

OPTICALLY ACTIVE AND FLAME-RETARDANT POLY(AMIDE-IMIDE)S BASED ON PHOSPHINE OXIDE MOIETY AND *N,N'*-(PYROMELLITOYL)BIS-L-AMINO ACID IN THE MAIN CHAIN: SYNTHESIS AND CHARACTERIZATION

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Abstract Six new optically active and flame-retardant poly(amide-imide)s PAIs **5a–5f** containing phosphine oxide moiety as a flame-retardant unit in the main chain were synthesized from direct polycondensation reaction of six chiral *N,N'*-(pyromellitoyl)-bis-L-amino acid **3a–3f** with bis(3-aminophenyl)phenyl phosphine oxide **4** in a medium consisting of *N*-methyl-2-pyrrolidone (NMP), triphenyl phosphite (TPP), calcium chloride (CaCl₂) and pyridine. The polymerization reactions produced a series of optically active poly(amide-imide)s with good yield and good inherent viscosity of 0.34–0.70 dLg^{−1}. The resulted polymers were fully characterized by means of FTIR and ¹H-NMR spectroscopy, gel permeation chromatography (GPC), elemental analyses, inherent viscosity and solubility tests. Thermal properties and flame-retardant behavior of the PAIs **5a–5f** were investigated using thermal gravimetric analysis (TGA and DTG) and limiting oxygen index (LOI). Data obtained by thermal analysis (TGA and DTG) revealed that these polymers showed good thermal stability. Furthermore, high char yield in TGA and good LOI values indicated that the resulting polymers were capable of exhibiting good flame retardant properties. *N,N'*-(pyromellitoyl)-bis-L-amino acids **3a–3f** were prepared in quantitative yields by the condensation reaction of pyromellitic dianhydride (1,2,4,5-benzenetetracarboxylic acid-1,2,4,5-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.

Keywords: Optically active; Flame-retardant polymers; Poly(amide-imide)s; Limiting oxygen index.

INTRODUCTION

Aromatic polyimides are well recognized as a class of high performance materials due to their remarkable thermal and oxidative stabilities and excellent electrical and mechanical properties for long time periods of operation^[1]. Unfortunately, strong interaction between polyimide chains and their rigid structure make them intractable. Poor thermoplastic fluidity and solubility are the major problems for wide application of polyimides. Thus, to overcome these processing problems various approaches have been carried out by incorporating flexible units such as —NHCO—, —O— and —SO₂—, and some of which are commercialized^[2–4]. Among them, polyamide-imide (PAI) is the most successful material, which combines the advantages of high-temperature stability and processability^[5–11].

Optically active polymers have found interesting applications because of their specific properties. For example, these polymers have the ability of molecular recognition, which cause to use them as a stationary phase in chromatography methods for enantiomer separations^[12–16]. They can also be used as chiral media for asymmetric synthesis and chiral liquid crystals in ferroelectric and nonlinear optical devices^[17].

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Phosphines, phosphine oxides, phosphonium compounds, phosphonates, elemental red phosphorus, phosphites and phosphate are all used as flame retardants^[18, 19]. 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)^[20–28]. 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^[29–32].

A triphenyl phosphite (TPP)-activated polycondensation (phosphorylation reaction) technique for the synthesis of polyamides was reported by Yamazaki *et al.*^[33]. Recently, this technique has been used for the preparation of high molecular weight polyamides as well as PAIs and is reported in the literature^[34, 35]. In this article, a series of new optically active PAIs **5a–5f** containing phosphine oxide moiety as a flame-retardant unit were synthesized by the direct polycondensation reaction of six chiral *N,N'*-(pyromellitoyl)-bis-L-amino acids **3a–3f** with bis(3-amino phenyl) phenyl phosphine oxide **4** in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (1,2,4,5-benzenetetracarboxylic acid-1,2,4,5-dianhydride) **1**, 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^[26, 27], bis(3-aminophenyl)phenyl phosphine oxide **4** was prepared from bis(3-nitrophenyl)phenyl phosphine oxide. Solvents: *N*-methyl-2-pyrrolidone (NMP; from Fluka), pyridine (from Acros), triphenyl phosphite (TPP; from Merck) were used as received. Commercially available calcium chloride (CaCl₂; from Merck) was dried under vacuum at 150°C for 6 h.

Measurements

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 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. Weight-average (*M_w*) and number-average (*M_n*) molecular weights were determined by gel permeation chromatography (GPC). The eluents were monitored with a UV detector (JMST Systems, USA, VUV-24) at 254 nm. Polystyrene was used as the standard. Limiting 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 a heating rate of 10 K/min. Elemental analyses were performed by a Vario EL equipment in Arak University.

Monomer Synthesis

Synthesis of *N,N'*-(pyromellitoyl)-bis-L-amino acid **3a–3f**

The diimide-diacids **3a–3f** were prepared by the following general procedure (using polymer **3f** as an example). 4.36 g (20.00 mmol) of pyromellitic dianhydride (1,2,4,5-benzenetetracarboxylic acid 1,2,4,5-dianhydride) **1**, 4.12 g (40.00 mmol) of L-2-aminobutyric acid **f**, 80 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 2.42 g (85%) compounds *N,N'*-(pyromellitoyl)-bis-L-2-aminobutyric acid **2f**. MP = 295–297°C. [α]_D²⁵ = +12.1 (Measured at a concentration of 0.5 g/dL in EtOH at 25°C). FTIR (KBr): 3500–2750 (m, br), 1776 (s, sh), 1770–1745 (s, br), 1456 (m), 1383 (s), 1282 (m), 1113 (s), 827 (m), 731 (m)

cm^{-1} . $^1\text{H-NMR}$ (300 MHz, DMSO-d_6): δ 0.85–0.90 (t, 6H), 2.10–2.17 (m, 4H), 4.72–4.77 (dd, 2H, $J = 6, 3$ Hz), 8.33 (s, 2H), 13.25 (s, br, 2H). Analysis: Calculated for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4$: C, 66.66; H, 4.93; N, 8.64; found: C, 66.58; H, 4.90; N, 8.66.

Bis(3-aminophenyl)phenyl phosphine oxide **4**

This compound was prepared according to our previous works^[30, 31].

Polymer Synthesis

The PAIs **5a–5f** were prepared by the following general procedure (using polymer **5a** as an example). *N,N'*-(pyromellitoyl)-bis-L-alanine **3a** (0.1 g, 0.277 mmol), bis(3-aminophenyl)phenyl phosphine oxide **4** (0.085 g, 0.277 mmol), calcium chloride (0.1 g, 0.9 mmol), triphenyl phosphite (0.84 mL, 3.00 mmol), pyridine (0.18 mL) and *N*-methyl-2-pyrrolidone (2.00 mL) 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 110°C for 8 h. 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 h under vacuum to leave 0.16 g (91%) white solid polymer **5a**.

FT-IR data of PAI **5a**: 3335 (m, br), 3063 (w), 2941 (w), 1776 (s), 1710 (s, br), 1680 (s, sh), 1591 (s), 1543 (s), 1481 (s), 1383 (s, sh), 1241 (m), 1165 (m), 1082 (m), 729 (m), 501 (m) cm^{-1} .

FT-IR data of PAI **5b**: 3330 (m, br), 3060 (w), 2940 (w), 1777 (m), 1710 (s, br), 1685 (s, sh), 1590 (s), 1543 (s), 1487 (s), 1383 (s, sh), 1240 (m), 1161 (m), 1080 (m), 730 (m), 506 (m) cm^{-1} .

FT-IR data of PAI **5c**: 3338 (m, br), 3067 (w), 2972 (w), 1776 (m), 1724 (s, br), 1678 (s, sh), 1589 (m), 1541 (m), 1483 (m), 1356 (m, sh), 1244 (m), 1165 (m), 1080 (w), 692 (w), 501 (w) cm^{-1} .

FT-IR data of PAI **5d**: 3325 (m, br), 3025 (w), 2970 (w), 1776 (w), 1720 (s, br), 1680 (s), 1589 (m), 1541 (m), 1483 (m), 1351 (m, br), 1240 (m), 1160 (m), 1082 (w), 691 (w), 506 (w) cm^{-1} .

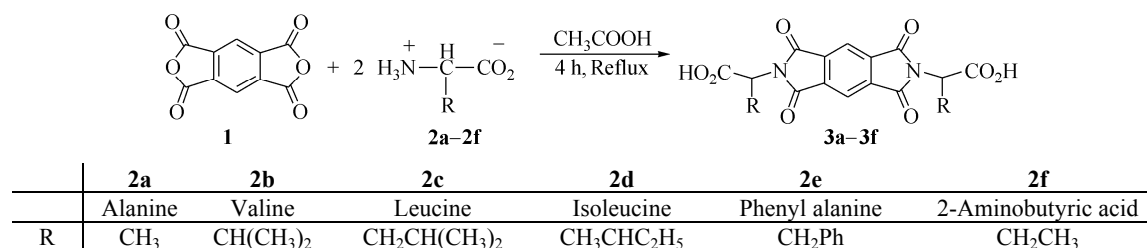
FT-IR data of PAI **5e**: 3275 (w, br), 3059 (w, sh), 1776 (m), 1724 (s, br), 1668 (m, sh), 1589 (m), 1541 (m), 1481 (m), 1356 (m), 1246 (w), 1109 (m), 698 (m), 501 (w) cm^{-1} .

FT-IR data of PAI **5f**: 3338 (m, br), 3060 (w), 2970 (w), 1776 (m), 1720 (s, br), 1688 (s), 1589 (m), 1541 (m), 1481 (m), 1356 (m), 1246 (w), 1109 (m), 698 (m), 506 (w) cm^{-1} .

RESULTS AND DISCUSSION

Monomer Synthesis

The asymmetric diimide-diacids **3a–3e** are synthesized previously^[8–10, 17], but diimide-diacid **3f** is a new compound that is synthesized by our research group. The diimide-diacids **3a–3f** were synthesized by the condensation reaction of pyromellitic dianhydride (1,2,4,5-benzenetetracarboxylic acid-1,2,4,5-dianhydride) **1** with two equivalents 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 1).



Scheme 1 Synthesis of diacids **3a–3f**

The FTIR spectrum of *N,N'*-(pyromellitoyl)-bis-L-2-aminobutyric acid **3f** showed a broad peak between 2500 and 3500 cm^{-1} , which was assigned to the COOH groups and two absorption bands at 1776 and 1726 cm^{-1} due to the carbonyl of imide (asymmetrical and symmetrical $\text{C}=\text{O}$ stretching vibration), and 1383, 1113, 731 cm^{-1} (imide ring deformation) (Fig. 1).

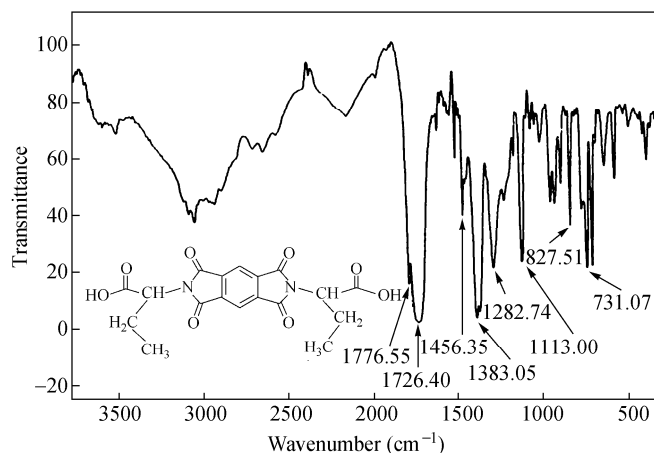


Fig. 1 FT-IR spectrum of *N,N'*-(pyromellitoyl)-bis-L-2-aminobutyric acid **3f**

The $^1\text{H-NMR}$ spectrum of diimide-diacid **3f** showed peaks between $\delta = 0.85$ and 0.90 as a triplet, which were assigned for two CH_3 (b), and peaks between $\delta = 2.10$ and 2.17 as a multiplet, which was assigned to the CH_2 (c), and peaks between $\delta = 4.72$ and 4.77 as a doublet of doublet ($J = 6$ and 3 Hz), which was assigned to the CH (d) proton, which is a chiral center. The peak at $\delta = 8.35$ was assigned to aromatic protons (e). Also a peak at $\delta = 13.25$ was assigned to COOH groups (Figs. 2 and 3).

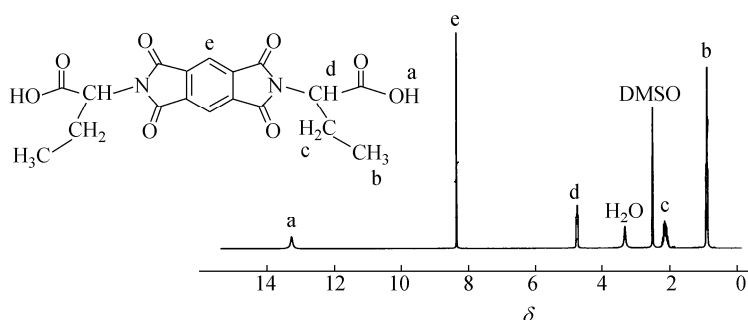


Fig. 2 $^1\text{H-NMR}$ spectrum of *N,N'*-(pyromellitoyl)-bis-L-2-aminobutyric acid **3f**

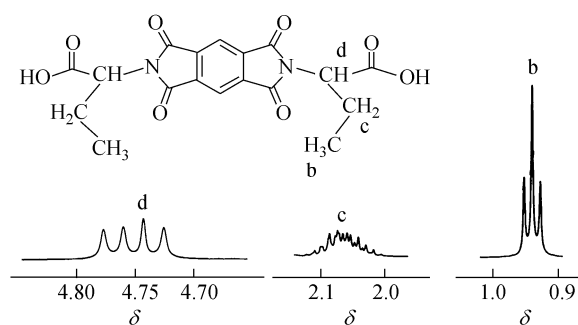
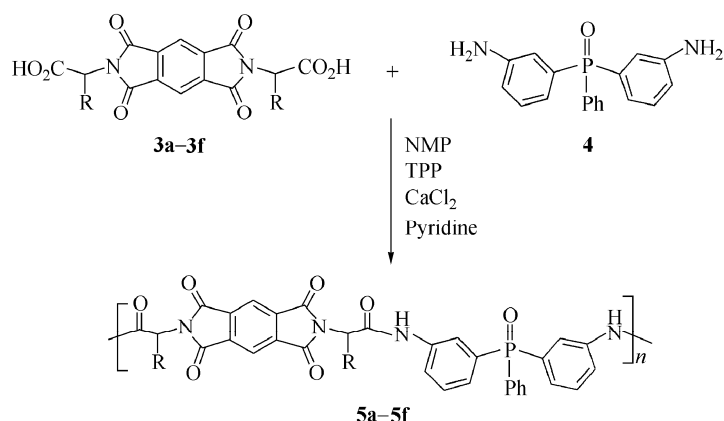


Fig. 3 $^1\text{H-NMR}$ spectrum of *N,N'*-(pyromellitoyl)-bis-L-2-aminobutyric acid **3f** [expanded]

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 **5a–5f** containing phosphine oxide moiety by the direct polycondensation reaction of an equimolar mixture of diimide-diacids **3a–3f** with bis(3-aminophenyl) phenyl phosphine oxide **4** in a medium consisting of *N*-methyl-2-pyrrolidone (NMP), triphenyl phosphite (TPP), calcium chloride (CaCl_2) and pyridine (Scheme 2).

**Scheme 2** Synthesis of PAIs **5a–5f**

The syntheses and some physical properties of these new PAIs **5a–5f** are given in Table 1. 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. The resulting polymers due to presence of chiral amino acids **2a–2f** in the polymer backbone were optically active and specific rotations can be measured at a concentration of 0.5 g/dL in DMSO at 25°C. These polymers exhibited number-average molecular weights (M_n) and weight-average molecular weights (M_w) in the range of 1.0×10^4 – 1.9×10^4 and 1.7×10^4 – 5.7×10^4 , respectively, as measured by GPC, relative to polystyrene standards, and due to presence of phosphine oxide moiety in their main chain, these polymers have flame-retardant property. Also the resulting polymers have a range of color between white and pale yellow.

Table 1. Synthesis and some physical properties of PAIs **5a–5f**

Diacid	Polymer	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_D^{25}$ ^a	M_n (10^4) ^b	M_w (10^4) ^b	PDI	Color ^c
3a	5a	91	0.57	+ 72	1.2	4.4	3.7	W
3b	5b	95	0.70	+ 58	1.9	5.7	3.0	W
3c	5c	90	0.34	+ 124	1.0	1.7	1.7	PY
3d	5d	90	0.37	+ 136	1.1	2.3	2.0	W
3e	5e	90	0.40	+ 94	1.3	4.2	3.2	PY
3f	5f	95	0.62	+ 87	1.4	4.9	3.5	W

^a Measured at a concentration of 0.5g/dL in DMSO at 25°C;^b Measured by GPC in DMF, polystyrene was used as standard;^c W = White, PY = Pale Yellow

Polymer Characterization

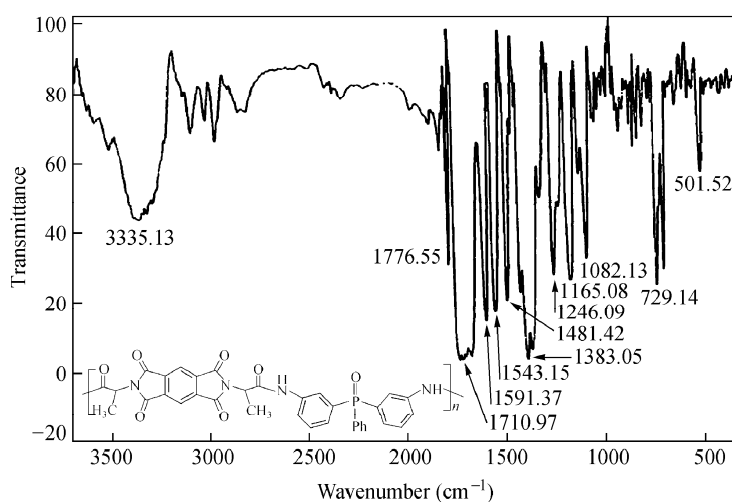
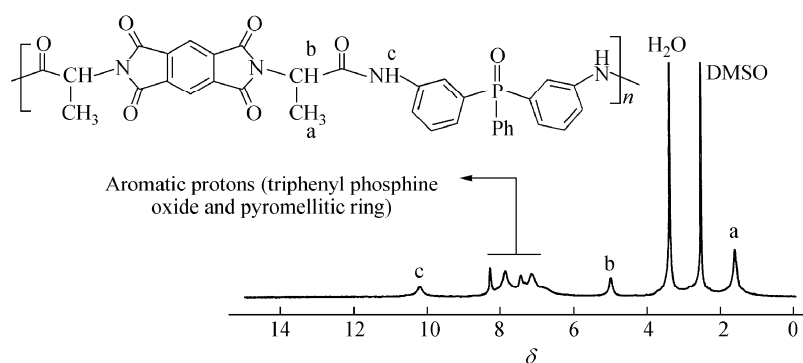
The elemental analyses of the resulting PAIs **5a–5f** were in good agreement with the calculated values for the proposed structure (Table 2).

The solubility of PAIs **5a–5f** was investigated by dissolving 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, DMAc and are insoluble in solvents such as chloroform, dichloromethane, methanol and ethanol.

The structure of these polymers was confirmed as PAIs by means of FTIR spectroscopy and elemental analyses. The representative FTIR spectrum of PAI **5a** is shown in Fig. 4. The polymer exhibited characteristic absorption bands at 1710 and 1776 cm⁻¹ for the imide ring (symmetric and asymmetric C=O stretching vibration), 1680 cm⁻¹ for the amide group (C=O stretching vibration) in the main chain, and bands at 1481 cm⁻¹ (P–Ph stretching vibration), 1383 cm⁻¹ (C–N stretching vibration) and 1165 cm⁻¹ (P=O stretching vibration). The absorption bands of amide groups appeared at 3335 cm⁻¹ (N–H stretching).

Table 2. Elemental analyses of PAIs **5a–5f**

Polymer	Formula		C (%)	H (%)	N (%)
5a	$C_{34}H_{25}N_4O_7P$	Calcd	64.55	3.95	8.86
	$(632.03)_n$	Found	62.85	3.80	8.42
5b	$C_{38}H_{32}N_4O_7P$	Calcd	66.37	4.65	8.15
	$(687.04)_n$	Found	64.93	3.95	8.01
5c	$C_{40}H_{37}N_4O_7P$	Calcd	67.03	5.16	7.82
	$(716.12)_n$	Found	66.78	5.01	7.70
5d	$C_{40}H_{37}N_4O_7P$	Calcd	67.03	5.16	7.82
	$(716.12)_n$	Found	65.84	5.06	7.23
5e	$C_{46}H_{32}N_4O_7P$	Calcd	70.49	4.08	7.15
	$(783.04)_n$	Found	68.52	3.90	7.01
5f	$C_{34}H_{29}N_4O_7P$	Calcd	64.15	4.55	8.80
	$(636.14)_n$	Found	62.88	4.05	8.78

**Fig. 4** FTIR spectrum of PAI **5a****Fig. 5** ^1H -NMR spectrum of PAI **5a**

The ^1H -NMR spectra of PAIs **5a** and **5e** showed peaks that confirm their chemical structures (Figs. 5 and 6). Figure 5 displays ^1H -NMR spectrum of PAI **5a**. The aromatic protons related to triphenyl phosphine oxide appeared in the region of $\delta = 6.94\text{--}7.84$ and the peak in the region of $\delta = 10.17$ is assigned for N–H of amide groups in the main chain of polymer. Figure 6 displays ^1H -NMR spectrum of PAI **5e**. The aromatic protons related to triphenyl phosphine oxide and aromatic proton related to diimide-diacid **3e** appeared in the region of

$\delta = 7.09$ – 8.16 , and the peak in the region of $\delta = 10.21$ 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 triphenyl phosphine oxide protons in the polymer chain, confirmed the proposed structure of these PAIs. Also Fig. 7 displays ^{31}P -NMR spectrum of PAI **5a**, and the peak in the region of $\delta = 23.27$ is related to P=O bond in the polymer backbone.

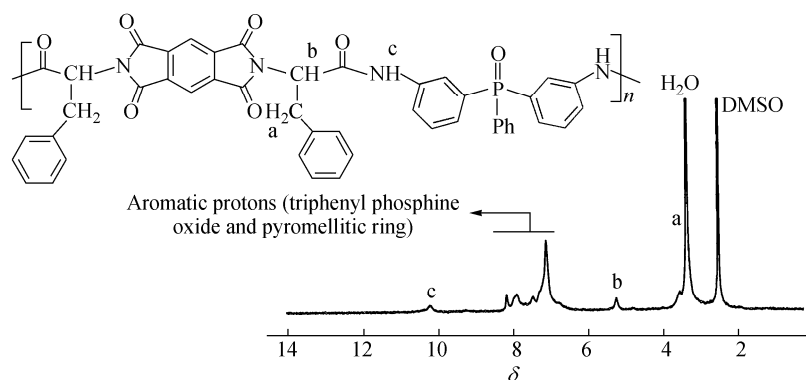


Fig. 6 ^1H -NMR spectrum of PAI **5e**

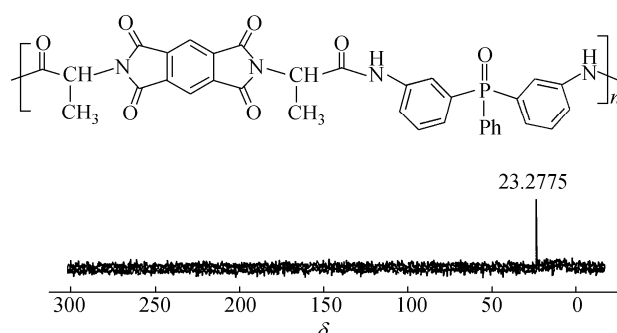


Fig. 7 ^{31}P -NMR spectrum of PAI **5a**

Thermal Properties

The thermal properties of PAIs **5a**, **5e** and **5f** were investigated by TGA in a nitrogen atmosphere at a heating rate of 10 K/min (Fig. 8). 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 3.

Table 3. Thermal behavior of PAIs **5a**, **5e** and **5f**

Polymer	T_5 (°C) ^a	T_{10} (°C) ^a	Char yield ^b	LOI ^c
5a	305	370	62.12	33
5e	280	330	64.89	32
5f	250	305	61.52	34

^a Temperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 10 K/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, Limiting Oxygen Index

These polymers exhibited good resistance to thermal decomposition up to 250°C in nitrogen and began to decompose gradually above that temperature. The temperature of 5% weight loss for all the polymers ranged from 250°C to 305°C, and the residual weight at 600°C ranged from 61.52% to 64.89% in nitrogen. Also the flame retardant property of these polymers was evaluated by measuring their LOI values. They showed LOI data between 32 and 34. Generally, materials exhibiting LOI values greater than 26 would show self-extinguishing behavior^[32] and were considered to be flame retardant. Therefore high char yield data, along with good LOI

values between 32 and 34, indicated that these polymers have good flame retardant properties. Char yield can be applied as decisive factor for estimating limiting oxygen index (LOI) of the polymers^[36].

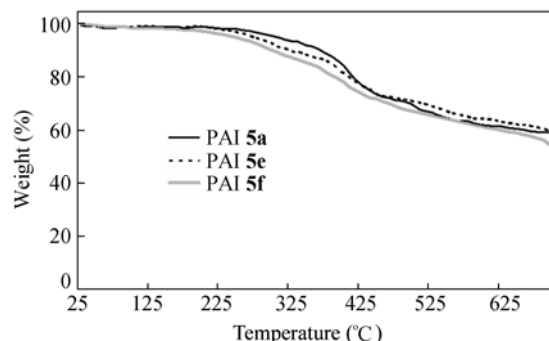


Fig. 8 TGA curves of PAIs 5a, 5e and 5f

CONCLUSIONS

A new series of PAIs **5a–5f** containing phosphine oxide moiety were synthesized by direct polycondensation reaction of six asymmetric diimide-diacids **3a–3f** with bis(3-aminophenyl)phenyl phosphine oxide **4** by using triphenyl phosphite, NMP, calcium chloride and pyridine as condensing agents. Due to the presence of chiral amino acids **2a–2f** in the main chain, these polymers are optically active and specific rotations can be measured at a concentration of 0.5 g/dL in DMSO at 25°C. The high char yields and good LOI data of these polymers showed that the introduction of phosphine oxide moiety into backbone increased the thermal stability and flame-retardant property. Optically active polymers with good thermal stability and flame-retardant behavior have potential to be used as a chiral stationary phase in chromatographic technique for the separation of racemic mixtures^[15, 16].

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