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# Structure Flammability Relationships of Phosphorus Containing Polystyrene Samples (I)

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## SUMMARY

Phosphonated polystyrene flammability is discussed in relation to their structure. It is shown that the oxygen Index of phosphonated polystyrenes depends mainly on the position of the phosphorus atoms on the backbone of the polymer and not on the absolute phosphorus content.

## INTRODUCTION

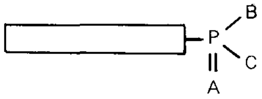
Investigations of structure-flammability relationships of organic polymers have attracted considerable interest over the past years, and different reviews were devoted to this subject (1-3). In general, a flame retardant unit incorporated into the polymer backbone is more effective than in a mixture with the polymer (1). However, a comparison of the degree of flame resistance, between polymers carrying the same flame retardant unit, attached to various positions of the polymer backbone is not well known.

The aim of this study is to investigate the difference in flame resistance between polystyrenes carrying phosphorus atoms fixed at various positions of the macromolecular backbone through a carbon-phosphorus bond.

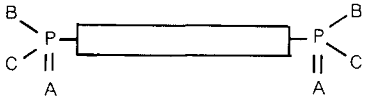
This paper concerns the study of structure-flammability relationships of the following two groups (I, II) of phosphonated polystyrenes. In the second part of this publication we will investigate similar relationships for another two groups of phosphonated polystyrenes.

## GROUP I

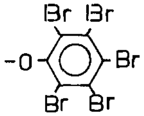
This group encloses polystyrenes carring phosphorus atoms bonded to one or both ends of the macromolecular chain



and



A = O,S

B, C = - Cl, - OMe, - OEt, - OH, - Me, - Ø, - $NMe_2$, - OØ, -O

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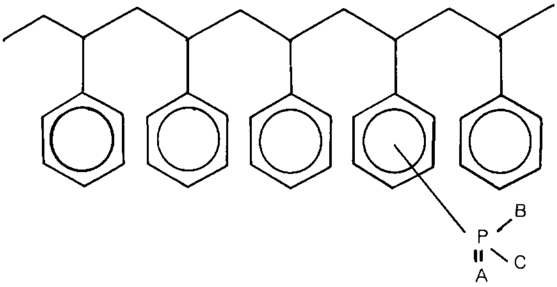
## GROUP II

The group II contains polystyrenes carrying phosphorus atoms bonded directly to the aromatic ring, and distributed statistically along the chain



A = O,S
B,C = - Cl, - OMe, - OEt, - OH

The flame retardancy properties of these groups of phosphonated polymers have been investigated using a modified oxygen index method $(OI)_m$. This method is defined as the oxygen percentage in a gas mixture of oxygen and nitrogen, just necessary to maintain in combustion, at least for 30 seconds, the polymer sample. We have used this modified technique of oxygen index in order to avoid dripping of the sample during combustion, which, in the case of the polystyrene, could lead to erroneous conclusions on the fire retardant properties (4).

With this testing method, it is possible to quantify the behaviour of the polymer towards flaming and it is also possible to compare the behaviour of homologous compounds, and to obtain relative values and a flammability scale.

## EXPERIMENTAL

### Synthesis of phosphonated polystyrenes

The phosphonated polystyrenes of group I, were prepared as described in ref. (5).

The multiphosphonated polystyrenes of group II were prepared according to the technique used in ref. (6).

### Determination of modified Oxygen Index $(OI)_m$

400 - 500 mg of polymer powder were placed in a glass cup (d = 25,6 mm, h = 4,5 mm) whose support is fitted to the sample holder of a stanton Redcroft Instrument.

An external flame is maintained in contact during 10 seconds with the powder of the polymer. The $(OI)_m$ was taken as the concentration of oxygen in the atmosphere ($O_2/N_2$) surrounding the sample just necessary to maintain its combustion for at least 30 seconds after ignition. The flow rate of the gas mixture ($O_2/N_2$) in the column is equal to 17 l/min. The temperature of the polymer's powder before any contact with the flame, is 20 °C. The precision of this measurement is ± 5 %.

Pure radical polystyrene possesses $(OI)_m \simeq 19$. For the pure polystyrene prepared by anionic polymerization, we found : $(OI)_m \simeq 26$.

TABLE 1

$(OI)_m$ of ω or α,ω phosphonated polystyrenes

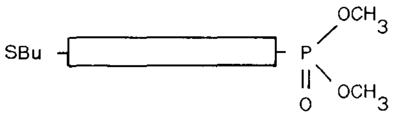
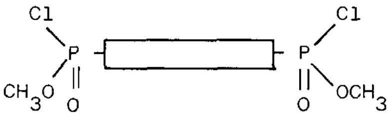
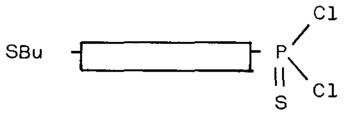
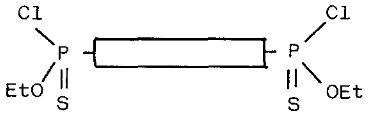
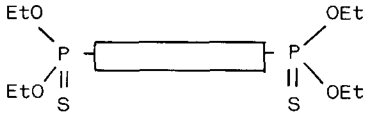
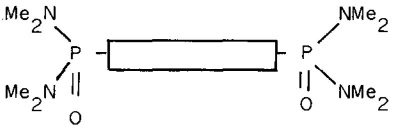
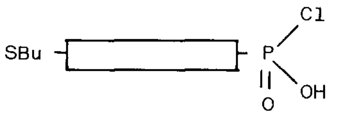
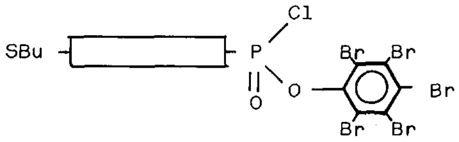
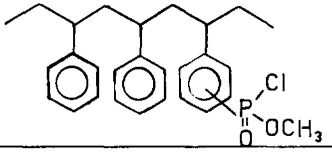
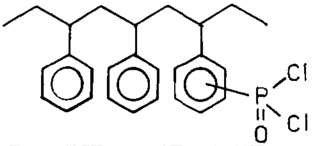
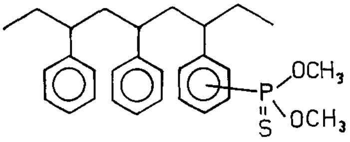
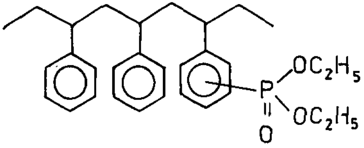
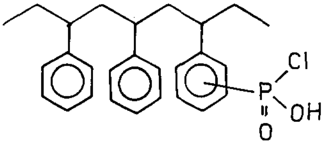
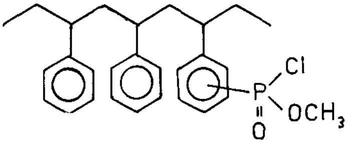
| Ref | Structure of the polymer | $\overline{M}_n$ (GPC) | % P (w/w) | % Cl (w/w) | $(OI)_m$ |
|---|---|---|---|---|---|
| 344 |  | 6,200 | 0.5 | 0 | 45 |
| 131 |  | 5,800 | 1.0 | 1.17 | 61 |
| 211 |  | 3,400 | 0.91 | 2.08 | 62 |
| 168 |  | 4,400 | 1.4 | 1.58 | 59 |
| 206 |  | 3,800 | 1.6 | 0 | 50 |
| 139 |  | 10,000 | 0.68 | 0 | 42 |
| 342 |  | 6,500 | 0.47 | 0.52 | 70 |
| 33B |  | 2,200 | 1.69 | 1.85 | 56 |

TABLE 2

Modified Oxygen Indexes $(OI)_m$, of polystyrenes carrying phosphorus atoms directly bonded to the aromatic ring (group II).

| Ref | Structure of the polymer | $\overline{Mn}$ (GPC) | % P (w/w) | % Cl (w/w) | $(OI)_m$ |
|---|---|---|---|---|---|
| 16 |  | 8,000 | 2.29 | 2.28 | 27 |
| 2 |  | 8,000 | 3.68 | 7.16 | 27 |
| 186 |  | 8,000 | 8.5 | 0 | 28 |
| 191 |  | 8,000 | 15.41 | 0 | 27 |
| 156 |  | 20,000 | 6.8 | 7.8 | 35 |
| 1 |  | 8,000 | 3.88 | 4.86 | 29 |

## RESULTS AND DISCUSSION

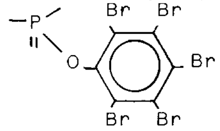
### Comparison of $(OI)_m$ of pure phosphonated polystyrenes (group I to II)

### 1 - Flame retardant properties of polystyrenes of group I

Table 1 lists $(OI)_m$ data for various ω and α,ω phosphonated polystyrenes. Qualitatively, from these data it is shown that.

- All polystyrenes carrying phosphonated end groups possess high $(OI)_m$. $[40 < (OI)_m < 70]$

- All end-phosphonated polystyrenes containing the P-Cl bond exhibit the highest observed values of $(OI)_m$

- An aromatic bromine introduced on the end of a polystyrene chain in a  group has little effect on his flammability (polymer 33 B).

By this investigation one can deduce that the phosphorus atom attached to one or both of the ends of the macromolecular chain of polystyrene exhibit interesting flame retardant properties.

### 2 - Flame retardant properties of polystyrenes of the group II

Table 2 lists data on $(OI)_m$ of multiphosphonated polystyrenes of the group II.

In spite of the high content in phosphorus and chlorine existing in these multifunctional polystyrenes where the phosphorus atom is directly bonded to the nucleus, their $(OI)_m$ is low and very close to those obtained for the unmodified anionic polystyrene.

The data show us that a phosphorus atom on the aromatic ring of polystyrene has only a small effect on his flammability.

## CONCLUSION

The α or α,ω phosphonated polystyrenes exhibit interesting fire retardant properties, in spite of their low content in phosphorus (0,5 - 1,7 %). On the other hand, multiphosphonated polystyrenes carrying higher do not possess improved flame resistance.

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