

New Optically Active and Thermally Stable Poly(amide-imide)s Containing *N,N'*-(Bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic)-bis-L-Alanine and Aromatic Diamines: Synthesis and Characterization

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Cinco novas poliamidas-iminas (PAIs) opticamente ativas **6a-e** foram preparadas pela reação de policondensação direta da *N,N'*-(bicyclo[2,2,2]octa-7-eno-2,3,5,6-tetracarboxila)-bis-L-alanina **4** com várias diaminas aromáticas **5a-e** usando solventes polares apróticos como a *N*-metil-2-pirrolidona (NMP). Neste procedimento, trifetil fosfito (TPP) e piridina foram usados como agentes de condensação para formar poliamidas-imidas através dos sais de *N*-fosfônio-piridina. Todos os polímeros foram obtidos com rendimentos quantitativos com uma viscosidade intrínseca entre 0,29-0,46 dL g⁻¹, sendo altamente solúveis em solventes polares apróticos como *N,N*-dimetil acetamida (DMAc), *N,N*-dimetilformamida (DMF), dimetil sulfoxido (DMSO), *N*-metil-2-pirrolidona (NMP) e ainda em solventes como o ácido sulfúrico. Os compostos foram caracterizados por espectroscopia de RMN ¹H, espectroscopia no infravermelho, análise elementar, viscosidade intrínseca, testes de solubilidade, rotação específica e as propriedades térmicas desses polímeros foram investigadas usando técnicas termogravimétricas de análise (TGA e DTG).

Five new optically active poly(amide-imide)s (PAIs) **6a-e** were prepared by direct polycondensation reaction of the newly synthesized *N,N'*-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic)-bis-L-alanine **4** with various aromatic diamines **5a-e** using polar aprotic solvents such as *N*-methyl-2-pyrrolidone (NMP). In this technique triphenyl phosphite (TPP) and pyridine were used as condensing agents to form poly(amide-imide)s through the *N*-phosphonium salts of pyridine. All of the polymers were obtained in quantitative yields with inherent viscosities between 0.29-0.46 dL g⁻¹ and were highly soluble in polar aprotic solvents such as *N,N*-dimethyl acetamide (DMAc), *N,N*-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP) and solvents such as sulfuric acid. They were fully characterized by means of ¹H NMR, FTIR spectroscopy, elemental analyses, inherent viscosity, solubility test, specific rotation and thermal properties of these polymers were investigated using thermogravimetric analysis techniques (TGA and DTG).

Keywords: Poly(amide-imide)s; optically active polymers; L-alanine

Introduction

Aromatic polyimides are widely employed in the aerospace, microelectronics, optoelectronics and composites for their excellent balance of thermal and mechanical properties.¹⁻² However their applications have been limited in some fields because the aromatic polyimides are normally insoluble in common organic solvents and have extremely high glass transition or melting temperatures. It is well known that the chemical composition and chain structure of aromatic polyimides were responsible for their prominent

properties and responsible for their poor processibility. Therefore one of the targets of polyimide chemistry is to incorporate new functionalities to make polyimides more easily processing without decreasing their many desirable properties such as excellent thermal stability and good mechanical resistance.³⁻⁴ For this purpose many efforts on chemical modifications of polyimides have been done, such as introduction of flexible linkages in their backbone, or incorporation of bulky side groups which results in good solubility and processability of the polyimides.⁵⁻¹¹ Synthesis of poly(amide-imide)s (PAIs) by incorporating amide functionality at regular intervals in the polyimide main chain is also used. Replacement of polyimides by

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copolyimides such as poly(amide-imide)s (PAIs) may be useful to tackle the intractability of polyimides¹²⁻¹³ and among them poly(amide-imide)s (PAIs) can improve the solubility. Recently we have synthesized thermally stable PAIs by different methods.¹⁴⁻¹⁸

Also polymers with optically active properties have been found interesting applications such as chiral stationary phase for enantiomeric separation in chromatography methods or chiral media for asymmetric synthesis.¹⁹⁻²⁴ In the polycondensation reactions we use amino acids as chiral inducing agents. These materials are naturally occurring compounds and synthetic polymers based on amino acids are expected to be biodegradable and biocompatible. Recently optically active polymers by the reaction of an optically active monomer with several diamines via solution polymerization have been synthesized.²⁵⁻²⁹

In this article, we described synthesis and characterization of a series of novel poly(amide-imide)s **6a-e** containing rigid segments such as bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide in the main chain. The resulting polymers were prepared by the direct polycondensation reaction of *N,N'*-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic)-bis-*L*-alanine **4** with 4,4'-diamino diphenyl ether **5a**, 4,4'-diamino diphenyl sulfone **5b**, 3,3'-diamino diphenyl sulfone **5c**, 1,4-diamino benzene **5d**, 1,5-diamino naphthalene **5e** in a medium consisting of *N*-methyl-2-pyrrolidone (NMP), triphenyl phosphite (TPP), calcium chloride (CaCl₂) and pyridine.

Experimental

Reagents

Bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1**, *L*-alanine **2**, 4,4'-diaminodiphenylether **5a**, 4,4'-diaminodiphenylsulfone **5b**, 3,3'-diaminodiphenylsulfone **5c**, 1,4-phenylenediamine **5d**, 1,5-diamino naphthalene **5e**, *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.

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) as solid by using KBr pellets. Vibration transition frequencies were

reported in wave number (cm⁻¹) and band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Technico 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⁻¹. Elemental analyses were measured by Vario EL equipment by Arak University.

Monomer synthesis

N,N'-(bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetra carboxylic) bis-*L*-alanine **4**

Into a 100 mL round-bottomed flask with a stirring bar were placed (1.24 g, 5.0 mmol) of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1**, (0.89 g, 10.0 mmol) of *L*-alanine **2** and 30 mL of concentrated 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 then 5 mL cold concentrated HCl was added to the residue until a white precipitate formed. The precipitate was washed with cold water and dried under reduced pressure to give 1.79 g (92%) of compound **4**, m.p. 248-251 °C; [α]_D²⁵ = -58.35° (0.05g in 10 mL DMF); IR (KBr, ν_{max} / cm⁻¹): 2400-3400 (m, br), 1770 (w), 1705 (s), 1628 (w), 1396 (m), 1309 (w), 1207 (m), 1126 (m), 976 (w), 819 (w), 675 (w), 611 (w), 353 (w); ¹H NMR (300 MHz, DMSO-d₆, TMS): δ 13.01(s, br, 2H), 5.95-5.98 (t, 2H), 4.50-4.57 (q, 2H), 3.37 (s, 2H), 3.22 (s, 4H), 1.23-1.25 (d, 6H); ¹³C NMR (300 MHz, DMSO-d₆): δ 176.82, 170.61, 130.64, 47.55, 42.47, 33.89, 14.49. Elemental Anal. Calc. for C₁₈H₁₈N₂O₈: C, 55.39; H, 4.65; N, 7.18; Found: C, 55.04; H, 4.46; N, 7.14.

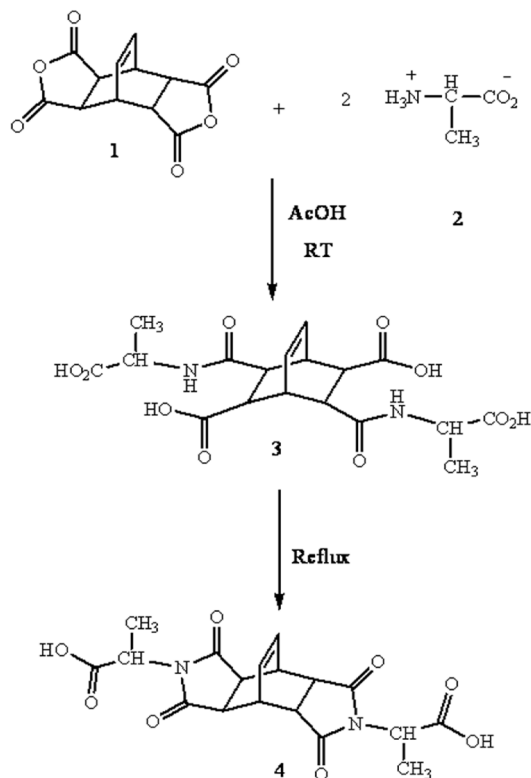
Polymer synthesis

As a typical example, PAI **6c** was prepared as follows: Into a 50 mL round-bottom flask with a stirring bar were placed (0.100 g, 0.326 mmol) diimide-diacid **4**, (0.065 g, 0.326 mmol) of 3,3'-diamino diphenyl sulfone **5c**, 0.10 g of calcium chloride, 1.0 mL of NMP, 0.8 mL of triphenyl phosphite and 0.3 mL of pyridine. 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 quenching growth of the polymer chain, the polymer solution was slowly trickled into a stirred methanol, giving a stringy precipitate. Then polymeric product was washed with hot methanol, collected by filtration and dried at 80 °C for 12 h under vacuum to leave 0.163 g (91%) of solid polymer **6c**.

Results and Discussion

Monomer synthesis

The asymmetric diimide-diacid **4** was synthesized by the condensation reaction of one equimolar of bicyclo[2,2,2]oct-7-



Scheme 1.

ene-2,3,5,6-tetracarboxylic dianhydride **1** with two equivalents of L-alanine **2** in an acetic acid solution (Scheme 1).

The chemical structure and purity of diimide-diacid **4** were proved by using elemental analysis, ^1H NMR, ^{13}C NMR and FTIR spectroscopy. The measured results in elemental analyses were closely corresponded to the calculated ones, demonstrating that the expected compound was obtained. Figure 1 displays FTIR spectrum of diimide-diacid **4**. Peaks appearing at $2400\text{--}3400\text{ cm}^{-1}$ (acid O-H stretching), 1770 cm^{-1} ($\text{C}=\text{O}$ asymmetric imide stretching), 1705 cm^{-1} ($\text{C}=\text{O}$ acid and symmetric imide stretching), 1396 and 675 cm^{-1} (imide characteristic ring vibration) confirmed the presence of imide rings and carboxylic groups in this compound.

The ^1H NMR spectrum of diimide-diacid **4** showed in Figure 2. H(a) protons relevant to O-H carboxylic groups, H(b) protons relevant to olefin hydrogens that appeared in region of $5.95\text{--}5.98\text{ ppm}$. Peaks in the region $4.50\text{--}4.57\text{ ppm}$ as a quartet were assigned to the CH(c) proton which is a chiral center.

The ^{13}C NMR spectrum of diimide-diacid **4** showed 7 signals including C(b) in carboxylic group that appeared in region of 176.82 ppm , C(d) was relevant to chiral carbon atom that appeared in region of 47.55 ppm (Figure 3). ^{13}C NMR and ^1H NMR spectra along with elemental analyses data confirmed the proposal structure of compound **4**.

Polymer synthesis

PAIs **6a-e** were synthesized by direct polycondensation reaction of an equimolar mixture of monomer **4** with five

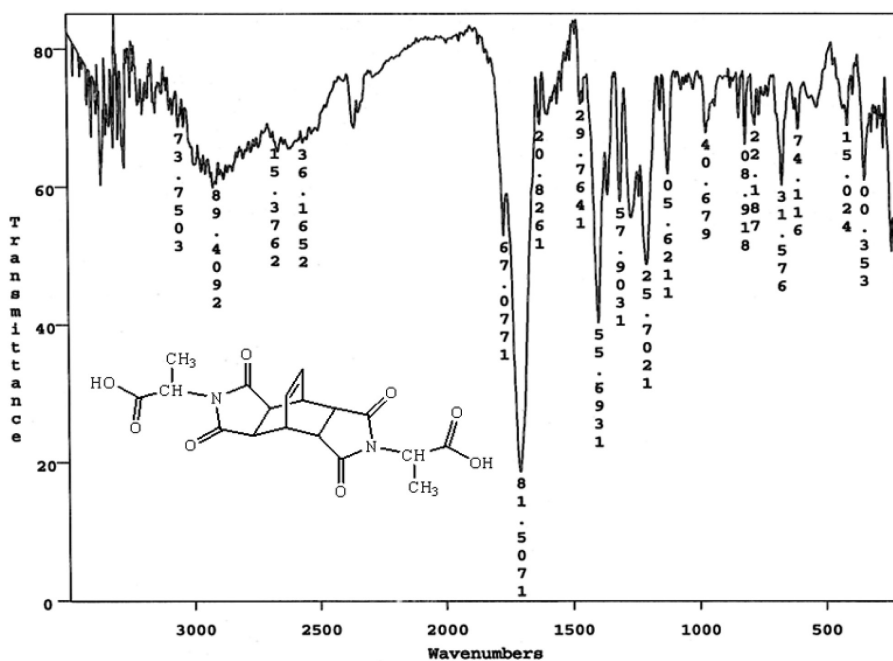


Figure 1. FTIR spectrum of diimide-diacid **4**.

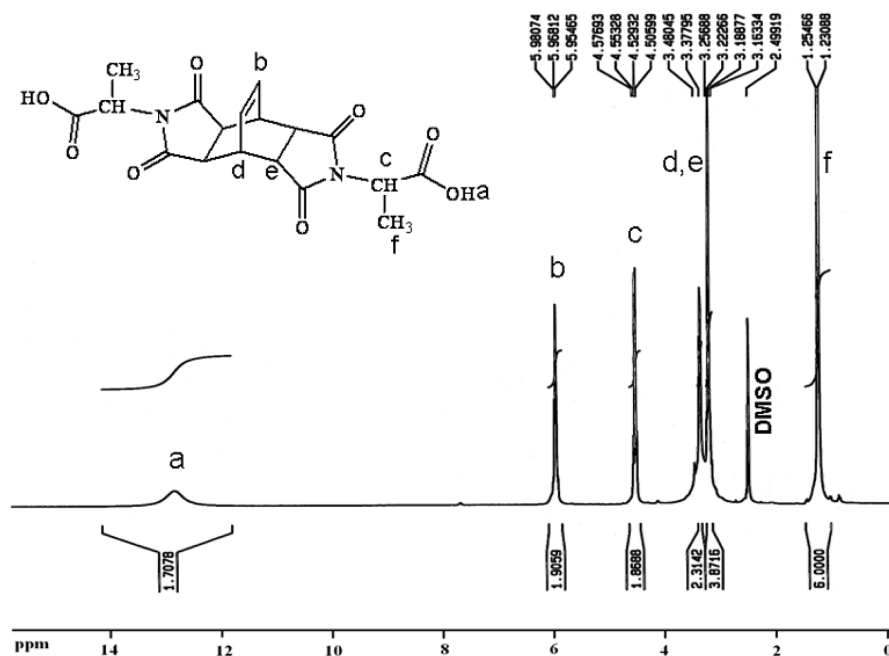


Figure 2. ^1H NMR spectrum of diimide-diacid 4.

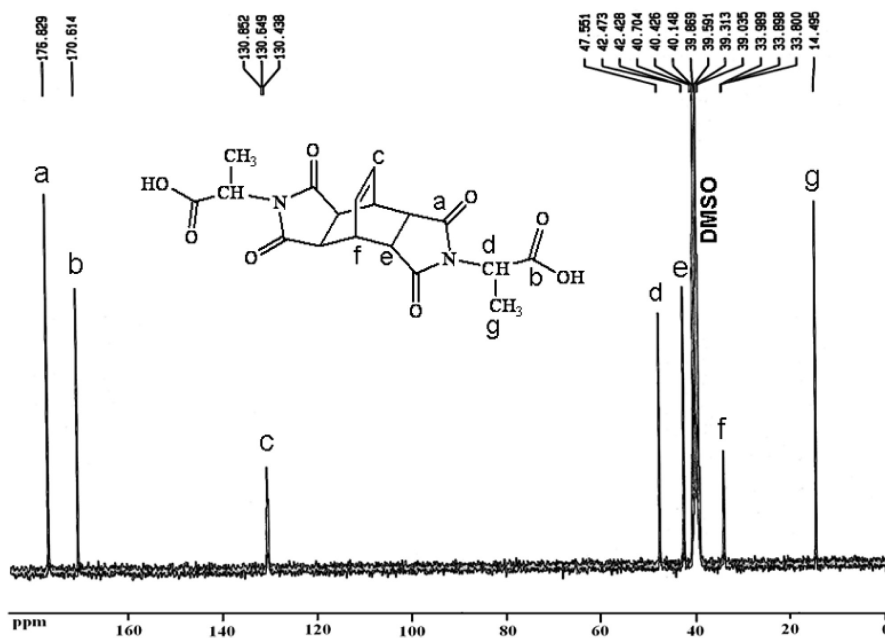


Figure 3. ^{13}C NMR spectrum of diimide-diacid 4.

different derivatives of aromatic diamine **5a-e** as shown in Scheme 2.

Synthesis and some physical properties of PAIs **6a-e** are summarized in Table 1. These polymers have inherent viscosities in range of 0.29-0.46 dL g⁻¹. All of the resulting polymers show optical rotations and have optical activities. Results show that PAIs **6b** and **6c** have higher inherent viscosities in comparing to other PAIs because they have

a rigid and polar moiety in the diamine structure such as sulfone moiety (Table 1).

Polymer characterization

The structures of these polymers were confirmed as PAIs by mean of FTIR, ^1H NMR spectroscopy and elemental analyses. FTIR spectroscopy of all PAIs are listed in Table 2.

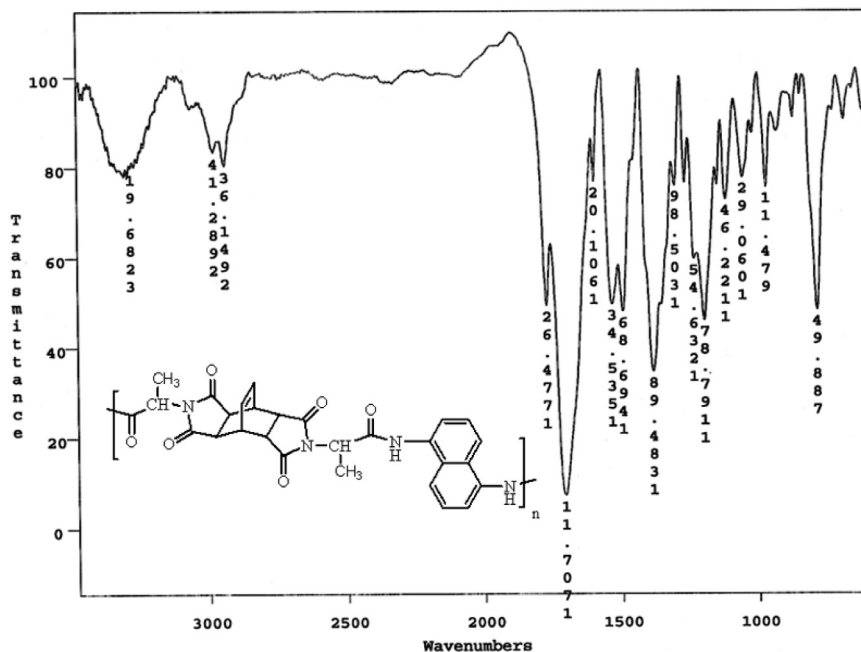
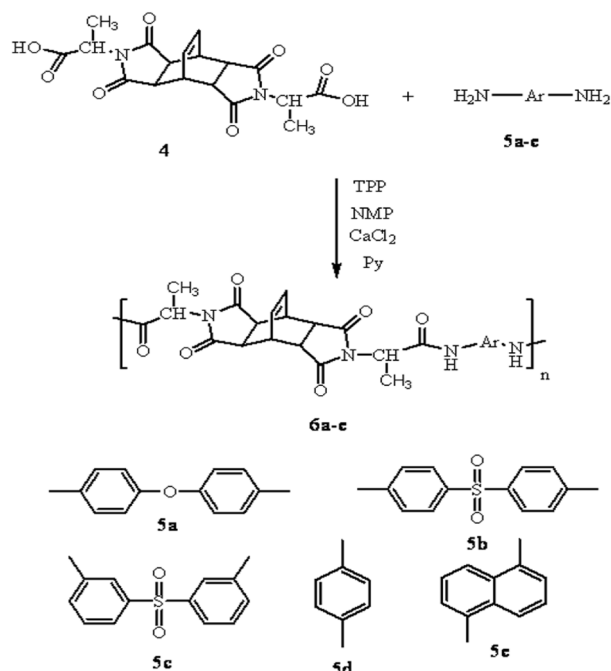


Figure 4. FTIR spectrum of PAI **6e**.

Table 1. Synthesis and some physical properties of PAIs **6a-e**

Aromatic Diamine	Polymer	Yield (%)	η_{inh} (dL g ⁻¹) ^a	$[\alpha]_D^{25}$	Color
5a	6a	90	0.35	-14.6	White
5b	6b	96	0.41	-36.7	Cream
5c	6c	91	0.46	-32.4	White
5d	6d	85	0.29	-28.5	White
5e	6e	87	0.37	-18.3	Cream

^a Measured at a concentration of 0.5 g dL⁻¹ in DMF at 25 °C.



Scheme 2.

The representative FTIR spectrum of PAI **6e** was shown in Figure 4. The polymer exhibited characteristic absorption bands at 1707-1774 cm⁻¹ to the imide ring (asymmetric and symmetric C=O stretching vibration) and 1384 cm⁻¹ (C-N stretching vibration). The absorption bands of amide groups appeared at 3286 cm⁻¹ (N-H stretching).

Figure 5 displays ¹H NMR spectrum of PAI **6d**. Peak at 9.60 ppm related to NH of amide groups in the polymer chain, aromatic protons related to 1,4-phenylene appeared in the region of 7.41 ppm and the peak in the region of 6.06 ppm related to olefin protons.

The elemental analyses of the resulting PAIs **6a-e** were in good agreement with the calculated values for the proposed structure (Table 3).

The solubility of PAIs **6a-e** was investigated by 0.01g of polymeric sample in 2.0 mL solvent. All of the polymers are soluble in organic solvents such as *N,N*-dimethyl acetamide (DMAc), *N,N*-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), NMP (*N*-methyl-2-pyrrolidone), sulfuric acid and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water (Table 4).

Thermal properties

The thermal properties of PAIs **6a** and **6c** were investigated by TGA and DTG in a N₂ atmosphere at a heating rate of 10 °C min⁻¹ as model for prepared polymers and the thermal data are summarized in Table 5 (Figure 6). The initial decomposition temperatures of 5% and 10%

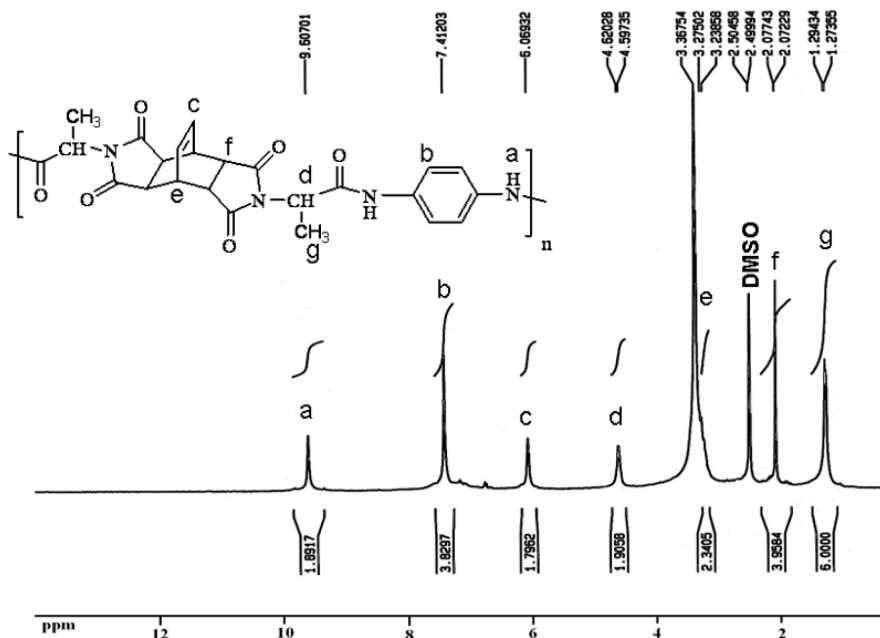


Figure 5. ^1H NMR spectrum PAI **6d**.

Table 2. FTIR Characterization of PAIs **6a-e**

Polymer	Spectra data
6a	IR peaks (cm^{-1}): 3202 (w), 2957 (m), 1776 (w), 1710 (s, br), 1604 (w), 1500 (s, sh), 1386 (m), 1305 (m), 1222 (m, sh), 1068 (m), 833 (w), 787 (w), 516 (w).
6b	IR peaks (cm^{-1}): 3254 (w), 2962 (w), 1774 (w), 1710 (s), 1664 (m, sh), 1591 (m), 1531 (m), 1479 (m), 1386 (m), 1305 (m), 1255 (w), 1188 (w), 1151 (m), 1107 (m), 839 (w), 790 (w), 721 (w), 690 (w).
6c	IR peaks (cm^{-1}): 3294 (w), 2876 (w), 1776 (w), 1709 (s, br), 1595 (m), 1535 (m), 1479 (m), 1384 (m), 1302 (m), 1244 (m), 1159 (m), 1149 (m), 995 (w), 784 (w), 746 (w).
6d	IR peaks (cm^{-1}): 3344 (w), 2960 (m), 2872 (w), 1774 (w), 1707 (s, br), 1610 (w), 1516 (s), 1386 (m), 1307 (w), 1236 (w), 1192 (m), 853 (w), 790 (w).
6e	IR peaks (cm^{-1}): 3286 (w, br), 2982 (w, sh), 1774 (w), 1707 (s, br), 1601 (w), 1535 (m), 1496 (m), 1384 (m, sh), 1305 (w), 1197 (m), 1122 (w), 974 (w), 788 (m).

Table 3. Elemental analyses of PAIs **6a-e**

Polymer	Formula		C%	H%	N%
6a	$\text{C}_{30}\text{H}_{28}\text{N}_4\text{O}_7$ (554.23) _n	Calc.	65.00	4.69	10.10
		Found	64.89	4.60	9.94
6b	$\text{C}_{30}\text{H}_{28}\text{N}_4\text{O}_8\text{S}$ (602.28) _n	Calc.	59.82	4.31	9.29
		Found	59.40	4.20	9.10
6c	$\text{C}_{30}\text{H}_{28}\text{N}_4\text{O}_8\text{S}$ (602.28) _n	Calc.	59.82	4.31	9.29
		Found	59.44	4.28	8.20
6d	$\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_6$ (462.18) _n	Calc.	62.36	4.76	12.11
		Found	62.10	4.64	11.98
6e	$\text{C}_{28}\text{H}_{24}\text{N}_4\text{O}_6$ (512.22) _n	Calc.	65.65	4.68	10.93
		Found	65.50	4.50	10.90

Table 4. Solubility of PAIs **6a-e**

Solvent	6a	6b	6c	6d	6e
H_2SO_4	+	+	+	+	+
DMAc	+	+	+	+	+
DMSO	+	+	+	+	+
DMF	+	+	+	+	+
NMP	+	+	+	+	+
MeOH	-	-	-	-	-
EtOH	-	-	-	-	-
CHCl_3	-	-	-	-	-
CH_2Cl_2	-	-	-	-	-
H_2O	-	-	-	-	-

Soluble (+) and insoluble (-) at room temperature.

weight losses (T_5 and T_{10}) and the char yield at $600\text{ }^\circ\text{C}$ are summarized in Table 5. These polymers exhibited good resistance to thermal decomposition up to 320 to $340\text{ }^\circ\text{C}$ in nitrogen and began to decompose gradually above

those temperatures. T_5 for these polymers ranged from 320 to $340\text{ }^\circ\text{C}$ and T_{10} for two polymers ranged from 345 to $355\text{ }^\circ\text{C}$ and the residual weights for these polymers at $600\text{ }^\circ\text{C}$ ranged from 38 and 58% in nitrogen. Results show

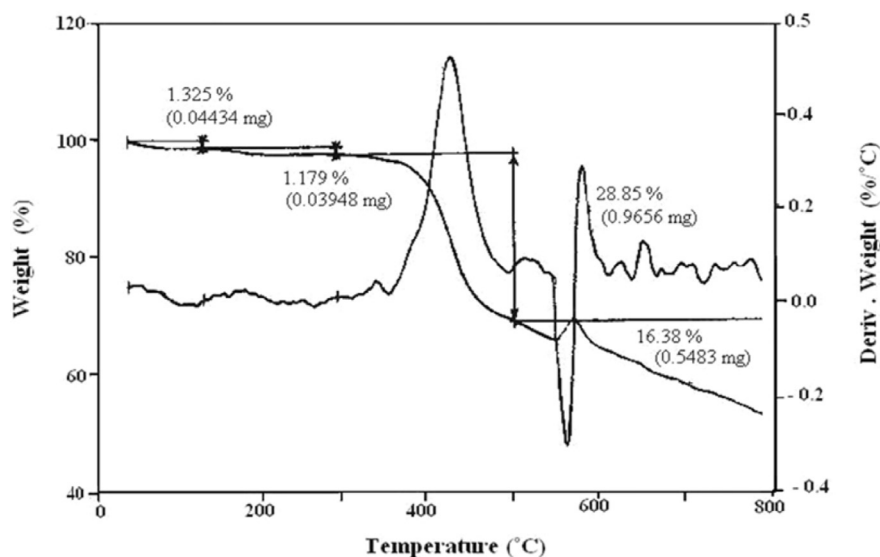


Figure 6. TGA and DTG thermogram of PAI 6a.

that PAI 6c containing sulfone moiety has higher thermal stability in comparing to PAI 6a because this polymer has a rigid and polar moiety in the diamine structure such as sulfone moiety (Table 5).

Table 5. Thermal behavior of PAIs 6a and 6c

Polymer	T ₅ (°C) ^a	T ₁₀ (°C) ^b	Char Yield ^c (%)
6a	320-330	345-355	58
6c	340-345	355-360	38

^{a,b} Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10 °C min⁻¹ in N₂ respectively. ^c Percentage weight of material left undecomposed after TGA analysis in 600 °C.

Conclusions

A new series of PAIs 6a-e containing bicyclo[2,2,2] oct-7-ene-2,3,5,6-tetracarboxylic diimide were synthesized by direct polycondensation reaction of *N,N'*-(bicyclo[2,2,2] oct-7-ene-2,3,5,6-tetracarboxylic)bis-L-alanine 4 with various aromatic diamins 5a-e using triphenyl phosphite, NMP, calcium chloride and pyridine as condensing agents. The high char yields of these polymers showed that the introduction of bicyclo and aromatic rings into the polymer backbone increased the thermal stability and solubility in polar amidic solvents. Since these optically active polymers have amino acid in the polymer architecture and they are expected to be biodegradable. Optically active and thermal stability properties can make these polymers 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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