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# Investigation of some Intrinsic Parameters Influencing the Flammability of $\omega$ or $\alpha, \omega$ Phosphonated Polystyrenes (III)

**A. Chiotis, G. Clouet and J. Brossas**

Centre de Recherches sur les Macromolécules, 6, rue Boussingault,
F-67083 Strasbourg cedex, France

## SUMMARY

This paper concerns the study of some chemical intrinsic parameters governing the fire retardant properties of polystyrenes carrying phosphorus atoms at one or both ends of their macromolecular chain. It is shown that their low flammability, depends on the presence of labile atoms, bonded, either directly to the phosphorus atom or in the α position to the phosphorus atom.

## INTRODUCTION

In a previous work (1) (2), the fire-retardant properties of polystyrenes carrying phosphorus atoms at various places of the macromolecular chain have been described. It was shown that ω or α,ω phosphonated polystyrenes possess high fire-resistance as measured by using a modified Oxygen Index method. However their fire-resistance was shown to depend on some intrinsic characteristics of the polymer.

## EXPERIMENTAL

### Synthesis of phosphonated polymers

ω or α,ω phosphonated polymers were prepared as described in ref. (3).

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

The modified Oxygen Index of the phosphonated polystyrenes is measured according to the technique described in ref. (1).

## RESULTS AND DISCUSSION

### 1. Effect of the presence of P-Cl bonds on the $(OI)_m$ values for the ω or α,ω phosphonated polystyrenes

Table 1 gives the $(OI)_m$ data of some ω or α,ω phosphonated polystyrenes with different end groups. One can observe from this table, that, for the same backbone but with homologous end groups :

$- PO(OR)_2$ (ref 344), $- POCl(OCH_3)$, $- PO(Cl)_2$

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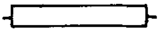
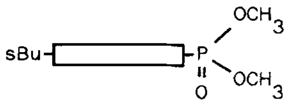
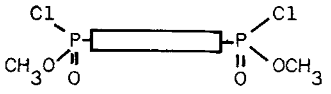
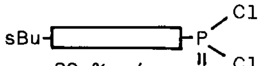
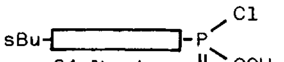
the oxygen index increases when chlorine atom is bonded to the phosphorus atom. This is another proof of the well-known synergism between phosphorus and halogen in the fire-retardancy of polymeric materials(4).

TABLE 1

$(OI)_m$ of ω or α,ω phosphonated polystyrenes with various contents of phosphorus and chlorine.  = Polystyrene

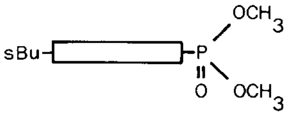
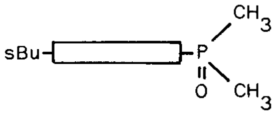
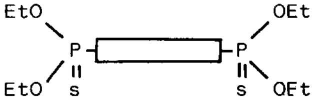
| Ref | Structure of polymer | $\bar{M}_n$ (GPC) | % P (w/w) | % Cl (w/w) | $(OI)_m$ |
|---|---|---|---|---|---|
| 344 |  | 6,200 | 0.5 | 0 | 45 |
| 131 |  | 5,800 | 1.0 | 1.17 | 61 |
| 331 |  39 % w/w<br> 61 % w/w | 2,000 | 1.55 | 2.46 | 65 |

## 2. Effect of the nature of other substituents on the phosphorus atom towards the $(OI)_m$ values of ω or α ,ω phosphonated polystyrenes

The following comparisons reveal that the $(OI)_m$ of ω or α,ω phosphonated polystyrenes depend on the nature of the phosphorus atom substituents. For the same length of the polystyrene chain, we have seen previously the efficient role of the chlorine atom. We have observed that the $(OI)_m$ is linearly correlated with the chlorine/phosphorus ratio and not with the absolute value of the phosphorus content. Then we have investigated the influence of other susbstituents bonded to the phosphorus atom.

Table 2

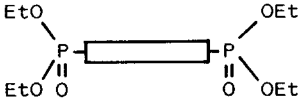
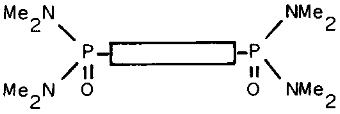
$(OI)_m$ of telechelic polystyrenes with phosphonic and phosphine oxide end groups

| Ref | Structure of polymer | $\bar{M}_n$ (GPC) | % P (w/w) | % Cl (w/w) | $(OI)_m$ |
|---|---|---|---|---|---|
| 344 |  | 6,200 | 0.5 | 0 | 45 |
| 122 |  | 5,500 | 0.4 | 0 | 52 |
| 206 |  | 3,800 | 1.6 | 0 | 50 |

Polystyrenes carring - $P(O)(CH_3)_2$ groups (Ref 122, Table 2) possess higher oxygen index than phosphonic compounds with methoxy group (ref. 344, Table 2). On the other hand, for the same backbone, thiophosphonic group (ref. 206, Table 2) is more resistant to fire than phosphonic group (ref. 344, Table 2).

Table 3

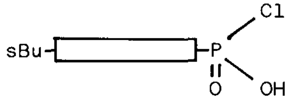
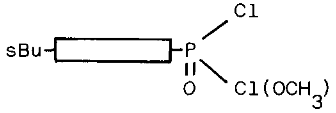
Comparison of $(OI)_m$ between phosphonic and phosphonamide groups

| Ref | Structure of polymer | $\bar{M}_n$ (GPC) | % P (w/w) | % Cl (w/w) | $(OI)_m$ |
|---|---|---|---|---|---|
| 137 |  | 10,000 | 0.62 | 0 | 47 |
| 139 |  | 10,000 | 0.68 | 0 | 42 |

The comparison between the oxygen index values of polystyrenes with phosphonic groups (ref. 137, Table 3) and phosphonamide groups (ref. 139, Table 3) indicate that the synergism which exist, between phosphorus and nitrogen in cellulosic compounds (5) is not observed in the case of the $\alpha,\omega$ phosphonated polystyrenes.

Table 4

Oxygen index comparisons between hydroxychlorophosphonic groups and chlorophosphonic groups

| Ref | Structure of polymer | $\bar{M}_n$ (GPC) | % P (w/w) | % Cl (w/w) | $(OI)_m$ |
|---|---|---|---|---|---|
| 342 |  | 6,500 | 0.47 | 0.52 | 70 |
| 331 |  | 2,000 | 1.55 | 2.46 | 65 |

The hydroxychlorophosphoryl group (ref. 342, Table 4) attached at the end of the polystyrene's chain exhibits the highest index $(OI)_m$ observed in the case of $\omega$ phosphonated polystyrene.

## 3. Effect of the presence of benzylic hydrogen atom at the $\alpha$ position to the phosphorus atom towards the $(OI)_m$ values

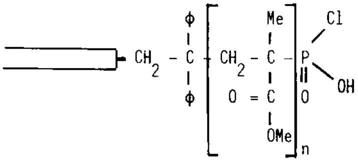
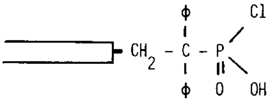
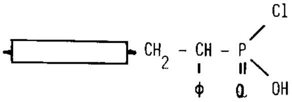
The data (Table 5) reveal that the presence of benzylic hydrogen in the $\alpha$ position to the phosphorus atom induces a significant increase of the oxygen index values $(OI)_m$.

The polymer (ref 135) has been prepared in adding 1,1-diphenylethylene on a living polystyrene. This monomer does not polymerize and so, we decrease the polystyrenic carbanion reactivity. It is possible in this condition to add methylmethacrylate monomer before the halogeno oxyphosphoryl deactivation.

On these polymer chains (ref. 135 and 321) we have no hydrogen in the $\alpha$ position to the phosphorus atom.

Table 5

Influence of the polymer unit in the α position to the phosphonic groups towards the $(OI)_m$ values

| Ref | Nature of phosphonted polystyrene | Structure of the end of the macromolecular chain | $M_n$ (GPC) | % P (w/w) | % Cl (w/w) | $(OI)_m$ |
|---|---|---|---|---|---|---|
| 135 | α,ω |  | 9,050 | 0.67 | 0.76 | 40 |
| 321 | α,ω |  | 7,000 | 0.80 | 1.0 | 44 |
| 342 | ω |  | 6,500 | 0.47 | 0.52 | 70 |

## CONCLUSIONS

ω or αω phosphonated polystyrene are highly effective flame retardant materials . We observe that their flame retardant effectiveness depends strongly on some intrinsic parameters of the polymer, such as :

- the presence of labile chlorine atoms on the phosphorus atom,
- the presence of labile benzylic hydrogen atom at the α position to the phosphorus atom,
- the chemical nature of the other substituents of the phosphorus atom (-Me, -Et, -OH, $-NMe_2$)

It is found that the most effective fire-retardant phosphonate group, when it is bonded at the end of the macromolecular chain of polystyrene, is the -PO(Cl)(OH) group.

## REFERENCES

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