

Novel Optically Active Poly(amide-imide)s from *N*-Trimellitylimido-*S*-valine and Aromatic Diamines by Direct Polycondensation Reaction

Shadpour Mallakpour*, Abdol-Reza Hajipour and
Mohammad H. Shahmohammadi.

Organic Polymer Chemistry Research Laboratory, College of Chemistry,
Isfahan University of Technology, Isfahan, 84156, I.R. Iran

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ABSTRACT

N-Trimellitylimido-*S*-valine **3** was prepared from the reaction of trimellitic anhydride **1** with (*S*)-(+)-valine(2-amino-3-methylbutyric acid) **2** in acetic acid solution at refluxing temperature. The direct polycondensation reaction of the monomer imide-diacid **3** with 1,4-phenylenediamine **4a**, diaminodiphenylmethane **4b**, 4,4'-diaminodiphenylsulphone **4c**, diaminodiphenylether **4d**, 1,5-naphthalenediamine **4e**, 2,4-diaminotoluene **4f** and 1,3-phenylenediamine **4g**, was carried out 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 stirred at room temperature in NMP solution and then it was heated at 60°C, 90°C, and finally at 130°C for different periods of time and the other method the reaction mixture was refluxed only for 1 min in the same solvent. The resulting poly(amide-imide)s **PAIs** having inherent viscosities 0.15-0.73 dL/g were obtained in high yield. All of the above compounds were fully characterized by IR, elemental analyses, and specific rotation. Some structural characterizations and physical properties of this new optically active **PAIs** are reported.

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Key Words:

N-trimellitylimido-*S*-valine;
direct polycondensation;
poly(amide-imide)s;
optically active polymers;
inherent viscosities;
thermally stable polymers.

INTRODUCTION

Aromatic polyimides and polyamides are thermally stable polymers which have received much interest over the past decade due to increasing demands for high performance polymers as replacement for ceramics or metals in the microelectronic, aero-

space and automotive industries [1-4]. However, most aromatic polyamides are intractable materials that do not melt before thermally decomposing, therefore, would be difficult for processing. However, aromatic poly(amide-imide)s (**PAIs**),

(*)To whom correspondence should be addressed.
E-mail: Mallak@cc.iut.ac.ir

are very useful high-performance materials that exhibit better processing characteristics when compared with polyimides of analogues structures

The synthesis and application of optically active polymers are the newly considerable topics which have been paid more attention recently. So we have synthesized optically active polymers by different methods [5-19].

In this article for the first time we wish to report the synthesis and characterization of new optically active PAIs from aromatic diamines and *N*-trimellitylimido-*S*-valine **3**, a monomer containing performed 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-deHaen 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'-Diaminodiphenylmethane **4b** was purified by recrystallization from water. 4,4'-Diaminodiphenylsulphone **4c** was purified by recrystallization from water/ethanol. 1,4-Phenylenediamine **4a**, 4,4'-diaminodiphenylether **4d**, 2,4-diaminotoluene **4f**, and 1,3-phenylenediamine **4g** were purified by sublimation.

Apparatus

Proton nuclear magnetic resonance (^1H NMR, 90MHz) spectra were recorded on a Varian EM-390 instrument. Tetramethylsilane (TMS) was used as an internal reference. IR Spectra were recorded on Shimadzu 435 IR spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (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 analyses were performed by Tarbiat Modarres University, Tehran, I.R. Iran.

Monomer Synthesis

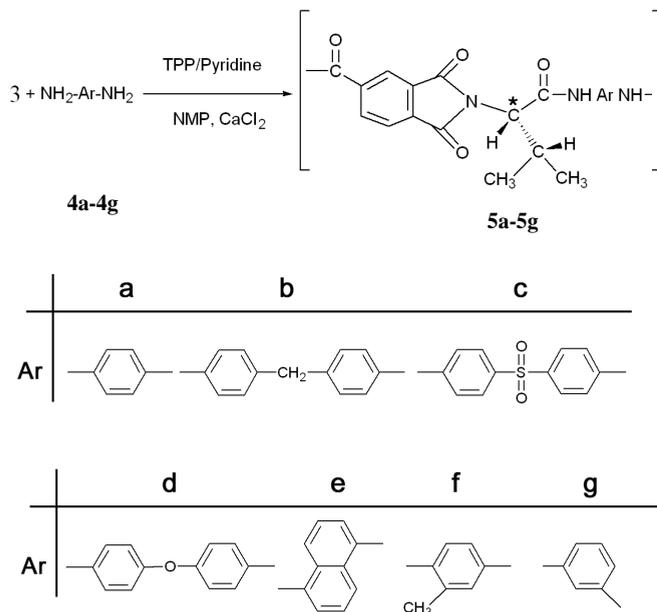
N-Trimellitylimido-*S*-valine **3**

Into a 25 mL round-bottomed flask which was equipped with a magnetic stirrer, 1.00 g (5.20×10^{-3} mol) of trimellitic anhydride **1**, 0.697 g (5.20×10^{-3} mol) of *S*-valine **2** and 12 mL of acetic acid were placed. The stirrer was started and the mixture was refluxed for 4 h. The mixture was poured into 10 mL of concentrated HCl solution and after 2 h, 20 mL of water was added. A white precipitate was formed, filtered off and dried in vacuo, to give 1.273 g (84%) of diacid **3**. Recrystallization from methanol/water gave white crystals mp = 292-293 C, $[\alpha]_D^{25} = -105.00$ (0.050 g in 10 mL DMF); IR (KBr): 3000 (s, br), 2650 (m, sh), 1780 (m), 1715 (s, br), 1600 (m), 1490 (m), 1420 (s), 1380 (s), 1290 (s), 1260 (s), 1200 (m), 1170 (m), 1140 (m), 1090 (m), 1070 (m), 1015 (w), 930 (w), 875 (m), 830 (w), 800 (w), 760 (m), 730 (s), 705 (m), 650 (m), 610 (w), 570 (w), 530 (w), cm^{-1} ; ^1H NMR (DMSO- d_6 , TMS, 90MHz): (0.70-1.05 (d, 3H, $J = 7.50$ Hz), 1.05-1.30 (d, 3H, $J = 7.50$ Hz), 2.45-2.90 (m, 1H), 4.50-4.70 (d, 1H, $J = 7.5$ Hz), 6.20-7.80 (a broad peak for two acidic OH protons), 8.15-8.35 (d, 1H, $J = 6.0$ Hz), 8.50 (s, 1H), 8.55-8.75 (d, 1H, $J = 6.0$ Hz) ppm; Elemental analysis. Calcd. for $\text{C}_{14}\text{H}_{13}\text{NO}_6$: C, 57.73%; H, 4.49%; N, 4.81%; Found: C, 57.95%; H, 4.43%; N, 4.82 %.

Polymerization

Synthesis of Polymer **5c**

PAIs were prepared by direct polycondensation using the following general procedure. Taking polymer **5c** as an example. Into a 10 mL round-bottomed flask fitted with a water cooled condenser and a magnetic stirrer, was placed 0.10 g (3.43×10^{-4} mol) of diacid **3**, 0.1 g of calcium chloride, 0.327 mL (1.27×10^{-3} mol) of triphenyl phosphite, 0.29 mL of pyridine, 0.085 g (3.43×10^{-4} mol) of diamine **4c** and 0.6 mL of NMP. The stirrer was started and the mixture was heated under nitrogen atmosphere in an oil bath at 60 C for 0.5 h, then at 90 C for 2 h and finally at 130 C for 8 h. The viscous reaction mixture was cooled and diluted with 0.5 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 to leave 0.1742 g (92%) of solid **5c** mp>300 C; IR (KBr): 3500 (m), 3300 (m, br), 3100 (m, sh), 2950 (m), 2810 (m, sh), 1775 (m), 1715 (s), 1680 (s, sh), 1590 (s), 1520 (s), 1490 (s, sh), 1425(w, sh), 1400 (m), 1380 (s), 1315 (s), 1250 (s), 1180 (m, sh), 1150 (s), 1100 (s), 1070 (m),



Scheme II

1 min during which better yield and viscosities were obtained. It is important to note that the amount of catalysts were changed compared to the first method. The synthesis and some physical properties of novel optically active PAIs, **5a'-5g'** and **5a-5g**, are given in Tables 1 and 2. All the polycondensation readily proceeded in a homogeneous solution. In most cases of the reaction, an additional amount of NMP must be supplemented to maintain a degree of agitation because the polymer solutions were too viscous to stir. Tough and

Table 1. Synthesis and Some Physical Properties of PAIs (**5a-5g**).

Diamine	Polymer				
	Code	Yield(%)	$\eta_{\text{inh}}(\text{dL/g})^{\text{a}}$	$[\alpha]_{\text{D}}^{25} \text{ }^{\text{b}}$	Colour ^c
4a	5a	85	0.32	-45.20	Y
4b	5b	97	0.30	-21.60	PY
4c	5c	92	0.14	-12.40	W
4d	5d	96	0.35	-27.40	Y
4e	5e	90	0.20	-7.60	LG
4f	5f	89	0.19	-14.00	off-W
4g	5g	97	0.25	-24.00	off-W

(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, LG=light-green.

Table 2. Synthesis and Some Physical Properties of PAIs (**5a-5g**).

Diamine	Polymer				
	Code	Yield(%)	$\eta_{\text{inh}}(\text{dL/g})^{\text{a}}$	$[\alpha]_{\text{D}}^{25}$	Colour ^b
4a	5a'	95	0.38	-13.80	Y
4b	5b'	95	0.32	-18.00	PY
4c	5c'	55	0.15	-11.80	W
4d	5d'	91	0.14	-25.20	Y
4e	5e'	92	0.20	-2.60	G
4f	5f'	90	0.67	-7.00	off-W
4g	5g'	85	0.73	-15.80	off-W

(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

stringy precipitates were formed when the viscous PAIs solutions were trickled into the stirring methanol. All of the polymers were obtained in quantitative yields with high inherent viscosities of 0.15-0.73 dL g⁻¹ and show optical rotation, therefore they are optically active.

Polymer Characterization

The formation of PAIs were confirmed by means of IR spectroscopy and elemental analysis. As example, the IR spectrum of PAIs **5c** (Figure 1) showed the characteristic absorptions of amide and imide groups occurred around 3300, 1770-1780, 1715-1720 and 1650-1675

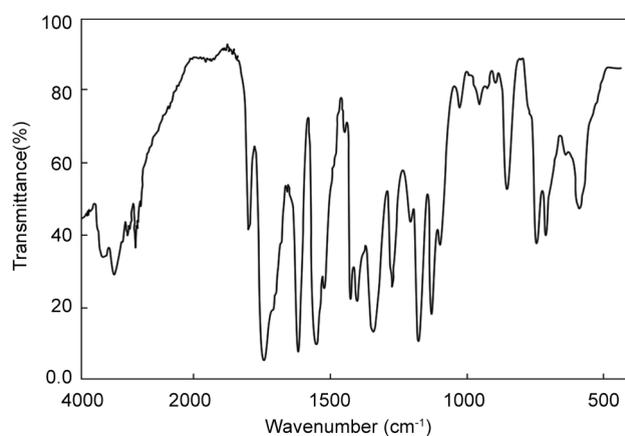


Figure 1. IR (KBr) spectrum of PAI **5c**.

Table 3. Elemental Analysis of PAIs (5a-5g).

Polymer	Formula		Elemental analysis (%)			Moisture intake(%) ^a
			C	H	N	
5a	(C ₂₀ H ₁₇ N ₃ O ₄) _n (363.37) _n	Calcd	66.11	4.71	11.56	1.98
		Found	64.14	4.81	10.64	
		Corr ^b	65.41	4.71	10.85	
5b	(C ₂₇ H ₂₃ N ₃ O ₄) _n (453.49) _n	Calcd	71.51	5.11	9.26	1.36
		Found	69.00	5.06	8.54	
		Corr ^b	69.94	5.00	8.56	
5c	(C ₂₆ H ₂₁ N ₃ O ₆ S) _n (503.53) _n	Calcd	62.02	4.20	8.34	1.66
		Found	60.87	4.37	7.78	
		Corr ^b	61.88	4.29	7.91	
5d	(C ₂₆ H ₂₁ N ₃ O ₆ S) _n (503.53) _n	Calcd	68.56	4.65	9.22	1.48
		Found	66.95	4.62	8.77	
		Corr ^b	67.94	4.55	8.90	
5e	(C ₂₆ H ₂₁ N ₃ O ₅) _n (413.43) _n	Calcd	69.72	4.63	10.16	1.61
		Found	67.58	4.71	9.55	
		Corr ^b	68.67	4.49	9.70	
5f	(C ₂₁ H ₁₉ N ₃ O ₄) _n (377.40) _n	Calcd	66.83	5.07	11.13	1.50
		Found	64.99	5.08	10.12	
		Corr ^b	65.96	5.00	10.27	
5g	(C ₂₀ H ₁₇ N ₃ O ₄) _n (363.37) _n	Calcd	66.11	4.71	11.56	1.32
		Found	64.00	4.69	10.01	
		Corr ^b	64.85	4.63	10.14	

(^a)Moisture intake(%) = $(W - W_0) / W_0 \times 100$, W = weight of polymer sample after standing at room and W₀ = weight of polymer sample after drying in vacuo at 100°C for 10 h. (^b)Corrected value for C and N = found value x (100 + moisture intake) / 100, and corrected value for H = found value temperature x (100 - moisture intake) / 100.

cm⁻¹, peculiar to N-H stretching and carbonyls stretching of imide and amide, respectively. All of these PAIs exhibited strong absorption at 1360-1380 cm⁻¹ and 720-730 cm⁻¹, that show the presence of the imide heterocycle in these polymers. The polymer 5c showed characteristic absorptions at 1315 and 1150 cm⁻¹ due to the sulphone moiety (SO₂ stretching). Elemental analysis values of the resulting polymers are listed in Table 3. PAIs derived from monomers 3 may range in colour from white to yellow and light-green.

The solubility of PAIs was tested quantitatively in various solvents and are listed in Table 4. All of the PAIs are soluble in organic solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethylsulphoxide (DMSO), NMP and

Table 4. Solubility of PAIs, (5a'-5g')^a and (5a'-5g').

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

(^a)Concentration: 5 mg mL⁻¹; + = soluble at room temperature, - = insoluble.

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, (**5f** and **5g'**) were evaluated by means of TGA/DTG under nitrogen atmosphere. All of these polymers show different decomposition behaviour. The PAI **5f** shows three different decomposition maxima. Thus, it shows the first decomposition with an end temperature at 225.7 C with a corresponding weight loss of 9.62%. The second decomposition occurs with an end temperature at 762.3 C, with a corresponding weight loss of 48.87%. The third decomposition occurs with an end temperature at 995.7 C with a corresponding weight loss of 15.25%. The char yield for this polymer at 996.3 C is 24.44%. On the other hand the PAI, (**5g'**), show two different decomposition maxima. Thus, it shows the first decomposition with an end temperature also at 225.7 C with a corresponding weight loss of 6.78%. The second decomposition occurs with an end temperature at 981.7 C, with a corresponding weight loss of 60.74%. The char yield for this polymer also at 996.3 C is 30.40%. Therefore, the PAI, (**5g'**), is more stable than PAI, (**5f**).

CONCLUSION

A series of optically active PAIs having inherent viscosities of 0.15-0.73 dL/g were synthesized for the first time by direct polycondensation of the optically active *N*-trimellitylimido-*S*-valine **3** having a preformed imide ring as an enlarged monomers containing one chiral *S*-valine group with some aromatic diamines. The best method for the preparation of these polymers is heating a mixture of monomers and catalysts in NMP as a solvent under refluxing temperature for 1 min, which saves lots of energies and time. These aromatic PAIs show optical rotation and they are readily soluble in various organic solvents and have moderate thermal stability. This could be due to the formation of some cyclic polymers instead of linear polymers.

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