# Novel flame retardant polyphosphoramide esters

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Several new polyphosphoramide esters have been synthesized by solution polycondensation of *N*,*N*′-bis(*p*-chloroformylphenyl)*N*″-phenyl phosphoric triamide with various aromatic diols. The polymers were characterized by i.r., $^1H$, $^{13}C$ and $^{31}P$ n.m.r. spectroscopy and by their inherent viscosity. Thermo-oxidative stability and flammability of the polymers were evaluated by thermogravimetry and limiting oxygen index values respectively.

**(Keywords: polyphosphoramide esters; flame retardation; phenyl phosphoric triamide; aromatic diols; infra-red spectroscopy; nuclear magnetic resonance spectroscopy; thermogravimetry; limiting oxygen index)**

## INTRODUCTION

Phosphorus-containing polymers, with predominantly aromatic structures, generally possess useful properties such as high chemical and thermo-oxidative stability and low flammability. The use of phosphorus-containing polyamides as fire retardant materials has received limited attention in comparison to their polyester counterparts[1–5]. A successful study of polyphosphate esters in this laboratory led us to undertake a renewed look into this class of polymers[6–13]. Literature on the phosphoramide-bearing polymers is scarce[14–17]. The present work deals with the syntheses and characterization of several hitherto unreported polyphosphoramide esters from *N*,*N*′-bis(*p*-chloroformylphenyl)*N*″-phenyl phosphoric triamide with different aromatic diols. The polymers were characterized by i.r., $^1H$, $^{13}C$ and $^{31}P$ n.m.r. spectroscopy. The inherent viscosity, thermal and flammability measurements were made by viscometry, thermogravimetry (t.g.) and limiting oxygen index (LOI) respectively.

## EXPERIMENTAL

### *Materials*

Benzene and tetrahydrofuran (THF) were purified as reported elsewhere[18]. Methanol, nitrobenzene, $POCl_3$ and aniline were distilled before use. Hydroquinone, biphenol, phenolphthalein, *p*-aminobenzoic acid (BDH) and bisphenol-A (Aldrich) were used as such. Bisphenol-S, tetrabromo-bisphenol-A and tetrabromo-phenolphthalein were prepared by the reported procedure[19,20].

### N,N′-*bis*(p-*chloroformylphenyl*)N″-*phenyl phosphoric triamide*

*N*-phenyl phosphoramidic dichloride was synthesized by a reported procedure[21]. *N*,*N*′-bis(*p*-carboxyphenyl)-*N*″-phenyl phosphoric triamide (CPPT) was obtained as follows. To a stirred solution of *N*-phenyl phosphoramide dichloride (1 mol), in dry THF at 0°C under $N_2$ atmosphere, the solution of *p*-aminobenzoic acid (2 mol) in dry THF was added dropwise over a period of 1 h. The stirring was maintained at this temperature for another 3 h, then the mixture was gradually allowed to attain room temperature. The precipitated product was filtered, washed with THF and dried *in vacuo*. The diacid, on treatment with thionyl chloride, gave the title compound (m.p. 221°C). I.r. (KBr): 1740 $cm^{-1}$ (-CO-), 1320 $cm^{-1}$ P-N-C(Ar).

### *Polymerization*

The polyphosphoramide esters were prepared by solution polycondensation. A typical procedure for the preparation of polymer *I* is described. CPPT (5 mmol) was dissolved in 20 ml nitrobenzene and the solution was maintained at 100°C with stirring. Hydroquinone (5 mmol) was added to the stirring solution and the reaction was carried out at that temperature for 12 h. The mixture was cooled and poured into a large quantity of methanol, the precipitated polymer was filtered and washed with water, acetone and hot methanol, followed by drying *in vacuo* at 80°C. The remaining polymers (*II*–*VII*) were prepared in a similar manner. The polymer yield was 30–50%. All the polymers are coloured and powdery, soluble under hot conditions in dimethylformamide (DMF), dimethylacetamide (DMAc), dimethylsulphoxide (DMSO) and *N*-methylpyrrolidone (NMP) but insoluble in common organic solvents such as chloroform and acetone.

### *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 in DMSO-$d_6$ using tetramethylsilane (TMS) as internal standard. $^{31}P$ n.m.r. spectra were recorded on a Brucker FT 200 spectrometer in DMSO-$d_6$ under broad band $^1H$ decoupling

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conditions. $D_2O$ and phosphoric acid (85%) were used as the external lock and external standard, respectively. The inherent viscosities of the polymers in DMF/$CF_3COOH$ (4:1 v/v) solutions (0.1 g $dl^{-1}$) were measured using an Ubbelohde viscometer at 30°C.

### *Thermal and flammability studies*

The t.g. studies were carried out using a Mettler TA 3000 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 an apparatus produced in accordance with standard ASTM-D 2863-70 and the measurements were made using a modified procedure[8].

## RESULTS AND DISCUSSION

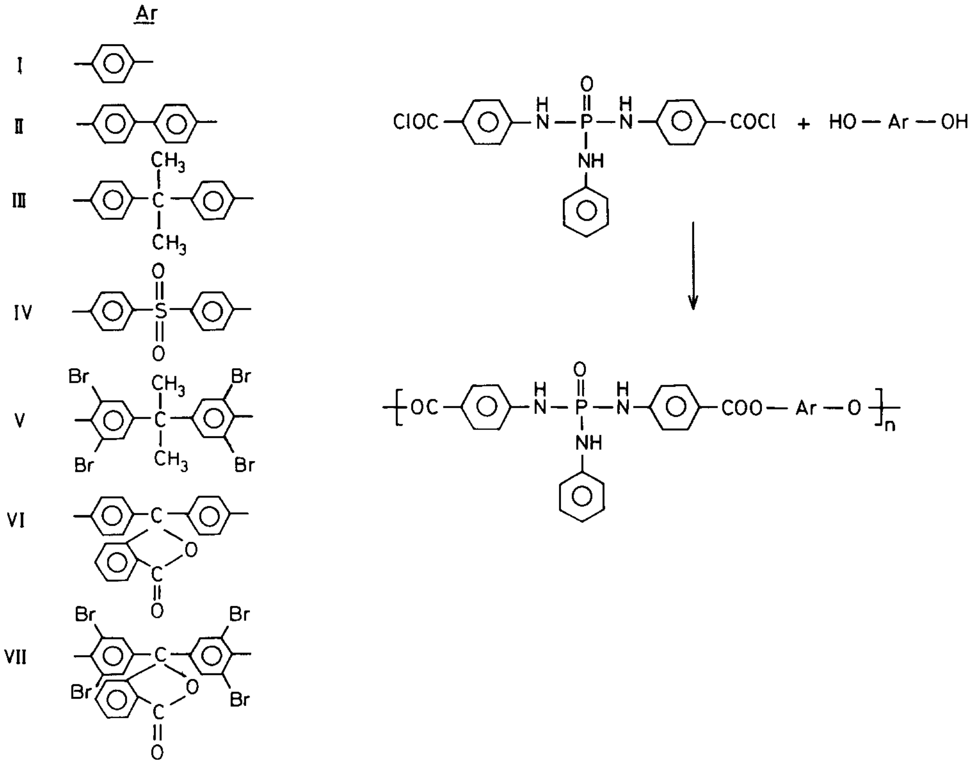
All polyphosphoramide esters, shown in the *Scheme 1*, were synthesized by solution polycondensation of CPPT with different aromatic diols. The reaction was carried out at refluxing temperature of nitrobenzene for 12 h and yielded a black, rigid, insoluble product. A prolonged reaction period (> 12 h) at 100°C also yielded insoluble, coloured products, which may be due to further molecular weight build-up. The polymerization reaction, carried out at 100°C, was terminated after 12 h in order to gain information on the structure of these polymers. The molecular weights of the polymers were reasonably high, as indicated by their inherent viscosities (*Table 1*). All the polymers were unaffected by aqueous media up to pH 10, at room temperature.

The polyphosphoramide esters were characterized by i.r. spectra. The absorption bands near 3280, 1300 $cm^{-1}$ corresponded to –NH– and P=O stretchings, respectively. All the polymers showed absorption bands around 1320, 1180 and 960 $cm^{-1}$ due to P–N–C(Ar) and P–O–C(Ar) stretchings[22,23]. The other absorption bands, dovetailed to aromatic or functional groups present in the polymers, varied with the structure to support the formation of polyphosphoramide esters. The representative $^1H$ n.m.r. spectrum of polymer *VI* is shown

**Table 1** Physical, thermal and flammability behaviour of polymers

| Polymer | Colour | Yield (%) | Inherent viscosity[a] (dl $g^{-1}$) | Temperature at 5% weight loss in t.g. (°C) | Char yield at 800°C (%) | LOI[b] (%) |
|---|---|---|---|---|---|---|
| *I* | Deep yellow | 35 | 0.31 | 400 | 60 | 52 |
| *II* | Pale yellow | 52 | –[c] | 450 | 78 | 54 |
| *III* | Yellow | 46 | 0.29 | 300 | 50 | 48 |
| *IV* | Brown | 48 | 0.41 | 320 | 62 | 51 |
| *V* | Deep yellow | 42 | 0.35 | 320 | 71 | 50 |
| *VI* | Deep yellow | 35 | 0.54 | 410 | 71 | 53 |
| *VII* | Brown | 32 | –[c] | 450 | 72 | 55 |

[a] Measured at a concentration of 0.1 g $dl^{-1}$ in DMF/$CF_3COOH$ (4:1 by volume) at 30°C
[b] Error ±1%
[c] Insoluble



**Scheme 1** Synthesis of polyphosphoramide esters

in *Figure 1*. The aromatic protons resonate in the region 6.2δ to 8.4δ; due to high aromaticity in the polymer backbone, the proton signals intermix and appear as a broad multiplet. The -NH- protons resonate downfield in the region 10.4δ. Typical $^{13}C$ n.m.r. spectra of polymers *III* and *VI* are shown in *Figure 2*. From the reported[24] $^{13}C$ n.m.r. spectra of aryl phosphoramidates, we have assigned the chemical shifts[25–27] which are indicated in the spectra. Clear distinction is observed between *ortho* and *meta* aromatic carbons. However, the *para* carbon was identified by its lower signal intensity. The resonances corresponding to C-10 (polymer III, *Figure 3a*) at 42.5, C-15 and C-16 (polymer VI, *Figure 3b*) around 126.4 and 125.5 merge with the solvent peak and other carbon resonances, respectively.

$^{31}P$ n.m.r. spectra of polymers showed negative chemical shifts which were observed in the region −4δ to −8δ as two doublets. The splitting of the phosphorus resonances by hydrogen in the P–N–H bond probably indicates the covalent character in the bond. The splitting

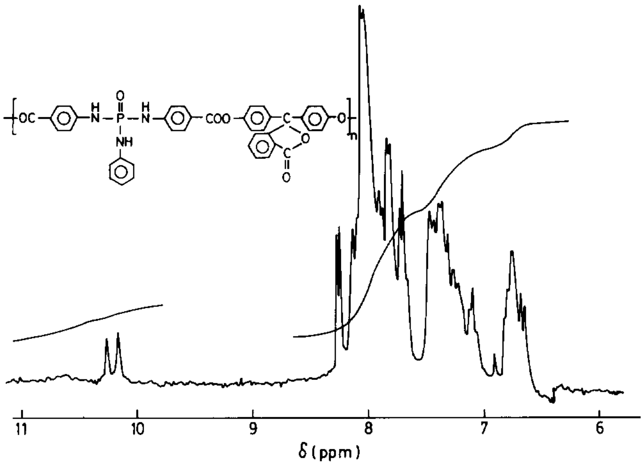


**Figure 1** $^{1}H$ n.m.r. spectrum of polymer *VI*

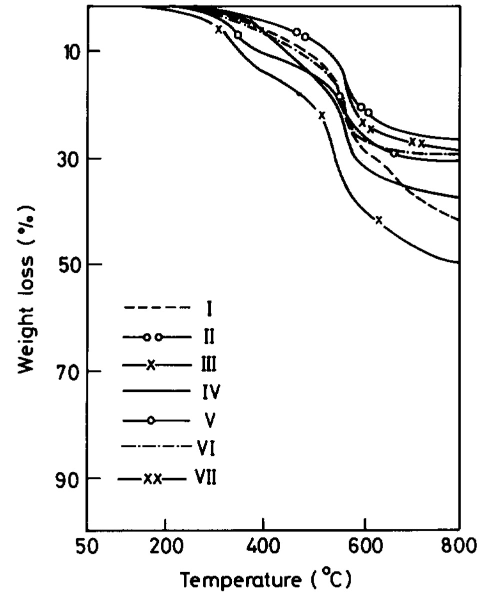


**Figure 3** Thermogravimetric traces of polymers *I–VII*

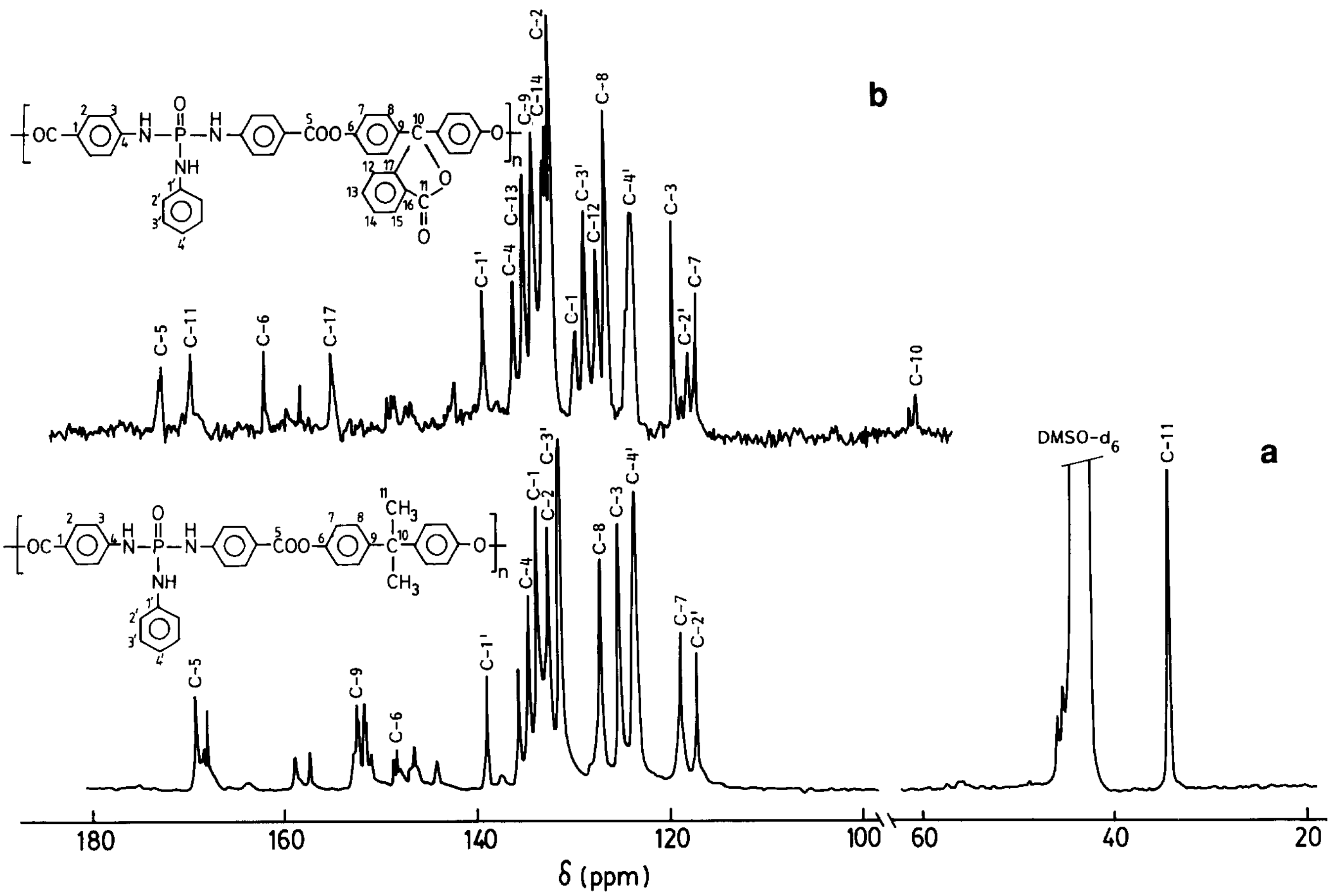


**Figure 2** Broad band decoupled $^{13}C$ n.m.r. spectra of (a) polymer *III* and (b) polymer *VI*

**Table 2** Comparison of data for phosphoramide esters and phosphate esters

| Polymer | LOI (%) | $T^{1/2a}$ | Char yield (%) | Phosphorus content (%) |
|---|---|---|---|---|
| Phosphoramide esters | 48–55 | >800 | 52–78 | 3–6 |
| Phosphate esters | 31–50 | 390–510 | 11–40 | 4–12 |

$^a T^{1/2}$ = temperature (°C) for 50% weight loss in t.g.

may also arise due to the electrical quadrupole moment of the interconnecting nitrogen nucleus[28].

The thermal and thermo-oxidative stability of polymers were ascertained by t.g. thermograms. *Figure 3* represents typical t.g. traces of all the polymers. The initial decomposition (5% weight loss) and the maximum polymer decomposition at 800°C, corresponding to the char yield in air, are summarized in *Table 1*. The results show that the polymers are stable in air up to 300–450°C and start degrading thereafter. Polymer *III* exhibited a significantly lower thermal stability than the others, due to the thermally sensitive aliphatic segment. The higher thermal stability of polymers *II*, *VI* and *VII* may be due to their rigid structures. All the polymers, however, afforded higher char yield irrespective of their structures. This may be attributed to the phosphoramide linkages in the polymer backbone.

The flame retardant properties of these polymers were compared from their LOI values (*Table 1*). The present class of polymers is distinguished by its low flammability, as demonstrated by higher LOI values. Let us now consider the flame retardation mechanism, in view of the significant structural difference of these polymers from the conventional polyphosphate polymers[6–13]. It has been shown in phosphate polymers[8] that the flame retardation, as displayed by LOI, is related to the phosphorus content and thermal stability of the polymers. To compare the flammability data of the present polymers with polyphosphates requires data on polyester–ester counterparts. Since such studies are not available, we have compared the results on similar phosphate polymers from our laboratory[6–13]. The thermal stability, phosphorus content and LOI data for aromatic polyphosphates[6–13] are collated in *Table 2*. The LOI, thermal stability data and char yield are higher in phosphoramide esters, showing that these polymers have superior non-flammable behaviour.

It is well known that thermal stability alone cannot bring about flame retardation in polymers. It has been shown that the phosphorus-containing polyamides have a higher degree of fire resistance than the corresponding common polyamides[29]. Obviously, combination of nitrogen and phosphorus is necessary for imparting fire resistance in polyamides. We cannot comment conclusively on the nitrogen–phosphorus synergism in phosphoramide esters; although it prevails in cellulosic polymers, not much is known regarding other polymers. The phosphorus–halogen and $Sb_2O_3$–halogen synergism, on the other hand, are well documented[30]. The conventional, so-called exclusive 'char formation mechanism' in organic polyphosphates has been debated[8,13] from the non-existence of any correlation between the char and LOI and the emergence of phosphorus-containing fragments[13] into the gas phase. On comparing the char proportion at 700°C, a wide difference is noticed in the char yield of these polymers, and they follow the same trend in LOI and thermal stability. The phosphorus content in phosphate esters is higher than in phosphoramide esters; if phosphorus content had prevailed over thermal stability, greater fire retardant properties would have been observed in phosphate esters than in phosphoramide esters, but the opposite trend was found. This prompts us to suggest that thermal stability is the dominating factor in curtailing the flammability of these polymers. The char yield is also higher in phosphoramide esters which is concordant with the suggestion of Lin and Pearce[31] that increase in the char yield promotes reduction of the polymer flammability. Considering the overall scenario, it may be stressed that thermal stability and char yield are both important in imparting flame retardant properties to polyphosphoramide esters.

## CONCLUSION

Phosphoramide-containing copolyphosphoramide esters have been synthesized and characterized spectroscopically. Although rigid insoluble polymers can be prepared by solution polycondensation under extreme conditions, we optimized the reaction to gain structural information. The thermal and flammability data indicate that this class of polymers can be used for potent heat resistant and fire retardant applications.

## ACKNOWLEDGEMENT

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