PREPARATION OF NEW OPTICALLY ACTIVE AND THERMALLY STABLE POLY(AMIDE-IMIDE) CONTAINING BICYCLO SEGMENT AND ETHER GROUP IN THE MAIN CHAIN BY DIRECT POLYCONDENSATION IN TWO DIFFERENT MEDIA

KHALIL FAGHIHI¹*, MEISAM SHABANIAN²

¹Polymer Research Laboratory, Department of Chemistry, Faculty of Science, Islamic Azad University, Arak Branch, Arak, Iran.

² Islamic Azad University, Arak Branch, Young Researchers Club, Araky, Iran

(Received: May 31, 2010 - Accepted: November 15, 2010)

ABSTRACT

A new series of optically active and thermally stable poly(amide-imide)s (PAIs) with good inherent viscosities based on bicyclo diacids and etheric diamine in the main chain were synthesized from the direct polycondensation reaction of *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-*L*-amino acids **3a-g** with 1,2-Bis[4-aminophenoxy]ethane **7** by direct polycondensation with two different media such as direct polycondensation in a medium consisting of *N*-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl₂)/pyridine (Py) and direct polycondensation in a tosyl chloride (TsCl)/pyridine (Py)/*N,N*-dimethylformamide (DMF) system. Also **3a-g** were synthesized by the condensation reaction of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1** with two equivalents of various amino acids such as *L*-alanine **2a**, *L*-valine **2b**, *L*-leucine **2c**, *L*-isoleucine **2d**, *L*-phenylalanine **2e**, *L*-2-aminobutyric acid **2f** and *L*-histidine **2g** in an acetic acid solution.

The polymerization reactions produced a series of thermally stable and optically active organosoluble PAIs. The resulting polymers were fully characterized by means of FT-IR and ¹H-NMR spectroscopy, elemental analyses, inherent viscosity, specific rotation, solubility tests and differential scanning calorimeter (DSC). Also thermal properties of the PAIs **8a-g** were investigated using thermal gravimetric analysis (TGA) and derivative of thermogravimetric (DTG) analysis.

Key word: Thermal properties; Optically active; Organosoluble; Poly(amide-imide)

INTRODUCTION

High-performance polymeric materials are currently receiving considerable attention for their potential applications in advanced technologies demands. Aromatic polyimides are well known high-performance polymers that show excellent thermal, mechanical and electrical properties.^{1,2} However, applications may be rather limited due to their high softening or melting temperatures and their insoluble nature in most organic solvents.³

Modification of high performance materials by increasing the solubility and lowering the transition temperatures while maintaining thermal stability are of particular interest. Copolycondensation is one of the possible ways for modification of polymer properties. Thus, for the processing of polyimides many copolyimides, such as poly(amide-imide)s, poly(ester-imide)s, and other copolymers have been prepared.⁴⁻⁹ Aromatic polymers that contain aryl ether linkages and other flexible units such as -NHCO- and -SO₂- generally have lower glass transition temperatures, greater chain flexibility and tractability in compare to their corresponding polymers these groups in the chain.¹⁰⁻¹² The lower glass transition temperatures and also improved solubility are attributed to the flexible linkages that provide a polymer chain with a lower energy of internal rotation.¹³

Nature uses chirality as one of the key structural factors to perform a series of complicated functionalities, such as molecular recognition and catalytic activities.¹⁴ 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 of optically active polymers as catalysts for asymmetric synthesis and as chiral stationary phases (CSP) for the direct optical resolution of enantiomers.¹⁵⁻¹⁷ 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.^{18, 19}

In this article, a series of new optically active and thermally stable organosoluble PAIs **8a-g** containing bicycle and ether moiety were synthesized by the direct polycondensation reactions of seven chiral *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-*L*-amino acids **3a-g** with 1,2-Bis[4-aminophenoxy]ethane **7** by two different media such as direct polycondensation in a medium consisting of *N*-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl₂)/pyridine (Py) and direct polycondensation in a tosyl chloride (TsCl)/pyridine (Py)/*N,N*-dimethylformamide (DMF) system.

EXPERIMENTAL

Materials

Bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1** (from Aldrich), *L*-alanine **2a**, *L*-valine **2b**, *L*-leucine **2c**, *L*-isoleucine **2d**, *L*-phenylalanine **2e** and *L*-2-aminobutyric acid **2f**, *L*-histidine **2g**, 1,2-dibromoethane **4**, *p*-nitrophenol **5** and tosyl chloride (TsCl; from Merck) were used without previous purification. Solvent: *N*-methyl-2-pyrrolidone (NMP; from Fluka), pyridine (from Acros), triphenyl phosphite (TPP; from Merck) and *N,N*-dimethylformamide (DMF; from Merck) were used as received. Commercially available calcium chloride (CaCl₂; from Merck) was dried under vacuum at 150°C for 6 hrs.

Techniques

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FT-IR) spectra were recorded on Galaxy series FT-IR 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 polymers were taken on a Mettler TA4000 System under N₂ atmosphere at rate of 10°C/min and differential scanning calorimetry (DSC) was conducted with a DSC Mettler 110 (Switzerland) at a heating rate of 10 °Cmin⁻¹ in a nitrogen atmosphere. The temperature range was from 25 to 350°C. The glass transition temperature (T_g) of PAI was recorded based on the second scanning. Elemental analyses were performed by Vario EL equipment in Arak University.

Monomer synthesis

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

1 g (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-g**, 50 mL of 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 hrs. 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 *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-*L*-amino acids **3a-g**.⁸

1,2-bis[4,4'-aminophenoxy]ethane **7**

1,2-bis[4-aminophenoxy]ethane **7** was synthesized according to the previous work.²⁰

Polymer synthesis

Poly(amide-imide)s **8a-g** were synthesized by two different methods that as an example the preparation of PAI **8a** explains in the following.

Method A: Direct polycondensation in a medium consisting of *N*-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl₂)/pyridine (Py)

0.107 g (0.275 mmol) of *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-*L*-alanine **3a**, 0.067 g (0.275 mmol) of 1,2-Bis [4-aminophenoxy] ethane **7**, 0.1 g (0.9 mmol) of calcium chloride, 0.84 mL, (3.00 mmol) of triphenyl phosphite, 0.1 mL of pyridine and 1.5 mL *N*-methyl-2-pyrrolidone (NMP) were placed into a 25-mL round-bottomed flask, which was fitted with a stirring bar. The reaction mixture was heated under reflux at 120°C for 8 hrs. Then, the reaction mixture was poured into 50 mL of methanol and the precipitated polymer was collected by filtration and washed thoroughly with hot methanol and dried at 60°C for 12 hrs under vacuum to leave 0.151 g (92%) pale yellow solid polymer **8a**.

Method B: Direct Polycondensation in a Tosyl Chloride (TsCl)/Pyridine (Py)/ *N,N*-Dimethylformamide (DMF) System

A solution of 0.1 mL pyridine, 0.078 g (0.411 mmol) of TsCl after 30 min stirring at room temperature was treated with 0.1 mL, (1.36 mmol) of DMF for additional 30 min. The reaction mixture was added dropwise to a solution 0.053 g (0.137 mmol) of diacid **3a** in 0.1 mL of pyridine. The mixture was maintained at room temperature for 30 min, and then to this mixture, a solution 0.033 g (0.137 mmol) of 1,2-Bis[4-aminophenoxy]ethane **7** in 0.1 mL of Pyridine was added dropwise and the whole solution was stirred at room temperature for 30 min and at 110°C for 2 hrs. As the reaction proceeded, the solution became viscous, then was precipitated in 30 mL of methanol and filtered off, dried under vacuum to leave 0.121 g (74%) brown solid polymer **8a**.

RESULTS AND DISCUSSION

Synthesis of monomers

The asymmetric diacids **3a-g** 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**, *L*-2-aminobutyric acid **2f** and *L*-histidine **2g** in an acetic acid solution (scheme 1). The yields and some physical properties of these compounds are shown in Table 1.

	2a	2b	2c	2d	2e	2f	2g
R	Alanine	Valine	Leucine	Isoleucine	Phenyl alanine	2-Aminobutyric acid	Histidine
	CH ₃	CH(CH ₃) ₂	CH ₂ CH(CH ₃) ₂	CH ₃ CHC(CH ₃) ₂ H	CH ₂ Ph	CH ₂ CH ₃	CH ₂ -imidazole

Scheme 1: Preparation of diacids **3a-g**

Table 1 Some physical properties of chiral diacid derivatives **3a-g**

Entry	Amino acid compound	R	Mp(°C)	Yield(%)	[α] _D ^a
3a	<i>L</i> -Alanine	CH ₃	249-250	92	+155.7
3b	<i>L</i> -Valine	(CH ₃) ₂ CH	318-320	93	+138.4
3c	<i>L</i> -Leucine	(CH ₃) ₂ CHCH ₂	289-290	94	+146.8
3d	<i>L</i> -Isoleucine	(C ₂ H ₅)(CH ₃)CH	293-295	92	+156.2
3e	<i>L</i> -Phenyl alanine	PhCH ₂	247-248	91	+160.2
3f	<i>L</i> -2-Aminobutyric acid	CH ₃ CH ₂	251-253	93	+130.2
3g	<i>L</i> -histidine	CH ₂ -imidazole	310-312	85	+128.4

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

The chemical structure and purity of the optically active diacids **3a-g** were proved by using elemental analysis, FT-IR, ¹H-NMR and ¹³C-NMR spectroscopic techniques and these data shown in Table 2.

Table 2 ¹H-NMR, ¹³C-NMR, FT-IR spectra and elemental analyses data of diacid derivatives **3a-g**.

Diimide-diacid	Spectral 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, J= 7 Hz), 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. FT-IR (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, J= 9 Hz), 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, J= 6 Hz), 0.66-0.68 (d, 6H, J= 6 Hz). 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. FT-IR (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. FT-IR (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, J= 9 Hz), 3.22-3.30 (m, 6H), 2.14-2.15 (d, 2H, J= 3 Hz), 1.30-1.37 (m, 2H), 0.89-0.91 (d, 6H, J= 6 Hz), 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. FT-IR (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. FT-IR (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. FT-IR (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.
3g	¹ H-NMR (DMSO-d ₆ , δ ppm): 14.48 (s, br, 4H), 9.11 (s, 2H), 7.30 (s, 2H), 5.38-5.80 (s, 2H), 4.98-5.01 (t, 2H), 3.03-3.32 (m, 10H). ¹³ C-NMR (DMSO-d ₆ , δ ppm): 176.53, 168.91, 134.22, 130.21, 128.84, 117.86, 51.49, 42.44, 33.31, 23.56. FT-IR (KBr, cm ⁻¹): 2500-3400 (s, br), 1770 (w), 1707 (s, br), 1626 (m), 1521 (w), 1383 (s), 1228 (s), 1163 (s), 1074 (m), 927 (w), 827 (s), 710 (m), 624 (m). Elemental analysis: calcd. for C ₂₄ H ₂₂ N ₂ O ₈ : C, 55.17; H, 4.24; N, 16.09; found: C, 55.03; H, 4.23; N, 16.00.

The FT-IR spectra of all *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-*L*-amino acids **3a-g** showed absorption around 2500 and 3400 cm⁻¹, which was assigned to the COOH groups. Peaks appearing at 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 ¹H-NMR spectrum of diacid **3f** is shown 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 CH₃(g), peak in 1.79-1.93 ppm were assigned to H(f). Protons relevant to olefin bicyclo 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 (Figure 2). These peaks in ¹H-NMR and ¹³C-NMR spectra along with elemental analyses data confirmed the proposed structure of compound **3f**.

Fig. 1: ¹H-NMR spectrum of diacid **3f**

Fig. 2: ¹³C-NMR spectrum of diacid **3f**

1,2-bis[4-aminophenoxy]ethane **7** was synthesized according this method: At first 1,2-bis[4,4'-nitrophenoxy] ethane **6** was prepared from the reaction of two equivalents p-nitrophenol **5** and one equivalent 1,2-dibromo ethane **4**. Then dinitro compound **6** was reduced by using 10% Pd-C, ethanol and hydrazine monohydrate (Scheme 1).

Scheme 2: Synthesis of diamine **7**

The chemical structure and purity of dinitro compound **6** were proved with elemental analysis, ¹H-NMR and FT-IR spectroscopy and diamine compound **7** were proved with elemental analysis, FT-IR, ¹H-NMR, and ¹³C-NMR 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 FT-IR spectrum of diamine **7** showed two peaks at 3406 and 3327 cm⁻¹, which were assigned to the NH₂ groups.

6.66-6.69 (d, 4H, J= 9 Hz), 6.48-6.51 (d, 4H, J= 9 Hz), 4.63 (s, 4H), 4.07 (s, 4H) ppm. ¹³C-NMR (300 MHz, DMSO-d₆): δ; 150.0, 143.0, 115.8, 115.3, 67.3 ppm. Elemental

¹H-NMR spectrum of diamine **7** showed peaks as a doublet of doublet at 6.66-6.69 ppm and 6.48-6.51 ppm were assigned to the H(a) and H(b) related to aromatic protons, and a singlet peak at 4.07 ppm which was assigned to the H(d) protons of the NH₂ groups in this compound (Fig. 3).

Fig. 3: ^1H -NMR spectrum of diamine 4

Polymer synthesis

The direct polycondensation of a dicarboxylic acid and diamine is one of the well-known methods for PAI synthesis. In this article, we synthesized PAIs **8a-g** containing dibenzalacetone moiety by the direct polycondensation reactions of seven chiral *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-*L*-amino acids **3a-g** with 1,2-bis[4,4'-aminophenoxy]ethane **7** in two different media such as direct polycondensation in a medium consisting of *N*-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl_2)/pyridine (Py) (method A, Scheme 3) and direct polycondensation in a tosyl chloride (TsCl)/pyridine (Py)/*N,N*-dimethylformamide (DMF) system (Media B, Scheme 3).

Scheme 3: Synthesis of PAIs **8a-g** in two different media

In media A for direct polycondensation used TPP/Py/ CaCl_2 as activating agent according to a typical procedure that was shown in Scheme 3. A triphenyl phosphite (TPP)-activated polycondensation (phosphorylation reaction) technique for the synthesis of polyamides was reported by Yamazaki et al.²¹

The syntheses and some physical properties of these new PAIs **8a-g** are given in Table 3. The entire polycondensation reaction readily proceeds in a homogeneous solution, tough and stringy precipitates formed when the viscous PAIs solution was obtained in good yields.

In method B for the direct polycondensation of diacids **3a-g** and aromatic diamine **7**, a Vilsmeier adduct was prepared by dissolving TsCl in a mixed solvent of Py and DMF. The polycondensation was carried out as the following way: TsCl was dissolved in Py and after a certain period of time (aging time);

the solution was treated with DMF for 30 min. The reaction mixture was added to a solution of diacid in Py. After 30 min, a solution of diamine in Py was added and the whole solution was maintained at room temperature, and then at refluxing temperature.²²

The polymers with high inherent viscosities were obtained at 2 hrs time. The syntheses and some physical properties of these new PAIs **8a-g** are given in Table 4. The entire polycondensation reaction readily proceeds in a homogeneous solution, tough and stringy precipitates formed when the viscous PAIs solution was obtained in moderate yields. Although PAIs **8a-g** obtained in a shorter period in media B, but these polymers obtained with higher inherent viscosities and good yields in media A.

One of the main methods for synthesis of optically active polymers is incorporation of chiral segments in the monomer structure. In this work we used of chiral amino acid moieties for synthesis of chiral diacids **3a-g**. Also Specific Rotations of the resulting polymers were measured at a concentration of 0.5 g/dL in DMF at 25°C (Table 3 and 4).

Table 3 Yield and some physical properties PAIs **8a-g** by media A.

Diacid	Polymer	Yield(%)	η_{inh} (dL/g) ^a	$[\alpha]_D^{25}$ ^a	Color ^b
3a	8a	92	0.75	+88	W
3b	8b	91	0.85	+110	Y
3c	8c	86	0.78	+110	W
3d	8d	91	0.59	+76	Y
3e	8e	91	0.66	+96	PY
3f	8f	92	0.69	+86	Y
3g	8g	83	0.51	+124	PY

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

^b, PY= Pale Yellow, Y=Yellow, W=White.

Table 4 Yield and some physical properties PAIs **8a-g** by media B.

Diacid	Polymer	Yield(%)	η_{inh} (dL/g) ^a		Color ^b
3a	8a	74	0.50	+102	B
3b	8b	77	0.38	+92	Y
3c	8c	83	0.46	+68	PB
3d	8d	75	0.28	+56	Y
3e	8e	81	0.61	+110	PY
3f	8f	68	0.54	+58	B
3g	8g	82	0.30	+62	PB

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

^b, B= Brown, PB= Pale Brown, PY= Pale Yellow, Y=Yellow.

Polymer properties

The Spectroscopic results such as CHN, FT-IR and ^1H -NMR data confirmed the structure of these polymers. The elemental analyses of the resulting PAIs **8a-g** were in good agreement with the calculated values for the proposed structure (Table 5).

Table 5 Elemental analysis results of PAIs **8a-g**.

Polymer	Formula		C%	H%	N%
8a	$C_{32}H_{30}N_4O_8$	Calcd.	64.21	5.05	9.36
	$(598.21)_n$	Found	63.64	4.98	9.18
8b	$C_{36}H_{38}N_4O_8$	Calcd.	66.04	5.85	8.56
	$(654.71)_n$	Found	63.54	5.79	8.22
8c	$C_{38}H_{42}N_4O_8$	Calcd.	66.85	6.20	8.21
	$(682.76)_n$	Found	66.11	6.21	8.04
8d	$C_{38}H_{42}N_4O_8$	Calcd.	66.85	6.20	8.21
	$(682.76)_n$	Found	66.08	6.18	7.98
8e	$C_{44}H_{38}N_4O_8$	Calcd.	70.39	5.10	7.46
	$(750.79)_n$	Found	70.02	5.06	7.27
8f	$C_{34}H_{34}N_4O_8$	Calcd.	65.17	5.47	8.94
	$(626.66)_n$	Found	64.89	5.39	8.80
8g	$C_{38}H_{34}N_4O_8$	Calcd.	62.46	4.69	15.33
	$(730.25)_n$	Found	61.98	4.62	14.98

The representative FT-IR spectrum of PAI **8f** was shown in Figure 4. The polymer exhibited characteristic absorption bands at 1772 cm^{-1} for the imide ring (asymmetric C=O stretching vibration), 1709 cm^{-1} (symmetric C=O stretching and amide stretching vibration) in the main chain, 1386 cm^{-1} (C-N stretching vibration). The absorption bands of amide groups appeared at 3335 cm^{-1} (N-H stretching). FT-IR characterizations of all PAIs are given in Table 6.

Fig. 4: FT-IR spectrum of PAI **8f****Table 6** FT-IR characterization of PAIs **8a-g**.

Polymer	Spectral data (ν , cm^{-1})
8a	3269 (w), 2915 (w), 1774 (w), 1709 (s), 1605 (m), 1518 (m), 1380 (m), 1219 (m), 1158 (m), 1065 (w), 969 (w), 830 (w), 725 (w).
8b	3246 (m), 2926 (m), 1776 (w), 1710 (s, br), 1605 (s), 1516 (s), 1383 (s), 1235 (s), 1178 (m), 1087 (w), 981 (m), 830 (m), 725 (w), 704 (w).
8c	3245 (w), 2915 (w), 1776 (w), 1712 (s), 1602 (m), 1518 (m), 1383 (m), 1219 (m), 1177 (m), 1065 (w), 929 (w), 832 (w), 725 (w).
8d	3252 (w), 2918 (w), 1774 (w), 1709 (s), 1605 (m), 1516 (m), 1382 (m), 1248 (m), 1115 (m), 1080 (s), 983 (w), 837 (w), 725 (w).
8e	3244 (w), 2928 (m), 1776 (w), 1712 (s), 1605 (m), 1516 (m), 1386 (m), 1250 (m), 1111 (m), 1082 (m), 983 (w), 837 (w), 729 (w).
8f	3238 (w), 3055 (w), 2928 (w), 1772 (w), 1709 (s), 1604 (w), 1510 (s), 1386 (m), 1305 (w), 1228 (s, br), 1120 (w), 1066 (w), 831 (w), 723 (w).
8g	3243 (w, br), 2918 (m, br), 1774 (w), 1710 (s, br), 1610 (m), 1510 (m), 1383 (m), 1251 (m), 1112 (m), 1082 (s), 983 (w), 837 (w), 725 (w).

Figure 5 displays ^1H -NMR spectrum of PAI **8a** that the aromatic protons related to diamine appeared in the region of 6.70-6.78 and 7.24-7.40 ppm and the peak in the region of 9.52 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 PAI **8a**.

Fig. 5: ^1H -NMR spectrum of PAI **8a**

Solubility of the PAIs

One of the main objectives of this study was producing modified poly(amide-imide)s with improved solubility. By the incorporation of monomers with ether and bicyclo moiety these polymers are expected to have higher solubility. The solubility of PAIs **8a-g** was investigated as 0.01 g of polymeric sample in 2 mL of solvent. Remarkably, all of these PAIs were easily soluble at room temperature in aprotic polar solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF) and insoluble in solvents such as acetone, chloroform, ethanol and methanol.

Thermal properties

TGA and derivative of thermogravimetric (DTGA) analysis at a rate of $10^{\circ}\text{Cmin}^{-1}$ in a nitrogen atmosphere were utilized to examine the thermal decomposition of these PAIs, and the obtained results are summarized in Table 7. Figure 6 show TGA results of all the PAIs.

The thermal stability of the polymers was studied on the basis of 5 and 10% weight losses (T_5 and T_{10} , respectively) of the polymers and the residue at 600°C (char yield). The results revealed that the PAIs were thermally stable up to 320°C . TGA data showed that the resulting polymers were good thermally stable. Also the DSC analyses for the polymers showed T_g between 175 and 215°C respectability (Table 7). Thermal stability and T_g value of the polymers **8e** and **8g** with aromatic rings were higher than the other polymers, because these polymers has a rigid aromatic structure in the side chain.

Table 7 Thermal behavior of all the PAIs.

Polymer	T_g^a	$T_5(^{\circ}\text{C})^b$	$T_{10}(^{\circ}\text{C})^b$	Char yield ^c
8a	200	330	370	44.5
8b	185	320	340	43.62
8c	175	275	360	42.52
8d	185	220	310	43.21
8e	210	330	380	51.83
8f	195	270	375	38.25
8g	215	260	370	47.91

^a Glass transition temperature was recorded at a heating rate of $10^{\circ}\text{Cmin}^{-1}$ in a nitrogen atmosphere.

^b Temperature at which 5% or 10% weight loss was recorded in TGA analysis at a heating rate of 10°C/min under N_2 .

^c Weight percentage of material left after TGA analysis at a maximum temperature of 600°C under N_2 .

REFERENCES

- Ghosh, M.K.; Mittal, K.L. *Polyimides: Fundamentals and Applications*. Marcel Dekker: New York (1996).
- Ghosh, A.; Banerjee, S. *Polym. Adv. Technol.*, **19**, 1486, (2008).
- Cassidy, P.E. *Thermally Stable Polymers*. Marcel Dekker: New York (1980).
- Saxena, A.; Rao, V.L.; Prabhakaran, P.V.; Ninan, K.N. *Eur. Polym. J.*, **39**, 401, (2003).
- Liaw, D.J.; Liaw, B.Y.; Hsu, P.N.; Hwang, C.Y. *Chem. Mater.*, **13**, 1811, (2001).
- Mallakpour, S.; Meratian, S. *High. Perform. Polym.*, **20**, 3, (2008).
- Faghihi, Kh.; Mozaffari, Z. *J. Appl. Polym. Sci.*, **108**, 1152, (2008).
- Faghihi, Kh.; Hajibeygi, M.; Shabanian, M. *Macromol. Res.*, **17**, 739, (2009).
- Faghihi, Kh.; Naghavi, H. *J. Appl. Polym. Sci.*, **96**, 1776, (2004).
- Zhang, Q.; Li, S.; Li, W.; Zhang, S. *Polymer*, **48**, 6246, (2007).
- Zhang, Q.; Chen, G.; Zhang, S. *Polymer*, **48**, 2250, (2007).
- Bottino, F.A.; Pasquale, G.D.; Scalia, L.; Pollicino, A. *Polymer*, **42**, 3323, (2001).
- Gutch, P.K.; Banerjee, S.; Jaiswal, D.K. *J. Appl. Polym. Sci.*, **89**, 691, (2003).
- Voet, D.; Voet, J.G.; Pratt, C.W. *Fundamentals of Biochemistry*. Wiley: New York (1999).
- Mallakpour, S.; Zamanlou M.R. *J. Appl. Polym. Sci.*, **91**, 3281, (2004).
- Liaw, D.J.; Chang, F.C.; Liu, J.H.; Wang, K.L.; Faghihi, Kh.; Huang, S.H.; Lee, K.R.; Lai, J.Y. *Polym. Degrad. Stabil.*, **92**, 323, (2007).
- Yeganeh, H.; Tamami, B.; Ghazi, I. *Eur. Polym. J.*, **38**, 2179, (2002).
- Faghihi, Kh. *J. Appl. Polym. Sci.*, **109**, 74, (2008).
- Faghihi, Kh.; Shabanian, M.; Hajibeygi, M. *Macromol. Res.*, **17**, 912, (2009).
- Eastmond, G.C.; Paprotny, J. *Polymer*, **43**, 3455, (2002).
- Yamazaki, N.; Matsumoto, M.; Higashi, F. *J. Polym. Sci. Part A: Polym. Chem.*, **13**, 1373, (1975).
- Mallakpour, S.; Kolahdoozan, M. *J. Appl. Polym. Sci.*, **104**, 1248, (2007).

Fig. 6: TGA curves of all the PAIs

CONCLUSIONS

A series of new thermally stable and optically active organosoluble PAIs **8a-g** containing bicyclo and ether groups moiety were synthesized by the direct polycondensation reactions of seven chiral diacids **3a-g** with diamine **7** by two different methods. By introducing ether and bicyclo moiety into the polymer backbone the rigid conformation of the chains is modified increasing the solubility in polar aprotic solvents. Because the resulting polymers contained optically pure *L*-amino acid moieties, they showed optical rotations and were optically active. The presented results also clearly demonstrate that incorporating the imide group into the polymer main chain as well as combination of the wholly aromatic backbone and several functional groups remarkably enhanced the thermal stability of the new polymers. Potential applications of amino acid based polymers include chiral stationary phases for the resolution of enantiomers in chromatographic techniques, and biomaterials.