A novel approach to structure–flammability correlation in polyphosphate esters

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The relationship between the structure and flammability of a number of polyphosphate esters has been examined. The conventional correlation of char residue with limiting oxygen index was found to be unproductive in these polymers, giving insight into the importance of gas-phase reactions in addition to condensed-phase reactions in determining their flammability. A novel approach was sought in understanding the structure–flammability relationships of these polymers relating thermal stability, phosphorus content and limiting oxygen index. An empirical relationship has been derived amongst these three parameters.

(Keywords: polyphosphate esters; flammability; limiting oxygen index; phosphorus content; thermal stability)

INTRODUCTION

The importance of structure in deciding the flammability of polymers has been recognized more in recent years[1–4]. Knowledge of such a relationship is helpful in understanding the mechanism of flame retardancy, in developing intrinsically flame-retardant polymers and in predicting the flammability of polymers. Of the limited number of studies available in this direction[5–29], the most systematic one is by Van Krevelen, who has obtained an empirical relationship between flammability as measured by limiting oxygen index (*LOI*) and char residue, studied in various aliphatic, aromatic and heterocyclic polymers. The halogen-containing polymers did not comply with this relationship owing to their well known gas-phase flame-retardant mechanism. It is surprising that phosphorus-containing polymers, which form one of the most efficient classes of flame-retardant polymers, were not considered by Van Krevelen; especially so, realizing the fact that the phosphorus compounds are known for their flame-retardant action through char formation[1,3]. The present investigation aims at understanding the structure–flammability relationship in phosphorus-containing polymers. We have chosen polyphosphate esters for study, where the literature is mostly patented[23,30–33], and such attempts are either non-existent or surreptitious. All the polymers employed were synthesized during the present investigation and many of them are new. The detailed spectroscopic studies are described elsewhere[34,35]. The correlation of char residue with flammability was found to be unproductive; but an excellent correlation relating thermal stability, phosphorus content and *LOI* has been derived empirically.

EXPERIMENTAL

The various polyphosphates (*Figure 1*) were synthesized by solution polycondensation of bisphenols with aryl or alkyl phosphorodichloridates. A typical procedure for the synthesis of polymer I is as follows. Bisphenol A (11.4 g) was taken in dry toluene (30 ml) and refluxed with phenyl phosphorodichloridate (8.4 ml) for 48 h with constant stirring. The polymer was then separated and refluxed with methanol (10 ml) for another 3 h to convert the P–Cl groups to P–O–CH_3. The polymer was purified by reprecipitation using excess methanol. The polymers II–V were prepared according to the same procedure. For the preparation of polymers VI–XI and XII–XIV, the solvents used were benzene and xylene, respectively. The polymer XV was prepared by converting tetrabromobisphenol A into its sodium derivative and then refluxing with the phosphorodichloridate. The polymers were either thick viscous liquids or powders and were soluble

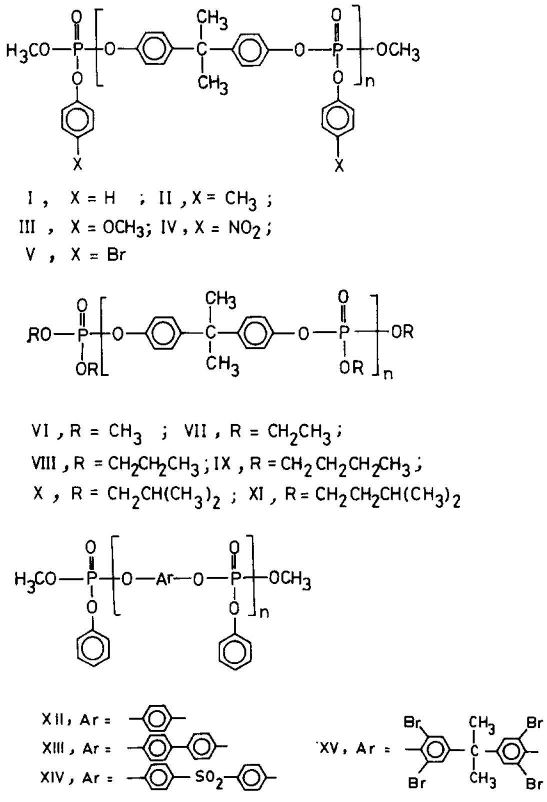

Figure 1 Structure of polyphosphates I–XV

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Table 1 Thermal stability, phosphorus content and oxygen index data of polymers

	Temperature (°C) corresponding to						
Polymer[a]	1% weight loss	inception of fast degradation	50% weight loss ($T_{1/2}$)	Char at 700°C (%)	Modified oxygen index, $(OI)_m$ (%)	Relative thermal stability, *TS* (%)	Phosphorus content, *PC* (%)
I	290	300	450	19	31.2	45	8.4
II	200	220	330	11	27.2	33	8.1
III	290	390	470	23	30.2	47	7.8
IV	260	270	530	28	30.7	53	7.5
V	270	360	400	25	36.9	40	7.0
VI	180	230	310	14	29.7	31	10.2
VII	180	230	300	12	29.7	30	9.7
VIII	190	230	320	20	27.8	32	9.3
IX	210	220	310	21	27.9	31	9.0
X	180	210	300	13	27.2	30	9.0
XI	170	220	330	20	27.9	33	8.6
XII	250	270	510	32	40.0	51	12.5
XIII	270	450	720	50	36.4	72	9.6
XIV	260	280	510	40	35.0	51	8.0
XV	270	340	390	25	50.0	39	4.5

[a] See *Figure 1*

in chloroform, acetone, dimethyl sulphoxide, etc. All the polyphosphates were characterized by i.r. and ^1H, ^{13}C and ^{31}P n.m.r. spectroscopy[34,35], and correspond to the structure given in *Figure 1*.

Thermogravimetric analysis (t.g.a.) was carried out on a Sinku-Riko TGD-500 model at a heating rate of 20°C min^{-1} in an argon atmosphere with sample weights of 3–5 mg. The oxygen index values were measured using the *LOI* apparatus constructed according to the specifications of ASTM D2863-70 standard. The *LOI* method used for self-supporting samples has been modified as described below to accommodate the viscous or powdery samples and the values are denoted $(OI)_m$. The measurement was carried out as follows. About 1 g of the polymer sample was placed in a glass cup (diameter 20 mm, height 10 mm) fitted to the specimen holder. An external flame of 20 mm length was maintained in contact, for 10 s, with the polymer. The $(OI)_m$ was taken as the minimum percentage of oxygen required in a nitrogen–oxygen atmosphere, surrounding the sample, to maintain its combustion for at least 30 s after ignition. The $(OI)_m$ was taken as the average of five experiments each. The experimental error was ±1%.

Pyrolysis gas chromatographic studies were carried out on a Shimadzu GC-4C gas chromatograph with attached PYR-1A pyrolyser using columns packed with 5% OV-17 coated on 80–100 mesh silanized Chromosorb. Nitrogen (35 ml min^{-1}) was used as the carrier gas. The samples were pyrolysed at 300 and 500°C and chromatographed on the column heated at 10°C min^{-1} from 60 to 300°C. The products were identified by comparison with retention times of pure compounds.

RESULTS AND DISCUSSION

The char residue or char-forming tendency of a polymer has been found to be a direct consequence of structure. In polymers in which condensed-phase reactions control flammability, the char residue has been found to be linearly related to their flammability[5–28]. Accordingly, an understanding of the structure–flammability relationship in polyphosphates will reveal their mechanism of flame-retardant action, viz. condensed phase, gas phase or a combination of both. With this in view, the char residue and $(OI)_m$ values of the various polymers were determined and their relationship examined.

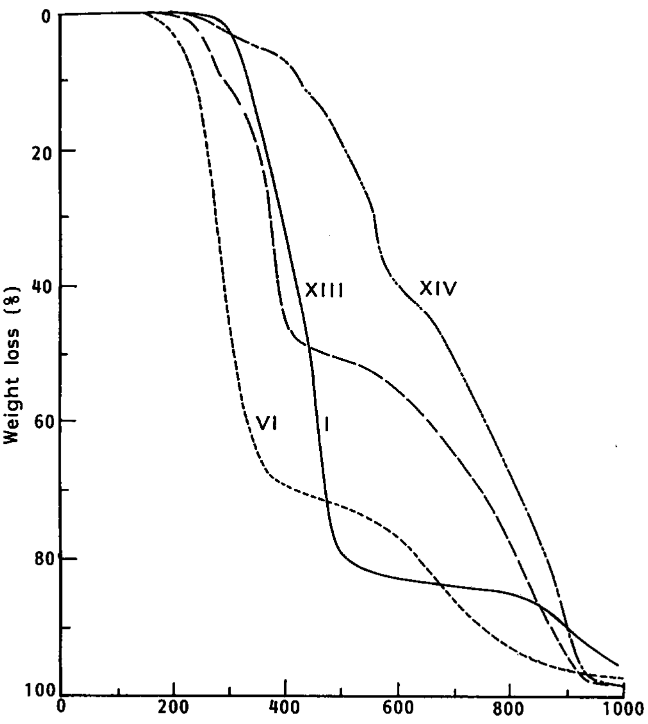

Figure 2 T.g. thermograms of polymers I, VI, XIII and XIV

The $(OI)_m$ for various polymers are given in *Table 1*. The char residue was determined by thermogravimetry and a few representative t.g. thermograms are shown in *Figure 2*. All polymers showed a two-step degradation, though the temperature corresponding to 1% or 50% weight loss varied depending on the structure (*Table 1*). It could be inferred from pyrolysis gas chromatographic (p.g.c.) studies of polymers I and VI that the first step corresponds to the formation of various phenols and phosphates with some amount of char that subsequently carbonizes in the second step. The amount of char residue has been taken as the percentage of char remaining, at a

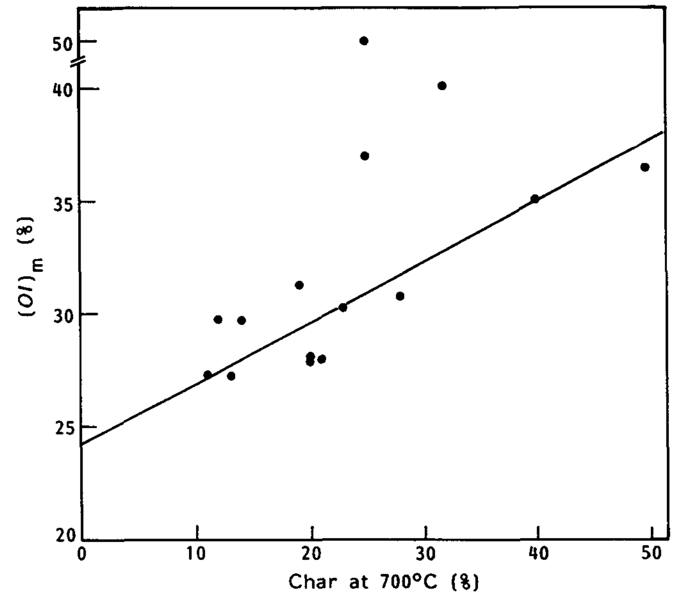

Figure 3 $(OI)_m$ as a function of char percentage for polymers I–IV and VI–XIV

fixed temperature in the t.g. thermogram. A temperature of 700°C was chosen since it falls well within the limits of the carbonization step (the second step) in all the polymers and the differences in the char residue remaining for various polymers were sufficient for a good comparison (*Table 1*). The char percentages, at 700°C, are plotted against $(OI)_m$ values in *Figure 3*. The halogen-containing polymers were found to behave differently from others (*Figure 3*), which might be due to their gas-phase mechanism[6]. Apart from the halogen-containing polymers, the largest deviation is shown by polymer XII. It may be pointed out that XII has a much higher phosphorus content compared to all other polyphosphates. However, even in the case of the rest of the polymers, the amount of char remaining did not have a significant correspondence with their flammability. A linear relationship could hardly be achieved, the correlation coefficient being only 0.86. This gives an indication that condensed-phase reactions are not the only criteria determining the flammability of polyphosphates; it may be possible that gas-phase reactions are also important in these polymers. Evidence obtained through p.g.c. studies justifies such a conclusion. Phosphate compounds like diphenylmethyl phosphate, dimethylphenyl phosphate, etc., were found to be present in the p.g.c. products. The fact that these types of phosphate compounds are effective flame inhibitors[36,37] supports the possibility of a gas-phase fire-retardant mechanism in polyphosphates.

Upon gathering that a combination of both condensed-phase and gas-phase mechanisms might be operative in polyphosphates, a different approach to the structure–flammability relationship in polyphosphates was envisaged. Studies on phosphorus-containing polymers have shown that the flammability of these polymers decreases with increase in phosphorus content[23–29]. A careful analysis of the thermogravimetric data of the polymers (*Table 1*) also suggests that the thermal stability of the polymers is a consequence of the structure. It can thus be said that thermal stability and phosphorus content are two independent variables that can be considered as controlling the flammability of polyphosphates. Phosphorus content (*PC*) has been taken as the percentage of phosphorus per repeat unit. The temperature corresponding to 50% weight loss ($T_{1/2}$) has been found to be a characteristic measure of thermal stability[38]. An examination of the $(OI)_m$, *PC* and $T_{1/2}$ values (*Table 1*) shows that the difference in the $(OI)_m$ values of the various polymers could be easily explained considering their phosphorus content and thermal stability. For instance, polymers XII and XIII, which have higher *PC* and $T_{1/2}$, exhibit higher values of $(OI)_m$. Also, though the $T_{1/2}$ of XII is less than that of XIII and XIV, it has the highest $(OI)_m$ value owing to its very high phosphorus content. Similar effects can be seen on comparing the flammability of polymers I–V with that of VI–XI. However, the $(OI)_m$ values of V and XV are very high, understandably due to the presence of halogen in them. Hence, these two polymers have not been considered in the new approach.

With this preliminary observation in mind, we have ventured to derive a relationship between $T_{1/2}$, *PC* and $(OI)_m$ in these polymers. Since the $(OI)_m$ and *PC* values were quantified in percentages, the $T_{1/2}$ data have also to be converted to a percentage scale. This was carried out by assuming that a polymer undergoing 50% weight loss in a dynamic t.g. run in an inert atmosphere at 1000°C has a 100% thermal stability while a polymer having 50% weight loss at 0°C has a zero percentage stability. The upper limit has been chosen based on the fact that, barring some exceptions[39,40], thermally stable polymers undergo around 50% weight loss in the temperature range 900–1000°C[41–44]. In the case of the lower limit, all the polymers follow this limit since they are stable at room temperature. It may be pointed out that this indexing was done only to compare the thermal stability of the various polyphosphates. The percentage thermal stability (*TS*) of the polyphosphates has thus been calculated as:

$$\text{percentage stability} = 100 - \text{percentage instability}$$

$$TS = 100 - \frac{1000 - T_{1/2}}{1000} \times 100 = \frac{T_{1/2}}{10} \tag{1}$$

The percentage stabilities obtained for various polymers are given in *Table 1*.

The functional dependence of $(OI)_m$ on *TS* and *PC* can be written as:

$$(OI)_m = K(TS)^{\alpha}(PC)^{\beta} \tag{2}$$

where α and β are exponents and K is a constant. Linear regression analysis of equation (2) was carried out to find α, β and K. From (2) we get:

$$\ln(OI)_m = \alpha \ln(TS) + \beta \ln(PC) + \ln K \tag{3}$$

or

$$Z = \alpha X + \beta Y + \gamma \tag{4}$$

where $Z = \ln(OI)_m$, $X = \ln(TS)$, $Y = \ln(PC)$ and $\gamma = \ln K$. Equations (5), (6) and (7) are obtained from equation (4):

$$\sum Z_i = \alpha \sum X_i + \beta \sum Y_i + \gamma N \tag{5}$$

$$\sum Z_i X_i = \alpha \sum X_i^2 + \beta \sum X_i Y_i + \gamma \sum X_i \tag{6}$$

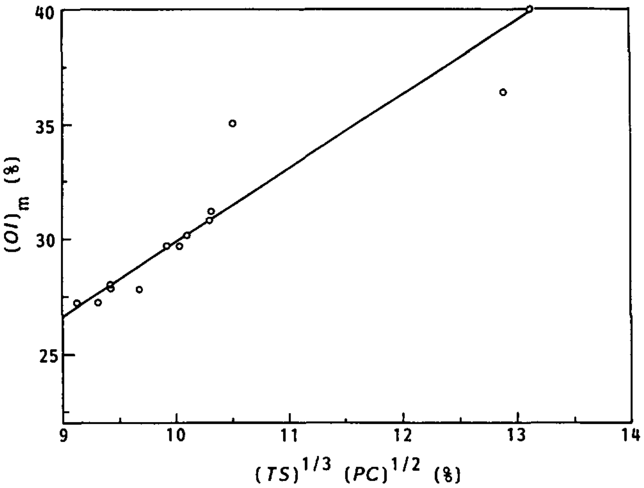

Figure 4 $(OI)_m$ as a function of $(TS)^{1/3}(PC)^{1/2}$ for polymers I–IV and VI–XII

$$\sum Z_iY_i=\alpha\sum X_iY_i+\beta\sum Y_i^2+\gamma\sum Y_i \qquad (7)$$

Equations (5), (6) and (7) are solved to obtain the values of α, β and K as 0.33, 0.5 and 3.0, respectively. Thus the $(OI)_m$ in (2) can now be written as:

$$(OI)_m=3.0(TS)^{1/3}(PC)^{1/2} \qquad (8)$$

A plot of $(OI)_m$ against $(TS)^{1/3}(PC)^{1/2}$ gives a good linear relationship (*Figure 4*) with a correlation coefficient of 0.95. It may be noted that the sulphone (XIV) and biphenol (XV) polymers deviate slightly from the straight line. The deviation of sulphone-based polymer could be due to the presence of sulphur, which is also a known flame-retardant element[45]. The reason for the deviation of the biphenol-based polymer is not clear. It can be seen that this polymer is highly stable compared to the others (*Table 1*). If the sulphone and biphenol polymers are excluded from the plot, it is seen that the correlation coefficient improves to 0.99 (*Figure 4*). This concludes that the flammability of a polyphosphate is directly proportional to the cube root of its thermal stability and square root of its phosphorus content.

This excellent empirical relation offers a new approach to structure–flammability correlation in polyphosphates, because the *TS* and *PC* are direct consequences of the structure itself. It may be noted that the possibility of this kind of a relationship could be tested in other phosphorus-containing polymers as well; however, only by realizing the significance of the power factors of *TS* and *PC*.

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