Journal of Thermal Analysis and Calorimetry, Vol. 85 (2006) 1, 73–78

THERMAL PROPERTIES OF POLY(STYRENE) CONTAINING BROMINATED ARYL PHOSPHATE ADDITIVES

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General purpose poly(styrene) is a large volume commodity polymer widely used in a range of applications. For many of these the presence of an additive to impart some flammability resistance is required. Most commonly, brominated aromatics are used for this purpose. As the polymer undergoes combustion these compounds decompose to generate bromine atoms and/or hydrogen bromide which escape to the gas phase and trap flame propagating radicals. While these species are effective in inhibiting flame propagation they present the opportunity for loss of halogen to the atmosphere. For this reason, the use of these compounds is being limited in some parts of the world. Phosphorus compounds, on the other had, impart a flame retarding influence by promoting char formation at the surface of the burning polymer. This prevents heat feedback to the polymer and consequent pyrolysis to generate fuel fragments. The combination of both bromine and phosphorus present in a single compound might generate a superior flame-retarding additive in that both modes of retardancy might be promoted simultaneously. Should this be the case smaller amounts of additive might be necessary to achieve a satisfactory level of flame retardancy. A series of such additives, brominated aryl phosphates, has been synthesized and fully characterized spectroscopically. Blends of these additives, at various levels, with poly(styrene) have been examined by DSC, TG and in the UL-94 flame test. The flammability of the polymer is dramatically diminished by the presence of the additive.

Keywords: *dual-action flame retardants, flame-retarded poly(styrene), flame-retarding additives, halogenated phosphorus flame retardants, thermal properties*

Introduction

Organohalogen compounds, particularly brominated aromatic compounds, are widely used as flame retardant additives for polymeric materials. In general, these additives are extremely effective and are available at low cost. These attributes have made them very popular with plastics formulators. However, there is increasing concern about the potential negative environmental impact of some of these compounds. Both pentabromodiphenyl ether and octabromodiphenyl ether have been voluntarily removed from the market. Two compounds, pentabromodiphenylether and hexabromobiphenyl, are under consideration for phaseout through the Stockholm Convention on Persistant Organic Pollutants [1]. In contrast, decabromodiphenylether remains the most widely used organohalogen flame retardant. Because of the concerns about the use of some organobromine compounds there is an increasing demand for more environmentally benign (i.e. 'greener') flame retardants. Effective flame retardants that contain lower levels of bromine (or no bromine at all) are needed to be responsive to this concern. Organohalogen compounds are gas-phase active flame retardants. They undergo degradation at the temperature of the burning polymer to liberate hydrogen halide and/or halogen atoms which are effective scavengers of flame propagating radicals, principally oxygen and hydroxyl radicals [2, 3]. Other additives promote flame retardancy by action in the solid phase. In the main, organophosphosphorus compounds function in this way. They facilitate the formation of a protective layer at the surface of the degrading polymer which inhibits heat feedback from the flame and limits the production of fuel fragments by thermal degradation of the polymers. Most solid-phase active flame retardants are compounds that can promote cross-linking and char formation. Cross-linking facilitates char formation by creating a carbon-carbon network whereby chain cleavage, which produces volatile components, is retarded [4–8].

A way of achieving enhanced flame retardant activity is to construct compounds which display more than a single mode of action or that are capable of a synergy of flame suppressant properties. Compounds containing both a high level of halogen, in particular bromine, and another element which may be converted to a cross-linking, char-promoting agent during the combustion process might display these characteristics. Accordingly, a series of (bromophenyl)diethylphosphates has been prepared. These compounds contain both bromine and phosphorus.

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1388–6150/$20.00

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Experimental

In general, synthesis reactions were performed under a static atmosphere of prepurified nitrogen in dry apparatus. The apparatus employed for synthesis consisted of a three-necked, round-bottomed flask fitted with a pressure-equalizing dropping funnel, a Trubore stirrer and an Allihn condenser bearing a gas-inlet tube. Prior to use all glassware was thoroughly cleaned, dried overnight in an oven controlled at 160°C, and allowed to cool under a stream of purified nitrogen. Polymerization was carried out in 25×200 mm Pyrex test tubes. Solutions were thoroughly degassed prior to polymerization (three freeze-thaw cycles; nitrogen purge). Size exclusion chromatography was accomplished using a Waters 150-CV unit equipped with Polymer Laboratories mixed bed columns, narrow distribution poly(styrene) standards, and tetrahydrofuran at 1 mL min^{-1} as eluent. Solutions for analysis (0.01 mass percent in THF) were filtered through a 0.45 μm nylon filter prior to injection. Nuclear magnetic resonance (NMR) spectra (^{1}H and ^{13}C) were obtained using a Varian Mercury Plus 300 MHz NMR spectrometer and a solution (10~30%) of the sample in deuterochloroform. The NMR chemical shifts were reported in parts per million (δ) relative to internal tetramethylsilane (TMS δ=0.00). The following standard abbreviations were used in describing NMR data: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and AB pattern. For ^{1}H NMR spectra, each abbreviation is followed by XH, where X is an integer indicating the number of protons represented by the peak. Infrared (IR) spectra were obtained using solid solutions (1~5%) in anhydrous potassium bromide in pellet form and a Nicolet MAGNA-IR 560 Spectrometer. Absorptions were recorded in wavenumbers (cm^{-1}), and absorption intensities were classified in the usual fashion as very weak (vw), weak (w), medium (m), strong (s) and very strong (vs) relative to the strongest band in the spectrum. Mass spectra were determined using a Hewlett-Packard 5995A Gas Chromatograph/Mass Spectrometer with an ionizing potential of 70 electron volts and temperature programmed elution into the spectrometer inlet (90~200°C). Thermal decomposition temperatures were determined by thermogravimetry in a flow of prepurified nitrogen (20 mL min^{-1}) at a heating rate of 40°C min^{-1} using a Perkin-Elmer Pyris 1 Thermogravimetric Analyzer (TG). Melting points were determined using a Perkin-Elmer Pyris Diamond DSC unit at a heating rate of 5°C min^{-1}. The cell was subject to a constant purge of prepurified nitrogen at a rate of 20 mL min^{-1}.

(2,4,6-Tribromophenyl)diethylphosphate

A mixture of 36.07 g (0.156 mol) of 2,4,6-tribromophenol and 16 mL (0.124 mol) of diethylphosphite in 150 mL of carbon tetrachloride was stirred at 5°C. After dissolution was complete, 29 mL of triethylamine (Et_3N) was added dropwise over a period of 0.5 h. The resulting mixture was allowed to warm to room temperature and was stirred overnight. Triethylammonium chloride was removed by filtration. The filtrate was washed successively, with 20 mL of 2 M aqueous sodium hydroxide solution and two 20-mL portions of water. The solution was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure to afford a colorless oil which solidified on standing at 0°C. The product (51.91 g, 89.7% yield) was collected and characterized using spectroscopic and thermal methods; *m.p.* 73°C (DSC); *d.p.* 259°C (TG); ^{1}H NMR (δ, $CDCl_3$) 7.69 (s, 2H, aromatic protons between bromines), 4.32 (q, 4H, methylene protons adjacent to oxygen), 1.39 (t, 6H, methyl protons); ^{13}C NMR (δ, $CDCl_3$) 145.8 (aromatic carbon atom adjacent to oxygen), 135.2 (two aromatic carbon atoms between bromines), 118.5 (aromatic carbon atom adjacent to 4-bromine), 117.5 (two aromatic carbon atoms adjacent to 2,4-bromines), 65.2 (two methylene carbon atoms adjacent to oxygen), 15.9 (two methyl carbon atoms); FTIR (cm^{-1}, NaCl) 3073 (s) (aromatic C–H stretching), 2979 (s) (aliphatic C–H stretching), 1441 (vs) (methylene C–H bending), 1372 (s) (methyl C–H bending), 1290 (vs) and 1248 (s) (P–O–C aromatic stretching), 1045 (vs) and 983 (s) (P–O–C aliphatic stretching); mass spectrum (*m*/*e*, % of base), 28(35), 63(5), 81(16), 109(14), 143(7), 250(17), 301(6), 331(100), 387(31), 466(M^+, 5).

(4-Bromophenyl)diethylphosphate

d.p. 231°C (TG); ^{1}H NMR (δ, $CDCl_3$) 7.28 (AB pattern, J_{AB}=8.7 Hz, 4H, aromatic protons), 4.21 (q, 4H, methylene protons adjacent to oxygen), 1.34 (t, 6H, methyl protons); ^{13}C NMR (δ, $CDCl_3$) 149.5 (aromatic carbon atom adjacent to oxygen), 132.5 (two aromatic carbon atoms *ortho* to bromine), 121.6 (two aromatic carbon atoms *ortho* to oxygen), 117.7 (aromatic carbon atom adjacent to bromine), 64.6 (two methylene carbon atoms adjacent to oxygen), 15.9 (two methyl carbon atoms); FTIR (cm^{-1}, NaCl) 3093 (vw) (aromatic C–H stretching), 2985 (s) (aliphatic C–H stretching), 1484 (vs) (methylene C–H bending), 1395 (w) (methyl C–H bending), 1281 (s) and 1220 (s) (P–O–C aromatic stretching), 1032 (vs) and 960 (P–O–C aliphatic stretching); mass spectrum (*m*/*e*, % of base), 28(20), 63(13), 81(25), 109(27), 143(19), 172(100), 184(48), 236(10), 252(31), 280(37), 308(M^+, 98).

(2,4-Dibromophenyl)diethylphosphate

d.p. 265°C (TG); ^{1}H NMR (δ, $CDCl_3$) 7.72 (s, 1H, aromatic proton between bromines), 7.41 (d, 1H, aromatic proton *ortho* to 4-bromine), 7.38 (A portion of AB pattern, 1H, aromatic proton *ortho* to oxygen), 4.27 (q, 4H, methylene protons adjacent to oxygen), 1.37 (t, 6H, methyl protons); ^{13}C NMR (δ, $CDCl_3$) 147.2 (aromatic carbon atom adjacent to oxygen), 135.7 (aromatic carbon atom between bromines), 131.5 (aromatic carbon atom *ortho* to bromine), 122.1 (aromatic carbon atom *ortho* to oxygen), 117.8 (aromatic carbon atom adjacent to 4-bromine), 115.3 (aromatic carbon atom adjacent to 2-bromine), 65.1 (two methylene carbon atoms adjacent to oxygen), 15.9 (two methyl carbon atoms); FTIR (cm^{-1}, NaCl) 3087 (w) (aromatic C–H stretching), 2984 (m) (aliphatic C–H stretching), 1471 (vs) (methylene C–H bending), 1372 (m) (methyl C–H bending), 1289 (s) and 1236 (s) (P–O–C aromatic stretching), 1038 (vs) and 956 (s) (P–O–C aliphatic stretching); mass spectrum (*m*/*e*, % of base), 28(20), 63(8), 81(12), 109(10), 143(3), 172(10), 223(11), 251(100), 281(24), 307(23), 343(2), 359(1), 388(M^+, 23).

(Pentabromophenyl)diethylphosphate

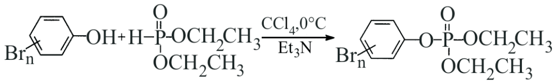
m.p. 137°C (DSC); *d.p.* 242°C (TG); ^{1}H NMR (δ, $CDCl_3$) 4.32 (q, 4H, methylene protons adjacent to oxygen), 1.41 (t, 6H, methyl protons); ^{13}C NMR (δ, $CDCl_3$) 147.1 (aromatic carbon atom adjacent to oxygen), 128.8 (two aromatic carbon atoms *ortho* to 4-bromine), 126.0 (aromatic carbon atom adjacent to 4-bromine), 120.4 (aromatic carbon atoms *ortho* to oxygen), 65.5 (two methylene carbon atoms adjacent to oxygen), 16.1 (two methyl carbon atoms); FTIR (cm^{-1}, NaCl) 2981 (m) (aliphatic C–H stretching), 1370 (m) (methylene C–H bending), 1319 (s) and 1292 (s) (P–O–C aromatic stretching), 1040 (s) and 970 (s) (P–O–C aliphatic stretching); mass spectrum (*m*/*e*, % of base), 81(43), 109(29), 141(15), 220(35), 301(45), 408(17), 461(17), 489(100), 625(M^+, 3).

Results and discussion

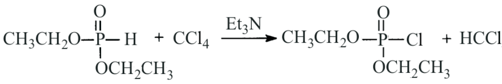
Organohalogen and organophosphorus compounds represent two major classes of flame retardants for polymeric materials. Organohalogen compounds, particularly brominated aromatics, are used in largest volume. This may be attributed to their effectiveness and low cost. Organohalogen compounds decompose at the temperature of the burning substrate to release halogen atoms and hydrogen halide into the vapor phase. These species scavenge flame-propagating radicals, particularly hydroxyl and oxygen radicals. Thus, the combustion cycle is interrupted. These compounds are referred to as gas-phase active. Organophosphorus compounds, unlike organohalogen compounds, are primarily solid-phase active. Some of these compounds display both solid-phase and gas-phase activity. The primary mode of action, particularly when these compounds are used in oxygenated polymers, is the formation of acids which promote crosslinking and char formation at the surface of the burning polymer. This char layer prevents heat feedback to the polymer and inhibits pyrolysis which generates fuel fragments necessary to feed the flame. Some phosphorus compounds may also emit radical scavenging species into the gas phase. For example, 9,10-dihydro-9-oxa-10-phosphaphenanthane-10-oxide (DOPO) releases the $PO^{\cdot}$ radical into the gas phase.

The combination of both bromine and phosphorus into the same compound would produce an additive that might be functional in both the solid phase and the gas phase. Such dual functional flame retardants may be generated by converting a brominated phenol into a phosphate ester. The starting material for this preparation is diethyl phosphite. Treatment of diethyl phosphite with a brominated phenol in carbon tetrachloride generates the corresponding phosphate (Scheme 1).

The actual reaction is between the chlorophosphite formed in situ (Scheme 2) and the phenol.



Scheme 1 Synthesis of [(bromo)$_n$phenyl]diethylphosphates



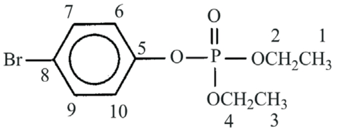
$$CH_3CH_2O-\overset{\displaystyle O}{\overset{\|}{P}}(OCH_2CH_3)-H + CCl_4 \xrightarrow{Et_3N} CH_3CH_2O-\overset{\displaystyle O}{\overset{\|}{P}}(OCH_2CH_3)-Cl + HCCl_3$$

Scheme 2 Generation of diethyl(chloro)phosphite

(4-Bromophenyl)diethylphosphate

(4-Bromophenyl)diethylphosphate was obtained as a yellowish oil (78.6% yield) from reaction of 4-bromophenol with diethylphosphite. This material was characterized by spectroscopic and thermal methods. The proton NMR spectrum of the phosphate is displayed below in Fig. 1.

The ^{13}C NMR spectral data are displayed in Table 1. The infrared spectrum contains characteristic absorptions at 3094 cm^{-1} (w) for aromatic C_{sp2}–H stretching, 2985 cm^{-1} (s) for aliphatic C_{sp3}–H stretching, 1584 cm^{-1} (w) and 1485 cm^{-1} (s) for the phenyl nucleus, 1281 cm^{-1} (s) and 1220 cm^{-1} (s) for aromatic P–O–C stretching, 1098 cm^{-1} (s) and 781 cm^{-1} (s) for O–P–O stretching, 1033 cm^{-1} (s) and 960 cm^{-1} (s) for P–O–C aliphatic stretching vibrations.



The molecular mass of this material is 308 g mol^{-1} as determined by mass spectrometry and its decomposition onset temperature (TG) is 231°C. The mass spectrum of this compound is displayed in Fig. 2. From the intensities of the M^+ and $[M+2]^+$ peaks, *m*/*z* 308 and 310, it is clear that the compound contains a single bromine atom.

Other [(bromo)$_n$phenyl]diethylphosphates, (2,4-dibromophenyl)diethylphosphate, (2,4,6-tribromophenyl)diethylphosphate, (pentabromophenyl)diethylphosphate] were characterized in an analogous manner.

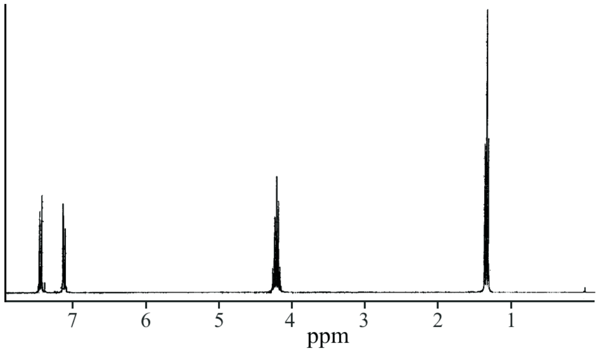


Fig. 1 ^{1}H NMR spectrum of (4-bromophenyl)diethylphosphate

Table 1 ^{13}C NMR spectral data for (4-bromophenyl)diethylphosphate

Chemical shift (δ)	Carbon atoms
15.9	C_1 and C_3
64.6	C_2 and C_4
117.7	C_8
121.6	C_6 and C_{10}
132.5	C_7 and C_9
149.5	C_5

Infrared analysis for phosphorus compounds

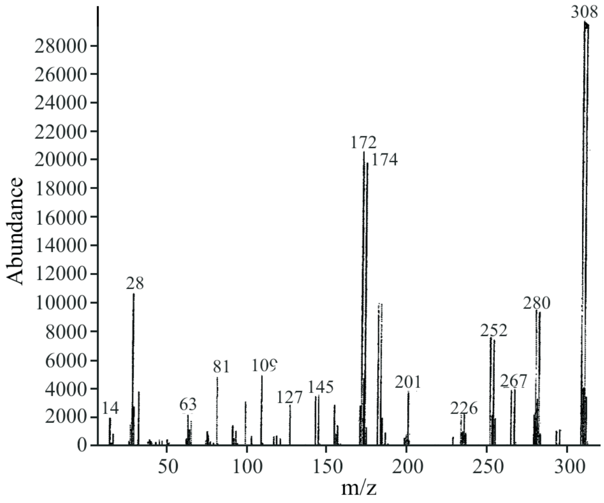


Fig. 2 Mass spectrum of (4-bromophenyl)diethylphosphate

The infrared spectra of all the (bromophenyl)diethylphosphates synthesized contain prominent bands for phosphorus-oxygen stretching. These bands represent one of the most widely used characterization features of organophosphorus compounds. Compounds containing a P–O–C unit are characterized by spectra containing intense absorption bonds near 1000 cm^{-1}. This absorption appears at somewhat higher frequency (905–1060 cm^{-1}) for pentavalent phosphorus compounds than for trivalent (850–1034 cm^{-1}) [9]. In addition, P–O–C (aromatic) stretching vibrations appear at higher frequency than do those of P–O–C (aliphatic). Both of these absorptions are prominent features in spectra of the compounds described here. These are collected in Table 2.

A prominent characteristic in the infrared spectra of organophosphorus compounds are bands arising from O–P–O stretching vibrations. These bands usually appear between 1101 and 780 cm^{-1}. These bands for the (bromophenyl)diethylphosphates described here are listed in Table 3.

These compounds were also characterized by thermal methods. The results are presented in Table 4. It might be noted that all undergo decomposition at approximately 250°C and that two are crystalline solids.

To evaluate the effectiveness of these compounds as flame retardants it was necessary to make polymer plaques, containing a level of the particular compound, of specific dimensions. Solutions of the appropriate concentration of flame retardant in styrene monomer

Table 2 Infrared absorptions for the P–O–C unit in [(bromo)$_n$phenyl]diethylphosphates

Flame retardant	Stretching vibration/cm^{-1}			
	P–O–C (aromatic)		P–O–C (aliphatic)	
(4-bromophenyl)diethylphosphate	1281	1220	1033	960
(2,4-dibromophenyl)diethylphosphate	1289	1236	1038	956
(2,4,6-tribromophenyl)diethylphosphate	1290	1248	1045	983
(pentabromophenyl)diethylphosphate	1319	1292	1040	970

Table 3 Infrared absorptions for the O–P–O unit in [(bromo)$_n$phenyl]diethylphosphates

Flame retardant	Stretching vibration/cm^{-1}	
	O–P–O	
(4-bromophenyl)diethylphosphate	1098	781
(2,4-dibromophenyl)diethylphosphate	1098	794
(2,4,6-tribromophenyl)diethylphosphate	1102	794
(pentabromophenyl)diethylphosphate	1088	818

were prepared, partially polymerized (AIBN initiation; 60°C) to generate a syrup which was poured into a Pyrex mold of 3.2×12.7×127 mm and cured in an oven at 65°C for 8 to 48 h. The plaques obtained were used for the UL-94 vertical burn test. These plaques contained, respectively, three percent and five percent by mass of the flame retardant well dispersed in a poly(styrene) matrix. The polymers generated were characterized by size exclusion chromatography. The results are presented in Table 5.

Thermal properties of poly(styrene) containing [(bromo)$_n$phenyl]diethylphosphates as flame retardants

The samples prepared as described above were subjected to the Underwriters Laboratories vertical burn test (UL-94). In this test a 3.2×12.7×127 mm specimen is held at one end in a vertical position. A burner flame is applied in a vertical direction to the free end of the specimen for two 10-s intervals separated by the time it takes for flaming combustion to cease after the first application. For this test not only the rate at which the flame of the burning polymer is extinguished but also whether or not flaming drips are formed is considered. If flaming drips capable of igniting a cotton sample placed under the test plaque are formed, the effectiveness of the flame retardant is lower than if this is not the case. Of the samples examined here only that containing no additive formed flaming drips. None of those containing flame retardant, even at a three percent level, formed flaming drips. The presence of any of the flame retardants had a positive effect on the flammability of the polymer. For the UL-94 test, results are presented as a series of designations reflecting the effectiveness of the flame retarding additive.

- V-2 Burning stops within 60 s after two applications of 10 s each of a flame to a test bar. Flaming drips ARE allowed.
- V-1 Burning stops within 60 s after two applications of 10 s each of a flame to a test bar. NO flaming drips are allowed.
- V-0 Burning stops within 10 s after two applications of 10 s each of a flame to a test bar. NO flaming drips are allowed.

A V-0 designation is the most desirable and is indicative of effective flame retardation. In this case, a V-0 designation was achieved for poly(styrene) using any of the (bromophenyl)diethylphosphates at a loading of 5 mass%.

(Pentabromophenyl)diethylphosphate was more effective with a V-0 rating being achieved with only a three mass% loading. The results of the flammability testing are collected in Table 6.

Table 4 Thermal characteristics of [(bromo)$_n$phenyl]diethylphosphates

Compound	Melting point (DSC)/°C	Decomposition onset (TG)/°C
(4-bromophenyl)diethylphosphate	–	231
(2,4-dibromophenyl)diethylphosphate	–	255
(2,4,6-tribromophenyl)diethylphosphate	73	258
(pentabromophenyl)diethylphosphate	133	254

Table 5 Size exclusion chromatographic characterization of poly(styrene) samples containing various levels of [(bromo)$_n$phenyl]diethylphosphates as flame retardant additives

Flame retardants	Level/%	Mn/g mol^{-1}	Mw/g mol^{-1}	Polydispersity
none	0	73446	105107	1.43
(4-bromophenyl)diethylphosphate	3	77090	115011	1.49
	5	170875	462432	2.71
(2,4-dibromophenyl)diethylphosphate	3	81830	122315	1.50
	5	184908	477163	2.58
(2,4,6-tribromophenyl)diethylphosphate	3	90006	145332	1.62
	5	247445	845781	3.42
(pentabromophenyl)diethylphosphate	3	88480	156319	1.77
	5	459827	1121817	2.44

Table 6 Flammability of poly(styrene) containing [(bromo)$_n$phenyl]diethylphosphates as flame retardant

Flame retardants	Level/ %	UL-94 rating
(4-bromophenyl)diethylphosphate	3 5	V-1 V-0
(2,4-dibromophenyl)diethylphosphate	3 5	V-1 V-0
(2,4,6-tribromophenyl)diethylphosphate	3 5	V-1 V-0
(pentabromophenyl)diethylphosphate	3 5	V-0 V-0

Conclusions

A series of [(bromo)$_n$phenyl]diethylphosphates has been synthesized, completely characterized by spectroscopic and thermal methods, and examined as flame retardants for poly(styrene). Two of these, (2,4,6-tribromophenyl)diethylphosphate (*m.p.* 73°C) and (pentabromophenyl)diethylphosphate (*m.p.* 137°C) are crystalline solids and offer good potential for development as commercial flame retardants. The effectiveness of these compounds as flame retardants for poly(styrene) has been demonstrated. They provide good flame retardancy at low loading in this polymer.

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DOI: 10.1007/s10973-005-7335-y