

Synthesis and Properties of New Thermally Stable and Optically Active Organosoluble Poly(ether-amide-imide)s Containing Bicyclo Segment in the Main Chain

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ABSTRACT: *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-*L*-amino acids **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 *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. Also 1,4-bis[4'-nitrophenoxy]butane **6** was prepared by reaction of 4-nitrophenol **4** with 1,4-dibromo butane **5** in DMF solution. Then dinitro **6** was reduced to 1,4-bis[4'-aminophenoxy]butane **7** by using 10% Pd-C, ethanol and hydrazine monohydrate. Then, six new poly(ether-amide-imide)s PEAs **8a-f** were synthesized through the direct polycondensation reaction of six chiral *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-*L*-amino acids **3a-f** with diamine **7** by direct polycondensation methods in a medium consist-

ing of *N*-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl₂)/pyridine (Py). The polymerization reaction produced a series of organosoluble and thermally stable poly(ether-amide-imide)s **8a-f** with high yield. The resulted polymers were fully characterized by means of FTIR, ¹H-NMR spectroscopy, elemental analyzes, inherent viscosity, specific rotation and solubility tests. Data obtained by thermal analysis (TGA and DTG) revealed that these polymers show good thermal stability. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1184–1192, 2010

Key words: poly(ether-amide-imide); optically active polymer; thermally stable polymers; direct polycondensation

INTRODUCTION

High-performance polymers are an important class of polymers and their applications are growing rapidly. Many studies of new polymer syntheses have been focused on the preparation of high-performance polymers. In general, they show high thermal stability, good chemical resistance, low flammability, and excellent mechanical properties. In the last few decades, thermally stable polymers have received extensive interest due to the increasing demands for high temperature polymers as replacements for metals or ceramics in the automotive, aerospace, and microelectronics industries. Aromatic polyimides, polyamides, poly benzazoles and other heterocyclic polymers are some of the most successful classes of high temperature polymers.^{1–4}

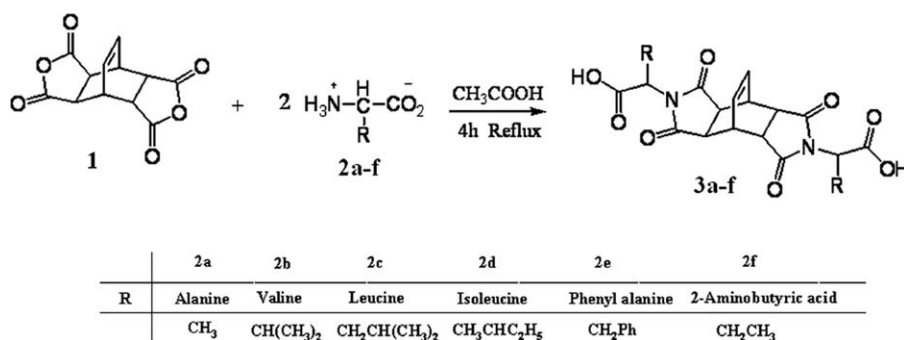
In recent years interest has been focused on the synthesis of rigid-rod polyimides and polyamides by incorporating aromatic rings into the polymer backbones. The increased number of aromatic rings enhances the rigidity of the polymer backbones.^{5–7}

Poly(amide-imide)s were developed from high-performance polymers which combine and inherit desirable characteristics from both polyamides and polyimides. They possess good thermal properties in compared to polyamides, and better melting processability than polyimides. To improve further solubility in organic solvents, flexible or asymmetrical linkages have been introduced in the polymer.^{8–16}

Synthesis of optically active polymers is an important field in macromolecular science as they find a wide variety of potential applications based on the chiral structure.^{17–19} One of the most practical and widely accepted applications of chiral polymers is the use as chiral stationary phase (CSP) for the separation of racemic mixtures by high-performance liquid chromatography (HPLC). Recently the optically active polymers have been synthesized by reaction of an optically active monomer with several diols or diamines via usual polymerization techniques.^{20–24}

In this article, a series of thermally stable PEAs **8a-f** containing bicyclo moiety were synthesized by the direct polycondensation reactions of six chiral *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-*L*-amino acids **3a-f** with 1,4-bis[4'-aminophenoxy]butane **7**. On other hand, due to presence chiral segments in polymer backbone, these PEAs are optically active.

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Scheme 1 Preparation of diacids 3a-f.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical (Switzerland), Aldrich Chemical (Milwaukee), Merck Chemical (Germany) and Acros Organics N.V/S.A (Belgium).

Techniques

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solid were performed by using KBr pellets. Vibration transition frequencies were 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 by using a Technico Regd Trad Mark Viscometer. Specific Rotations were measured by an A-Kruss polarimeter. Thermal Gravimetric Analysis (TGA and DTG) data for the polymers were taken on a Mettler TA4000 System under N₂ atmosphere at rate of 10°C/min. Elemental analyzes were performed by Vario EL equipment.

Monomer synthesis

N,N'-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids 3a-f

One gram (4.03 mmol) of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1**, 8.06 mmol of L-amino acids **2a-f**, 50 mL of acetic acid and a stirring bar were placed in 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 compounds **3a-f**.

1,4-bis[4'-nitrophenoxy]butane **6**

In a 100 mL round-bottomed flask were added (6.00 g, 43.11 mmol) of 4-nitrophenol **4** and (2.97 g, 21.55 mmol) of dry K₂CO₃ in 30 mL dimethyl formamide (DMF). Then a solution of (4.46 g, 20.67 mmol) 1,4-dibromo butane **5** in 5 mL dry dimethyl formamide was added drop-wise to reaction mixture. The reaction mixture was heated for 6 hrs at 120°C, then was cooled and poured onto crushed ice. The precipitated white product was collected by filtration, dissolved in CH₂Cl₂ and washed successively with NaOH (2 M), HCl (1 M) and water. The CH₂Cl₂

TABLE I
Synthesis and Some Physical Properties of Diimide-Diacid Derivatives 3a-f

Entry	Amino acid compound	R	Mp (°C)	Yield (%)	[α] _D ²⁵ ^a
3a	L-Alanine	CH ₃	249–250	92	+155.7
3b	L-Valine	(CH ₃) ₂ CH	318–320	93	+138.4
3c	L-Leucine	(CH ₃) ₂ CHCH ₂	289–290	94	+146.8
3d	L-Isoleucine	(C ₂ H 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 ₃ CH ₂	251–253	93	+130.2

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

TABLE II
 1H-NMR, 13C-NMR, FTIR Spectra and Elemental Analyses Data of Diacids 3a-f

Diimide-diacid	Spectra data
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 ₂ O ₈ : C, 55.39; H, 4.65; N, 7.18; found: C, 54.45; H, 4.56; N, 7.11.
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 ₂ O exchange, s, 2H), 3.18–3.25 (D ₂ O 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 ₂ O ₈ : C, 59.19; H, 5.87; N, 6.27; found: C, 58.98; H, 5.87; N, 6.25.
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 ₂ O ₈ : C, 60.75; H, 6.37; N, 5.90; found: C, 60.25; H, 6.22; N, 5.88.
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 ₂ O ₈ : C, 60.75; H, 6.37; N, 5.90; found: C, 60.45; H, 6.21; N, 5.91.
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 ₂ O ₈ : C, 66.41; H, 4.83; N, 5.16; found: C, 66.41; H, 4.82; N, 5.10.
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 ₂ O-exchang, s, br, 2H), 3.20–3.27 (D ₂ O-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 ₂ O ₈ : C, 57.41; H, 5.30; N, 6.70; found: C, 57.34; H, 5.29; N, 6.70.

solution was then dried over Na₂SO₄ and concentrated in vacuum and product was recrystallized from ethanol, affording 4.59 g (65.4%) of white solid 6, mp: 140–142°C, FTIR (KBr, cm⁻¹): 3058 (w), 1609

(s), 1534 (s), 1411 (m), 1348 (s), 1181 (s), 1111 (s), 987 (s), 852 (s), 756 (m), 702 (s), 543 (m).

¹H-NMR (300 MHz, DMSO-d₆, TMS): δ; 8.17–8.20 (t, 4H), 7.12–7.15 (t, 4H), 4.19 (s, 4H), 1.92 (s, 4H)

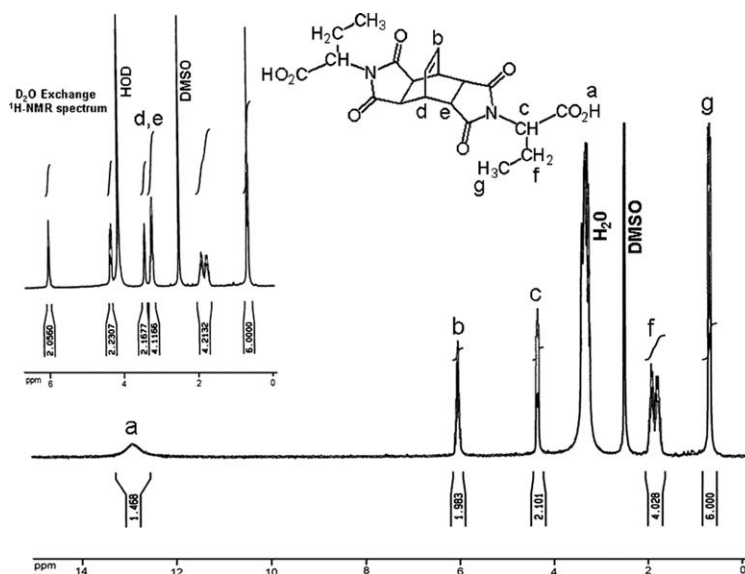


Figure 1 ¹H-NMR spectrum of diimide-diacid 3f.

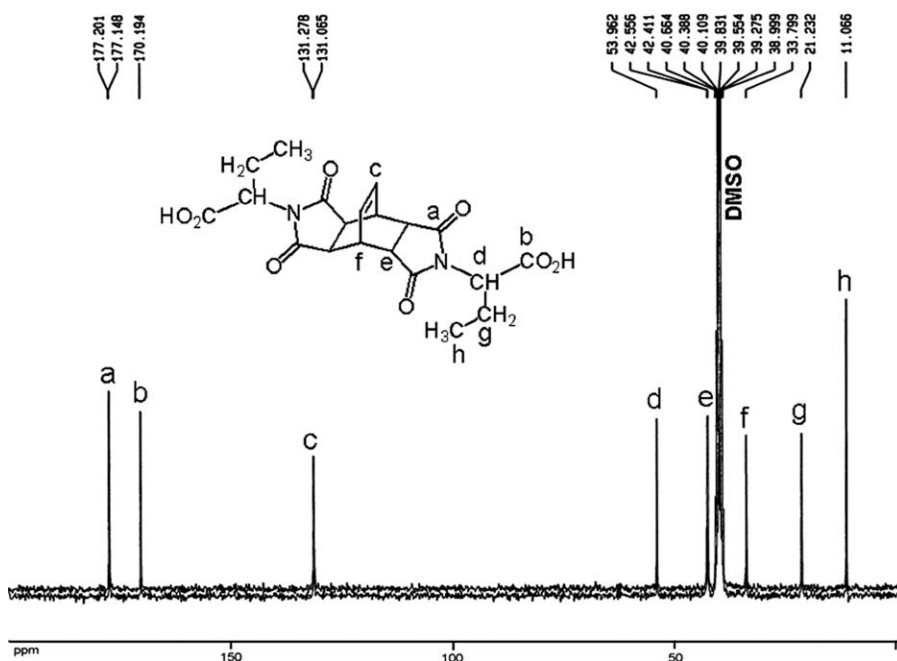
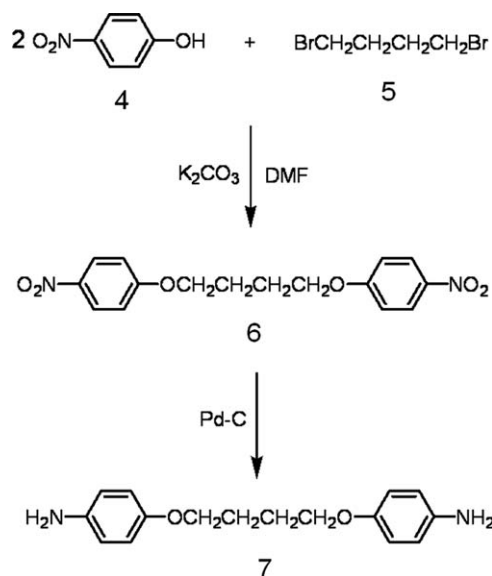


Figure 2 ^{13}C -NMR spectrum of diimide-diacid **3f**.

ppm. ^{13}C -NMR (300 MHz, DMSO-d_6): δ ; 164.37, 142.78, 126.31, 115.41, 68.10, 26.17 ppm. Elemental analysis: calculated for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_6$: C, 57.83; H, 4.85; N, 8.43; found: C, 57.68; H, 4.81; N, 8.33.

1,4-bis[4'-aminophenoxy]butane **7**

In a 100 mL round-bottomed flask were added (1.00 g, 3.67 mmol) of 1,4-bis[4'-nitrophenoxy]butane **6** and 0.1 g of 10% Pd-C, and 20 mL of ethanol were



Scheme 2 Synthesis of diamine **7**.

introduced into a 100-mL round-bottomed flask to which 7 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 reflux temperature for another 5 h. Then, the mixture was filtered to remove the Pd-C and the filtrate was poured into water and dried to afford 0.71 g (87%). Mp: $152\text{--}154^\circ\text{C}$. FTIR (KBr, cm^{-1}): 3322 (m), 3214 (m), 3032 (w), 2906 (w), 1604 (m), 1591 (s), 1504 (s), 1438 (m), 1307 (m), 1282 (m), 1172 (s), 1107 (m), 985 (w), 829 (m), 511 (m) cm^{-1} .

^1H -NMR (300 MHz, DMSO-d_6 , TMS): δ ; 6.62–6.65 (d, 4H), 6.47.650 (d, 4H), 4.58 (s, 4H), 3.85 (s, 4H), 1.76 (s, 4H) ppm. ^{13}C -NMR (300 MHz, DMSO-d_6): δ ; 150.40, 142.72, 126.33, 115.42–115.81, 68.11, 26.14 ppm. Elemental analysis: calculated for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2$: C, 70.56; H, 7.40; N, 10.29; found: C, 70.28; H, 7.36; N, 10.21.

Polymer synthesis

PEAIs **8a-f** were synthesized by direct polycondensation that as an example the preparation of PEAI **8b** explains in the following: 0.145 g (0.326 mmol) of diacid **3b**, 0.088 g (0.326 mmol) of diamine **7**, 0.1 g (0.9 mmol) of CaCl_2 , 0.84 mL (3.00 mmol) of triphenyl phosphite, 0.8 mL of pyridine and 1.00 mL of NMP were placed into a 50-mL round-bottomed flask, which was fitted with a stirring bar. The reaction mixture was heated under reflux on an oil bath at 120°C for 8 h. Then was precipitated in 50 mL of

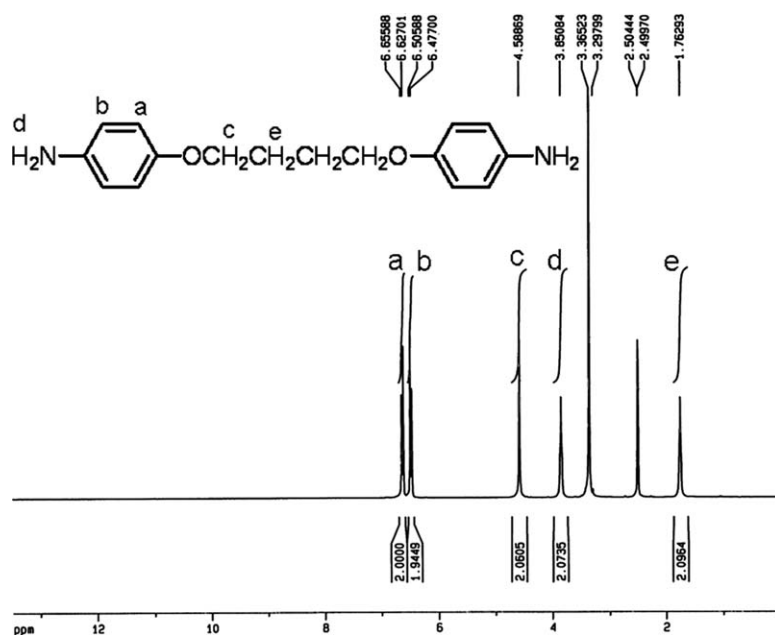


Figure 3 $^1\text{H-NMR}$ spectrum of diamine 7.

methanol and filtered off, dried under vacuum to leave 0.195 g (88%) white solid polymer **8b**.

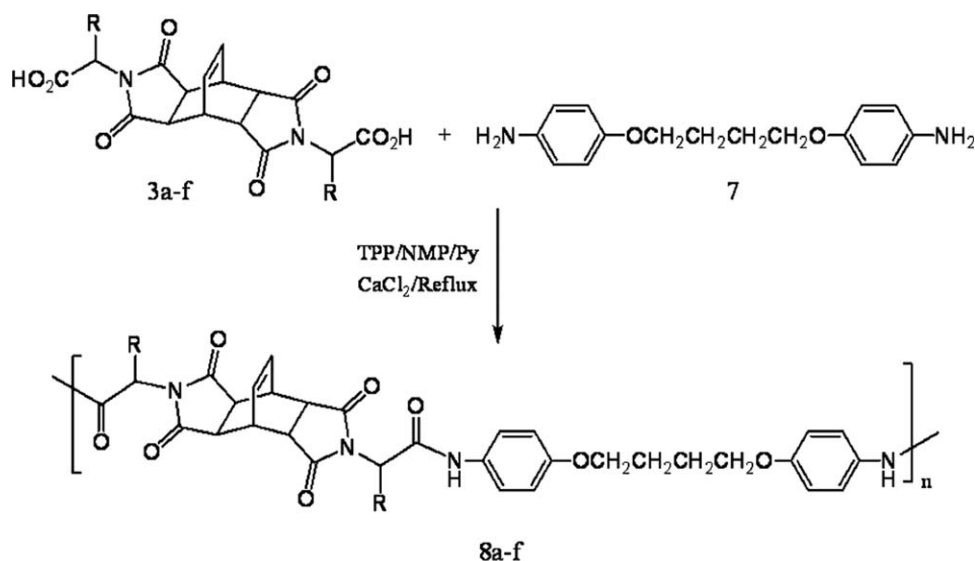
RESULTS AND DISCUSSION

Monomer synthesis

The asymmetric diimide-diacids **3a-f** were synthesized by the condensation reaction of dianhydride **1** with two equivalents of various amino acids **2a-f** in an acetic acid solution (Scheme 1). The yields and some physical properties of these compounds are shown in Table I.

The chemical structure and purity of the optically active diimide-diacids **3a-f** were proved by using elemental analysis, FTIR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopic techniques and these data shown in Table II.

As an example, the $^1\text{H-NMR}$ spectrum of diacid **3f** showed in Figure 1. The protons H(a) relevant to O-H carboxylic groups appeared at 12.95 ppm. Peak in 4.33–4.38 ppm as a doublet of doublet which were assigned to the H(c) protons, which is a chiral center, peaks between 0.66–0.71 ppm were assigned to aliphatic CH_3 (g), peak in 1.79–1.93 ppm were assigned to H(f). Protons relevant to olefin bicyclo



Scheme 3 Synthesis of PEAs **8a-f**.

TABLE III
Synthesis and Some Physical Properties of PEAs 8a-f

Diimide-diacid	Polymer	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_D^{25}$ ^a	Color
3a	8a	93	0.52	+85.6	W
3b	8b	88	0.65	+92.4	W
3c	8c	95	0.67	+85.4	C
3d	8d	82	0.83	+58.2	C
3e	8e	88	0.38	+69.2	C
3f	8f	79	0.53	+87.5	W

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

^b W, white; C, cream.

ring appeared at 6.01–6.10 ppm, H(b). Peaks between 3.20–3.43 ppm were assigned to H(e) (4H) and H(d) (2H), that appeared in D₂O exchange ¹H-NMR spectrum. Also the ¹³C-NMR spectrum of diacid 3f showed 8 signals, including C(b) and C(a) in carboxylic acids and carbonyl imide rings, and C(c) in carbon atoms olefin in bicyclo (Fig. 2). These peaks in ¹H-NMR and ¹³C-NMR spectra along with elemental analyzes data confirmed the proposed structure of compound 3f.

Also 1,4-bis[4'-aminophenoxy]butane 7 was synthesized by using a two-step reaction. At first 1,4-bis[4'-nitrophenoxy]butane 6 was prepared from the reaction of two equimolars 4-nitrophenol 4 and one 1,4-dibromo butane 5 in DMF and dry K₂CO₃. Then dinitro compound 6 was reduced by using 10% Pd-C, ethanol and hydrazine monohydrate (Scheme 2).

The chemical structure and purity of compound 6 and 7 were proved with elemental analysis, ¹H-NMR and FTIR spectroscopy.

The measured results in elemental analyzes 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 3322 and 3214 cm⁻¹, which were assigned to the NH₂ groups.

TABLE V
FTIR Characterization of PEAs 8a-f

Polymer	Spectral data
8a	FTIR Peaks (cm ⁻¹): 3321 (m), 3067 (w), 2943 (w), 1774 (w), 1707 (s, br), 1602 (w), 1510 (s), 1386 (s), 1303 (w), 1234 (s, br), 1116 (w), 829 (m), 723 (w), 522 (w).
8b	FTIR Peaks (cm ⁻¹): 3325 (m, br), 3067 (w), 2966 (m), 1774 (w), 1709 (s, br), 1602 (w), 1510 (s), 1381 (m, br), 1236 (m), 1197 (m), 1016 (w), 829 (s), 692 (w).
8c	FTIR Peaks (cm ⁻¹): 3340 (m, br), 3067 (w), 2957 (s), 1774 (w), 1710 (s, br), 1602 (w), 1510 (s), 1386 (m, br), 1305 (w), 1234 (m), 1190 (w), 829 (s), 729 (w), 522 (w).
8d	FTIR Peaks (cm ⁻¹): 3325 (m, br), 2966 (m), 1774 (w), 1710 (s, br), 1602 (w), 1510 (s), 1383 (m, br), 1303 (w), 1234 (m), 1194 (w), 1024 (w), 829 (m), 736 (w).
8e	FTIR Peaks (cm ⁻¹): 3338 (m, br), 3063 (w), 2941 (m), 1774 (w), 1707 (s, br), 1602 (w), 1510 (s), 1384 (s, br), 1305 (w), 1236 (m), 1174 (w), 829 (m), 729 (w), 698 (m).
8f	FTIR Peaks (cm ⁻¹): 3321 (w), 3061 (w), 2951 (w), 1772 (w), 1709 (s, br), 1601 (w), 1510 (s), 1386 (s, br), 1307 (w), 1234 (m), 1195 (w), 1064 (w), 831 (m), 522 (w).

TABLE IV
Elemental Analysis of PEAs 8a-f

Polymer	Formula		C%	H%	N%
8a	C ₃₄ H ₃₄ N ₄ O ₈	Calcd	65.17	5.47	8.94
	(626.66) _n	Found	64.65	5.56	8.74
8b	C ₃₈ H ₄₂ N ₄ O ₈	Calcd	66.85	6.20	8.21
	(682.76) _n	Found	66.08	6.13	7.95
8c	C ₄₀ H ₄₆ N ₄ O ₈	Calcd	67.59	6.52	7.88
	(710.82) _n	Found	66.94	6.51	7.73
8d	C ₄₀ H ₄₆ N ₄ O ₈	Calcd	67.59	6.52	7.88
	(710.82) _n	Found	66.92	5.50	7.84
8e	C ₄₆ H ₄₂ N ₄ O ₈	Calcd	70.94	5.44	7.19
	(778.85) _n	Found	70.19	5.40	7.11
8f	C ₃₆ H ₃₈ N ₄ O ₈	Calcd	66.04	5.85	8.56
	(654.71) _n	Found	65.73	5.81	8.41

¹H-NMR spectrum of compound 7 showed peaks as a doublet of doublet at 6.62–6.65 ppm and 6.47–6.50 ppm were assigned to the H(a) and H(b) related to aromatic protons, and a singlet peak at 3.85 ppm which was assigned to the H(e) proton of the NH₂ group in this compound (Fig. 3). The protons of the methylene groups in compounds 6 and 7 are equivalent and equivalent nuclei have the same resonance frequency, and couplings between equivalent nuclei cannot be observed in the ¹H-NMR spectra.

Polymer synthesis

PEAs 8a-f were synthesized by reaction of an equimolar mixture of diimide-diacids 3a-f with diamine 7 by direct polycondensation (Scheme 3).

In this method for direct polycondensation used TPP/Py/CaCl₂ as activating agent according to a typical procedure that was shown in Scheme 3. The syntheses and some physical properties of these PEAs 8a-f are given in Table III.

Polymer characterization

The elemental analyzes of the resulting PEAs 8a-f were in good agreement with the calculated values for the proposed structure (Table IV). The solubility

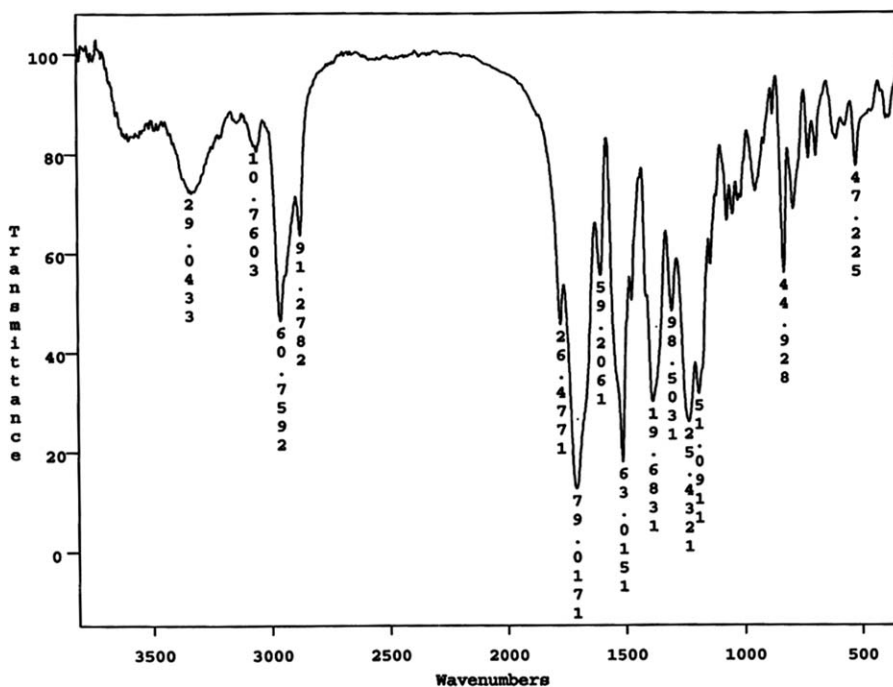
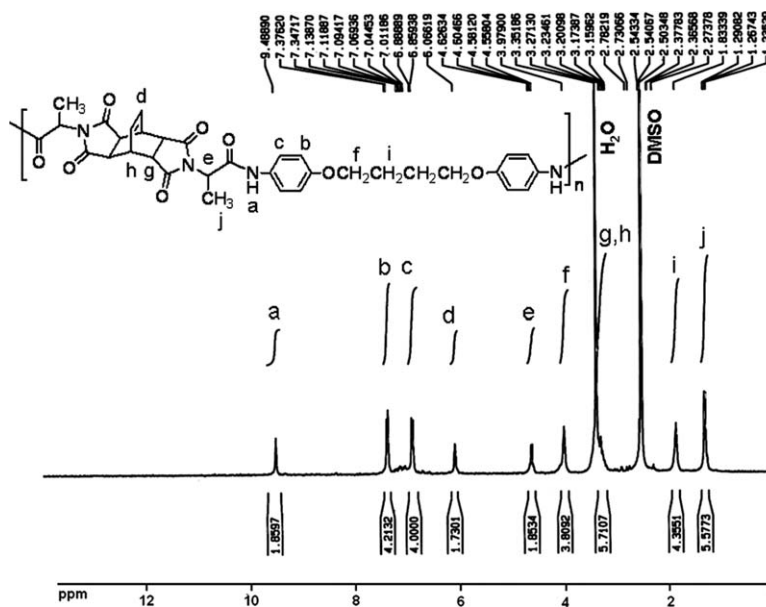


Figure 4 FTIR spectrum of PEAI 8c.

Figure 5 $^1\text{H-NMR}$ spectrum of PEAI 8a.

of PEAs 8a-f was investigated as 0.01 g of polymeric sample in 2 mL of solvent. All of the polymers are soluble in DMSO, DMF, NMP, DMAc and H_2SO_4 and are insoluble in solvents such as chloroform, dichloromethane, methanol and ethanol.

The structures of these polymers were confirmed as PEAs by means FTIR, $^1\text{H-NMR}$ spectroscopy and elemental analyzes. FTIR characterizations of all PEAs are listed in Table V. The representative FTIR spectrum of PEAI 8c was shown in Figure 4. The

TABLE VI
Thermal Behavior of PEAs 8d, 8e, and 8f

Polymer	$T_5(^{\circ}\text{C})^a$	$T_{10}(^{\circ}\text{C})^a$	Char yield ^b
8d	350–355	385–390	37.83
8e	380–385	395–400	45.88
8f	365–370	390–395	34.95

^a Temperature at which 5 or 10% weight loss was recorded by TGA at a heating rate of $10^{\circ}\text{C}/\text{min}$ under N_2 .

^b Weight percentage of material left after TGA analysis at a maximum temperature of 800°C under N_2 .

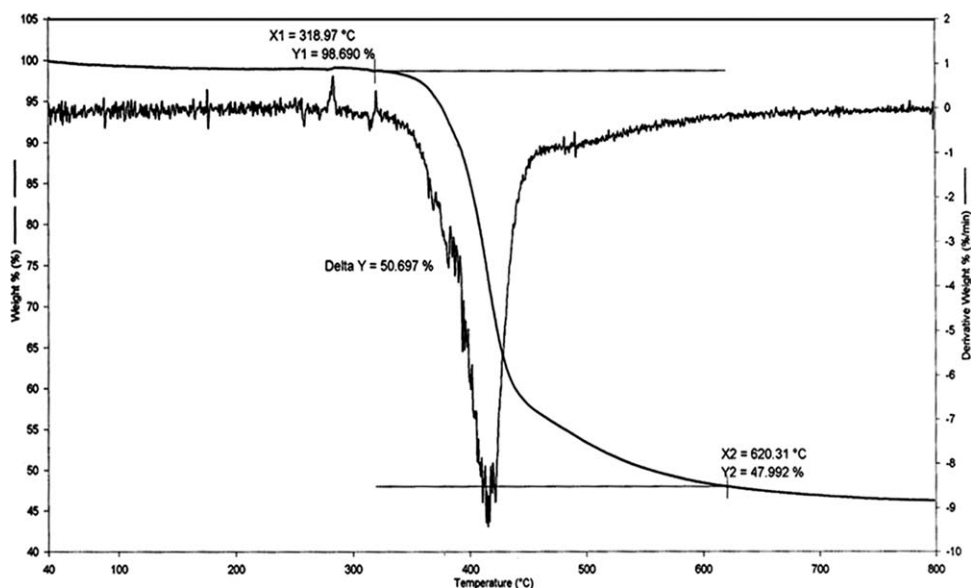


Figure 6 TGA and DTG thermogram of PEAI 8e.

polymer exhibited characteristic absorption bands at 1710 and 1774 cm^{-1} for the imide ring (symmetric and asymmetric C=O stretching vibration), broad peak approximately at 1690 cm^{-1} related to amide groups (C=O stretching vibration), 1386 cm^{-1} (C–N stretching vibration). The absorption bands of amide groups appeared at 3340 cm^{-1} (N–H stretching).

The $^1\text{H-NMR}$ spectrum of PEAI 8a showed peaks that confirm its chemical structure (Fig. 5). The aromatic protons related to diamine appeared in the region of 6.85–6.88 and 7.34–7.37 ppm and the peak in the region of 9.48 ppm is assigned for N–H of amide groups in the main chain of polymer. Decaying peak related to carboxylic acid protons and appearing peaks related to amide groups and aromatic protons of diamine in the polymer chain, confirmed the proposed structure of PEAI 8a.

Thermal properties

The thermal properties of PEAI 8d, 8e, and 8f were investigated by TGA in a nitrogen atmosphere at a heating rate of 10°C/min. All of these polymers showed similar decomposition behavior. Initial decomposition temperature, 5 and 10% weight loss temperature (T_5 , T_{10}), and char yields summarized in Table VI.

These polymers exhibited good resistance to thermal decomposition up to 350–380°C in nitrogen and began to decompose gradually above that temperature. The temperature of 5% weight loss for all the polymers ranged from 355 to 385°C and the residual weight at 800°C ranged from 34.95 to 45.88% in nitrogen. The high char yields at 800°C, T_5 and T_{10} of these PEAI at high temperature region are important. It shows that these polymers have good

thermal stability. Thermal stability of polymer 8e with phenyl alanine moiety was higher than other polymers, because this polymer has a rigid aromatic structure in the polymer backbone (Fig. 6).

CONCLUSIONS

A series of new optically active and organosoluble PEAI 8a–f containing dibenzalacetone moiety were synthesized by six chiral *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids 3a–f with 1,4-bis[4'-aminophenoxy]butane 7 by direct polycondensation reaction. Because of presence of ether group and bicyclo moiety in polymer backbone, these PEAI are expected to have higher solubility. Because the resulting polymers contained optically pure L-amino acid moieties, they showed optical rotations and were optically active. These properties could make these PEAI attractive for practical applications, such as processable high-performance engineering plastics, used as chiral stationary phase and chiral media for asymmetric synthesis.

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