

Pyrolysis gas chromatographic studies on polyphosphate esters of bisphenol A

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SUMMARY:

Pyrolysis gas chromatographic studies were carried out on two polyphosphate esters of bisphenol A^{b)}. The gaseous pyrolysis products were found to be mainly phenols and a few phosphate compounds. The identification of phosphorus compounds in the gas phase proves a gas phase mechanism of flame retardant action for polyphosphates. The presence of phosphoric acid in the char residue supports the existence of the conventional condensed-phase mechanism. Thus, the study demonstrates that both condensed-phase and gas-phase mechanisms are operative in the flame-retardant action of polyphosphates.

Introduction

Pyrolysis gas chromatography (PGC) finds excellent use in the analysis of thermal degradation products of polymers^{1–4)}. In the case of flame-retardant polymers, such a study is of great importance in understanding the mechanism of flame retardancy. Phosphorus-based flame retardants are generally believed to act in the condensed phase^{5–8)}, though a few of them have been found to act in the gas phase as well^{9,10)}. Recently, we have reported the synthesis and characterization of a series of polyphosphate esters, which are found to be efficient flame-retardant polymers^{11–13)}. However, a detailed information on the mechanism of flame retardant action of polyphosphates is not available due to the lack of pyrolysis studies of these polymers. In the present investigation, of the various polyphosphates synthesized, two typical ones (**I** and **II**) have been chosen for a detailed PGC study. Since both polymers are based on bisphenol A (BPA), its pyrolysis products have also been analyzed to understand the degradation of the above polymers.

Experimental part

The polyphosphate esters were synthesized according to a procedure reported elsewhere^{11,12)}. The pyrolysis gas chromatographic (PGC) studies were carried out on a Shimadzu GC-4C gas chromatograph equipped with a PYR-1A pyrolyzer unit and a flame ionization detector (FID). Stainless steel columns, 2 m × 3 mm inner diameter, packed with OV-17 (5%) coated on 80/100 mesh chromosorb silanized, were used to separate the compounds. The injector and detector temperatures were 325 °C. The column temperature was programmed from 60 to 300 °C at a rate of 10 °C/min. Nitrogen, at a flow rate of 35 mL/min, was used as the carrier gas. The samples (1 mg) were pyrolyzed for 15 s, at the desired temperatures, viz. 300, 400 and 500 °C, and then

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^{b)} Systematic name: 2,2'-isopropylidendiphenol.

chromatographed. The products were identified by comparison with the retention times of pure compounds under identical conditions. However, all the products could not be identified by the retention time data alone and therefore the following method was adopted. The polymers were pyrolyzed at 300 °C in a separate furnace and the gaseous products were collected at low temperatures (–50 °C); the liquid pyrolyzate, thus obtained, was separated by thin-layer chromatography (TLC) and analyzed by ^1H and ^{31}P NMR spectroscopic techniques. In the PGC study, the relative concentrations of the various products were obtained in terms of relative peak areas of the recorder response. The response is found to be highest for hydrocarbons and less for compounds containing heteroelements like N, S, P etc.¹⁴⁾. Therefore, the “relative peak areas” reflect the “true relative concentrations” only in a first approximation.

The IR spectra of neat samples were recorded on a Perkin Elmer 715 IR spectrophotometer between KBr discs. The ^1H NMR spectra were obtained using a Varian T-60 spectrometer with TMS as the internal standard and CDCl_3 as the solvent. The ^{31}P NMR spectra were recorded on a Varian PT 80A (32,2 MHz) spectrometer. The spectra were recorded in CHCl_3 under broadband ^1H decoupling conditions. D_2O provided the external lock.

The char residue obtained after the pyrolysis of these polymers (after keeping in a furnace at 350 °C for 48 h) was shaken with water and filtered. The filtrate was tested for phosphate¹⁵⁾ using ammonium molybdate, thick yellow precipitate confirming it.

Results and discussion

Pyrolysis of bisphenol A

The pyrograms of BPA at 300, 400 and 500 °C are shown in Fig. 1 and the relative concentrations of the various products are summarized in Tab. 1. The pyrolysis of BPA at 300 °C gives two products, identified as phenol and *p*-isopropenylphenol (the peak at the highest retention time corresponds to undecomposed BPA). The formation of these two products may be represented as shown in Scheme 1 (pathway a). BPA (1) undergoes cleavage at the isopropylidene group giving rise to radicals **a** and **b**. While **a** abstracts one H^\bullet , **b** eliminates on H^\bullet , giving rise to phenol (2) and *p*-isopropenylphenol (3), respectively.

The pyrogram at 400 °C was similar to that at 300 °C except for two additional peaks corresponding to lower aliphatic hydrocarbons and toluene. The pyrolysis of BPA at 500 °C gives a large number of products (Fig. 1 c). The lower-boiling products were aliphatic hydrocarbons, benzene and toluene. The higher-boiling products identified were phenol, *p*-cresol, *p*-ethylphenol, *p*-isopropylphenol and *p*-isopropenylphenol, concordant with the observations of Sugita¹⁶⁾. Possible mechanisms for the formation of these products are shown in Scheme 1 (pathways a and b). The formation of radical **e** by the cleavage of the methyl group of BPA has been reported in BPA-based epoxy resins¹⁷⁾. There is a possibility of radical **c** eliminating a H^\bullet and forming *p*-vinylphenol (pathway c); such a compound has, however, not been identified but probably is amongst the few unidentified peaks. Benzene and toluene may be formed by the cleavage of the C—O bond.

Pyrolysis of polymer I

The pyrolysis of polymer I (Scheme 2) at 300 °C (Figure 2a) gives rise to a large number of products compared to BPA pyrolyzed at the same temperature, indicating

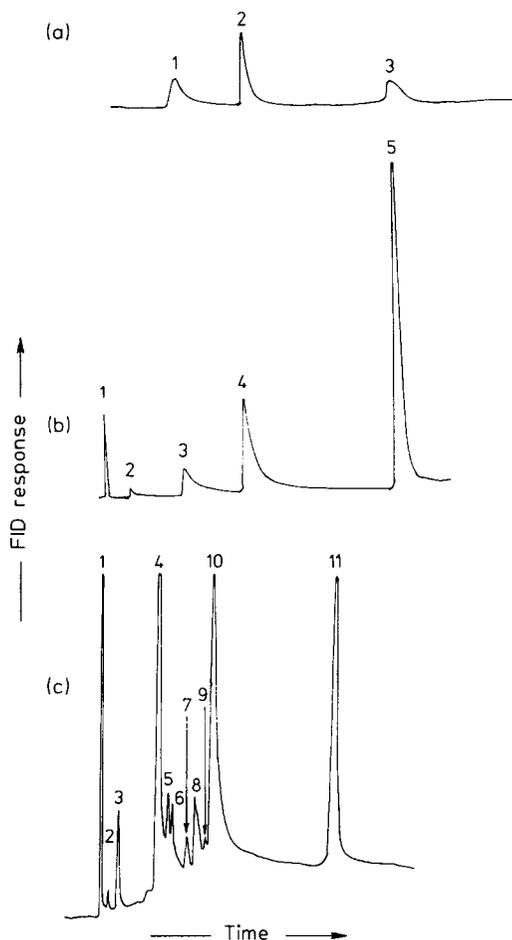
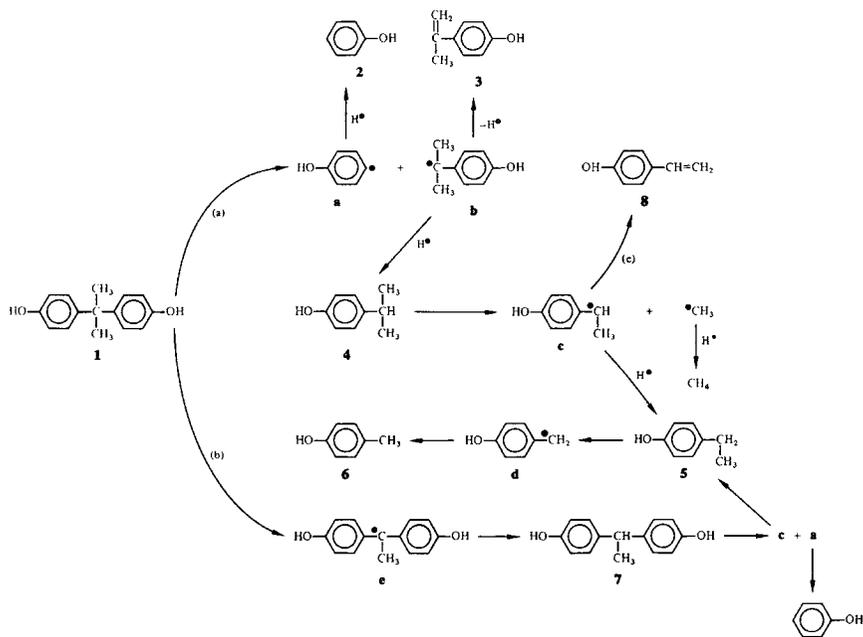


Fig. 1. Pyrograms of BPA: Pyrolysis temperature (a) 300 °C; (B) 400 °C, and (c) 500 °C. The peaks are numbered according to Tab. 1

that the polymer is less thermally stable than BPA. All the compounds identified in the pyrogram of BPA at 500 °C were found to be present in the pyrolysis products of polymer I at 300 °C, though the concentrations were different (Tab. 2). Cumene was identified as an additional product from the polymer. The peak at 9,0 and 11,0 min could not be identified by the retention time. The pyrolysis products were collected, separated into two major fractions by TLC, using 90 vol.-% hexane + 10 vol.-% ethyl acetate eluent, and characterized by IR and NMR spectroscopy.

The IR spectrum of the top fraction (TF-1) shows the absorption characteristic of phenols (3200 , 1350 and 1260 cm^{-1}) whereas that of the bottom portion (BP-1) shows the absorptions of alkyl and aryl phosphates¹⁸⁾ ($\nu_{\text{P=O}} = 1300\text{ cm}^{-1}$, $\nu_{\text{P-O-C}}$ (aromatic) = 1120 and 980 cm^{-1} , and $\nu_{\text{P-O-C}}$ (aliphatic) = 1050 cm^{-1}). The ^1H NMR spectrum of TF-1 indicates that it is a mixture; GC analysis confirmed that it is a mixture of cumene and the 5 different phenols which were obtained in the case of BPA.

Scheme 1: The mechanism of BPA degradation



Tab. 1. Pyrolysis products of BPA at different temperatures

Pyrolysis temperature in °C	Peak No.	Pyrolysis products	Retention time in min	Relative peak areas in %
300	1	Phenol	5,5	37
	2	<i>p</i> -Isopropenylphenol	10,4	42
	3	Bisphenol A	21,1	20
400	1	Aliphatic hydrocarbons	0,6	3
	2	Toluene	2,1	2
	3	Phenol	5,6	25
	4	<i>p</i> -Isopropenylphenol	10,5	29
	5	Bisphenol A	21,3	40
500	1	Aliphatic hydrocarbons	0,6	16
	2	Benzene	1,4	1
	3	Toluene	2,2	3
	4	Phenol	5,5	26
	5	Unidentified	6,5	2
	6	<i>p</i> -Cresol	6,9	5
	7	<i>p</i> -Ethylphenol	8,3	3
	8	<i>p</i> -Isopropylphenol	9,0	5
	9	Unidentified	9,9	1
	10	<i>p</i> -Isopropenylphenol	10,3	23
	11	Bisphenol A	21,1	15

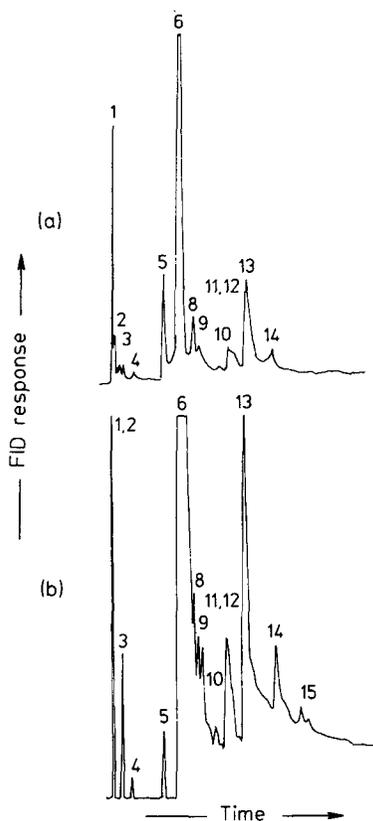


Fig. 2. Pyrograms of polymer I: Pyrolysis temperature (a) 300°C, and (b) 500°C. The peaks are numbered according to Tab. 2

Tab. 2. Pyrolysis products of polymers I and II

Peak No.	Pyrolysis products	Retention time in min	Relative peak areas in % at			
			300°C		500°C	
			I	II	I	II
1, 2	Aliphatic hydrocarbons	0,4-1,0	5	2	10	8
3	Benzene	1-1,2	1	1	4	9
4	Toluene	1,8-1,9	1	2	3	2
5	Cumene	4,1	7	13	5	4
6	Phenol	5,5-5,7	56	31	39	32
7	Trimethyl phosphate	5,8	—	—	—	8
8	Unidentified	6,3	4	—	3	—
9	<i>p</i> -Cresol	6,9	2	20	3	3
10	<i>p</i> -Ethylphenol	8,2	1	—	2	6
11, 12	<i>p</i> -Isopropylphenol, Dimethyl phenyl phosphate	8,7-8,9	5	15	9	10
13	<i>p</i> -Isopropenylphenol	10,2-10,3	15	10	14	8
14	Diphenyl methyl phosphate	11,5-12,0	3	5	6	6
15	Unidentified	13,8	—	—	2	—

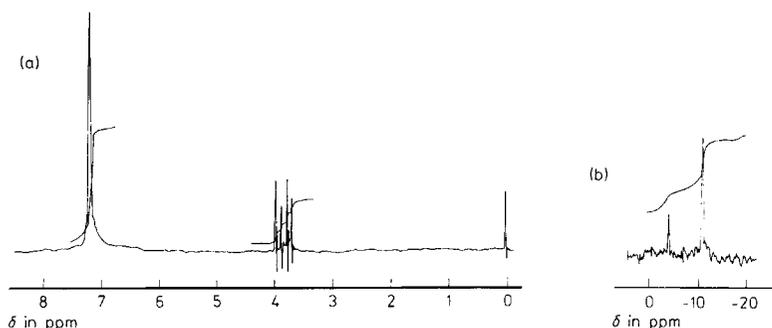
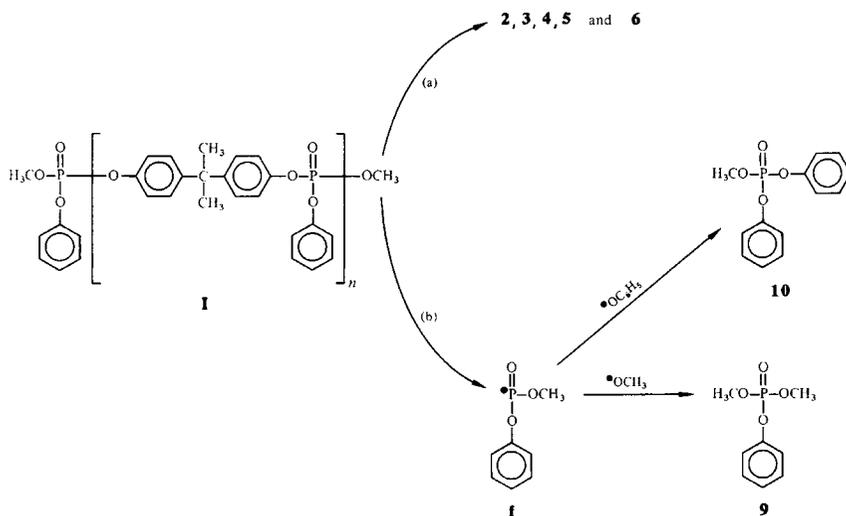


Fig. 3. (a) ^1H , and (b) ^{31}P (^1H decoupled) NMR spectra of pyrolysis products (bottom fraction of TLC) of polymer I at 300°C

The ^1H decoupled ^{31}P NMR spectrum of BF-1 (Fig. 3b) shows two singlets; one at $\delta = -4,6$ corresponding to dialkyl aryl phosphate and the other at $\delta = -11,4$ corresponding to diaryl alkyl phosphate¹⁹. The ^1H NMR spectrum (Fig. 3a) shows two doublets, one at $\delta = 3,8$ and the other at $\delta = 3,9$ with a coupling constant of 11 Hz, in addition to a broad singlet at $\delta = 7,2$. It can then be concluded that the two phosphate compounds are dimethyl phenyl phosphate (9) and diphenyl methyl phosphate (10), where the doublets at $\delta = 3,8$ and $\delta = 3,9$ correspond to $\text{P}-\text{O}-\text{CH}_3$ groups of the former and latter, respectively^{20,21}. The resonances corresponding to $\text{P}-\text{O}-\text{C}_6\text{H}_5$ groups of both the compounds have merged together giving rise to a

Scheme 2: A possible mechanism of degradation of polymer I



pseudo-singlet at $\delta = 7.2$. The mole ratio of **9** to **10** is found to be 1 : 2 from both ^1H and ^{31}P spectral integration. Flame ionization detection is not sensitive to phosphorus compounds and therefore the peak areas given in Tab. 2 are less than their actual concentrations.

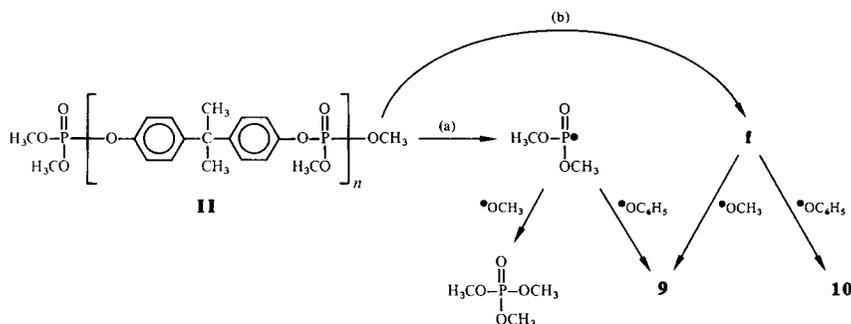
A possible mechanism for the formation of the phosphate compounds is shown in Scheme 2 (pathway b). The various phenols (pathway a) would have formed from the bisphenol part of the polymer as shown in Scheme 1. Some phenol would have also formed by the cleavage of the pendant phenyl group.

Pyrolysis of polymer **I** at higher temperatures, e. g. 500°C , gave the same products (Fig. 2b). The low-retention-time products increase in concentration as the pyrolysis temperature increases because the primary products get decomposed into smaller fragments (Tab. 2).

Pyrolysis of polymer **II**

The pyrograms of polymer **II** (Scheme 3) at 300 and 500°C are given in Fig. 4. Most of the pyrolysis products (Tab. 2) were the same as those identified in the case of polymer **I**. In order to confirm the structure of different phosphate compounds, spectral analysis of the products was carried out as in the previous case.

Scheme 3: A possible mechanism for the formation of phosphate compounds from polymer **II**



The products were separated by TLC (see previous chapter) into two major fractions; the top fraction (TF-2) was again found to be a mixture of various phenols. The bottom portion (BF-2) showed the IR absorptions characteristic of aryl and alkyl phosphate compounds. The ^{31}P NMR spectrum (Fig. 5 a) shows that BF-2 is a mixture of 3 phosphate compounds¹⁹⁾: trialkyl phosphate ($\delta = 0,0$), dialkyl aryl phosphate ($\delta = -5,0$) and diaryl alkyl phosphate ($\delta = -11,0$) in the mole ratio 3 : 2 : 1, respectively. By using 80 vol.-% hexane + 20 vol.-% ethyl acetate eluent, BF-2 was separated into two fractions. The ^1H NMR spectrum (Fig. 5 b) of one of these fractions corresponds to diphenyl methyl phosphate (doublet at $\delta = 3,9$, $^3J_{\text{PH}} + 11$ Hz and singlet at $\delta = 7,2$), and the other fraction corresponds to a mixture of trimethyl phosphate²¹⁾ (doublet at

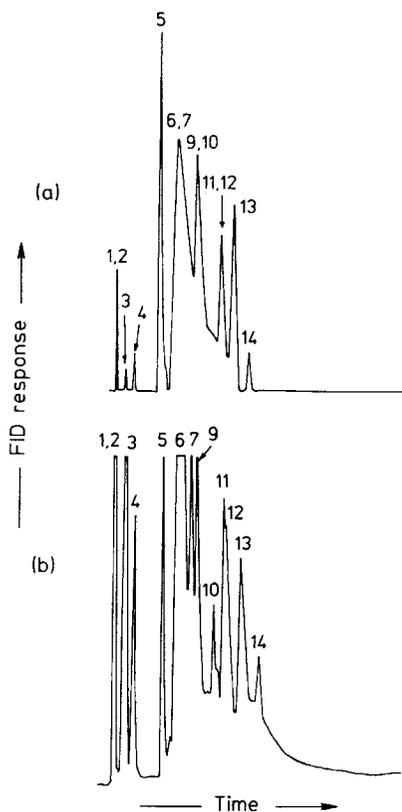


Fig. 4. Pyrograms of polymer II: Pyrolysis temperature: (a) 300 °C, and (b) 500 °C. The peaks are numbered according to Tab. 2

$\delta = 3,7$, $^3J_{\text{PH}} = 11$ Hz) and dimethyl phenyl phosphate (pseudo-singlet at $\delta = 7,2$) (Fig. 5c). The retention time of trimethyl phosphate is found to be 5,7 min. It may be noted that it merged with the phenol peak in the pyrogram of polymer II at 300 °C (Fig. 4a); however, in the pyrogram obtained at 500 °C (Fig. 4b) the two products are resolved. A possible mechanism for the formation of the three phosphate compounds is given in Scheme 3. The pyrolysis products of polymer II at higher temperature (Tab. 2) remain the same.

Mechanism of the flame-retardant action of polyphosphates

Phosphorus-based flame retardants are well known for their condensed-phase mechanism of flame-retardant action. Very few examples are available where they have been found to act in the gas phase. The present pyrolysis studies on polyphosphates have shown that phosphate compounds are present in the pyrolysis products. Studies^{22, 23)} on phosphate compounds have shown that they are efficient flame inhibitors. The phosphate compounds may be breaking in the flame to give radicals like

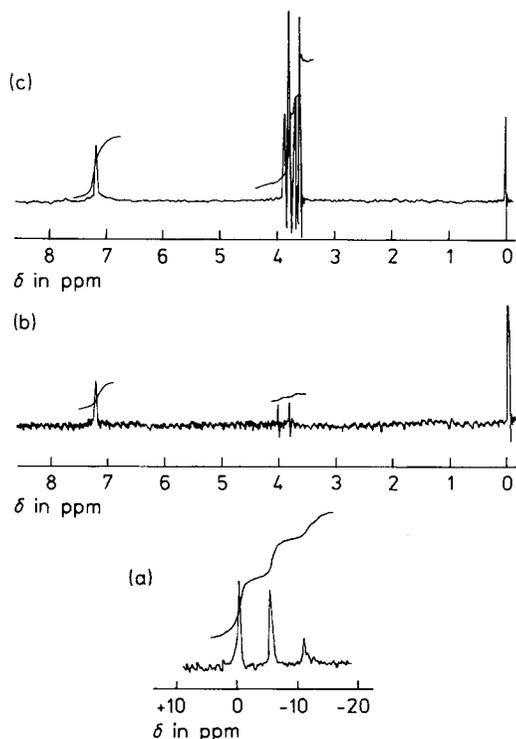


Fig. 5. NMR spectra of pyrolysis products (bottom fraction of TLC) of polymer II at 300°C. (a): ^{31}P (^1H decoupled) NMR spectrum; (b) and (c): ^1H NMR spectra of 2-sub-fractions

PO^\bullet which scavenge the propagating radicals like H^\bullet and CH^\bullet and thus reduce the energetics of the flame reactions.

Analysis of the other residue showed the presence of phosphoric acid which is known for its action in the condensed phase through charring. This suggests that the flame retardant action of polyphosphates works by a combination of condensed-phase and gas-phase mechanisms. The precise contributions of condensed-phase and gas-phase inhibitions are not known and need further investigation.

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