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The Fire-Resistance Properties of Polycarbonates

II. New Fire-Resistant Copolycarbonates Containing Salts of Phosphonic Acid Hemi-Esters

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SUMMARY

This paper describes new fire-resistant bisphenol A and monoalkyl monoalkaline bis(hydroxy-4 phenyl) alkyl phosphonate copolycarbonates.

We show that inclusion of minute quantities (in molar percentages of 0.5 to 1%) of monoalkaline potassium salts of bis(hydroxy-4 phenyl)-alkyl phosphonic acid considerably improves the fire-resistant of the bisphenol A polycarbonate.

We obtain oxygen indices of 34 to 35.

INTRODUCTION

As demonstrated in part I (1), the inclusion of the phosphorus atom in certain structures considerably improves the fire-resistant properties of the polycarbonate.

It was shown, for instance, that dimethyl bis(hydroxy -4 phenyl)-2,2 propyl phosphonate homopolycarbonate, which has a phosphorus content of 7.7 %, has an oxygen index of 36.5.

The phosphonic diester group very readily forms a hemi-salt and we considered it interesting to use molecules corresponding to formula 1 to make use of the combustion-inhibiting properties of phosphorus and the alkali metals. The alkali metals would act as catalysts for the re-integration of free radicals and would exert their activity within the flame (2).

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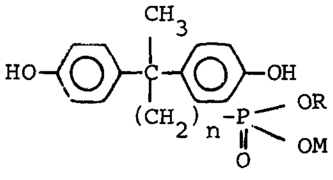

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Accordingly, it seemed possible to reduce the molar percentage of phosphorus and at the same time to maintain a favourable oxygen index.

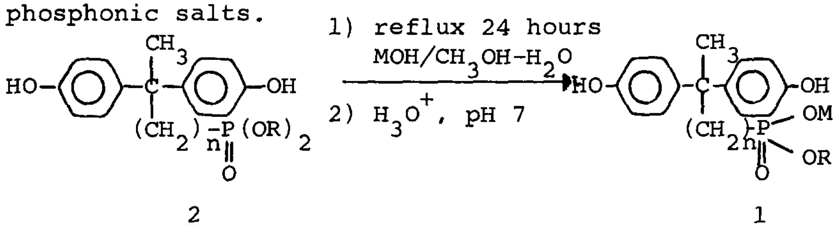
The inclusion of a minute quantity of an active additive in salt form should be possible without interfering with the mechanical properties and the thermal stability of polymers thus obtained.

RESULTS AND DISCUSSION

a) Preparation of monomers

The monoalkyl monoalkaline bisphenol phosphonates 1 are obtained by the alkaline hydrolysis of dialkyl bisphenol phosphonates 2.
This process is carried out by refluxing an aqueous alcoholic solution of the mixture. The refluxing must be continued for a sufficiently long period (24 hours) to avoid the formation of a mixture of the diester 2 and the hemi-ester 1. A partial hydrolysis is easily monitored by ^{1}H-NMR, allowing separation of diester 2 OCH_3 protons from hemi-ester 1 OCH_3 protons.

Once hydrolysis is complete, the reaction medium is neutralised using concentrated HCl until a pH of 7 is obtained. This neutralisation permits complete neutralisation of the phenolic groups while retaining the phosphonic salts.



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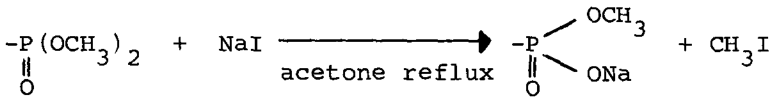
Besides analysis for phosphorus and alkali metals, the compounds obtained (see table 1) were characterised essentially by ^{1}H and ^{13}C-NMR spectroscopy.

Sodium salts can also be obtained by the action of NaI in a reaction medium containing a ketone (3) on dimethyl bisphenol phosphonates.



$$-P(=O)(OCH_3)_2 + NaI \xrightarrow[\text{acetone reflux}]{} -P(=O)(OCH_3)(ONa) + CH_3I$$

TABLE 1

Monoalkyl monoalkaline bisphenol phosphonates of structure 1

Compound N°	n	M	R	Yield (%)	T(°C) decomp.[a]	^{1}H-NMR, solvent D_2O δ (ppm from TMS)
1a	0	Na	CH_3	90	260	$\delta = 3.32$ (OCH_3)
1b	0	K	CH_3	82	220-225	$\delta = 3.47$ (OCH_3)
1c	1	Na	CH_3	95	220-225	$\delta = 3.20$ (OCH_3)
1d	1	K	CH_3	84	235	$\delta = 3.20$ (OCH_3)
1e	1	Na	Et	30	220-225	$\delta = 3.5$ ($\underline{OCH_2}CH_3$)
1f	1	K	Et	-	220-230	
1g	2	Na	CH_3	58[b]	240	$\delta = 3.41$ (OCH_3)

a The temperature at which decomposition took place was mesured using differential thermal analysis (DTA) and by thermogravimetric analysis.

b Obtained upon reaction with NaI.

The compounds obtained are white powders which are hygroscopic and decompose on melting.

b) The polycondensation process

The polycondensation process used consisted of interfacial phosgenation as described in part I (1).

c) Bisphenol A and methyl and sodium bis(hydroxy-4 phenyl)-1,1 ethyl phosphonate 1a copolycarbonates

We carried out a preliminary series of tests in which we varied the molar percentage of compound 1a from 10 to 0.75 %.Triethylamine was used as a catalyst.

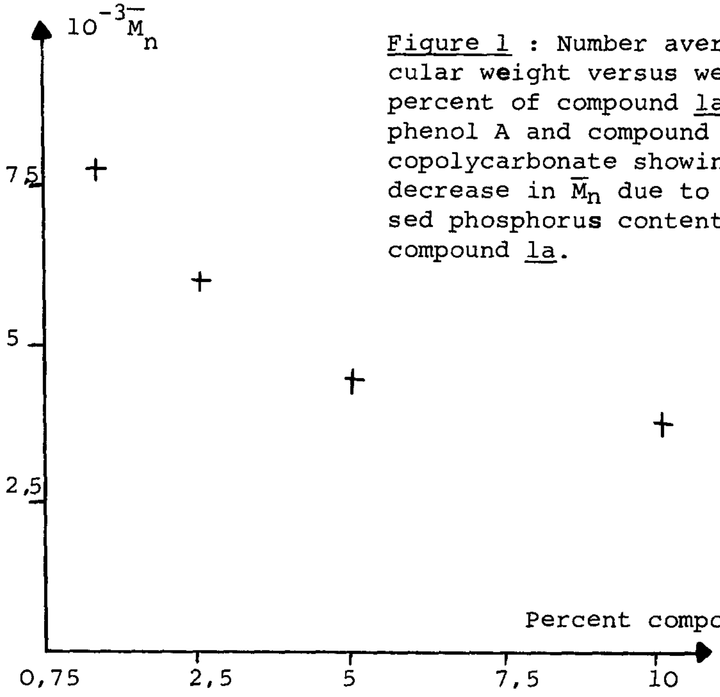
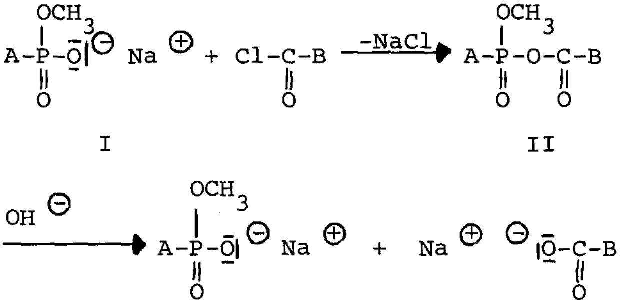


Figure 1 : Number average molecular weight versus weight percent of compound 1a in bisphenol A and compound 1a copolycarbonate showing the decrease in $\bar{M}_n$ due to increased phosphorus content of compound 1a.

It can be seen from figure 1 that there is a marked decrease in molecular mass as the percentage phosphorus content in compound 1a increases. This observation led us to put forward the hypothesis that this salted active additive could act as a chain limiting factor by reacting with the active chlorines and the salted phosphonic ester group.

The reaction is shown below :



$$A-\underset{\underset{O}{\|}}{\overset{\overset{OCH_3}{|}}{P}}-\bar{O}|^{\ominus}\ Na^{\oplus} + Cl-\underset{\underset{O}{\|}}{C}-B \xrightarrow{-NaCl} A-\underset{\underset{O}{\|}}{\overset{\overset{OCH_3}{|}}{P}}-O-\underset{\underset{O}{\|}}{C}-B$$

I II

$$\xrightarrow{OH^{\ominus}} A-\underset{\underset{O}{\|}}{\overset{\overset{OCH_3}{|}}{P}}-\bar{O}|^{\ominus}\ Na^{\oplus} + Na^{\oplus}\ {}^{\ominus}|\bar{O}-\underset{\underset{O}{\|}}{C}-B$$

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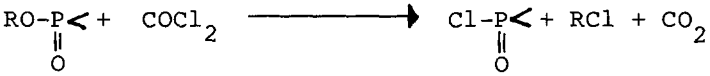
The mixed anhydride II thus formed would then be hydrolysed, regenerating the phosphorated salt I and a sodium carbonate.

It is known that phosgene is able to react with alkyl esters if acids derived from tetra-substituted phosphorus. The reaction is shown as follows (4,5) :



$$RO-\underset{\underset{O}{\|}}{P}< + COCl_2 \longrightarrow Cl-\underset{\underset{O}{\|}}{P}< + RCl + CO_2$$

Unwanted side reactions would perhaps be minimised by choosing a catalyst which speeds up the polycondensation reaction.

As it was found impossible in practice to synthesise compounds richer in phosphonate salts due to the small molecular masses obtained and to the presence of large quantities of NaCl (6), we were forced to centre our interest on the use of these additives in low concentrations (0.5 to 2 %).

d) Bisphenol A and methyl and sodium bisphenol phosphosnate copolycarbonates

Table 2 shows the most important results obtained using triethylbenzylammonium chloride as catalyst for substances containing 1 % molar of phosphorated component.

TABLE 2

BISPHENOL A AND METHYL AND SODIUM[a] BIS(HYDROXY-4 PHENYL)ALKYL PHOSPHONATE COPOLYCARBONATES

Test	Phosphorated comp. Molar Percent	$\bar{M}_w$ [b]	$\bar{M}_n$ [b]	Yield (%)	Phosphorus		Na		OI[c]
					calc.%	exp.%	calc.%	exp.%	
1	1a 1 %	43200	14600	84	0.12	0.017	0.089	0.13	31/32
2	1b 1 %	50800	14200	83.8	0.12	0.067	0.09	0.1	31/32
3	1g 1 %	38100	10300	81.6	0.12	0.076	0.09	0.13	31

[a] For 0.1 mole of bisphenols, 150 ml of a 1.56 N aqueous sodium hydroxide solution, 170 ml of CH_2Cl_2, 0.35 g of catalyst (1.5 % molar/bisphenols), 0.1 g of phenol (1 % molar/bisphenols) and 58 ml of a 20 % solution of $COCl_2$ in toluene (0.11 mole of $COCl_2$) were used.
The addition of the $COCl_2$ was carried out over a period of 1 hour at $5 < T(°C) < 15$ $pH > 9$.

[b] The molecular masses were determined by GPC.

[c] The oxygen indices OI were determined using a Michigan Chemical Corporation apparatus conforming to standard ASTM D 2863-70.

It can be seen that with this catalyst, the products obtained have the greatest molecular mass $\overline{M}_n$ The products also possess good thermal stability as their weight loss after heating at 250°C for 2 hours is of the order of 0.05 to 0.1 %.

These tests demonstrate that small amounts of phosphorus and sodium, present as active additives in the form of salts at a concentration of 1 % molar, clearly improve the fire-resistant properties of bisphenol A polycarbonate. In general, the oxygen indices obtained were 31.

e) Bisphenol A and monoalkyl and potassium bisphenol phosphonate copolycarbonates

Examination of research conducted on the combustion-inhibiting properties of various alkali metals reveals that the K^+ cation is somewhat superior to the Na^+ cation (2.7).

For this reason we carried out a number of tests using potassium salts, with triethylbenzyl ammonium chloride as catalyst, this catalyst having already demonstrated its favourable effect in obtaining large molecular masses.

Table 3 shows the results obtained. On examining the variation in molecular mass, the chain-limiting factor previously mentioned seems to be present.

The products obtained which have a high yield and also good thermal stability at 250°C possess excellent fire-resistant properties.

In fact, the oxygen indices are within the range 33 to 35 for molar percentages of phosphorated compound within the range 0.5 to 2 %.

As found in part I, it is necessary to use a molar percentage of at least 50 % of dimethyl bisphenol phosphonate to obtain identical oxygen indices (Part I).

In addition, we consider it important to report that we have verified experimentally that these differing bisphenol phosphonates used as inert additives in polycarbonates on the market did not significantly improve fire-resistant properties because the oxygen indices did not exceed 29.

TABLE 3

BISPHENOL A AND MONOALKYL AND POTASSIUM BIS (HYDROXY-4 PHENYL) ALKYL PHOSPHONATE COPOLYCARBONATES[a]

Test	Phospho. compound Molar Per.	$\overline{M}_w$	$\overline{M}_n$	Yield (%)	Phosphorus		K		Na percent	OI
					calc. %	% exp.	calc. %	% exp.		
4	1b 1 %	42300	14300	81.6	0.12	0.082	0.15	0.11	0.1	34/35
5	1d 0.5%	59600	18800	86	0.063	0.072	0.076	0.07	0.11	34/35
6	1d 1 %	35000	12700	86.8	0.12	0.0035	0.15	0.12	0.065	33/34
7	1d 2 %	27000	10700	85.8	0.24	0.0037	0.30	0.055	0.105	34
8	1f 1 %	51100	22200	83.5	0.12	0.09	0.15	0.13	0.08	35

[a] For experimental conditions, see table 2.

The mechanical characteristics were considerably damaged by this addition.

f) Characterisation of the compounds

We wish to emphasise here the problems in testing the conditions under which incorporation of salted molecules took place.

The physico-chemical methods used for the caracterisation of the dialkyl bisphenol phosphonate polycarbonates are not sensitive enough.

Also, we could only rely on elemental analysis of the different elements. In this manner, the assays for phosphorus using the usual methods gave practically negative results.

These methods necessitate an initial mineralisation of the polymer to convert the phosphonated compound into phosphoric acid and it is thought that the mineralisation process degrades the material releasing volatile phosphorated susbtances (dry mineralisation) or that the process does not bring about sufficient degradation ("wet" mineralisation).

Only the method of neutron activation enabled us to assay the small amounts of phosphorus incorporated in our products.

However, the amounts of phosphorus found were sometimes very different from the theoretical values.

The same observations can be made for the bisphenol A polycarbonates to which actives additives are added and for which the problem of incorporation does not exist.

On the other lands, the determination of alkaline cations using atomic absorption seems to confirm good incorporation.

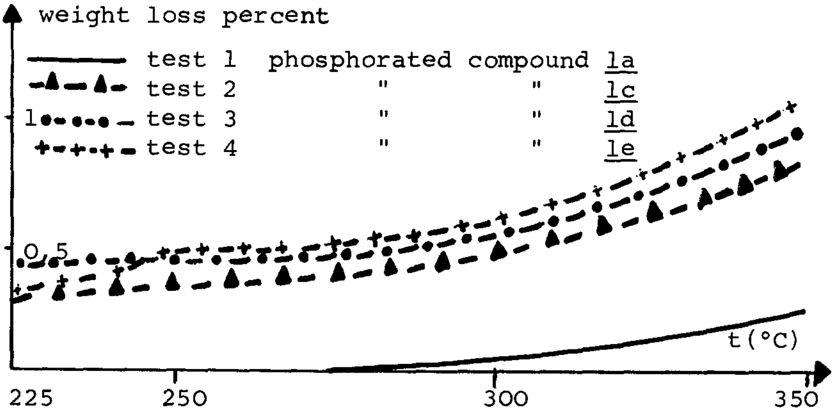
Finally, the oxygen values of as high as 35 and the measured thermal stability of our products are the most significant proofs of the presence of these phosphorus entities in the macromolecular chain of the polycarbonate.

In fact, whilst bisphenol A - synthesised under the same experimental conditions - undergoes no weight loss on heating to 350°C, our products undergo considerable decomposition above 300°C (see diagram 2) ;

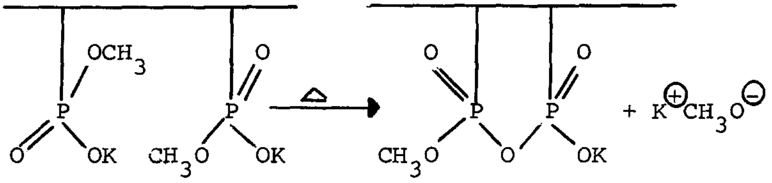
this decomposition is most marked in presence of potassium salts.

DIAGRAM 2

Weight loss expressed as percent plotted againts temperature, in bisphenol A and salted bisphenol phosphonate copolycarbonates



A possible mechanism for the degradation of the potassium salts can be postulated by drawing an analogy with the mechanism cited previously (8). In an initial step, $KOCH_3$ would be released :



Traces of water would lead to the formation of potassium hydroxide as follows :

$$K^{\oplus}\,CH_3O^{\ominus} + H_2O \longrightarrow K^{\oplus}OH^{\ominus} + CH_3OH$$

Thus, the presence of K^+ and KOH could contribute to the degradation of the polycarbonate and could also serve as effective entity in the inhibition of combustion and in the improvment of the fire-resistant properties of bisphenol A polycarbonate.

CONCLUSION

We have shown that in using the sodium, or better still the potassium salts of bis(hydroxy-4 phenyl) alkyl phosphonic acid in a copolycondensation reaction with bisphenol A, oxygen indices of 34 and 35 could be obtained on employing active additives in the form of salts, in molar percentages of 0.5 to 1 % ; use of inert additives does not significantly improve fire-resistant properties.

REFERENCES

1.- P. POISSON and G. STURTZ, Polymer Bulletin

2.- K. SRIDHAR, SUSAN WOLLOWITZ and W.E. KASKAN,"The Mechanism of Flame Inhibition by Sodium Salts" Synt. Int. Combustion, 1975, 329.

3.- R. KLUGER, J. Org. Chem., 1973, 38, 2721

4.- J.I.G.CADOGAN; K. Chem. Soc., 1957, 3604

5.- M. GREEN and R.F. HUDSON, J. Chem. Soc., 1963,1004

6.- A.A.BERLIN, I.I. LEVANTOUSKAYA, B.M. KOVARSKAYA, G.V. DRALYUK and L.M. RAGINSKAYA, Vysokomol.Soyed., 1968,A10, 1103 (Polymer Science U.S.S.R., 1968, A10, 1278)

7.- J.D. BIRCHALL, Combustion and Flame, 1970, 14, 85

8.- A. HAMOUDI and I.C. McNEILL, European Polymer J., 1978, 14, 951

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