THERMAL PROPERTIES OF COMPOUNDS POSSESSING BOTH SOLID-PHASE AND GAS-PHASE FLAME RETARDANT POTENTIAL

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Effective additives are required to impart a measure of fire retardancy to polymeric materials used in a variety of applications. Traditionally, these have been gas-phase active additives, most commonly organohalogen compounds, or solid-phase active agents, often organophosphorus compounds. Organosphosphorus flame retardants are often very effective but may suffer from a cost disadvantage when compared with their organobromine counterparts. Organohalogen flame retardants are usually quite effective but their use is subject to several environmental concerns. The development of additives that could simultaneously promote both types of fire retardant action could make available flame retardants that are both more cost effective and more environmentally friendly than those currently in use. Several sets of compounds including bromoanilino triazine derivatives and bromoaryl phosphates with the potential to display both solid-phase and gas-phase flame retardant activity have been prepared and evaluated by a variety of thermal methods.

Introduction

Currently, there are three forces driving the development of new flame retardant agents for polymers. The first is the ever-increasing need to expand the use range of these materials, i.e., to utilize them in applications at the limits permitted by the properties of the materials – at high temperatures or high stress loads, for example. Flame retardants must be found which are effective under these conditions. Secondly, formulators wish to use as little flame retardant as possible – largely, to reduce the cost of the finished article. Thirdly, there is an ever-increasing demand for more environmentally benign (i.e. 'greener') flame retardants. Not withstanding their superior effectiveness, limitations on the use of organohalogen flame retardants are now being sought in many parts of the world. Effective flame retardants that contain lower levels of halogen (or no halogen at all) are needed to be responsive to this concern.

All these considerations require that more effective flame retardants be found. In particular, if compounds which would simultaneously promote char formation at the surface of the polymer and at the same time display effective gas-phase disruption of the flame propagating reactions could be found a significant advance in flame retardant technology might be possible. In fact, there is some evidence that such agents might display a synergy of action (i.e., that the effectiveness of either mode of action might be enhanced in the presence of the other) [1–3]. This would mean that smaller amounts of total additive would be required to impart the desired level of flame retardancy. This should both lower the cost required to achieve an acceptable level of flammability and reduce the potential environmental impact that might accompany decomposition or release of the additive.

Experimental

Methods and instrumentation

All new materials were fully characterized by spectroscopic, thermal and chromatographic methods. Nuclear magnetic resonance spectra (^{1}H and ^{13}C) were obtained using solutions in deuterochloroform, dimethyl sulfoxide-d_6 or toluene-d_8 containing tetramethylsilane (TMS) as an internal reference and a General Electric QE-300 spectrometer. Infrared spectra were obtained using solid solutions (1%) in anhydrous potassium bromide (as pellets) or thin films between sodium chloride discs using a model 560 Nicolet MAGN-IR spectrophotometer.

Melting points were determined by differential scanning calorimetry (DSC) using a TA Instruments Thermal Analyst model 2100 system equipped with a model 2910 MDSC cell. The sample compartment was subject to a constant purge of dry nitrogen at 50 mL min^{-1}. Thermal degradation characteristics were examined by thermogravimetry using a TA In-
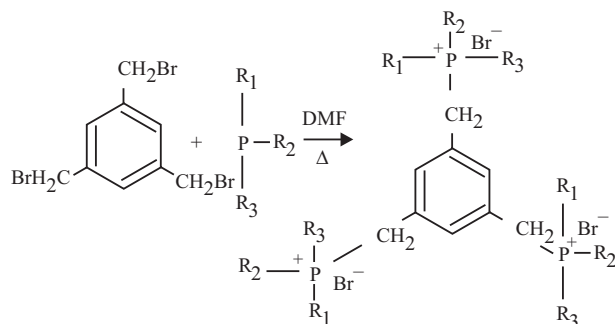
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struments model 2950 TG unit interfaced with the Thermal Analyst Control module. The TG cell was swept with nitrogen at 50 mL min^{-1} during degradation runs. The sample size was 5–10 mg in a platinum sample pan. The temperature was ramped at a rate of 5°C min^{-1}.

Results and discussion

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. Organic compounds, which promote char formation, are those containing phosphorus, nitrogen, sulfur, phenoxy oxygen, and a few other heteroatoms. Many organophosphorus compounds are very effective solid phase flame retardants particularly when used with oxygen-containing polymers. Nitrogen compounds such melamine, melamine phosphate, melamine polyphosphate, ethylenediamine phosphate are frequently used as synergists to reinforce the effect of phosphorus compounds [4–7]. Currently nitrogen-containing flame retardants are mainly used in the textile industry.

Organohalogen compounds, particularly brominated aromatics, continue to be among the most widely used flame retardants [8, 9]. The widespread use of these compounds reflect both their effectiveness and their relatively low cost. They function by liberating, upon thermal decomposition, hydrogen halide or halogen atoms, which interrupt gas phase flame propagating reactions. The incorporation of bromine into a compound containing phosphorous, nitrogen, or other element known to enhance char formation at the surface of burning polymers might generate flame retardant agents which while retaining the good gas phase activity characteristic of organohalogen compounds would also display good solid phase activity. Several series of compounds with the potential to display unique flame retardant characteristics have been prepared and examined by thermogravimetry. Phosphonium salts were prepared by treating 1,3,5-tri(bromomethyl)benzene with phosphines. Examination of the decomposition of these materials by thermogravimety revealed that several of them have decomposition temperatures of greater than 300°C (Fig. 1) [10]. These may be useful for flame retarding polymeric materials that undergo combustion at relatively high temperatures. The symmetrical tri(bromomethyl) benzene has also been uti-
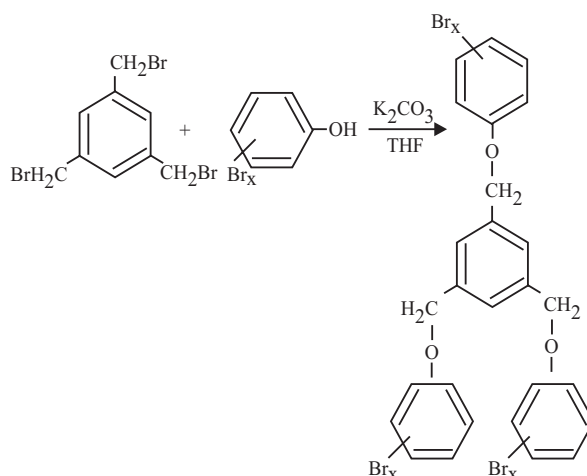

R1, R2, R3	Yield/%	Decomp. temp./°C
Triphenyl	97.3	364
n-Butyldiphenyl	91.9	297
n-Propyldiphenyl	97.6	293
Di-t-butylphenyl	87.0	244
Benzyldiphenyl	96.1	344
Methyldiphenyl	95.0	324
Tri-p-chlorophenyl	87.7	330
Tri-t-butyl	70.2	250

Fig. 1 Thermal decomposition characteristics of phosphonium salts derived from 1,3,5-tri(bromomethyl)benzene

lized as a substrate for the preparation of a series of brominated aryl ethers (Scheme 1) [11].

The thermal properties of these compounds may be found in Table 1. Three of these are solids with good potential as flame retardant agents.
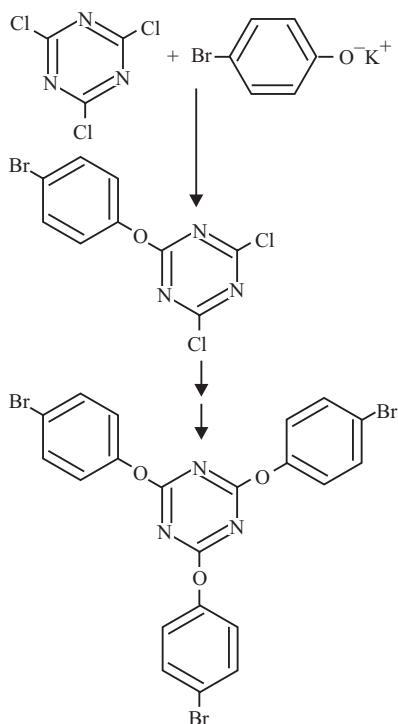
Two series of compounds which contain high levels of nitrogen as well as halogen have been generated by treating 2,4,6-trichloro-1,3,5-triazine with an appropriate nucleophilic reagent. The first was a series of bromophenoxy derivatives obtained by treating the trichlorotriazine with the corresponding phenoxide [12]. This is illustrated in Scheme 2 for the

Scheme 1 Preparation of 1,3,5-tri[(bromo)$_x$phenoxymethyl]benzene

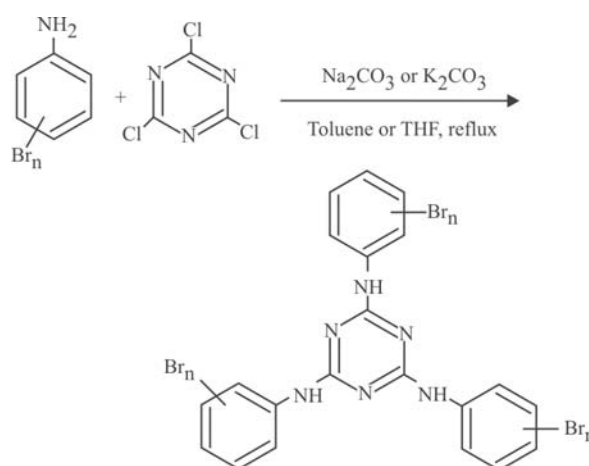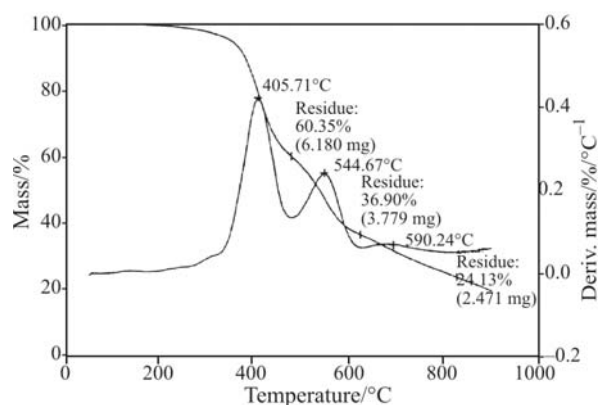**Table 1** Thermal characteristics of variously brominated 1,3,5-(phenoxymethyl)benzenes

Compound (Bromophenoxy substituent)	Melting point/ °C, DSC	Decomp. temp./ °C, DTG
4-Bromophenoxy		255
2,4-Dibromophenoxy	152	307
2,4,6-Tribromophenoxy	277	295
Pentabromophenoxy	290	299

Scheme 3 Synthesis of 2,4,6-tri[(bromo)$_x$anilino]-1,3,5-tri-azines

Scheme 2 Synthesis of 2,4,6-tri(4-bromophenoxy)-1,3,5-triazine

Table 2 Thermal characteristics of 2,4,6-tri(bromo$_x$phenoxy)-1,3,5-triazines

Compound (Bromophenoxy substituent)	Melting point/ °C, DSC	Decomp. temp./ °C, DTG
4-Bromophenoxy	235	372
2,4-Dibromophenoxy	179	385
2,4,6-Tribromophenoxy	229	398
Pentabromophenoxy	371	408

Fig. 2 Thermal decomposition of 2,4,6-tri(4-bromoanilino)-1,3,5-triazine

preparation of 2,4,6-tri(4-bromophenoxy)-1,3,5-triazine. The thermal characteristics of these compounds are displayed in Table 2.

A second series, containing a higher level of nitrogen, was obtained using brominated anilines as the nucleophile. This is illustrated in Scheme 3 [13, 14]. All these compounds are stable solids and contain high levels of both nitrogen (six nitrogen atoms per molecule) and bromine (three to fifteen bromine atoms per molecule). The thermal degradation characteristics for these compounds were determined by thermogravimetry. A thermogram for the decomposition of 2,4,6-tri(4-bromoanilino)-1,3,5-triazine is shown in Fig. 2. The decomposition process consists of three stages. The first centered at 406°C represents a loss of 39.7% of the initial mass and probably reflects the loss of a 4-bromoanilino group.

The second stage is centered at 545°C and corresponds to an additional loss of mass (23% of the initial mass present) and probably reflects the loss of a second bromoanilino group. The final stage of decomposition is centered at 690°C and corresponds to the loss of the final 4-bromoanilino group. The residue, 24.13% of the initial mass of the sample, corresponds to the triazine core of the compound. Other (bromoanilino)triazines degrade similarly. The degradation data are collected in Table 3.

Table 3 Decomposition data for 2,4,6-tri[(bromo)$_x$anilino]-1,3,5-triazines

Compound (No. of bromine atoms)	First stage		Second stage		Third stage		
	dp[a]/ °C, DTG	Mass loss[b]/ %	dp[a]/ °C, DTG	Mass loss[b]/ %	dp[a]/ °C, DTG	Mass loss[b]/ %	Residue/ %
1	405.7	39.65	544.7	23.45	690.2	12.77	24.13
2	418.9	42.05	551.3	25.06	865.6	29.21	3.68
3	447.1	38.02	534.7	36.57	758.1	23.06	2.35
5	430.5	42.41	529.8	39.92	691.9	15.32	2.35

[a]Decomposition point taken as the maximum in a derivative plot of mass loss *vs.* temperature, [b]Mass loss as a percentage of the initial sample mass
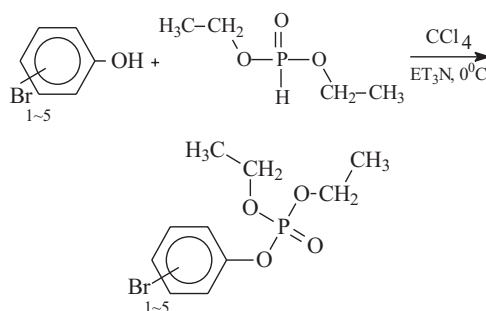
All these compounds undergo initial decomposition at temperatures greater than 400°C and degradation occurs in a stepwise manner reflecting, in the main, sequential loss of bromoanilino groups. As the level of bromine present increases the initial decomposition temperature increases somewhat. These observations suggest that the compounds may be good candidates for high temperature flame retardants and further that both gas-phase action (volatilization of bromine-containing fragments) and solid phase action (formation of a nitrogen-rich residue) will be present.

A series of bromoarylphosphates which could simultaneously promote char formation at the surface of a burning polymer and at the same time display effective gas-phase disruption of flame propagating reactions has been prepared from bromophenols and diethylphosphite [15, 16]. This is illustrated in Scheme 4.

The thermal degradation characteristics of these compounds are shown in Table 4.

The effectiveness of these compounds as flame retardants for poly(styrene) was evaluated using the UL-94 vertical burn test (ASTM D3801) [17]. Plaques for testing were prepared by dissolving the flame retardant in styrene monomer at the appropriate concentration, carrying out partial polymerization (AIBN-initiated) to generate a syrup, and curing the syrup in a mold of dimensions 2×13×127 mm. The re-

sults of the flame test are collected in Table 5. As can be seen all the additives are quite effective as flame retardants for poly(styrene) at the 5% level. Even at a low loading of 3% an appreciable flame retarding influence is observed.

Scheme 4 Synthesis of [(bromo)$_x$phenyl]diethylphosphate

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

Compound (Bromophenyl substituent)	Melting point/ °C, DSC	Decomp. temp./ °C, DTG
4-Bromophenyl		231
2,4-Dibromophenyl		265
2,4,6-Tribromophenyl	73	259
Pentabromophenyl	137	242

Table 5 Impact of the presence of brominated aryl phosphates on the flammability of poly(styrene)

Flame retardant	Loading/mass%	UL-94 rating[a]
(4-Bromophenyl)diethylphosphate		V-1
(2,4-Dibromophenyl)diethylphosphate		V-1
(2,4,6-Tribromophenyl)diethylphosphate	3	V-1
(Pentabromophenyl)diethylphosphate		V-0
(4-Bromophenyl)diethylphosphate		V-0
(2,4-Dibromophenyl)diethylphosphate		V-0
(2,4,6-Tribromophenyl)diethylphosphate	5	V-0
(Pentabromophenyl)diethylphosphate		V-0

[a]A UL-94 rating of V-1 indicates that burning stops (without flaming drips) within 60 sec after two applications of 10 sec each of a flame to a test bar; V-0 indicates that burning stops (without flaming drips) within 10 sec after two applications of 10 sec each of a flame to a test bar and is the most desirable performance rating

Conclusions

A variety of approaches have been utilized to generate compounds containing both halogen (bromine) and either phosphorous or nitrogen. These compounds range from phosphonium bromide salts which display relatively high decomposition temperatures to (bromo-aryl)phosphates which undergo decomposition at much more modest temperatures. These compounds offer the potential to display dual functional behavior as flame retardants, i.e., to maintain the excellent gas phase activity associated with organohalogen compounds while, at the same time, promoting the development of protective char at the solid phase.

References

1 G. Avondo, G. C. Vovelle and R. Delbourge, Comb. Flame, 31 (1987) 7.
2 J. Green, J. Fire Sci., 12 (1994) 257.
3 J. Green, J. Fire Sci., 12 (1994) 338.
4 A. W. van der Made and R. H. van der Made, J. Org. Chem., 58 (1993) 1262.
5 D. J. Berry and B. J. Wakefield, J. Chem Soc. C, (1969) 2342.
6 W. M. Koopes and H. G. Adolph, J. Org. Chem., 46 (1981) 406.
7 A. Ninagawa and H. Matsuda, Macromol. Chem., 180 (1979) 2123.
8 F. A. Pettigrew, Halogenated Flame Retardants, Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, 1993, Vol. 10.
9 P. Georlette, J. Simons and L. Costa, 'Halogen-Containing Fire-Retardant Compounds', in A. F. Grand and C. W. Wilkie, Eds, 'Fire Retardancy of Polymeric Materials', Marcel Dekker Inc., New York, NY, 2000, Ch. 8, pp. 245–284.
10 B. A. Howell, W. Zeng and F. M. Uhl, Polym. Mater. Sci. Eng., 83 (2000) 100.
11 B. A. Howell, K. F. Johnston and C. Liu, Phosphorus, Sulfur Silicon, 147 (1999) 100.
12 B. A. Howell and F. M. Uhl, Polym. Mater. Sci. Eng., 77 (1998) 101.
13 B. A. Howell and H. Wu, Polym. Mater. Sci. Eng., 83 (2000) 72.
14 B. A. Howell and H. Wu, J. Therm. Anal. Cal., 83 (2006) 79.
15 B. A. Howell and Y.-J. Cho, Polym. Mater. Sci. Eng., 93 (2005) 963.
16 B. A. Howell and Y.-J. Cho, J. Therm. Anal. Cal., 85 (2006) 73.
17 B. A. King, 'Flame Retardant Polystyrene: Theory and Practice' in J. Schiers and D. B. Priddy, Eds, 'Modern Styrenic Polymers: Polystyrenes and Styrenic Copolymers', John Wiley and Sons, Inc., New York, NY, 2003, pp. 685–701.