Synthesis and spectral studies of polyamide–phosphate esters from phosphine-oxide-containing diols with aryl phosphorodichloridates and their thermal and flammability behaviour

P. Kannan, Gangadhara and K. Kishore*
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

(Received 9 February 1990; revised 13 June 1990; accepted 25 June 1990)

Polyamide–phosphate esters were synthesized by interfacial polycondensation of aryl phosphorodichloridates with the diols of phenoxaphosphine and phosphine oxide in the presence of a phase-transfer catalyst. The polymers were characterized by infra-red and ^{1}H, ^{13}C and ^{31}P nuclear magnetic resonance (n.m.r.) spectroscopy. The molecular weights were determined by end-group analysis using ^{31}P n.m.r. spectral data. The phenoxaphosphine-containing polymers showed superior thermostability and flame retardancy over the phosphine-oxide-containing polymers.

(Keywords: polyamide–phosphate esters; flame retardancy; aryl phosphorodichloridates; infra-red and nuclear magnetic resonance spectroscopy; thermogravimetry; limiting oxygen index)

INTRODUCTION

Phosphorus-containing polymers are well recognised for their flame-retardant properties, and they are increasingly gaining popularity over their halogen counterparts as they generally give off non-toxic combustion products. Recently, we have reported on the synthesis and flammability of various alkyl and aryl polyphosphate esters based on phosphorodichloridates[1,2]. Furthermore, studies of their structure–flammability relationship have yielded valuable information not only from the mechanistic angle but also on the characteristic role of thermal stability in curtailing their flammability[2]. It would be ideal if the polymers were to possess both fire retardancy as well as thermal stability. It was therefore resolved to attempt the synthesis of polyphosphate esters with a greater aromatic content. Phosphine oxide compounds are sufficiently heat-stable and impart a high degree of flame retardancy[3–9]. The present investigation attempts to synthesize polymers in which both the condensing monomers contain phosphorus atoms, e.g. phosphine-oxide-containing diols and aryl phosphorodichloridates. Efficient polymerization has been achieved by interfacial polycondensation using a phase-transfer catalyst. The thermal stability and flammability of these polymers have been evaluated by thermogravimetry and limiting oxygen index (*LOI*) respectively.

EXPERIMENTAL

Synthesis of monomers

4,4′-Bis(p-*hydroxyphenylamidophenyl*)*phenyl phosphine oxide* (*PPAD*). The compound 4,4′-bis(methylphenyl)-phenyl phosphine oxide, which was prepared from the Grignard reagent *p*-methylphenyl magnesium bromide and phenyl dichlorophosphine oxide (2:1 mol), was oxidized with alkaline $KMnO_4$ to give 4,4′-bis(carboxyphenyl)phenyl phosphine oxide[10]. The latter is subsequently converted into 4,4′-bis(chloroformylphenyl)-phenyl phosphine oxide by reacting it with thionyl chloride[11]. Treatment of 4,4′-bis(chloroformylphenyl)-phenyl phosphine oxide with *p*-aminophenol (2 mol) in dry dimethylacetamide (DMAc) at 0°C gave the title compound PPAD (m.p. 210°C).

2,8-Bis (p-*hydroxyphenylamido*)*-10-phenyl phenoxaphosphine-10-oxide* (*POAD*). The product obtained from the reaction of 4,4′-ditolyl ether and phenyl dichlorophosphine under Friedel–Crafts conditions was oxidized with alkaline $KMnO_4$ to give 2,8-dicarboxy-10-phenyl phenoxaphosphine-10-oxide, which on subsequent treatment with thionyl chloride gave 2,8-dichloroformyl-10-phenyl phenoxaphosphine-10-oxide[12]. This compound on further reacting with *p*-aminophenol (2 mol) at 0°C gave the title compound POAD (m.p. 221°C).

Aryl phosphorodichloridates (*APC*). The aryl phosphorodichloridates were prepared from $POCl_3$ with the corresponding phenols/naphthol by the reported procedure[13,14].

Polymerization

All the polymers were prepared by interfacial polycondensation using a phase-transfer catalyst, viz. tetrabutyl ammonium bromide (TBAB). A typical procedure for the synthesis of polymer I is as follows. In a solution of diol (1 mmol) in 20 ml of aqueous sodium hydroxide (1 N), TBAB (2 wt% of the diol) was dissolved. Sub-

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*To whom correspondence should be addressed

0032-3861/91/101909-05

sequently, 20 ml chloroform solution of phenyl phosphorodichloridate (1.1 mmol) was added to this mixture with vigorous stirring at 20°C. After 10 min the precipitated polymer was filtered and washed with chloroform and water; further purification was done by repeated precipitation from dimethylsulphoxide (DMSO) solution using methanol as the non-solvent. It was then dried to constant weight *in vacuo* at 80°C; the yield was more than 95%. The other polymers (II–XIV) were also prepared in a similar manner. All the polymers were light brown coloured powders. These polymers were insoluble in common organic solvents such as acetone and chloroform, but they were soluble, at room temperature, in concentrated sulphuric acid, trifluoroacetic acid and dipolar aprotic solvents such as dimethylformamide (DMF), dimethylacetamide (DMAc) and *N*-methylpyrrolidone (NMP).

Characterization

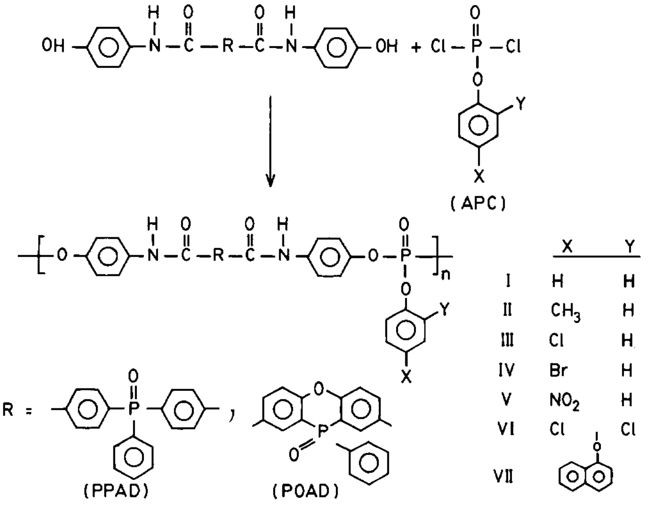
The i.r. spectra of the polymers were recorded in KBr pellets on a Perkin-Elmer model 715 spectrophotometer. The ^1H and ^{13}C n.m.r. spectra were recorded on a Brucker FT 270 spectrometer (67.89 MHz) in DMSO-d_6 using tetramethylsilane (TMS) as the internal standard. ^{31}P n.m.r. spectra were recorded on a Varian FT 80A (32.2 MHz) spectrometer in DMSO-d_6 under broadband ^1H decoupling conditions. D_2O and phosphoric acid (85%) were used as the external lock and external standard respectively.

Thermal and flammability studies

The thermogravimetric studies were carried out using a Sinku-Riko TGD 5000 thermal analyser in air at a heating rate of 20°C min^{-1} with a sample of 3–5 mg. The *LOI* data were obtained on a home-made assembly[2].

RESULTS AND DISCUSSION

A series of polyamide–phosphate esters containing phosphine oxide and phenoxaphosphine units were prepared by interfacial polycondensation at 20°C using TBAB as phase-transfer catalyst, with more than 95% yield (*Scheme 1*). In all the polymers, the diol to phosphorodichloridate ratio was kept at 1:1.1 to incorporate phosphate end-groups in the polymers.



	X	Y
I	H	H
II	CH_3	H
III	Cl	H
IV	Br	H
V	NO_2	H
VI	Cl	Cl
VII		

Scheme 1 Synthesis of polyamide–phosphate esters I–XIV

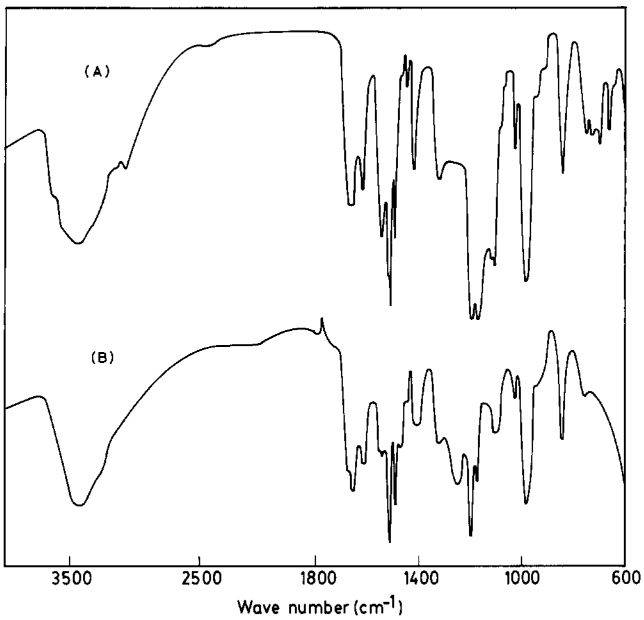


Figure 1 I.r. spectra of polymers IV (A) and X (B)

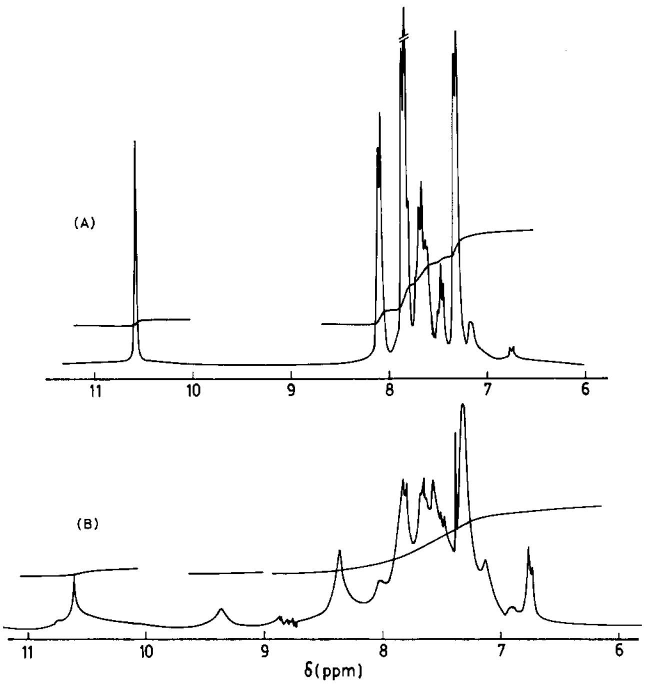


Figure 2 ^1H n.m.r. spectra of polymers I (A) and XI (B)

The i.r. spectra of the polymers are shown in *Figure 1*. The characteristic absorption bands are near 3300 and 1660 cm^{-1} for –NH– and amide carbonyl, respectively, for polymers I–VII; in addition to these, the absorption band at 1265 cm^{-1} due to ether linkage appeared for polymers VII–XIV[15]. All the polymers showed absorption at 1380, 1180 and 980 cm^{-1} for P–Ph and P–O–C (aromatic) respectively. Similarly, the absorption around 1300 cm^{-1} is due to the P=O stretching of the phosphate ester groups[16,17].

Representative ^1H and ^{13}C n.m.r. spectra are shown in *Figures 2–4*. The aromatic protons of the main chain and the pendent phenyl appear as broad multiplets in the region $\delta = 6.2$ to 8.2 ppm. In some spectra the phenolic–OH protons appeared as a singlet at $\delta = 10.6$ ppm. The ^{13}C resonance of all the phenyl carbons

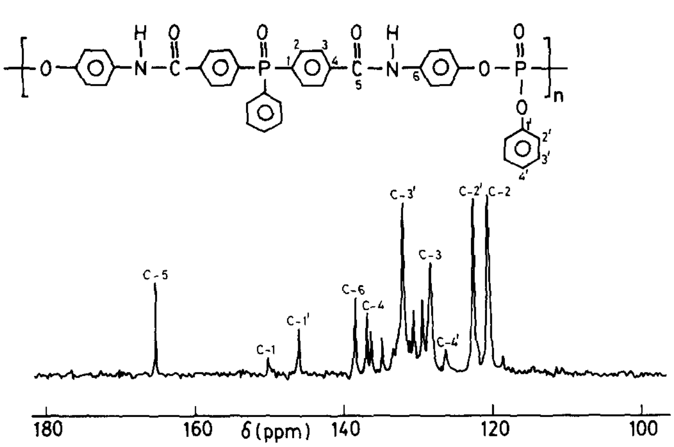


Figure 3 Broad-band decoupled ^{13}C n.m.r. spectrum of polymer I

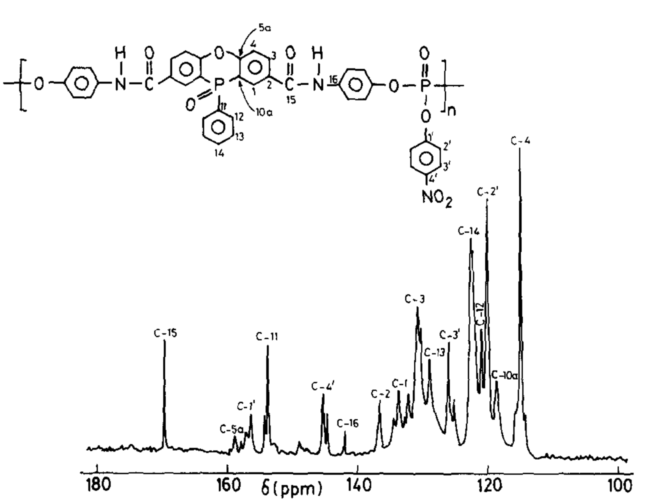


Figure 4 Broad-band decoupled ^{13}C n.m.r. spectrum of polymer XII

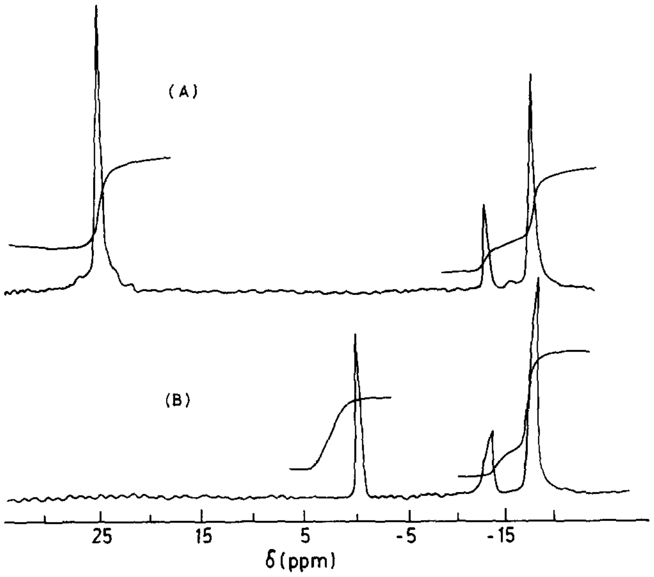


Figure 5 ^{31}P n.m.r. spectra of polymers I (A) and XII (B)

is centred from $\delta = 119.7$ to 136 ppm and the characteristic carbon resonances are indicated in the spectra[18–20]. The signal corresponding to –CONH– carbon emerges at $\delta = 165$ ppm[21].

The ^{31}P n.m.r. spectra of all the polymers show two intense signals and one weak signal (*Figure 5*, *Table 1*). The intense signals correspond to the P′ of phosphine oxide and P of phosphorophenyl of the repeat units, respectively, and the other weak signal corresponds to the P present at the end-group of the phosphate ester. The deshielded phosphine oxide and phenoxaphosphine oxide appeared at low field of $\delta \sim 24.6$ ppm and $\delta \sim -0.25$ ppm respectively[22], but the more shielded P in the repeat unit connected to three aryloxy groups appeared at $\delta \sim -11.6$ ppm. The end-group P appears at $\delta \sim -16.6$ ppm. The substitution on the phenyl ring does not cause any significant change in the δ values[23].

The molecular weights of the polymers were calculated from the ^{31}P n.m.r. spectral data using the ratio of the integration of the P in the repeat unit and the chain end of phosphate groups. Accordingly, in the case of polymer VII, the ratio of integration is found to be 2:5, and the number-average molecular weight ($\bar{M}_n$) is 4130; for other polymers $\bar{M}_n$ are given in *Table 1*.

The thermograms of various polymers are shown in *Figures 6* and *7*. The temperature corresponding to 1% and 50% weight loss, and the char remaining at 700°C are given in *Table 2*. All the polymers exhibit good

Table 1 ^{31}P n.m.r. spectral data and molecular weights of the polymers

	Chemical shift (ppm)				
Polymer	P′ in repeat unit	P at chain end	P in repeat unit	Ratio of integration (P end/ P repeat)	Molecular weight[a] ($\bar{M}_n$)
I (PPAD–APC)	25.0	−11.7	−16.7	1:4	3060
II	24.8	−11.6	−16.8	2:4	3140
III	25.0	−11.6	−17.0	2:4	3530
IV	25.6	−11.7	−16.8	1:3	2770
V	24.9	−12.1	−17.1	2:4	3290
VI	25.0	−11.1	−16.5	2:4	3270
VII	25.0	−11.0	−16.5	2:5	4130
VIII (POAD–APC)	−0.27	−11.8	−16.0	1:5	3680
IX	−0.24	−11.6	−16.8	2:4	2890
X	−0.24	−11.7	−15.9	1:4	3150
XI	−0.25	−12.0	−16.2	1:5	4150
XII	−0.24	−12.1	−16.1	2:4	3200
XIII	−0.29	−11.7	−16.1	2:4	3320
XIV	−0.25	−11.9	−16.0	2:5	3980

[a] Error ±2%

Table 2 Thermogravimetric and *LOI* data of polymers I–XIV

	Temperature (°C) corresponding to				
Polymer	1% weight loss	50% weight loss	Char percentage at 700°C	Phosphorus content (%)	*LOI*[a]
I	310	630	37	10.5	45.0
II	300	650	30	9.8	43.0
III	290	570	31	8.5	43.5
IV	330	760	50	8.9	49.0
V	320	620	42	9.5	44.5
VI	320	590	41	9.4	47.0
VII	340	690	49	9.8	52.0
VIII	290	620	30	8.8	44.5
IX	320	620	42	8.7	45.0
X	300	580	35	8.5	46.0
XI	310	640	44	8.0	51.0
XII	330	620	40	8.3	49.0
XIII	320	610	42	8.7	47.0
XIV	350	650	45	8.3	53.0

[a] The experimental error was ±1%

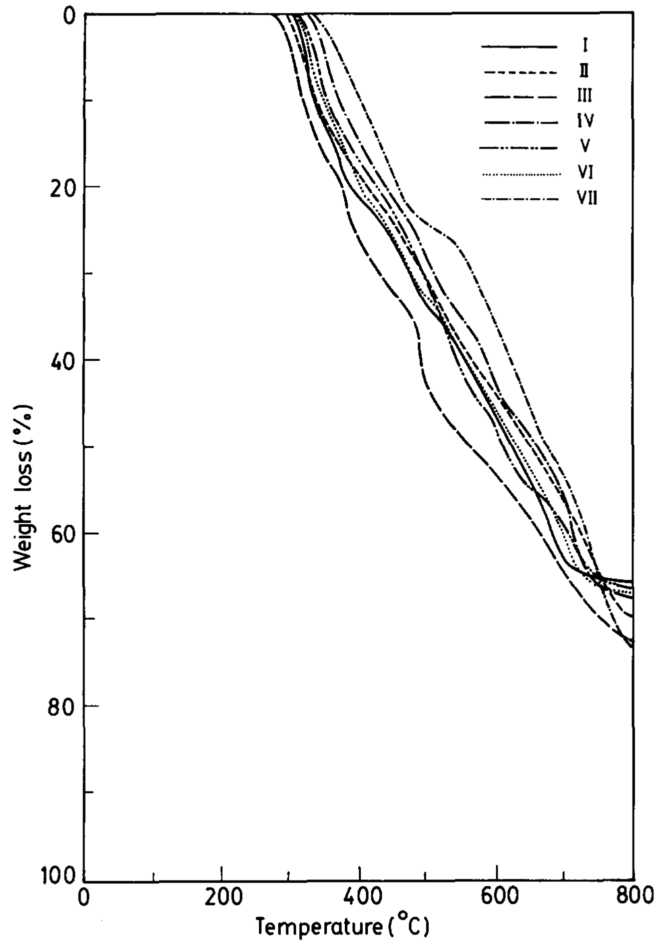


Figure 6 Thermogravimetric traces of polymers I–VII

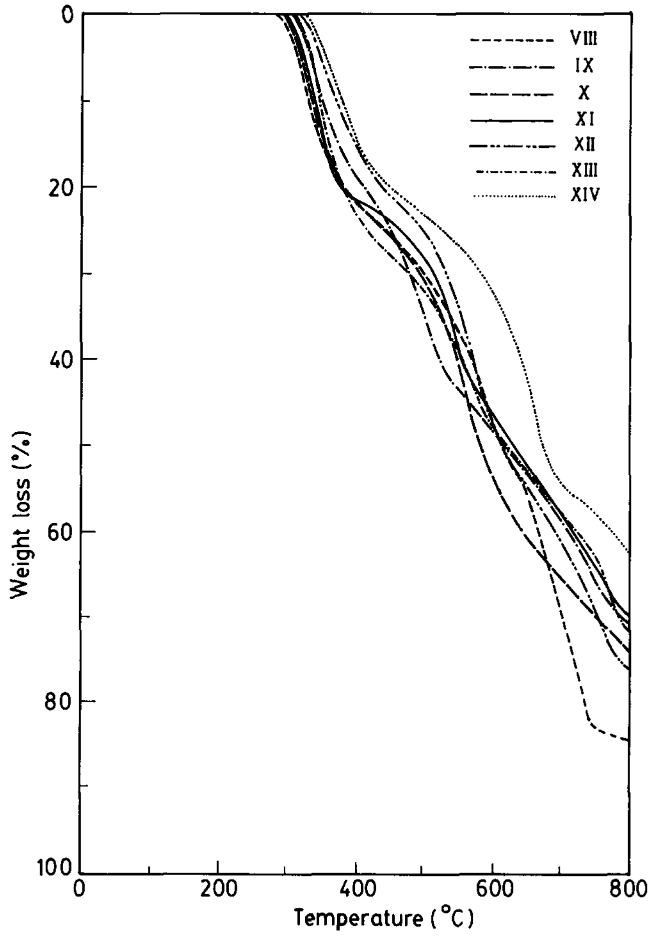


Figure 7 Thermogravimetric traces of polymers VIII–XIV

thermal stability up to $\sim$300°C and start to degrade between 320 and 410°C in air. The pendent naphthyl and bromine-substituted phenyl polymers (IV, VII, XI and XIV) show better thermal stability than the other polymers. The degradation occurs in the usual two-step process like our previous polyphosphate esters[1,2]. The polymers VIII–XIV (POAD–APC) showed improved thermal stability and an edge over the char percentages compared to the polymers derived from PPAD–APC. This may be attributed to the double-strand heterocyclic units of the phenoxaphosphine compared to the open-chain linkages of the phosphine units. In general, the char yield at 700°C varied from 30 to 50% for these polymers, depending on the backbone structures.

The *LOI* and phosphorus content (%) of the polymers are given in *Table 2*. These polyamide–phosphate esters showed considerably higher *LOI* values and good flame retardancy. The polymers VII and XIV produced superior *LOI* values than the remaining polymers. The *LOI* values decreased in the different sequences for PPAD–APC and POAD–APC polymers respectively, which may be ascribed to the structural differences of the polymers:

PPAD–APC: $Br > diCl_2 > NO_2 > H > Cl > CH_3$

POAD–APC $Br > NO_2 > diCl_2 > Cl > CH_3 > H$

The phenoxaphosphine-containing polyamide–phosphate esters exhibit better *LOI* than the corresponding phosphine-oxide-containing polymers.

CONCLUSIONS

Various new polyamide–phosphate esters bearing phosphine oxide and phenoxaphosphine units were synthesized and characterized spectroscopically. The molecular weights were determined from ^{31}P n.m.r. spectral data. The thermal stability of the polymers was found to vary depending on their side-chain structure. The introduction of a naphthyl unit in the side-chain was found to reduce the flammability substantially.

ACKNOWLEDGEMENT

The authors are grateful to the Department of Science and Technology, New Delhi, for financial support.

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