

# Synthesis and Properties of 4-Hydroxy-2,3,5,6-Tetrabromobenzyl Phosphonates and Effects of Their Flame Retardance on Impact Polystyrene

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## Synopsis

*p*-Cresol was converted into 2,3,5,6-tetrabromocresol by  $\text{AlCl}_3$  catalyst bromination, and then further brominated to 4-hydroxy-2,3,5,6-tetrabromobenzyl bromide (HTBBB) in benzene by light. HTBBB reacted easily with trialkyl phosphite to produce 4-hydroxy-2,3,5,6-tetrabromobenzyl phosphonates (HTBBPs) in solvents. Although the reaction of HTBBB with triaryl phosphite was slower than that with trialkyl phosphite, it does produce corresponding phosphonate with ease. Except for DMF, DMAc, chloroform, and tetrahydrofuran, HTBBP was difficult to dissolve in ordinary organic solvents. Of all the synthesized HTBBP, dimethyl hydroxy-2,3,5,6-tetrabromobenzyl phosphonate showed the poorest solubility. With the addition of these new compounds containing bromine and phosphorus atoms to HIPS as flame retardants, the results of oxygen index measurement showed that the flame resistance of these compounds was greater than the additive effect of the two corresponding individual brominated compound and phosphorus-containing compound. It means that these new compounds seem to act synergistically as flame retardants in HIPS. Simultaneous addition of brominated compound and phosphorus-containing compound to HIPS ends up with a similar effect as mentioned above, but the new compounds can prevent the exclusion of phosphorus-containing compound from polymer matrix.

## INTRODUCTION

In recent years, polymer materials have been widely used with increasing consumption day by day, but almost all the organic polymers are combustible. To reduce the combustibility of polymers, it is necessary to add fire retardants to the polymeric materials.

Halogenated or phosphorus-containing compounds are widely used as fire retardants for polymers.<sup>1-13</sup> In general, the halogenated compounds influence the flammability by producing hydrogen halide as radical traps in high temperature or by depressing the flammable gas mixture available for burning.<sup>14,15</sup> Phosphorus-containing compounds are in a position to reduce the flammability, because they can promote the char formation and inhibit the glowing reaction.<sup>16</sup>

The fire retardants used in industry are almost bromine-containing organic compounds such as tetrabromobisphenol A, decabromodiphenyl ether, and octabromodiphenyl ether, because these bromine-containing compounds have better compatibility with polymer. But most of phosphorus-containing compounds are incompatible with the polymeric system and have high manufacturing cost. Some papers mentioned that phosphorus-con-

taining compounds were used as fire retardants, among them being red phosphorus,<sup>7</sup> cellulose phenylthiophosphonate,<sup>8</sup> ammonium polyphosphate,<sup>9,11</sup> etc.

There are some articles describing the flame retardance of halogenated and phosphorus-containing compounds in plastic, like halogenated phosphates on PET<sup>17</sup> and tris(2,3-dibromopropyl) phosphate on PP<sup>18</sup>. A fire resistance copolymer was also obtained<sup>10</sup> by copolymerization of vinyl bromide and bis(beta-chloroethyl)vinyl phosphonate.

The simultaneous addition of the halogenated compound and phosphorus-containing compound to plastic may get better flame-retardancy effects for they could produce radical traps and reduce the density of flammable gas on the one hand and promote the char formation and inhibit the glowing reaction on the other. But there have been not many papers describing the combined effects of the halogenated compound and phosphorus-containing compound on polymers. Granzow and Savides<sup>9</sup> found the synergistic effect of phosphonium bromide and ammonium polyphosphate on PP and HIPS. Ballistreri and his co-workers<sup>11</sup> also obtained synergistic effect in polyacrylonitrile-ammonium polyphosphate-hexabromocyclododecane system.

The aims of this study are to synthesize some new phenolic bromine-containing and phosphorus-containing compounds to be as flame retardants for plastic and to compare their flame-retardancy effect with the individual and combined effects of corresponding brominated compound and phosphite on HIPS.

## EXPERIMENTAL

### Materials

Bromine, aluminum chloride, *p*-cresol, and dichloromethane were all first grade and purchased from Wako Pure Chemicals, Ltd., Japan; sodium sulfite was obtained from Hayashi Pure Chemicals, Ltd., Japan.

Trimethyl phosphite, triethyl phosphite, and tris(2-chloroethyl) phosphite were all E.P. reagents, obtained from T.C.I., Japan and triphenyl phosphite from Wako Pure Chemicals; benzene was obtained from Shimakyu's Pure Chemicals.

HIPS was supplied by Shang-Chih Chemicals; tetrabromobisphenol A was obtained from local suppliers. Pentabromophenol was prepared from the bromination of phenol. Tetrahydrofuran used in film preparation was first grade and purchased from Wako Pure Chemicals.

### Instrument

Melting points were measured in capillaries on a Yamato mp apparatus (Model MP-21) and uncorrected. Infrared measurements were recorded on the Jasco IRA-2 spectrometer. The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were taken at 30°C on a Jeol JNM-FX90Q FT NMR spectrometer with tetramethylsilane as an internal standard.

DSC measurements were carried out by using a DuPont 910 Differential Scanning Calorimeter with a 1090B Programmer-recorder. The program heating rate was 5°C/min and Indium was used as a standard. TG curves

were recorded on a DuPont 951 Thermogravimetric Analyzer with a 1090B Programmer-recorder and a heating rate of 20°C/min, in the presence of N<sub>2</sub>. Oxygen index determinations were made with a Suga ON-1 meter.

### Testing Methods

#### *DSC Measurement: Determination of Fusion Energy*

Indium,  $\Delta H_f = 28.4$  J/g, was used as a standard, and the fusion energy of each sample was obtained from the following equation:

$$\Delta H_{fd} = \Delta H_{fs} \times (A_d \times m_s) / (m_d \times A_s)$$

where  $\Delta H_f$  = fusion energy (J/g); m = the mass (mg); A = the peak area; s = standard (Indium), and d = detected sample.

#### *Oxygen Index Measurement*

**Film Preparation.** Sixty milliliters of tetrahydrofuran was heated to dissolve a proper amount of a flame retardant and 10 g of high impact polystyrene (HIPS). The blending solution was poured to a 20 cm × 20 cm × 0.13 mm glass mold. After drying in room temperature, the film escaped from the mold was dipped into water for 12 h to dissolve out the residuary tetrahydrofuran, and then it was dried at 70°C for 24 h and vacuum drying more than 1 day to give a smooth and uniform HIPS films.

**Oxygen Index Determination.** The flammability of the samples was determined in terms of the oxygen index according to ASTM D2863-77.

**1. Oxygen Index Measurement of HIPS Blended with Brominated Compound.** HIPS was blended with various kinds of brominated compounds to make the oxygen index measurement in various additive amounts.

**2. Oxygen Index Measurements of HIPS Blended with HTBBP.** HIPS was blended with various kinds of HTBBP to make the oxygen index measurement in various additive amounts.

**3. Oxygen Index Measurement of HIPS Blended with Phosphite.** HIPS was blended with various kinds of phosphite to make the oxygen index measurement in various additive amounts.

**4. Simultaneously Additive Effect of Bromine-Containing and Phosphorus Containing Compounds.**

The flame retardancy effects of the following conditions were compared: the individual effects of brominated compound and phosphite on HIPS, the combined effects of brominated compound and phosphite on HIPS, and the effects of corresponding HTBBP on HIPS.

### Synthesis

#### *Preparation of Tetrabromo-p-Cresol (TBPC)*

To a 500 mL three-necked flask, 214 g (1.34 mol) of liquid bromine and 3 g of aluminum chloride were added. The mixture was agitated to allow the catalyst to dissolve in the bromine completely. The bromine-AlCl<sub>3</sub>

mixture was then cooled to about 5°C by an ice bath, and the flask was covered with black cloth to prevent the light rays from seeping through.

Twenty-nine grams (0.27 mol) of *p*-cresol dissolved in 40 mL of dichloromethane was added gradually to the mixture during a period of 1 h. The ice bath was removed, and later the mixture was heated to about 60°C, at which temperature the bromine solution was refluxed for about 3 h. The reaction mixture was then heated to a higher temperature and the excess bromine was removed by distillation. After a few minutes, 200 mL of water was slowly added to the flask with continuous heat to remove the residual bromine.

The solid product was filtered and washed with hot sodium sulfite solution and hot water, respectively. After drying, the slightly yellow solids weighed 107 g and had a melting point of 190–194°C and a yield of 94%. Recrystallizing from acetone–methanol gave the compound as needle crystals, m.p. 202–204°C (lit.,<sup>19</sup> 199°C).

#### *Preparation of 4-Hydroxy-2,3,5,6-Tetrabromobenzyl Bromide (HTBBB)*

In a 400 mL flask, 250 mL of benzene was heated to dissolve 14 g (0.028 mol) of tetrabromo-*p*-cresol. The benzene solution was lighted by a 250 W reflector lamp at a distance of 5 cm and agitated with a stirrer. The reaction solution was refluxed by the heat from the lighting lamp.

A solution of 5.4 g of bromine and 10 mL of benzene was added to the above solution. As soon as the bromine–benzene solution was added, the reaction mixture became red and soon turned back to yellow with the evolution of hydrogen bromide.

After the bromine–benzene solution was added in the course of about 20 min, the reaction mixture was lighted and agitated to maintain continuous reflux for 3 h. The lamp was removed, and the agitating was stopped before the mixture was filtered. The cooled filtrate was stood in an ice box overnight to precipitate the product. The solid product was filtered and washed with benzene. The dried product weighed 14.3 g and had a melting point of 174–176°C and a yield of 86.1%. Two-thirds of benzene in filtrate evaporated under reduced pressure. The residue was cooled to precipitate the solid product. The precipitate was collected and dried to give the same product (1.3 g) as above. A total yield of 93.9% was obtained. The product was recrystallized from carbon tetrachloride to yield needle crystals, m.p. 185–186°C.

ANAL. Calcd for  $C_7H_3Br_5O$  (502.5): C, 16.71%; H, 0.59%; Br, 79.50%. Found: C, 16.91%; H, 0.59%; Br, 79.30%.

#### *Preparation of Dimethyl 4-Hydroxy-2,3,5,6-Tetrabromobenzyl Phosphonate (HTBBP<sub>M</sub>)*

Trimethyl phosphite (3.25 g, 0.026 mol) was added to a solution of 12 g (0.024 mol) of HTBBB in 120 mL of benzene. About 1 min after adding trimethyl phosphite, white solid was precipitated from benzene. The mixture was stirred and refluxed for 30 min. The solid was filtered, washed several times with benzene, and dried to give 14.3 g (88.2%) of HTBBP<sub>M</sub>,

m.p. 260–261°C. The filtrate and washings were combined, and the solvent was evaporated. The residue was washed with methanol, filtered, and dried to get 0.68 g HTBBP<sub>M</sub>. A total yield of 93.4% was obtained. After recrystallizing from DMSO, HTBBP<sub>M</sub> had a melting point of 263°C.

ANAL. Calcd for C<sub>9</sub>H<sub>9</sub>Br<sub>4</sub>PO<sub>4</sub> (531.6): C, 20.32%; H, 1.69%; Br, 60.12%; P, 5.83%. Found: C, 20.33%; H, 1.71%; Br, 60.15%; P, 5.72%.

*Preparation of Diethyl 4-Hydroxy-2,3,5,6-Tetrabromobenzyl Phosphonate (HTBBP<sub>E</sub>)*

Triethyl phosphite (3.63 g, 0.022 mol) was added to a solution of HTBBB (10 g, 0.020 mol) in 100 mL of benzene. About 2 min after adding triethyl phosphite, white solid was precipitated from benzene. The mixture was stirred and refluxed for 60 min. The solid was filtered, washed several times with benzene, and dried to give 9.22 g (82.3%) of HTBBP<sub>E</sub>, m.p. 214°C. The filtrate and washings were combined, and the solvent was evaporated. The solid residue was washed several times with methanol, filtered, and dried to get 1.04 g of HTBBP<sub>E</sub>, m.p. 198–202°C. A total yield of 91.6% was obtained. After recrystallizing from DMSO, HTBBP<sub>E</sub> had a melting point of 218°C.

ANAL. Calcd for C<sub>11</sub>H<sub>13</sub>Br<sub>4</sub>PO<sub>4</sub> (559.6): C, 23.59%; H, 2.32%; Br, 57.11%; P, 5.54%. Found: C, 23.63%; H, 2.31%; Br, 57.12%; P, 5.41%.

*Preparation of Diphenyl 4-Hydroxy-2,3,5,6-Tetrabromobenzyl Phosphonate (HTBBP<sub>P</sub>)*

Triphenyl phosphite (3.4 g, 0.11 mol) was added to a solution of HTBBB (5 g, 0.01 mol) in 50 mL of benzene. About 20 min after adding triphenyl phosphite, white precipitate was found in benzene solution. The mixture was stirred and refluxed for 3 h. Then the solid product was filtered, washed with *n*-hexane, and dried to give 4.54 g (69.6%) of HTBBP<sub>P</sub>, m.p. 181°C. The filtrate and washings were combined and the solvent was evaporated; the residue was washed with a water–methanol solution (80% methanol in solvent by volume), filtered, and dried to get 1.43 g of HTBBP<sub>P</sub>, m.p. 164–166°C. A total yield of 91.6% was obtained.

Recrystallizing from tetrahydrofuran–methanol solution gave the compound as white needle crystals, m.p. 185–186°C.

ANAL. Calcd for C<sub>19</sub>H<sub>13</sub>Br<sub>4</sub>PO<sub>4</sub> (655.4): C, 34.78%; H, 1.98%; Br, 48.73%; P, 4.73%. Found: C, 34.80%; H, 1.96%; Br, 48.61%; P, 4.77%.

*Preparation of Di(2-Chloroethyl) 4-Hydroxy-2,3,5,6-Tetrabromobenzyl Phosphonate (HTBBP<sub>CE</sub>)*

Tris(2-chloroethyl) phosphite (4.43 g, 0.0165 mol) was added to a solution of HTBBB (7.5 g, 0.015 mol) in 75 mL of benzene. The mixture was stirred and refluxed for 40 min. Benzene was evaporated under reduced pressure and the residue was washed with water–methanol solution (80% methanol in solvent by volume). After drying, the product weighed 8.41 g with a yield

of 89.5% and a melting point of 153°C. Recrystallizing from acetone-methanol solution gave the compound as white crystals, m.p. 162°C.

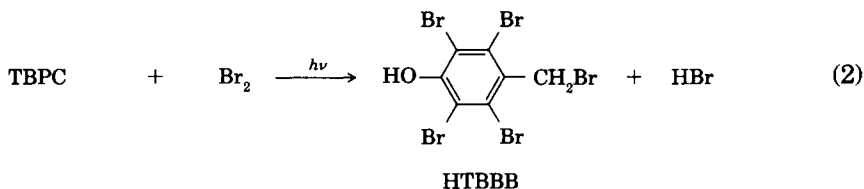
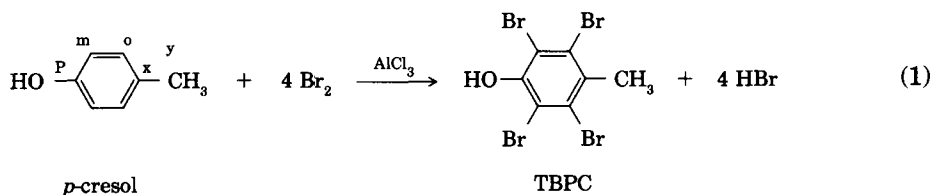
ANAL. Calcd for  $C_{11}H_{11}Br_4Cl_2PO_4$  (628.6): C, 20.99%; H, 1.75%; Br, 50.84%; Cl, 11.29%; P, 4.93%. Found: C, 21.15%; H, 1.78%; Br, 50.67%; Cl, 11.22%; P, 4.95%.

## RESULTS AND DISCUSSION

### Synthesis and Properties of 4-Hydroxy-2,3,5,6-Tetrabromobenzyl Bromide

The bromination of *p*-cresol is faster than those of ordinary aromatic compounds, because the hydroxyl group, —OH group, in *p*-cresol shows strongly activating effects on the aromatic ring. In a halogenated solvent such as dichloromethane or in the bromine as a solvent, *p*-cresol reacts with bromine to produce 2,6-dibromo-*p*-cresol. Catalyst is necessary for the complete bromination in aromatic ring of *p*-cresol as shown in eq. (1), because it needs more strongly electrophilic positive bromine to attack the meta position of the aromatic ring. Under the conditions of heating and excess bromine, the methyl group of *p*-cresol will proceed with radical bromination in the presence of light rays. So, it is necessary to prevent the presence of light during the bromination of *p*-cresol.

2,3,5,6-Tetrabromo-*p*-cresol (TBPC) dissolved in benzene or carbon tetrachloride is further photobrominated to corresponding 4-hydroxy-tetrabromobenzyl bromide (HTBBB) as shown in eq. (2).



The solvents used in this reaction should not contain aliphatic chains like alkyl group to prevent the bromination of the solvents. Benzene solution lighted by the reflector lamp almost boils while bromination proceeds rapidly. That the color of the reaction mixture changes from red to light yellow means no more existence of bromine. When the end point of bromination is reached, the red color of added bromine will not fade away. After the reaction was completed, the reaction solution was stored in refrigerator overnight to precipitate the product which could be recrystallized from benzene, carbon tetrachloride, or acetone-acetonitrile solution.

As shown in Figure 1, strong absorption at  $1370 \text{ cm}^{-1}$  confirms the pres-

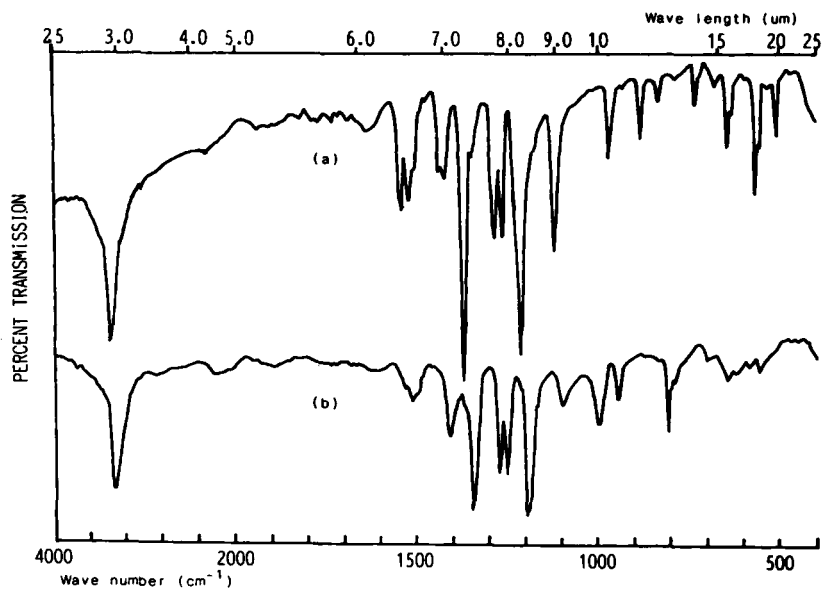


Fig. 1. IR spectra of HTBBB(a) and TBPC(b).

ence of  $-\text{CH}_2\text{Br}$  group in HTBBB (curve a) and absorption at  $1355\text{ cm}^{-1}$  is attributable to  $-\text{CH}_3$  group in TBPC (curve b).

The NMR spectra of TBPC and HTBBB are shown in Figure 2. In the  $^1\text{H}$ -NMR spectra, absorption by the methyl protons ( $-\text{CH}_3$ ) of TBPC appears upfield ( $\delta = 2.9\text{ ppm}$ ,  $\text{CCl}_4$ ), but the absorption by methylene protons

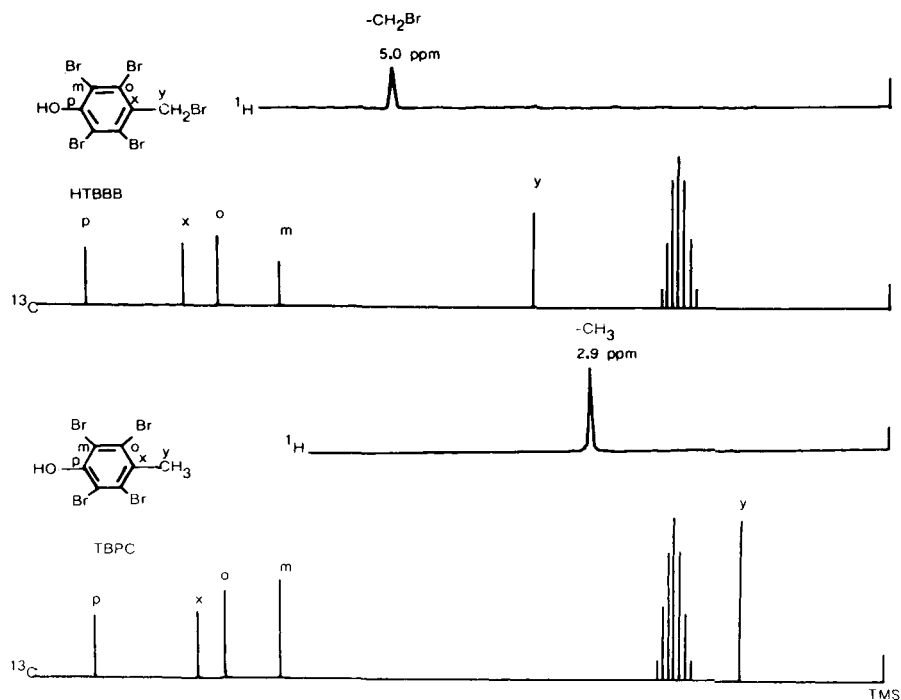


Fig. 2.  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of TBPC and HTBBB.

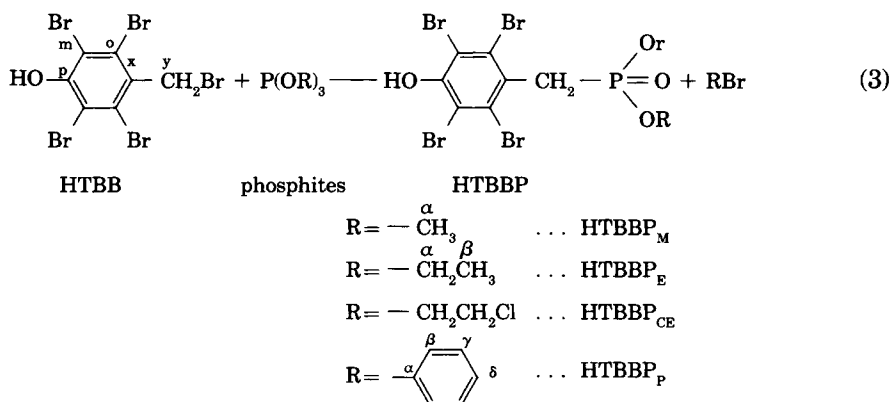
(—CH<sub>2</sub>—Br) of HTBBB shifts to downfield ( $\delta = 5.0$  ppm, CCl<sub>4</sub>) due to the inductive effect of bromine.

In the <sup>13</sup>C-NMR spectra, the chemical shift for the —CH<sub>3</sub> group of TBPC appears at 27.12 ppm, but that for the —CH<sub>2</sub>—Br group of HTBBB shifts to 71.1 ppm. The chemical shifts for aromatic carbon of TBPC are 131.23 (x), 126.08 (o), 115.30 (m), and 150.94 (p) ppm but those for HTBBB are 135.19 (x), 128.13 (o), 116.72 (m), and 153.56 (p). The spectral difference between these two compounds are listed in Table I.

It has been found that *p*-hydroxy-2,3,5,6-tetrabromobenzyl bromide, prepared from the bromination of *p*-cresol, is easy to react with alcohols, amines, and phosphite but not with water.

## Synthesis and Properties of HTBBP

### Synthesis of HTBBP




4-Hydroxy-2,3,5,6-tetrabromobenzyl bromide (HTBBB) in benzene reacts with trialkyl phosphite to produce 4-hydroxy-2,3,5,6-tetrabromobenzyl phosphonate (HTBBP) as shown in eq.(3). This reaction proceeds very rapidly even in a dilute solution. Due to the poor solubilities in benzene, HTBBP<sub>M</sub> and HTBBP<sub>E</sub> precipitate immediately when they form during the reaction. The yields obtained in various conditions are listed in Table II. The reaction

TABLE I  
<sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and IR Spectral Data for TBPC and HTBBB

Spectral	Compound	TBPC	HTBBB
IR		—CH <sub>3</sub> 1355 cm <sup>-1</sup>	—CH <sub>2</sub> Br 1370 cm <sup>-1</sup>
H-NMR ( $\delta$ ppm, CCl <sub>4</sub> )		—CH <sub>3</sub> $\delta = 2.9$ ppm	—CH <sub>2</sub> Br $\delta = 5.0$ ppm
<sup>13</sup> C-NMR	y	27.12	71.10
	x	131.23	135.19
$\delta$ ppm,	o	126.08	128.13
DMSO-d <sub>6</sub>	m	115.30	116.72
	p	150.94	153.56



TABLE II  
The Influence of Reaction Conditions to the Reaction Yield of HTBBB with Phosphite

R	HTBBB/P(OR) <sub>3</sub>	Reaction time (min)	Yield (%)
—CH <sub>3</sub>	1:2.0	10	93.1
	1:2.0	30	93.7
	1:2.0	60	93.5
	1:1.1	30	92.0
—C <sub>2</sub> H <sub>5</sub>	1:2.0	30	91.4
	1:2.0	120	92.0
	1:1.1	20	90.9
	1:1.1	60	91.6
—CH <sub>2</sub> CH <sub>2</sub> Cl	1:2.0	30	88.9
	1:2.0	90	89.2
	1:1.1	30	89.4
	1:1.1	60	89.6
	1:2.0	30	77.2
	1:2.0	120	85.4
	1:2.0	180	91.3
	1:1.1	30	55.9
	1:1.1	60	72.4
	1:1.1	120	86.6
	1:1.1	180	91.5

yield does not increase even with increasing reaction time. It shows that it just needs 10 min to complete the reaction of HTBBB and trialkyl phosphite in benzene. These reactions seem to be irreversible reactions with constant yields.

Although triphenyl phosphite does react with HTBBB as fast as trialkyl phosphite does, the reaction rate accelerates with the increase of the reaction amount of triphenyl phosphite. It needs 3 h to complete this reaction, as shown in Figure 3.

#### *Spectra Identification of HTBBP*

The IR spectra of the four HTBBP are shown in Figures 4 and 5. Strong absorptions around 1240 cm<sup>-1</sup> are attributable to P = O group, strong absorption around 980–1060 cm<sup>-1</sup> confirm the presence of the P—O—C (alkyl) group, and strong absorption at 940 cm<sup>-1</sup> corresponds to the P—O—Ph group.

The <sup>1</sup>H-NMR spectra, listed in Table III, shows a doublet at 3.67–4.38 ppm with  $J = 21$  Hz corresponding to the —CH<sub>2</sub>P(O)— group. The methyl protons in HTBBP<sub>M</sub> are split by the phosphorus atom with a coupling constant  $J_{PH} = 12$  Hz.

The <sup>13</sup>C-NMR spectral data given in Table IV consists of a characteristic doublet at 34.51–42.15 ppm attributed to the carbon of the —CH<sub>2</sub>P(O)— group.

#### *Solubility of HTBBP*

The various R groups in each of HTBBP cause the large difference among the solubilities of these bromine-containing phosphonates. The qualitative solubilities, as shown in Table V, are obtained by adding 0.2 g of each kind of HTBBP to 4 mL of various solvents, respectively.

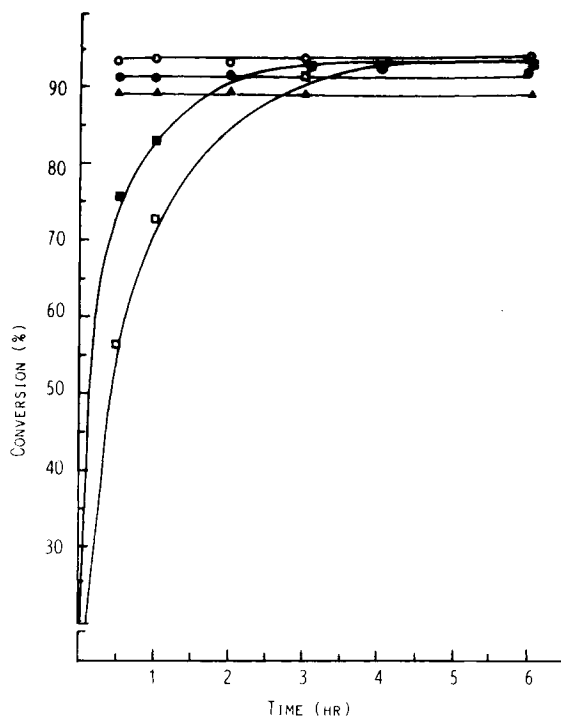


Fig. 3. The effects of molar ratio and reaction time on the reaction of HTBBB with phosphite in benzene: (○) HTBBB with trimethyl phosphite (1.0:1.1),  $R - CH_3$ ; (●) HTBBB with triethyl phosphite (1.0:1.1),  $R - CH_2CH_3$ ; (▲) HTBBB with tris(2-chloroethyl) phosphite (1.0:1.1),  $R - CH_2CH_2Cl$ ; (■) HTBBB with triphenyl phosphite (1.0:2.0),  $R - \text{C}_6\text{H}_5$ ; (□) HTBBB with triphenyl phosphite (1.0:1.1),  $R - \text{C}_6\text{H}_5$ .

All the four HTBBP are not dissolved in methanol, acetonitrile, dichloromethane, carbon tetrachloride, *n*-hexane, cyclohexane, ethyl ether, and ethyl acetate but dissolved in DMF, DMAc, and acetic acid. They are also dissolved in hot DMSO but precipitate when cooled. So, DMSO can be used as a recrystallizing solvent for HTBBP. Except for HTBBP<sub>M</sub>, which is the most difficult one to dissolve in any kind of solvent, the three other HTBBP also dissolved in chloroform and tetrahydrofuran.

#### TGA and DSC Measurements

TG curves of the four HTBBP are shown in Figure 6. The threshold temperatures for weight loss and amounts of residual product at different temperatures are listed in Table VI.

The threshold temperature for HTBBP<sub>P</sub> is 280°C and the amount of residual product at 700°C is 26 wt %. The threshold temperatures for HTBBP<sub>M</sub>, HTBBP<sub>E</sub>, and HTBBP<sub>CE</sub> are 255, 268, and 270°C, respectively, and the amounts of residual products at 700°C are all about 15%. Both the threshold temperature and residual amount at different temperatures are higher for HTBBP<sub>P</sub> than for the three others as a result of heat stabilization of aromatic rings. The threshold temperatures for HTBBP<sub>E</sub> and HTBBP<sub>CE</sub>

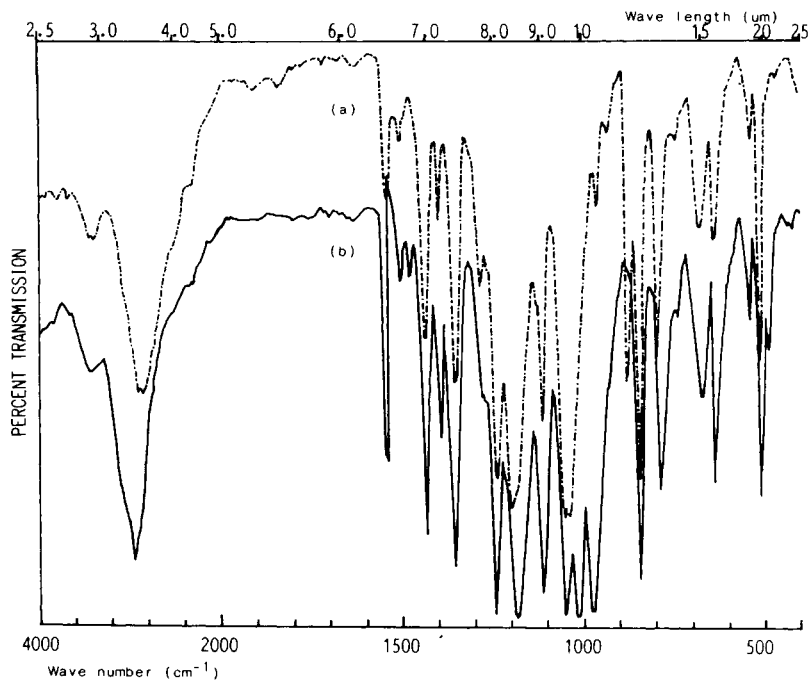


Fig. 4. IR spectra of HTBBP<sub>M</sub> (a) and HTBBP<sub>E</sub> (b).

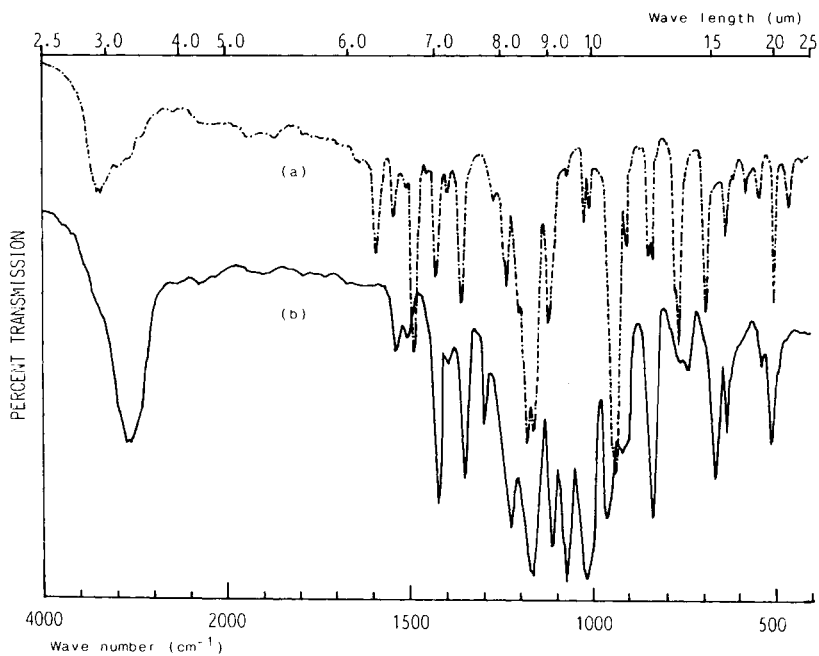


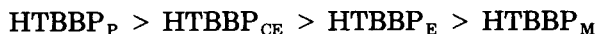
Fig. 5. IR spectra of HTBBP<sub>P</sub> (a) and HTBBP<sub>CE</sub> (b).

TABLE III  
<sup>1</sup>H-NMR Spectral Data for HTBBP

Compound	<sup>1</sup> H-NMR (ppm, DMSO-d <sub>6</sub> )
HTBBP <sub>M</sub>	3.69, 3.91 (2H, d, —CH <sub>2</sub> P(O)—) 3.55, 3.69 (6H, d, —OCH <sub>3</sub> )
HTBBP <sub>E</sub>	3.67, 3.90 (2H, d, —CH <sub>2</sub> P(O)—) 3.81-4.13 (4H, m, —OCH <sub>2</sub> —) 1.19 (6H, t, —CH <sub>3</sub> )
HTBBP <sub>CE</sub>	4.02, 4.26 (2H, d, —CH <sub>2</sub> P(O)—) 4.13-4.33 (4H, m, —OCH <sub>2</sub> —) 3.78 (4H, t, —CH <sub>2</sub> —Cl)
HTBBP <sub>P</sub>	4.13, 4.38 (2H, d, —CH <sub>2</sub> P(O)—) 7.04-7.42 (10H, m, aromatic protons)

are higher than that for HTBBP<sub>M</sub>, but the residual amounts at different temperatures are lower for HTBBP<sub>E</sub> and HTBBP<sub>CE</sub> due to their longer side chains.

As shown in Table VII, fusion energies of the four HTBBP are determined by DSC measurement using Indium ( $\Delta H = 28.4$  J/g) as a standard. The fusion energies of HTBBP<sub>M</sub>, HTBBP<sub>E</sub>, HTBBP<sub>CE</sub>, and HTBBP<sub>P</sub> are 61.1, 72.8, 67.1, and 102.1 J/g, respectively. HTBBP<sub>P</sub> has the highest gram fusion energy; HTBBP<sub>E</sub> the second. The conversion of gram fusion energies into molar fusion energies is found to be the following order:



### Flame-Retardancy Effects of Phenolic Brominated Compounds on HIPS

Pentabromophenol (PBP), tetrabromobisphenol A (TBBPA), and tetrabromo-*p*-cresol (TBPC) are used as phenolic brominated compounds to add to HIPS. Their flame-retardancy effects on the oxygen index of HIPS are shown in Figure 7. The oxygen index increases with the increase in the additive amount of brominated compound. And there is a linear relationship between oxygen index and additive amount up to 10 phr. Equations (4)–(6) show the linear dependence of the oxygen index on the additive amount of brominated compound:

$$\text{OI(HIPS)} \cong 17.3 + 0.37 \times \text{phr(PBP)} \quad (4)$$

$$\text{OI(HIPS)} \cong 17.3 + 0.27 \times \text{phr(TBBPA)} \quad (5)$$

$$\text{OI(HIPS)} \cong 17.3 + 0.33 \times \text{phr(TBPC)} \quad (6)$$

The intercepts in the above equations correspond to the oxygen index values of the pure HIPS, while the slopes give the increase of the oxygen index per phr brominated compound present in HIPS. The flame-retardancy effect of PBP in HIPS is higher than those of the two others with the same additive amount, because PBP contains higher bromine concentration.

The dependence of oxygen index on the bromine concentration is shown in Figure 8. The oxygen index increases with the increase of bromine concentration. The efficiency curves for these three compounds are linear and have the same slope. It is described by Eq. (7):

$$\text{OI(HIPS)} \cong 17.3 + 0.45 \text{ phr(Br)} \quad (7)$$

TABLE IV  
<sup>13</sup>C-NMR Data for HTBBP

Compound	<sup>13</sup> C-NMR chemical shift (ppm)									
	P	M	O	X	Y	α	β	γ	δ	δ
HTBBP <sub>M</sub>	151.84	115.81	127.05	127.11	40.63 34.51	52.45	—	—	—	—
HTBBP <sub>E</sub>	151.64	115.76	126.92	127.46	41.55 35.58	61.63	16.07	—	—	—
HTBBP <sub>CE</sub>	151.90	115.76	127.06	126.75	41.39 35.22	65.70	43.70	—	—	—
HTBBP <sub>P</sub>	151.27	115.92	127.32	125.86	42.15 35.87	149.78	129.76	120.12	—	125.16

TABLE V  
The Solubilities<sup>a</sup> of HTBBP in Various Solvents

	HTBBP <sub>M</sub>	HTBBP <sub>E</sub>	HTBBP <sub>CE</sub>	HTBBP <sub>P</sub>
Methanol	-	-	±	-
Acetone	-	-	±	±
Acetonitrile	-	-	-	-
Dichloromethane	-	-	-	-
Chloroform	-	+	+	+
Carbon tetrachloride	-	-	-	-
Tetrahydrofuran	±	+	+	+
<i>n</i> -Hexane	-	-	-	-
Cyclohexane	-	-	-	-
Benzene	-	-	±	±
Toluene	-	-	±	±
Ethyl ether	-	-	-	-
Ethyl acetate	-	-	-	-
Acetic acid	+	+	+	+
Xylene	-	±	±	±
DMF	+	+	+	+
DMAc	+	+	+	+
DMSO	A	A	A	A

<sup>a</sup> Solubility keys: (+) soluble; (±) partially soluble; (-) insoluble; (A) heat to soluble, cool to precipitate.

It means that the same bromine concentration among these three brominated compounds will have the same flame-retardancy effect on HIPS.

### Flame-Retardancy Effects of HTBBP on HIPS

The flame-retardancy effects of these new HTBBP on the oxygen index of HIPS are shown in Figure 9. The oxygen index increases with the increase of the additive amount of each HTBBP. Adding the same amount of HTBBP to HIPS, respectively, HTBBP<sub>CE</sub> has the best flame-retardancy effect; HTBBP<sub>P</sub>, the second best.

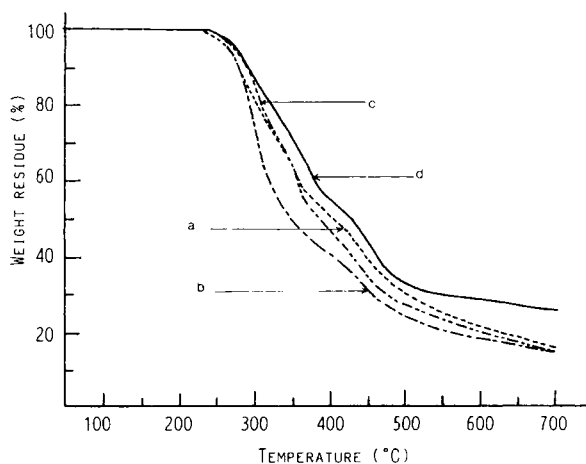


Fig. 6. TGA curves of HTBBP in N<sub>2</sub>—(a) HTBBP<sub>M</sub>; (b) HTBBP<sub>E</sub>; (c) HTBBP<sub>CE</sub>; (d) HTBBP<sub>P</sub>—with heating rate 20°C/min.

TABLE VI  
TGA Data for HTBBP

Compound	Threshold temperature for wt loss (°C)	Residue (%) at various temperatures (°C)					
		250	300	400	500	600	700
HTBBP <sub>M</sub>	255	97	81	50	30	21	16
HTBBP <sub>E</sub>	268	100	72	40	25	17	15
HTBBP <sub>CE</sub>	270	100	85	46	27	16	15
HTBBP <sub>P</sub>	280	100	86	54	32	28	26

The efficiency curves for HTBBP are linear in HIPS; they are described by

$$OI(\text{HIPS}) \cong 17.3 + 0.46 \text{ phr}(\text{HTBBP}_E) \quad (8)$$

$$OI(\text{HIPS}) \cong 17.3 + 0.49 \text{ phr}(\text{HTBBP}_M) \quad (9)$$

$$OI(\text{HIPS}) \cong 17.3 + 0.63 \text{ phr}(\text{HTBBP}_P) \quad (10)$$

$$OI(\text{HIPS}) \cong 17.3 + 0.77 \text{ phr}(\text{HTBBP}_{CE}) \quad (11)$$

The oxygen index increases with the increase of the additive bromine concentration and relates linearly to it, as shown in Figure 10. The efficiency curves for HTBBP<sub>E</sub> and HTBBP<sub>M</sub> have the same slope due to the similar components which cause similar flame-retardancy effects on HIPS. With the same additive bromine and phosphorus concentrations, HTBBP<sub>CE</sub> shows the best flame-retardancy effect due to the presence of chlorine atoms in itself. The flame-retardancy effect of aromatic ring may be better than that of alkyl group, so that HTBBP<sub>P</sub> shows better effect on the oxygen index of HIPS than HTBBP<sub>M</sub> and HTBBP<sub>E</sub> do at the same bromine concentration.

### The Flame-Retardancy Effects of Phosphite on HIPS

Among the four phosphorus-supplying compounds used in this experiment, trimethyl phosphite, and triethyl phosphite have higher volatility and offensive odor, but tris(2-chloroethyl) phosphite (TCEP) and triphenyl phosphite (TPP) have high boiling points and low volatility. So, TCEP and TPP are added to HIPS as flame retardants, and their flame-retardancy

TABLE VII  
DSC Data and Fusion Energies of HTBBP

Compound	Peak temperature (°C)	<i>m</i> (mg)	<i>A</i> (mg)	$\Delta H_f$	
				(J/g)	(J/mol)
Standard (In)	156	27.4	50.88	28.4	
HTBBP <sub>M</sub>	262	9.9	39.52	61.1	32,505
HTBBP <sub>E</sub>	218	13.2	62.84	72.8	34,216
HTBBP <sub>CE</sub>	162	12.9	56.52	67.1	45,864
HTBBP <sub>P</sub>	185	10.0	66.76	102.1	66,978

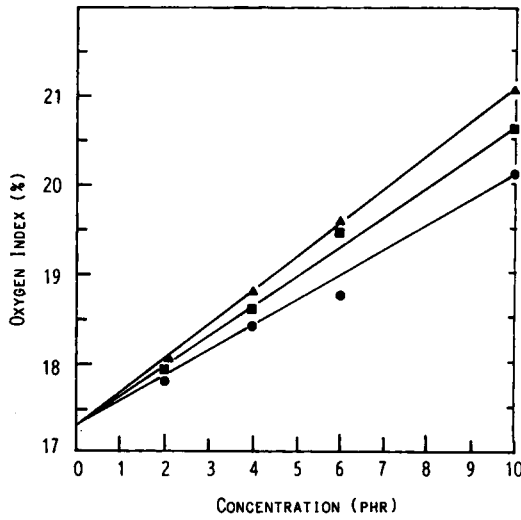


Fig. 7. Plots of oxygen index vs. additive concentration of phenolic brominated compound in HIPS: (▲) PBP; (■) TBPC; (●) TBBPA.

effects are shown in Figure 11. The oxygen index increases with the increase of the additive amounts of TCEP and TPP and relates linearly to them. The efficiency curves are described

$$\text{OI(HIPS)} \cong 17.3 + 0.36 \text{ phr(TPP)} \quad (12)$$

$$\text{OI(HIPS)} \cong 17.3 + 0.70 \text{ phr(TCEP)} \quad (13)$$

The flame-retardancy effect is higher for TCEP than for TPP with the same additive amount.

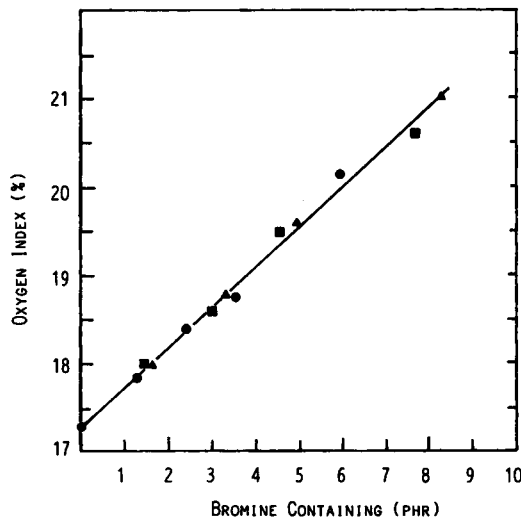


Fig. 8. Plot of oxygen index vs. bromine concentration of phenolic brominated compound in HIPS: (▲) PBP; (■) TBPC; (●) TBBPA.



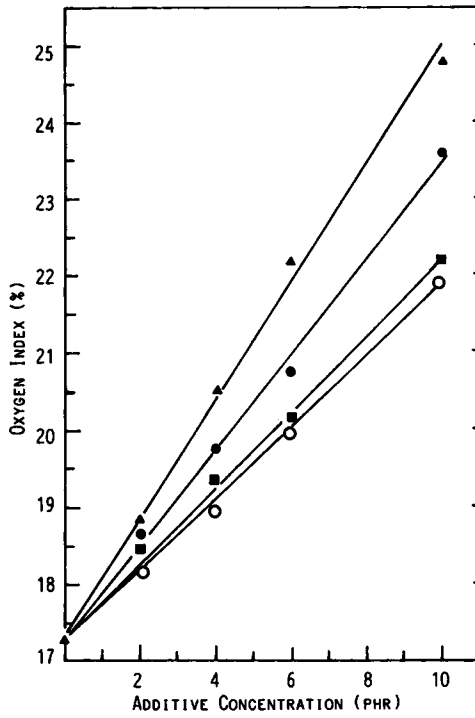


Fig. 9. Plots of oxygen index vs. additive concentration of HTBBP in HIPS: (■) HTBBP<sub>M</sub>; (○) HTBBP<sub>E</sub>; (●) HTBBP<sub>P</sub>; (▲) HTBBP<sub>CE</sub>.

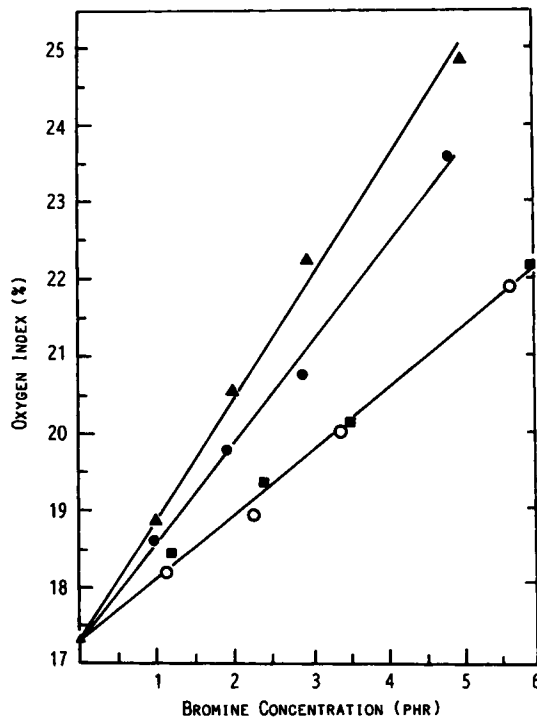


Fig. 10. Plots of oxygen index vs. bromine concentration of HTBBP in HIPS: (■) HTBBP<sub>M</sub>; (○) HTBBP<sub>E</sub>; (●) HTBBP<sub>P</sub>; (▲) HTBBP<sub>CE</sub>.

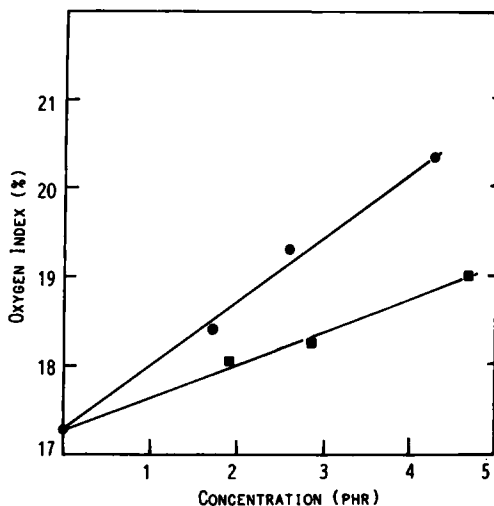


Fig. 11. Plots of oxygen index vs. additive concentration of phosphite in HIPS: (●) TCEP; (■) TPP.

As shown in Figure 12, the oxygen index relates linearly to the phosphorus concentration. The above relation can be described by

$$\text{OI(HIPS)} \cong 17.3 + 3.6 \text{ phr(P in TPP)} \quad (14)$$

$$\text{OI(HIPS)} \cong 17.3 + 6.12 \text{ phr(P in TCEP)} \quad (15)$$

That the flame-retardancy effect for TCEP is better is seemingly due to the presence of chlorine atoms which may assist phosphorus atoms to reduce the flammability of HIPS. But the low molecular-weight phosphite is unstable in plastic, easily dissolved out, or excluded from polymer matrix.

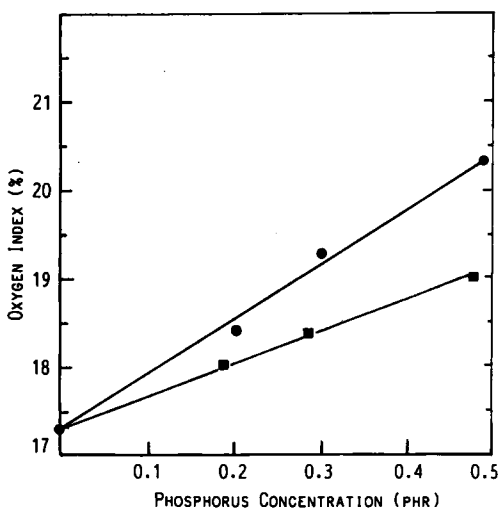


Fig. 12. Plots of oxygen index vs. phosphorus concentration of phosphite in HIPS: (●) TCEP; (■) TPP.

### Simultaneously Additive Effect of Bromine-Containing and Phosphorus-Containing Compounds

As shown in Figure 13, the individual effects of TPP and TBPC on HIPS are shown by lines a and b respectively. Line c corresponds to the calculated values with simultaneous additions of TPP and TBPC; line d shows the measured values. The measured values are larger than calculated ones. It seems that TPP and TBPC act synergistically as flame retardants in HIPS. As shown by line e, the flame-retardancy effects of HTBBP<sub>P</sub> on HIPS are better than not only those expected in line c but also the combined effects of TBPC and TPP as shown by line d. The better flame-retardancy effects of HTBBP<sub>P</sub> show that bromine-containing and phosphorus-containing compounds seem to act synergistically and that the effects are higher for the chemical combination of the brominated compound and phosphorus-containing compound than for the physical mixing of them. The physically combined effects of TPP and TBPC on HIPS are less than those of chemically combined compound (HTBBP<sub>P</sub>). The probable reasons are the heterogenous mixing of TPP and TBPC, the exclusion of TPP from polymer matrix, and the contribution of chemical bond in HTBBP<sub>P</sub>.

Figure 14 shows the comparison of oxygen index of HTBBP<sub>CE</sub> and TBPC plus TCEP on HIPS. Both the oxygen index values of HIPS with simultaneous additions of TCEP and TBPC and those of HIPS with HTBBP<sub>CE</sub> are better than those expected in line c.

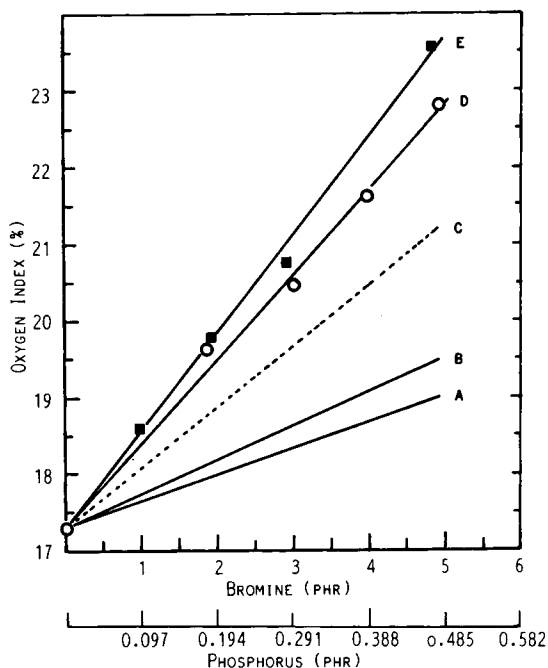


Fig. 13. Synergistic effects of brominated phosphonate (HTBBP<sub>P</sub>) and brominated compound (TBPC) plus phosphorus-containing compound (TPP) on HIPS: (a) TPP; (b) TBPC; (c) additive values; (d) measured values with TPP and TBPC; (e) HTBBP<sub>P</sub>.

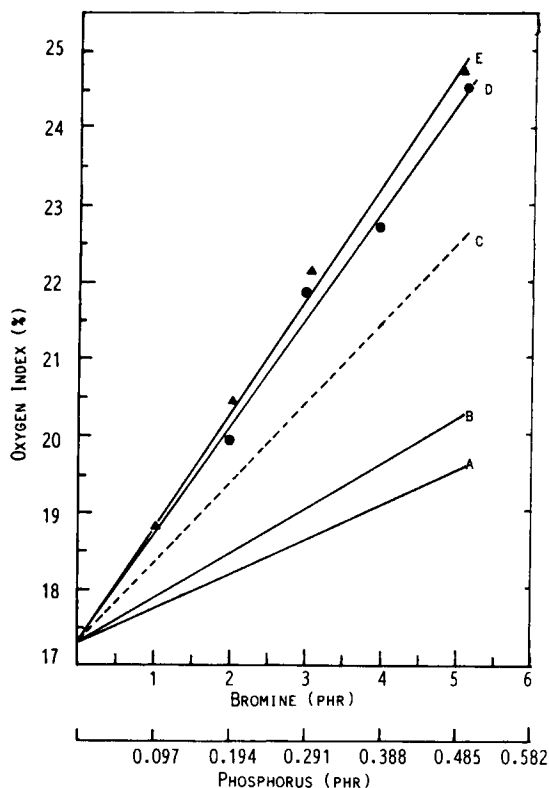


Fig. 14. Synergistic effects of brominated phosphonate ( $\text{HTBBP}_{\text{CE}}$ ) and brominated compound (TBPC) plus phosphorus-containing compound (TCEP) on HIPS: (a) TBPC; (b) TCEP; (c) additive values; (d) measured values with TCEP and TBPC; (e)  $\text{HTBBP}_{\text{CE}}$ .

The flame-retardancy effects of  $\text{HTBBP}_{\text{P}}$  and  $\text{HTBBP}_{\text{CE}}$  on HIPS show that either the brominated compound and phosphorus-containing compound seem to act synergistically or the effects of bromine atoms and phosphorus atom in the same compound are better than those of brominated compound and phosphorus-containing compound combined by physical mixing.

## CONCLUSIONS

1. 4-Hydroxy-2,3,5,6-tetrabromobenzyl bromide ( $\text{HTBBB}$ ) can be easily prepared with high yield by the bromination of *p*-cresol.

2. It is easy for  $\text{HTBBB}$  to react with trialkyl phosphite and triaryl phosphite to produce corresponding 4-hydroxy-2,3,5,6-tetrabromobenzyl phosphonate ( $\text{HTBBP}$ ).

3.  $\text{HTBBP}_{\text{M}}$  and  $\text{HTBBP}_{\text{E}}$  can dissolve in DMAc, DMSO, DMF, and acetic acid but can hardly dissolve in other ordinary organic solvents. In general, the solubilities of  $\text{HTBBP}_{\text{E}}$  and  $\text{HTBBP}_{\text{P}}$  are better than those of  $\text{HTBBP}_{\text{M}}$  and  $\text{HTBBP}_{\text{E}}$ .

4. TG measurements show that  $\text{HTBBP}_{\text{P}}$  has the best thermal stability of the four  $\text{HTBBP}$ . As obtained from DSC measurement, the fusion energies of  $\text{HTBBP}_{\text{M}}$ ,  $\text{HTBBP}_{\text{E}}$ ,  $\text{HTBBP}_{\text{CE}}$ , and  $\text{HTBBP}_{\text{P}}$  are 61.1, 72.8, 67.1, and 102.1 J/g, respectively.

5. For the phenolic brominated compounds, there is a linear relationship between the oxygen index values of HIPS and additive amounts, respectively. Bromine concentrations and oxygen index values also indicate linearity and the points representing measurements for the three compounds scatter along the same line.

6. The efficiency curves for phosphite are linear in HIPS and the flame-retardancy effects are better for TCEP than for TPP.

7. With individual addition of the four HTBBP to HIPS, HTBBP<sub>CE</sub> has the best flame-retardancy effect; HTBBP<sub>P</sub> the second best. With the same bromine concentration and phosphorus concentration, HTBBP<sub>CE</sub> also shows the best effects on HIPS and the points representing measurements for HTBBP<sub>M</sub> and HTBBP<sub>E</sub> scatter along the same line.

8. Brominated compound and phosphorus-containing compound seem to act synergistically as flame retardants in HIPS, but with the addition of HTBBP on HIPS we can get much better synergistic effects and prevent the phosphite from being dissolved out or excluded from the polymer matrix.

The authors are thankful to Dr. T. S. Lin, president of the Tatung Institute of Technology, for his support. Thanks also to Dr. W. C. Kuo for his valuable discussion.

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Received August 14, 1985

Accepted January 6, 1986