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Phase Separation of Phosphonated Polystyrenes in the Solid State

4. Influence of this Phenomenon on their Flame Retardency Properties

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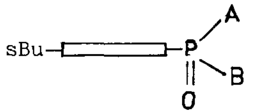
SUMMARY

The goal of this is to point out, using the Electron Spectroscopy for Chemical Analysis (ESCA) method, that the repartition of phosphorus atoms of phosphonated telechelic polystyrenes in the solid state, is not homogeneous. On the other hand, a correlation is established between the P/C ratio in a thin superficial layer of the polymer and his flammability data.

INTRODUCTION

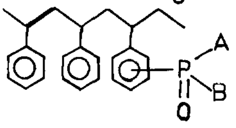
It is well know the Electron Spectroscopy for Chemical Analysis can be applied with success onto polymers, to elucidate fundamental aspects of their surface chemistry (D.T. Clark, 1977, D.W. Dwinght et al. 1978). Furthermore, this method can provide data concerning the relative concentration of various elements in a thin superficial layer of polymer. This study compares the P/C ratio obtained from ESCA analysis with the P/C values derived from chemical analysis for different phosphonated polymers. Those data are obtained from the following structure of polymers :

group I :



A,B = Cl, OCH_3,OH

group II :



A,B = -OEt

The above investigation was undertaken to understand the different behaviour of the two polymer types towards fire.

EXPERIMENTAL

Synthesis of ω-phosphonated polystyrene (group I)

The ω-phosphonated polystyrenes were synthesized as described (G. Clouet et al. 1981).

Synthesis of multiphosphonated polystyrene (groupe II)

This multiphosphonated polystyrene is prepared using the method of (I. Cabasso et al. 1974).

ESCA analysis of polymers of groups I and II

Powder samples of phosphonated polystyrenes were pressed and then irradiated with X-Rays (Al Kα : 1486.6 eV) under vacuum (10^{-9} torr) in a VG ESCA III spectrometer. ESCA spectra exhibited signals, at 286.5 eV (C 1s electrons) with a shake-up satellite at 294.4 eV and at 135-136 eV (2p e of P). No modifications in the position and the shape of the peaks were detected. The P/C molar ratios were estimated using the following relationship :

$$\frac{P}{C} = \frac{\text{height of the P peak}}{\text{height of the C peak}} \cdot \frac{\text{ionization cross section of C}}{\text{ionization cross section of P}}$$

The cross sections were taken from Leckey (R.C.G. Leckey,1976) who gives 0.127 and 0.141 for C and P, respectively. This method is justified since the binding energies of C and P do not differ very much so that the corresponding escape depths are quite close.

RESULTATS AND DISCUSSION

1) Phase separation of polystyrenes with phosphonated end groups

Table 1 lists data about P/C ratios, obtained by ESCA analysis and elemental analysis, for various plhosphonated samples.

For polymer N° 1 (table 1) carrying a $-POCl(OCH_3)$ terminal group, a significant difference is observed between superficial and bulk P/C ratio. The phosphorus content is very high in the surface layer as compared to the chemical analysis value. One can deduct, that in this case the phosphorus group has migrated into the thin superficial layer of the polymer.

The above migration is not observed nevertheless, for polymers N° 2 and N° 3 carrying -POCl(OH) terminal groups, before any thermal treatment.

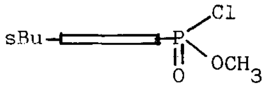
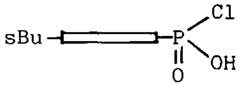
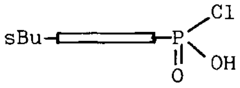
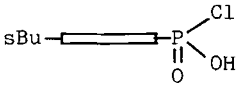
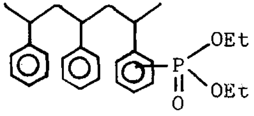
However if polymer N° 3 is heated at 105°C for 1 hour under Argon, the ESCA analysis results show a reorganization of the material. The phosphonated chain ends have migrated into the superficical layer (samples N°4, 5, table 1).

On the other hand, polymers carrying pendent phosphorus groups, such as polymers N° 6 and 7, exhibit superficial P/C ratios lower than those obtained by elemental analysis. Thus, the phosphorus groups of such a polymer tend to migrate inside the material. Furthermore, on the polymer N° 7 with pendent phosphorus groups it seems that there is no significant effect of any thermal treatment, on the above migration tendancy observed previously.

2) Relationship between superficial organization of phosphorus groups and flame retardancy properties

It is well established (A. Chiotis et al. 1982) that flame retardancy properties of phosphonated polystyrenes depend mainly on the relative position of the phosphorus atoms along the chains and not on the absolute phosphorus content. Polystyrenes carrying phosphorus groups bound to one or both ends of the macromolecular chain, are highly effective flame retardant polymers, whereas polystyrenes carrying pendent phosphorus groups are generally not effective. As it can be seen from table 1, the general tendency of phosphorus groups bound to the end of the chain is to migrate to the surface of the material while the oppositive tendency is observed for polymers with pendent phosphorus groups. Thus it is probable that this

Table 1 - P/C molar ratio for phosphonated polystyrenes

Réf	Polymer Structure	Thermal Treatment	$\overline{M}_n$	P/C x 100 molar ratio from ESCA Analysis	P/C x 100 molar ratio from Elemental Analysis	$(OI)_m$
1		-	6 000	1.7	0.24	67
2		-	2 000	0.54	0.49	70
3		-	6 500	0.26	0.20	72
4		1 h at 105° C under argon	6 500	1.04	0.20	72
5		10"in contact with a flame (1 000° C)	6 500	0.485	0.20	72
6		-	32 200	3.4	8	36
7	Same as ref. 6	3 h at 105° C under argon	32 200	3.05	8	36

behaviour is responsible for the different fire retardancy properties observed.

CONCLUSION

Our ESCA data (table 1) show that there is an organization of polymer material when polymer end chains are phosphonated groups with $-PO(OCH_3)Cl$ chain end groups : we observe an important phase separation which exists in the raw material. The phosphorus end chains are located in higher concentration in the surface layer as compared to the bulk. With -PO(OH)Cl chain end groups, the phase separation is not clear in the raw material, but the migration tendency to the surface, increases when the material is heated. This phosphonated layer thus formed, protects the material against the flames, corroborating the oxygen index values (table 1) and the experimental observations (G. Camino et al. 1979) which are given by the kinetic degradation studies.

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