

Synthesis and Properties of Novel Flame-Retardant and Thermally Stable Poly(amide-imide)s from *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino Acids and Phosphine Oxide Moiety by Two Different Methods

Khalil Faghihi*, Mohsen Hajibeygi, and Meisam Shabanian

Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, Arak University, Arak 38156, Iran

Received November 13, 2008; Revised March 9, 2009; Accepted March 10, 2009

Abstract: *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **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 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. Seven new poly(amide-imide)s PAIs **5a-g** were synthesized through the direct polycondensation reaction of seven chiral *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **3a-g** with bis(3-amino phenyl) phenyl phosphine oxide **4** by two different methods: 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. The polymerization reaction produced a series of flame-retardant and thermally stable poly(amide-imide)s **5a-g** with high yield. The resulted polymers were fully characterized by FTIR, ¹H NMR spectroscopy, elemental analyses, inherent viscosity, specific rotation and solubility tests. Data obtained by thermal analysis (TGA and DTG) revealed that the good thermal stability of these polymers. These polymers can be potentially utilized in flame retardant thermoplastic materials.

Keywords: high-performance polymer, phosphine oxide, thermally stable poly(amide-imide), optically active polymer.

Introduction

Aromatic polyamides possess excellent mechanical properties and thermal stability; however, they are difficult to process because of limited solubility and high glass transition (T_g) or melt temperature due to chain stiffness and intermolecular hydrogen bonding between amide groups.¹ The processing of these thermoplastic polymers has been greatly hindered because they lack softening or melting behavior at usual processing temperature, and they tend to degrade before or at the softening temperature.² Various attempts have been made to bring down the T_g or melting temperature of aromatic polyamides to make them processable, either by introducing linked and flexible bridging units³⁻⁵ into the polymers chain. Unfortunately, the loss of thermal stability and significant decrease in mechanical properties on heating are usually a consequence of the reduced chain stiffness. Aromatic poly(amide-imide)s PAIs are high performance materials with good compromise between thermal stability and processability when com-

pared with polyamides or polyimides of analogous structures.⁶⁻¹⁸

Phosphines, phosphine oxides, phosphonium compounds, phosphonates, elemental red phosphorus, phosphites and phosphate are all used as flame retardants.¹⁹⁻²³ The general types of phosphorus moieties have been incorporated into different polymeric backbones, such as epoxy resin, poly(amic acid), polycarbonate, poly(vinyl chloride), polyester, polyimide and poly(methyl methacrylate).²⁴⁻³¹ Among the polymers with phosphorus moieties, the polymers with phosphine oxide moieties have major advantages, such as good flame-retardant properties, high thermal oxidative stability, enhanced solubility in organic solvents, improved miscibility and good adhesion to other compounds.³²⁻³⁸

In this article, a series of novel flame-retardant PAIs **5a-g** containing phosphine oxide 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 bis(3-amino phenyl) phenyl phosphine oxide **4**. On other hand, due to presence chiral segments in polymer backbone, these PAIs are optically active. The synthesis and application of optically active polymers are the newly con-

*Corresponding Author. E-mail: k-faghihi@araku.ac.ir

siderable topics,³⁹⁻⁴² which have been paid more attention, because these polymers for biologically effects are very important.

Experimental

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

Apparatus and 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 wavenumber (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. Limited oxygen indexes (LOI) were measured on a Stanton Redcraft flamemeter. 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. Elemental analyses were performed by Vario EL equipment by Arak University.

Monomer Synthesis.

***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 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-g**.

Bis(3-amino phenyl) Phenyl Phosphine Oxide 4: This

compound was prepared according to our previous works.^{35,36}

Polymer Synthesis. PAIs **5a-g** were synthesized by two different methods that as an example the preparation of PAI **5b** 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)

0.145 g (0.326 mmol) of diacid **3b**, 0.1 g (0.326 mmol) of diamine **4**, 0.1 g (0.9 mmol) of CaCl₂, 0.84 mL (3.00 mmol) of triphenyl phosphite, 0.18 mL of pyridine and 2.00 mL of NMP were placed into a 25 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 methanol and filtered off, dried under vacuum to leave 0.194 g (83%) white solid polymer **5b**.

Method B: Direct polycondensation in a tosyl chloride (TsCl)/pyridine (Py)/*N,N*-dimethylformamide (DMF) system

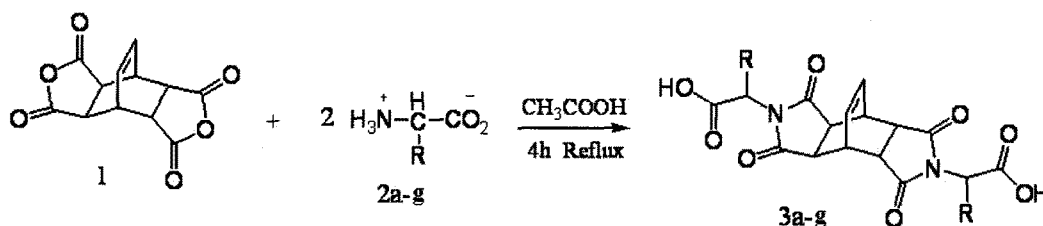
A solution of 0.1 mL pyridine, 0.0078 g (0.411 mmol) of TsCl after 30 min stirring at room temperature was treated with 0.1 mL, (1.36 mmol) of DMF for additional 30 min. The reaction mixture was added dropwise to a solution 0.061 g (0.137 mmol) of diacid **3b** in 0.1 mL of pyridine. The mixture was maintained at room temperature for 30 min, and then to this mixture, a solution 0.042 g (0.137 mmol) of diamine **4** in 0.4 mL of pyridine was added dropwise and the whole solution was stirred at room temperature for 30 min and at 100 °C for 2 h. As the reaction proceeded, the solution became viscous, then was precipitated in 20 mL of methanol and filtered off, dried under vacuum to leave 0.079 g (80%) white solid polymer **5b**.¹⁵

Results and Discussion

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

The chemical structure and purity of the optically active

Scheme I



	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 ₂ H ₅	CH ₂ Ph	CH ₂ CH ₃	CH ₂ -imidazole

Table I. Synthesis and Some Physical Properties of Diimide-Diacid Derivatives 3a-g

Entry	Amino Acid Compound	R	Mp(°C)	Yield(%)	$[\alpha]_D^{25a}$
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
3g	L-Histidine	CH ₂ -imidazole	310-312	85	+128.4

^aMeasured 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 Diacid Derivatives 3a-g

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.
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 (d, 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. FTIR (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 ₆ O ₈ : C, 55.17; H, 4.24; N, 16.09; found: C, 55.03; H, 4.23; N, 16.00.

diimide-diacids **3a-g** were proved by using elemental analysis, FTIR, ¹H NMR and ¹³C NMR spectroscopic techniques and these data shown in Table II.

As an example, The FTIR spectrum of diimide-diacid **3g** showed a broad peak between 2500 and 3400 cm⁻¹, which was assigned to the COOH groups. Peaks appearing at 1770 cm⁻¹ (C=O asymmetric imide stretching), 1707 (br) cm⁻¹

(acid C=O and symmetric imide stretching), 1383 and 710 cm⁻¹ (imide characteristic ring vibration) confirmed the presence of imide ring and carboxylic groups in this compound (Figure 1).

The ¹H NMR spectrum of diimide-diacid **3g** showed in Figure 2. The protons H(a) and H(b) relevant to O-H carboxylic groups and NH for imidazole ring, respectively, that

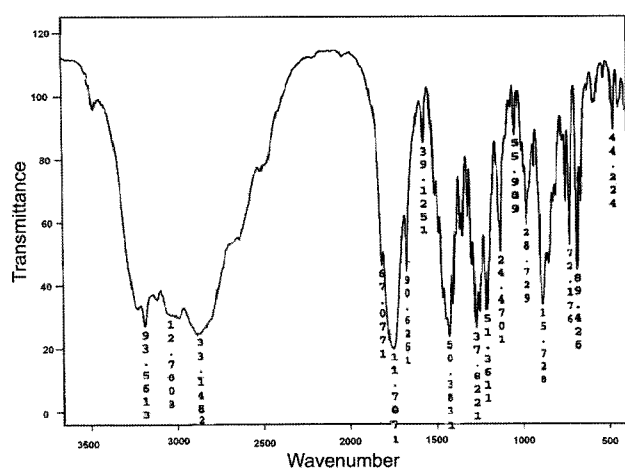


Figure 1. FTIR spectrum of diimide-diacid **3g**.

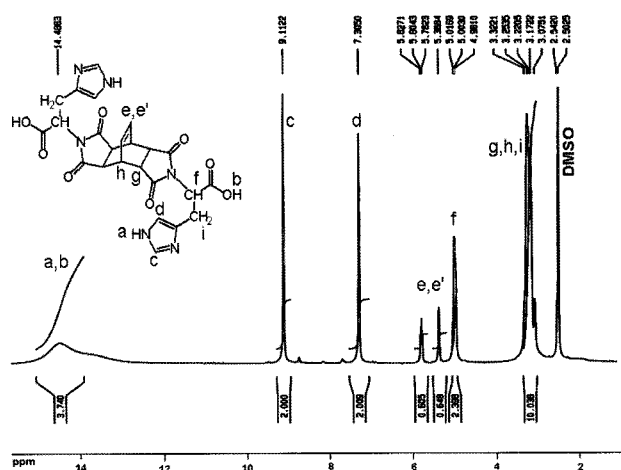


Figure 2. ¹H NMR spectrum of diimide-diacid **3g**.

appeared at 14.48 ppm. Peak in 4.98–5.01 ppm as a doublet which were assigned to the CH(f) protons, which is a chiral center. Protons relevant to olefin bicyclo ring appeared at 5.38–5.80 ppm, H(e, e'), which due to presence of imidazole ring in this compound, these protons are appeared in separate regions. Also the ¹³C NMR spectrum of diimide-diacid **3g** showed 10 signals, which confirmed the proposal structure of compound **3g** (Figure 3).

Polymer Synthesis. PAIs **5a–g** were synthesized by direct polycondensation reaction of an equimolar mixture of diimide-diacids **3a–g** with diamine **4** by two different methods (Scheme II).

In method A for direct polycondensation used TPP/Py/CaCl₂ as activating agent according to a typical procedure that was shown in Scheme II. The syntheses and some physical properties of these PAIs **5a–g** are given in Table III.

In method B for the direct polycondensation of diacids **2a–g** and aromatic diamine **4**, a Vilsmeier adduct was prepared by dissolving TsCl in a mixed solvent of Py and DMF.¹⁵ The syntheses and some physical properties of these PAIs

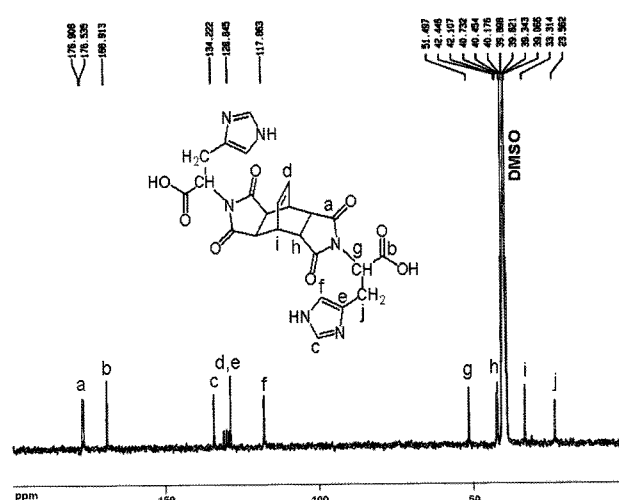


Figure 3. ¹³C NMR spectrum of diimide-diacid **3g**.

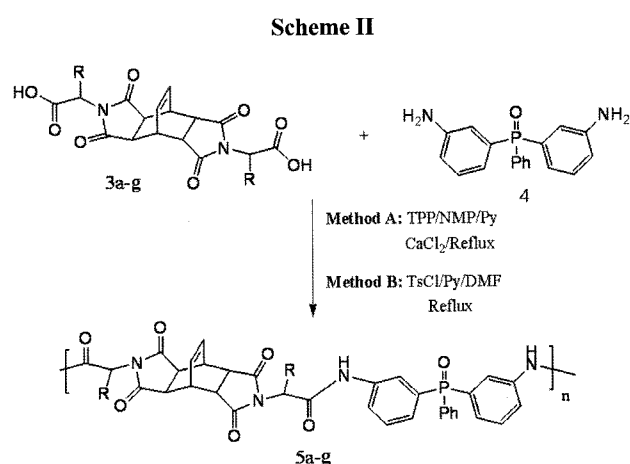


Table III. Synthesis and Some Physical Properties of PAIs **5a–g** by Method A

Diimide-Diacid	Polymer	Yield(%)	η_{inh} (dL/g) ^b	$[\alpha]_D^{25a}$	Color ^b
3a	5a	89	0.41	+65.2	PY
3b	5b	83	0.45	+71.6	W
3c	5c	85	0.47	+81.0	W
3d	5d	81	0.83	+68.3	W
3e	5e	80	0.39	+81.2	PY
3f	5f	83	0.48	+77.8	W
3g	5g	83	0.44	+65.34	PY

^aMeasured at a concentration of 0.5 g/dL in DMSO at 25 °C. ^bW=White, PY=Pale Yellow.

5a–g are given in Table IV. Although PAIs **5a–g** obtained in a shorter period by method B, but these polymers obtained with higher inherent viscosities by method A.

Polymer Characterization. The elemental analyses of the resulting PAIs **5a–g** were in good agreement with the calculated values for the proposed structure (Table V). The

Table IV. Synthesis and Some Physical Properties of PAIs 5a-g by Method B

Diimide-Diacid Polymer	Yield(%)	η_{inh} (dL/g)	$[\alpha]_D^{25a}$	Color ^b	
3a	5a	79	0.34	+88.2	W
3b	5b	80	0.36	+92.3	W
3c	5c	78	0.38	+79.9	PY
3d	5d	80	0.38	+75.4	PY
3e	5e	77	0.39	+83.7	PY
3f	5f	82	0.39	+65.32	W
3g	5g	79	0.28	+76.76	Y

^aMeasured at a concentration of 0.5 g/dL in DMSO at 25 °C. ^bW=White, PY=Pale Yellow, Y=Yellow.

Table V. Elemental Analysis of PAIs 5a-g

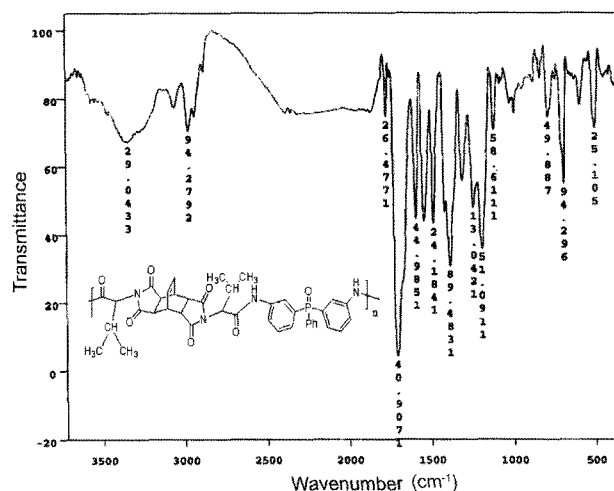
Polymer	Formula		C%	H%	N%
5a	C ₃₆ H ₃₁ N ₄ O ₇ P	Calcd	65.25	4.72	8.46
	(662.63) _n	Found	64.15	4.66	8.34
5b	C ₄₀ H ₃₉ N ₄ O ₇ P	Calcd	66.84	5.47	7.80
	(718.74) _n	Found	65.78	5.23	7.65
5c	C ₄₂ H ₄₃ N ₄ O ₇ P	Calcd	67.55	5.80	7.50
	(746.79) _n	Found	66.14	5.21	7.13
5d	C ₄₂ H ₄₃ N ₄ O ₇ P	Calcd	67.55	5.80	7.50
	(746.79) _n	Found	66.04	5.35	7.34
5e	C ₄₈ H ₃₉ N ₄ O ₇ P	Calcd	70.75	4.82	6.88
	(814.01) _n	Found	68.89	4.64	6.71
5f	C ₃₈ H ₃₅ N ₄ O ₇ P	Calcd	66.08	5.11	8.11
	(690.03) _n	Found	65.23	5.01	8.01
5g	C ₄₂ H ₃₅ N ₈ O ₇ P	Calcd	63.47	4.44	14.09
	(794.75) _n	Found	62.23	4.35	13.98

solubility of PAIs **5a-g** was investigated as 0.01 g of polymeric sample in 2 mL of solvent. All of the polymers are soluble in DMSO and H₂SO₄ and partially soluble in organic solvents such as DMF, NMP and DMAc and are insoluble in solvents such as chloroform, dichloromethane, methanol and ethanol.

The structures of these polymers were confirmed as PAIs by means FTIR, ¹H NMR spectroscopy and elemental analyses. FTIR characterizations of all PAIs are listed in Table VI. The representative FTIR spectrum of PAI **5b** was shown in Figure 4. The polymer exhibited characteristic absorption bands at 1709 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), 1384 cm⁻¹ (C-N stretching vibration). The absorption bands of amide groups appeared at 3340 cm⁻¹

Table VI. FTIR Characterization of PAIs 5a-g

Polymer	Spectra Data
5a	FTIR Peaks (cm⁻¹): 3330 (m, br), 2966 (w, sh), 1774 (w), 1709 (s, br), 1589 (m), 1541 (m), 1481 (m), 1412 (m, sh), 1380 (m, br), 1308 (w), 1192 (m), 1116 (w), 692 (m).
5b	FTIR Peaks (cm⁻¹): 3340 (m, br), 2972 (w, sh), 1774 (w), 1709 (s, br), 1589 (m), 1541 (m), 1481 (m), 1415 (m, sh), 1384 (m, br), 1309 (w), 1190 (m), 1116 (w), 788 (w), 692 (m).
5c	FTIR Peaks (cm⁻¹): 3340 (m, br), 2957 (m), 1774 (w), 1709 (s, br), 1589 (m), 1541 (m), 1481 (m), 1415 (m), 1384 (m, sh), 1309 (w), 1186 (m), 690 (m), 501 (w).
5d	FT IR Peaks (cm⁻¹): 3331 (m,br), 2966 (m), 1774 (w), 1709 (s, br), 1589 (m), 1541 (m), 1481 (m), 1412 (m, sh), 1380 (m, br), 1308 (w), 1192 (m), 1114 (w), 692 (m), 499 (w).
5e	FTIR Peaks (cm⁻¹): 3352 (m, br), 2972 (w), 1774 (w), 1709 (s, br), 1589 (m), 1541 (m), 1481 (m), 1384 (s), 1309 (w), 1190 (m), 1186 (m), 787 (w), 692 (m), 501 (w).
5f	FT IR Peaks (cm⁻¹): 3329 (m, br), 2960 (m, sh), 1774 (w), 1709 (s, br), 1589(m), 1540 (m), 1480 (m), 1383 (s), 1190 (m), 1187(m), 787 (m), 692 (m), 501 (w).
5g	FTIR Peaks (cm⁻¹): 3276 (w), 3162(w), 3016 (w), 2500-3000 (br), 1780 (m), 1722 (s), 1668 (w), 1658(w), 1608 (w), 1539 (m), 1487 (m), 1425 (w), 1380 (m), 1256 (m, sh), 1188 (m), 727(m), 624 (m) cm ⁻¹ .


Figure 4. FTIR spectrum of PAI 5b.

(N-H stretching).

The ¹H NMR spectra of PAIs **5c** and **5f** showed peaks that confirm their chemical structures (Figures 5 and 6). Figure 5 displays ¹H-NMR spectrum of PAI **5c**. The aromatic protons related to triphenyl phosphine oxide appeared in the region of 7.13-7.87 ppm and the peak in the region of 10.01 ppm is assigned for N-H of amide groups in the main chain of polymer, and Figure 6 displays ¹H NMR spectrum of PAI **5f**. Decaying peak related to carboxylic acid protons and appearing peaks related to amide groups and triphenyl phosphine oxide protons in the polymer chain, confirmed the

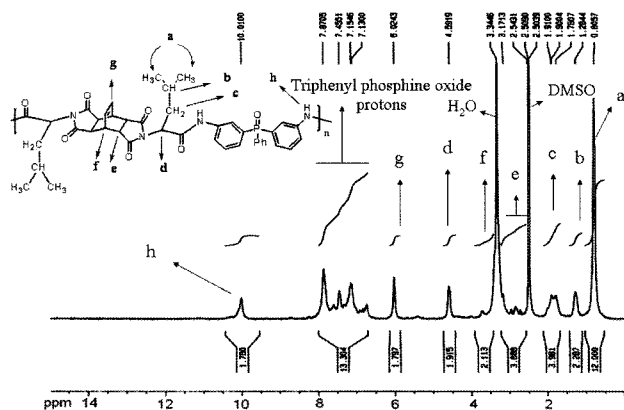


Figure 5. ^1H NMR spectrum of PAI **5c**.

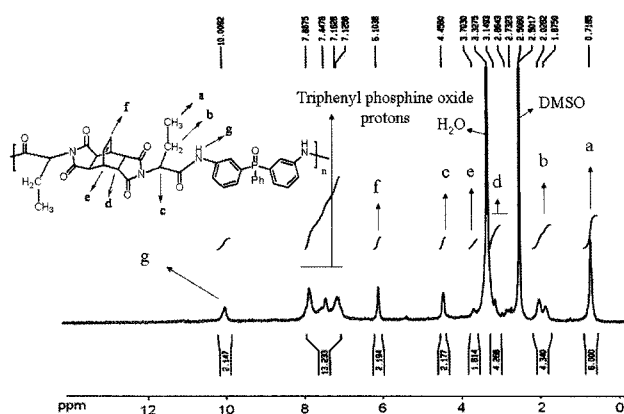


Figure 6. ^1H NMR spectrum of PAI **5f**.

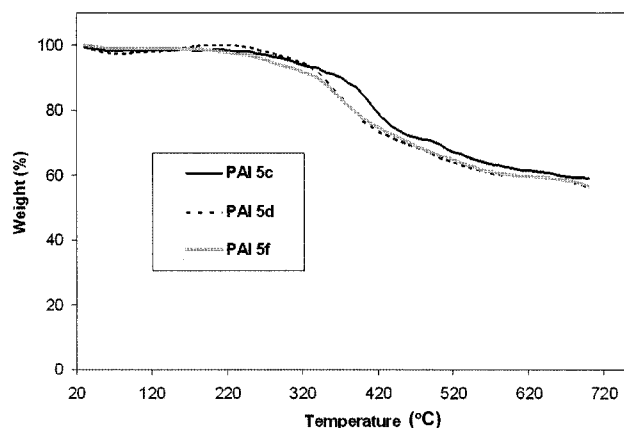


Figure 7. TGA curves of PAIs **5c**, **5d** and **5f** (in nitrogen at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$).

proposed structure of PAIs **5a-g**.

Thermal Properties. The thermal properties of PAIs **5c**, **5d** and **5f** were investigated by TGA in a nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ (Figure 7). All of these polymers showed similar decomposition behavior. Initial decomposition temperature, 5 and 10% weight loss temper-

Table VII. Thermal Behavior of PALs **5c**, **5d** and **5f**

Polymer	$T_5(\text{C})^a$	$T_{10}(\text{C})^a$	Char Yield ^b	LOI ^c
5c	300-305	365-370	62.12	32
5d	310-315	345-350	59.99	31
5f	270-275	335-340	60.03	33

^aTemperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under N_2 . ^bWeight percentage of material left after TGA analysis at a maximum temperature of $600\text{ }^\circ\text{C}$ under N_2 . ^cLOI, Limited oxygen index.

ature (T_5 , T_{10}), and char yields summarized in Table VII.

These polymers exhibited good resistance to thermal decomposition up to $270\text{--}310\text{ }^\circ\text{C}$ in nitrogen and began to decompose gradually above that temperature. The temperature of 5% weight loss for all the polymers ranged from 270 to $310\text{ }^\circ\text{C}$ and the residual weight at $600\text{ }^\circ\text{C}$ ranged from 59.99 to 62.16% in nitrogen. The high char yields of these PAIs at high temperature region are important. It shows that these polymers have good thermal stability. Also the flame retardant property of these polymers was evaluated by measuring their LOI values. They showed LOI data between 31 and 33.

Generally, materials exhibiting limiting oxygen index (LOI) values greater than 26 would show self-extinguishing behavior³⁸ and were considered to be flame retardant. Therefore high char yield data, along with good LOI values between 31 and 33, indicated that these polymers have good flame retardant properties. Char yield can be applied as decisive factor for estimating LOI of the polymers.⁴³

Conclusions

A new series of PAIs **5a-g** containing phosphine oxide moieties were synthesized by direct polycondensation reaction of six asymmetric diacids **3a-g** with bis(3-amino phenyl) phenyl phosphine oxide **4** by using triphenyl phosphite, NMP, calcium chloride and pyridine as condensing agents. The high char yields and good LOI data of these polymers showed that the introduction of phosphine oxide moieties into backbone increased the thermal stability and flame-retardant property. These properties can make these polymers attractive for practical applications such as processable high-performance engineering plastics.

References

- (1) A. Saxena, V. L. Rao, P. V. Prabhakaran, and K. N. Ninan, *Eur. Polym. J.*, **39**, 401 (2003).
- (2) G. Bier, *Adv. Chem. Ser.*, **91**, 612 (1969).
- (3) C. P. Yang, Y. P. Chen, and E. M. Woo, *Polymer*, **45**, 5279 (2004).
- (4) A. Boulares, M. Tessier, and E. Marechal, *Polymer*, **41**, 3561 (2000).

- (5) Z. Ge, S. Yang, Z. Tao, J. Liu, and L. Fan, *Polymer*, **45**, 3627 (2004).
- (6) D. J. Liaw, P. N. Hsu, W. H. Chen, and S. L. Lin, *Macromolecules*, **35**, 4669 (2002).
- (7) S. G. Hahm, S. Choi, S. H. Hong, T. J. Lee, S. Park, D. M. Kim, W. S. Kwon, K. Kim, O. Kim, and M. Ree, *Adv. Funct. Mater.*, **18**, 3276 (2008).
- (8) S. G. Hahm, S. W. Lee, T. J. Lee, S. A. Cho, B. Chae, Y. M. Jung, S. B. Kim, and M. Ree, *J. Phys. Chem. B*, **112**, 4900 (2008).
- (9) S. G. Hahm, T. J. Lee, and M. Ree, *Adv. Funct. Mater.*, **17**, 1359 (2007).
- (10) S. G. Hahm, T. J. Lee, T. Chang, J. C. Jung, W. C. Zin, and M. Ree, *Macromolecules*, **39**, 5385 (2006).
- (11) M. Ree, *Macromol. Res.*, **14**, 1 (2006).
- (12) M. Ree, T. J. Shin, and S. W. Lee, *Korea Polym. J.*, **9**, 1 (2001).
- (13) Kh. Faghihi and M. Hagibeygi, *Macromol. Res.*, **13**, 14 (2005).
- (14) Kh. Faghihi and H. Naghavi, *J. Appl. Polym. Sci.*, **96**, 1776 (2005).
- (15) S. Mallakpour and M. Kolehdozan, *J. Appl. Polym. Sci.*, **104**, 1248 (2007).
- (16) H. S. Jin, J. H. Chang, and J. C. Kim, *Macromol. Res.*, **16**, 503 (2008).
- (17) A. S. Mathews, I. Kim, and C. S. Ha, *Macromol. Res.*, **15**, 114 (2007).
- (18) C. H. Jung and Y. M. Lee, *Macromol. Res.*, **16**, 555 (2008).
- (19) C. Nguyen and A. Kim, *Macromol. Res.*, **16**, 620 (2008).
- (20) E. D. Weil, S. V. Levchik, M. Ravey, and W. M. Zhu, *Phosphorus Sulfur Silicon Relat. Elem.*, **146**, 17 (1999).
- (21) J. Green, *J. Fire Sci.*, **10**, 470 (1992).
- (22) A. M. Aaronson, *Phosphorus flame retardant for a changing world. Phosphorus Chemistry*, Developments in American Science, ACS Symposium Series 486, Washington, 1992, ACS, p 218.
- (23) K. S. Annakutty and K. Kishore, *J. Sci. Ind. Res.*, **48**, 479 (1989).
- (24) J. Xu, Y. Jiao, B. Zhang, H. Qu, and G. Yang, *J. Appl. Polym. Sci.*, **101**, 731 (2006).
- (25) S. C. Yang and J. P. Kim, *J. Appl. Polym. Sci.*, **108**, 2297 (2008).
- (26) C. Tian, H. Wang, X. Liu, Z. Ma, H. Guo, and J. Xu, *J. Appl. Polym. Sci.*, **89**, 3137 (2003).
- (27) H. Galip, H. Hasipoglu, and G. Gunduz, *J. Appl. Polym. Sci.*, **74**, 2906 (1999).
- (28) J. Liu, Y. Gao, F. Wang, and M. Wu, *J. Appl. Polym. Sci.*, **75**, 384 (2000).
- (29) T. Kashiwagi, A. B. Morgan, J. M. Antonucci, M. R. Vandlingham, R. H. Harris, W. H. Award, and J. R. Shields, *J. Appl. Polym. Sci.*, **89**, 2072 (2003).
- (30) Q. Wu, J. Lu, and B. Qu, *Polym. Int.*, **52**, 1326 (2003).
- (31) Z. Y. Wang, Z. Q. Feng, and Q. Liu, *J. Appl. Polym. Sci.*, **105**, 3317 (2007).
- (32) M. A. Espinosa, M. Galia, and V. Cadiz, *J. Polym. Sci. Part A: Polym. Chem.*, **42**, 3516 (2004).
- (33) Y. L. Liu, R. J. Jeng, and Y. S. Chiu, *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 1716 (2001).
- (34) L. A. Rusch-Salazar and V. V. Sheares, *J. Polym. Sci. Part A: Polym. Chem.*, **41**, 2277 (2003).
- (35) Kh. Faghihi and Kh. Zamani, *J. Appl. Polym. Sci.*, **101**, 4263 (2006).
- (36) Kh. Faghihi, *J. Appl. Polym. Sci.*, **102**, 5062 (2006).
- (37) Kh. Faghihi and M. Hajibeygi, *J. Appl. Polym. Sci.*, **92**, 3447 (2004).
- (38) L. Ying-Ling, C. Yie-Chan, and C. Tsung-Yu, *Polym. Inter.*, **52**, 1256 (2003).
- (39) Kh. Faghihi, *Macromol. Res.*, **12**, 258 (2004).
- (40) L. Cianga, *Eur. Polym. J.*, **39**, 2271 (2003).
- (41) Kh. Faghihi, *J. Appl. Polym. Sci.*, **109**, 74 (2008).
- (42) L. Angiolini, T. Benelli, L. Giorgini, and E. Salatelli, *Polymer*, **46**, 2424 (2005).
- (43) D. W. Van Krevelen and P. J. Hoftyzer, *Properties of Polymer*, Elsevier Scientific Publishing Company, New York, 1976.