

Flame-Retardant Effect of Tris(2,3-dibromopropyl) Phosphate on Polystyrene

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Synopsis

The flame-retardant effect of tris(2,3-dibromopropyl) phosphate (TBPP) on polystyrene was investigated using thermogravimetry, infrared spectroscopy, gel permeation chromatography, and electron spectroscopy for chemical analysis (ESCA). The following results and conclusions were obtained: (1) The addition of TBPP (about 3 wt%) to polystyrene had flame-retardant properties. (2) The addition of TBPP resulted in lowering the temperature of the burning surface and the amount of volatile products. TBPP increased the thermal stability of polystyrene. (3) TBPP inhibited oxidative attack on polystyrene. In the presence of TBPP the formation of peroxide groups at the burning surface was inhibited. It is inferred that this inhibition decreases the evolution of flammable fuels from the burning surface and contributes flame-retardant properties. There is a lesser possibility that TBPP acts as a physical barrier that limits oxygen access. At present there is no idea of why TBPP inhibits thermoxidative reactions of polystyrene.

INTRODUCTION

Tris(2,3-dibromopropyl) phosphate (TBPP) is one of the effectual flame retardants for polymers—poly(ethylene terephthalate), polystyrene, etc.^{1,2} In order to research more effectual flame retardants, attention has been directed to a mode of flame-retardant action on polymers.

A burning polymer constitutes a more complex system compared to conventional diffusion flames. The fuel generation process in the condensed phase and the fuel consumption process in the gas phase take place simultaneously, and the rates of these processes must be in equilibrium to maintain a steady state of combustion. Acceleration or deceleration of either process leads to the blow out of the flame. The rate of fuel generation is considered to be controlled by the energy flux, which is provided by radiative and conductive components from the flame zone.

Recently a few workers³⁻⁶ reported on the burning behavior of polymers. Stuetz *et al.*⁶ have pointed out the following:

- (1) Conductive and radiative contributions from the gas phase played a minor role in maintaining fuel formation.
- (2) Fuel production at the burning surface took place via simultaneous oxidative and pyrolytic degradations of the polymer.
- (3) The degradation processes were successfully modeled in the thermogravimetric experiments.

Brauman⁷ has thermogravimetrically studied interactions between polystyrene and an antimony trioxide-halogen compound system used as a flame retardant.

We also have reported on the flame-retardant effect of TBPP on poly(ethylene terephthalate) fabric.⁸ In this paper a thermogravimetric investigation was carried out in order to explain the flame-retardant action of TBPP on polystyrene.

EXPERIMENTAL

Polymer Samples

Polystyrene (Asahi-Dow Co. Ltd., Styron C1B56-475S-H27) was used. Polystyrene was mixed with TBPP (Marubishi Oil Co.) at 180°C using an extruder (Nakatani Machine Industry Co., Model AS-30), and chips were formed. The chips were processed to give 10 × 90 × 40 mm³ specimens using an injection molding machine (Yamashiro-Seiki Seisakujo, Model SAU 301). The polymer samples used in this study are shown in Table I together with TBPP contents.

Flammability Test

The oxygen index test (ASTM-D-2863-70) was used to evaluate a limiting oxygen index of the polymer samples.

Thermogravimetry

A Shinku-Riko thermogravimetric analyzer DGC-3 was used. Ground samples (80 mesh) of about 50 mg were weighed in quartz pans (8 mm i.d. × 8 mm), and then the pans were placed on the top of a chromel-alumel thermocouple and heated under vacuum (10⁻³ torr) or in air at a programmed rate of 4°C/min.

Gel Permeation Chromatography

A Toyo Soda model HLC-801A chromatograph was used. The separating system consisted of two columns (Toyo Soda TSK G3000H8, G5000H6; 7.5 mm i.d. × 610 mm) connected in series. The flow of solvent, tetrahydrofuran, was maintained at 1.4 ml/min at 40°C. Anionic polystyrene standards (Toyo Soda,

TABLE I
Flame-Retardant Effect of Tris(2,3-dibromopropyl) Phosphate on Polystyrene

Sample	Added TBPP ^a (%)	Loi (%)	Surface temperature of burning polymer (°C)	Number average Molecular weight of burning part (× 10 ⁻³)
PS-0	0	18.4	350	5.6
PS-P-0.5	0.53	22.8	310	5.0
PS-P-1	0.98	23.7		
PS-P-2	2.37	26.3		
PS-P-3	3.25	27.2	290	4.8
PS-P-5	5.15	27.9		
PS-P-10	10.6	31.1	260	3.3

^a Calculated from phosphorus content.

$M_n = 1.26 \times 10^6, 4.22 \times 10^5, 4.28 \times 10^4, 1.02 \times 10^4, 6.0 \times 10^3, 8.00$) were used to plot a calibration curve.

Infrared Spectroscopy

Infrared spectra were examined as KBr disks using a Nihon-Bunko spectrometer IRA-3.

Electron Spectroscopy for Chemical Analysis (ESCA)

A sample was analyzed on a DuPont model 650B. Spectra were recorded at a scan rate of 0.05 V/sec.

Phosphorus and Bromine Analyses

Phosphorus contents were determined by a colorimetric method. Samples were decomposed with a mixture of concentrated sulfonic acid and perchloric acid. The resulting solution was treated with ammonium molybdate, and the absorbance at 830 nm was measured.

Bromine contents were determined by a potentiometric titration method. Samples (10 mg) were burned in a Shoniger combustion flask. The resulting hydrogen bromide was absorbed in an aqueous solution of sodium hydroxide and hydrazine sulfate. The solution was titrated with a silver nitrate solution, using a Metrohm Herisau automatic titrator E436E.

RESULTS AND DISCUSSION

The flame-retardant effect of TBPP was determined using an oxygen index tester. This result is shown in Table I together with the surface temperature of a burning polystyrene stick and the number average of the molecular weight of the burning part (< 0.1 mm depth from the surface). The addition of TBPP brought about the flame-retardant properties, and at a level of about 3 wt% TBPP, polystyrene was self-extinguished; also, the surface temperature of the burning stick, where polystyrene was melted and yielded flammable gases, was lowered with increased TBPP content. The number average of the molecular weight of the burning part was also decreased. These decreases in the surface temperature and molecular weight with TBPP content indicate a possible alternative degradation reaction near the surface of polystyrene.

Stuetz *et al.*⁶ have pointed out that oxidative degradation of a polymer near the burning surface plays an important role in the combustion of the polymer. The contribution of heat conduction and radiation from the flame plays a minor role in maintaining flammable products from polymer. The degradation process occurring near the surface of a burning polymer could successfully be modeled in thermogravimetric experiments.

Effect of TBPP on Thermal Degradation of Polystyrene

In order to investigate degradation process occurring near the surface of burning polystyrene, thermogravimetric curves in air were measured (Fig. 1). The weight loss for the PS-0 sample (polystyrene) was initiated at 250°C and

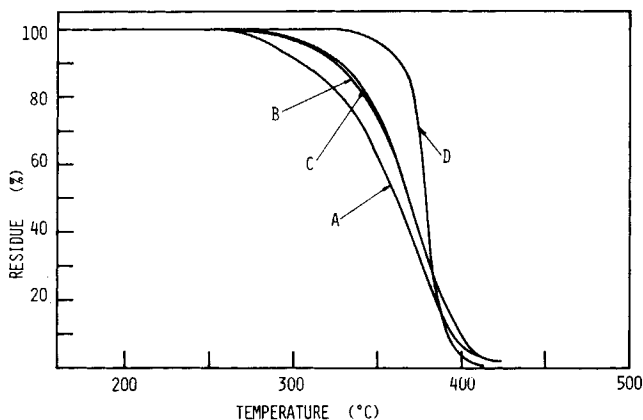


Fig. 1. Thermogravimetric curves for polystyrene and TBPP-containing polystyrene in air: A, PS-0; B, PS-P-1; C, PS-P-5; D, PS-0 under vacuum.

finished at 400°C. This curve is different from that under vacuum, e.g., the threshold temperature for weight loss in air was lower by about 100°C than that under vacuum. Contribution of some oxidative attack is inferred. For the PS-P samples the threshold temperature for weight loss was shifted to high-temperature regions, and the thermal stability was increased. It is recognized that the addition of TBPP results in a retardation of the weight loss. From a comparison of curves B and C, the power of this retardation is independent of the amount of added TBPP. The influence of TBPP on thermal reactions of polystyrene was further examined by using infrared spectroscopy.

Infrared spectra for residual products of the PS-0 and PS-P-10 samples after heating in air in the temperature range from 200 to 350°C for 1 hr are shown in Figures 2 and 3. When the PS-0 sample was heated at 200°C, a new absorption band at 1690 cm^{-1} due to C=O groups appeared. Other new absorption bands, except for this band, could not be detected even when heating at temperatures of more than 200°C. This spectral result indicates that before weight loss an oxidative attack, probably on the α -carbon of the polystyrene, occurs. On the other hand, for the PS-P-10 sample appearance of the band of C=O groups could not be observed up to 350°C. The intensity of this absorption, appearing at 350°C, was weak. The absorption band at 1050 cm^{-1} due to P-O-C groups of TBPP became less intense at 250°C and disappeared at 300°C. These spectral comparisons of the PS-0 and PS-P-10 samples indicate that the addition of TBPP inhibits oxidative attack on polystyrene at α -carbon. This assumption was supported by the following experiment. The PS-0 and PS-P-10 samples were heated in the temperature ranges from 200 to 350°C for 1 hr under vacuum, in air, or in an oxygen atmosphere, and the number-average molecular weight of the residual products was determined (Table II). The formation of volatile products is depressed by the addition of TBPP. The decrease of the molecular weight of the residual products from the PS-0 sample was sensitive to oxygen, but the decrease for the PS-P-10 sample was insensitive. For the PS-P-10 sample, the residual products degraded in air had a comparable molecular weight to those under vacuum.

As shown in the infrared spectra of the PS-P-10 sample, the disappearance of the absorption due to P-O-C groups indicates that the β -elimination of

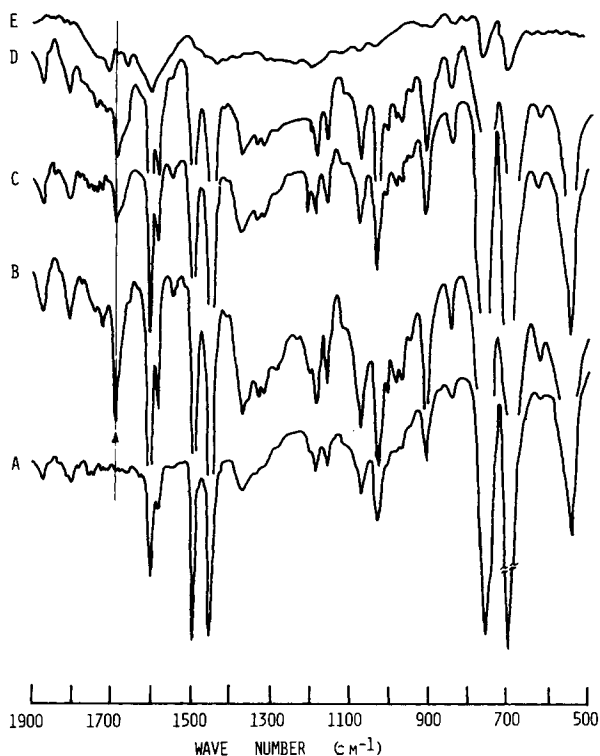


Fig. 2. Infrared spectra of residual products from PS-0 sample after heating for 1 hr: A, untreated; B, at 200°C; C, 250°C; D, 300°C; E, 350°C.

phosphorus ester groups may occur. Elemental analyses show that no amount of bromine atoms could be detected in the residual products at 250°C, but a comparable amount of phosphorus atoms to that initially added was present in residual products even at 350°C. It is not unreasonable that TBPP incorporated into polystyrene could be transformed into phosphoric acid or pyrophosphoric

TABLE II
Change of Molecular Weight of Polystyrene after Heating Treatment

Sample	Temperature (°C)	Residual Product ^a (wt %)	Number-average molecular weight		
			Vacuum	Air	Oxygen
PS-0	Untreated		9.6×10^4	9.6×10^4	9.6×10^4
	200	97.2	4.2×10^4	4.2×10^4	4.2×10^4
	250	73.2	3.2×10^4	1.1×10^4	3.4×10^3
	300	11.2	4.0×10^4	2.0×10^3	3.7×10^2
	350	0.9	8.8×10^3		
PS-P-10	Untreated		8.1×10^4	8.1×10^4	8.1×10^4
	200	96.2	6.2×10^4	6.2×10^4	6.2×10^4
	250	91.1	6.6×10^3	4.8×10^3	3.4×10^3
	300	70.0	1.9×10^3	1.9×10^3	4.9×10^2
	350	12.5	9.0×10^2	1.3×10^3	

^a Heated in air.

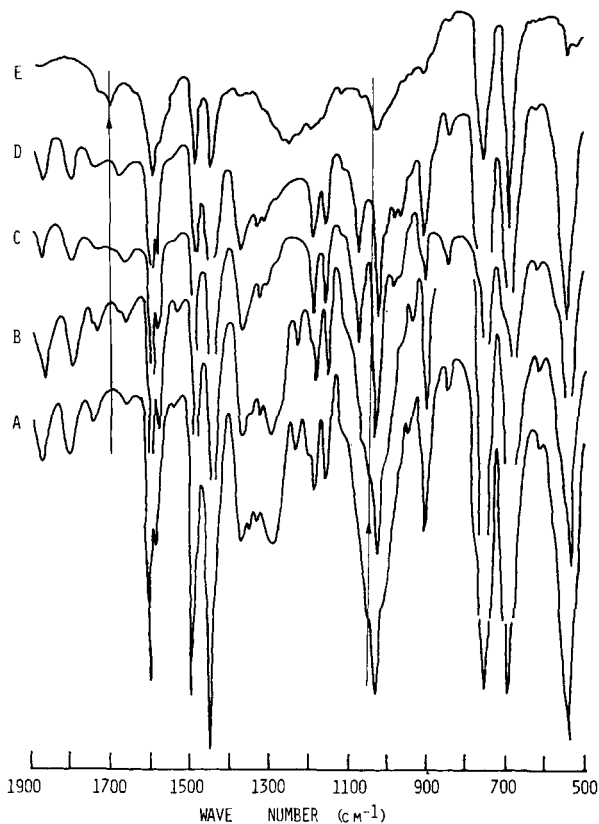


Fig. 3. Infrared spectra of residual products from PS-P-10 sample after heating for 1 hr: A, untreated; B, at 200°C; C, 250°C; D, 300°C; E, 350°C.

acid before polystyrene is degraded at the burning surface and that bromine atoms in TBPP could play a minor role in the flame-retardant action.

Thermal Degradation of Polystyrene near Burning Surface

From thermogravimetric and infrared spectral investigations a mode of flame-retardant action of TBPP is assumed to be the inhibition of oxidative reactions. Some additional experiments on thermal degradation near the burning surface were carried out. Burning polymer specimens were quenched rapidly with nitrogen gas and the infrared spectra of the quenched portion within a 0.1 mm depth of the burned surface were examined (Fig. 4). For the PS-0 sample new intense absorption bands at 3615 (OH), 1775, 1730, and 860 cm^{-1} (peroxide) appeared. This alternative spectrum shows that oxidative thermal reactions near the burning surface occur and that they yield peroxide groups. While for the PS-P-3 sample, the appearance of these new absorption bands could not be detected. This spectral result confirms that the incorporation of TBPP into polystyrene inhibits oxidative reactions near the burning surface.

ESCA spectrum for the burned surface of the PS-P-3 sample (Fig. 5) shows the distribution of added TBPP to polystyrene on burning. No phosphorus or bromine atoms could be detected on the burning surface. It is not unreasonable

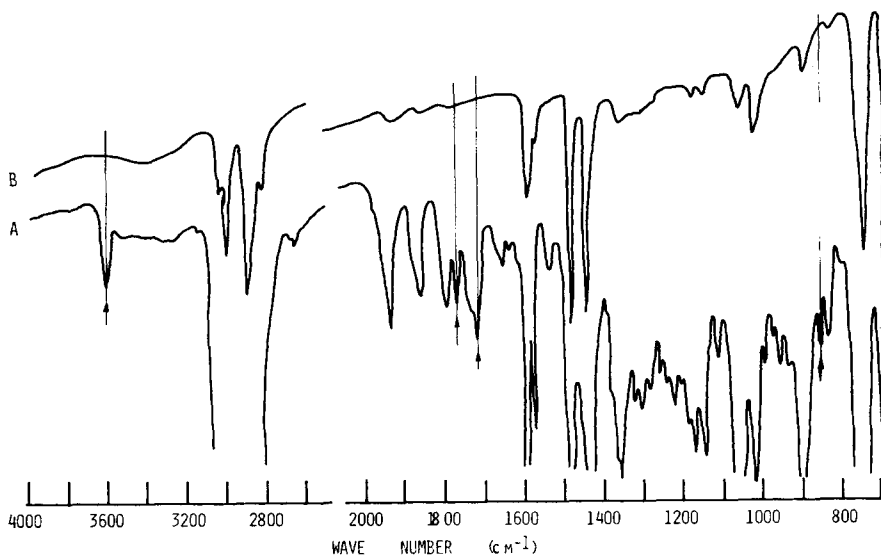


Fig. 4. Infrared spectra of burned part (within 0.1 mm depth of the burned surface): A, PS-0; B, PS-P-3.

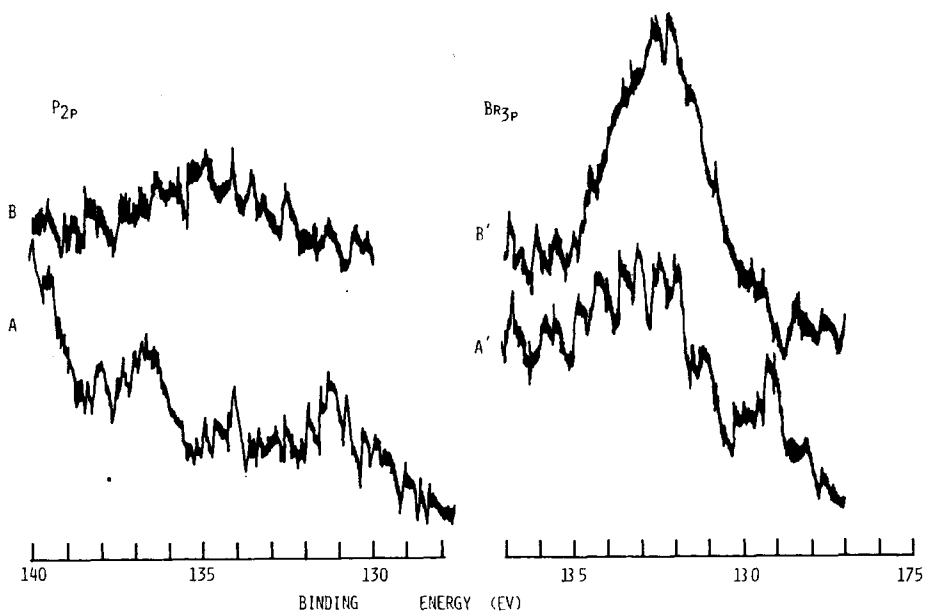


Fig. 5. ESCA spectra of burned surface of PS-P-3 sample: A, A', burned; B, B', unburned.

that the absence of bromine atoms on the burning surface is due to β -elimination of phosphorus ester groups. Taking into account the isothermal degradation result that a comparable amount of phosphorus atoms to those initially added remain in the degraded products even at 350°C for 1 hr, it is inferred that phosphorus atoms could not vaporize from the surface, but could sink into the polymer. There is less possibility that TBPP acts as a physical barrier that limits oxygen access. Other modes of action of TBPP should be taken into account.

At present there is no idea of why TBPP inhibits thermoxidative reactions of polystyrene.

From this experiment the following conclusions were obtained:

(1) The addition of TBPP (about 3 wt%) to polystyrene had flame-retardant properties.

(2) The addition of TBPP resulted in lowering the temperature of the burning surface and the amount of volatile products. TBPP increased the thermal stability of polystyrene.

(3) TBPP inhibited oxidative attack on polystyrene. In the presence of TBPP the formation of peroxide groups at the burning surface was inhibited. It is inferred that this inhibition decreases the evolution of flammable fuels from the burning surface and contributes flame-retardant properties.

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