% HCl solution. A white precipitate was formed, filtered off, and dried, to give 1.90 g (92.5%) of diacid (**3**). Recrystallization from methanol/water gave white crystals, mp = 246–247°C, $[\alpha]_D^{25} = +1.8$ (0.050 g in 10 ml DMF).

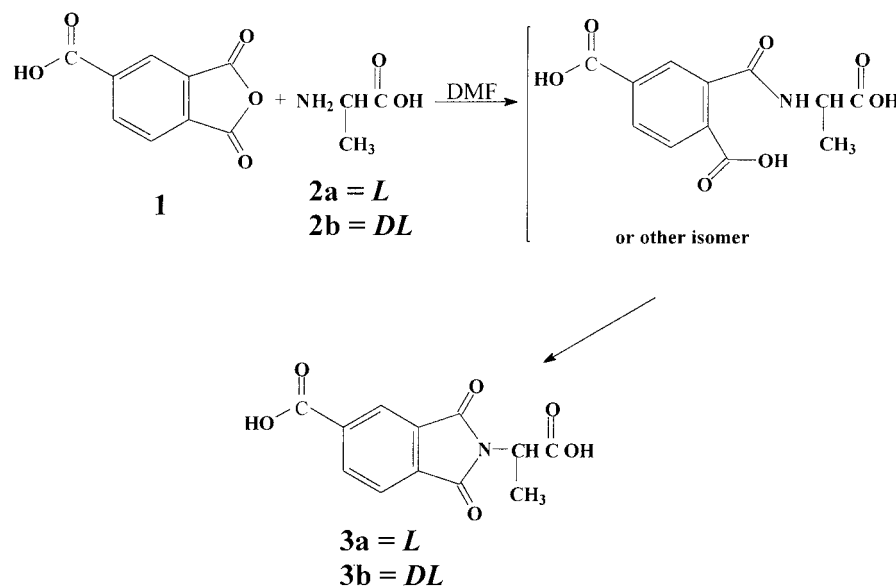
IR (KBr): 3300–2700 (m, br), 2650 (m), 2550 (m), 1700 (s, br), 1620 (m, sh), 1600 (m, sh), 1480 (w), 1380 (s), 1350 (m), 1320 (w), 1270 (s), 1250 (s), 1190 (m), 1170 (w), 1140 (m), 1090 (s), 1020 (s), 920 (s), 880 (m), 840 (w), 800 (m), 730 (s), 700 (m), 630 cm⁻¹; ¹H-NMR (DMSO-*d*₆, TMS, 90 MHz): δ 1.68 (d, 3H, *J* = 9 Hz), 4.85–5.24 (q, 1H, *J* = 9 Hz), 8.26 (d, 1H, *J* = 9 Hz), 8.61 (s, 1H), 8.70 (d, 1H, *J* = 9 Hz), 10.65 (s, br, 2H) ppm.

N-Trimellitylimido-DL-alanine (**3b**) was prepared by a procedure similar to that just described.

Polymerization: Synthesis of Polymer **5c'**

The poly(amide-imide)s were prepared by direct polycondensation using the following general procedure. Taking polymer **5c'** as an example. Into a 10-ml round-bottom flask, fitted with a water-cooled condenser and a magnetic stirrer, was placed 0.10 g (3.80×10^{-4} mol) of diacid (**3b**), 0.062 g of calcium chloride, 0.249 ml (9.50×10^{-4} mol) of triphenyl phosphite, 0.228 ml (2.83×10^{-3} mol) of pyridine, 0.0415 g (3.80×10^{-4} mol) of diamine (**4c**), and 0.7 ml of NMP. The stirrer was started and the mixture was heated under nitrogen atmosphere in an oil bath at 60°C for 1 h, then at 80°C for 2 h, and finally at 120°C for 12 h. The viscous reaction mixture was poured into 50 ml of warm methanol. The precipitated polymer was collected by filtration and was dried at 100°C for 15 h under vacuum to yield 0.130 g (96.7%) of solid (**5c**) mp > 300°C.

IR (KBr): 3300 (m, br), 3020 (m), 2950 (m), 1780 (m), 1715 (s, br), 1670 (s, br), 1610 (m), 1550 (m, sh), 1510 (s), 1430 (w), 1400 (m), 1380 (s), 1310 (s), 1250 (m), 1170 (m, sh), 1100 (m), 1080 (m), 1020 (w), 950 (w), 930 (w), 890 (w), 830 (m), 720 (m), 690 (m, br) cm⁻¹.



Scheme 1

The other PAIs **5a'**, **5b'**, **5d'**, **5e'**, **5f'**, and **5a-5f** were prepared by a procedure similar to that described earlier.

Polymer 5a'

IR (KBr): 3350 (m, br), 3100 (m), 2900 (m), 1780 (m), 1720 (s, br), 1680 (s, br), 1590 (s), 1530 (s, br), 1490 (s), 1400 (m), 1380 (m), 1310 (m), 1250 (m), 1150 (s), 1100

(m), 1070 (m), 1010 (m), 940 (w), 830 (m), 720 (m), 690 (m), 560 (m, br) cm^{-1} .

Polymer 5b'

IR (KBr): 3300 (m, br), 3100 (m), 2900 (m), 1780 (m), 1720 (s), 1665 (s), 1600 (m), 1530 (s, sh), 1510 (s), 1410 (m), 1380 (s), 1320 (m), 1250 (m), 1100 (w), 1075 (m), 1020 (m), 950 (w), 860 (w), 815 (m), 770 (w), 730 (m), 510 (w, br) cm^{-1} .

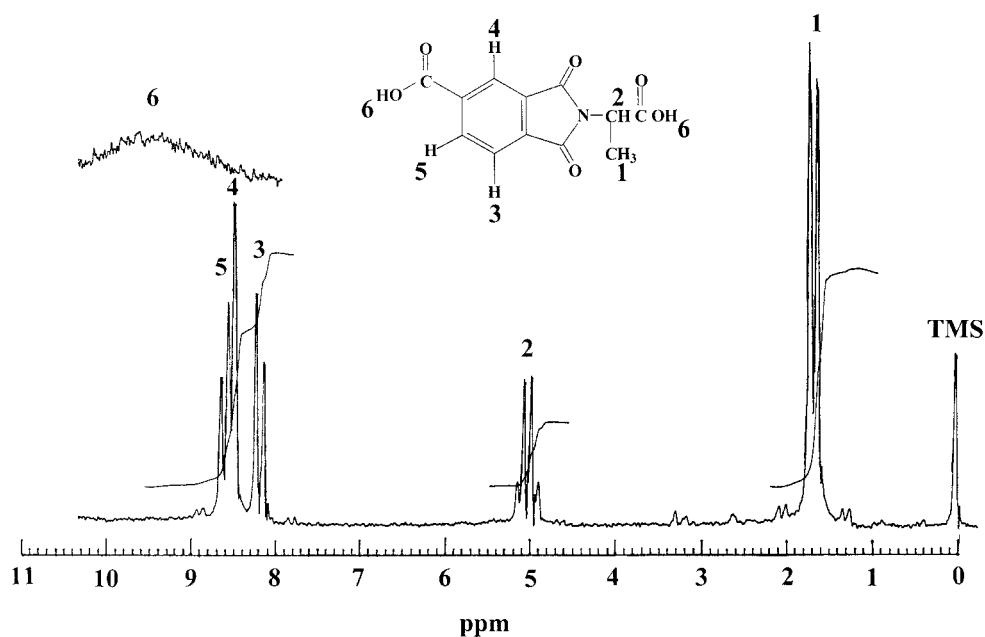
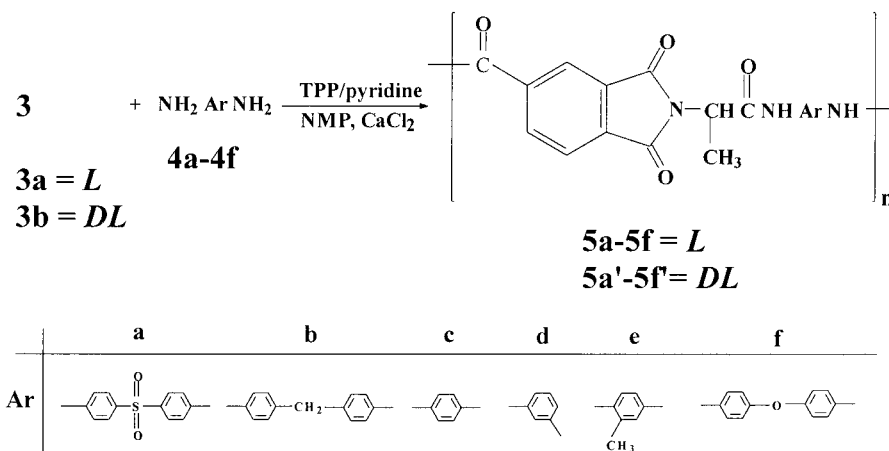


Figure 1 $^1\text{H-NMR}$ (90 MHz) spectrum of monomer **3a** in $\text{DMSO-}d_6$ at right. The protons no. 6 are offset by 2 ppm.



Scheme 2

Polymer 5d'

IR (KBr): 3300 (m, br), 3050 (m), 2900 (m), 1775 (m), 1710 (s, br), 1660 (s, br), 1600 (s), 1530 (s, br), 1485 (s), 1420 (m), 1380 (s), 1330 (m), 1300 (m), 1240 (m, br), 1160 (m), 1090 (m), 1020 (m), 940 (w), 920 (w), 890 (w), 860 (m), 780 (m), 720 (m), 680 (m), 580 (w, br) cm^{-1} .

Polymer 5e'

IR (KBr): 3310 (m, br), 3100 (m), 2950 (m), 1780 (m), 1720 (s, br), 1670 (s, br), 1600 (s), 1530 (s), 1500 (s), 1460 (m), 1380 (s), 1340 (m), 1320 (m), 1260 (m), 1220 (m, sh), 1170 (m), 1060 (m), 1020 (m), 950 (m), 895 (w), 870 (m), 830 (m), 780 (m), 740 (s), 700 (m), 610 (w, br) cm^{-1} .

Polymer 5f'

IR (KBr): 3300 (m, br), 3050 (m), 2900 (m), 1780 (m), 1715 (s, br), 1660 (s, br), 1600 (m), 1530 (s), 1500 (s), 1410 (m), 1380 (s), 1320 (m), 1220 (s, br), 1160 (m), 1100 (m), 1090 (m), 1010 (m), 950 (m), 890 (m), 860 (m), 830 (m), 760 (w), 720 (m), 500 (m, br) cm^{-1} .

The optically active polymers **5a-5f** show similar IR spectra patterns.

RESULTS AND DISCUSSION**Monomer Synthesis**

N-Trimellitylimido-*L*-alanine (**3a**) and *N*-trimellitylimido-*DL*-alanine (**3b**) were prepared in a similar way. Thus, the unsymmetric diacid compounds (**3a**, **3b**) were synthesized by the condensation reaction of an equimolar mixture of anhydride (**1**) and *L*-alanine (**2a**) or *DL*-alanine

(**2b**) in refluxing DMF. The white diacids were obtained from 5% HCl solution (Scheme 1).

Chemical structure and purity of the optically active and optically inactive monomers (**3a**, **3b**) were proved using IR and $^1\text{H-NMR}$ (Fig. 1) spectroscopic techniques.

Polymer Synthesis

PAIs 5a-5f and **5a'-5f'** were synthesized by direct solution polycondensation reactions of an equimolar mixture of monomer (**3a**) or (**3b**) with six different aromatic diamines (**4a-4f**) using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 2). The synthesis and some physical properties of novel optically active **PAIs 5a-5f** and optically inactive **PAIs 5a'-5f'** are given in Tables I and II. All polycondensation reactions readily proceeded in a homogeneous so-

Table I Synthesis and Some Physical Properties of PAIs **5a-5f**

		Polymer			
Diamine	Code	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_D^{25}$ ^a	Color ^b
4a	5a	98.7	0.32	-0.6	W
4b	5b	98.2	0.45	-0.2	PY
4c	5c	97.0	0.50	-0.2	Y
4d	5d	97.0	0.37	-0.6	PY
4e	5e	97.0	0.41	-0.2	PY
4f	5f	98.7	0.66	-0.2	Y

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

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

Table II Synthesis and Some Physical Properties of PAIs 5a'–5f'

Diamine	Code	Polymer			
		Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_D^{25}$	Color ^b
4a	5a'	98.1	0.36	—	W
4b	5b'	98.8	0.49	—	PY
4c	5c'	96.7	0.51	—	Y
4d	5d'	96.3	0.38	—	PY
4e	5e'	96.9	0.39	—	PY
4f	5f'	95.3	0.45	—	Y

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

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

lution. In most reactions an additional amount of NMP must be added to maintain a degree of agitation because the polymer solutions were too viscous to stir. Tough and stringy precipitates formed when the viscous PAI solutions were slowly poured into the methanol, under stirring. All of the polymers were obtained in quantitative yields with moderate inherent viscosities of 0.32–

0.66 dL/g and in the case of 5a–5f, show optical rotation and, therefore, are optically active.

Polymer Characterization

The formation of PAIs was confirmed by means of IR spectroscopy and elemental analysis. For example, the IR spectrum of PAIs 5a' showed the characteristic absorptions of amide and imide groups occurring around 3350, 1780, 1720, and 1680 cm^{-1} , characteristic of N–H stretching and carbonyl stretching of imide and amide, respectively. All of these PAIs exhibited strong absorption at 1380 and 720–730 cm^{-1} , showing the presence of the imide heterocycle in these polymers. Polymers 5a and 5a' showed characteristic absorptions at 1310 and 1150 cm^{-1} as a result of the sulfone moiety (SO_2 stretching). Figure 2 shows a typical IR spectrum (polymer 5e'). Elemental analysis values of the resulting polymers are listed in Table III. PAIs derived from monomers 3a and 3b may range in color from white to yellow.

The solubility of PAIs was tested quantitatively in various solvents, values of which are listed in Table IV. All of the PAIs are soluble in

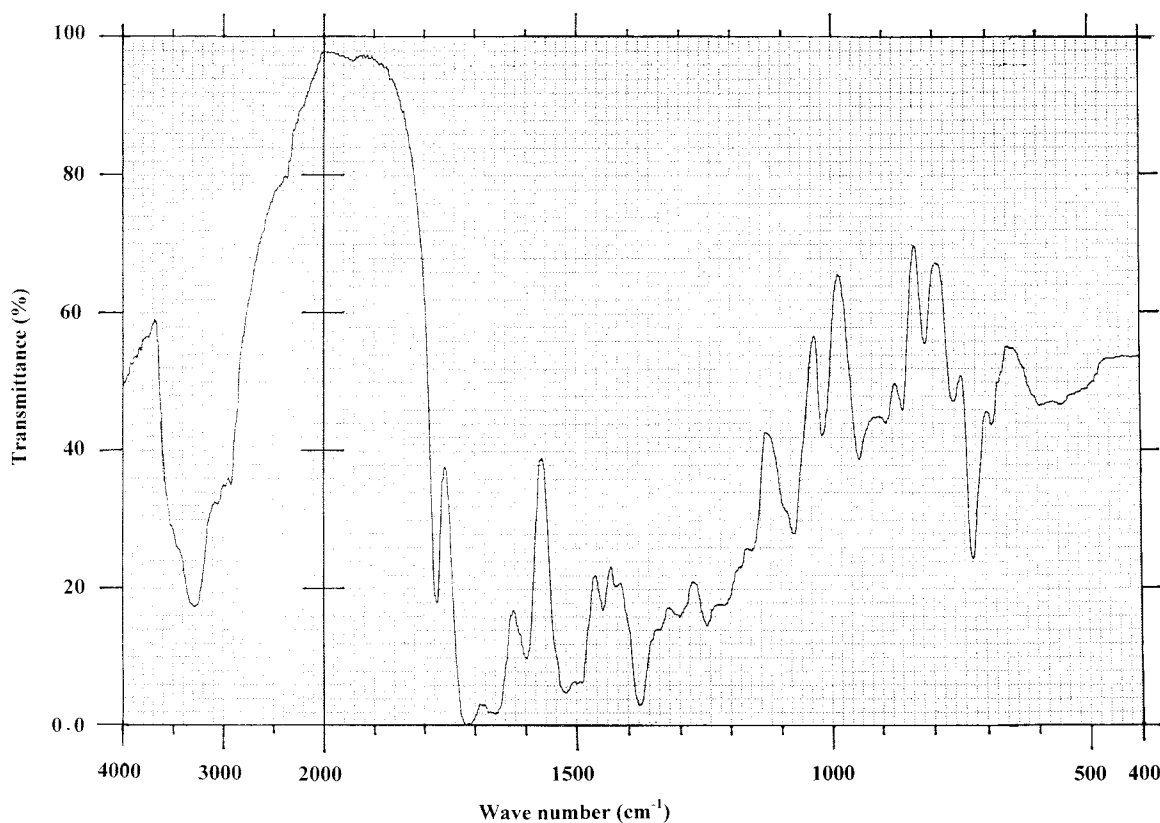


Figure 2 IR (KBr) spectrum of PAI 5e'.

Table III Elemental Analysis of PAIs **5a–5f** and **5a'–5e'**

Polymer	Formula	Elemental Analysis (%)			Moisture Intake (%) ^a	
			C	H		N
5a	(C ₂₄ H ₁₇ N ₃ O ₆ S) _n (475) _n	Calcd	60.62	3.61	8.84	4.04
		Found	58.50	4.30	8.60	
		Corr ^b	60.86	4.13	8.95	
5b	(C ₂₅ H ₁₉ N ₃ O ₄) _n (425) _n	Calcd	70.58	4.50	9.88	3.54
		Found	66.50	5.00	10.20	
		Corr ^b	68.86	4.82	10.56	
5c	(C ₁₈ H ₁₃ N ₃ O ₄) _n (335) _n	Calcd	64.48	3.91	12.53	4.17
		Found	61.20	4.80	12.20	
		Corr ^b	63.75	4.60	12.71	
5d	(C ₁₈ H ₁₃ N ₃ O ₄) _n (335) _n	Calcd	64.47	3.91	12.53	3.21
		Found	60.20	4.60	11.40	
		Corr ^b	62.13	4.45	11.77	
5e	(C ₁₉ H ₁₅ N ₃ O ₄) _n (349) _n	Calcd	65.32	4.33	12.03	3.21
		Found	62.70	4.20	11.90	
		Corr ^b	64.71	4.10	12.28	
5f	(C ₂₄ H ₁₇ N ₃ O ₅) _n (427) _n	Calcd	67.44	4.01	9.83	2.38
		Found	66.00	4.20	9.70	
		Corr ^b	67.57	4.10	9.93	
5a'	(C ₂₄ H ₁₇ N ₃ O ₆ S) _n (475) _n	Calcd	60.62	3.61	8.84	4.49
		Found	58.00	4.30	9.60	
		Corr ^b	60.60	4.10	10.03	
5b'	(C ₂₅ H ₁₉ N ₃ O ₄) _n (425) _n	Calcd	70.58	4.50	9.88	4.35
		Found	67.00	4.80	10.30	
		Corr ^b	69.91	4.59	10.75	
5c'	(C ₁₈ H ₁₃ N ₃ O ₄) _n (335) _n	Calcd	64.48	3.91	12.53	3.64
		Found	61.50	4.50	12.00	
		Corr ^b	63.74	4.34	12.44	
5d'	(C ₁₈ H ₁₃ N ₃ O ₄) _n (335) _n	Calcd	64.48	3.91	12.53	3.55
		Found	61.50	4.00	10.60	
		Corr ^b	63.68	3.86	10.98	
5e'	(C ₁₉ H ₁₅ N ₃ O ₄) _n (349) _n	Calcd	65.32	4.33	12.03	4.09
		Found	63.70	4.50	11.00	
		Corr ^b	66.31	4.32	11.45	

^a Moisture Intake (%) = $(W - W_0)/W_0 \times 100$, W = weight of polymer sample after standing at room temperature and W_0 = weight of polymer sample after dried in vacuum at 100°C for 10 h.

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

organic solvents such as DMF, *N,N*-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), NMP, and H₂SO₄ at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water.

Thermal Properties

The thermal properties of PAIs (**5b'**, **5c'**, **5f'**) were evaluated by means of TGA/DTG under nitrogen atmosphere. All of these polymers show similar decomposition behavior. The PAIs **5b'**

and **5f'** show three different decomposition maxima, but PAIs **5c'** shows five different decomposition maxima. Thus, PAIs (**5b'**, **5c'**, **5f'**) show first decomposition with end temperatures at 228.3, 98.3, and 115.00°C with a corresponding weight loss of 6.80, 3.3, and 1.70%, respectively. The second decomposition occurs with end temperatures at 568.30, 248.30, and 228.30°C with a corresponding weight loss of 32.38, 6.60, and 1.72%, respectively. The third decomposition occurs with end temperatures at 695.00, 345.00,

Table IV Solubility of PAIs (5a–5f)^a and (5a'–5f')

Solvent	5a/5a'	5b/5b'	5c/5c'	5d/5d'	5e/5e'	5f/5f'
DMAc	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
H ₂ SO ₄	+	+	+	+	+	+
MeOH	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
CHCl ₃	–	–	–	–	–	–
CH ₂ Cl ₂	–	–	–	–	–	–
H ₂ O	–	–	–	–	–	–

^a Concentration: 5 mg/ml; +, soluble at room temperature; –, insoluble.

and 685.00°C with a corresponding weight loss of 34.02, 6.33, and 42.49%, respectively, for the **PAI 5c'**. The fourth decomposition occurs with an end temperature at 541.70°C with a corresponding weight loss of 25.41% and the fifth and final decomposition occurs with an end temperature at 695.0°C with a corresponding weight loss of 32.32%. The char yields of these **PAIs (5b', 5c', 5f')** at 700.0°C in nitrogen atmosphere are 20.74, 21.63, and 50.66%, respectively.

CONCLUSIONS

A series of optically active **PAIs**, with inherent viscosities of 0.32–0.66 dL/g, was synthesized for the first time by direct polycondensation of the optically active *N*-trimellitylimido-*L*-alanine (**3a**) and optically inactive *N*-trimellitylimido-*DL*-alanine (**3b**) as a diacid having a performed imide ring as an “enlarged” monomer containing one chiral *L*-alanine group with some aromatic diamines. These aromatic **PAIs** show optical rotation and are readily soluble in various organic solvents and have moderate thermal stability, which could result from the formation of some cyclic polymers instead of linear polymers.

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