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Structure Flammability Relationships of Phosphorus Containing Polystyrene Samples (II)

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Summary

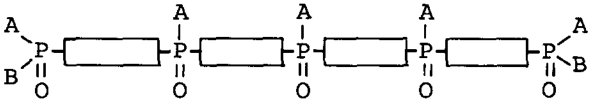
In the first part of this publication the flammability of two groups of phosphonated polystyrenes was discussed in relation to their structure. It was shown that the flammability of these two groups of phosphonated polystyrenes depends mainly on the position of phosphorus atoms on the backbone of the polymer and not on the absolute phosphorus content. This hypothesis is confirmed in this paper by the study of flammability-structure relationships for another two groups of phoshonated polystyrenes.

INTRODUCTION

Previous work (1) indicates that there is a strong dependence between the flammability of phosphonated polystyrenes and the relative position of phosphorus atom on the backbone of the chain. In order to confirm this correlation, we have synthesized and investigated the flammability of the following groups of phosphonated polystyrenes.

Group III

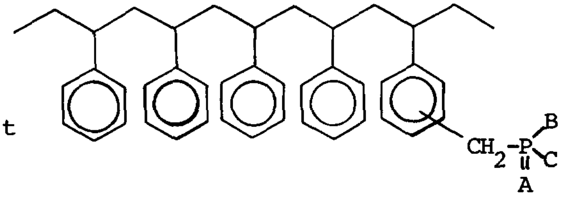
The group contains regular block polystyrenes with phosphorus knuckles:



▭ = polystyrene   A,B = Cl, - OMe $1 \leqslant n \leqslant 20$

Group IV

The fourth group contains polystyrenes carrying phosphorus atoms separated from the aromatic ring by a carbon atom, and distributed statistically along the macromolecular chain.



A = O   B,C = OEt

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The flame retardancy properties of these groups of phosphonated polystyrenes have been investigated using a modified oxygen index method.

EXPERIMENTAL

Synthesis of phosphonated polystyrenes

The polymers of group III were synthesized according to the experimental method described in ref. (2).

The multiphosphonated polystyrenes of group IV were prepared as described in ref. (3).

Determination of modified oxygen index $(OI)_m$

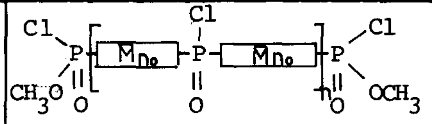
The $(OI)_m$ of phosphonated polystyrene samples was determined as described in ref. (1).

RESULTS AND DISCUSSION

1 - Flame retardant properties of phosphonated polystyrenes of group III

Table 1 collects $(OI)_m$ data for block polystyrenes carrying phosphorus knuckles. As may be seen from these data, all these polymers possess $(OI)_m$ in the range 47 to 49. It may be concluded that incorporation of phosphorus atoms into the aliphatic backbone of polystyrene improves significatively their intrinsic flame resistance.

TABLE 1

Ref.	Structure of the polymer	$\bar{M}_{n,o}$ (GPC)	$\bar{M}_n$ (GPC)	$(OI)_m$
17		3,700	7,600	49
21 PM	"	4,700	10,350	46
21 C	"	4,700	15,200	47
21 F5	"	4,700	36,600	48
21 F4	"	4,700	102,700	48

$(OI)_m$ of phosphonated polystyrenes of group III

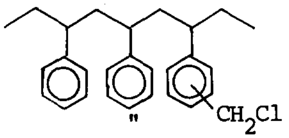
2 - Flame retardant properties of phosphonated polystyrenes group IV

The Michaelis-Arbuzov reaction between styrene/chloromethylated styrene copolymers and trialkylphosphites, used for the synthesis of these multiphosphonated polystyrenes (3) is not quantitative, and in the final phosphonated polymer we have a residual percentage of chlorine.

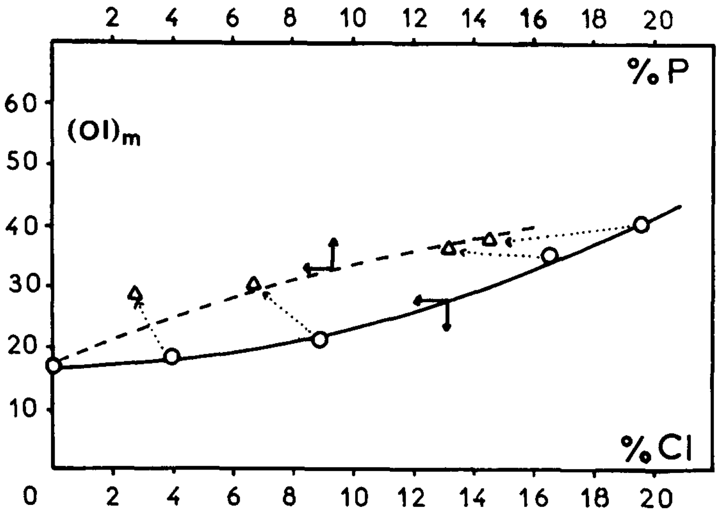
2.1 - $(OI)_m$ of the initial copolymers styrene/chloromethylated polystyrene

As one can see from the results summarized in Table 2, the $(OI)_m$ of copolymers styrene/chloromethylated styrene generally increases with the content in chlorine (see also fig.1).

TABLE 2

Ref.	Structure of polymer	$\bar{M}_n$ (GPC)	% Cl (w/w)	$(OI)_m$
1		47,000	4.29	18
2	"	17,700	9.41	20
3	"	32,000	16.39	35
4	"	35,900	19.4	40

$(OI)_m$ of styrene/chloromethylated styrene copolymers



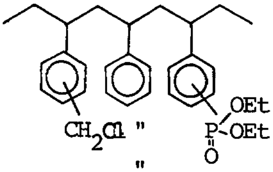
O : Copolymer styrene / chloromethylated styrene
Δ : phosphonated polystyrene

Figure 1. $(OI)_m$ of styrene / chloromethylated copolymers and of multiphosponated polystyrenes of group II

2.2 - $(OI)_m$ of multiphosphonated polystyrenes of the group IV

Table 3 lists data on $(OI)_m$ of multiphosphonated polystyrenes synthesized via an Arbuzov reaction between polymers of Table 2 and triethylphosphite.

TABLE 3

Ref.	Structure of polymer	% P (w/w)	Residual chlorine (% (w/w)	$(OI)_m$
1'		2.9	0.97	29
2'		6.8	1.6	30
3'	"	13.2	2.27	36
4'	"	14.6	2.8	37

$(OI)_m$ of multiphosphonated polystyrenes of group IV

Data of Table 3 indicate that substitution of a Cl-atom of a copolymer of Table 2, by a - P(O)OEt)$_2$ group, causes some further increase of their $(OI)_m$, if the initial chlorine content is lower than 10% (w/w). For an initial chlorine content higher than 10% (w/w), the same subtitution does not endow them with a higher $(OI)_m$ (see also fig.1).

On the basis of the comparison between $(OI)_m$ data of Tables 2 (ref. 1) and 3, it may be deduced that phosphorus atom separated from the ring by an atom of carbon is more effective in flame retardancy than directly bounded to the aromatic ring of polystyrene.

CONCLUSION

It is well established that the flame retardant properties of phosphonated polystyrenes depend strongly on the relative position of phosphorus atom on the backbone of the macromolecular chain. We have determined a relative scale of flame resistance for the four groups of phosphonated polystyrenes that we have synthesized (see also ref.(1).

We have observed the following decreasing order towards the flame retardant properties

Group I > Group III > Group IV > Group II

References

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