Fire-Retardant Action of Resorcinol Bis(diphenyl Phosphate) in PC-ABS Blend. II. Reactions in the Condensed Phase

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ABSTRACT: The thermal decomposition of polycarbonate (PC), PC containing resorcinol bis(diphenyl phosphate) (RDP), and PC—acrylonitrile-butadiene-styrene (PC-ABS) blend containing RDP was studied by thermogravimetry. Volatile and solid products of thermal decomposition were collected at different steps of thermal decomposition and characterized either by gas chromatography-mass spectrometry or infrared and chemical analysis. It was found that phosphorus accumulates in the condensed phase. Upon combustion of the fire-retardant mixture PC-ABS + RDP, accumulation of phosphorus is observed in the charred layer, at the surface of the burning specimens. It is suggested that PC undergoes a Fries-type rearrangement upon thermal decomposition, and RDP reacts with the formed phenolic groups through a trans-esterification mechanism. Kinetic analysis of the thermal decomposition of PC containing RDP supports the proposed mechanism. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1863–1872, 1999

Key words: resorcinol bis(diphenyl phosphate); fire retardancy; polycarbonate—ac-rylonitrile–butadiene–styrene blend; solid residue; trans-esterification

INTRODUCTION

Poly[2,2-propane-(bisphenol) carbonate] (PC) and acrylonitrile-butadiene-styrene (ABS) copolymer are easily blended. PC-ABS blend is mostly used in computer housings. It combines the ease of processing of ABS with the high physical properties of PC and presents advantages for fire retardancy since it contains readily charrable PC. Thermal decomposition studies of PC, which are important to understanding fire-retardant modes of action, were extensively reported in the literature.¹⁻¹⁷

In the earlier studies, it was noted¹ that PC undergoes extensive crosslinking when heated in an open vessel or in vacuum under continuous

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removal of volatile products,² whereas in a sealed tube, chain scission without gelation is a predominant process. The major gaseous product evolved from PC is CO_2 , which indicates that, in general, carbonate linkages are destroyed³ initially. The evolution of CO and CH_4 observed at low level at the beginning of decomposition becomes more important at higher temperatures. A large variety of phenols is formed during thermal decomposition of PC.³ It was assumed² that removal of phenols by vacuum promotes crosslinking of PC. Based on these results, it was postulated^{4,5} that the carbonate group can rearrange to form a pendant carboxyl group, ortho, to an ether linkage in the main chain. The carboxyl group might either split out CO_2 or react with a carbonate group to produce an ester crosslink.

The fact that PC undergoes crosslinking upon removal of volatile decomposition products was also confirmed by Abas.⁶ Using kinetic considerations, he 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) is indicative of the contribution of molecular mechanisms.

Evidence of the rearrangement of the carbonate group to the carboxyl group was observed⁷ by pyrolytic mass spectrometry, where some peaks were attributed to xanthone or antraquinones, which are the secondary products of this rearrangement. However, no direct evidence of the rearrangement was provided by infrared (IR) study of the solid residue performed in the same study.

Lee⁸ studied the thermal decomposition of PC in air and in nitrogen. He suggested that oxygen primarily attacks the isopropylidene linkage of the polymer, causing chain splitting; whereas in an inert atmosphere, the carbonate linkages undergo decomposition. The high yield of bisphenol A was assumed to result from hydrolysis by water traces present in the polymer at 400°C.

Mass spectrometry investigation of PC and its model compounds showed^{9–12} that cyclic oligomers are probably the primary products of PC fragmentation. Loss of methylene or carbon dioxide leads to the series of secondary products usually observed in mass spectrometry. It was proposed that ionic ester exchange is the governing process of thermal decomposition of polycarbonates.

McNeill and Rincon^{13,14} disputed the ionic mechanism. In their work on decomposition of PC under vacuum using thermal volatilization analysis, the nature of the products evolved was in favor of an homolytic chain scission rather than hydrolysis or ester interchange. The discussion that continued in the literature between Montaudo and Puglisi¹² and McNeill and Rincon¹⁴ did not give convincing preferences to the ionic or radical mechanisms.

All suggested mechanisms of PC thermal decomposition were based mainly on the volatile products. The authors paid little or no attention to the solid residue, though PC is a highly charrable polymer. The only investigations of PC chars that we found in the literature were carried out by Politou et al.^{15,16} and by Factor.¹⁷ They showed that above 440°C, a highly crosslinked structure with diaryl ester, ether, and unsaturated carbonaceous bridges is formed.

Various fire-retardant additives were used to impart fire retardancy to PC and its blends. Zinc borate,¹⁸ triphenyl phosphate, or brominated phosphates^{19–21} were found to be efficient in PCcontaining materials. Aromatic sulfonate salts at a very low level (0.1 wt %) provide fire-retardant properties to pure PC,^{21,22} but not its blends.

Resorcinol bis(diphenyl phosphate) (RDP) is the most widely used fire-retardant additive for PC-ABS.^{23,24} The gas phase mechanism of fireretardant action was implied²¹ for RDP based on the fact that higher molecular weight oligomeric phosphates showed a decrease in fire-retardant efficiency.

In Part I of this publication,²⁵ we studied the combustion performance of PC–ABS fire-retarded with RDP. We showed that gas phase fire-retardant coadditives, that is, melamine and its derivatives, are antagonistic with RDP; on the other hand, coadditives that may promote additional charring or improve the char quality exhibit some synergism. Thermogravimetric analysis (TGA) of the fire-retardant formulations proved that condensed phase coadditives increase char yield. Therefore, it is reasonable to suggest that RDP may interfere with the thermal decomposition of the polymers.

The main goal of this work was to explore possible interaction between PC-ABS and RDP, which might support or reject the condensed phase activity of RDP.

EXPERIMENTAL

Materials

Bisphenol A polycarbonate (PC; LEXAN 141), acrylonitrile-butadiene-styrene copolymer (ABS; DOW 9010) and PC-ABS blend (GE CYCOLOY C 1110) were used as received. Resorcinol bis(diphenyl phosphate) (RDP; Fyroflex® RDP, Akzo Nobel)



is a commercial product containing about 65% of the low-molecular-weight product (n = 1), 30 wt % of higher oligomers (n = 2 to 8), and up to 5 wt % of triphenyl phosphate. Novolak Durez 29295 (OxyChem) was used in our study.

Samples Preparation

All components of the formulation were thoroughly premixed with the polymer at room temperature. Melt compounding was carried out at 250°C at 30–60 rev min for 5 min in a closed chamber of a homemade mixer of the Brabender type. Slabs of $\frac{1}{16}$ in. thickness were pressed at 250°C. Samples for combustion, thermal degradation, or characterization experiments were cut from the slabs.

Thermal Analysis

Thermal decomposition behavior of either pure polymers or additives or formulations was investigated by TGA using a Mettler TA 3000 thermal analyzer. Experiments were carried out either in inert atmosphere of argon or in air flow, both at 60 cm^3 min and a heating rate 10° C min.

Kinetics

Kinetic analysis was carried out by using a set of thermogravimetric curves recorded at different heating rates (1.25, 2.5, 5.0, 10, 20, and 40°C min). The dependence of the activation energy on the advancement of the degradation reaction was estimated using modified Ozawa method.^{26,27}

Chemical Analysis for Phosphorus

Four bars of dimensions of $\frac{1}{4} \times \frac{1}{16} \times 5$ in. were used to collect combustion char and were marked every 1 cm from the top down. Each bar was vertically clamped and burned from the top using a Bunsen burner. The first one was burned to the 1-cm mark, the second to the 2-cm mark, the third to the 4-cm mark, and the last one to the 6-cm mark. The char collected from the specimens was separated from the unburned polymer. Chars formed during pyrolysis of the polymer were prepared in a conventional oven, in air under isothermal conditions. The obtained chars were dissolved by oxidation in hot concentrated H₂SO₄ and HNO₃ and then by addition of H₂O₂. The phosphorus content was measured by a standard vanadium molybdate complex method.²⁸

Infrared of Solid Residues

Solid residues of thermal decomposition of neat polymers, PC–ABS blend, or formulations were collected in thermogravimetry at different steps of thermal decomposition. TGA experiments were interrupted at a chosen temperature, and the sample was cooled down in inert atmosphere. Infrared spectra were recorded on a Perkin–Elmer 1750 spectrometer. KBr pellets were used.

Volatile Products Analysis

Thermal decomposition of PC–ABS containing RDP was carried out under vacuum in sealed glass ampoules. The bottom part of the ampoules containing the samples was heated at 10°C min, whereas the upper part was continuously cooled by running water to condense the high boiling products. The heating was interrupted either at 470 or 540°C. A gas probe, taken after ampoule cooling, was analyzed by gas chromatography (Shimadzu GC-17A) coupled with quadruple mass spectrometry (Shimadzu QP-5000). High boiling products were scrapped from the walls of the ampoule and analyzed by IR study.

RESULTS AND DISCUSSION

Kinetics

Resorcinol bis(diphenyl phosphate) undergoes volatilization at $320-470^{\circ}$ C, which is much lower than the temperature of decomposition of PC (500-550°C); however, it matches the decomposition temperature profile of ABS ($370-440^{\circ}$ C; Fig. 1). Addition of 15 wt % of RDP to ABS does not influence its thermal stability. The onset of weight loss of PC + 15% RDP is lower than that of neat PC due to partial volatilization of the additive²⁵; however the main step of weight loss of the polymer occurs at the same temperature.

From these thermogravimetric data, one would expect very little effect of RDP on the kinetic parameters of the thermal decomposition of the resins. However, as shown in Figure 2, it is rather notice-



Figure 1 Thermogravimetric curves of RDP, PC, ABS, PC, and ABS with added RDP (15 wt %). Argon flow was 60 cm³ min; heating rate was 10°C min.

able. Neat RDP has low activation energy of volatilization, which decreases during the decomposition from 125 to 90 kJ mol. These low values indicate that evaporation governs RDP volatilization.

Neat ABS has a high activation energy (approximately 200–210 kJ mol), which is typical of a radical decomposition mechanism. At low degree of decomposition, E_a is low, which can be explained by the breaking of weak bonds or volatilization of some oligomers. At a high degree of decomposition, E_a increases, probably because of decomposition of crosslinked structures. The E_a of the formulation ABS + 15% RDP is very close to that of neat ABS. The slight decrease observed is apparently related to RDP evaporation.

Neat PC shows a similar dependence to that of neat ABS; however, the values of E_a at the main stage are lower (approximately 170–190 kcal mol). This indicates the contribution of molecular mechanisms. The PC + 15% RDP mixture exhibits low E_a at 0.1 degree of decomposition. Then E_a increases until the degree of decomposition is 0.35. Partial evaporation of RDP at the beginning of thermal decomposition (see Fig. 1) may be responsible for this phenomenon. However, when the degree of decomposition reaches 0.35, the activation energy levels off at approximately 230 kJ mol. RDP seems to stabilize PC by suppressing molecular mechanisms of decomposition and promoting free radical scissions.

Phosphorus Content

The concentration of phosphorus found in the combustion chars is reported in Table I. The data



Figure 2 Dependencies of the activation energy on degree of decomposition of RDP, PC, ABS, PC and ABS with added RDP (15 wt %).

Table I Phosphorus Content in the								
Combustion	Chars from PC-ABS + 15% RDP							

No	Burned Part of Specimen (cm)	P Content (wt %)	
1	Unburned	1.6	
2	1	1.8	
3	2	2.2	
4	4	2.6	
5	6	2.8	

indicate an accumulation of phosphorus. The rate of accumulation is higher at the beginning of combustion, when less than 2 cm of the specimen is consumed; it slows down after, probably because of approaching some stationary equilibrium concentration.

Table II shows the phosphorus content in pyrolysis chars prepared in an oven. Both ABS and PC–ABS accumulate phosphorus; however, the ratio of retained phosphorus versus the volatilized phosphorus is higher for PC–ABS. For example, at 75% weight loss, the ABS/RDP combination keeps about 52% of the original phosphorus, whereas PC–ABS retains 90%. It is conceivable that PC is responsible for the phosphorus accumulation.

In PC-ABS blend, no phosphorus volatilization is observed at 10% of weight loss. These data seem to conflict with the thermogravimetric results where lower onset of weight loss and low activation energy at the beginning of thermal decomposition were attributed to partial volatilization of RDP. This discrepancy may arise from the difference in experimental conditions (linear heating in inert atmosphere versus isothermal pyrolysis in air).

Infrared of Solid Residues of Neat PC

Figure 3 shows IR spectra of neat PC and its solid residues of thermal decomposition. Characteristic absorptions of PC are as follows¹⁵: 2980–2860 cm⁻¹, CH₃ stretching; 1777 cm⁻¹, C=O stretching; 1600 and 1506 cm⁻¹, quadrant and semicircle of aromatic rings, respectively; 1233 and 1160 cm⁻¹, asymmetrical O—C(O)—O stretching; 1192 cm⁻¹, (CH₃)—C—(CH₃) skeletal vibration; 1011 cm⁻¹, C—C in-plane bending; 885 cm⁻¹, symmetrical O—C(O)—O stretching; 830 cm⁻¹, aromatic C—H out-of-plane deformation; 764 cm⁻¹, O—C(O)—O skeletal vibration.

The IR pattern of PC changes at 20% weight loss. A decrease in relative intensities at 1233

No	Weight Loss (%)	ABS + RDP		PC–ABS + RDP	
		P Content (%)	P Retained (%)	P Content (%)	P Retained (%)
1	0	1.6	100	1.6	100
2	10			1.8	100
3	17	1.65	85		
4	35			2.3	92
5	42	2.2	79		
6	75	3.35	52	5.8	90
7	80			6.9	85
8	83			7.7	81
9	95	5.9	18		

Table II Phosphorus Content in the Pyrolysis Chars from ABS + 15% RDP and PC-ABS + 15% RDP

and 1160 cm⁻¹ clearly indicate some loss of O—C(O)—O functionalities. The broadening of the peak at 1777 cm⁻¹ is probably due to the appearance of C=O stretchings other than carbonate. The intense band at 3470 cm⁻¹ is characteristic of OH stretching.

At 40% weight loss, the position of C=O stretching changes from 1777 to 1744 cm⁻¹, which points to complete decomposition of the carbonate groups and the appearance of ester groups instead.²⁹ Decomposition of the carbonate groups is also confirmed by the disappearance of strong absorptions at 1233 and 1160 cm^{-1} and medium intensity absorption at 885 cm^{-1} . The band at 1240 cm^{-1} , which appears first at 20% of weight loss as a shoulder at approximately 1260 cm⁻¹, is likely to belong to aromatic ethers.²⁹ At 40% weight loss, distinct changes are also observed in the region of aromatic C-H out-ofplane deformations $(900-700 \text{ cm}^{-1})$, which are in agreement with changes of the order of substitution in the aromatic rings. Disappearance of the isopropylidene skeletal vibration at 1192 cm^{-1} is suggestive of chain scission or some other secondary reactions at this group.

At a high degree of decomposition (73% weight loss), PC shows a typical spectrum of highly carbonized materials.¹⁵ An absorption at 1621 cm⁻¹ is due to small polynuclear aromatic systems. The band at 1494 cm⁻¹ demonstrates the presence of individual aromatic rings. The presence of aliphatic bridges is seen by weak absorptions at 2925 and 2856 cm⁻¹. Bands at 3438, 1269, and 1103 cm⁻¹ are likely to belong to remaining phenolic and ether groups.

Mechanism of Thermal Decomposition of Neat PC

Our IR study of the solid residue is in agreement with the work of Politou et al. 15,16 and Factor. 17

However, our data do not support the mechanism suggested by Davis and Golden^{4,5} since carboxylic groups were not detected in our experiments. In their study, Politou et al.,¹⁵ in addition to IR analysis, also performed chemical analysis but found no carboxylic groups. In our study, as in the work of Politou et al.¹⁵ or Factor,¹⁷ a high content of phenolic functionalities was detected; this was not discussed in many other publications.

In the literature on PC degradation induced by γ -irradiation³⁰⁻³² or by ultraviolet (UV) irradiation,³³⁻³⁵ it is generally accepted that the carbonate group undergoes a Fries-type rearrangement. Green²¹ suggested that the Fries rearrangement in PC is catalyzed by aromatic sulfonate salts. To explain our data, we assume that PC might partially undergo the Fries rearrangement upon heating without catalysts, as follows:



Appearance of phenolic and ester groups, as well as the change in the order of aromatics substitutions observed by IR, are in agreement with this rearrangement. It is often reported in the literature that CO_2 is the major gaseous product evolved from PC. We assume that the rearrangement suggested by Davis and Golden^{4,5} may also take place in PC. Since carboxylic groups are known to split out CO_2 , as soon as they form, they could not be detected in the solid residue, as follows:





Figure 3 Infrared spectra of initial PC and of solid residues collected in thermogravimetry at different steps of thermal decomposition in an inert atmosphere (pellets in KBr).

The fact that ether functionalities are found in the solid residue favor this mechanism. On the other hand, ethers can also be produced upon condensation of phenolic groups [eq. (3)] formed in the course of a Fries-type rearrangement, as follows:



Similar to novolak,³⁶ phenolic groups in PC can probably react with methyl groups, producing aliphatic

crosslink bridges [eq. (4)], which are detected by IR analysis in the high-temperature solid residue.



If the volatile products containing phenolic groups are not lost during decomposition of the polymer, one can suspect that they will participate in the condensation reactions [eqs. (3) and (4)] and prevent crosslinking of solid residue. This observation was mentioned in early articles on



Figure 4 Infrared spectra of neat RDP, initial PC with added RDP (15 wt %), and of solid residues of PC + RDP collected in thermogravimetry at different steps of thermal decomposition in inert atmosphere (pellets in KBr).

thermal decomposition of $PC^{2,3,6}$ without proper explanation.

Infrared Spectra of Solid Residues of PC + RDP and PC-ABS + RDP

Figure 4 shows the IR spectra of RDP, initial PC + 15 wt % RDP, and solid residues from the PC + RDP formulation. Besides P—O stretching at 962 cm⁻¹, all other major characteristic absorptions of RDP overlap with the strong bands of PC. The band at 962 cm⁻¹ can be used to label RDP.

The initial PC + RDP formulation has relatively strong absorption at 3436 cm^{-1} , which

probably belongs to phenolic OH stretching.²⁹ It is likely that already during compounding, some PC undergoes a Fries-type rearrangement [eq. (1)], which may be catalyzed by RDP.

At 40% weight loss, a further increase in phenolic content is observed. A shoulder, which appears at 1744 cm⁻¹, indicates the formation of ester bonds according to eq. (1). The amount of RDP in the polymer seems to decline, as shown by the lower relative intensity of the absorption at 962 cm⁻¹.

The solid residue at 70% weight loss is similar to that of neat PC (Fig. 3). This suggests that, apart from catalysis of the Fries rearrangement,



Figure 5 Infrared spectra of initial PC-ABS with added RDP (15 wt %) and of its solid residues collected in thermogravimetry at different steps of thermal decomposition inert atmosphere (pellets in KBr).

RDP does not have other detectable effects on the charring of PC.

The IR spectra of initial PC–ABS + 15% weight RDP formulation and solid residues from its thermal decomposition are shown in Figure 5. Characteristic absorptions of ABS that do not overlap with PC or RDP are C=N stretching at 2237 cm⁻¹, the quadrant of aromatic ring at 1454 cm⁻¹, and C—H out-of-plane deformations of aromatics at 758 and 700 cm⁻¹.

At 50% weight loss, a major part of ABS has been volatilized, as indicated by a strong decrease of its characteristic absorptions. On the other hand, the IR pattern of PC shows only minor modifications, which are similar to that of neat PC at 20% weight loss (Fig. 3). The increase in relative intensity of RDP's characteristic P—O stretching indicates an accumulation of RDP in the solid residue, which is in agreement with the phosphorus chemical analysis. Further accumulation of RDP is observed at 70% weight loss. At this stage, P—O stretching becomes as pronounced as the other PC absorptions. RDP is also detectable in the solid residue at 80% weight loss, which corresponds to the temperature range of 530–540°C.

Volatile Products of Thermal Decomposition of PC-ABS + RDP

Carbon dioxide and 2-propenitrile are the major gaseous products found at 470°C. It is likely that 2-propenitrile originates from the ABS part of the blend, whereas CO_2 comes from the PC part. Acetonitrile and 1,3-butadiene, which are present in a relatively high concentration, probably split off from the ABS rubber. At a higher temperature (540°C), 2-propenitrile remains the major gas evolved, whereas the concentration of CO_2 becomes very low. Aromatic gases (benzene, toluene, etc.), which may originate from both PC and ABS, are produced at relatively high concentration at 540°C. No phosphorus-containing gases are detected.

The IR pattern of high boiling products evolved from PC-ABS + RDP is similar to that of neat PC-ABS blend (see Fig. 5), which shows that mostly polymer chain fragments make up the high boiling products. However, the intensity of the characteristic peaks of ABS versus those of PC is higher in the volatile products than in the virgin blends, which is in favor of preferential volatilization of ABS and retention of PC in the solid residue. This is in agreement with the IR analysis of the solid residue.

Phosphorus-containing functional groups (absorption at 952 cm⁻¹) are detected in a relatively small concentration in the high boiling products collected at 470°C and in a very low concentration at 540°C.

Fire-Retardant Action of RDP in PC-ABS

The above results show that PC–ABS blend can efficiently accumulate RDP in the course of combustion or thermal decomposition. It is likely that RDP reacts with the decomposing polymer, probably with the PC. Upon Fries rearrangement, PC generates phenolic groups [eq. (1)], which may react with RDP by a trans-esterification mechanism, as follows:



Figure 6 Thermogravimetry curves of RDP, novolak, and RDP–novolak mixtures at different ratios (experimental) and the calculated curve for a RDP–novolak (5 : 1) mixture. Argon flow was 60 cm³ min; heating rate was 10°C min.



Since RDP contains several reactive P—O—C bonds, it might be expected to react with another PC chain to produce crosslinking. However, as shown by thermogravimetry, RDP does not substantially increase the char yield of PC–ABS or pure polymers.

Chemical analysis of the extinguished combustion specimens showed a distinct accumulation of phosphorus in the relatively thin layer of the decomposing polymer and charring material. Since combustible gases, which feed the flame, evaporate mostly from the surface, a high concentration of relatively nonvolatile, noncombustible phosphorus species can greatly affect flame propagation and cause its extinction. If the phosphorus species on the surface are in the form of phosphoric acid due to oxidation of RDP, they will also provide an additional barrier effect against diffusion of combustible gases to the flame.

Independent Evidence for RDP Reaction with Phenolics

In Part I of this work,²⁵ we showed that novolak is an efficient coadditive to RDP and helps to increase the char yield. Since novolak has phenolic OH groups in the molecule, an attempt was made to ascertain if these groups can react with RDP. Figure 6 shows thermogravimetric curves of neat novolak, neat RDP, their mixtures at different ratios, and the calculated curve at the ratio of 5 : 1. The experimental and calculated curves match up to 30% weight loss (415°C). After that point, weight loss in the experimental curve slows down significantly, which indicates interaction between the components of the mixture. Although the calculated curve predicts approximately 20% of solid residue at 600°C, the experimental curve shows 35%.

Increasing the novolak content (2 : 1 ratio) leads to a further increase in solid residue up to 40%. However, there is no increase in residue at a 1 : 1 ratio. In fact, calculations based on the reaction shown in eq. (5) predict that the optimum ratio between low-molecular-weight RDP and novolak should be 2.7 to 1. Since RDP contains up to 35% of oligomeric products and some triphenyl phosphate, the optimum ratio may be slightly different. Reaction of RDP with novolak provides additional evidence the fact that RDP can react with phenolic groups from PC decomposition.

CONCLUSIONS

It was shown that PC undergoes a Fries-type rearrangement upon thermal decomposition. The phenolic groups formed are likely to be responsible for crosslinking of chains and char formation. We found that phosphorus accumulates in the condensed phase upon thermal decomposition of PC-ABS + RDP mixture. In combustion, accumulation of phosphorus was detected in the charred layer, which is formed on the top of burning specimen. Kinetic analysis showed that RDP increases the activation energy of thermal decomposition of PC, probably promoting homolytic scissions at the expense of molecular mechanisms. We also demonstrated that RDP reacts with PC probably through trans-esterification. Phosphorus accumulated on the surface of the burning polymer is likely to interfere with the delivery of combustible gases to the flame.

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