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Review

Overview of recent developments in the flame retardancy of polycarbonates

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Abstract: This paper presents an overview of the recent literature on flame retardancy of polycarbonate (PC) and polycarbonate-based resins. A brief survey of the major mechanisms of thermal decomposition of PC is also presented because it gives insight in the mechanisms of flame retardant action. Mostly industrial laboratories are involved in the development of new flame retardants for PC and, to a much lesser extent, academic laboratories are doing research on the mechanistic aspects of flame retardancy. The number of patents published annually on the flame retardancy of PC and its blends significantly exceeds the number of patents on flame retardancy of any other polymer. Because PC is a naturally high charring polymer, the condensed phase active flame retardants, in particular phosphorus-based ones, are widely used in PC-based blends. Plain PC can pass stringent flame retardant tests with very low additions of some sulfur- or silicone-based flame retardants.

Keywords: polycarbonate; combustion; thermal decomposition; flame retardancy; aromatic phosphates; sulfonates; polysiloxanes

INTRODUCTION

Although some aliphatic polycarbonates are known for special applications, the largest commercial products are aromatic polycarbonates and, particularly, poly[2,2-propane(bisphenol) carbonate] (here called polycarbonate or PC) manufactured from bisphenol A. The annual volume of this polymer exceeds 1 million metric tons. PC is an amorphous polymer with a relatively high glass transition temperature, T_g, = 140–150 °C.[1] Because PC possesses a high heat distortion temperature (132–138 °C), this makes polycarbonate particularly useful for structural elements operating at elevated temperatures. Another advantage of polycarbonate relates to its transparency and exceptional clarity. Because of relatively high tendency to charring, PC by itself shows a V-2 rating in the UL-94 test. However, more stringent flame retardant performance is often required.

In order to improve impact toughness, which tends significantly to decrease with PC aging, elastomeric polymers like styrene–butadiene–styrene triblock copolymer (SBS) or styrene-acrylonitrile (SAN) are added to PC. However, the most common blend is a blend with acrylonitrile–butadiene–styrene copolymer, PC/ABS. The optimum content of ABS is in the range of 30–40 wt%; however in flame retardant formulations it is usually lower. By varying the polycarbonate and ABS grades and proportions, it has been possible to close the technological gap between ABS and bisphenol A polycarbonate.[2] The mechanical properties vary with the composition of the blend.

The flammability of PC/ABS blends very much depends on the ratio PC/ABS. Although PC is relatively easy to flame retard, ABS is very combustible and tends to generate heavy black smoke. The conventional flame retardants that are used in the individual resins may not perform as well in PC/ABS.[3] Other commercial blends based on PC are blends with poly(ethylene terephthalate), PC/PET, and blends with high impact polystyrene, PC/HIPS. There are flame-retardant commercial formulations classified either V-2 or V-0 under the UL 94 protocol. Glass-fiber-reinforced grades are also available.

This paper presents an overview of recent developments in flame retardancy of polycarbonate and polycarbonate-based blends. The literature of the last seven years is mostly cited; however, if an older publication provides fundamentals for understanding recent developments it is also discussed. A short overview of the thermal decomposition of polycarbonate is also presented in order to provide a better understanding of the flame-retardant mechanisms.

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THERMAL DECOMPOSITION OF POLYCARBONATE

Polycarbonate possesses a high degree of thermal stability and undergoes little decomposition below 250 °C. The most important volatile degradation products are carbon dioxide and bisphenol A.[4,5] Other products formed in significant amounts are carbon monoxide, methane, phenol, diphenyl carbonate, and 2-(4-hydroxyphenyl)-2-phenylpropane. In addition to these products, ethylphenol, isopropenylphenol, isopropylphenol and cresol were detected as minor products.[6] These are thought to result from breakdown of the primary product, bisphenol A. The only highly volatile and highly combustible gases formed are CO and methane. These gases are most likely important for PC ignition but since the concentration of CO and CH_4 is relatively low, it is difficult to ignite the polymer.

In the earlier studies, it was noted[7] that PC undergoes extensive crosslinking when heated in an open vessel or in a vacuum under continuous removal of volatile products,[8] whereas in a sealed tube chain scission without gelation is a predominant process. Since the major gaseous product evolved from PC is CO_2, this is indicative that mostly carbonate linkages are destroyed initially. On the basis of these results, it was postulated[9] that the carbonate group can undergo a rearrangement to form a pendant carboxyl group, *ortho* to an ether linkage in the main chain. The carboxyl group quickly splits out CO_2 or H_2O (Reaction 1) and therefore it was not detected in the condensed phase or with volatilized chain fragments.

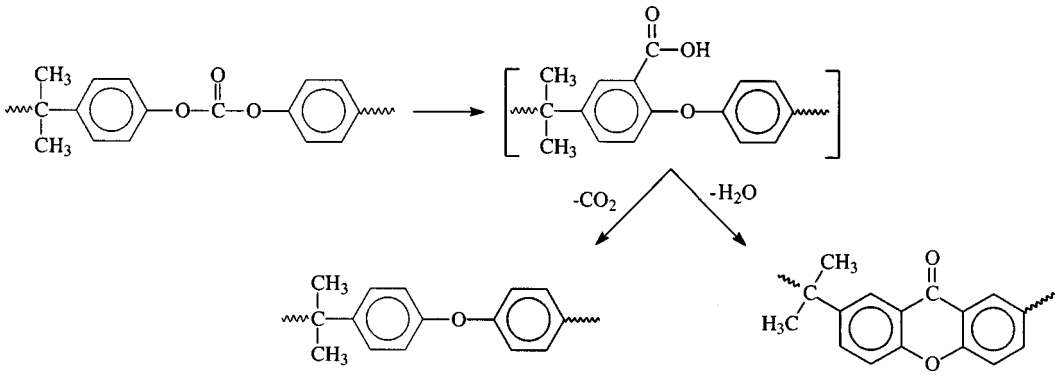
In both cases the linear polymer structure remains intact. Evidence of the rearrangement of the carbonate group to the carboxyl group was also obtained[10] by pyrolytic mass spectrometry, where some peaks were attributed to xanthone or anthraquinones, which are the secondary products of this rearrangement. Apart from the rearrangement mechanism (Reaction 1) CO_2 can be also generated via homolytic scission or 1,3-shift of the carbonate group.

Although formation of the xanthone ring structure is not a dominant process, it is important for understanding further chain breaking of polycarbonate with participation of H_2O and the formation of bisphenol A. Water evolved in this process, also some moisture present in the original polymer, is very detrimental to carbonate linkages and is responsible for chain scission[11] (Reaction 2).

It was believed that free phenols, bisphenol A and small fragments with phenolic chain ends are also detrimental for carbonate linkages, because they transesterify the carbonate linkages and thus break the polymer into smaller fragments (Reaction 3).

Intermediate 2-phenoxybenzoic acid structures formed in Reaction 1 can attack polycarbonate and form crosslinks. Bisphenol A-terminated chain-ends are formed which lead to the evolution of bisphenol A at further decomposition (Reaction 4).

This set of reactions satisfactorily interprets the dependence of crosslinking on the removal of degradation products. Thus, branching will occur via Reactions 1 and 4, whether or not volatiles are removed from the system. However, this will only result in gelation if the scission processes, Reactions



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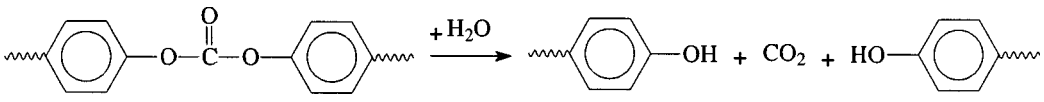

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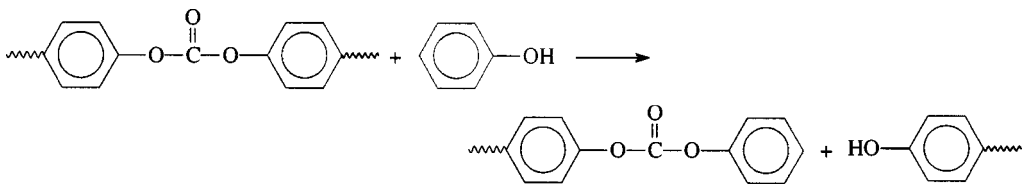

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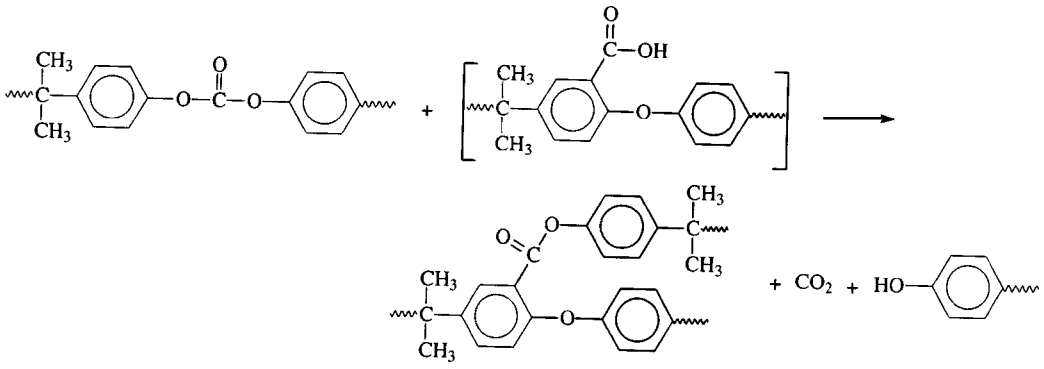
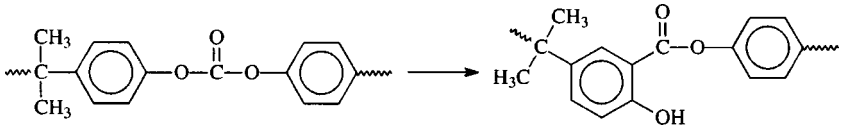


(Reaction 4)



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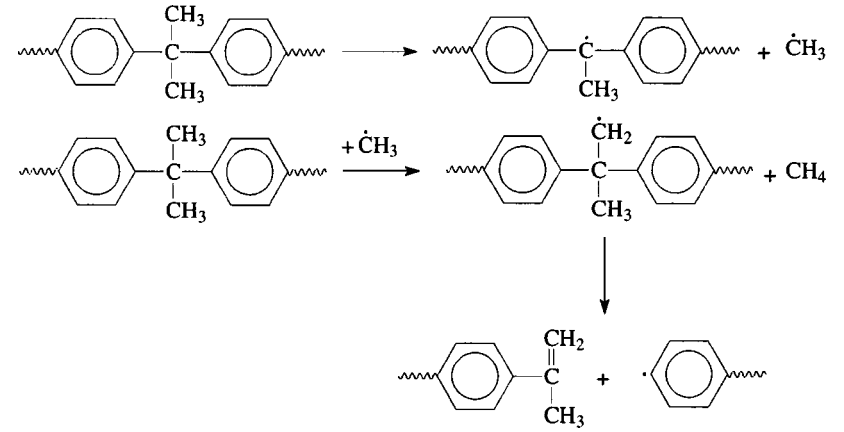


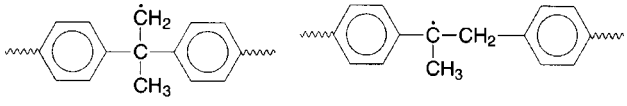
(Reaction 6)

2 and 3, are suppressed by removal of free hydroxyl groups (water or phenols) from the system. However, if these volatiles are left, scission will predominate and gel formation will not occur. Using kinetic considerations, Abbas[12] proved that the chain scission of PC in a closed system does not fit with the random free-radical model. A relatively low value of activation energy (112 kJ mol^{-1}) is indicative of the contribution of molecular mechanisms, which could be Reactions 2 and 3.

Another rearrangement which takes place in polycarbonate chains is Fries rearrangement (Reaction 5). Although both phenolic OH groups and aromatic ester groups were found in decomposing polycarbonate by many authors, the most convincing proofs were provided by pyrolysis mass spectrometry based on evolved volatile fragments.[13,14]

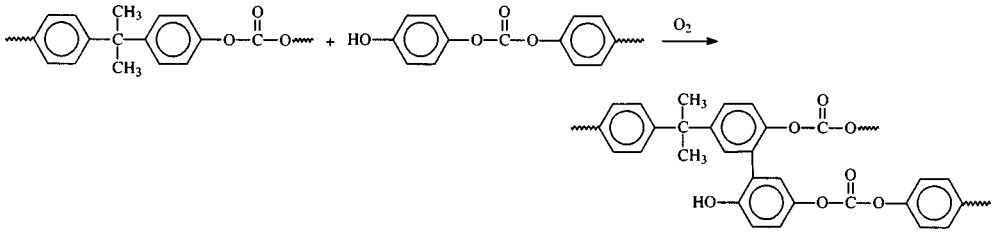
The evolution of CH_4 observed at a low level at the beginning of decomposition becomes more important at higher temperatures. Evolution of CH_4 is a part of the free-radical reactions leading to scission of the isopropylidene moiety[15] (Reaction 6).

Mass-spectrometric investigation of PC and its model compounds under mild ionization conditions showed that cyclic oligomers are the primary products of PC fragmentation.[16–19] It was proposed that ionic ester exchange is the governing process of thermal decomposition of polycarbonates. Loss of methylene or carbon dioxide resulted in the series of secondary products. McNeill and Rincon[20,21] have disputed this ionic mechanism. In their experiments, carried out under vacuum, the nature of the products evolved was in favor of the homolytic chain scission rather than hydrolysis or ester interchange. The discussion which has continued in the literature between these two groups of investigators has not given convincing preference to the ionic or the radical mechanism.



(I) (II)

Lee[6] studied the thermal decomposition of PC in air. The initial site attacked by oxygen was not clearly defined but likely it was the isopropylidene linkage. After the hydrogen from the methyl group is abstracted, an unstable radical (**I**) is formed, but it would immediately rearrange to a stable radical (**II**). This radical is then readily attacked by oxygen to form a hydroperoxide. At temperatures above 300 °C, the hydroperoxide may cleave homolytically to give a reactive hydroxyl radical and an alkoxyl radical.



(Reaction 7)

Through hydrogen abstraction, the hydroxyl radical would produce a molecule of water, and the alkoxyl radical would form a compound with a hydroxyl group. Both water and hydroxyl compounds will induce further degradation (Reactions 2 and 3).

A primary oxidation mechanism leading to the initial formation of methylene radicals which undergo rearrangement to a more stable benzylic radical was also proven by matrix-assisted laser-desorption ionization—time-of-flight (MALDI–TOF) mass spectrometry.[22] Oxidative coupling of phenol end groups with the polycarbonate chain leading to a biphenyl crosslink (Reaction 7) responsible for the formation of the insoluble gel fraction was also shown by this technique.

All the above-discussed mechanisms of thermal and thermal oxidative decomposition were supported by the analysis of volatile products. Although PC is a highly charrable polymer, the researchers paid little or no attention to the solid residue. The only investigations of PC chars which we found in the literature were carried out by Low and coworkers,[23,24] Factor[25] and Jang and Wilkie.[26] They showed that above 440 °C, a highly crosslinked structure with diaryl ester, ether and unsaturated carbonaceous bridges is formed.

FLAME RETARDANT POLYCARBONATE

Halogenated flame retardants

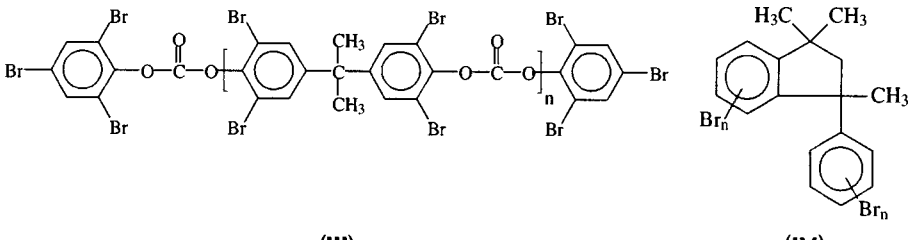
Known for many years, epoxy oligomers made from tetrabromobisphenol A are still used in polycarbonate because they minimally affect the heat distortion temperature and even show a positive effect on impact strength.[27] About 6–9 wt% of the epoxy oligomer is required for achieving V-0 rating and a thermotropic liquid crystal polyester helps to improve melt flow, so that thin-walled parts can be molded.[28] Antimony trioxide is not normally used in combination with halogen-containing additives in PC, because it causes loss of clarity.

An alternative to the epoxy oligomer is a low molecular weight polycarbonate made from tetrabromobisphenol A and end-capped with tribromophenoxy groups (**III**) or with phenoxy groups. The brominated polycarbonate oligomer is more costly but allows better physical properties to be maintained in comparison with epoxy oligomers. About 14 wt% is required in order to provide V-0 in polycarbonate.[29] Inherently flame-retarded copolycarbonate can be made by copolymerizing tetrabromobisphenol A and straight bisphenol A.[30] This copolycarbonate did not find commercial acceptance because of lower thermal properties.

Polybrominated trimethylphenylindane (**IV**) manufactured by Dead Sea Bromine Group (FR-1808) is very compatible with polycarbonate.[31] Polycarbonate keeps its transparent appearance upon addition of 15–40 wt% FR-1808.

Phosphorus-containing flame retardants

Although aromatic phosphates are currently the products of choice for flame-retarding PC-based blends, phosphate esters are rarely used in plain PC because of partial loss of clarity, tendency to stress-cracking and somewhat reduced hydrolytic stability.



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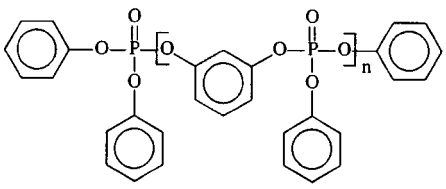

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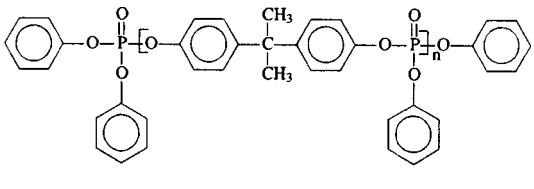


(VI)

Resorcinol bis(diphenyl phosphate) (RDP) (**V**) and bisphenol A bis(diphenyl phosphate) (BDP) (**VI**) are oligomeric phosphates manufactured by a number of flame-retardant producers in the USA, Europe, Japan and China. Both RDP[28] and BDP[32] are very efficient in PC providing a V-0 rating at only 6 wt% loading. Poly(ethylene–maleic anhydride) copolymer added to PC helps with flame retardancy, because only 2 wt% RDP is needed for V-0 rating.[33]

BDP was shown to be synergistic with poly(methyl phenylsiloxane), because 3 wt% BDP and 0.5 wt% of the polysiloxane gave a V-0 rating in PC containing 5 wt% ABS.[34] PC-containing ABS is normally more combustible than pure PC. Polysiloxane can also be copolymerized with PC giving some advantages in physical properties.[35] The blend of RDP with triphenyl phosphate (TPP) shows 'phosphorus–phosphorus synergism' because it is more effective than pure RDP.[36] V-0 has been achieved at 1.5 wt% RDP/TPP = 3:1 in PC added with 3.6 wt% ABS. In contrast, talc seems to be antagonistic with RDP, because 9 wt% RDP and 8 wt% talc are needed for a V-0 rating in PC.[37] Nanosize AlO(OH) (0.7 wt%) is also disadvantageous for flame retardancy in combination with RDP, but it helps to improve physical properties while keeping good transparency.[38]

When certain multifunctional phosphonates are added to PC, the polymer can be crosslinked to produce a flame-retardant thermoset resin. For example, low molecular weight 4-substituted phenol–formaldehyde resins were reacted with phosphonic dichlorides to obtain poly(cyclic phosphonate) resins (eg 4-phenylphenolformaldehyde phenylphosphonate (**VII**)).[39] The T_g, of the commercial polycarbonate is 150 °C but after being cured with poly(cyclic phosphonate) at 350 °C for 30 min, the T_g increased to 200 °C. When the polycarbonate was cured in the presence of 5 wt% of a poly(cyclic phenylphosphonate), the char yield increased to 45 % and it increased further to 50 % with 15 % of the phosphonates. It was believed that the polycarbonate when crosslinked with the phosphonates is more flame retardant than the non-crosslinked material.

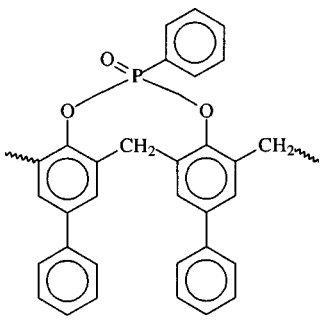
A phosphorus-containing copolycarbonate (**VIII**) was prepared via melt polycondensation of diphenyl carbonate, bisphenol A and 2-(6-oxido-6*H*-dibenz [c,e] 1,2 oxaphosphorin-6-yl)-1,4-benzenediol.[40] Owing to the rigid phosphorinane structure in the pendant group, the resulting phosphorus-containing copolycarbonates exhibited better flame retardancy, higher char yield, higher degradation temperature and thermal stability than homopolymers of polycarbonate. A high oxygen index (OI) value and UL 94 V-0 rating were achieved with a phosphorus content of 0.75 wt% and no fumes or toxic gas emissions were detected.

Red phosphorus is not particularly active in this PC; 4 wt% is needed for V-0 rating.[41] Comparison of this phosphorus concentration with the phosphorus loading in RDP- or BDP-based formulations makes red phosphorus appear very disadvantageous with respect to these two phosphates. Phosphate salts are also relatively ineffective in PC, eg 19 wt% ethylenediamine phosphate and 4 wt% vermiculite are required for V-0 performance.[42]

Sulfur-containing additives

In the early 1970s, it was shown in patents[43] that alkali metal perfluoroalkylsulfonates are highly effective flame retardants for PC. At General Electric, it was found that very low additions (<1 wt%) of alkali or earth alkali metals salts of certain arylsulfonates provide self-extinguishing performance to polycarbonate. Although numerous metal sulfonates were tested and patented[44] (most patents show Victor Mark as inventor) two salts were selected for further commercial development: potassium diphenylsulfone sulfonate (KSS) (**IX**) and sodium trichlorobenzene sulfonate (STB) (**X**).[45] Later, another very efficient salt, potassium perfluorobutane sulfonate (KPFBS) (**XI**), was redeveloped at 3M laboratories. All these sulfonates are particularly effective in polycarbonates providing V-0 ratings at as low as 0.05–0.1 wt% loading.[46–48]

Although potassium sulfonates are used at very low loading, they can cause some hazing of polycarbonate. The sulfonate (**IX**) (KSS) allows the greater clarity. Also, co-addition of octaphenylcyclotetrasiloxane,[49] poly(methyl siloxane) or poly(methylphenyl siloxane)[50] helps to prevent hazing while fire retardant performance does not suffer. If clarity of the polycarbonate is not important, poly(tetraflurorethylene) (PTFE), carbon black, organic fibers, mineral fillers and other polymers can enhance the FR properties of the sulfonates.[45] KSS (**IX**) is mostly used in halogen-free transparent



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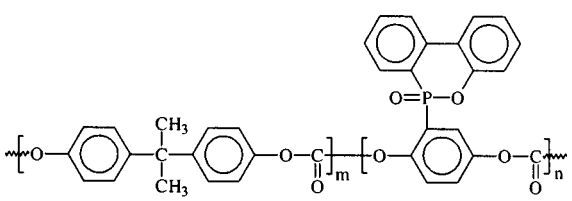

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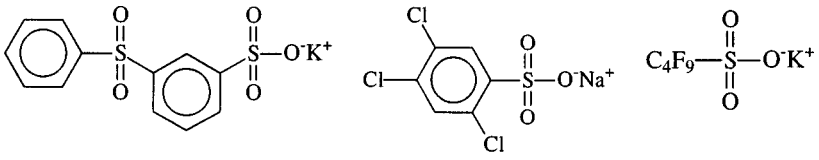


(IX) (X) (XI)

applications, whereas STB (**X**) either by itself or in combination with brominated polycarbonate is often the FR of choice when halogen is acceptable for the application. The brominated polycarbonate oligomers are used at 1–4 wt% along with 0.5 wt% STB.

Poly(styrenesulfonic acid sodium salt) (**XII**) was shown to work at the relatively high level of 10 wt%; however it gave good physical properties and only moderate thermal destabilization of PC.[51,52] A series of fluoroalkylsulfonamidate salts, eg (**XIII, XIV**) was recently synthesized at 3M and tested in PC.[53] These fluoroalkylsulfonamidates are effective at only 0.04 wt% providing a V-0 rating in the UL-94 test.

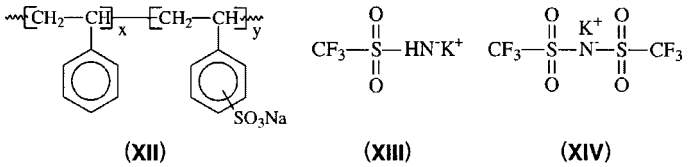
The mechanism of the flame-retardant action of these sulfonate salts is not completely clear. Ballistreri *et al*[54] studied the dependence of OI on the concentration of potassium 2,4,5-trichlorobenzene sulfonate and compared it with another combustion index where N_2O is used as an oxidizer instead of oxygen (NOI). This method allows the modes of action of the flame retardant in the gas phase and condensed phases to be distinguished. It was found[54] that OI and NOI traces have parallel trends, implying that the sulfonate acts in the condensed phase and that the contribution to the flame inhibition in the gas-phase is negligible in spite of the presence of chlorine in the molecule. The thermogravimetric runs revealed that the aromatic sulfonate decomposes at about 400–500 °C, ie in the same temperature range as polycarbonate. However, even at 1 % loading level, the sulfonate significantly accelerates the thermal decomposition rate of polycarbonate. In another study,[55] using kinetic analysis of the thermogravimetry runs, it was shown that KSS (**IX**) also significantly destabilizes PC.

Mass-spectroscopic analysis of the evolved products showed that the aromatic sulfonates induce only a change of the abundance of products of thermal degradation of PC and no new products were detected.[54] It was believed that aromatic sulfonates promote isomerization of polycarbonate (Reaction 1), which leads to higher concentrations of CO_2 and dilution of combustion products as well as faster crosslinking and char formation. In another study,[56] it was speculated that aromatic sulfonates accelerate Fries-type rearrangement (Reaction 5), which results in faster decomposition and crosslinking as well. The temperature just below the burning surface was measured by a thermocouple embedded in plain PC and in PC-containing potassium-2,4,5-trichlorobenzenesulfonate.[54] It was noted that in the presence of aromatic sulfonate the temperature remained low for a relatively long time, whereas for the pure PC sample it reaches high values in a short time. Although these results have been interpreted as formation of a thermally insulating char, the explanation can be different and strictly related to the acceleration of thermal decomposition and effective removal of the heat due to the melt flow. Taking into consideration the very small amount of aromatic sulfonate used, this explanation seems more plausible than charring.

Siloxanes

The beneficial effect of siloxanes, eg octaphenylcyclotetrasiloxane or branched methylphenyl siloxanes, in combination with metal salts of organosulfonic acids was discovered a long time ago at the GE laboratories.[57] In view of the halogen-free approach taking more attention, branched methylphenyl siloxanes were recently reexamined and studied in detail.[58–66] Normally 5 wt% of the branched siloxane in combination with PTFE provides a significant increase of OI from 26 to 33–40[59,60] and only 2 wt% is required for a V-0 rating in the UL-94 test.[61,62,66] As was mentioned above, octaphenylcyclotetrasiloxane[49] or branched methylphenylsiloxanes[50,52,65,67] are preferably used in combination with potassium or sodium salts of organosulfonic acids. If branched methylphenylsiloxane is added at a relatively high level (10 wt%), then simple alkali metal halides, eg 0.015 wt% NaCl, help to ensure a V-0 rating in the UL-94 test.[64] Branched phenylmethylsiloxanes showed utility not only in extinguishing small flames (as in UL-94 and OI), but also in decreasing the heat release rate and smoke evolution as measured by Ohio State University (OSU) calorimeter.[68]

Poly[(phenyl silsesquioxane)-*co*-(dimethylsiloxane)] (**XV**) apparently shows the benefits of siloxanes and nanoparticles simultaneously, because it has rigid and



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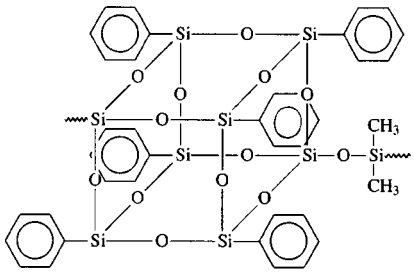

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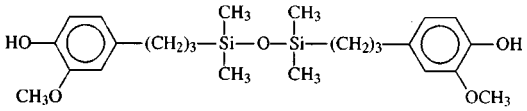
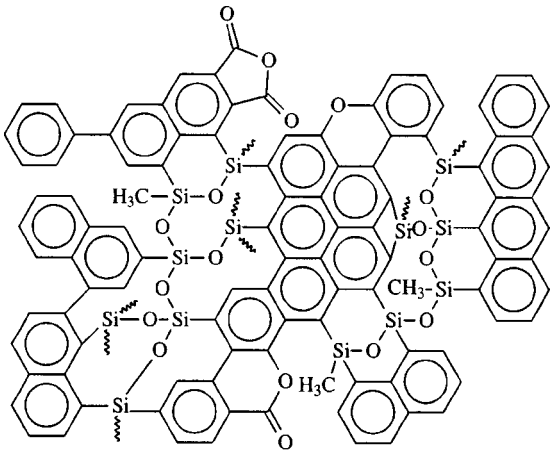


(XVI)

bulky fragments in the polymeric chain. Thus 5 wt% of this or related silsesquioxane provide a V-0 rating in PC;[69] however if the effective siloxane is used in combination with sodium toluene sulfonate (0.03 wt%) only 0.8 wt% is required for a V-0 rating.[70] A mixture of siloxanes and silanes upon processing can give crosslinked localized polysiloxanes, which may be considered as nanoparticles in PC.[71] Another way to improve the physical properties is copolymerization of phenol-terminated dimethylsiloxanes (**XVI**) in the polycarbonate chain.[72]

The mechanism of flame-retardant action of branched methylphenylsiloxanes was assessed by Iji and Serizawa.[73,74] It was found that, because of the inclusion of the aromatic groups in the siloxane, it becomes significantly more soluble and more easily dispersed in PC than the purely aliphatic siloxane. The low reactivity of the terminal groups also facilities dispersion by preventing gelation. Using X-ray photoelectron microscopy, it was shown that the siloxanes tend to migrate from the inside of the PC resin to the surface during combustion and quickly accumulate on the surface. Such movement resulted from differences in viscosity and solubility between the siloxane and the PC at high temperatures. The branched methylphenylsiloxanes showed much higher thermal stability and tendency to charring than linear methyl siloxanes. This was attributed to the presence of aromatic groups, which can form condensed aromatic compounds with high flame resistance (hypothetical structure **XVII**), and also attributed to its branched structure which prevents unzipping-type depolymerization.

An alternative mechanism for fire retardant action of methylphenylsiloxanes, which actively involves polycarbonate in the charring process was suggested by Hayashida *et al*.[75] In the gas chromatographic pyrogram of the solid residue of flame-retardant PC, which was insoluble because of crosslinking, the peaks

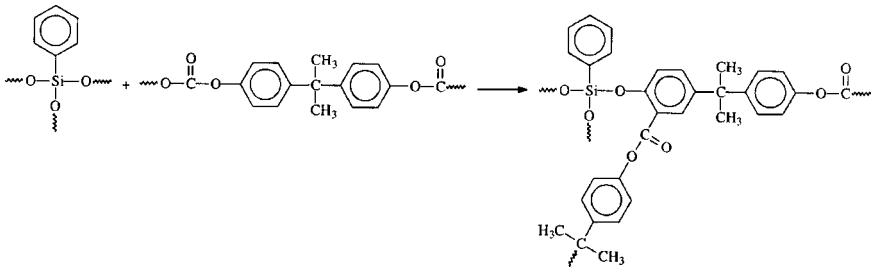


(XVII)

reflecting decarboxylation (Reaction 1) or Fries rearrangement (Reaction 5) were observed in much larger intensity than those on the pyrogram of plain PC.

A possible formation of the carboxyl-branching structure during combustion of PC with added methylphenyl branched polysiloxane is shown in Reaction 8. In this case, the silyl group attacks the OH groups generated during the simultaneous Fries rearrangement and as a result, the phenyl silyl ether crosslink structure is formed.

In contrast, Nishihara *et al*[76,77] showed that linear polysiloxanes are more advantageous flame retardants in PC than branched polysiloxanes. It was conversely shown in this study that the aromatic units and branched structures are of little importance. The flame retardant effect of the linear polysiloxanes was found to be superior to that of branched structure, apparently because of their high mobility in the plastic under combustion. In addition, it was claimed that linear polysiloxanes addition does not affect PC recyclability, whereas the branched structures tend to lower recyclability due to interaction of PC with the



(Reaction 8)

numerous chain ends of branched polysiloxane and eventual crosslinking.

Miscellaneous

Although boron-containing compounds are not effective flame retardants by themselves in PC, they are synergistic in combination with polysiloxanes. For example, the use of 2 wt% boron oxide helped to pass V-0 rating in PC/polysiloxane copolymer containing 5 wt% ABS.[78] In another study a silyl borate was made by reacting an alkylsilanol fluid with boron oxide.[79] This compound was used in combination with some (2 wt%) bisphenol A bis(diphenyl phosphate) (**VI**) in order to cut after-flaming time in PC containing small amounts of ABS.

Two boronic acids, 1,4-benzenediboronic and 1,3,5-benzenetriboronic acids were made using a nickel catalyst and pinacol borane.[80] Loadings of 10 wt% in PC gave a UL-94 V-2 rating, little different from that of PC with no additives. However, loading of 2.5 wt% of diboronic acid gave a V-1, and a 5 wt% loading gave a V-0 result. It is interesting that large amounts of char were seen to form during the flame test at all concentrations. It was suggested that the boroxine network is formed already during blending with the polymer (eg 1,4-benzenediboronic acid in Reaction 9) and then it assists with the char formation during combustion.

At Mitsui laboratories in Japan, diguanamines (eg (**XVIII**)) or their methylol derivatives were recently found efficient in polycarbonate at 10 wt%.[81] In order to ensure a V-0 rating, co-addition of 3 wt% cyanuric acid was required. Guanidine sulfate or guanidine carbonate found use at very low loading (0.01 wt%) in PC sheeting materials used for construction which required passing the French radiant panel test NF-P-92-505.[82] Poly[(1,4-cyclohexanedimethanol)-*co*-(1,4-dicarboxylate)][83] (**XIX**) manufactured by Eastman or pentaerythritol tetrastearate[84] were also found beneficial in this test by preventing flammable drips.

PC-BASED BLENDS

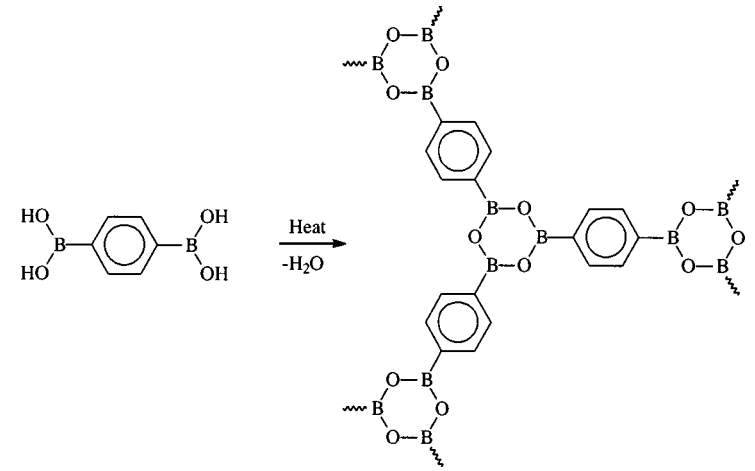
Halogenated flame retardants

Similar to plain PC, brominated polycarbonate oligomers[85] or polybrominated epoxy resin oligomers[28] are used in PC/ABS blends; however, this choice is rather infrequent. Tetrabromobisphenol A-based polycarbonate (58 wt% Br) is not compatible with PC/ABS at the 80:20 PC/ABS ratio.[86] Methacrylate–butadiene–styrene (MBS), ethylene–vinyl acetate (EVA), or styrene–maleic anhydride (SMA) can be used to improve the physical properties of PC/ABS containing brominated PC oligomer. Contrary to the phosphorus-containing flame retardants, halogenated oligomers do not provide advantages of flow enhancement, but flow properties can be optimized by varying the composition of the ABS. For example, decreasing the acrylonitrile content results in decrease of shear viscosity in PC/ABS flame-retarded with brominated epoxy oligomer.[87] Brominated epoxy oligomer may help with tensile and flexural strength of PC/ABS blend, however impact strength will suffer because of the presence of reactive epoxy groups.[88]

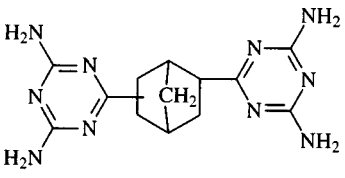
Phosphorus-containing flame retardants

Phosphate esters

There are at least five commercial aromatic phosphates which are or were widely used in PC/ABS. The most cost-effective additive is triphenyl phosphate.[89–93]



(Reaction 9)



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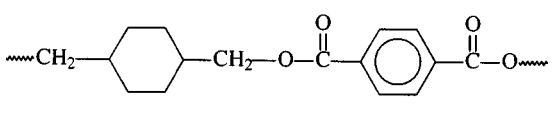

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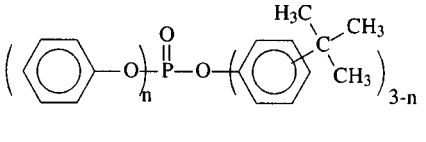

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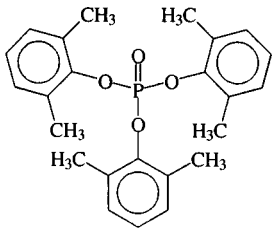


(XXI)

This additive is effective in PC/ABS blend at 12–18 wt% depending on the PC:ABS ratio.[94] Co-addition of a high charring polymer helps to increase efficiency of TPP. For example, only 4 wt% TPP is needed in PC/HIPS (3:2) if 7 wt% poly(phenylene ether) is added.[95] Combustion performance and Vicat softening temperature of PC/ABS composites could be improved by co-addition of various natural alumosilicates and in particular of zeolites.[96]

Although TPP is reasonably effective as a flame retardant, it creates serious problems during compounding because of its relatively low melting point[97] (causing bridging in the feeding equipment) and relatively high volatilization[98] (causing loss of the additive during extrusion and molding). Mixed tri(*t*-butylphenyl phenyl) phosphate (**XX**) has advantages over TPP, because it is liquid, has better retention in the resin and better hydrolytic stability[99] and resistance to cracking,[100,101] however its volatility is still relatively high.

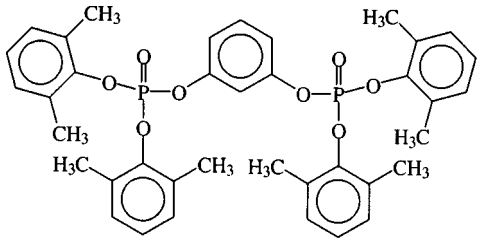
Another commercial aryl phosphate, tris(2,6-xylyl) phosphate (**XXI**), is often cited in the patent literature, especially from Japan.[91,92] This trixylyl phosphate is slightly less efficient than other aromatic phosphates, since 12–15 wt% is required for a V-0 rating in the UL 94 test, however it has obvious advantages of high hydrolytic stability. The extent of commercial use of this aromatic phosphate in PC/ABS blends is unclear.

Bridged aromatic diphenyl phosphates seem to be finding much broader application because of good thermal stability and low volatility. Resorcinol bis(diphenyl phosphate) (RDP, **V**) is a mixture of oligomers with two to five phosphorus atoms, but with distribution shifted towards mostly the diphosphate.[102] In the commercial PC/ABS blends where the ABS content normally does not exceed 25 %, RDP provides a V-0 rating at 8–12 wt% loading.[103–106] PTFE is a necessary component of the formulation, usually at <0.5 wt% loading, to retard dripping.[107,108] RDP is often used in PC/PET and it is very effective. For example, only 4 wt% RDP is required in PC/PET (5:1) in order to pass UL 94 at a V-0 rating.[109] A triple PC/ABS/PET blend flame retarded with RDP has been patented by Bayer.[110] It was shown that presence of PET helps to improve toughness compare with similar PC/ABS blend without PET. RDP is also more efficient in PC/HIPS blend than in PC/ABS. For example, RDP helps to pass V-0 rating PC/HIPS (4:1) at only 7–10 wt% loading.[111,112]

RDP suffers hydrolytic instability, which leads to deteriorated aging performance of PC-based blends because PC is sensitive to acids. The improved properties of RDP are achieved by addition of acid scavengers like epoxies,[113] epoxidized soybean oil,[114] oxazolines, or ortho esters (eg triethyl orthobenzoate)[113] or residual MgO remaining from the catalyst after synthesis.[115]

In the early patent to Bayer[116] it was shown that co-addition of highly dispersed inorganic materials like TiN (70 nm), or TiO_2 (5 nm) or boehmite (12 nm) helps significantly decrease the after-flaming time of PC/ABS compositions containing RDP. Later it was noticed that some inorganic co-additives like highly dispersed silica[117] or talc[118,119] or zeolite[89] help to improve physical properties, especially high temperature dimensional stability. Co-addition of aluminum flakes[120] or organoclay[121] provide better flame retardancy by decreasing after-flaming time.

Bisphenol A bis(diphenyl phosphate) (BDP, **VI**), commercially available from several manufacturers, is more thermally and hydrolytically stable than RDP (**V**).[91] However, it is significantly more viscous and therefore more difficult to handle. It has less phosphorus content and as a result is less effective than RDP. In some formulations BDP shows higher HDT.[122,123] PC/ABS with ABS content $\leqslant$ 25 wt% usually requires $\geqslant$ 12 wt% BDP with co-addition of PTFE in order to secure a V-0 rating.[124–127] Although BDP is hydrolytically very stable, further improvement of long-term stability,[128] and as a result of aging performance, of PC/ABS[129] can be achieved by using epoxy acid scavengers. Co-addition of a mineral filler in the form of wollastonite fibers[130] or carbon fibers[131] or a highly charring polymer, phenoxy resin,[132] helps with impact resistance and also cuts after-flame time.



(XXII)

Resorcinol bis(di-2,6-xylyl phosphate) (RBXP, **XXII**) is another diphosphate manufactured on a commercial scale, but exclusively in Japan. Because

of steric hindrance of 2,6-xylyl groups this product shows higher hydrolytic stability than BDP. Its fire retardant efficiency is comparable to BDP, because it provides V-0 rating in PC/ABS blends at 12–16 wt% loading.[92,133,134] Because both PC and PET are acid sensitive, use of more hydrolytically stable tris(2,6-xylyl phosphate) (**XXI**) or RBXP[109,135] or similar sterically hindered phosphates[136] is preferable rather than RDP (**V**) or BDP (**VI**) in PC/PET blends. In hydrolytically critical applications tris(2,6-xylyl phosphate) (**XXI**)[137] or RBXP (**XXII**)[138] are also preferable in PC/HIPS blends. In contrast to RDP and BDP, RBXP is a solid which is often considered as an advantage by compounders, however its relatively high cost retards significant use of this product.

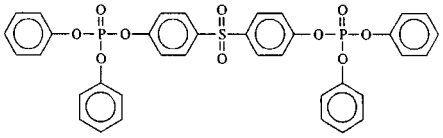
Increasing the average molecular weight of RDP[139] or BDP[140,141] gives some improvement of physical properties, however the additives become very viscous and difficult to handle. Although the phosphorus content of oligomeric RDP and BDP increases with increase of average molecular weight, this increase apparently does not result in an improvement of fire-retardant performance. However, a combination of RDP or BDP with TPP[142–145] or mixed tri(*t*-butylphenyl diphenyl) phosphate (**XX**),[142] or even a combination of BDP and RDP,[146] are more advantageous in terms of flame-retardant efficiency because the loading can be reduced to 10 wt% while still preserving the V-0 rating. This is probably related to the combination of condensed phase and gas phase actions of aromatic phosphates.[98]

Various other aromatic diphosphates or oligomeric phosphates have been described in the technical literature. For example, bisphenol S bis(diphenyl phosphate) (**XXIII**) is more effective than RDP or BDP.[147] This product did not find commercial application, probably because of relative hydrolytic instability. Mixed oligomeric phosphates, for example resorcinol–bisphenol A phenyl phosphates (**XXIV**) or bisphenol A–bisphenol S phenyl phosphates, were also synthesized.[148] Their efficiency was not higher than that of RDP and BDP, but these products showed some benefit to the physical properties of the resultant PC/ABS.

Biphenyl bis(diphenyl phosphate) (**XXV**) is one of the most thermally stable bisphosphates. Although it is applied at the same level as BDP (11–14 wt%) for V-0 rating, it provides essential advantages of high temperature performance in PC/ABS.[149–151] A combination of biphenyl bis(diphenyl phosphate) with a phosphazene seems to be even more advantageous in terms of thermal properties.[152] Combinations with diphenyl naphthyl phosphate provided good charring performance and high thermal properties.[151]

A number of bisphosphates with cycloalkyl structures in the bridging units (eg (**XXVI**)) were recently patented by Bayer.[153] These bisphosphates are not particularly effective and provide a V-0 rating in PC/ABS = 5:1 at a loading $\geqslant$ 12.5 wt%. In contrast, pentaerythritol spirophosphates (**XXVII** and **XXVIII**) are very efficient in PC/ABS.[154] For example, only 3.8 wt% of the spirophosphate in combination with 3.5 wt% TPP is enough for a V-0 rating in PC/ABS (4:1). Relatively high volatility and probably some water solubility apparently prevent these compounds from being commercialized.

Numerous alkylphenyl diphosphates are described in the patent literature[155,156] (eg (**XXIX**)[156]). Efficiency of these diphosphates is lower than most of the



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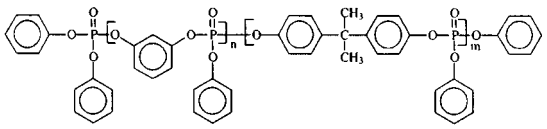

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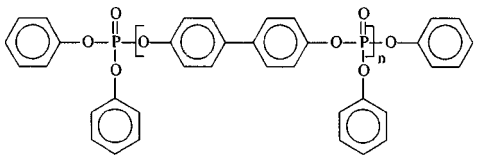

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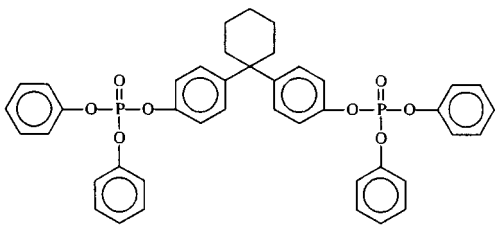

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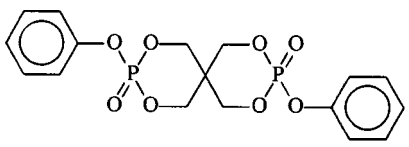

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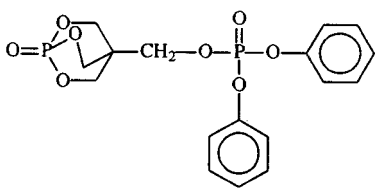

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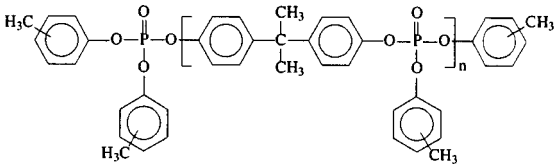

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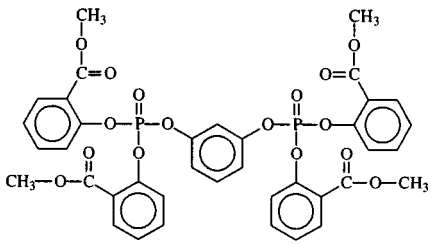

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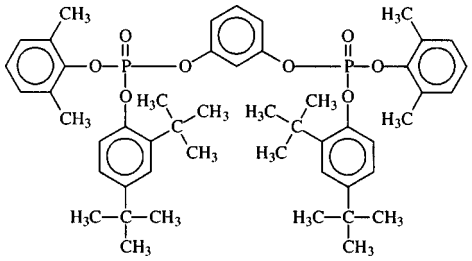

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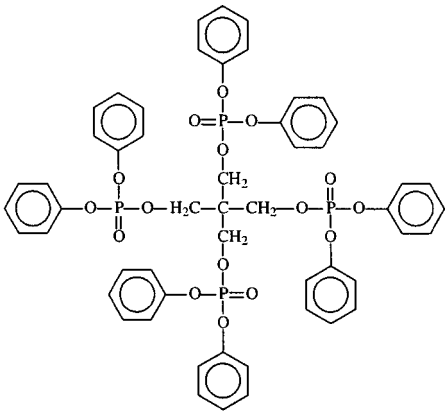


(XXXII)

commercial bisphosphates; however they show reasonable performance in combination with highly volatile phosphates like TPP. Rhodia recently patented phosphates of salicylic acid[157] (eg (**XXX**)), however these phosphates give only a V-2 rating in PC/ABS even at 16 wt% loading.

Improvement of the hydrolytic stability of bisphosphates was achieved by incorporation of *o,p-tert*-butylphenyl groups[158] (eg (**XXXI**)). This compound in spite of lower phosphorus content is surprisingly more effective than the analogous xylenyl phosphate (**XXII**). Another approach to make hydrolytically stable esters has been to use a branchy bridging group. For example, pentaerythritol tetrakis(diphenyl phosphate) (**XXXII**) and trimethylolpropane tris(diphenyl phosphate) were tested in PC/ABS (3:1), where they showed V-0 ratings at 11.5–16.5wt%.[159]

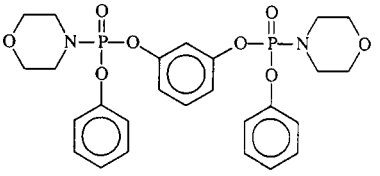
A series of new bisphosphamidates with one or few phenyl groups replaced with morpholine rings were recently prepared in the Cheil laboratories[160,161] (eg (**XXXIII**)). They are effective in PC/ABS (4:1) at 12 wt% loading. Moreover, in combination with epoxy novolac (8 wt%) they provide high OI (39) and a V-0 UL 94 rating in PC/ABS blend low in PC (2:3).[162]

A wide variety of phosphate ester salts (eg magnesium salt of diphenyl phosphoric acid (**XXXIV**)) were claimed as synergists with bisphosphates.[163] Co-addition of 0.1–0.2 wt% of these salts helped to cut the loading of RDP to 9 wt%. A magnesium salt (**XXXIV**) was also suggested as a main flame-retardant component for the PC/ABS blend;[164] however the loading required for passing the UL-94 test was not defined. Tetraphenyl pyrophosphate (**XXXV**) was found[165] to be a very efficient co-additive to RDP and TPP, because it helped significantly to decrease after-flaming time at a loading of only 1.0 wt%. Nevertheless, practical use of this co-additive seems to be doubtful because of high hydrolytic instability.

Mechanism of fire retardant action of aromatic phosphates

Levchik *et al*[166,167] studied flammability of PC/ABS with different ratios of PC to ABS flame retarded with TPP, RDP or BDP. All three phosphates showed comparable fire-retardant efficiency at the same phosphorus level as measured by OI. However, TPP was less efficient than RDP or BDP in the UL-94 test. In cone calorimetry, aromatic phosphates provided only a moderate decrease of the peak heat release. However, they efficiently increase the time to ignition.

Intuitively, it was always believed that the mechanism of fire-retardant action of aromatic phosphates



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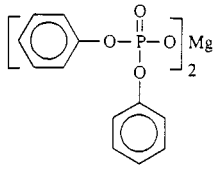

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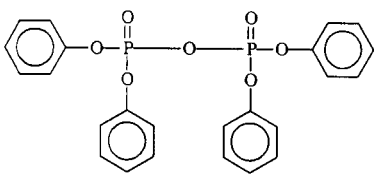


(XXXV)

relates to the charring of the PC component of the blend.[168] Because the fire-retardant efficiency of aromatic phosphates strongly depends on the content of polycarbonate in PC/ABS blends, this is considered as indication of condensed phase action.[166] However, the complex dependence of OI on the composition of PC/ABS blend and increase of CO evolution in the presence of aryl phosphates are in favor of gas phase activity.

Murashko *et al*[169,170] studied the mechanism of fire retardant action of RDP in PC/ABS blends. They found that pure RDP is relatively effective in PC, but it shows only moderate action in ABS. Systematic testing of various co-additives to RDP showed that gas-phase-active co-additives (melamines) are not effective or even antagonistic with RDP, whereas condensed-phase-active co-additives which provide additional char or improve char structure have a positive effect. Novolac shows outstanding behavior by suppressing dripping and improving char.

It was found[170] that phosphorus accumulates in the condensed phase during thermal decomposition or combustion. Thermogravimetry proved that RDP protects the char from oxidation at high temperature, whereas condensed-phase-active co-additives increase the char yield. It was shown that polycarbonate undergoes Fries-type rearrangement (Reaction 5) upon thermal decomposition, and aromatic phosphates may catalyze these rearrangements. RDP reacts with PC probably through trans-esterification which leads to accumulation of phosphorus and additional charring of PC (Reaction 10).

The gas-phase activity of aromatic phosphates has been always disputed in the literature. For example, Carnahan *et al*[171] and Bright *et al*[172] reported a decrease in fire-retardant efficiency with increasing molecular weight of the aromatic phosphates (oligomerization), which was related to the absence of a volatile phosphate fraction. In contrast, Deanin and Ali[173] showed that the flame-retardant efficiency of poly(aryl phosphate)s increases with increase of molecular weight. It is also well established[167,174] that RDP is more efficient in PC/ABS than the more volatile TPP.

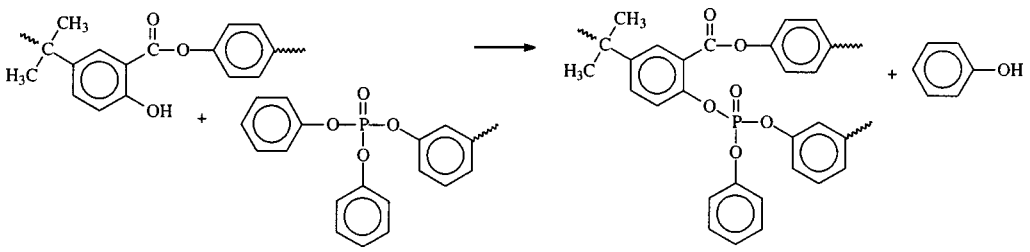
Levchik *et al*[98] carried out a cone calorimeter study of PC/ABS blend fire-retarded with RDP and RDP/TPP (3/1) at heat fluxes of 35 and 75 kW m^{-2}. The RDP/TPP combination showed lower peak values of heat release rate than RDP at a heat flux of 35 kW m^{-2}, which was related to the gas phase contribution of TPP. However, the order of fire retardant efficiency reversed at the heat flux of 75 kW m^{-2}, eg RDP alone showed lower peak values of heat-release rate than RDP/TPP. The gas phase contribution of TPP apparently becomes unimportant or even negative at the high temperature of the flame.

A possible explanation of this phenomenon comes from the reversible nature of the inhibition action of some flame retardants in the gas phase.[175] Phosphorus-containing species, which normally inhibit flame propagation,[176] become effective catalysts of combustion in the high temperature flames.[177] TPP can apparently reverse its inhibition action, or at least become ineffective in high temperature flames. This also explains synergistic action between low volatility and high volatility phosphates eg RDP/TPP or BDP/TPP mixtures.[142,145] RDP or BDP, which are mostly condensed phase active additives, tend to involve more PC into charring, thus decreasing fuel supply to the flame and effectively decreasing the temperature of the flame. TPP becomes more and more effective in the gas phase with decreasing temperature of the flame.

Brominated phosphate esters

These esters were developed at FMC laboratories in the 1980s aiming at PC-based blends. A brominated triphenyl phosphate coded as PB-460, later identified as tris(2,4-dibromophenyl) phosphate, was compared with plain triphenyl phosphate (TPP).[178–180] The compositions PC/ABS (3:1) containing 6 wt% brominated phosphate pass the UL-94 test with a V-0 rating whereas, with PC/ABS ratios down to 1:1, 14 wt% of brominated phosphate was required. In contrast, 14 wt% TPP was needed for a V-0 rating in PC/ABS (3:1), while PC/ABS (2:1) failed the UL-94 test at 14 wt% TPP. Cone calorimetry showed a significantly longer time to ignition, a lower total heat release and a lower peak heat release rate for the brominated phosphate. Mechanical properties were also assessed. The brominated phosphate, PB-460, had a heat distortion temperature of 105 °C which is 17 °C higher than for the TPP-based formulation. The phosphorus-bromine-based product had also a higher flexural strength. Because of relatively low volatility, the brominated phosphate does not tend to 'juice out'.

Brominated triphenyl phosphate esters were found particularly effective in PC/PET.[181] It was found that PC/PET (2:1) blend with an oxygen index



(Reaction 10)

of 32 requires 16.7 wt% brominated polycarbonate oligomer, or 12 wt% TPP, or only 6 wt% PB-460. The brominated phosphate gave 40–50 % more char by weight than when bromine, phosphorus or blends of the two were used.[182] Analyses of the chars showed no bromine, but considerable amounts of phosphorus. It was believed that the polycarbonate and the PET undergo transesterification during pyrolysis above 400 °C and the brominated phosphate acts as a transesterification inhibitor or stabilizer. When the brominated phosphate was used the char had a fine porous structure and thick solid skin, whereas other chars showed poorer structure and less to no skin.

Phosphine oxides and phosphonates

Aromatic phosphine oxides or phosphonates are often solids and inherently less plasticizing than phosphates, therefore they could be beneficial for high temperature dimensional stability. Phosphine oxides and phosphonates are more hydrolytically stable then phosphates, therefore they may perform better in the long-term aging tests. Nevertheless, these two classes of phosphorus-containing products are relatively rarely tested in PC/ABS which is related to their low or negligible solubility in PC/ABS. Insoluble particles usually deteriorate the impact performance of PC and PC-based blends.

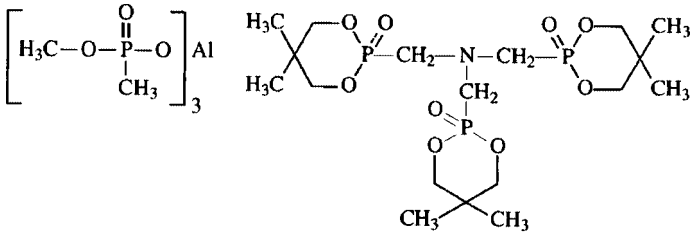
Triphenyl phosphine oxide was tested in PC/ABS (4:1) in the Bayer laboratories and was found efficient in the UL 94 test for V-0 rating at the relatively low loading of 10 wt%.[183] The aluminum salt of methyl methylphosphonic acid (**XXXVI**) showed very high efficiency, providing a V-0 rating at only 6 wt%.[184] However, in spite of a short commercial introduction by Ciba, it was not successful and has been removed from the market. A tricyclic phosphonate (**XXXVII**) relatively rich in phosphorus (18.5 wt%) was tested alone[185] or in combination with an inorganic co-additive, AlO(OH)[186] or aromatic phosphates, RDP/TPP.[187] Although this phosphonate is relatively efficient, showing a V-0 rating at 10.8 wt% it does not dissolve in PC/ABS.

Phosphorus–nitrogen containing products

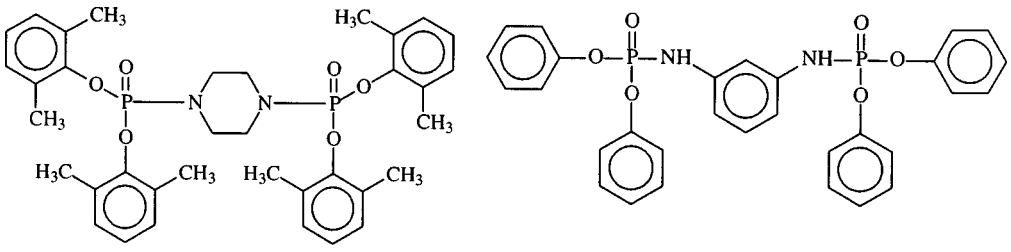
Phosphorus–nitrogen-containing products were not of high interest in PC/ABS until recently. This is related to the miniaturization of electronic devices and the growing demand for polymeric materials with better high temperature dimensional stability. Since most of phosphoramides are high melting solids it was thought that they may allow retention of the high heat distortion temperature (HDT) of PC/ABS, which suffers from addition of plasticizing aromatic phosphates.

Recently, GE patented a series of bisphosphoramidates with a piperazine bridging unit (eg (**XXXVIII**)).[188–190] These products are effective in PC/ABS (V-0 rating) at 12 wt% and as expected they provided high HDT. Compounds containing these bisphosphoramidates performed satisfactory not only in the UL-94 test but also in the Glow Wire Test at 960 °C.[191,192] Synergism was shown with boron phosphate,[193] potassium diphenylsulphone 3-sulfonate or organoclay.[193,194] A phosphoramidate with a 1,3-phenylenediamine bridging group (**XXXIX**) was also recently tested in PC/ABS and found efficient at *ca* 1 wt% phosphorus content, which corresponds to 12 wt% loading.[195]

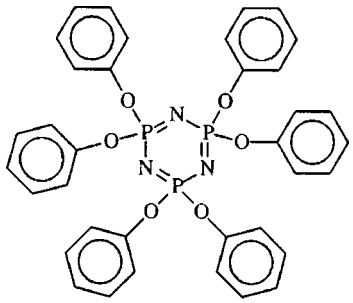
Cyclic phenoxyphosphazenes (eg hexaphenoxytricyclophosphazene (**XL**)) are thermally stable phosphorus–nitrogen products. The blend consisting of mostly tri- and tetraphosphazenes as well as some large rings was found effective in PC/ABS at 12–5 wt% loading.[196,197] Some of these cyclophosphazenes may be finding commercial use in the Far East. Aromatic bisphosphates (RDP or BDP) or monophosphates (TPP) were found to be synergistic with the cyclic



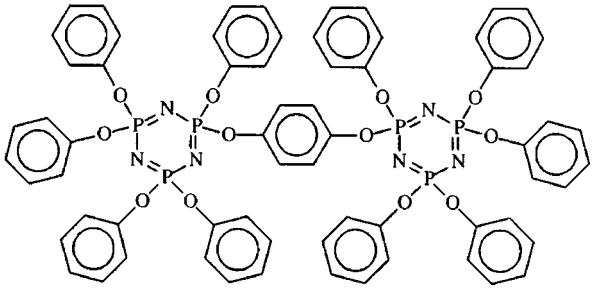
(XXXVI) **(XXXVII)**



(XXXVIII) **(XXXIX)**



(XL)



(XLI)

phosphazenes.[198,199] Bridged cyclic phenoxyphosphazenes (eg hydroquinone-bridged bistricyclophosphazene (**XLI**)) showed higher efficiency (11 wt%) than the blend of cyclic phosphazenes.[200] The bridged cyclophosphazenes are also synergistic with aromatic bisphosphates.[201] Cyclic phosphazenes with the reactive OH groups on the phenyl ring can be reacted in the polycarbonate polymeric chain.[202]

Miscellaneous

Red phosphorus is very efficient in PC/ABS blends. At a loading as low as 0.7 wt% in combination with 9 wt% talc it provided a V-0 rating in PC/ABS = 7:3.[203] Very small amount of natural China tannin is effective in PC/ABS because it helps to achieve HB rating at 1 wt% loading.[204] Mica can be used in PC/ABS as a filler and flame retardant additive simultaneously. According to Pastorini and Nunes[205] 25 wt% is an optimum loading of mica, which provides good physical properties and low flame spread.

There is contradicting information in the patent literature regarding the efficiency of silicone-based products in PC/ABS blends. The patents show that silicones are effective in PC/PET but not in PC/ABS blends. For example, branched methylphenylsiloxanes[63] or branched methyl aminosiloxanes[206] are effective in PC/PET at the low loading of 3 wt%. Nevertheless, a recent patent to NEC[58] shows that branched methylphenylsiloxane at 4 wt% helps to increase OI from 19 to 26 in a PC/ABS blend. A similar polysiloxane at 13 wt% provides a V-0 rating in PC/ABS (9:1).[207] A linear or cyclic phenylpolysiloxane also shows a V-0 rating in PC/ABS (3:2) (a low in PC formulation) at only 10 wt% according to a recent patent to Wacker-Chemie and Asahi Kasei.[208] Only 2 wt% of phenylmethyl siloxane with some residual Si–H groups and 0.1 wt% KPFBS (**IX**) apparently ensure a V-0 rating in PC/ABS (4:1).[209] The only publication in the recent literature on use of silicone-based flame retardants in PC/HIPS is a patent to Asahi Kasei, showing that 13 wt% of poly(methyl siloxane) or mixed poly(methylphenylsiloxane) provides a V-0 rating in PC/HIPS (9:1) at 13 wt% loading.[210]

CONCLUSIONS

Polycarbonate is a thermally stable engineering resin which is relatively difficult to ignite. Depending on temperature, the thermal decomposition of PC involves both ionic and free-radical processes. PC undergoes extensive crosslinking when heated with continuous removal of volatile products or in an open atmosphere. It is believed that the carbonate group can rearrange into pendant carboxyl group which may further decarboxylate with evolution of carbon dioxide. The phenoxybenzoic acid groups formed during this rearrangement are actively involved in the crosslinking. A highly crosslinked structure with diaryl ester, ether and unsaturated carbonaceous bridges is formed at a high temperature.

Epoxy oligomers and polycarbonate oligomers made from tetrabromobisphenol A have a long-standing history of use as flame retardants in polycarbonate. Potassium diphenylsulfone sulfonate, sodium trichlorobenzene sulfonate and potassium perfluorobutane sulfonate are effective in polycarbonate at one tenth of a per cent level and these salts are used on a commercial scale. Mechanistic studies showed that the sulfonate salts are mostly active in the condensed phase where they strongly destabilize PC upon heating thus promoting fast decomposition and melt flow which removes heat.

Although the fire-retardant efficiency of polysiloxanes has been known for a long time, recently this class of products is gaining special attention because of demands for halogen-free flame retardants. Branched methylphenyl siloxanes were reexamined and studied very attentively and it was found that because of the presence of aromatic groups these siloxanes are more soluble and easily dispersed in PC than aliphatic siloxanes. The mechanistic studies proved that the siloxanes tend to migrate from the inside of the PC resin to the surface during combustion and quickly accumulate on the surface. Phosphate esters are rarely used in plain PC because of partial loss of clarity, tendency to stress-cracking and rather low hydrolytic stability.

Aromatic phosphates comprise the class of the most widely used flame retardants in PC/ABS blends. Triphenyl phosphate and mixed tri(*t*-butylphenyl phenyl) phosphate are reasonably effective in PC/ABS and are used commercially, however they have the disadvantage of relatively high volatility. Bridged aromatic diphenyl phosphates, especially resorcinol bis(diphenyl phosphate) and bisphenol A bis(diphenyl phosphate) have found much broader application

than monophosphates because of good thermal stability, high efficiency and low volatility. Resorcinol bis(di-2,6-xylyl phosphate) is another diphosphate manufactured on a commercial scale. Because of steric hindrance around the phosphate groups it has very high hydrolytic stability. Combinations of bridged diphenyl phosphates and monophosphates are advantageous because of synergism between the condensed phase and gas phase action of phosphorus. Numerous other aromatic phosphates are presented in the patent literature, some of them having advantages of high efficiency, others of improved physical properties and even others of high hydrolytic stability. It was shown that nano-scale inorganic materials help to improve fire-retardant performance of aromatic phosphates and provide enhanced thermal dimensional stability for PC/ABS.

A mechanistic study of fire-retardant action of aromatic phosphates revealed an accumulation of phosphorus in the condensed phase during combustion. It was also proven that aromatic phosphates protect the char from oxidation at high temperature. Apparently aromatic phosphates catalyze carbonate–ether and Fries rearrangements in polycarbonate. The phosphate esters transesterify phenolic groups formed on PC after the Fries rearrangement thus retarding volatilization of the polymer and building char.

Brominated aromatic phosphates were briefly introduced to the market for PC/ABS and most of all for PC/PET applications. These phosphates are very effective in both of the blends. Phosphine oxides and phosphonates were occasionally tested in PC/ABS, however they did not find application because of limited solubility in the resin and deterioration of physical properties. Aromatic phosphoramidates are very attractive for PC-based blends, because of relatively high melting points. Some of these products, particularly phosphazenes, may be finding their way to commercialization.

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