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ORIGINAL PAPER

Synthesis and characterization of new optically active poly(amide-imide)s containing 1,3,4-oxadiazole moiety in the main chain

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Abstract Six new optically active poly(amide-imide)s were synthesized by poly condensation reaction of 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (**8**) with six chiral *N*,*N*′-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic)-bis-L-amino acids (**3a**–**f**) in a medium consisting of *N*-methyl-2-pyrrolidone (NMP), triphenylphosphite (TPP), calcium chloride ($CaCl_2$), and pyridine. Chiral *N*,*N*′-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic)-bis-L-amino acids (**3a**–**f**) were obtained by the reaction of bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (**1**) with two equimolar of L-alanine (**2a**), L-valine (**2b**), L-leucine (**2c**), L-isoleucine (**2d**), L-phenyl alanine (**2e**), and L-2-aminobutyric acid (**2f**) in acetic acid. The poly condensation reaction produced a series of novel poly(amide-imide)s (**9a**–**f**) in high yield and with inherent viscosities between 0.30 and 0.52 dL/g. The resulting polymers were characterized by elemental analysis, viscosity measurement, solubility testing, thermo-gravimetric analysis (TGA), ^{1}H-NMR, and FT-IR techniques.

Keywords Poly(amide-imide) · 1,3,4-Oxadiazole · Polycondensation · Optically active polymer

Introduction

Thermally stable polymers have received more interest over the past decade, due to increasing demands for high-performance polymers to be replaced for ceramics or metals in the microelectronic, aerospace, and automotive industries [1–3].

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Poly(amide-imide)s (PAIs) are a class of high-performance polymers which show excellent mechanical and thermal properties and are also solvent resistant [4, 5]. There is a growing interest in PAIs for a variety of applications, as they retain good mechanical properties at high temperatures and are more processable than other aromatic thermostable polymers, such as polyamides and polyimides [6]. Several attempts have been made to modify the PAIs structure by introducing the functional groups or substitutions which are capable of reducing the chain rigidity and further increasing their tractability and applicability [7–9].

Nature uses chirality as one of the key structural factors to perform a series of complicated functionalities such as molecular recognition and catalytic activities [10]. Synthesis and characterization of optically active polymers have been a challenging theme in the field of polymer synthesis in recent years for their important applications as catalysts for asymmetric synthesis and as chiral stationary phases (CSP) for the direct optical resolution of enantiomers [11–13]. Optically active polymers can be obtained by polymerization of optically active monomers or by stereo selective polymerization of racemic or prochiral monomers using optically active catalysts.

Recently, we have synthesized a variety of optically active polymers by incorporation of optically active segments in polymer's backbone. In addition to optical properties of these polymers, the solubility of them was improved without significant loss of mechanical and thermal properties [14–18].

On the other hand, it was shown that aromatic polymers containing 1,3,4-oxadiazole rings in the main chain exhibit high thermal resistance in oxidative atmosphere, good hydrolytic stability, low dielectric permittivity, high toughness, and other special properties which are determined by the electronic structure of this particular heterocycle [19–23]. The incorporation of oxadiazole and imide rings together with flexible groups in the polymer chain is expected to provide a combination of high-performance properties and processability, particularly in thin films and coatings.

In this report, we have described synthesis and characterization of new optically active PAIs containing 1,3,4-oxadiazole unit in the main chain, which were obtained by the polycondensation reaction of 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (**8**) with six chiral *N*,*N*′-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic)-bis-L-amino acids (**3a**–**f**) using *N*-methyl-2-pyrrolidone (NMP), triphenylphosphite (TPP), and pyridine as condensing agents.

Experimental

Materials

All chemicals were purchased from Fluka Chemical Co. and Aldrich Chemical Co. *N*,*N*-dimethyl acetamide (DMAc), NMP, and acetic anhydride were purified by distillation under reduced pressure. Commercially obtained calcium chloride was dried under vacuum at 150 °C for 10 h before use.

Measurements

IR spectra were recorded on Galaxy series FT-IR 5000 spectrophotometer (England). Band intensities are assigned as weak (w), medium (m), and strong (s), and band shapes as shoulder (sh), sharp (s), and broad (br). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 300 MHz instrument (Germany). Inherent viscosity was measured by a standard procedure using a Technico® viscometer. Specific rotations were measured by an A-Kruss polarimeter. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TA 4000 System under N_2 atmosphere at the rate of 10 °C/min. Elemental analyses were performed by Vario EL equipment by Arak University.

Monomer synthesis

*Synthesis of N,N′-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic)-bis-*L*-amino acids (**3a–f**)*

Into a 250-mL round-bottomed flask were placed (1.250 g, 5 mmol) of bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (**1**), 10 mmol of L-amino acids (**2a–f**), and 100 mL concentrate acetic acid. The mixture was stirred at room temperature for 8 h and then refluxed for 5 h. The solvent was removed under reduced pressure and 5 mL cold concentrated HCl added to the residue until a white precipitate formed. The precipitate was washed with cold water and dried under reduced pressure to give compounds *N,N′*-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic)-bis-L-amino acids **3a–f**.

Diacid (**3a**): ^{1}H-NMR (DMSO-d_6, δ ppm): 12.87–12.93 (s, br, 2H), 5.95–5.98 (t, 2H), 4.50–4.57 (q, 1H), 3.37 (s, 2H), 3.16–3.25 (m, 4H), 1.23–1.25 (d, 6H). ^{13}C-NMR (DMSO-d_6, δ ppm): 176.82, 170.61, 130.64, 47.55, 42.47, 33.89, 14.49. FTIR (KBr, cm^{-1}): 2561–3100 (m, sh, br), 1770 (w), 1705 (s, br), 1628 (w), 1467 (w), 1396 (m), 1309 (m), 1207 (m), 1126 (w), 976 (w), 675 (w), 611 (w). Elemental analysis: calcd for $C_{18}H_{18}N_2O_8$: C, 55.39; H, 4.65; N, 7.18; found: C, 54.45; H, 4.56; N, 7.11.

Diacid (**3b**): ^{1}H-NMR (DMSO-d_6, δ ppm): 12.88 (s, br, 2H), 5.99–6.09 (m, 2H), 4.12–4.15 (d, 2H), 3.45 (D_2O exchange, s, 2H), 3.18–3.25 (D_2O exchange, t, 4H), 2.32–2.39 (m, 2H), 0.92–0.94 (d, 6H), 0.66–0.68 (d, 6H). ^{13}C-NMR (DMSO-d_6, δ ppm): 177.23, 169.55, 131.51, 57.70, 42.61, 33.84, 27.96, 21.28, 19.60. FTIR (KBr, cm^{-1}): 2500–3400 (m, br), 1709–1770 (s, br), 1390 (s), 1199 (s, sh), 1068 (m), 775 (w), 700 (m), 603 (w). Elemental analysis: calcd for $C_{22}H_{26}N_2O_8$: C, 59.19; H, 5.87; N, 6.27; found: C, 58.98; H, 5.87; N, 6.25.

Diacid (**3c**): ^{1}H-NMR (DMSO-d_6, δ ppm): 12.70 (s, br, 2H), 5.93–6.01 (m, 2H), 4.44–4.49 (dd, 2H, $J = 6, 3$ Hz), 3.40 (s, 2H), 3.21–3.30 (m, 4H), 1.85 (m, 2H), 1.65 (m, 2H), 1.25 (m, br, 2H), 0.75–0.81 (q, 12H). ^{13}C-NMR (DMSO-d_6, δ ppm): 177.09, 170.46, 130.97, 50.73, 42.44, 36.62, 33.80, 24.60, 23.47, 21.14. FTIR (KBr, cm^{-1}): 2500–3200 (m, br), 1770 (w), 1710 (s, br), 1628 (w), 1460 (m), 1380 (m), 1309 (m), 1207 (w), 1126 (w), 976 (w), 670 (w), 600 (w). Elemental analysis: calcd for $C_{24}H_{30}N_2O_8$: C, 60.75; H, 6.37; N, 5.90; found: C, 60.25; H, 6.22; N, 5.88.

Diacid (**3d**): ^{1}H-NMR (DMSO-d$_6$, δ ppm): 12.8 (s, br, 2H), 5.97–6.03 (m, 2H), 4.18–4.21 (d, 2H), 3.22–3.30 (m, 6H), 2.14–2.19 (m, 2H), 1.30–1.37 (m, 2H), 0.85–0.91 (d, 6H), 0.71–0.74 (t, 6H). ^{13}C-NMR (DMSO-d$_6$, δ ppm): 177.59, 169.66, 131.27, 57.03, 42.40, 33.67, 25.24, 16.90, 10.87. FTIR (KBr, cm^{-1}): 2500–3400 (m, br), 1772 (w), 1744 (s, sh), 1709 (s, sh), 1390 (s), 1232 (w), 1225 (m), 806 (w), 717 (w), 599 (w), 314 (m). Elemental analysis: calcd for $C_{24}H_{30}N_2O_8$: C, 60.75; H, 6.37; N, 5.90; found: C, 60.45; H, 6.21; N, 5.91.

Diacid (**3e**): ^{1}H-NMR (DMSO-d$_6$, δ ppm): 13.15 (s, br, 2H), 7.21–7.23 (q, 6H), 7.02–7.03 (t, 4H), 4.85–4.91 (dd, br, 2H, $J = 6, 6$ Hz), 3.25–3.31 (dd, 2H, $J = 12, 3$ Hz), 3.10–3.12 (d, 2H, $J = 6$ Hz), 3.01–3.05 (d, 4H, $J = 12$ Hz), 2.92–2.94 (d, 2H, $J = 6$ Hz). ^{13}C-NMR (DMSO-d$_6$, δ ppm): 176.69, 169.94, 132.02, 129.32, 128.53, 126.98, 53.07, 42.24, 42.11, 33.45, 33.24. FTIR (KBr, cm^{-1}): 2600–3500 (m, br), 1776 (w), 1703 (s, br), 1498 (w), 1398 (w), 1394 (s), 1234 (m, br), 1174 (s), 933 (w), 698 (m). Elemental analysis: calcd for $C_{30}H_{26}N_2O_8$: C, 66.41; H, 4.83; N, 5.16; found: C, 66.41; H, 4.82; N, 5.10.

Diacid (**3f**): ^{1}H-NMR (DMSO-d$_6$, δ ppm): 12.95 (s, br, 2H), 6.01–6.10 (m, 2H), 4.33–4.38 (dd, 2H, $J = 6, 3$ Hz), 3.43 (D_2O-exchang, s, br, 2H), 3.20–3.27 (D_2O-exchang, q, 4H), 1.91–1.93 (m, 2H), 1.79–1.81 (m, 2H), 0.66–0.71 (t, 6H). ^{13}C-NMR (DMSO-d$_6$, δ ppm): 177.14, 170.19, 131.06, 56.50, 42.41, 33.79, 21.23, 11.06. FTIR (KBr, cm^{-1}): 2650–3400 (m, br), 1776 (s, br), 1498 (w), 1390 (s), 1224 (m, br), 1170 (s), 933 (w), 698 (m). Elemental analysis: calcd for $C_{20}H_{22}N_2O_8$: C, 57.41; H, 5.30; N, 6.70; found: C, 57.34; H, 5.29; N, 6.70.

*Synthesis of N′-(4-nitrobenzoyl)-4-nitrobenzohydrazide (**6**)*

Into a 100-mL round-bottomed flask fitted with a magnetic stirrer was placed a solution of 4-nitrobenzoyl chloride (10 g, 53.9 mmol) and triethylamine (4 mL) in 40 mL of dry dimethylacetamide (DMAc). The reaction mixture was cooled in an ice water bath. To this solution, 6 mL of hydrazine monohydrate 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 100 °C to yield **6** (6.5 g, 73%). Mp = 290–292 °C, FT-IR: 3221 (s, br), 3111 (w), 1619 (s), 1587 (s), 1529 (s), 1465 (s), 1348 (s), 1261 (w), 1109 (w), 837 (m), 715 (m) cm^{-1}.

*Synthesis of 2,5-bis(4-nitrophenyl)-1,3,4-oxadiazole (**7**)*

Into a 50-mL round-bottomed flask, 4 g (12.0 mmol) of *N′*-(4-nitrobenzoyl)-4-nitrobenzohydrazide (**6**), 30 mL of phosphoryl trichloride, and a stirring bar were placed. The stirrer was started, and the mixture was refluxed for 12 h. The reaction mixture was cooled at room temperature and poured into ice-water then precipitated. The precipitate was filtered, washed with water, and then dried to afford **7** (3.5 g, 87%). Mp $\geq$ 300 °C, FT-IR: 3109 (w), 1612 (m), 1583 (s), 1515 (s), 1469 (m), 1350 (s), 1109 (w), 866 (m), 717 (m) cm^{-1}.

Synthesis of 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (BAO) (8)

Two grams (6.4 mmol) of the 2,5-bis(4-nitrophenyl)-1,3,4-oxadiazole (**7**), 0.2 g of 10% Pd–C and 50 mL of ethanol were introduced into a 100-mL round-bottomed flask to which 12 mL of hydrazine monohydrate was added dropwise over a period of 1 h at 85 °C. After the complete addition, the reaction was continued at reflex temperature for another 5 h. Then, the mixture was filtered to remove the Pd–C, and the filtrate was poured into water. The product was filtered off, washed with water, and dried to afford **8** (1.2 g, 74%). Mp = 260–261 °C, FT-IR: 3325 (m), 3215 (m), 1608 (s), 1493 (s), 1438 (w), 1273 (w), 1178 (m), 1080 (w), 831 (w), 746 (w) cm^{-1}. ^{1}H-NMR (DMDO-d$_6$): $\delta = 7.71$ (d, $J = 8.7$, 4H), 6.69 (d, $J = 8.7$, 4H), 5.86 (s, 4H) ppm. ^{13}C-NMR (DMDO-d$_6$): $\delta = 168.6$, 157.2, 133.0, 118.8, 115.4.

Polymer synthesis

As a typical example, PAI **9d** was prepared as follows. Into a 50-mL round-bottom flask, 0.309 g (0.652 mmol) of *N*,*N*′-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic)-bis-L-isoleucine (**3d**), 0.164 g (0.652 mmol) 2,5-bis(4-nitrophenyl)-1,3,4-oxadiazole (**8**), 0.1 g of calcium chloride, 1 mL of NMP, 0.8 mL of triphenyl phophite, and 0.3 mL of pyridine and a stirring bar were placed. The mixture was stirred at room temperature for 2 h and then was heated while stirring at 120–130 °C for 8 h. At the end of the reaction, for quench growth polymer chain, the polymer solution was slowly trickled into stirred methanol, giving rise to a stringy precipitate, which was washed thoroughly with hot methanol, collected by filtration and dried at 80 °C for 12 h under vacuum to leave 0.378 g (84%) of solid polymer (**9d**).

The PAIs (**9a–f**) were analyzed using FT-IR spectroscopy:

Polymer (**9a**): FT-IR (KBr): 3360 (m, br), 2945 (w), 1772 (w), 1707 (s), 1606 (m), 1525 (w), 1496 (s), 1390 (s), 1317 (m), 1249 (w), 1182 (m), 1122 (w), 1066 (w), 846 (w), 746 (w) cm^{-1}.

Polymer (**9b**): FT-IR (KBr): 3344 (m, br), 3117 (w), 2964 (w), 1772 (w), 1709 (s), 1606 (m), 1525 (w), 1494 (s), 1381 (m), 1313 (m), 1182 (m), 1068 (w), 1012 (w), 912 (w), 848 (m), 748 (w), 704 (w) cm^{-1}.

Polymer (**9c**): FT-IR (KBr): 3381 (m, br), 2960 (m), 1774 (w), 1709 (s), 1608 (m), 1525 (w), 1496 (s), 1386 (m), 1313 (w), 1251 (w), 1182 (m), 1068 (w), 846(w), 748 (w) cm^{-1}.

Polymer (**9d**): FT-IR (KBr): 3390 (w, br), 2968 (w), 1774 (w), 1710 (s), 1608 (m), 1494 (m), 1381 (m), 1313 (w), 1253 (w), 1184 (m), 1068 (w), 848 (w), 748 (w) cm^{-1}.

Polymer (**9e**): FT-IR (KBr): 3367 (m, br), 3030 (w), 2930 (w), 1774 (w), 1709 (s), 1606 (s), 1525 (w), 1496 (s), 1315 (m), 1249 (m), 1180 (s), 1070 (w), 939 (w), 844 (w), 746 (m), 698 (m) cm^{-1}.

Polymer (**9f**): FT-IR (KBr): 3381 (m, br), 2974 (w), 1774 (w), 1709 (s), 1606 (m), 1525 (w), 1496 (s), 1384 (s), 1317 (m), 1248 (w), 1182 (m), 1068 (w), 844 (w), 746 (w) cm^{-1}.

Results and discussion

Monomer synthesis

The new asymmetric diacid series **3a–f** were synthesized by the condensation reaction of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1** with two equimolars of various amino acids such as L-alanine **2a**, L-valine **2b**, L-leucine **2c**, L-isoleucine **2d**, L-phenyl alanine **2e**, and L-2-aminobutyric acid **2f** in an acetic acid solution (Scheme 1). The yields and some physical properties of these compounds are shown in Table 1.

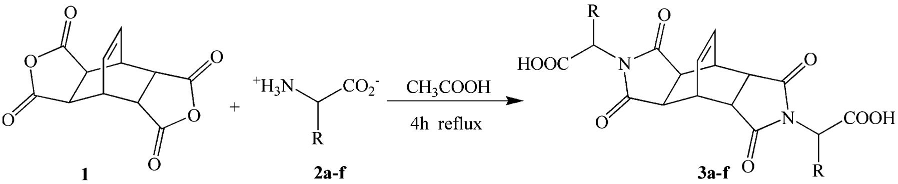
The chemical structure and purity of the optically active diacids **3a–f** were proved using elemental analysis, FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopic techniques.

The FT-IR spectra of all *N*,*N*′-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **3a–f** showed absorption around 2500 and 3400 cm^{-1}, which was assigned to the COOH groups. Peaks appearing around 1700–1770 cm^{-1} (acid C=O and symmetric imide stretching), 1390 and 700 cm^{-1} (imide characteristic ring vibration) confirmed the presence of imide ring and carboxylic groups in these compounds.

As an example, the ^{1}H-NMR spectrum of diacid **3d** is shown in Fig. 1. The peak relevant to O–H carboxylic acid groups appeared at 12.82 ppm. The peak in 4.19–4.21 ppm as a doublet which was assigned to CH(b) protons as a chiral center, peaks between 0.72 and 0.92 ppm were assigned to aliphatic CH_3(e, f). Also olefin protons (H_i) in bicyclo ring appeared in 5.00–5.02 ppm.

The ^{13}C-NMR spectrum of diacid (**3d**) shown 10 signals, including C_h and C_i in carboxylic acid and imide rings, C_g was related to carbon atoms olefin and C_f was relevant to chiral carbon atoms (Fig. 2).

Also, 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (**8**) was synthesized by using a three-step reaction. At first *N*′-(4-nitrobenzoyl)-4-nitrobenzohydrazide (**6**) was prepared from condensation of two equivalents of 4-nitrobenzoyl chloride (**4**) with hydrazine monohydrate (**5**) at triethylamine in DMAc solution (Scheme 2).



	2a	2b	2c	2d	2e	2f
R	Alanine	Valine	Leucine	Isoleucine	Phenyl alanine	2-Aminobutyric acid
	CH_3	$CH(CH_3)_2$	$CH_2CH(CH_3)_2$	$CH_3CHC_2H_5$	CH_2Ph	CH_2CH_3

Scheme 1 Preparation of asymmetric diacids (**3a–f**)

Table 1 Synthesis and some physical properties of diacid derivatives **3a–f**

Entry	Amino acid compound	R	Mp (°C)	Yield (%)	$[\alpha]_{25}^{D}$ [a]
3a	L-Alanine	CH_3	249–250	92	+155.7
3b	L-Valine	$(CH_3)_2CH$	318–320	93	+138.4
3c	L-Leucine	$(CH_3)_2CHCH_2$	389–390	94	+146.8
3d	L-Isoleucine	$(C_2H_5)(CH_3)CH$	293–295	92	+156.2
3e	L-Phenyl alanine	$PhCH_2$	247–248	91	+160.2
3f	L-2-Aminobutyric acid	CH_3CH_2	251–253	93	+130.2

[a] Measured at a concentration of 0.5 g/dL in DMF at 25 °C

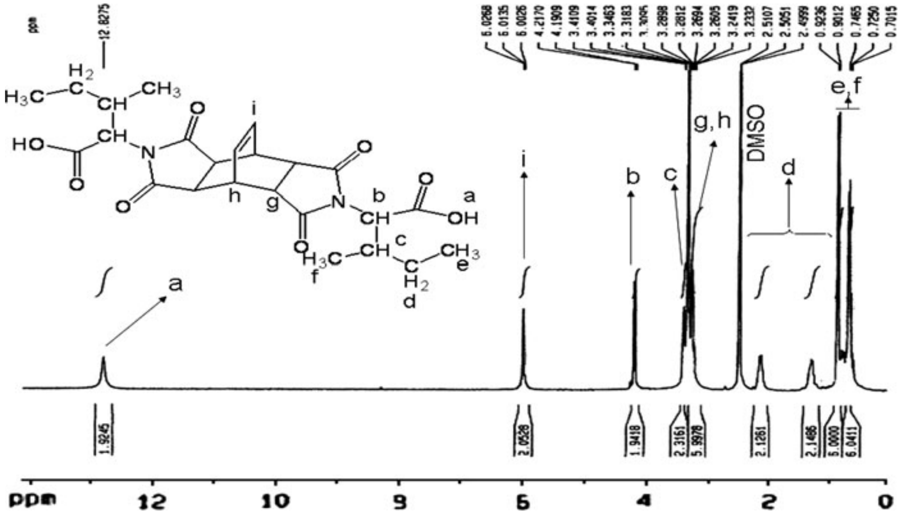


Fig. 1 ^{1}H-NMR spectrum of diacid **3b**

Then *N′*-(4-nitrobenzoyl)-4-nitrobenzohydrazide (**6**) was cyclized to 2,5-bis(4-nitrophenyl)-1,3,4-oxadiazole (**7**) with phosphorus oxychloride as anhydrous reagent under reflux conditions. Finally, the 2,5-bis(4-nitrophenyl)-1,3,4-oxadiazole (**7**) reduced by using Pd/C to produce 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (**8**) (Scheme 2). The chemical structure and purity of compound **8** were determined by elemental analysis, FT-IR, and ^{1}H-NMR spectroscopic techniques. The ^{1}H-NMR spectrum of compound **8** showed a peak at 5.86 ppm, which was assigned to the H(c) protons of the NH_2 groups. Peaks at $\delta = 6.60$ and $\delta = 7.72$ were assigned to the H(b) and H(a) protons of the phenyl rings (Fig. 3).

Polymer synthesis

Poly(amide-imide)s **9a–f** were synthesized by direct polycondensation reaction of an equimolar mixture of diacids (**3a–f)** with diamine (**8**) (Scheme 3).

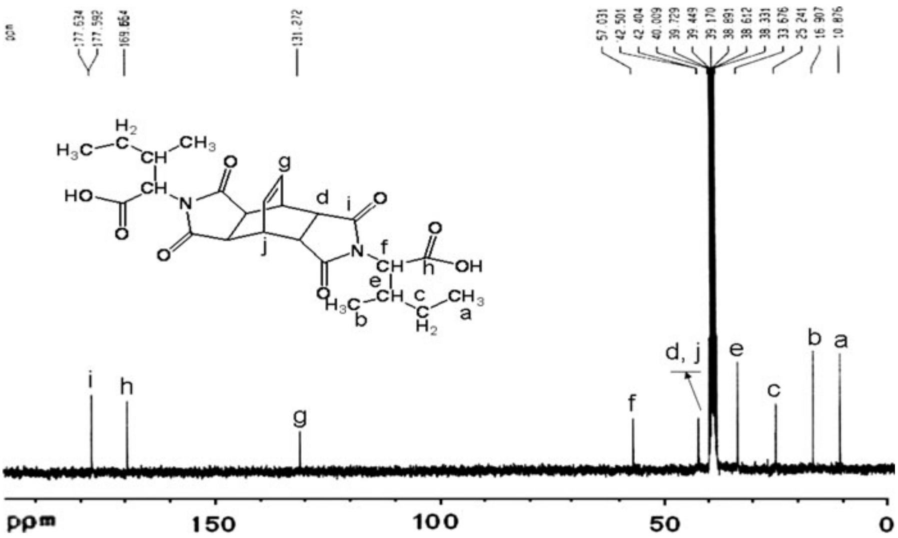
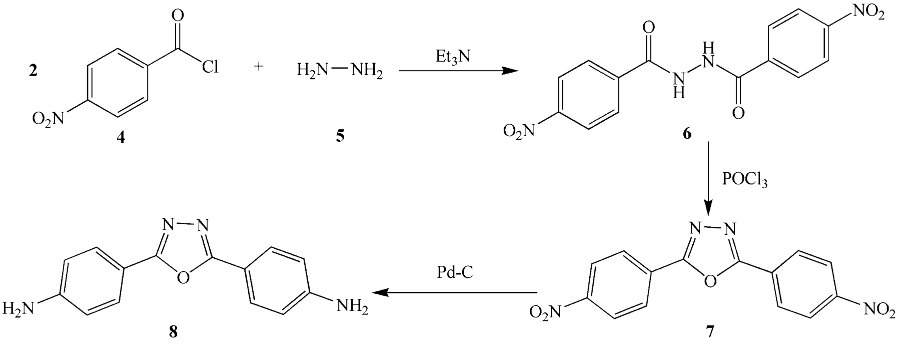


Fig. 2 ^{13}C-NMR spectrum of diacid **3b**



Scheme 2 Synthesis of 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (**8**)

The synthesis and some physical properties of these novel optically active PAIs are given in Table 2. The entire polycondensation readily proceeded in a homogeneous solution. Tough and stringy precipitates formed when the viscous PAIs solutions were trickled into the stirred methanol. All the polymers were obtained in quantitative yields with moderate inherent viscosities (0.30–0.52 dL/g).

One of the main methods for synthesis of optically active polymers is incorporation of chiral segments in monomer structure. In this study, we used chiral amino acids **2a–f** for synthesis of chiral diacids **3a–f**. Also resulting polymers due to the presence of chiral amino acid moieties **2a–f** in the polymer backbone are optically active and specific rotations measured at a concentration of 0.5 g/dL in DMF at 25 °C.

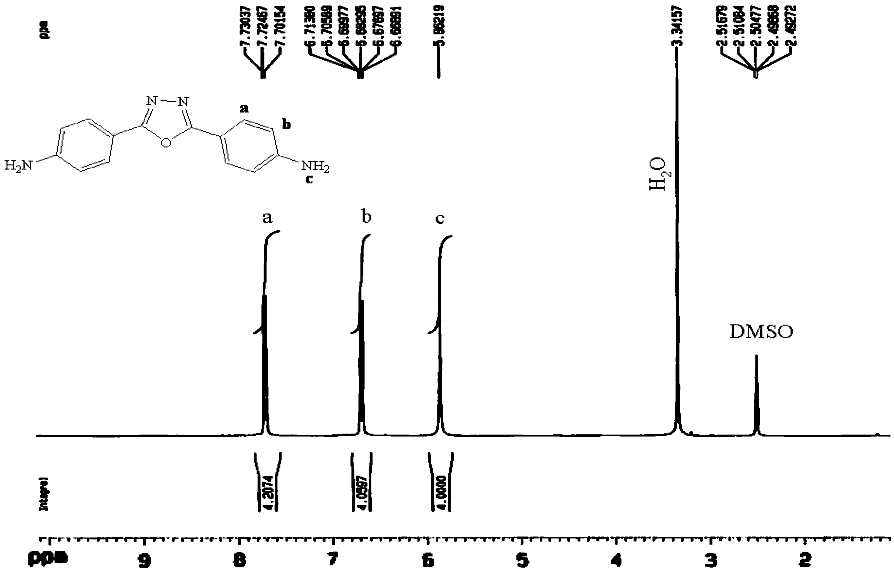
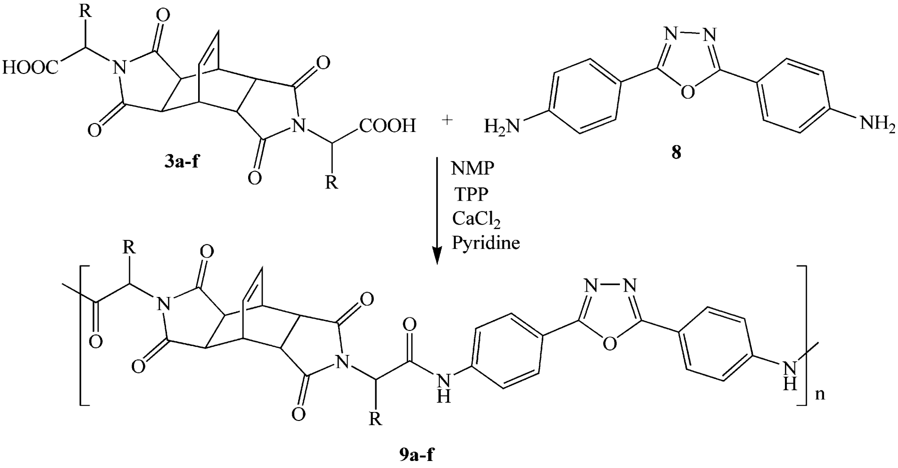


Fig. 3 ^{1}H-NMR spectrum of 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (**8**)



Scheme 3 Synthesis of polyamideimides (**9a–f**)

Polymer characterization

The elemental analysis values of the resulting polymers are in good agreement with the calculated values for the proposed structures (Table 3).

The solubility of PAIs was tested quantitatively in various solvents. The solubility of PAIs is listed in Table 4. Most of the PAIs are soluble in organic polar aprotic solvents such as DMF, *N*,*N*-dimethylacetamide (DMAc), dimethyl sulfoxide

Table 2 Synthesis and some physical properties PAIs **9a–f**

Diimide-diacid	Polymer	Yield (%)	η_{inh} (dL/g)[a]	$[\alpha]_{25}^{D}$ [a]
3a	**9a**	89	0.50	+105
3b	**9b**	87	0.47	+108
3c	**9c**	85	0.30	+118
3d	**9d**	84	0.35	+123
3e	**9e**	98	0.41	+94
3f	**9f**	90	0.52	+132

[a] Measured at a concentration of 0.5 g/dL in DMSO at 25 °C

Table 3 Elemental analysis of PAIs (**9a–f**)

Polymer	Formula		C%	H%	N%
9a	$C_{32}H_{26}N_6O_7$	Calcd	63.36	4.32	13.85
	$(606.58)_n$	Found	62.11	4.46	13.66
9b	$C_{36}H_{34}N_6O_7$	Calcd	65.25	5.17	12.68
	$(662.69)_n$	Found	64.10	5.15	12.48
9c	$C_{38}H_{38}N_6O_7$	Calcd	66.07	5.54	12.17
	$(690.74)_n$	Found	64.95	5.68	12.29
9d	$C_{38}H_{38}N_6O_7$	Calcd	66.07	5.54	12.17
	$(690.74)_n$	Found	65.20	5.70	12.11
9e	$C_{44}H_{34}N_6O_7$	Calcd	69.65	4.52	11.08
	$(758.78)_n$	Found	68.76	4.73	10.87
9f	$C_{34}H_{30}N_6O_7$	Calcd	64.35	4.76	13.24
	$(634.64)_n$	Found	63.46	4.97	13.39

Table 4 Solubility of PAIs (**9a–f**)

Solvent	**9a**	**9b**	**9c**	**9d**	**9e**	**9f**
H_2SO_4	+	+	+	+	+	+
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
MeOH	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
$CHCl_3$	–	–	–	–	–	–
CH_2Cl_2	–	–	–	–	–	–
H_2O	–	–	–	–	–	–

+ Soluble at room temperature, – insoluble at room temperature

(DMSO), 1-methyl-2-pyrrolidone (NMP), and polar protic solvents such as H_2SO_4 at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water. These PAIs in comparison with polyimides containing bicyclo segments in the main chain had better solubility in organic solvents, probably due to the presence of amide groups [24].

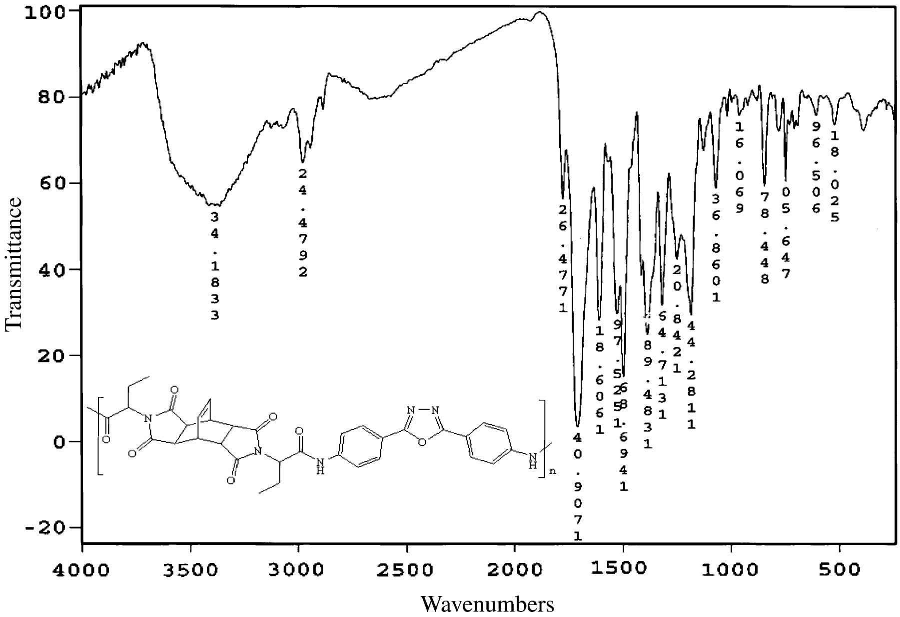


Fig. 4 FT-IR spectrum of PAI **9f**

The structures of these polymers were confirmed as PAIs by means of FT-IR, ^{1}H-NMR spectroscopy, and elemental analyses. The representative FT-IR spectrum of PAI (**9e**) was shown in Fig. 4. The FT-IR spectra of the polymer exhibited characteristic absorption bands at 1774 cm^{-1} for the imide ring (asymmetric C=O stretching vibration), 1709 (br) cm^{-1} (symmetric C=O stretching and amide stretching vibration) in the main chain and 1384 cm^{-1} (C–N stretching vibration). The absorption bands of amide groups appeared at 3380 cm^{-1} (N–H stretching). FT-IR characterizations of all PAIs are given in "Experimental" section.

The ^{1}H-NMR spectrum of PAI (**9e**) showed peaks that confirm its chemical structure. Figure 5 displays ^{1}H-NMR spectrum of PAI (**9e**). The aromatic protons related to oxadiazole unit, H_c and H_b, were appeared in the region of 8.08–8.11 ppm and 7.79–7.81 ppm, respectively.

The peaks in the region of 7.03–7.28 ppm are assigned for H_f, H_h and H_g related to phenyl groups of phenyl alanine units. The peak for olefin protons were appeared in the region of 5.07 ppm while the proton of the chiral center (H_a) appeared at 4.83 ppm. Decaying peak related to carboxylic acid protons and appearing peaks related to amide groups, oxadiazole moiety and phenyl ring protons in the polymer chain, confirmed the proposed structure of PAIs (**9e**).

Thermal properties

The thermal stability of the polymers **9a** and **9c** was characterized by TGA conducted in nitrogen at a heating rate of 10 °C/min (Fig. 6). In all cases, the thermal stability is very good. The temperature, at which the decomposition starts, is

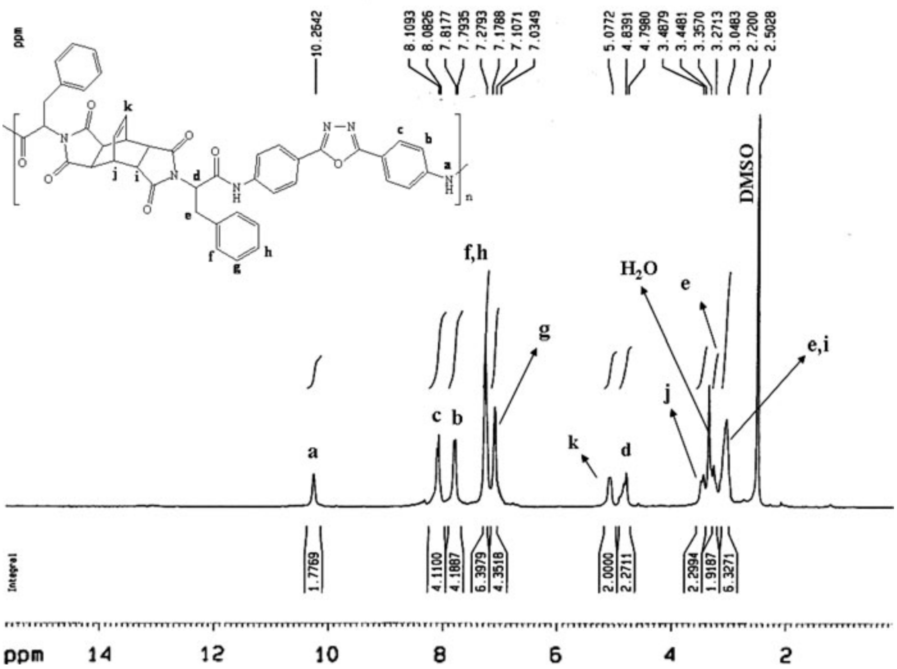


Fig. 5 ^{1}H-NMR spectrum of PAI **9e**

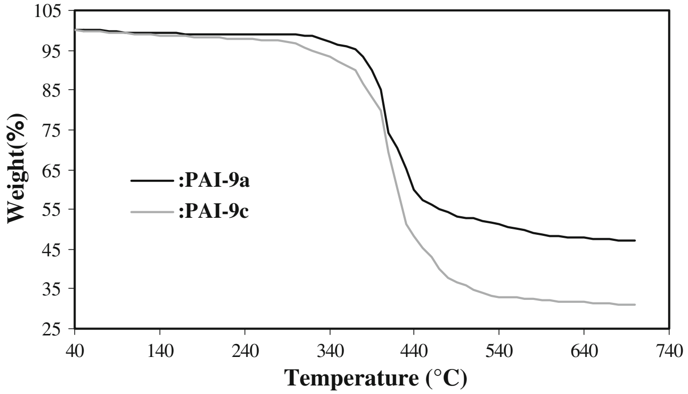


Fig. 6 TGA curves of PAIs **9a** and **9c**

never under 300 °C. The temperatures of 5 and 10% weight loss together with char yield at 600 °C for PAIs **9a** and **9c** have been calculated from their thermograms. As a result, these polymers are thermally stable. The thermo analysis data of PAIs **9a** and **9c** are summarized in Table 5.

Table 5 Thermal properties of PAIs (**9a**) and (**9c**)

Polymer	T_5 (°C)[a]	T_{10} (°C)[b]	Char yield (%)[c]
9a	375	395	48.42
9c	315	375	32.07

[a,b] Temperature at which 5 or 10% weight loss was recorded TGA at a heating rate of 10 °C/min in N_2

[c] Weight percentage of material left after TGA analysis at maximum temperature 600 °C in N_2

Conclusion

The present study involved the synthesis of several new optically active PAIs (**9a**–**f**) by the solution polycondensation reaction of 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (**8**) with six asymmetric diimide-diacids **3a**–**f**, triphenyl phosphite, NMP, calcium chloride, and pyridine as condensing agents. These PAIs were soluble in various organic solvents and shown moderate to good thermal stability. Since the resulting polymers are optically active and have good thermal stability, they have potential to be used as achiral stationary phase in chromatography technique for the separation of racemic mixtures.

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