Journal of the Chinese Chemical Society, **2009**, *56*, 609-618

Novel Flame-retardant and Thermally Stable Poly(amide-imide)s Based on Bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic Diimide and Phosphine Oxide in the Main Chain: Synthesis and Characterization

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Six novel poly(amide-imide)s PAIs **5a-f** were synthesized through the direct polycondensation reaction of six chiral *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **3a-f** with bis(3-amino phenyl) phenyl phosphine oxide **4** in a medium consisting of *N*-methyl-2-pyrrolidone (NMP), triphenyl phosphite (TPP), calcium chloride ($CaCl_2$) and pyridine. The polymerization reaction produced a series of flame-retardant and thermally stable poly(amide-imide)s **5a-f** with high yield and good inherent viscosity of 0.39-0.83 dLg^{-1}. The resultant polymers were fully characterized by means of FTIR, ^1H NMR spectroscopy, elemental analyses, inherent viscosity, specific rotation and solubility tests. Thermal properties and flame retardant behavior of the PAIs **5a-f** were investigated using thermal gravimetric analysis (TGA and DTG) and limited oxygen index (LOI). Data obtained by thermal analysis (TGA and DTG) revealed that these polymers show good thermal stability. Furthermore, high char yields in TGA and good LOI values indicated that resultant polymers exhibited good flame retardant properties. *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **3a-f** were prepared in quantitative yields by the condensation reaction of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1** with L-alanine **2a**, L-valine **2b**, L-leucine **2c**, L-isoleucine **2d**, L-phenyl alanine **2e** and L-2-aminobutyric acid **2f** in acetic acid solution. These polymers can be potentially utilized in flame retardant thermoplastic materials.

Keywords: Flame-retardant polymers; Poly(amide-imide)s; Thermally stable polymers; Chiral amino acid.

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 temperatures, 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 by introducing linked and flexible bridging units[3-5] into the polymer chains. 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 a good compromise between thermal stability and processability when compared with polyamides or polyimides of analogous structures.[6,7]

Phosphines, phosphine oxides, phosphonium compounds, phosphonates, elemental red phosphorus, phosphites and phosphate are all used as flame retardants.[8-11] 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).[12-19] 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.[20-26]

In this article, a series of novel flame-retardant PAIs

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5a-f containing phosphine oxide moiety were synthesized by the direct polycondensation reactions of six chiral *N,N'*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-amino acids **3a-f** with bis(3-amino phenyl) phenyl phosphine oxide **4** in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine. These polymers that have phosphine oxide moieties in the main chain show flame retardant and thermally stable behavior. These properties can make these polymers attractive for practical application such as processable high-performance engineering plastics. On the other hand, due to the presence of chiral segments in the polymer backbone, these PAIs are optically active. The synthesis and application of optically active polymers are novel topics worthy of consideration.[27-30]

RESULTS AND DISCUSSION

Monomer synthesis

The asymmetric diimide-diacids **3a-f** were synthesized by the condensation reaction of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1** with two equimolars of L-alanine **2a**, L-valine **2b**, L-leucine **2c**, L-isoleucine **2d**, L-phenyl alanine **2e** and L-2-aminobutyric acid **2f** in an acetic acid solution (Scheme I). The yields and some physical properties of these compounds are shown in Table 1.

The chemical structure and purity of the optically active diimide-diacids **3a-f** were proved by using elemental analysis, FTIR, ^{1}H NMR and ^{13}C NMR spectroscopic techniques and these data shown in Table 2.

As an example, the FTIR spectrum of *N,N'*-(bicyclo-[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-valine **3b** showed a broad peak between 2500 and 3400 cm^{-1}, which was assigned to the COOH groups. Peaks appearing at 1709-1751 cm^{-1} (acid C=O and symmetric imide stretching), 1390 and 700 cm^{-1} (imide characteristic ring vibration) confirmed the presence of an imide ring and carboxylic groups in this compound (Fig. 1).

The ^{1}H NMR spectrum of diimide-diacid **3b** is shown in Fig. 2. The protons H(a) relevant to O-H carboxylic groups appeared at 12.88 ppm. Peaks in 4.12-4.15 ppm appearing as doublets were assigned to the CH(b) protons, which is a chiral center; peaks between 0.66-0.94 ppm were assigned to aliphatic CH_3(c,d); peaks in 2.32-2.39 ppm were assigned to H(e). Protons relevant to the olefin bicyclo ring appeared at 5.99-6.09 ppm, H(h). Peaks between 3.24-3.42 ppm were assigned to H(f) (4H) and H(g) (2H).

The ^{13}C NMR spectrum of diimide-diacid **3b** showed 9 signals, including C_1 and C_6 in carboxylic acids and carbonyl imide rings, and C_7, C_8 in carbon atoms olefin in a

Scheme I

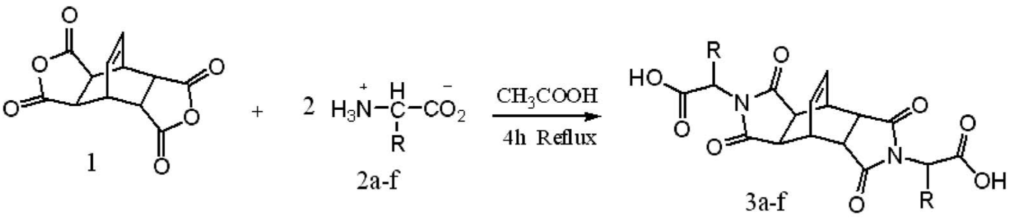

Table 1. Synthesis and some physical properties of chiral diimide-diacid derivatives **3a-f**

Diacid	Amino acid compound	R	Mp (°C)	Yield (%)	$[\alpha]_D^{25}$ [a]
3a	L-Alanine	CH_3	249-250	92	+155.7
3b	L-Valine	$(CH_3)_2CH$	318-320	93	+138.4
3c	L-Leucine	$(CH_3)_2CHCH_2$	289-290	94	+146.8
3d	L-Isoleucine	$(C_2H_5)(CH_3)CH$	293-295	92	+156.2
3e	L-Phenyl alanine	$PhCH_2$	247-248	91	+160.2
3f	L-2-Aminobutyric acid	CH_3CH_2	251-253	93	+130.2

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

Table 2. ^{1}H-NMR, ^{13}C-NMR, FTIR spectra and elemental analyses data of diacid derivatives **3a-f**

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), 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 $C_{18}H_{18}N_2O_8$: 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_2O exchange, s, 2H), 3.18-3.25 (D_2O 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 $C_{22}H_{26}N_2O_8$: 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 $C_{24}H_{30}N_2O_8$: 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 $C_{24}H_{30}N_2O_8$: 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 $C_{30}H_{26}N_2O_8$: 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_2O-exchang, s, br, 2H), 3.20-3.27 (D_2O-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 $C_{20}H_{22}N_2O_8$: C, 57.41; H, 5.30; N, 6.70; found: C, 57.34; H, 5.29; N, 6.70.

bicyclo ring (Fig. 3). These peaks in the ^{13}C NMR spectrum along with elemental analyses data confirmed the proposed structure of compound **3b**.

Polymer synthesis

PAIs **5a-f** were synthesized by direct polycondensation reaction of an equimolar mixture of diimide-diacids **3a-f** with bis(3-amino phenyl) phenyl phosphine oxide **4** in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine (Scheme II). The syntheses and some physical properties of these novel PAIs **5a-f** are given in Table 3. The entire polycondensation reaction readily proceeded in a homogeneous solution; tough and stringy precipitates formed when the viscous PAIs solution was obtained in good yields. The resultant polymers due to the presence of chiral amino acids **2a-f** in the main

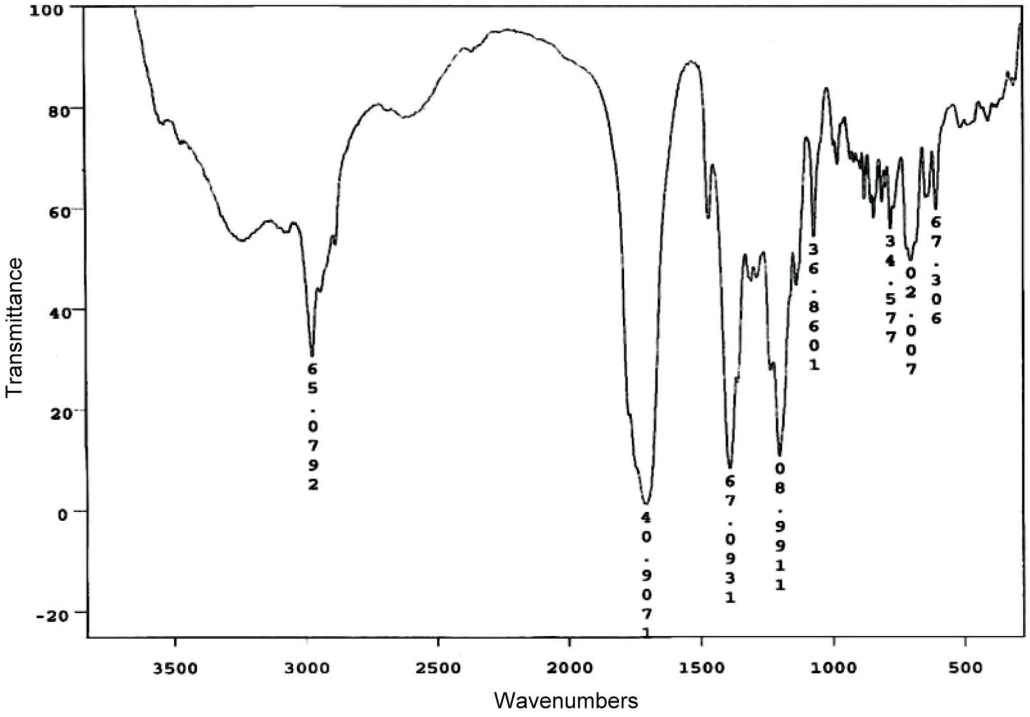

Fig. 1. FTIR spectrum of diimide-diacid **3b**.

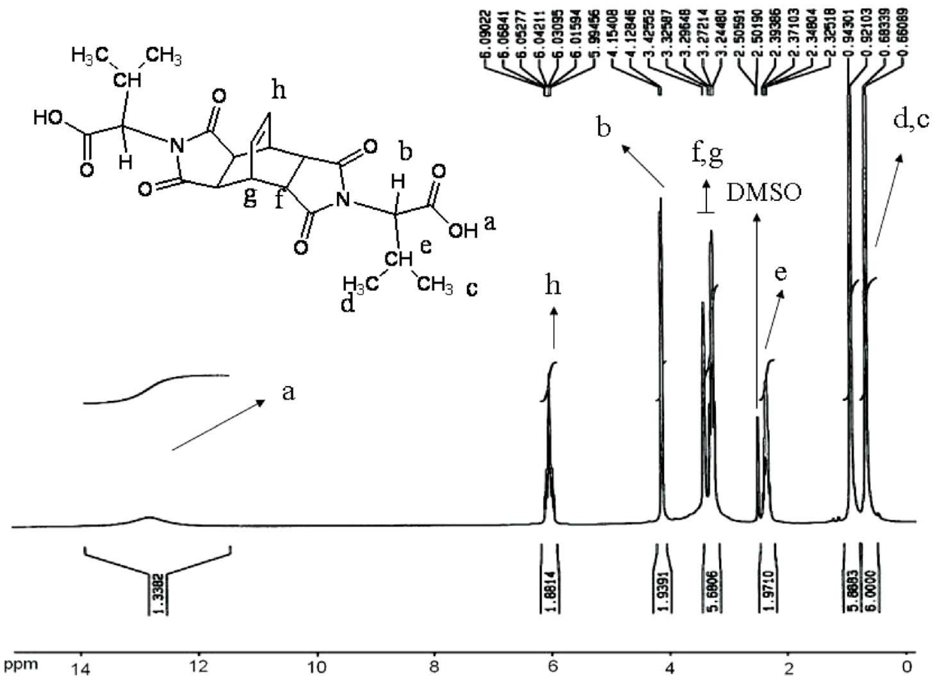

Fig. 2. ^{1}H NMR spectrum of diimide-diacid **3b**.

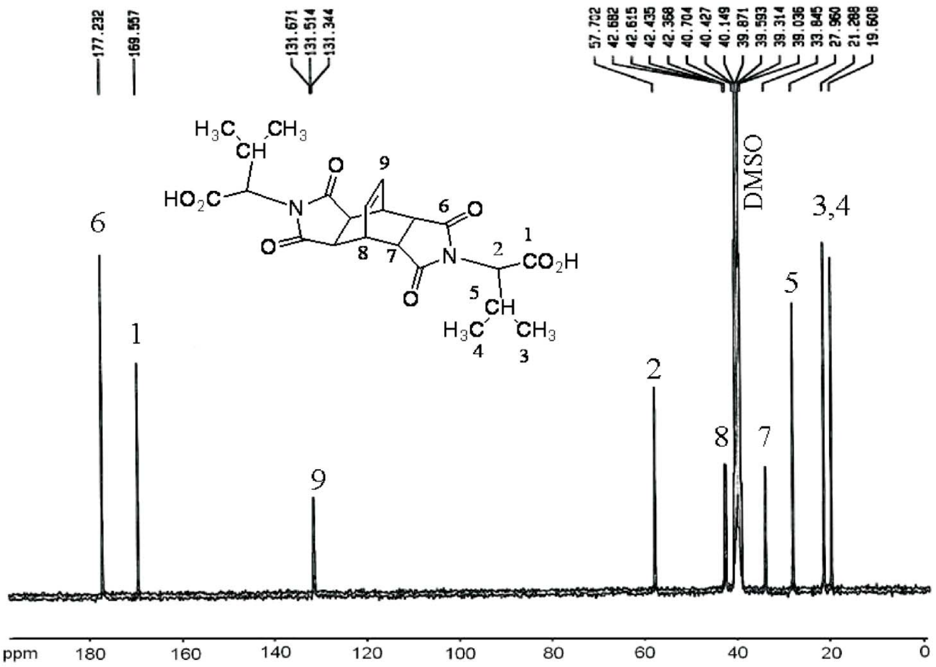

Fig. 3. ^{13}C NMR spectrum of diimide-diacid **3b**.

chain of polymers are optically active and Specific Rotations were measured at a concentration of 0.5 g/dL in DMSO at 25 °C. Also the resultant polymers have a range of color between white and pale yellow.

Polymer characterization

The elemental analyses of the resultant PAIs **5a-f** were in good agreement with the calculated values for the proposed structure (Table 4). The solubility of PAIs **5a-f** was investigated as 0.01 g of polymeric sample in 2 mL of solvent. All of the polymers are soluble in DMSO and H_2SO_4 and partially soluble in organic solvents such as DMF, NMP and DMAc and are insoluble in solvents such as chloroform, dichloromethane, methanol and ethanol.

Scheme II

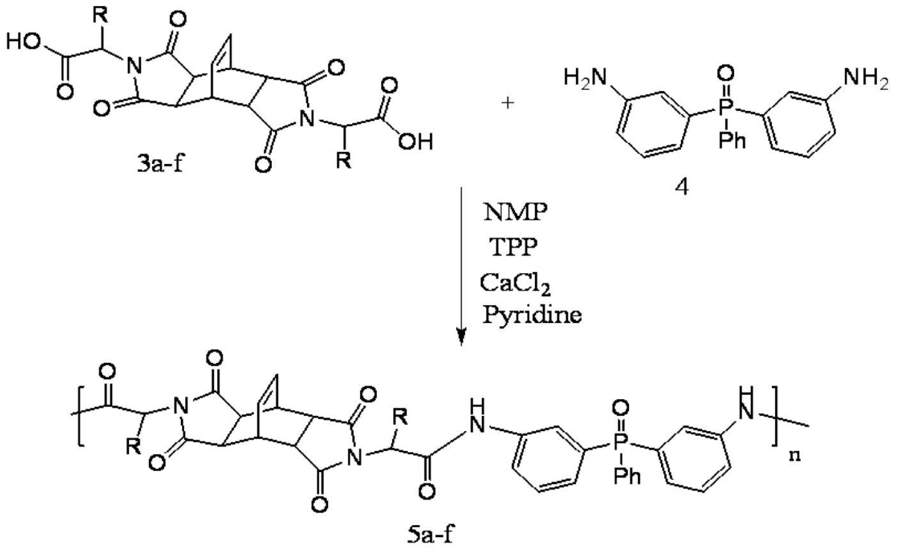

Table 3. Synthesis and some physical properties of PAIs **5a-f**

Diimide-diacid	Polymer	Yield (%)	η_{inh} (dL/g)^a	$[\alpha]_D^{25\,a}$	Color
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

[a] Measured at a concentration of 0.5 g/dL in DMSO at 25 °C.

[b] W = White, PY = Pale Yellow

The structures of these polymers were confirmed as PAIs by means of FTIR, ^{1}H-MNR spectroscopy and elemental analyses. FTIR characterizations of all PAIs are listed in Table 5. The representative FTIR spectrum of PAI **5b** is shown in Fig. 4. The polymer exhibited characteristic absorption bands at 1709 and 1774 cm^{-1} for the imide ring (symmetric and asymmetric C=O stretching vibration), a broad peak approximately at 1690 cm^{-1} related to amide groups (C=O stretching vibration), and 1384 cm^{-1} (C-N stretching vibration). The absorption bands of amide groups appeared at 3340 cm^{-1} (N-H stretching).

The ^{1}H NMR spectra of PAIs **5b** and **5f** showed peaks that confirm their chemical structures (Figs. 5, 6). Fig. 5 displays the ^{1}H-NMR spectrum of PAI **5c**. The aromatic protons related to tiphenyl phosphine oxide appeared in the region of 7.13-7.87 ppm and the peak in the region of 10.01 ppm is assigned to N-H of the amide groups in the main chain of the polymer. And Fig. 6 displays the ^{1}H NMR spectrum of PAI **5f**. The aromatic protons related to triphenyl phosphine oxide appeared in the region of 7.12-7.86 ppm, and the peak in the region of 10.00 ppm is assigned to N-H of the amide groups in the main chain of the polymer. A decaying peak related to carboxylic acid's protons and peaks appearing related to amide groups and triphenyl phosphine oxide protons in the polymer chain, confirmed the proposed structure of PAIs **5a-f**.

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 °C/min (Fig. 7). All of these polymers showed similar decomposition behavior. Initial decomposition temperature, 5 and 10% weight loss temperature (T_5, T_{10}), and char yields are summarized in Table 6.

Table 4. Elemental analysis of PAIs **5a-f**

Polymer	Formula		C%	H%	N%
5a	$C_{36}H_{31}N_4O_7P$	Calcd	65.25	4.72	8.46
	$(662.63)_n$	Found	64.15	4.66	8.34
5b	$C_{40}H_{39}N_4O_7P$	Calcd	66.84	5.47	7.80
	$(718.74)_n$	Found	65.78	5.23	7.65
5c	$C_{42}H_{43}N_4O_7P$	Calcd	67.55	5.80	7.50
	$(746.79)_n$	Found	66.14	5.21	7.13
5d	$C_{42}H_{43}N_4O_7P$	Calcd	67.55	5.80	7.50
	$(746.79)_n$	Found	66.04	5.35	7.34
5e	$C_{48}H_{39}N_4O_7P$	Calcd	70.75	4.82	6.88
	$(814.01)_n$	Found	68.89	4.64	6.71
5f	$C_{38}H_{35}N_4O_7P$	Calcd	66.08	5.11	8.11
	$(690.03)_n$	Found	65.23	5.01	8.01

Table 5. FTIR Charcterization of PAIs **5a-f**

Polymer	Spectral data
5a	**FT-IR 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	**FT-IR 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	**FT-IR 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	**FT-IR 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).

These polymers exhibited good resistance to thermal decomposition up to 270-310 °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 °C and the residual weight at 600 °C ranged from 59.99 to 62.16% in nitrogen. The high char yields of these PAIs in the 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 LOI values greater than 26 would show self-extinguishing behavior[26] and are 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 prop-

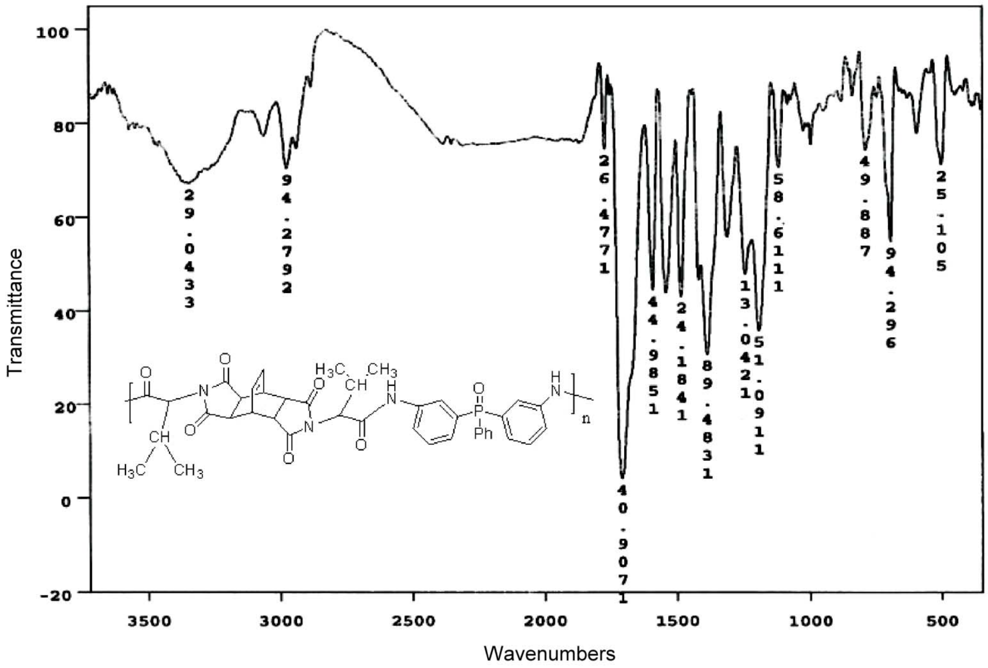

Fig. 4. FTIR spectrum of PAI **5b**.

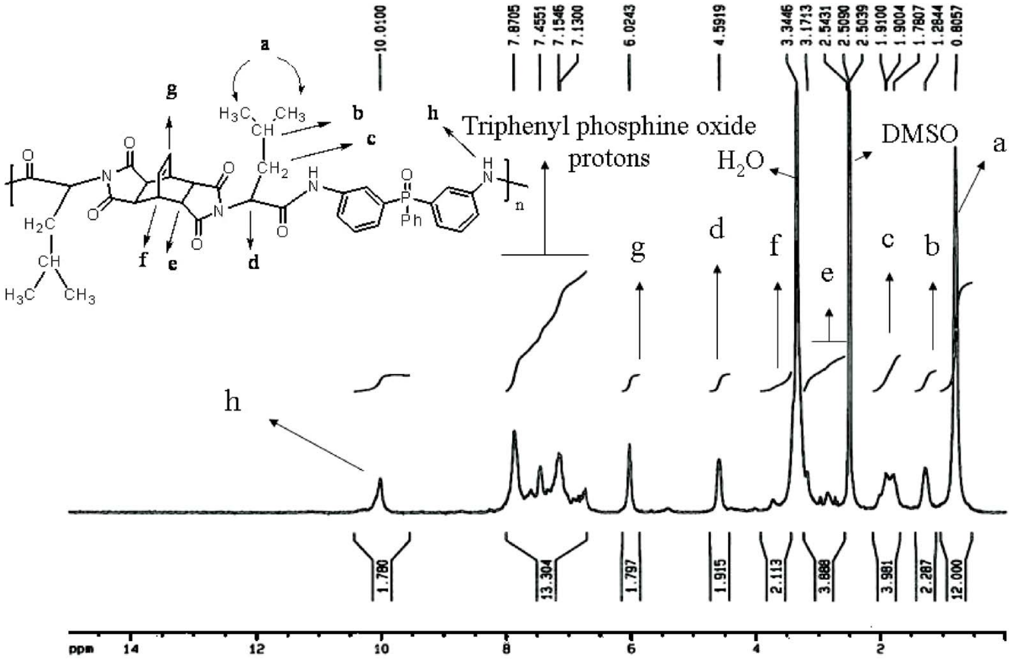

Fig. 5. ^{1}H NMR spectrum of PAI **5c**.

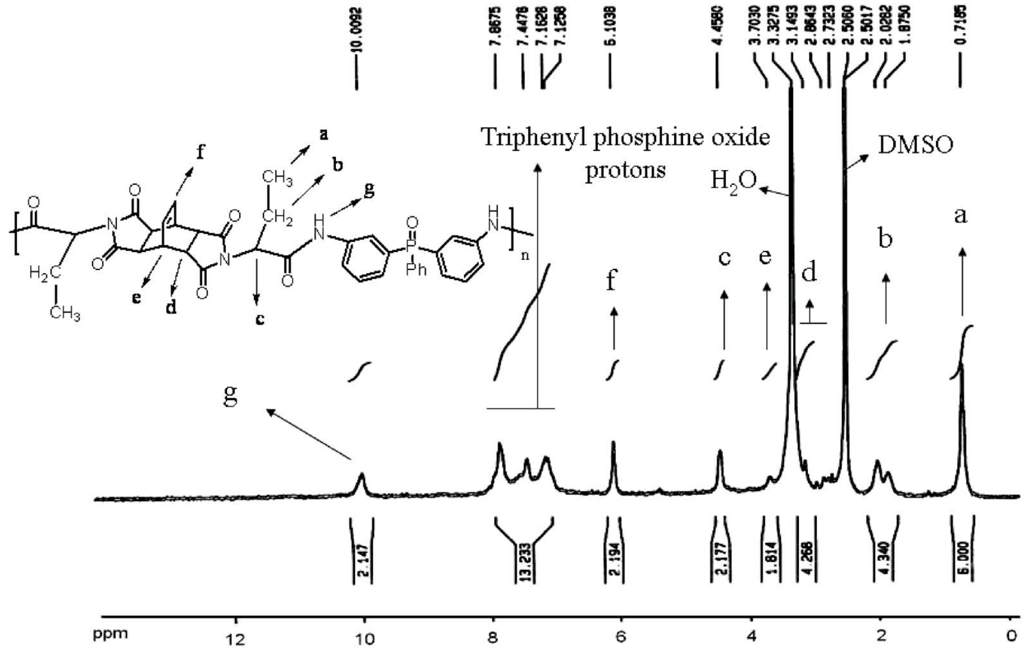

Fig. 6. ^{1}H NMR spectrum of PAI **5f**.

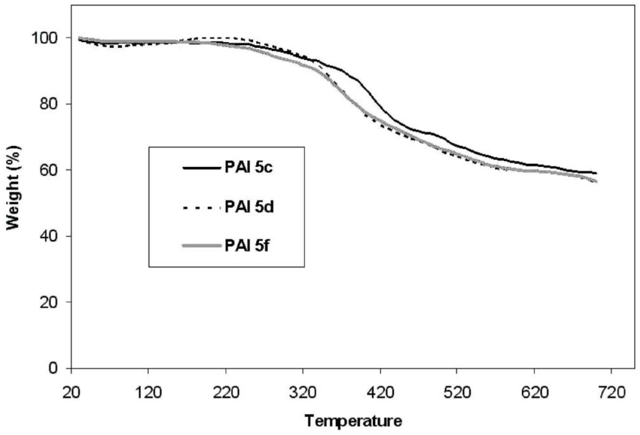

Fig. 7. TGA curves of PAIs **5c**, **5d** and **5f**.

erties.

CONCLUSIONS

A novel series of PAIs **5a-f** containing phosphine oxide moieties were synthesized by direct polycondensation reaction of six asymmetric diacids **3a-f** 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 the backbone increased the thermal stability and flame-retardant properties. These properties can make these polymers attractive for practical applications such as processable high-performance engineering plastics.

Table 6. Thermal behavior of PALs **5c**, **5d** and **5f**

Polymer	T_5 (°C)[a]	T_{10} (°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

[a] Temperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 10 °C/min under N_2.

[b] Weight percentage of material left after TGA analysis at a maximum temperature of 600 °C under N_2.

[c] LOI, Limited oxygen index

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-phenyl alanine **2e** and L-2-aminobutyric acid **2f** (from Merck) were used without previous purification. According to the synthetic procedure reported previously,[23-24] bis(3-amino phenyl) phenyl phosphine oxide **4** was prepared from bis(3-nitro phenyl) phenyl phosphine oxide. Solvent: *N*-methyl-2-pyrrolidone (NMP; from Fluka), pyridine (from Acros), triphenyl phosphite (TPP; from Merck) were used as received. Commercially available calcium chloride ($CaCl_2$; from Merck) was dried under vacuum at 150 °C for 6 hrs.

Apparatus and techniques

^{1}H NMR and ^{13}C 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 numbers (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 Trade Mark Viscometer. Specific Rotations were measured by an A-Kruss polarimeter. Limited oxygen indexes (LOI) were measured on a Stanton Redcroft flame meter. Thermal Gravimetric Analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N_2 atmosphere at a rate of 10 °C/min. Elemental analyses were performed on Vario EL equipment by Arak University.

Monomer synthesis

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

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-f**, 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 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-f**.

Bis(3-amino phenyl) phenyl phosphine oxide 4

This compound was prepared according to our previous methods.[23-24]

Polymer synthesis

The PAIs **5a-f** were prepared by the following general procedure: Taking polymer **5b** as an example: 0.145 g (0.326 mmol) of *N,N′*-(bicyclo[2,2,2]oct-7-ene-tetracarboxylic)-bis-L-valine **3b**, 0.1 g (0.326 mmol) of bis(3-amino phenyl) phenyl phosphine oxide **4**, 0.1 g (0.9 mmol) of calcium chloride, 0.84 mL (3.00 mmol) of triphenyl phosphite, 0.18 mL of pyridine and 2.00 mL of *N*-methy-2-pyrrolidone 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 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 0.194 g (83%) white solid polymer **5b**.

Received November 14, 2008.

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