

New Optically Active Poly(amide-imide)s Based on *N,N'*-(Pyromellitoyl)-bis-L-amino Acid and 1,3-Bis(4-aminophenoxy) Propane: Synthesis and Characterization

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ABSTRACT: Five new poly(amide-imide)s **8a–e** were synthesized through the direct polycondensation reaction of five chiral *N,N'*-(pyromellitoyl)-bis-L-amino acids **3a–e** with 1,3-bis(4-aminophenoxy) propane **7** in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride, and pyridine. The polycondensation reaction produced a series of novel poly(amide-imide)s containing trimethylene moiety in the main chain in high yield with inherent viscosities between 0.34 and 0.65 dL/g. The resulted polymers were fully characterized by means of FTIR spectroscopy, elemental analyses, inherent viscosity, and solubility tests. Thermal properties of these polymers were investigated by using thermal gravimetric analysis (TGA) and differential thermal gravimetric (DTG). All of the polymers were soluble at room temperature in polar solvents such as *N,N*-dimethyl acetamide, *N,N*-

dimethyl formamide, dimethyl sulfoxide, and *N*-methyl-2-pyrrolidone. *N,N'*-(pyromellitoyl)-bis-L-amino acids **3a–e** were prepared in quantitative yields by the condensation reaction of pyromellitic dianhydride (1,2,4,5-benzenetetracarboxylic acid 1,2,4,5-dianhydride) **1** with L-alanine **2a**, L-valine **2b**, L-leucine **2c**, L-isoleucine **2d**, and L-phenyl alanine **2e** in acetic acid. Also 1,3-bis(4-aminophenoxy) propane **7** was synthesized by using a two-step reaction. At first 1,3-bis(4-nitrophenoxy) propane **6** was prepared from the reaction of 4-nitrophenol **4** with 1,3-dibromopropane **5** in NaOH solution. Then, dinitro compound **6** was reduced by using Na₂S. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 74–81, 2008

Key words: direct polycondensation; optically active polymers; poly(amide-imide)s

INTRODUCTION

Aromatic polyimides show high thermal stabilities and good mechanical properties and chemical resistance, but their high softening or melting temperatures and poor solubility in common organic solvents cause their low processability and limit their applications.^{1,2} To overcome these drawbacks, many investigations were focused on the modifications of their chemical structure, for example, through the introduction of flexible linkages, asymmetric units, or bulky substituents into the polymer backbones.^{3–8} In addition, various copolyimides such as poly(amide-imide)s have been proposed in many reports.^{9–12} There is a growing interest in poly(amide-imide)s (PAIs) for a variety of applications as they retain good mechanical properties at high temperatures and show easier processability in comparison with other aromatic thermostable polymers such as polyamides and polyimides.¹³ They are finding numerous applications in adhesives, electronic wire enamel, injection molding, extrusion products, and membranes.^{14,15}

In this article, a series of novel optically active PAIs **8a–e** containing trimethylene moiety as a flexible segment were synthesized by the direct polycondensation reactions of five chiral *N,N'*-(pyromellitoyl)-bis-L-amino acids **3a–e** with 1,3-bis(4-aminophenoxy) propane **7** in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride, and pyridine. Introduction of trimethylene segments in the main chain improved solubility of these polymers in comparison to aromatic poly(amide-imide)s.

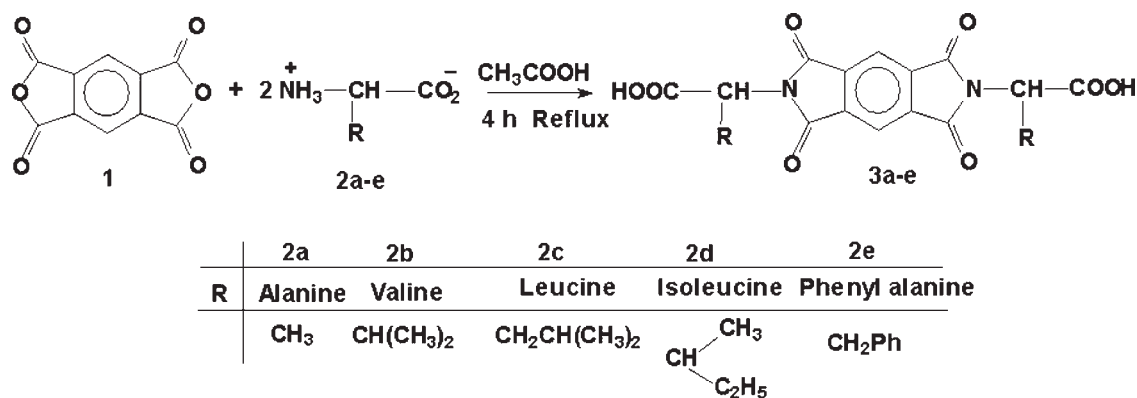
Furthermore, the synthesis and application of optically active polymers are the newly considerable topics, which have been paid more attention, because chiral polymers are biologically very important. Recently, we have synthesized optically active polymers by different methods.^{16–22}

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Switzerland), Aldrich Chemical Co. (Milwaukee, WI), and Merck Chemical Co. (Germany).

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Scheme 1

Techniques

¹H NMR spectra were recorded on a Bruker 500 MHz instrument. Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solids were performed by using KBr pellets. Vibrational transition frequencies are reported in wave number (cm⁻¹). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure using a Technico registered trade mark viscometer. Specific Rotations were measured by an A-Kruss polarimeter. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TA4000 System under N₂ atmosphere at a rate of 10°C/min. Elemental analyses were performed by the Research Institute of Petroleum Industry, Tehran, I. R. Iran.

Monomer synthesis

N,N'-(Pyromellitoyl)-bis-*L*-amino acid 3a-e

These compounds were prepared according to a typical procedure that was shown in Scheme 1.¹⁸

4.36 g, 20.00 mmol of pyromellitic dianhydride (1,2,4,5-benzenetetracarboxylic acid 1,2,4,5-dianhydride) **1**, 40.00 mmol of *L*-amino acid (**2a-e**), 80 mL of mixture in acetic acid, and a stirring bar were placed into a 250-mL round-bottomed flask. The mixture was stirred at room temperature for overnight and

refluxed for 4 h. The solvent was removed under reduced pressure, and the residue was dissolved in 100 mL of cold water, then the solution was decanted and 5 mL of concentrated HCl was added. A white precipitate was formed, filtered off, and dried to give a compound *N,N'*-(pyromellitoyl)-bis-*L*-amino acid **3a-e**. The yields and some physical properties of these compounds are shown in Table I.

1,3-Bis(4-nitrophenoxy) propane **6**

6.00 g, 43.11 mmol of 4-nitrophenol and 2.97 g, 21.55 mmol of K₂CO₃ were added to dimethylformamide (30 mL). A solution of 1,3-dibromopropane (4.17 g, 2.1 mL, 20.67 mmol) in dimethylformamide (4.31 mL) was added dropwise. The reaction mixture was heated for 6 h at 120°C, then cooled and poured onto crushed ice. The precipitated yellow product was isolated by filtration, dissolved in CH₂Cl₂, and washed successively with NaOH (2M), HCl (1M) and water. The CH₂Cl₂ solution was then dried over Na₂SO₄ and concentrated in vacuum, and the product was recrystallized from ethanol, affording 2.33 g (35.5%) of yellow solid, m.p. 134–135°C.

FTIR (KBr, cm⁻¹): 3092 (w), 2962 (w), 2833 (w), 1604 (s,sh), 1504 (s,sh), 1469 (m), 1340 (s,sh), 1259 (s), 1172 (m), 1111 (s), 1053 (m), 966 (m), 841 (s), 752 (m), 688 (m), 650 (m), 534 (w), 499 (w). ANAL. Calcd for C₁₅H₁₄N₂O₆: C, 56.6%; H, 4.4%; N, 8.8%. Found: C, 56.3%; H, 4.5%; N, 8.5%.

TABLE I
Synthesis of Chiral Diimide-acid Derivatives 3a-e

Entry	Amino acid compound	R	Mp (°C)	Yield of compound 3 (%)	[α] _D ^{25a}
3a	<i>L</i> -Alanine	CH ₃	291–293	72	-6.5
3b	<i>L</i> -Valine	(CH ₃) ₂ CH	277–279	76	-3.0
3c	<i>L</i> -Lucine	(CH ₃) ₂ CHCH ₂	292–294	88	+0.2
3d	<i>L</i> -Isoleucine	(C ₂ H ₅)(CH ₃)CH	266–268	86	-8.0
3e	<i>L</i> -phenyl alanine	PhCH ₂	295–297	70	+0.2

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

TABLE II
¹H NMR and FTIR Spectral and Elemental Analyses Data of Diimide-acid Derivatives 3a–e

Diimide-acid	Spectral data
3a	¹ H NMR (500MHz, DMSO-d ₆): δ 1.58–1.60 (d, 6H), 4.93–4.98 (q, 2H), 8.29 (s, 2H), 12.50–12.56 (s, br, 2H) ppm. FTIR (KBr): 3555(m, br), 2900–3100 (s, br), 1782 (s, sh), 1722 (s, br), 1485 (m), 1383 (s), 1257 (s), 1170 (m), 1024 (m), 850 (m), 728 (m) cm ⁻¹ . Analysis: Calculated for C ₁₆ H ₁₂ N ₂ O ₈ : C, 53.31; H, 3.33; N, 7.77; found: C, 53.24, H, 3.38, N, 7.24.
3b	¹ H NMR (500MHz, DMSO-d ₆): δ 0.84–0.85 (d, 6H), 1.06–1.07 (d, 6H), 2.54–2.617 (m, 2H), 4.52–4.54 (d, 2H), 8.32–8.33 (s, 2H), 12.50–13.50 (br, 2H) ppm. FT IR (KBr): 3400–2800 (m, br), 1780 (s, sh), 1730–1700 (s, br), 1471 (m), 1381 (s, br), 1370–1360 (s), 1290 (m), 1234 (m), 1153 (m), 1085 (s), 914 (m), 871 (m), 727 (m) cm ⁻¹ . Analysis: Calculated for C ₂₀ H ₂₀ N ₂ O ₈ : C, 57.69; H, 4.80; N, 6.73; found: C, 58.1; H, 4.9; N, 6.4.
3c	¹ H NMR (500MHz, DMSO-d ₆): δ 0.90–0.95 (d, 6H), 1.70–1.90 (m, 1H), 2.40–2.60 (m, 2H), 4.20–4.30 (t, 1H), 8.10–8.20 (m, 2H), 12.20–13.30 (s, br, 1H), ppm. 3000–3650 (m, br), 2980 (m), 1780 (m), 1760 (s), 1710 (s, br), 1460 (w), 1385 (s), 1370 (m), 1275 (m), 1240 (m), 1160 (m), 1120 (m), 1090 (m), 1060 (m), 820 (m), 830(m), 740 (m), 630 (m) cm ⁻¹ . Analysis: Calculated for C ₂₂ H ₂₄ N ₂ O ₈ : C, 59.40; H, 5.40; N, 6.30; found: C, 59.48; H, 5.46; N, 6.38.
3d	¹ H NMR (500MHz, DMSO-d ₆) δ 0.70–1.8 (m, 16H), 2.50 (m, 2H), 4.70 (dd, 2H, J = 9 Hz), 8.60 (s, 2H), 10.9 ppm (br, 2H). FTIR (KBr): 3000–3400 (s, br), 1775 (s), 1720 (s, br), 1460 (m), 1380 (s), 1360 (s), 1280 (s), 1170 (m), 1080 (s), 1010 (m), 925 (m, sh), 820 (w), 775 (m), 740 (m), 700 (m), 630 (m) cm ⁻¹ . Analysis: Calculated for C ₂₂ H ₂₄ N ₂ O ₈ : C, 59.45; H, 5.44; N, 6.30; found: C, 59.52; H, 5.49; N, 5.84.
3e	¹ H NMR (500MHz, DMSO-d ₆): δ 3.29–3.34 (dd, 2H); 3.49–3.53 (dd, 2H); 5.16–5.20 (dd, 2H); 7.09–7.11 (m, 2H); 7.15–7.16 (d, 8H); 8.20–8.21 (s, 2H); 8.57–8.58 (br, 2H) ppm. FTIR (KBr): 3500–2800 (m, br), 1776 (sh), 1740–1700 (s, br), 1383 (s), 1363 (s, sh), 1278 (m, br), 1101 (s), 941 (w), 883 (w), 827 (m), 756 (m), 727 (m) cm ⁻¹ . Analysis: Calculated for C ₂₈ H ₂₀ N ₂ O ₈ : C, 65.61; H, 3.93; N, 5.46; found: C, 65.80; H, 4.20; N, 5.20.

1,3-Bis(4-aminophenoxy) propane 7

A mixture of 1.00 g, 3.10 mmol of 1,3-bis (4-nitrophenoxy) propane **6** and 4.90 g of sodium sulfide in 150 mL of ethanol and 30 mL of water was refluxed for 10 h. After removal of the solvents by evaporation, the

residue was washed with water and dried under vacuum to afford 0.32 g (39.5%) of yellow solid, m.p: 109–112°C.

FTIR (KBr, cm⁻¹): 3391 (m), 3304 (w), 2958 (w), 2885 (w), 1620 (w), 1512 (s), 1471 (m), 1381 (w), 1336 (w),

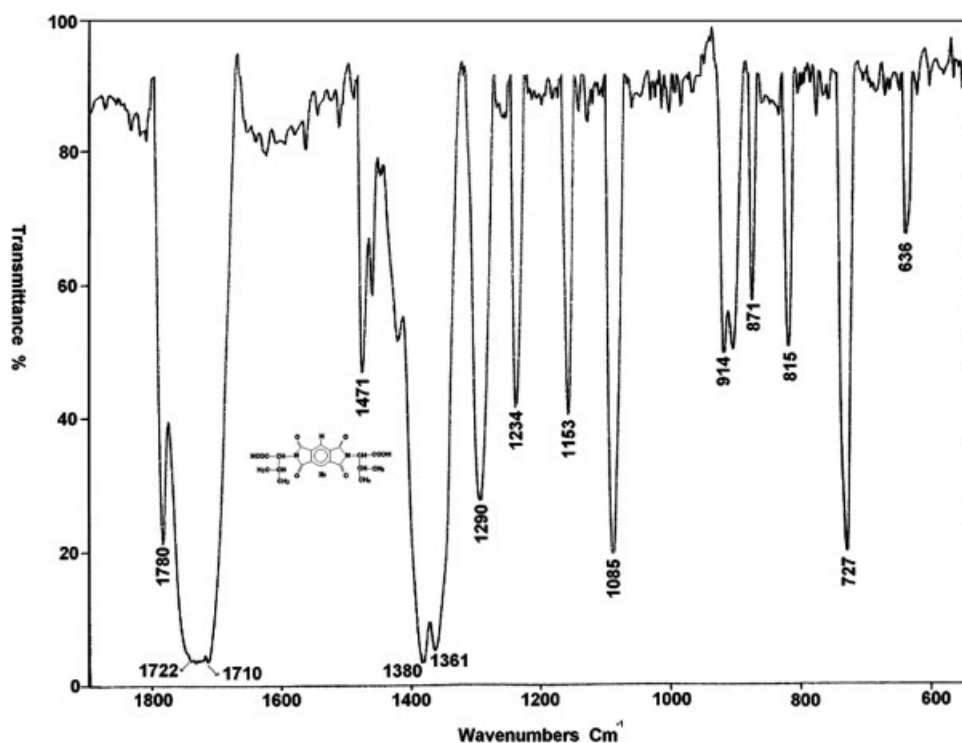


Figure 1 FTIR Spectra of *N,N'*-(pyromellitoyl)-bis-L-valine (**3b**).

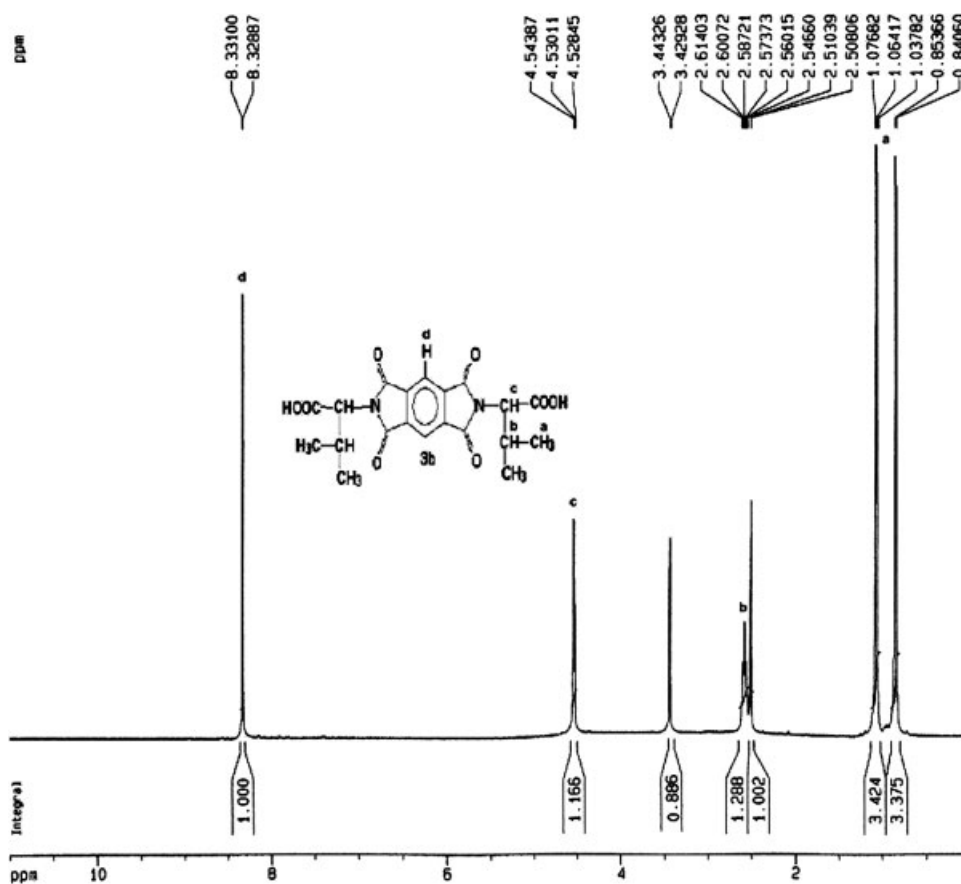


Figure 2 ¹H NMR Spectra of *N,N'*-(pyromellitoyl)-bis-L-valine (3b).

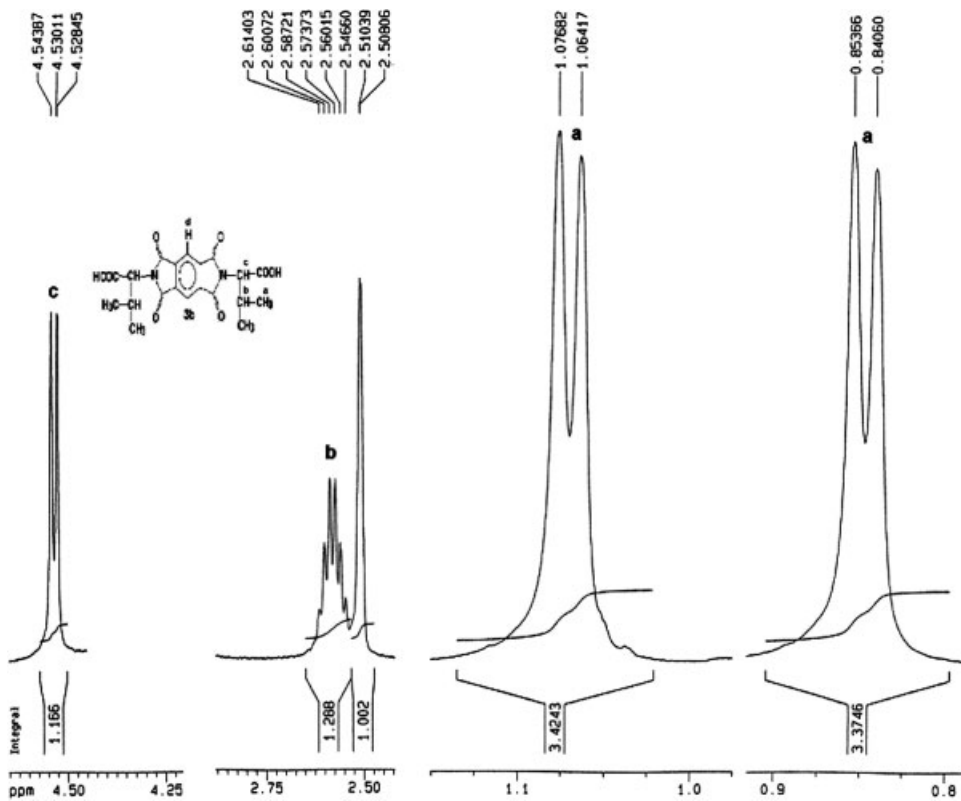
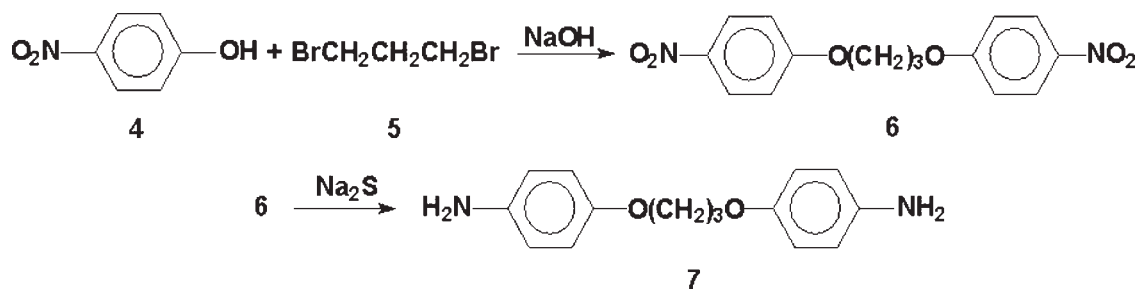


Figure 3 ¹H NMR Spectra of *N,N'*-(pyromellitoyl)-bis-L-valine (3b) [expanded].



Scheme 2

1296 (w), 1240 (s), 1170 (w), 1101 (w), 1062 (m), 997 (m), 972 (m), 825 (s), 723 (m), 690 (w), 520 (w). ^1H NMR (chloroform (CDCl_3), TMS, δ): 2.15–2.20 (m, 2H), 3.41 (br, 2H), 4.05–4.09 (t, 4H), 6.62–6.66 (d, 4H), 6.74–6.78 (d, 4H) ppm. ^{13}C NMR ($\text{DMSO}-d_6$, δ): 27 (1C, CH_2), 66 (2C, OCH_2), 114 (4C), 115 (4C), 142 (1C), 149 (1C) ppm. ANAL. Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_2$: C, 69.7%; H, 6.9%; N, 10.8%. Found: C, 69.6%; H, 6.7%; N, 10.6%.

Polymer synthesis

The PAIs **8a–e** were prepared by the following general procedure (using polymer **8a** as an example). *N,N'*-(pyromellitoyl)-bis-*L*-alanine **3a** (0.115 g, 0.32 mmol), 1,3-bis(4-aminophenoxy) propane **7** (0.082 g, 0.32 mmol), calcium chloride (0.100 g, 0.90 mmol), triphenyl phosphite (0.84 mL, 3.00 mmol), pyridine (0.18 mL), and *N*-methyl-2-pyrrolidone (0.80 mL) were placed into a 25-mL round-bottomed flask, which was fitted with a stirring bar. The reaction mixture was heated under reflux on an oil bath at 100°C for 6 h.

Then, the reaction mixture was poured into 50 mL of methanol and the precipitated polymer was collected by filtration and washed thoroughly with hot water and methanol and dried at 60°C for 12 h under vacuum to leave 0.171 g (92%) white solid polymer **8a**. The PAIs **8a–e** were analyzed by using FTIR spectroscopy.

RESULTS AND DISCUSSION

Monomer synthesis

The asymmetric diimide acids **3a–e** were synthesized by the condensation reaction of pyromellitic dianhydride (1,2,4,5-benzenetetracarboxylic acid 1,2,4,5-dianhydride) **1** with two equimolar of *L*-alanine **2a**, *L*-valine **2b**, *L*-leucine **2c**, *L*-isoleucine **2d**, and *L*-phenyl alanine **2e** in an acetic acid solution. The chemical structure and purity of the optically active diimide acids **3a–e** were proved by using elemental analysis, FTIR, and ^1H NMR spectroscopic techniques and

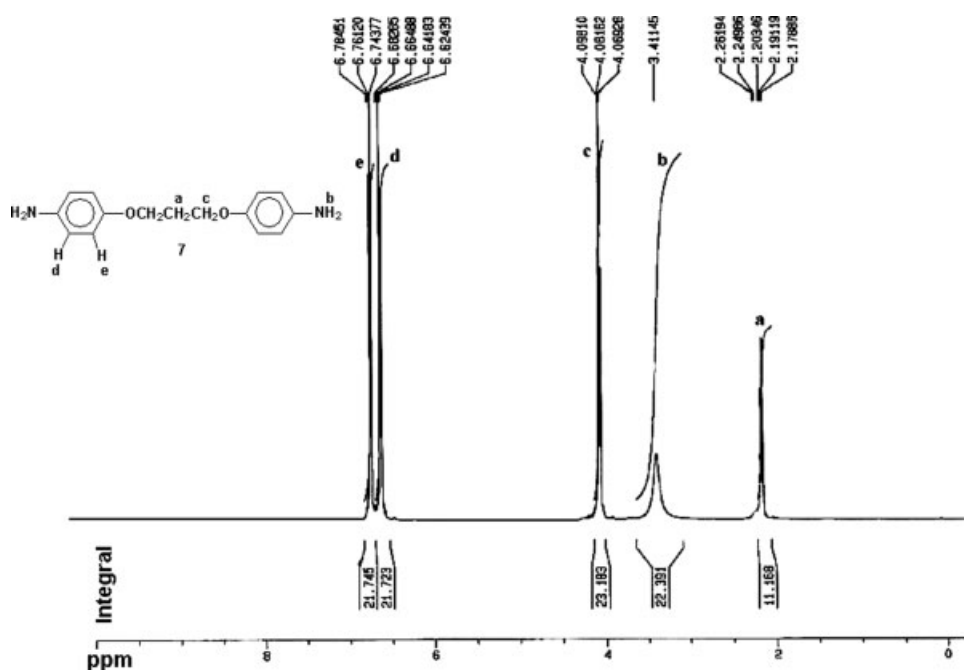
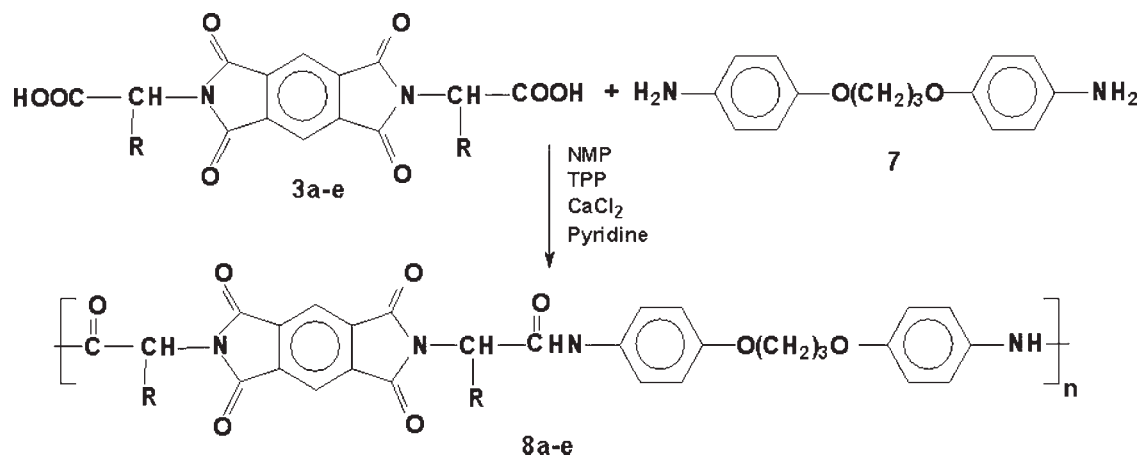


Figure 4 ^1H NMR Spectra of 1,3-Bis(4-aminophenoxy) propane 7.



Scheme 3

these data were shown in Table II. As an example, the FTIR spectrum of *N,N'*-(pyromellitoyl)-bis-*L*-valine **3b** showed a broad peak between 2800 and 3400 cm^{-1} , which was assigned to the COOH groups and two absorption bands at 1780 and 1722 cm^{-1} due to carbonyl of imide (asymmetrical and symmetrical C=O stretching vibration), 1710 cm^{-1} (C=O stretching of acidic group), and 1380, 1085, 727 cm^{-1} (imide ring deformation) (Fig. 1).

The ^1H NMR spectrum of diacid **3b** showed peaks between 0.84 and 1.07 ppm as a doublet of doublet, which were assigned for two CH_3 (a) of isopropyl groups that show a diastrotopic splitting manner, and peaks between 2.54 and 2.61 ppm as a multiplet, which was assigned to the CH (b) proton of isopropyl groups, and peaks between 4.52 and 4.54 ppm as a doublet, which was assigned to the CH(c) proton, which is a chiral center. The peak at 8.32 ppm was assigned to aromatic proton (d). Also a broad peak between 12.5 and 13.5 ppm was assigned to COOH group (Figs. 2 and 3).

Also 1,3-bis(4-aminophenoxy) propane **7** was synthesized by using a two-step reaction. At first 1,3-bis(4-nitrophenoxy) propane **6** was prepared from the reaction of 4-nitrophenol **4** with 1,3-dibromopropane **5** in NaOH solution. Then, the dinitro compound **6** was reduced by using Na_2S (Scheme 2). The chemical

structure and purity of compounds **6** and **7** were proved with elemental analysis, ^1H NMR, ^{13}C NMR and FTIR spectroscopy. The measured results in elemental analyses of these compounds were closely corresponded to the calculated ones, demonstrating that the expected compounds were obtained. The FTIR spectrum of compound **7** showed two peaks at 3391 and 3304 cm^{-1} , which were assigned to the NH_2 groups.

^1H NMR spectrum of compound **7** showed a peak as a multiple at 2.17–2.26 ppm was assigned to the H_a protons of the methylene and a peak as a triplet at 4.06–4.09 ppm, which was assigned to the H_c protons of the methylene bonded to oxygen. Also a broad singlet peak at 3.41 ppm which was assigned to the H_b protons of the NH_2 groups. Peaks between 6.62 and 6.78 ppm (as a doublet) which were assigned to the H_d and H_e protons of the aromatic ring (Fig. 4). Also ^{13}C NMR spectrum of compound **7** showed six different carbon atoms.

Polymer synthesis

PAIs **8a–e** were synthesized by the direct polycondensation reaction of an equimolar mixture of diacid **3a–e**

TABLE IV
Elemental Analysis of Aromatic PAIs **8a–e**

Polymer	Formula		C%	H%	N%
8a	$\text{C}_{31}\text{H}_{26}\text{N}_4\text{O}_8$ (582.31) _n	Calcd	63.93	4.46	9.61
		Found	63.00	4.20	9.10
8b	$\text{C}_{35}\text{H}_{34}\text{N}_4\text{O}_8$ (638.35) _n	Calcd	65.84	5.32	8.77
		Found	65.20	5.00	8.10
8c	$\text{C}_{37}\text{H}_{38}\text{N}_4\text{O}_8$ (666.37) _n	Calcd	66.68	5.70	8.40
		Found	66.00	5.40	7.90
8d	$\text{C}_{37}\text{H}_{38}\text{N}_4\text{O}_8$ (666.37) _n	Calcd	66.68	5.70	8.40
		Found	66.00	5.20	8.10
8e	$\text{C}_{43}\text{H}_{34}\text{N}_4\text{O}_8$ (734.43) _n	Calcd	70.31	4.62	7.62
		Found	69.90	4.30	7.00

TABLE III
Synthesis and Some Physical Properties of PAIs **8a–e**

Diimide-acid	Polymer	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_{\text{D}}^{25}$ ^a
3a	8a	92	0.34	−11.5
3b	8b	90	0.46	−9.0
3c	8c	88	0.44	−6.2
3d	8d	91	0.65	−14.0
3e	8e	93	0.60	−18.0

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

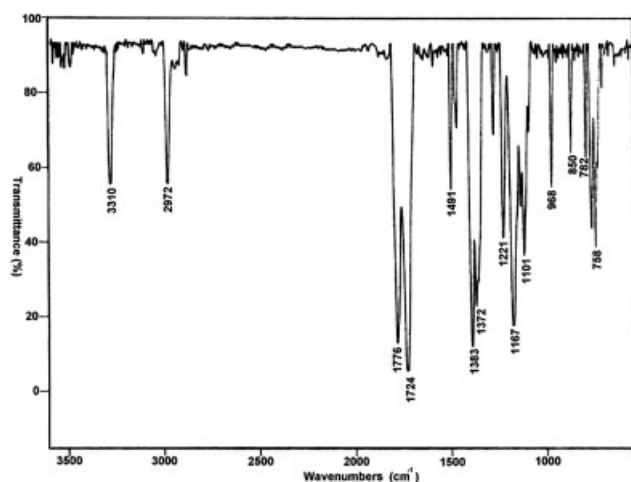


Figure 5 FTIR Spectra of PAIs 8b.

with 1,3-bis(4-aminophenoxy) propane 7 in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine (Scheme 3). The syntheses and some physical properties of these new PAIs 8a–e are given in Table III. The entire polycondensation reaction readily proceeded in a homogeneous solution, tough and stringy precipitates formed when the viscous PAIs solution was obtained in good yields.

Polymer characterization

The syntheses and some physical properties of PAIs 8a–e are summarized in Table III. These polymers had inherent viscosities around 0.34–0.65 dL/g and show white crystal. These polymers were confirmed to be PAIs with FTIR spectroscopy and elemental analyses (Table IV). A representative FTIR spectrum of polymer 8b is shown in Figure 5. FTIR spectrum shows N–H stretching vibration of amide group at 3310 cm^{-1} and disappearing of OH stretching vibration of COOH groups in this polymer.

TABLE V
Thermal Behavior of Aromatic PAIs 8a–e

Polymer	T_g (°C)	T_5 (°C) ^a	T_{10} (°C) ^a	Char yield ^b
8a	150	375–380	400–405	30
8b	130	350–355	360–365	35
8c	135	315–320	355–360	11
8d	140	345–350	385–390	62
8e	160	380–385	410–415	56

^a Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10°C/min in N_2 , respectively.

^b Percentage weight of material left undecomposed after TGA analysis at 600°C.

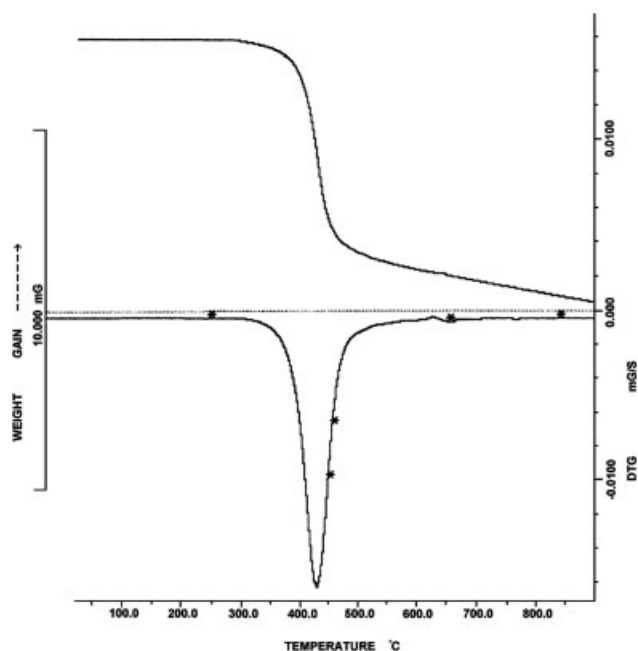


Figure 6 TGA and DTG thermograms of PAIs 8a.

The elemental analyses of the resulting polymers are in good agreement with the calculated values for the proposed structures (Table IV).

The solubility of PAs 8a–e was investigated with 0.01 g polymeric samples in 2 mL of solvent. All of the polymers are dissolved in organic solvents such as DMF, DMAC, DMSO, and NMP at room temperature and are insoluble in solvent such as chloroform, methylene chloride, methanol, ethanol, and water.

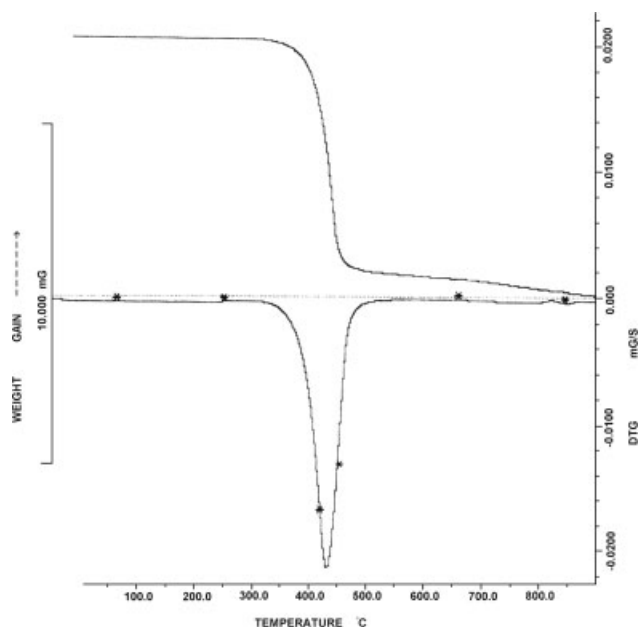


Figure 7 TGA and DTG thermograms of PAIs 8c.

Thermal properties

The thermal properties of polyamides **8a–e** were investigated by TGA and DTG in a nitrogen atmosphere at a rate of heating of $10^{\circ}\text{C}/\text{min}^{-1}$, and the thermal data are summarized in Table V (Figs. 6 and 7). The initial decomposition temperatures of 5 and 10% weight losses (T_5 and T_{10}) and the char yield at 600°C for them are summarized in Table V. These polymers exhibited good resistance to thermal decomposition, up to $375\text{--}385^{\circ}\text{C}$ in nitrogen, and began to decompose gradually above that temperature. T_5 for polymers ranged from 375 to 385°C and T_{10} for all polymers ranged from 400 to 415°C , and the residual weight for these polymers at 600°C ranged from 11 to 19% in nitrogen. Results show that PAIs **8a** and **8e** have better thermal stability and higher Tg temperatures. This is because of the presence of methyl and benzyl as a side chain in the structure of these polymers.

CONCLUSIONS

This work involved the syntheses of several new PAIs **8a–e** through the direct polycondensation reaction of five chiral diacids **3a–e** with 1,3-bis(4-aminophenoxy)propane **7** by using triphenyl phosphite, NMP, calcium chloride, and pyridine as condensing agents. These new PAIs are optically active, are soluble in various organic solvents and have good thermal stability. These resulting novel polymers have the potential to be used in column chromatography technique for the separation of the enantiomeric mixtures.

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