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Preparation and Characterization of New Optically Active Poly(amide-imide)s from N,N'-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetra carboxylic)-bis-L-isoleucine and Aromatic Diamines

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Preparation and Characterization of New Optically Active Poly(amide-imide)s from N,N'-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetra carboxylic)-bis-L-isoleucine and Aromatic Diamines

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Five new optically active aromatic poly(amide-imide)s (PAIs) **5a–e** were prepared from a direct polycondensation reaction of a new diacid of N,N'-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetra carboxylic)-bis-L-isoleucine **3** with various aromatic diamines **4a–e** in a medium consisting of triphenyl phosphite (TPP), calcium chloride (CaCl₂), pyridine (Py) and N-methyl-2-pyrrolidone (NMP). The polycondensation reaction produced a series of novel poly(amide-imide)s **5a–e** in quantitative yields with inherent viscosities of 0.39–0.51 dL/g. The resulting polymers were fully characterized by means of ¹H-NMR, FT-IR spectroscopy, elemental analyses, inherent viscosity, solubility test, specific rotation and thermal properties of them were investigated using TGA/DTG and differential scanning calorimeter (DSC). The diacid **4** was synthesized by the condensation reaction of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1** with L-isoleucine **2** in acetic acid solution.

Keywords: Optically active, polycondensation, poly(amide-imide), isoleucine, specific rotation

1 Introduction

Aromatic polyimides (PI) possess many desirable characteristics such as high thermal stability and excellent physical properties and they have been used in the fields of adhesives, composites, fibers, films and electrical materials (1–2). However, they are generally insoluble and infusible after conversion from their poly(amic-acid) precursors to polyimides (3–5). Replacement of polyimides by copolyimides such as poly(amide-imide)s (PAIs) may be useful to tackle the intractability of polyimides (6–9). PAIs are also expected to have the advantages of polyamides and polyimides, such as solvent resistance. Several attempts have been made to modify the PAIs structure by introducing the functional groups or substations capable of reducing the chain rigidity and further increasing their tractability and applicability (10–12).

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 (13–15). 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 diamines via usual polymerization techniques (16–24).

In this article, synthesis and characterization a new series of PAIs **5a–e** containing rigid segments bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide in the main chain was described. PAIs **5a–e** were synthesized by direct polycondensation reaction of diacid **3** with 4,4'-diamino diphenyl ether **4a**, 4,4'-diamino diphenyl sulfone **4b**, 3,3'-diamino diphenyl sulfone **4c**, 1,4-phenylenediamine **4d**, 1,5-diamino naphthalene **4e**, in a medium consisting of N-methyl-2-pyrrolidone (NMP), triphenyl phosphite (TPP), calcium chloride (CaCl₂) and pyridine (Py). Results showed these new polymers with amide-imide groups and bicyclo segment in the main chain have better solubility in organic solvents in compared to aromatic polyimides.

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2 Experimental

2.1 Materials

Bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1** (from Aldrich), L-isoleucine **2**, 4,4'-diaminodiphenyl ether **4a**, 4,4'-diaminodiphenylsulfone **4b**, 3,3'-diaminodiphenylsulfone **4c**, 1,4-phenylenediamine **4d**, 1,5-diamino naphthalene **4e**, N-methyl-2-pyrrolidone (NMP), pyridine and triphenyl phosphite (TPP) were purchased from Merck Chemical Company and used without previous purification. Commercially available calcium chloride (CaCl₂) was purchased from Merck Chemical Company and dried under vacuum at 150°C for 6 h.

2.2 Techniques

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded on a 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 Merk 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 calorimeter (DSC) was conducted with a DSC Mettler 110 (Switzerland) at a heating and heating rate of 10°Cmin⁻¹ in a nitrogen atmosphere. Elemental analyses were performed by Vario EL equipment by Arak University.

2.3 Monomer Synthesis

2.3.1. N,N'-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic)-bis-L-isoleucine **3**

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**, (1.310 g, 10 mmol) of L-isoleucine **2** 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 2.198 g (92%) of compound **3**. M.p. = 293–295°C, [α]_D²⁵ = 156° (0.05 g in 10 mL DMF). FT-IR (KBr): 2400–3400 (m, br), 1772 (w), 1744 (s), 1709 (s), 1390 (m), 1232 (w), 1390 (m), 806 (w), 717 (w), 599 (w) cm⁻¹. ¹H-NMR (300 MHz, DMSO-d₆, 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). ¹³C-NMR (300 MHz,

DMSO-d₆, δ ppm): 177.59, 169.66, 131.27, 57.03, 42.50, 42.40, 33.67, 25.24, 16.90, 10.87. Elemental analysis: calcd for C₂₄H₃₀N₂O₈: C, 60.75%; H, 6.37%; N, 5.90%; found: C, 60.45%; H, 6.21%; N, 5.91%.

2.4 Polymer Synthesis

As a typical example, PAI **5b** was prepared as follows: into a 50 mL round-bottom flask, (0.309 g, 0.652 mmol) of diacid **3**, (0.130 g, 0.652 mmol) of 4,4-diamino diphenyl sulfone **4b**, 0.1 g of calcium chloride, 1 mL of NMP, 0.8 mL of triphenyl phosphite and 0.3 mL of pyridine and a stirring bar were placed. The mixture was stirred at room temperature for 2 h and then heated with 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 in to 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 0.395 g (95%) of solid polymer **5b**.

FT-IR (KBr) data for Polymer **5a**: 3190 (m, br), 2970 (m), 1774 (w), 1710 (s), 1606 (w), 1498 (s), 1381 (m), 1305 (w), 1224 (m), 835 (w) cm⁻¹.

FT-IR (KBr) data for Polymer **5b**: 3336 (m, br), 2969 (m), 1775 (m), 1698 (s, br), 1593 (s), 1528 (s), 1380 (s), 1313 (s), 1194 (s), 1107 (s), 928 (w), 839 (m), 689 (m) cm⁻¹.

FT-IR (KBr) data for Polymer **5c**: 3393 (m, br), 2969 (m), 1773 (w), 1713 (s), 1595 (s), 1481 (m), 1302 (m), 1151 (m), 1097 (m), 927 (m), 766 (m), 689 (m) cm⁻¹.

FT-IR (KBr) data for Polymer **5d**: 3313 (m), 2964 (m), 1774 (w), 1710 (s, br), 1535 (m), 1493 (m), 1381 (m), 1194 (m), 1066 (w), 785 (m), 601 (w) cm⁻¹.

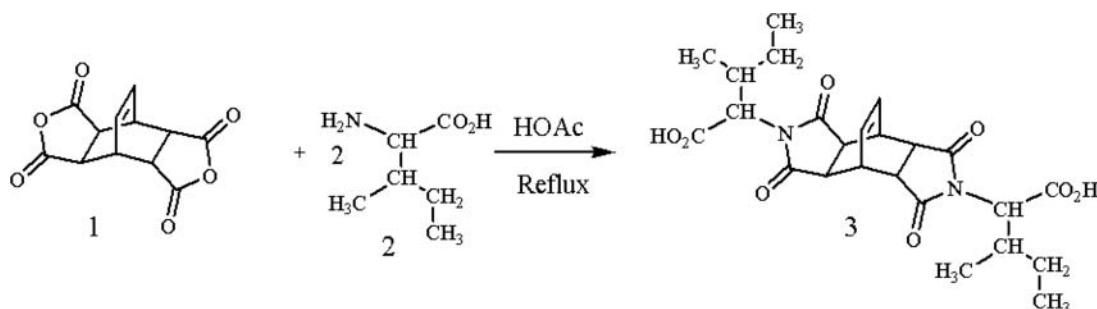
FT-IR (KBr) data for Polymer **5e**: 3271 (m), 2966 (m), 1774 (w), 1695 (s, br), 1606 (m), 1518 (s, sh), 1464 (w), 1348 (m, sh), 1307 (m), 1195 (m), 1064 (w), 835 (w), 756 (w), 609 (w) cm⁻¹.

3 Results and Discussion

3.1 Monomer Synthesis

N,N'-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetra carboxylic)-bis-L-isoleucine **3** was prepared by a one-step reaction as shown in Scheme 1. This compound was synthesized by the condensation reaction of one equimolar of dianhydride **1** with two equimolar of L-isoleucine **2** in acetic acid solution. Dissolving the residue in cold water gives a gummy-like solid that breaks by adding concentrated HCl and gave a white color solid.

The chemical structure and purities of diacid **3** were also analyzed by elemental analysis, ¹H-NMR, ¹³C-NMR and FT-IR spectroscopy. The measured results in elemental analyses closely corresponded to the calculated ones, demonstrating that the expected compound was obtained. Figure 1 displays FT-IR spectrum of diacid **3**. Peaks



Sch. 1. Synthesis of diacid 3.

appearing at $2400\text{--}3400\text{ cm}^{-1}$ (acid O–H stretching), 1772 and 1709 cm^{-1} (asymmetric and symmetric imide stretching), 1744 cm^{-1} (acid C=O and stretching), 1390 and 717 cm^{-1} (imide characteristic ring vibration) confirmed the presence of imide rings and carboxylic groups in this compound.

The $^1\text{H-NMR}$ spectrum of diacid 3 was shown in Figure 2. The peak relevant to O–H carboxylic acid groups appeared at 12.82 ppm . The peak in $4.19\text{--}4.21\text{ ppm}$ as a doublet was assigned to the CH(b) protons as a chiral center, peaks between $0.72\text{--}0.92\text{ ppm}$ were assigned to aliphatic CH_3 (e, f). Also olefin protons (H_i) in bicyclo ring appeared in $5.00\text{--}5.02\text{ ppm}$.

The $^{13}\text{C-NMR}$ spectrum of diacid 3 showed 10 signals, including C(h) and C(i) in carboxylic acid and imide rings, C(g) related to carbon atoms olefin and C(f) relevant to chiral carbon atoms (Fig. 3).

3.2 Synthesis of Polymer

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 5a–e containing bicyclo segment by direct polycondensation reaction of diacid 4 with five different derivatives of aromatic diamines 4a–e in a medium consisting of N-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl_2)/pyridine (py) system, as shown in Scheme 2.

Table 1. Some physical properties of PAIs 5a–e

Diamine	Polymer	Yield (%)	$\eta_{inh}(\text{dL/g})^a$	$[\alpha]_D^{25a}$	Color
4a	5a	95	0.42	+178.1	Cream
4b	5b	94	0.39	+118.9	White
4c	5c	90	0.47	+105.0	White
4d	5d	90	0.51	+220.5	Cream
4e	5e	85	0.43	+170.2	White

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

Synthesis and some physical properties of PAIs 5a–e are summarized in Table 1. These polymers have inherent viscosities in a range of $0.39\text{--}0.51\text{ dL/g}$. PAIs derived from monomer 3 may range in color from cream or white. All of the resulting polymers show optical rotation and are optically active.

3.3 Polymer Characterization

The structures of these polymers were confirmed as PAIs by mean of FT-IR, $^1\text{H-NMR}$ spectroscopy and elemental analyses. The representative FT-IR spectrum of PAI 5a was shown in Figure 4. The polymer exhibited characteristic absorption bands at $1710\text{--}1774\text{ cm}^{-1}$ for the imide ring (asymmetric and symmetric C=O stretching vibration), 1381 cm^{-1} (C–N stretching vibration). The absorption bands of amide groups appeared at 3190 cm^{-1} (N–H stretching).

The $^1\text{H-NMR}$ spectrum of polymer 5a showed some peaks that confirm the chemical structure (Fig. 5). The aromatic protons related to diphenyl ether appeared in the region of $6.90\text{--}7.51\text{ ppm}$ and the peak in the region of 9.85 ppm is assigned for NH of amide groups in the polymer backbone.

The elemental analyses of the resulting PAIs 5a–e were in good agreement with the calculated values for the proposed structure (Table 2).

Table 2. Elemental analysis of PAIs 5a–e

Polymer	Formula		C%	H%	N%
5a	$\text{C}_{36}\text{H}_{38}\text{N}_4\text{O}_7$	Calcd	67.71	5.96	8.78
	$(638.29)_n$	Found	66.81	5.83	7.86
5b	$\text{C}_{36}\text{H}_{38}\text{N}_4\text{O}_8\text{S}$	Calcd	62.97	5.54	8.16
	$(686.34)_n$	Found	61.53	5.38	7.36
5c	$\text{C}_{36}\text{H}_{38}\text{N}_4\text{O}_8\text{S}$	Calcd	62.97	5.54	8.16
	$(686.34)_n$	Found	62.20	5.11	7.82
5d	$\text{C}_{34}\text{H}_{36}\text{N}_4\text{O}_6$	Calcd	68.46	6.04	9.39
	$(596.28)_n$	Found	66.92	5.90	8.73
5e	$\text{C}_{30}\text{H}_{34}\text{N}_4\text{O}_6$	Calcd	65.91	6.23	10.26
	$(546.24)_n$	Found	64.54	6.00	9.45

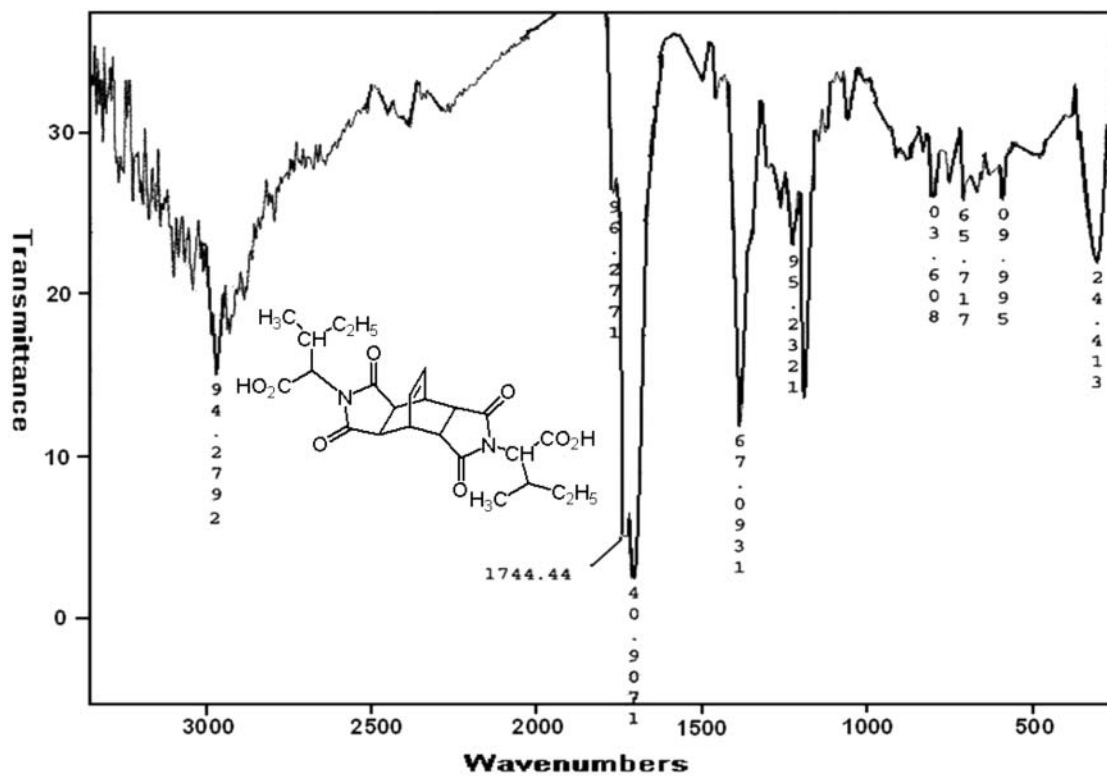


Fig. 1. FT-IR spectrum of diacid 3.

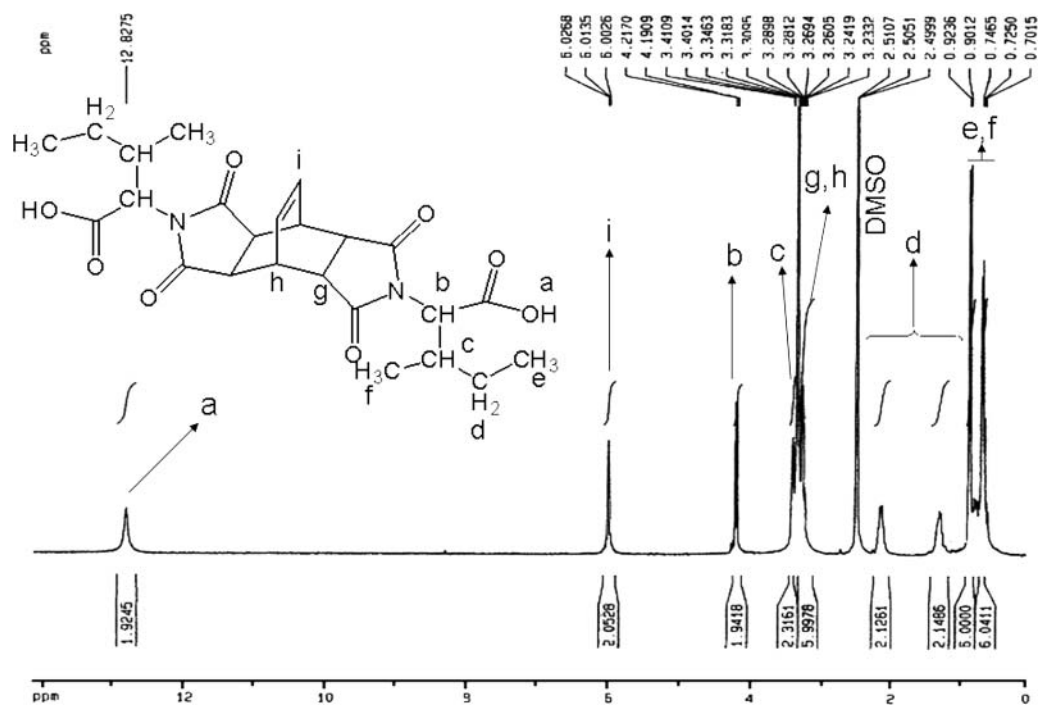


Fig. 2. ¹H-NMR spectrum of diacid 3.

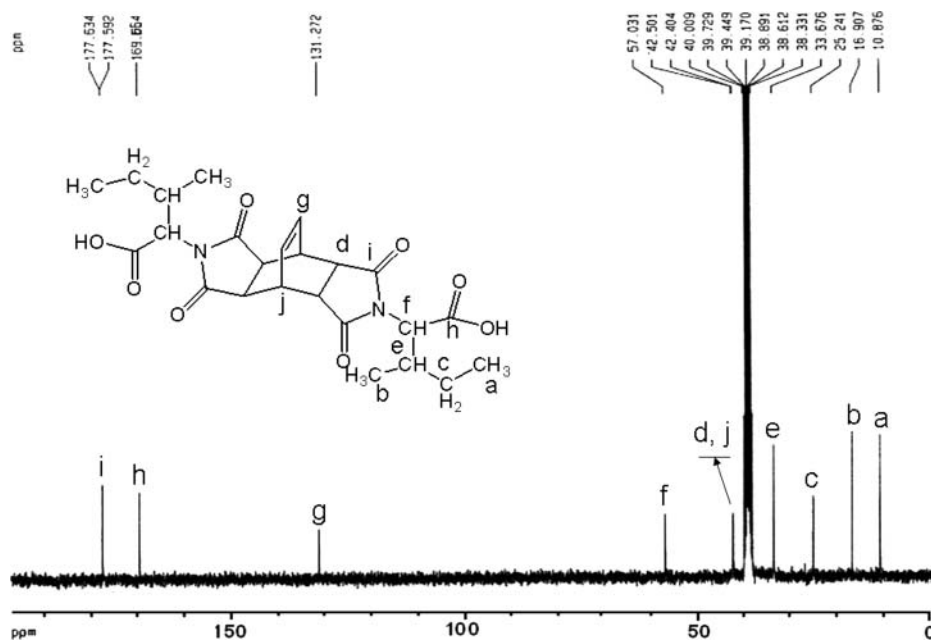


Fig. 3. ^{13}C -NMR spectrum of diacid **3**.

Table 3. Solubility of PAIs **5a–e**

Solvent	5a	5b	5c	5d	5e
DMAc	+	+	+	+	+
DMF	+	+	+	+	+
DMSO	+	+	+	+	+
NMP	+	+	+	+	+
CH_3OH	–	–	–	–	–
$\text{C}_2\text{H}_5\text{OH}$	–	–	–	–	–
CHCl_3	–	–	–	–	–
CH_2Cl_2	–	–	–	–	–
H_2O	–	–	–	–	–

+, Soluble at room temperature. –, Insoluble at room temperature.

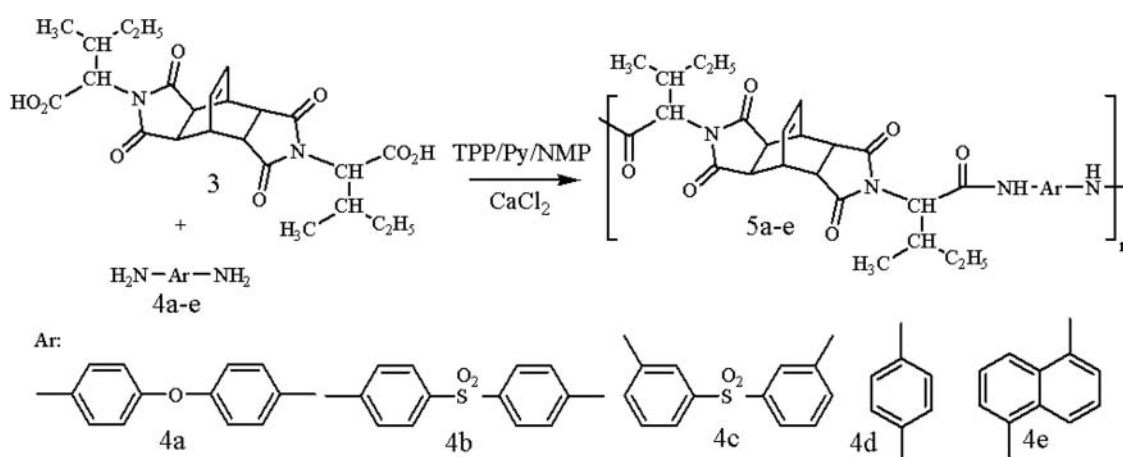
Table 4. Thermal behavior of PAIs **5b**, **5c** and **5e**

Polymer	T_g^a	$T_5(^{\circ}\text{C})^b$	$T_{10}(^{\circ}\text{C})^b$	Char yield ^c
5b	188	320	370	39.00
5c	171	345	370	32.27
5e	201	360	380	37.72

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

^b Temperature at which 5% or 10% weight loss was recorded by TGA 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 .



Sch. 2. Synthesis of PAIs **5a–e**.

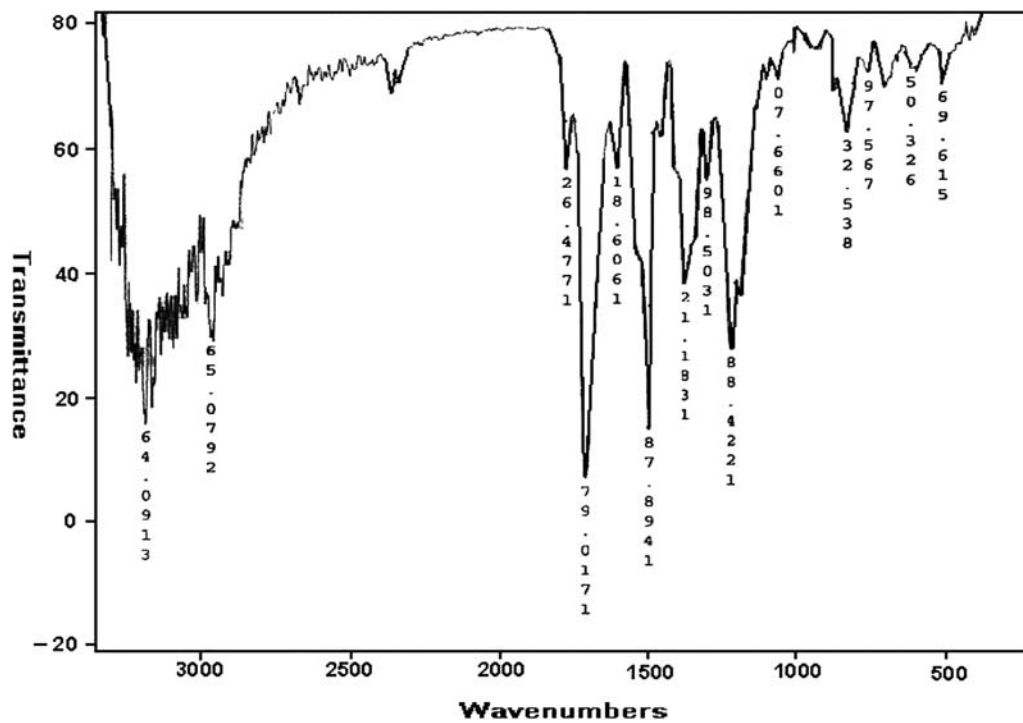
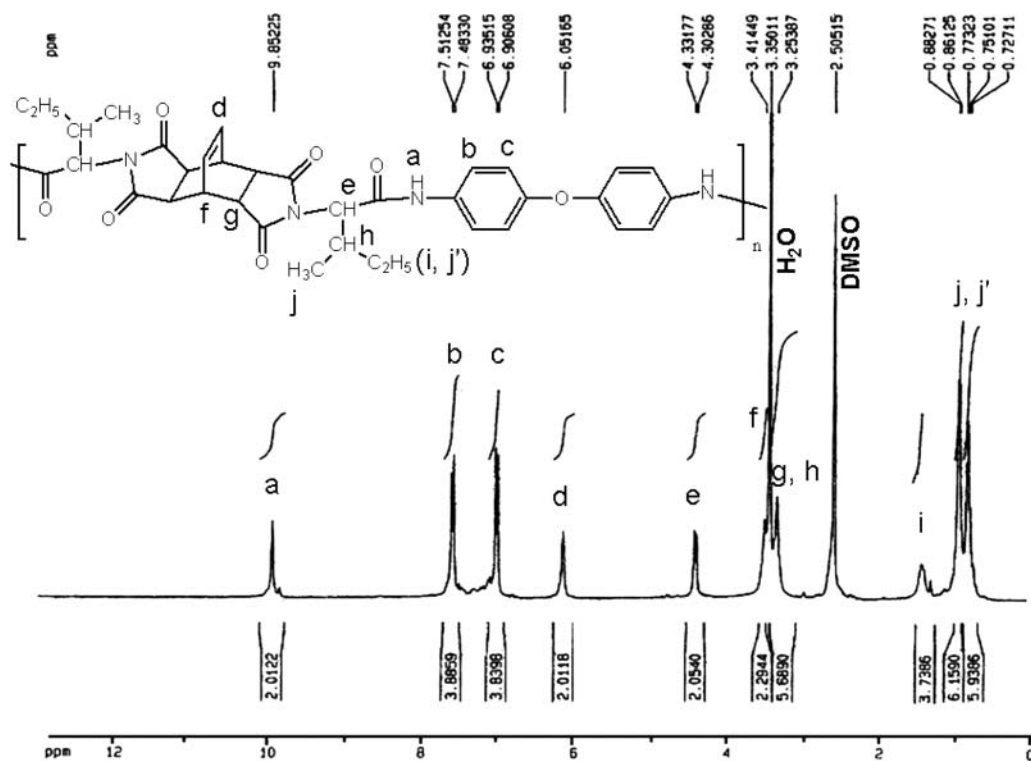


Fig. 4. FT-IR spectrum of PAI 5a.

Fig. 5. ¹H-NMR spectrum of PAI 5a.

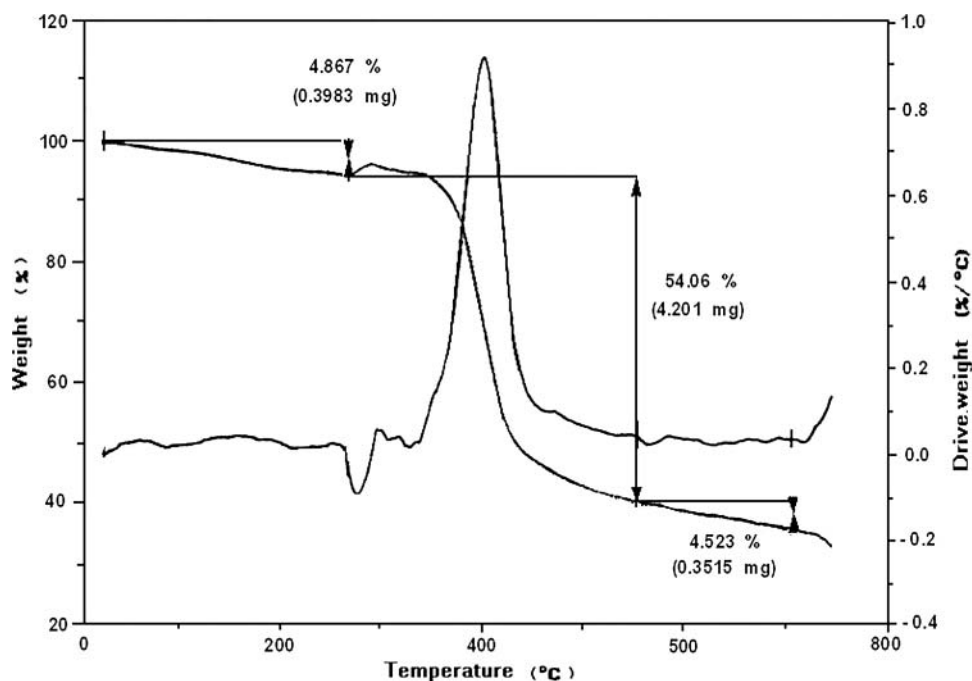


Fig. 6. TGA and DTG thermogram of PAI 5b.

The solubility of PAIs 5a-e was investigated as 0.01 g of polymeric sample in 2 mL of solvent. All of the polymers are soluble in organic solvents such as DMF, DMSO and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water (Table 3). Due to presence of isoleucine moiety in the polymer chain, and its aliphatic pendant group, these synthesized poly(amide-imide)s had

better solubility than polymers containing amide and imide groups in the main chain of polymer.

3.4 Thermal Properties

TGA and derivative of thermogravimetric (DTG) analysis at a rate of $10^{\circ}\text{Cmin}^{-1}$ in a nitrogen atmosphere were

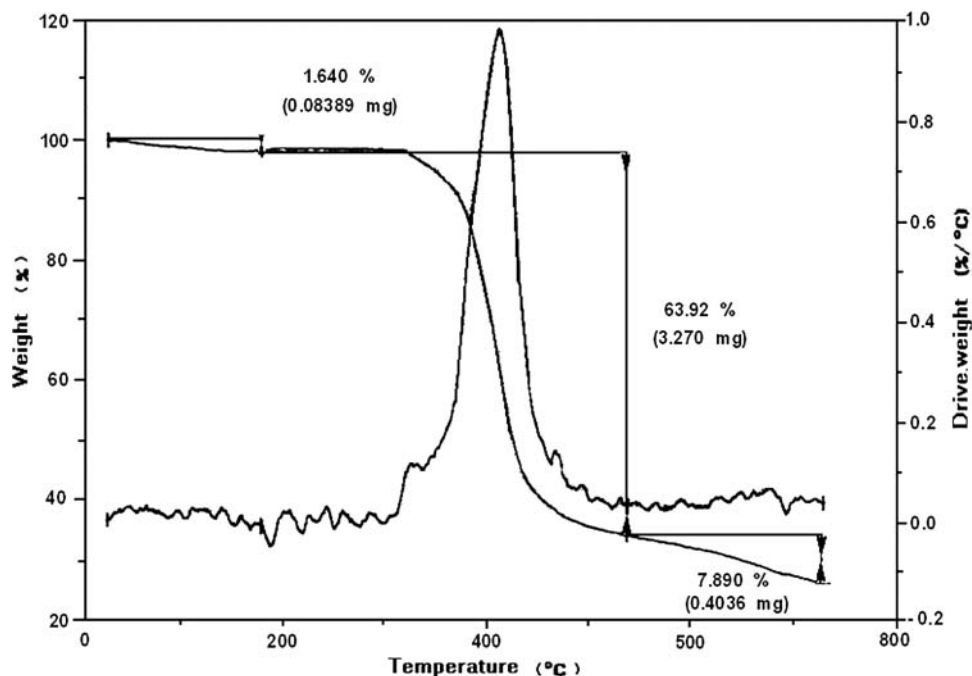


Fig. 7. TGA and DTG thermogram of PAI 5c.

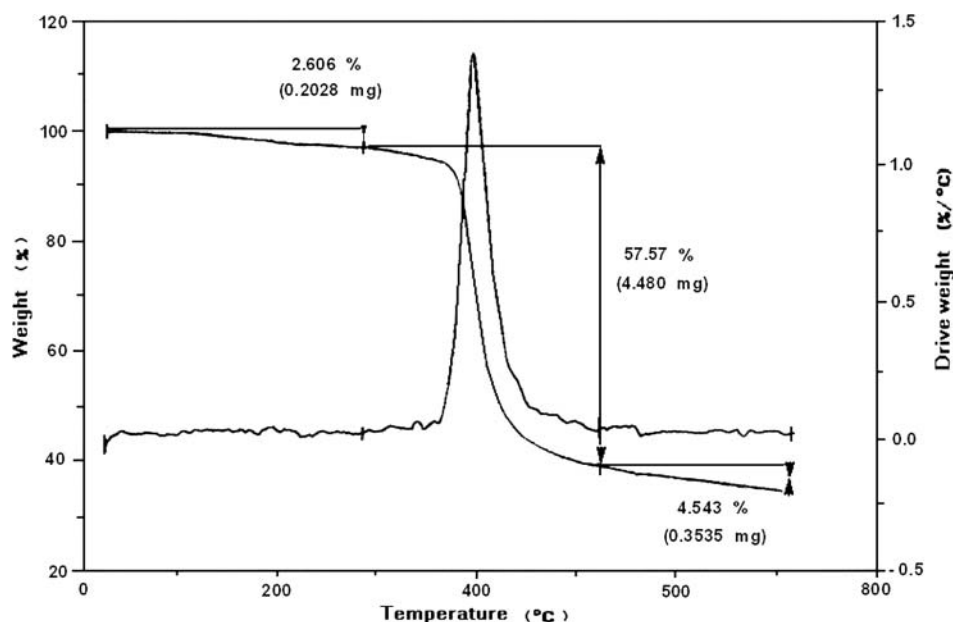


Fig. 8. TGA and DTG thermogram of PAI 5e.

utilized to examine the thermal properties of PAIs **5b**, **5c** and **5e**, and the obtained results are summarized in Table 4.

The initial decomposition temperatures of 5% and 10% weight losses (T_5 and T_{10}) and the char yield at 600°C are summarized in Table 4. Figures 6–8 show TGA and DTG results of PAIs **5b**, **5c** and **5e**, respectively.

These polymers exhibited good resistance to thermal decomposition, up to 320 to 360°C in nitrogen, and began to decompose gradually above those temperatures. T_5 for these polymers from 320 to 360°C and T_{10} for all polymers ranged from 370 to 380°C, and the residual weight for these polymers at 600°C ranged from 32.27 and 39.0% in nitrogen. Also the DSC analyses for PAIs showed T_g around 171–201°C (Table 4).

4 Conclusions

The present work has shown that N,N'-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic)bis-L-isoleucine **3** is an interesting monomer which contains both imide groups as well as a chiral L-isoleucine groups. This compound was used to synthesis a series of new optically active PAIs **5a–e** by polycondensation reaction with five aromatic diamines **4a–e**. These PAIs are optically active, are soluble in various organic solvents and have good thermal stability. These resulting new polymers have the potential to be used in column chromatography technique for the separation of the enantiomeric mixtures.

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