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The Fire-Resistance Properties of Polycarbonates

I. New Fire-Resistant Polycarbonates Containing Phosphonic Acid Diester Groups

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SUMMARY

The present paper describes two types of polycarbonates possessing fire-resistance. The first type is obtained by reacting dialkyl bis(hydroxy-4 - phenyl)alkyl phosphonates with phosgene and the second type is a copolymer of bisphenol A and dialkyl bisphenol phosphonates.

We show that the incorporation of dialkyl bisphenol phosphonates into the bisphenol A polycarbonate chains can be satisfactorily carried out using interfacial polycondensation.

The products with groups-$P(OCH_3)_2$ possess high oxygen indices (OI).

INTRODUCTION

Because of their excellent mechanical and electrical properties, as well as their high degree of transparency, polycarbonates are used in a number of fields (glazing, lighting, electromechanical structures).

Although relatively non-inflammable among organic polymers (the oxygen index for a bisphenol A polycarbonate is between 26 and 28), it seemed necessary to carry out research into polymers with better fire-resistant properties.

Numerous fire-resistant additives have been incorporated in polycarbonates to increase their resistance to combustion. Halogen compounds (tetrabromo bisphenol A, decabromo diphenyl ether) were used extensively, but have since been found to release toxic and corrosive gases (halohydric acids) on combustion.

In order to avoid such problems and to endeavour to

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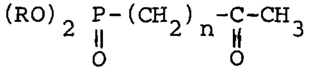
improve the fire-resistance of the polycarbonates, we decided to make use of the combustion-inhibiting properties of the phosphorus atom.

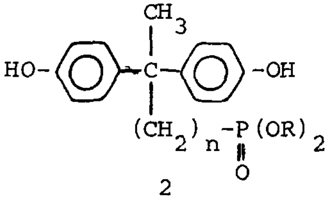
Some studies (1 to 4) have already demonstrated that this element can be incorporated in the macromolecular chain of the polycarbonates. The substances thus obtained exhibit, however, a certain degree of instability towards hydrolysis (3) or involve monomer syntheses which are very difficult to perform in practice (4).

ILIOPULOS et al (5) were able to synthesise a self-extinguishing polycarbonate which contained "hanging" phosphonate groups by using a reaction involving dimethyl bis(hydroxy-4 phenyl)-1,1 ethyl phosphonate with phosgene. The various modes of attachment of phosgene to β and γ ketophosphonates (7) of general formula 1,


$$(RO)_2\underset{\underset{O}{\|}}{P}-(CH_2)_n-\underset{\underset{O}{\|}}{C}-CH_3$$

1

are familiar from the reaction described by ILIOPULOS (5,6) for α ketophosphonates. Such substances are less stable than those obtained from β and γ ketophosphonates and hence it seemed feasible that dialkyl bisphenol phosphonates possessing structure 2 could be synthesized.



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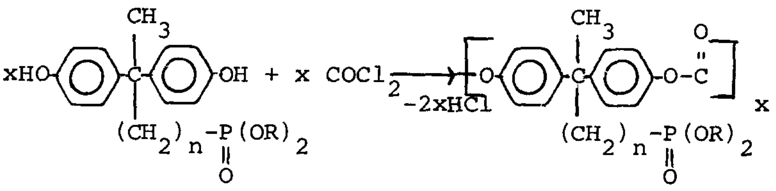
This paper describes two new polymers : polycarbonates 3 obtained by reacting dialkyl bisphenol phosphonates 2 with phosgene and copolymers 4 of bisphenol A and dialkyl bisphenol phosphonates 2, both types of polymer possessing improved fire-resistance.



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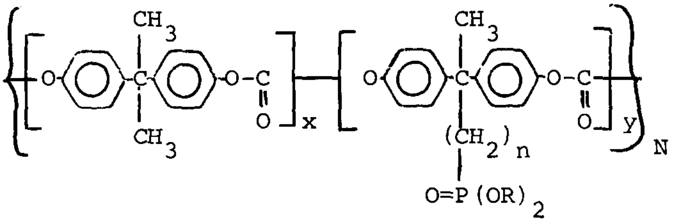

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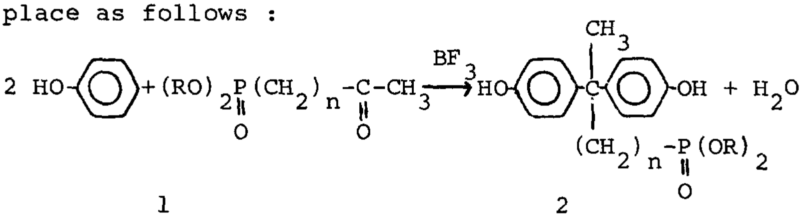
(x and y represent the molar ratios in the recurring unit, N indicates the number of times the unit is repeated).

RESULTS AND DISCUSSION

a) Preparation of monomers

The dialkyl bisphenol phosphonates 2 are obtained by condensing ketophosphonates 1 (7 to 9) with phenol in the presence of boron trifluoride. The reaction takes place as follows :



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A mixture of phenol in excess (6 moles)and ketophosphonate in boron trifluoride (at around 15°C) is saturated. The viscous liquid thus obtained is then heated between 40 and 45°C and maintained at this temperature for one hour. On cooling, the liquid is then dissolved in 500 ml of acetic acid and the solution thus obtained is poured into 12 l of water vigourous stirring.

A white oil which gradually hardens is precipitated (24 to 72 hours). The solidified product is removed from the water, washed, dried and then crystallised.

As well as elemental analysis for carbon, hydrogen and phosphorus, the substances obtained were characterised by various methods of spectroscopy, namely - infra-red, ^{1}H and ^{13}C-NMR. See table 1.

TABLE 1

Dialkyl bisphenol phosphonates possessing structure 2 (see text)

Compound					^{1}H-NMR, solvent DMSO d_6
N°	n	R	Yield	M.P. (°C)	δ (ppm from TMS)
2a	1	CH_3-	71	185	δ=2.62($-CH_2-$),δ=3.28(OCH_3)
2b	1	Et-	69	152	δ=3.9($-\underline{OCH_2}CH_3$,δ=1.15($-OCH_2\underline{CH_3}$)
2c	2	CH_3-	88	170	δ= 3.58($-OCH_3$)
2d	3	Et-	-	115	δ=3.85($-\underline{OCH_2}CH_3$),δ=1.15 ($-OCH_2\underline{CH_3}$)

b) The polycondensation process

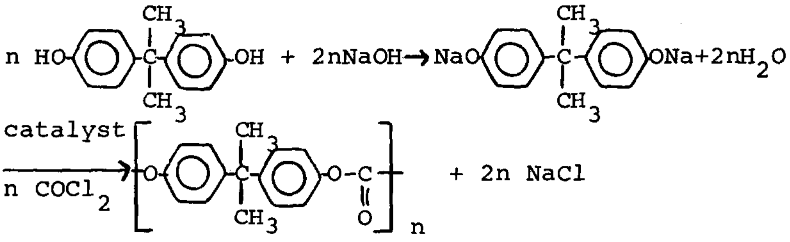
Several processes already exist for obtaining polycarbonates. We have chosen the process of interfacial phosgenation.

This process consists of the reaction of phosgene (a 20 % solution in toluene) with sodium bisphenolate in aqueous alkaline solution in the presence of CH_2Cl_2 (non-miscible), which dissolves the polycarbonate formed.

The reaction which takes place at a temperature between 5 and 15°C can be catalysed by tertiary amines, ammonium and phosphonium salts.

The polycondensation reaction is carried out at a temperature of 30°C for 1 hour.

The polycarbonate is recovered by precipitation in ether.
The diagram of the reaction is as follows :

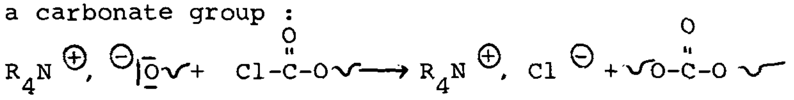


Preliminary tests carried out using bisphenol A and the compound 2b in the presence of various catalysts (triethylamine, ammonium salts) enabled us to determine the most favourable conditions for the reaction. In this manner we found that triethylbenzyl ammonium chloride is the best catalyst for obtaining the largest molecular masses with a well-defined distribution. According to SMIRNOVA et al (11), the catalytic activity consists of the formation of salts produced by the joint ionic interaction of the cation R_4N^+ and phenolic anions :

$$R_4N^{\oplus}, Cl^{\ominus} \rightleftharpoons R_4N^{\oplus} + Cl^{\ominus}$$

$$R_4N^{\oplus} + {}^{\ominus}|\overline{\underline{O}}\sim \longrightarrow R_4N^{\oplus}, {}^{\ominus}|\overline{\underline{O}}\sim$$

These salts react with chloroformic end groups to form a carbonate group :



$$R_4N^{\oplus}, {}^{\ominus}|\overline{\underline{O}}\sim + Cl-\overset{O}{\overset{\|}{C}}-O\sim \longrightarrow R_4N^{\oplus}, Cl^{\ominus} + \sim O-\overset{O}{\overset{\|}{C}}-O\sim$$

c) Bisphenol A and diethyl bis(hydroxy-4 phenyl)-2,2 propyl phosphonate 2b Copolycarbonates

Using triethylbenzyl ammonium as catalyst, we synthesised a series of copolycarbonates 4 possessing different phosphorus contents. These compounds were synthesised from bisphenol A and compound 2b (see table 2).

We obtained high molecular masses but observed a progressive reduction in molecular mass as the phosphorus content of the copolycarbonate increased.

This increase in phosphorus content was also responsible for a reduction in the glass transition temperature Tg. The group $-\underset{\underset{O}{\|}}{P}(OEt)_2$ acts as an internal plasticizer. This plasticizing effect has the advantage of being permanent and can permit the use of lower temperatures.

It is, however, surprising to note that a raised phosphorus content does not produce a significant increase in fire-retardant activity in these materials.

In fact, no correlation could be found between the oxygen indices OI of about 29 and the percentage of

TABLE 2

Bisphenol A and diethyl bis(hydroxy-4 phenyl)-2,2 propyl phosphonate 2b[a] copolycarbonates

Test	Molar percent in compound 2b	$\overline{M}_w$ [b]	$\overline{M}_n$ [b]	Yield (%)	Phosphorus calc.%	Phosphorus Exp.%	OI[c]	Tg(°C)[d]
1	0	69600	20500	87	-	-	27.5	155
2	25	47500	16800	78	2.65	2.04	28	140
3	50	37650	12200	77.5	4.81	4.84	29	127
4	75	25800	10100	81	6.5	6.22	29.5	123
5	100	20700	7600	76.5	7.90	8.27	29	118

a) For 0.1 mole of bisphenol A the following was used : 150 ml of an aqueous 1.56 N alkaline solution, 170 ml CH_2Cl_2, 0.35 g of triethyl benzyl ammonium chloride as catalyst (1.5 molar in relation to bisphenols), 0.1 g of phenol (1% molar in relation to bisphenols), 58 ml of a 20 % solution of $CO\ Cl_2$ in toluene (0.11 mole of $COCl_2$).
The addition of the $COCl_2$ was carried out over a pediod of 1 hour at $5 < t \leqslant 15$°C and pH $>$ 9.

b) The molecular masses $\overline{M}_w$ and $\overline{M}_n$ were determined using gel permeation chromatography.

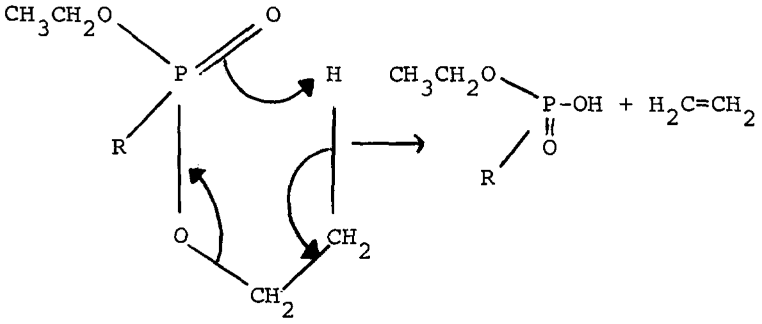
c) The oxygen indices OI were determined using a Michigan Chemical Corporation apparatus conforming to standard ASTM.D 2863.70.

d) The glass transition temperatures were determined by DSC.

phosphorus in the compound.

Information obtained from thermal stability studies on these compounds may explain these results. In fact, although relatively stable at around 200-220°C, these copolycarbonates decompose rapidly as soon as the temperature is raised. Using coupled chromatography-mass spectroscopy, we analysed the volatile substances given off on decomposition of these copolycarbonates. These volatile substances consisted of CO_2 and ethylene.

The probable mechanism for the release of ethylene is by an electron transfer passing through an intermediate 6-centred transition stage (10) :



The presence of the P-OH group may give rise to the formation of P-O-P with the release of water, which may in turn give rise to the hydrolysis of the carbonate group, with the release of CO_2.

Thus, the decomposition reactions seemed to limit considerably the value of these compounds as fire-resistant substances.

For this reason, it was apparent that the dimethyl bisphenol phosphonates, which do not undergo this type of degradation, would be more effective.

d) Bisphenol A and dimethyl bis(hydroxy-4 phenyl)-2,2 propyl phosphonate 2a copolycarbonates

We synthesised a series of copolycarbonates of bisphenol A and dimethyl bis(hydroxy-4 phenyl)-2,2 propyl-phosphonate 2a using the same procedure as described previously for the phosgenation.

Table 3 shows the most important results obtained. It can be seen that there is a considerable decrease in molecular mass as the phosphorus content of the compound 2a increases in the composition of the copolycarbonate . By extension, the polycarbonate 3a (test 9) can be considered as being an oligomer.

These products also possess good thermal stability and also show much improved fire-resistant properties compared with bisphenol A polycarbonate (test 1, table 1). For a phosphorus content of 2.3 % an oxygen index of 33 is obtained.

Although it is not possible to offer a completely satisfactory explanation for the reduction in molecular mass observed, it is obvious that carrying out the tests in a very alkaline medium favours the hydrolysis of the methyl ester group.

It also seemed to us to be possible to decrease these side reactions by increasing the speed of the reaction.

For this reason, we carried out the tests in the presence of benzyltriphenyl phosphonium chloride (as catalyst) and in the absence of a chain limiting factor, under the conditions given below (see table 4).

These substances possess much larger molecular masses but the same reduction in molecular mass with increasing phosphorus content is observed.

The tested substances are transparent and pliable, have good thermal stability and excellent fire-resistant properties. In fact, for compound 3a (test 13) an OI of 36.5 is obtained for a phosphorus content of 7.7 %.

e) Modification of properties according to the structure of the bisphenol phosphonate (n=0,1,2)

In table 5 the fire-resistant properties of dimethyl bisphenol phosphonate polycarbonates having a similar phosphorus content but different structures are compared.

TABLE 3

Bisphenol A and dimethyl bis(hydroxy-4 phenyl)-2,2 propyl phosphonate 2a copolycarbonates

Test	Molar percent in compound 2a	$\overline{M_w}$	$\overline{M_n}$	Yield(%)	Phosphorus calc (%)	Phosphorus Exp (%)	OI	Tg(°C)
6	10	38680	13160	86	1.16	1.01	31	152
7	25	25050	9870	77	2.73	2.33	33	152
8	50	15400	6120	71	4.99	4.20	34	141
9	100	3700	1980	88.6	8.51	7.7	$\simeq 35$[a]	139

[a] Breakable test tubes, OI determined on the pieces.

TABLE 4

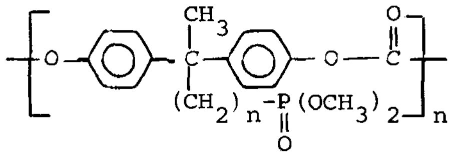
Bisphenol A and dimethyl bis(hydroxy-4 phenyl)-2,2 propyl phosphonate 2a copolycarbonates[a]

Test	Molar percent in compound 2a	$\overline{M}_w$	$\overline{M}_n$	Yield (%)	Phosphorus		OI
					calc (%)	Exp (%)	
10	25	319000	77000	70	2.73	2.32	33
11	50	157600	15000	65	4.99	4.80	35
12	75			69	6.88	5.80	36
13	100	31100	9200	80.2	8.5	7.72	36.5

[a] For 0.1 mole of bisphenol, 400 ml of 0.75 N sodium hydroxide, 200 ml of CH_2Cl_2 and 2 g of triphenyl benzyl phosphonium chloride (5 % molar with respect to the bisphenols) were used.

TABLE 5

Phosphorated polycarbonates[a] having the structure :



n	Polycarbonate	$\overline{M}_w$	$\overline{M}_n$	Yield (%)	Phosphorus calc (%)	Phosphorus Exp (%)	OI	Tg(°C)
0		58800	15800	82.6	8.84	7.64	35.5	160
1	3a	31100	9200	80.2	8.5	7.72	36.5	142
2	3c	4200	2200	68	8.20	7.68	≃35[b]	101

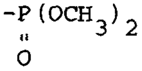
[a] For experimental details of polycondensation, see table 4.

[b] Breakable test tube, OI determined on the pieces.

The best fire-resistant properties were exhibited by the polycarbonate 3a. There is a progressive diminution in molecular mass and yield as the side chain length increases. The latter probably influences reaction speed. There is also a reduction in the temperature at which glass transition of the principal chain occurs, being proportional to the increase in length of the side chain (160°C for n=0 and 101°C for n=2).

CONCLUSION

We have shown that the insertion of dialkyl bisphenol phosphonates 2 into the chain of bisphenol A polycarbonate can be satisfactorily carried out using interfacial polycondensation.

The products obtained possess very different fire-resistant properties, these differences being dependent on their structure. The group of choice is the group  $-\underset{\underset{O}{\|}}{P}(OCH_3)_2$ because the best oxygen indices ($>$30) were obtained in polycarbonates containing this group.

Of these substances possessing high oxygen indices, the homopolycarbonate 3a (OI=36.5) is the substance of choice.

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