Materials Science-Poland, *Vol. 28*, *No. 2*, *2010*

New flame retardant and optically active poly(amide-imide)s based on N-trimellitylimido--L-amino acid and phosphine oxide moiety in the main chain: synthesis and characterization

KH. FAGHIHI*, M. HAJIBEYGI

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

Six new flame retardant and optically active poly(amide-imide)s (PAIs) containing phosphine oxide moiety in the main chain were synthesized by direct polycondensation reactions of six chiral N-trimellitylimido-L-amino acids with bis(3-amino phenyl) phenyl phosphine oxide in a medium consisting of N-methyl-2-pyrrolidone (NMP), triphenyl phosphite (TPP), calcium chloride ($CaCl_2$) and pyridine (Py). The polymerization reactions produced a series of flame retardant and optically active PAIs with high yields and good inherent viscosities in the range of 0.43–0.71 $dm^3 \cdot g^{-1}$. The resulting polymers were fully characterized by means of FTIR and ^{1}H-NMR spectroscopy, elemental analyses, inherent viscosity, specific rotation and solubility tests. The thermal properties and flame retardant behaviour of the PAIs were investigated using thermal gravimetric analyses the limiting oxygen index (LOI) tests. Data obtained by the thermal analyses revealed that the polymers showed good thermal stability and also high char yields, in the TGA data, and good LOI values indicating that PAIs have good flame retardant properties.

Keywords: *poly(amide-imide); flame retardant; polycondensation*

1. Introduction

Aromatic polyamides such as e.g. Kevlar and Nomex, synthesized from aromatic diamines and aromatic dicarboxylic acids, possess excellent mechanical properties and outstanding thermal stability [1–6]. Aromatic polyimides are also recognised as high performance polymer materials, for their excellent mechanical strength and high thermal stability, as well as balanced mechanical and electric properties [7, 8]. However, most polyimides are difficult to process, due to their rigidity and poor solubility in organic solvents. To overcome this drawback, several copolymers have been devel-

*Corresponding author: e-mail: k-faghihi@araku.ac.ir

oped. Replacement of polyimides by copolyimides such as poly(amide-imide)s (PAIs), may be useful to tackle the intractability of polyimides [9, 10] and, among them, poly(amide-imide)s (PAIs) can improve solubility. PAIs are usually fabricated by low temperature polycondensation of an aromatic diamine with acyl chloride of trimellitic anhydride [11, 12] or with acyl chlorides of aromatic diacids containing preformed imide rings [13–16]. The former method requires high temperatures or chemical cyclodehydration step of the poly(amic acid) formed, while the latter method requires a two step synthesis of diacyl chloride monomers. Recently, we have synthesized thermally stable PAIs by various methods [17–21].

Polymers containing phosphorus are generally flame retardant. They are also characterized by good adhesion to substrates, metal ion binding properties and increased polarity [22, 23]. Major advantages have polymers with phosphine oxide moieties. Phosphine oxide groups possess have hydrolytically stable P–C and P–O–C bonds and oxidatively stable P=O bonds. Polymers containing phosphine oxide moieties typically display good flame resistance, high thermal oxidative stability, enhanced solubility and improved miscibility and adhesion [24–26].

Also, interesting applications have been found for optically active polymers because of their specific properties. For example, these polymers have the ability of molecular recognition which justifies their use as a stationary phase in chromatography methods for separations of enantiomers [27, 28]. They can also be used as chiral media for asymmetric synthesis and as chiral liquid crystals in ferroelectric and nonlinear optical devices [29].

In the paper, syntheses of a series of new flame retardant PAIs containing phosphine oxide moieties were synthesized by the reactions of direct polycondensation of six chiral N-trimellitylimido-L-amino acids with bis(3-amino phenyl) phenyl phosphine oxide in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine. The synthesis and application of optically active polymers are new topics, recently extensively studied [30].

2. Experimental

Materials. Trimellitic anhydride (**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; bis(3-amino phenyl) phenyl phosphine oxide ((**4**)) was prepared from bis(3-nitro phenyl) phenyl phosphine oxide [24, 25]. Solvents: N-methyl-2-pyrrolidone (NM, Fluka), pyridine (Acros), triphenyl phosphite (TPP, Merck) were used as received. Commercially available calcium chloride ($CaCl_2$, Merck) was dried under vacuum at 150 °C for 6 h.

Apparatus and techniques. ^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded with a Galaxy series FTIR 5000 spectrophotometer (UK). Spectra of

solids were recorded in KBr pellets. Band intensities were classified 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 with an A-Kruss polarimeter. Limiting oxygen indexes (LOI) were measured with a Stanton Redcraft flame meter. Thermal gravimetric analysis (TGA and DTG curves) for polymers were taken on a Mettler TA4000 System under a N_2 atmosphere at rate of 10°C/min. Elemental analyses were performed with Vario EL equipment manufactured/provided by Arak University.

Syntheses of monomers. N-trimellitylimido-L-amino acids ((**3a–f**)) were synthesized as follows: 2 g (10 mmol) of trimellitic anhydride (**1**), 10 mmol of L-amino acid (**2a–f**), and 50 cm^3 of acetic acid were placed in a 250 cm^3 round-bottomed flask equipped with a stirring bar. The mixture was stirred at room temperature overnight and refluxed for 4 h. The solvent was removed under reduced pressure, and the residue was dissolved in 80 cm^3 of cold water, then the solution was decanted and 5 cm^3 of concentrated HCl was added. A white precipitate was filtered off, and dried to give N-trimellitylimido-L-amino acid ((**3a–f**)).

Bis(3-amino phenyl) phenyl phosphine oxide ((**4**)) was prepared according to the method described elsewhere [24, 25].

Syntheses of polymers. The PAIs (**5a–f**) were prepared by the following general procedure, taking polymer (**5a**) as an example: 0.10 g (0.38 mmol) of N-trimellitylimido-L-alanine (**3a**), 0.11 g (0.38 mmol) of bis(3-amino phenyl) phenyl phosphine oxide (**4**), 0.1 g (0.9 mmol) of calcium chloride, 0.84 cm^3 (3.00 mmol) of triphenyl phosphite, 0.18 cm^3 of pyridine and 2.00 cm^3 of N-methy-2-pyrrolidone were placed in a 25-cm^3 round-bottomed flask, which was equipped with a stirring bar. The reaction mixture was heated under reflux at 110 °C for 8 h. Then, the reaction mixture was poured into 50 cm^3 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 0.2 g (98.5%) white solid polymer (**5a**).

Polymer (**5a**): FTIR (KBr): 3310 (m, br), 3061 (m, sh), 1778 (w), 1718 (s), 1670 (s), 1589 (m), 1541 (m), 1481 (m), 1381 (m), 1248 (m), 1168 (m), 1082 (w), 949 (w), 690 (w), 588 (w), 503 (w) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm): 10.81 (s, 1H), 10.14 (s, 1H), 7.09-8.36 (m, 16H), 4.93 (s, 1H), 1.55 (s, 3H).

Polymer (**5b**): FTIR (KBr): 3337 (m, br), 3059 (w), 2962 (m), 1776 (w), 1720 (s), 1670 (s), 1589 (m), 1543 (m), 1481 (m), 1415 (m), 1377 (m), 1307 (m), 1248 (m), 1170 (m), 1114 (w), 1082 (m), 941 (w), 690 (m) cm^{-1}. ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm): 10.82 (s, 1H), 10.21 (s, 1H), 7.11-8.41 (m, 16H), 4.57 (s, 1H), 2.63-2.73 (m, 1H), 0.99 (d, 3H), 0.81 (d, 3H).

Polymer (**5c**): FTIR (KBr): 3330 (m, br), 3060 (w), 2960 (m), 1778 (w), 1722 (s), 1670 (s), 1589 (m), 1543 (m), 1485 (m), 1418 (m), 1383 (m), 1311 (m), 1248 (m), 1171 (m), 1117 (w), 1082 (m), 943 (w), 693 (m) cm^{-1}.

Polymer (**5d**): FTIR (KBr): 3294 (m, br), 3059 (w), 2962 (w), 1776 (w), 1720 (s), 1668 (s), 1589 (m), 1541 (m), 1479 (m), 1415 (m), 1375 (m), 1303 (m), 1246 (m), 1167 (m), 1082 (m), 939 (w), 790 (w), 690 (m), 499 (w) cm^{-1}.

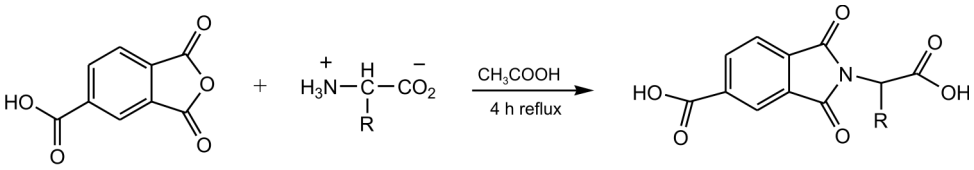
Polymer (**5e**): FTIR (KBr): 3308 (m, br), 3061 (m), 2930 (w), 1178 (w), 1720 (s), 1670 (s), 1591 (m), 1541 (m), 1481 (m), 1415 (m), 1377 (m), 1307 (m), 1246 (m), 1170 (m), 1105 (m), 939 (w), 692 (m), 503 (w) cm^{-1}.

Polymer (**5f**): FTIR (KBr): 3308 (m, br), 3067 (w), 2974 (w), 1178 (w), 1718 (s), 1662 (s), 1670 (m), 1541 (m), 1477 (m), 1377 (m), 1303 (m), 1244 (m), 1165 (m), 688 (m), 499 (m) cm^{-1}.

3. Results and discussion

3.1. Syntheses of monomers

Asymmetric diacids (**3a–f**) were synthesized by the condensation of trimellitic anhydride (**1**) with equivalent quantities of L-amino acids [31] such as L-alanine (**2a**), L-valine (**2b**), L-leucine (**2c**), L-isoleucine (**2d**), L-phenyl alanine (**2e**) and L-2-aminobutyric acid (**2f**) in solution of acetic acid (Scheme 1). The yields and some physical properties of these compounds are given in Table 1.



1 **2a–f** **3a–f**

Scheme 1. Synthesis of N-trimellitylimido-L-amino acids (**3a–f**)

Table 1. Yields and some physical properties of diacids (**3a–f**)

Entry	Amino acid compound	R	Mp [°C]	Yield [%]	$[\alpha]_D^{25a}$
3a	L-Alanine	CH_3	272-275	92	+122.4
3b	L-Valine	$(CH_3)_2CH$	208-210	94	+128.9
3c	L-Leucine	$(CH_3)_2CHCH_2$	194-197	92	+117.3
3d	L-Isoleucine	$(C_2H_5)(CH_3)CH$	200-203	94	+131.5
3e	L-Phenyl alanine	$PhCH_2$	215-218	90	+128.7
3f	L-2-Aminobutyric acid	CH_3CH_2	234-237	95	+139.8

[a]Measured at the concentration of 0.5 g/dm^3 in DMF at 25 °C.

The chemical structure and purity of the optically active diacids (**3a–f**) were confirmed by elemental analyses, FTIR and ^{1}H-NMR spectroscopic techniques (Table 2).

Table 2. ^{1}H-NMR, FTIR spectra and elemental analyses data of diacid (**3a–f**)

Imide diacid	Spectral data
(**3a**)	^{1}H–NMR (300 MHz, DMSO–d_6, δ, ppm): 13.5 (s, br, 2H), 8.39–8.40 (d, 1H, *J* = 9 Hz), 8.26 (s, 1H), 8.04–8.07 (d, 1H, *J* = 9 Hz), 4.91 (q, 1H), 1.55 (d, 3H). FTIR (KBr): 2500–3400 (s, br), 1728 (s, sh), 1722 (s, br), 1604 (w, sh), 1487 (w, sh), 1423 (s, sh), 1384 (s), 1290 (s), 1095 (m), 927 (m), 731 (s), 655 (m), 532 (w) cm^{-1}. ELEM. ANAL. Calc. For $C_{12}H_9NO_6$ (263..04): C, 54.76; H, 3.45; N, 5.32. Found: C, 54.63; H, 3.40; N, 5.30.
(**3b**)	^{1}H–NMR (300 MHz, DMSO–d_6, δ, ppm): 13.64 (s, br, 2H), 8.51–8.54 (d, 1H, *J* = 9 Hz), 8.25 (s, 1H), 8.02–8.05 (d, 1H, *J* = 9 Hz), 5.02 (d, 1H), 2.32 (m, 1H), 1.06–1.08 (d, 3H), 0.83–0.85 (d, 3H). FTIR (KBr): 2500–3400 (m, br), 1782 (m, sh), 1722 (s, br), 1487 (w), 1384 (s), 1290 (s), 1095 (w), 929 (m), 733 (s), 609 (w), 532 (w) cm^{-1}. ELEM. ANAL. Calc. For $C_{14}H_{13}NO_6$ (291.07): C, 57.73; H, 4.50; N, 4.81. Found: C, 57.41; H, 4.50; N, 4.79.
(**3c**)	^{1}H–NMR (300 MHz, DMSO–d_6, δ, ppm): 13.07 (s, br, 2H), 8.51–8.54 (d, 1H, *J* = 9 Hz), 8.41 (s, 1H), 8.02–8.05 (d, 1H, *J* = 9 Hz), 4.78–4.83 (dd, 1H, *J* = 6, 3 Hz), 1.52 (m, 2H), 1.49 (s, 1H), 0.85–0.87 (d, 6H). FTIR (KBr): 2500–3400 (m, br), 1780 (m, sh), 1733 (s, br), 1485(w), 1380(s), 1295(s), 1095 (w), 920 (m), 743 (s), 609 (w), 533 (w) cm^{-1}. ELEM. ANAL. Calc. For $C_{15}H_{15}NO_6$ (305.09): C, 59.01; H, 4.95; N, 4.59. Found: C, 58.95; H, 4.95; N, 4.56.
(**3d**)	^{1}H–NMR (300 MHz, DMSO–d_6, δ, ppm): 13.39 (s, br, 2H), 8.38–8.41 (d, 1H, *J* = 9 Hz), 8.27 (s, 1H), 8.02–8.05 (d, 1H, *J* = 9 Hz), 4.53–4.56 (d, 1H), 2.36–2.38 (m, 1H), 1.46–1.52 (s, 2H), 1.00–1.06 (d, 3H), 0.77–0.82 (t, 3H). FTIR (KBr): 2400 –3500 (s, br), 1778 (s, sh), 1722 (s, br), 1379 (s), 1286 (s), 1093 (m), 929 (w), 733 (m), 538 (w) cm^{-1}. ELEM. ANAL. Calc. For $C_{15}H_{15}NO_6$ (305.09): C, 59.01; H, 4.95; N, 4.59. Found: C, 58.88; H, 4.96; N, 4.52.
(**3e**)	^{1}H–NMR (300 MHz, DMSO–d_6, δ, ppm): 13.57 (s, br, 2H), 8.33–8.53 (d, 1H, *J* = 6 Hz), 8.19 (s, 1H), 7.94–7.97 (d, 1H, *J* = 6 Hz), 7.15 (s, 5H), 5.12–5.17 (dd, 1H, *J* = 9, 3 Hz), 3.46–3.52 (dd, 1H, *J* = 9, 3 Hz), 3.29–3.35 (dd, 1H, *J* = 9, 3 Hz). FTIR (KBr): 2400–3500 (s, br), 1770 (s, sh), 1720 (s, br), 1383 (s), 1278 (s), 1091 (m), 925 (w), 731 (m), 539 (w) cm^{-1}. ELEM. ANAL. Calc. For $C_{18}H_{13}NO_6$ (339.07): C, 63.72; H, 3.86; N, 4.13. Found: C, 63.55; H, 3.78; N, 4.10.
(**3f**)	^{1}H–NMR (300 MHz, DMSO–d_6, δ, ppm): 13.45 (s, br, 2H), 8.37–8.40 (d, 1H, *J* = 9 Hz), 8.26 (s, 1H), 8.01–8.04 (d, 1H, *J* = 9 Hz), 4.66–4.71 (dd, 1H, *J* = 6, 3 Hz), 2.01–2.19 (m, 2H), 0.82–0.87 (t, 3H). FTIR (KBr): 2400–3500 (s, br), 1780 (s, sh), 1720 (s, br), 1604 (m), 1487 (m), 1383 (s), 1284 (s, sh), 1082 (s), 879 (s), 729 (s), 638 (m), 472 (w), 314 (w) cm^{-1}. ELEM. ANAL. Calc. For $C_{13}H_{11}NO_6$ (277.06): C, 56.32; H, 4.00; N, 5.05. Found: C, 56.11; H, 4.10; N, 5.15.

Exemplary FTIR spectrum of N-trimellitylimido-L-2-aminobutyric acid (**3f**) showed a broad peak between 2500 and 3400 cm^{-1}, assigned to COOH groups. Peaks appearing at 1780 cm^{-1} (asymmetric imide stretching), and a broad peak at 1710–1760 cm^{-1} (symmetric imide stretching and carbonyl group for carboxylic acids), 1383 and 729 cm^{-1} (imide characteristic ring vibration) confirmed the presence of an imide ring and carboxylic groups in the compound (Fig. 1).

The ^{1}H-NMR spectrum of diacid (**3f**) **is** shown in Fig 2. Carboxylic groups appeared at 13.45 ppm. Peaks in 4.66–4.71 ppm (*J* = 6, 3 Hz) were assigned to the CH(b)

proton, that is a chiral centre, peaks at 0.82–0.87 ppm were assigned to aliphatic CH_3(d), a multiplet at 2.01–2.19 ppm was assigned to H(c). Aromatic protons were detected at 8.01–8.4 ppm.

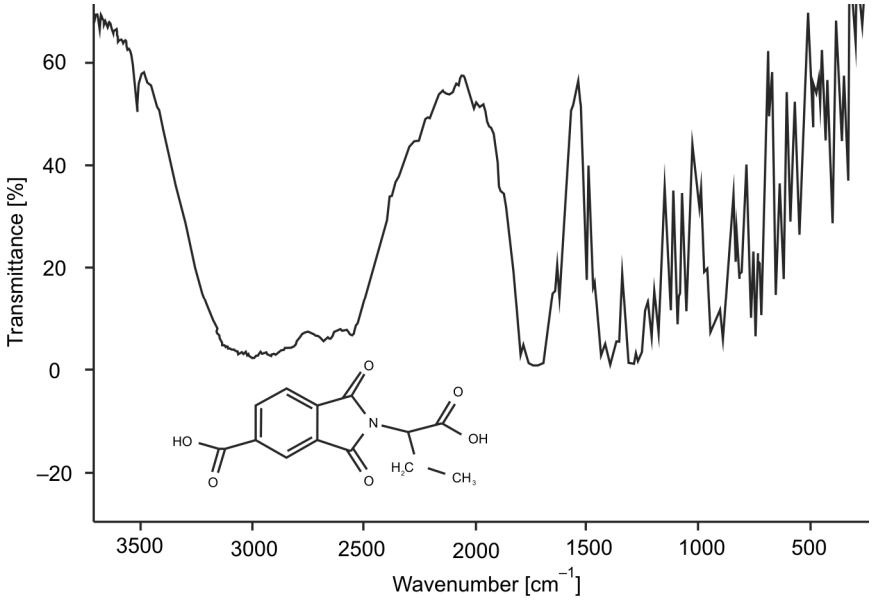


Fig. 1. FTIR spectrum of diacid (**3f**)

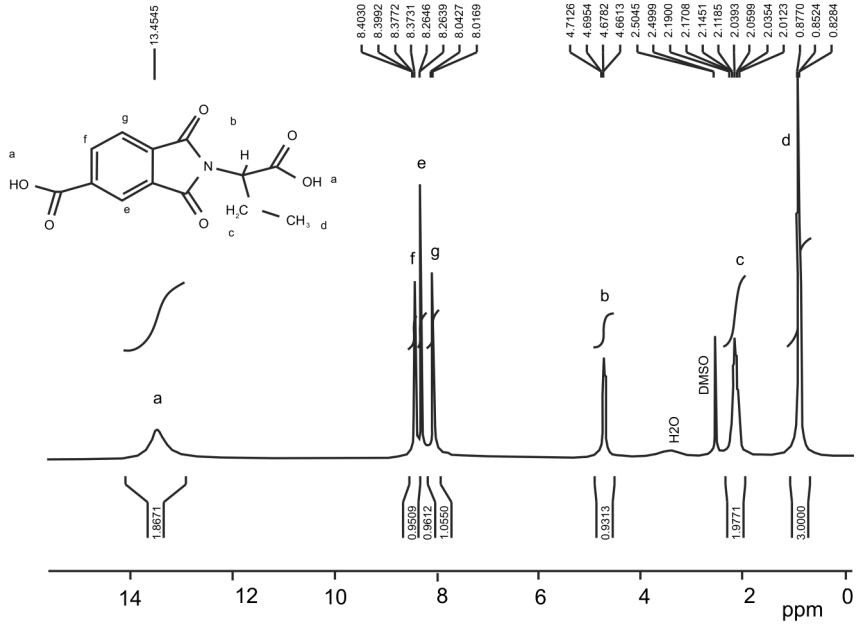
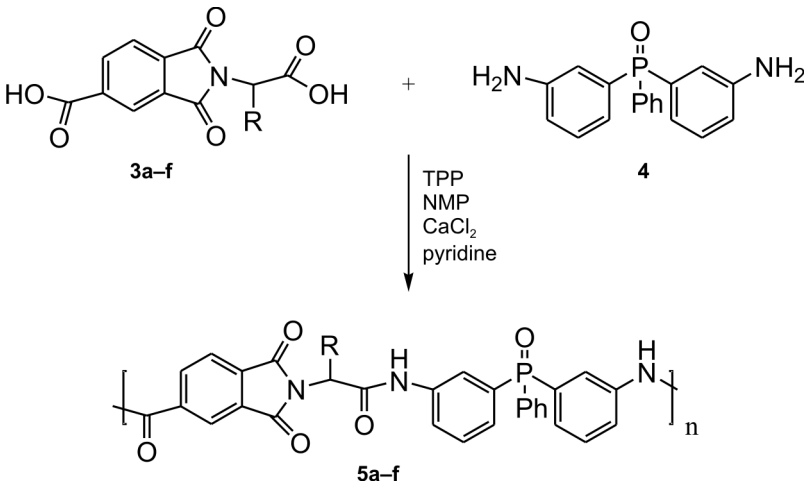


Fig. 2. ^{1}H-NMR spectrum of diacid (**3f**)

3.2. Syntheses of polymers

PAIs (**5a–f**) were synthesized by direct polycondensation of equimolar mixtures of 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 2).



Scheme 2. Synthesis of PAIs (**5a–f**)

Table 3. Yields and some physical properties of PAIs (**5a–f**)

Diimide-diacid	Polymer	Yield [%]	η_{inh} [dm^3/g]	$[\alpha]_D^{25a}$	Colour[b]
3a	**5a**	98	0.58	+72.1	PY
3b	**5b**	95	0.71	+58.5	W
3c	**5c**	94	0.48	+124.3	W
3d	**5d**	96	0.43	+136.4	W
3e	**5e**	94	0.59	+94.8	PY
3f	**5f**	96	0.48	+114.4	PY

[a]Measured at the concentration of 0.5g/dm^3 in DMSO at 25 °C.
[b]W – white, PY – pale yellow.

The yields and some physical properties of the new PAIs (5a–f) are given in Table 3. The resulting polymers, due to the presence of chiral amino acid moieties (**2a–f**) in the main chain of polymer, are optically active, as shown by specific rotation measurements at the concentration of 0.5 g/dm^3 in DMSO at 25 °C. Also, the resulting polymers have a spectrum of colour between white and pale yellow. The entire polycondensation reaction readily proceeded in a homogeneous solution, tough and stringy precipitates formed when viscous PAIs solution was obtained in good yields.

3.3. Polymer characterization

The elemental analyses of the resulting PAIs (**5a–f**) were in good agreement with the calculated values for the proposed structure (Table 4).

Table 4. Results of elemental analyses of PAIs (**5a–f**)

Polymer	Formula		C [%]	H [%]	N [%]
(**5a**)	$C_{30}H_{22}N_3O_5P$	calculated	67.28	4.11	7.85
	$(535.04)_n$	found	66.15	4.66	7.34
(**5b**)	$C_{32}H_{26}N_3O_5P$	calculated	68.20	4.61	7.46
	$(563.21)_n$	found	67.78	4.23	7.65
(**5c**)	$C_{33}H_{28}N_3O_5P$	calculated	68.63	4.85	7.27
	$(577.11)_n$	found	67.14	4.21	7.13
(**5d**)	$C_{33}H_{28}N_3O_5P$	calculated	68.63	4.85	7.27
	$(577.11)_n$	found	67.04	4.35	7.33
(**5e**)	$C_{36}H_{26}N_3O_5P$	calculated	70.70	4.25	6.87
	$(611.15)_n$	found	69.98	4.46	6.17
(**5f**)	$C_{31}H_{24}N_3O_5P$	calculated	67.75	4.37	7.65
	$(549.17)_n$	found	66.23	4.01	7.01

To investigate the solubility of PAIs (**5a–f**), 0.01 g polymeric samples were dissolved in 2 cm^3 of various solvents. All PAIs are soluble in DMSO, DMAc and H_2SO_4, and partially soluble in organic solvents such as DMF, NMP, and insoluble in solvents such as chloroform, dichloromethane, methanol and ethanol. The results are given in Table 5; +means soluble at room temperature, ± partially soluble at room temperature and soluble after heating, – insoluble.

Table 5. Solubility of PAIs (**5a–f**)

Solvent	(**5a**)	(**5b**)	(**5c**)	(**5d**)	(**5e**)	**5f**
H_2SO_4	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	±	±	+	+	±	±
NMP	±	±	+	+	±	±
DMAc	+	+	+	+	+	+
$CHCl_3$	–	–	–	–	–	–
CH_2Cl_2	–	–	–	–	–	–
MeOH	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
Acetone	–	–	–	–	–	–

The structures of these polymers were confirmed by means of FTIR, ^{1}H-MNR spectroscopy and elemental analyses. An exemplary FTIR spectrum of PAI (**5a**) is shown in Fig 3. The polymer exhibited characteristic absorption bands at 1778 and

1718 cm^{-1} for the imide ring (asymmetric and symmetric C=O stretching vibration), 1718 cm^{-1} (C= O stretching vibration for amide group) and 1381 cm^{-1} (C–N stretching vibration). The absorption bands of amide groups appeared at 3310 cm^{-1} (N–H stretching).

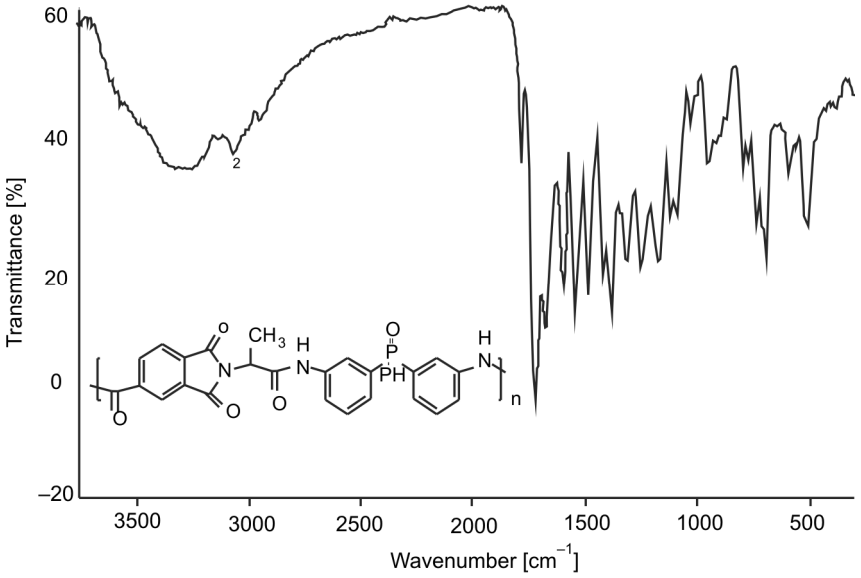


Fig. 3. FTIR spectrum of PAI (**5a**)

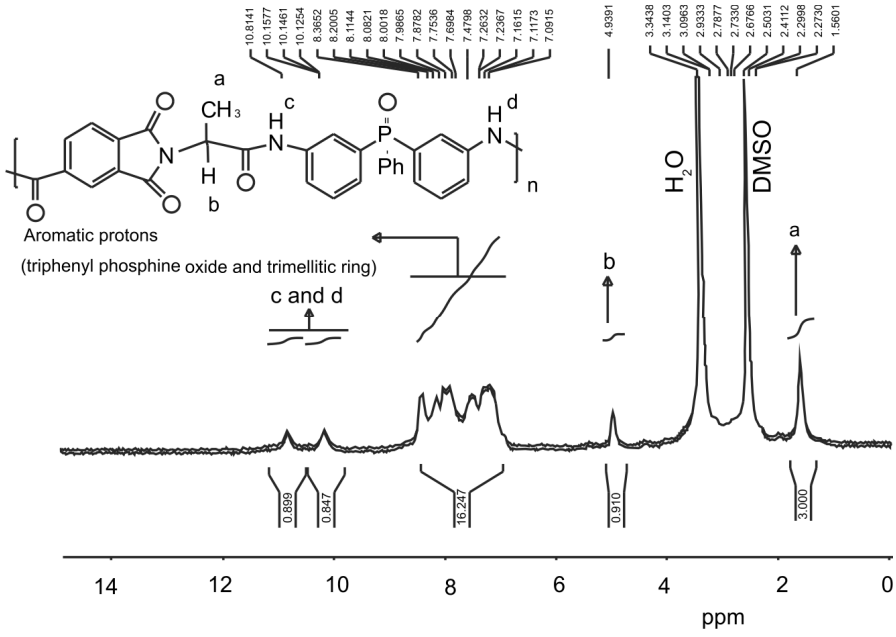


Fig. 4. ^{1}H-NMR spectrum of PAI (**5a**)

The ^{1}H-NMR spectrum of PAI (**5a**) is shown in Fig. 4. Thirteen protons related to triphenyl phosphine oxide and three protons related to trimellitic ring in the region of 7.09–8.36 ppm, and peaks in the regions of 10.14 and 10.81 ppm corresponded to N–H of various amide groups in the main chain. Decaying peak related to protons of carboxylic acid and peaks related to amide groups and triphenyl phosphine oxide protons in the polymer chain confirmed the proposed structures of PAIs (**5a**).

3.4. Thermal properties

Thermal properties of PAIs (**5a**), (**5b**) and (**5e**) in nitrogen atmosphere were investigated by TGA (with the heating rate of 10 °C/min). All the polymers showed approximately similar decomposition behaviour (Fig. 5).

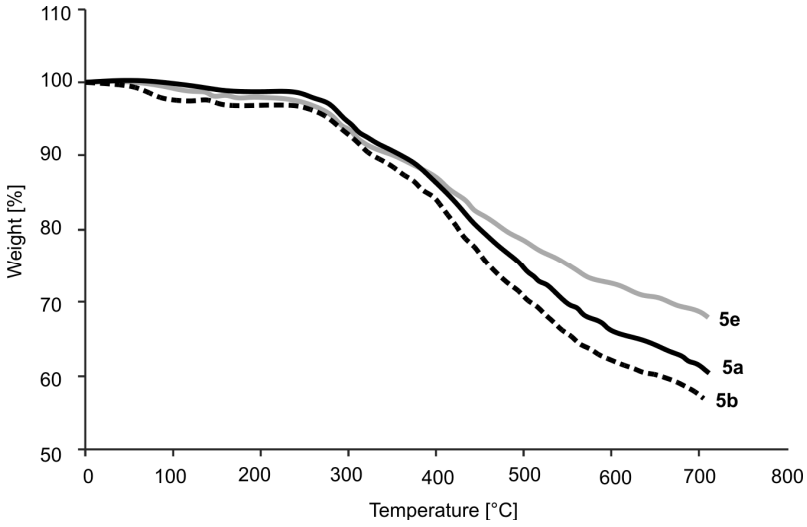


Fig. 5. TGA curves of PAIs (**5a**), (**5b**) and (**5e**)

The temperatures of initial decomposition, and of the 5% and 10% weight losses (T_5, T_{10}), and the char yields are given in Table 6.

Table 6. Thermal behaviour of PAIs (**5a**), (**5b**) and (**5e**)

Polymer	T_5 [°C][a]	T_{10} [°C][a]	Char yield[b]	LOI[c]
(**5a**)	290–295	350–355	66.17	35
(**5b**)	270–275	320–325	61.94	33
(**5e**)	275–280	345–350	72.47	30

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

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

[c]LOI, Limited oxygen index.

The polymers exhibited good resistance to thermal decomposition up to 270–290 °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 290 °C, and the residual weight at 600 °C ranged from 61.94 to 72.47% in nitrogen. The high char yields of the PAIs in the high temperature region show that these polymers have good thermal stability. According to the TGA thermogram of PAIs (**5a**), (**5b**) and (**5e**), PAI (**5e**) has the highest thermal resistance. It is due to the presence of aromatic rings related to phenyl alanine in the polymer. The flame retardation of the polymers was evaluated by measuring their limiting oxygen index (LOI) values: the higher the LOI value, the more effective the flame-retardation. The (LOI) data of these polymers ranged between 30 and 35. Generally, materials exhibiting (LOI) values greater than 26 would show self-extinguishing behaviour [26], and were considered to be flame retardant. Therefore, a high char yield, alongside with good (LOI) values indicated that these polymers have good flame retardant properties.

4. Conclusions

A new series of PAIs (**5a–f**) containing phosphine oxide moiety were synthesized by a direct polycondensation reaction of six asymmetric diacids (**3a–f**) with bis (3-aminophenyl)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 moiety into the backbone improved their flame retardation. Also, due to the presence of chiral amino acid moieties in the main chain, the synthesized polymers are optically active. Optically active flame retardant polymers with good thermal stability have the potential to be used as a chiral stationary phase in chromatographic techniques for the separation of racemic mixtures [32, 33]. These properties can make these polymers attractive for processable, high-performance engineering plastics.

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Received 2 July 2009
Revised 27 August 2009