Studies of degradation enhancement of polystyrene by flame retardant additives

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ABSTRACT

Experimental methods as well as thermodynamic modeling techniques were utilized to explore potential gas and condensed-phase contributions of various flame retardant (FR) additives with polystyrene polymer. FR additives investigated include hexabromocyclododecane (HBCD), triphenyl phosphine oxide (TPPO), triphenyl phosphate (TPP), triphenyl phosphine sulfide (TPPS), and sulfur. Flame studies of fundamental FR activity were also employed using molecular beam mass spectrometry analysis of FR active species directly in a flame system. The flame studies show direct evidence for active bromine (HBr, Br) species for HBCD and active phosphorous species (HPO_2, PO, PO_2 HPO_3) species for TPPO and TPP which provide high potential for gas-phase activity for these FR additives. Various experimental measurements were also done to assess the degradation species and the degree of degradation of polystyrene by the FR additives. These studies support enhanced degradation of the base polystyrene polymer by the FR additive as a major pathway for condensed FR activity for HBCD and sulfur FR additives. Phosphorous based structures appear to show little enhancement of polystyrene degradation.

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1. Introduction

Flame retardant (FR) additives are blended with many polymers to provide improved fire resistance so that they can be used in certain commercial applications. Flame retardants can act in a variety of ways to provide increased fire resistance: by raising the ignition temperature, reducing the rate of burning, reducing flame spread, and reducing smoke generation. The two principle modes of action for flame retardants are based on gas-phase and condensed-phase activity. For gas-phase activity, the flame retardant produces an active species in the vapor or gas phase that impacts the burning/combustion process. An example of gas-phase activity is a bromine-based FR molecule such as hexabromocyclododecane (HBCD) that can degrade to produce HBr in the gas phase [1]. The HBr molecule serves as a radical scavenger of key combustion radicals (OH, H) to effectively shut down the combustion process [2].

Condensed-phase activity involves action in the solid or melt phase of the polymer to impact/reduce the burning process. An example of condensed activity is the formation of a char layer that can insulate or isolate the remaining bulk material from the combustion process. Another example of condensed activity is FR interaction with the base polymer to cause enhanced polymer degradation and increased polymer melt flow during the burning process. Many phosphorous-based FRs such as triphenyl phosphate are thought to provide both char forming condensed-phase as well as gas-phase activity [3].

To qualify polymeric materials for commercial applications, the materials must pass certain regulatory fire tests. These fire tests attempt to duplicate real-life fire scenarios, and most tests typically involve burning test samples under various conditions. The type of FR mechanistic activity can be very important when trying to pass a given fire test. For example, increased condensed-phase polymer melt flow is thought to influence the limiting oxygen index (LOI) or ASTM D 2863 test [4].

Experimental studies and thermodynamic modeling calculations were conducted to identify the primary FR mechanism for

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improved fire performance as exhibited by LOI and extinguishment-time testing for polystyrene formulations that contain bromine, phosphorus and sulfur-based FRs. FR additives investigated include HBCD, triphenyl phosphate (TPP), triphenyl phosphine oxide (TPPO), triphenyl phosphine sulfide (TPPS), and sulfur. HBCD was chosen as a control in the present work since it has been thoroughly studied and provides a high degree of FR activity [1,5,6]. Sulfur and TPP are examined because of the unique fire performance observed when both FR additives are blended together in polystyrene [7].

To evaluate the potential for gas-phase FR activity, flame studies were employed using molecular beam mass spectrometry (MBMS) analysis of FR active species directly in a flame system. The MBMS experiments involve only the FR in a fuel-rich flame and simplify the FR burning process by neglecting possible polymer–FR interactions. These flame studies support the role of bromine and phosphorous-containing FRs as active gas-phase radical scavengers whereas sulfur shows only minimal activity.

Previous studies have suggested enhanced degradation of polystyrene as a major FR mechanism for bromine-containing FR additives in polystyrene [1]. This enhanced degradation would be a type of condensed-phase FR activity that is based upon an FR radical abstracting a hydrogen atom off the polystyrene backbone and followed by β scission of the polystyrene radical. Several experimental techniques were used to investigate the degree of condensed-phase FR activity based on the FR-enhanced degradation of polystyrene. Studies included the use of thermogravimetric analysis (TGA), size-exclusion chromatography (SEC), and pyrolysis-mass spectrometry techniques to assess the degradation species and the degree of degradation of polystyrene by various FR additives. Data show clear evidence for the enhanced degradation of polystyrene in the presence of certain sulfur and bromine FRs whereas phosphorus shows no enhancement for the FRs studied. Comparison of data for pure sulfur and triphenyl phosphine sulfide showed that the nature of the sulfur structure is very important for enhanced degradation of polystyrene. These studies support enhanced degradation of the base polystyrene polymer by the FR additives as a major pathway for condensed FR activity for bromine and sulfur FR additives. Phosphorous-based structures appear to show little enhancement of polystyrene degradation, and the primary FR mechanism for phosphorous FR additives is based on gas-phase flame inhibition and radical scavenging chemistry. Molecular modeling was employed to evaluate the thermodynamic potential for a condensed-phase mechanism of FR decomposition to radicals and radical-induced hydrogen abstraction off the polystyrene backbone. The modeling calculations support the experimental measurements for enhanced polystyrene degradation by certain bromine and sulfur FR additives compared with little enhancement for phosphorous-based FR additives.

2. Experimental

2.1. Chemicals and blending

Pure flame retardants were obtained from Albemarle (HBCD), Aldrich (TPP, TPPO, TPPS), and Martin Resources, Inc. (sulfur). Blends were prepared using a Haake RHEOCORD™ 90 apparatus that has a Haake 24124 controller and an attached Rheomix 800 mixing bowl containing roller blade mixers. Each batch or blend contained a total of 50 g of polymer resin and additives. The bowl was heated to 180 °C and polystyrene (PS) was added under low RPM. After the resin softened, the speed was increased to 40 and the FR was added. Blending was continued for 8 min.

Polymer/FR blends were ground to ensure uniform mixing of FR into the polymer (Wiley lab grinder and a 3 mm screen size) before molding into plaques. Plaques measuring 100 mm × 100 mm × 1.5 mm were compression molded using 25–27 g aliquots of the ground material. A Pasadena Hydraulic Platen Press (Model # BL444-C-6M2-DX2357) was used with a set-point temperature of 180 °C and pressure (25,000 pounds per square inch (psi) (172 megapascals (MPa))) application time of 5 min. A small band saw was used to cut the molded plaques into strips for fire tests.

2.2. FR activity testing of blends of FR additives and PS

LOI testing was performed in accord with a modified version of the American Society for Testing and Materials (ASTM) Test D 2863. The modification involves using samples cut from molded plaques that measure 100 mm × 6.5 mm × 1.5 mm.

Ingram describes the FP-7 test as a small scale "resistance to ignition" test [8] that is similar to the widely used UL-94 test but for a horizontal sample. The apparatus operates to automatically move a micro-burner ignition source under the first 6 mm of the plaque sample to apply a flame from the source to the sample for a period of 3 s. The flame is removed and a timer starts automatically. FP-7 values represent the time to flame extinguishment. An FP-7 value for a sample is an average of six different test samples from a single plaque.

2.3. Molecular beam mass spectrometry

To test the potential of flame retardants to provide gas-phase activity, a molecular beam mass spectrometry (MBMS) system was utilized to sample the flame system and measure active radical species after addition of the pure flame retardant. For these studies, a premixed $CH_4/O_2/N_2$ (9.18/15.54/75.28) flame stabilized with a Mache–Hebra nozzle burner [9] at atmospheric pressure was used. The Mach–Hebra burner used a quartz tube that was tapered at one end. This resulted in uniform distribution of flow velocity over the cross section of the burner's outlet and formation of a regular cone for the flame. The flow rate of the combustible mixture varied from 1.5 to 2.16 slpm (standard liter per minute) so as to keep the height of the flame cone at about 10 mm. Fire retardants under investigation (HBCD, TPP, TPPO, and sulfur) were added to the combustible mixture at loadings of 0.018–0.19% by volume as vapors.

A flame-sampling MBMS instrument that employed a tunable soft ionization by electron impact was used for these studies [10]. The instrument consisted of an atmospheric-pressure flame chamber, a differentially pumped molecular beam flame-sampling system, and a MS 7302 quadrupole mass spectrometer (Experimental Plant of the Russian Academy of Sciences). Detailed descriptions of the instrument, burner, flame-sampling system, and experimental procedures are given elsewhere [11]. The mass spectrometer utilized an ion source that allowed fine adjustment of the electron energy [12] to permit identification of species with adiabatic ionization energies (IEs) that differ only slightly from the ionization thresholds of fragmentary ions at the same m/z. This fine adjustment allows operation at low IEs relative to the ionization potentials of ambiguous species – atoms, radicals, and unstable molecules.

The calibration coefficients for H and OH radicals were determined by comparing their final concentrations in the post flame zone without additives. The coefficients were calculated by assuming a partial equilibrium of the three most rapid reactions ($H_2 + OH = H_2O + H$; $H_2 + O = H + OH$; $O_2 + H = OH + O$) and using a method described earlier [13].

2.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using either a TA Instruments 2950 or a TA Instruments Q5000IR TGA. Samples

(5–20 mg) for TGA analysis were heated at 10 °C/min to 500 or 600 °C under helium or nitrogen.

2.5. Direct insertion probe mass spectrometry

Pure FR and FR blends were analyzed by direct probe insertion mass spectrometry (DIP-MS) using the direct insertion probe with an aluminum crucible. The probe was programmed to heat from 25 °C to 400 °C at 38 °C/min and then held at 400 °C for 5 min.

A Finnigan MAT 95 spectrometer was scanned from m/z 10 to 900 at 1 s/decade. Instrument resolution was over 1000 which allowed low mass isobaric ions to be distinguished for purposes of discriminating between ions like m/z 79, 80, 81 and 82 for Br and HBr from organic ions of the same mass range.

2.6. Pyrolysis gas chromatography-mass spectrometry

Pyrolysis gas chromatography-mass spectrometry (PyGCMS) was performed using the Frontier Laboratories Pyrolysis 2020 unit mounted on a Thermo Scientific Trace gas chromatography/mass spectrometry (GC/MS) instrument. The instrument was configured with a 30 m × 250 μm × 1.0 μm GC column with 5% phenyl methyl siloxane film (DB-5MS from Agilent Technologies). The PyGCMS system used a nitrogen cooled micro-cryo trapping device, which trapped all of the analytes in a 0.5 cm section at the front end of the chromatographic column during the heating phase. Mass spectral measurements used an electron ionization (EI) source along with a detector voltage of 270 V and spectral scans from m/z 26 to 566 at 1.5 scans/s. The emission current and source current were 100 μA and 325 μA, respectively. GC parameters used a split injection port at 320 °C, MS transfer line at 300 °C, a split ratio at 30:1, and a GC oven program: 40 °C for 0.5 min, 40 °C–120 °C at 10 °C/min, 120 °C–310 °C at 16 °C/min, 310 °C for 12 min.

2.7. Dynamic mechanical spectroscopy

Dynamic mechanical spectroscopy (DMS) was carried out on a RDSII Rheometrics Dynamic Spectrometer (made by Rheometrics Scientific, which is now part of TA Instruments). A parallel plate geometry was used. Compression molded discs were 25 mm in diameter and 1.6 mm in thickness. Temperature sweep was 180 °C–400 °C at 10 °C/min. Frequency was 10 rad/s, strain was 5%, maximum applied strain was 10%, maximum allowed torque was 150 g cm, strain adjustment was 25% of the current strain, data sampling occurred every 30 s. Air was forced through the oven during measurements.

2.8. Condensed-phase TGA-SEC measurements

Samples were heated under helium atmosphere using a TA Q5000IR TGA. The heating profile consisted of rapid heating of 100 °C/min up to 350 °C, hold for 5 min, and cooling back to room temperature. After heat treatment, the samples were analyzed for molecular weight distribution (MWD) characterization by size-exclusion chromatography (SEC) analysis. Separation was via a tetrahydrofuran (THF) mobile phase and two Polymer Laboratories 5 μm Mixed-C columns at 35 °C. Samples were prepared by shaking approximately 0.02 g of sample in 10 mL of the eluent (THF). The solutions were filtered through an Alltech 0.2 micron PTFE filter with a syringe prior to injection.

The SEC instrument consisted of a Waters 410 DRI detector and a Waters model 2690 pump (1 mL/min) and injector. Data were collected with a Polymer Laboratories Calibre GPC/SEC, acquisition version 6.0 and reanalysis version 7.04. Narrow molecular weight distribution polystyrene standards were used for calibration. Thus,

Table 1
Fire testing data for FR blends of polystyrene

	% FR loading	% Br/% P/% S	LOI test	FP-7 test, s
PS			18.8	>25
2.5% HBCD in PS	2.5	1.8% Br	24.0	1.1
5% TPP in PS	5.0	0.5% P	20.7	9.5
1.0% sulfur in PS	1.0	1.0% S	21.0	5.3
1.0% S/5.0% TPP in PS	1.0/5.0	0.5% P/1.0% S	25.5	3.9
5.0% TPPO in PS	5.0	0.6% P	21.5	13.1
5.0% TPPS in PS	5.0	0.5% P/0.5% S	21.2	13.7

all molecular weight averages and molecular weight distributions reported are PS-equivalent data.

2.9. Molecular modeling

Molecular modeling was used to compute the bond dissociation energies (BDE) and other reaction energies associated with polystyrene degradation. The bond dissociation energy is the energy required for the homolysis of a certain bond in a molecule. All reaction energies were computed from the difference between product molecular energies and reactant molecular energies. As an example, in ethane, the C–C bond dissociation energy can be computed as the sum of the energies of the two methyl radicals minus the energy of ethane.
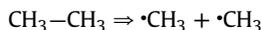
$$CH_3-CH_3 \Rightarrow {}^\bullet CH_3 + {}^\bullet CH_3$$

$$BDE(C-C) = 2 \times E_{{}^\bullet CH_3} - E_{CH_3CH_3}$$

The structures and energies of all the species considered were optimized using density functional theory (B3LYP) [14,15] and the 6-31G* basis set [16–18] contained in either the Spartan 06 or Gaussian 03 molecular orbital software [19,20].

3. Results

3.1. Fire performance testing

Results of LOI and FP-7 fire performance testing are shown in Table 1 for FR blends of polystyrene. The HBCD blend represents a common commercial loading and shows higher LOI and lower FP-7
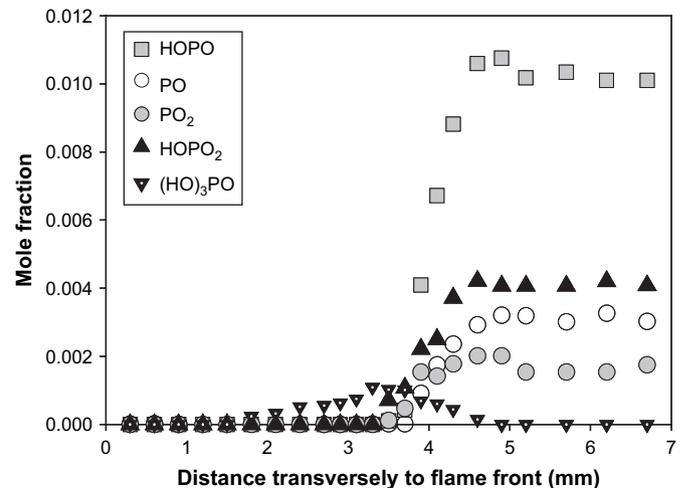
Fig. 1. Concentration profiles of phosphorous-containing compounds in $CH_4/O_2/N_2$ flame after addition of TPPO.
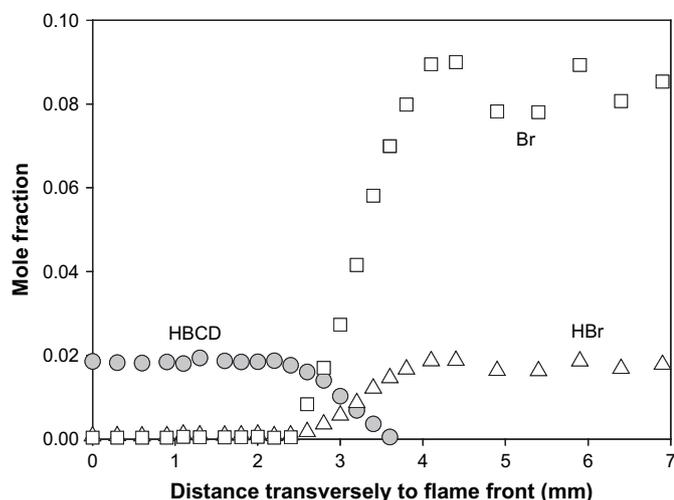
Fig. 2. Concentration profiles of bromine-containing compounds in $CH_4/O_2/N_2$ flame after addition of HBCD.

values for good fire performance. For phosphorous-containing FRs, all show lower fire performance (lower LOI and higher FP-7) except for the blend that contains a mixture of both TPP and sulfur. When compared with the TPP-only and sulfur-only blends, unique FR activity is observed with the TPP and sulfur combination. This combination performs at a level very near to that observed for the bromine HBCD blend.

3.2. Fundamental gas-phase activity

To understand the potential of each FR to provide gas-phase activity, MBMS was used to assess each FR to provide flame inhibition after addition to a stable flame system. Fig. 1 profiles the concentration of phosphorus-containing products after addition of TPPO to a flame and shows the formation of PO, PO_2, HOPO, $HOPO_2$ and $(HO)_3PO$. The HOPO species comprises about 60% of the total phosphorus that was added to the flame. A similar profile of phosphorous species was observed after addition of trimethyl-phosphate to a laminar premixed $CH_4/O_2/Ar$ flame ($\phi = 1.2$) [21]. These types of H_xPO_y species formed by the destruction of organic phosphorous compounds in a flame are known to catalyze
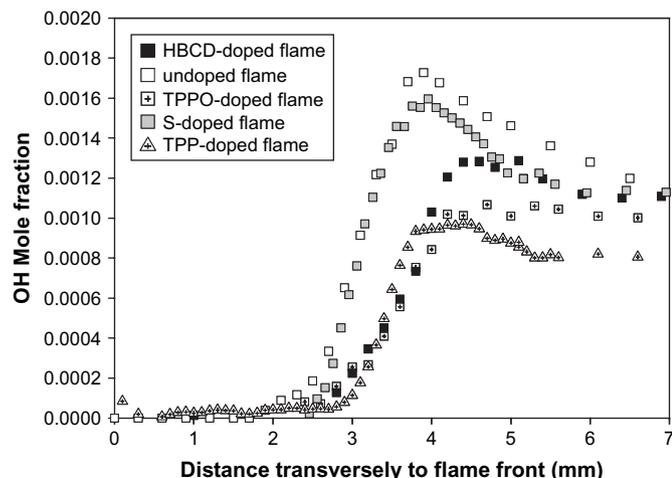
Fig. 3. Profiles of concentration of OH radical in $CH_4/O_2/N_2$ flame; open symbols – flame without additive, filled symbols – doped with 0.018% HBCD, 0.019% TPPO, 0.018% TPP, 0.16% S (by volume).
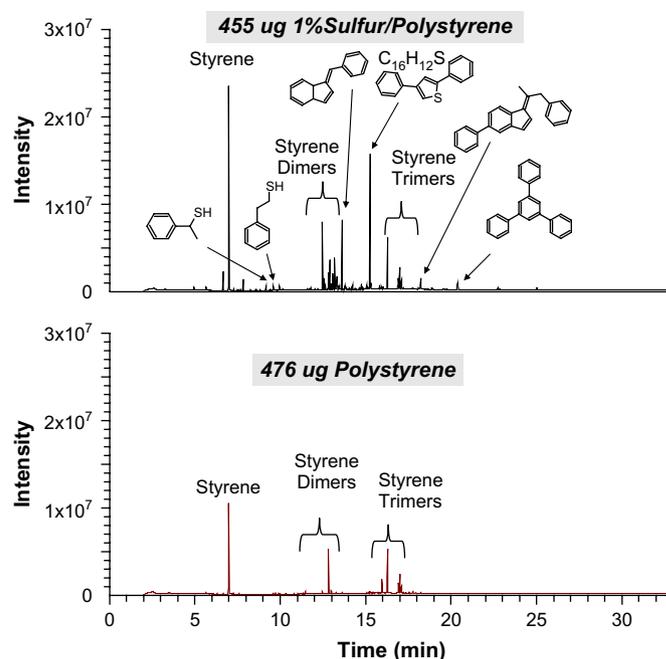
Fig. 4. Pyrolysis GCMS study of 1% sulfur in polystyrene blend (top) versus pure polystyrene (bottom). Total ion current (TIC) plots are shown for pyrolysis heating of 400 °C for 30 s in helium.

recombination of H and OH radicals and provide strong inhibition of flames [22].

Bromine-containing compounds are known to be effective inhibitors due to the formation of HBr, which catalyzes the recombination of H atoms: $HBr + H = Br + H_2$; $Br + H = HBr$. Fig. 2 shows the emission of HBr and Br in the flame front as the HBCD concentration decreases. It is noteworthy that Br-containing products are formed faster than P-containing ones as denoted by the onset of species formation in the flame (Fig. 1 versus Fig. 2). However, organic phosphorous compounds are known as more effective inhibitors based on a simple one-to-one atom basis of
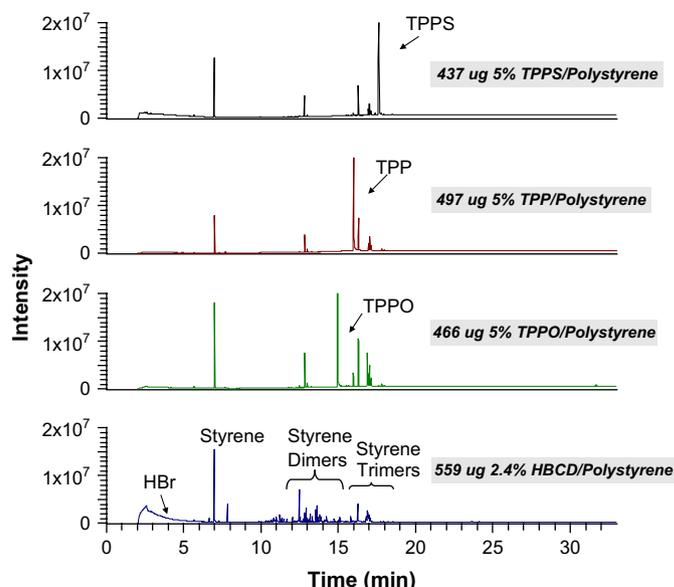
Fig. 5. Pyrolysis GCMS study of blends of 5% TPPS, TPP, TPPO and 2.5% HBCD in polystyrene. Total ion current (TIC) plots are shown for pyrolysis heating of 400 °C for 30 s in helium.
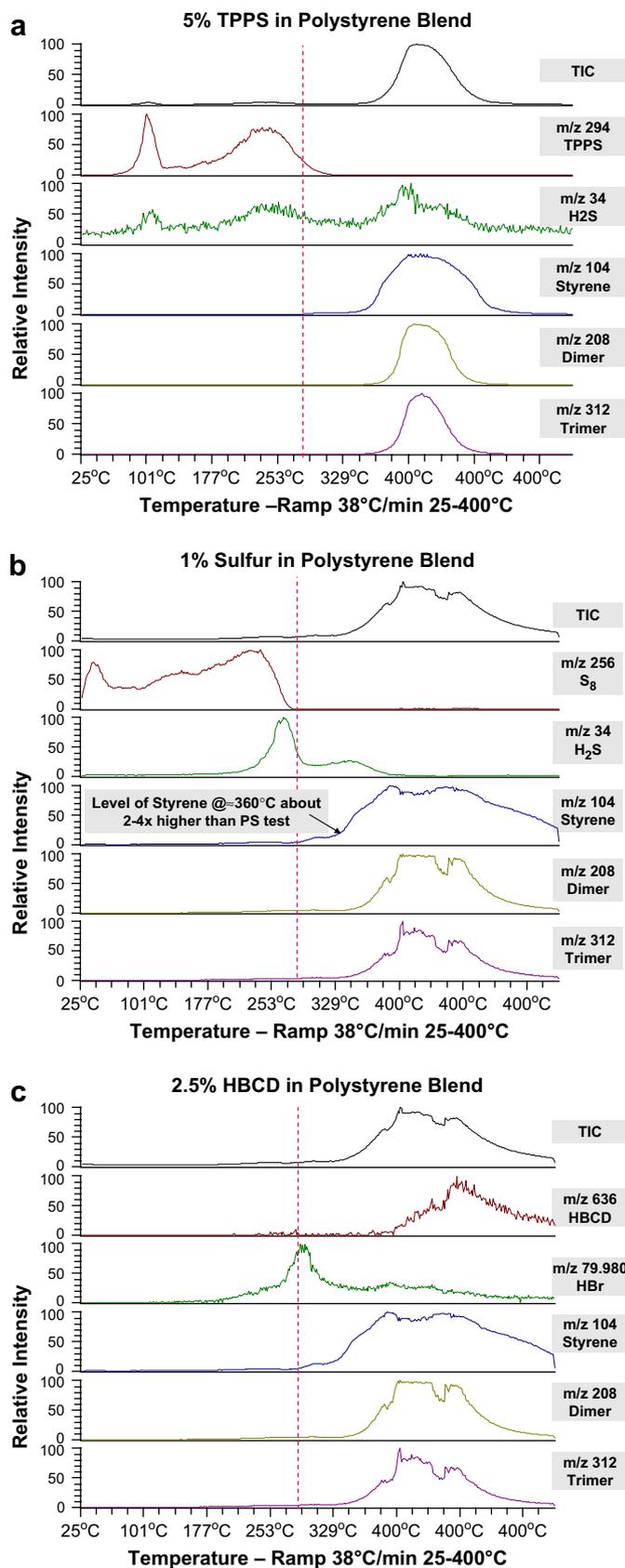
Fig. 6. Temperature profiles (DIP-MS study) of various fragments from the heating of (a) 5% TPPS in polystyrene blend (b) 1% sulfur in polystyrene blend (c) 2.5% HBCD in polystyrene blend. Heating profile was 25 °C–400 °C at 38 °C/min and then held at 400 °C. TIC represents the total ion current – all species.
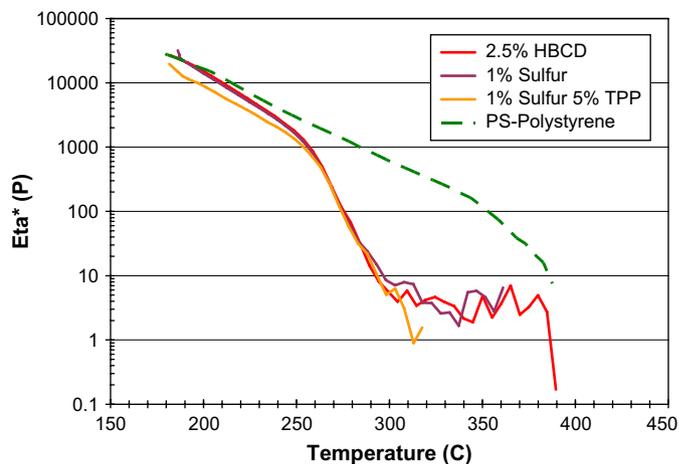
Fig. 7. DMS viscosity–temperature profiles for polystyrene blends of HBCD, sulfur and sulfur/TPP at 10 °C/min.

phosphorous compared with bromine [23]. Fig. 3 presents a comparative activity of various fire retardants and shows a decreasing molar concentration of the OH radical after addition of the FR into a premixed $CH_4/O_2/N_2$ flame. A similar trend was also observed with H radical measurements. Several studies have demonstrated that sulfur species can provide a degree of inhibition of H or OH radicals. Zachariah [24] and Rasmussen [25] have studied the inhibition by SO_2 based on an inhibition mechanism via the catalytic cycle $H + SO_2 + M = HOSO + M$ and $H + HOSO = H_2 + SO_2$, i.e. $H + H = H_2$. This cycle is similar to catalytic cycles in a phosphorus mechanism for flame inhibition.

HBCD provides a drop in the OH radical concentration of about 25% and provides a high level of activity at scavenging active flame species. TPPO and TPP decrease the maximal OH radical concentration by about 40% which indicates very high gas-phase activity for P-containing fire retardants. The drop in OH radical concentration for sulfur is lower than that exhibited by either HBCD or TPP and TPPO. In terms of relative effectiveness of the major atoms, the FR trends for combustion activity agree with the work of Babushok and Tsang [26], which ranked the relative effectiveness of atoms for inhibition as $P > Br > S$.

As for the higher efficiency of phosphorus in comparison with bromine and sulfur, a previous study by Rumminger et al. [27] showed that an effective inhibitor should provide activity at
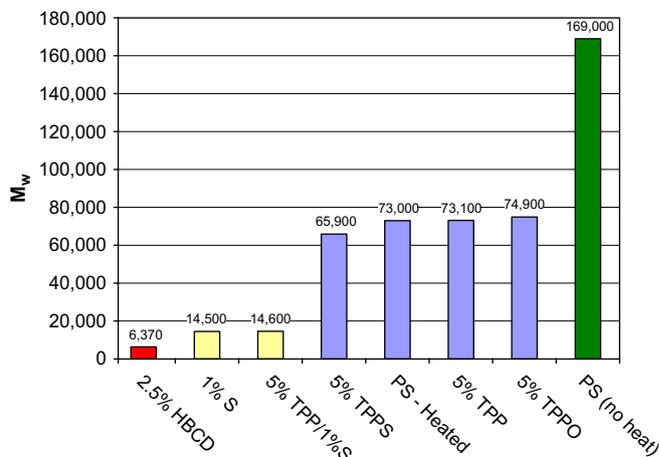
Fig. 8. Molecular weight analysis results for heat-treated FR-PS blends. Heat treatment was for 5 min at 350 °C in helium.

$$FR \rightarrow FR\bullet \ + \ FR^*\bullet \qquad \text{Homolytic cleavage} \qquad (1)$$

$$FR^*\bullet \ + \ H\text{-}PS \rightarrow PS\bullet \ + \ H\text{-}FR \qquad \text{FR abstraction of H} \qquad (2)$$

$$FR^*\bullet \ + \ PS\bullet \rightarrow PS(=) \ + \ H\text{-}FR \qquad \text{Termination} \qquad (3)$$

$$PS\bullet \rightarrow \ \text{--}CH_2C(Ph)=CH_2 \ + \ Ph\bullet CHCH_2\text{--} \qquad \beta \text{ scission} \qquad (4)$$
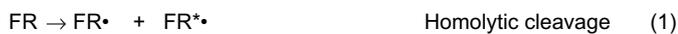
Scheme 1. Mechanism for enhanced polystyrene degradation.

temperatures of about 1700 K and not lose its activity at higher temperatures. This implies that an inhibitor, which functions at lower temperatures, is less effective. The maximum level of FR activity or inhibition occurs when the maximum in chain termination rate (in catalytic reactions) spatially coincides with the region of high radical volume fraction of H or OH [27]. These conclusions were made on the basis of calculations of flame speed, structure and rate of production of radicals along the combustion zone. A follow-up analysis of a kinetic model with TPPO data from the present study showed that the most effective flame inhibition occurs when the peak levels of the OH radical (formed via the chain branching $H + O_2 = OH + O$ reaction) coincide with the maximum consumption rate of the OH radical in a catalytic reaction of recombination (caused by the flame retardant). Thus, peak OH and H radical production is reflective of higher temperature regions in the flame and more effective flame inhibitors (phosphorous based FRs) will show activity in these regions.

MBMS experiments show the fundamental potential of each FR to provide gas-phase activity via flame inhibition chemistry. The experiments are a simplification that utilizes a fuel-rich flame to mimic a polymer burn. The experiments neglect potential FR–polymer interactions and the time/temperature delivery or mass-transfer of the FR via degradation or volatization. Nevertheless, the experiments provide a clue as to the overall gas-phase potential of each FR as well as direct and semi-quantitative information on the degree of flame inhibition radical chemistry.

3.3. Degradation studies of polystyrene-FR blends

Studies of FR degradation were done with FR-polystyrene blends to try and understand the potential of FR-enhanced condensed activity. PyGCMS measurements of blends of sulfur and pure polystyrene are shown in Fig. 4 after pyrolysis for 30 s at 400 °C. Pure polystyrene degrades to form styrene as well as several dimer and trimer related species. In contrast, the sulfur blend shows several sulfide aromatic and thiophene aromatic species as well as several branched aromatic species. Of particular interest is the high level of polystyrene related species (styrene, dimer, and trimer) relative to pure PS. Sulfur facilitates polystyrene degradation as is evident by the higher level and number of polystyrene related degradation species formed. Sulfur also shows extensive

degradation as no parent species (S_8 or other S_n species) are evident.

Fig. 5 shows results for similar PyGCMS experiments for polystyrene blends of HBCD, TPPS, TPP, and TPPO. As was the case with the sulfur blend, the HBCD blend shows enhanced polystyrene degradation via the formation of high levels of styrene and multiple dimer and trimer species. HBCD also shows complete FR degradation via extensive HBr formation and no evidence for the FR parent molecule. Phosphorus-containing species show little evidence for enhanced polystyrene degradation and only a minor amount of actual FR degradation with a very small amount of phenol formation. Large parent FR peaks for phosphorous FRs indicate FR volatization versus degradation.

Time/temperature profiles of the evolution of FR and polystyrene degradation species were measured with DIP-MS. Fig. 6 shows select fragment profiles for heating of polystyrene blends of TPPS, sulfur, and HBCD. Profiles shown in Fig. 6 include TIC (represents all fragments), the pure FR, styrene (m/z 104), dimer (m/z 208), and trimer (m/z 312) fragments related to polystyrene degradation. Also shown are the profiles for H_2S (m/z 34) sulfur species and HBr (m/z 79.980) for HBCD which represent the possible species related to FR activity. For TPPS, polystyrene degradation becomes apparent (based upon the styrene profile m/z 104) at about 325 °C compared with sulfur and HBCD which show polystyrene degradation at 280 °C (based on the dashed line in Fig. 6). The approximate levels of styrene formation for polystyrene blends of HBCD, sulfur and sulfur/TPP were about 2–4 times that of pure polystyrene or polystyrene blends of phosphorous-containing FRs. Also evident in Fig. 6 are distinct maximum levels for H_2S (sulfur) and HBr (HBCD) that occur during the onset of styrene formation. Thus, enhanced and earlier polystyrene degradation is clearly evident in polystyrene blends of sulfur and HBCD. TPPS does not exhibit a distinct profile for H_2S formation or an early onset of styrene formation and shows no evidence for enhanced polystyrene degradation.

3.4. Measurements of condensed-phase activity via enhanced polymer degradation

DMS temperature profiles show the change in viscosity for polystyrene and FR-polystyrene blends as shown in Fig. 7. In the temperature sweep (10 °C/min) of the DMS, the polystyrene viscosity gradually decreases until the temperature reaches about 350 °C. Above this temperature, polystyrene chains start degrading at a more rapid rate and there is a departure from the gradual viscosity decrease. Blends of sulfur and HBCD show a sharp drop in viscosity at 250 °C and clear enhanced melt flow of polystyrene caused by a decrease in viscosity and further evidence for FR-enhanced polystyrene degradation.

Isothermal heat experiments of polystyrene and FR-polystyrene blends at 350 °C and the subsequent molecular weight analysis are shown in Fig. 8. At 350 °C, the degradation of polystyrene is clearly evident based on the drop in M_w to about 70,000 from 168,000 for an unheated polystyrene sample. Phosphorous-only containing FRs (TPP, TPPO) show no evidence for enhanced polystyrene degradation. The TPPS (bound sulfur and phosphorous) polystyrene blend shows a very minor decrease in M_w. Sulfur polystyrene and the
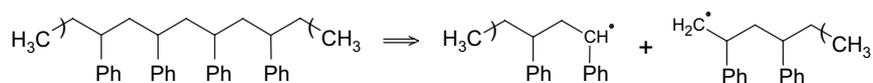
E = 273 kJ/mol (65.1 kcal/mol)

Scheme 2. Polystyrene degradation initiation.
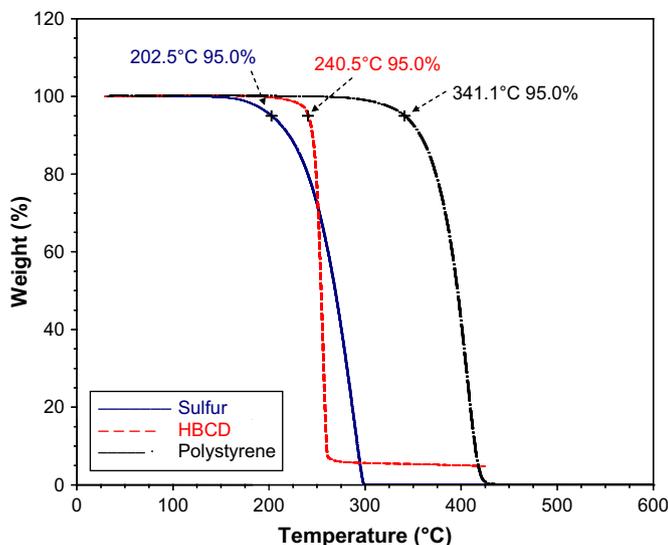
Fig. 9. TGA curves of polystyrene, pure HBCD, and pure sulfur.

HBCD blends show a large decrease in M_w and further evidence for FR-enhanced degradation of polystyrene.

3.5. Molecular modeling and mechanism

Polystyrene degradation proceeds via a chain scission pathway [28]. The enhanced degradation of polystyrene in the presence of brominated FRs and other molecules has been reviewed in several studies [1,29–32]. The accepted mechanism for enhancement involves formation of a free radical initiator that abstracts hydrogen off the polystyrene backbone to form a polystyrene radical (Scheme 1).

The polystyrene radical then undergoes β scission of the polystyrene C–C bond. Molecular modeling was completed to better understand the thermodynamic energies associated with this mechanism and to better understand the enhanced polystyrene degradation observed with HBCD and sulfur polystyrene blends versus phosphorous FR-polystyrene blends. Molecular modeling of polystyrene degradation shows that the BDE for the breaking of the aliphatic C–C bond has an energy of 273 kJ/mol (Scheme 2).

The formation of an initiator radical via homolytic cleavage (reaction 1 in Scheme 1) must occur with a BDE below 273 kJ/mol to provide enhanced polystyrene degradation. TGA data for the degradation of polystyrene in Fig. 9 indicate that the onset of degradation starts experimentally at about 341 °C and suggest the breakage of the C–C bonds for polystyrene degradation (273 kJ/mol) starts occurring at about this temperature. Both sulfur and HBCD show TGA activity below 341 °C as exhibited by the TGA curves in Fig. 9. The lower onsets for degradation of both HBCD and sulfur point to BDEs that are below the estimated energy for the degradation of polystyrene. Scheme 3 shows the energy calculations for the HBCD mechanism and a BDE of 249 kJ/mol for the homolytic cleavage of the first C–Br bond on HBCD. The subsequent FR abstraction of the hydrogen off polystyrene can proceed by two pathways: 3° carbon H abstraction or 2° carbon H abstraction. The 3° carbon H abstraction is more favorable at 8.0 kJ/mol. All energies associated with the FR-enhanced mechanism are favorable compared with 273 kJ/mol required for pure polystyrene degradation with no enhancement as shown previously in Scheme 1.

Scheme 4 shows a similar sequence for sulfur and enhanced polystyrene degradation. Pure sulfur is of the form S_8 but the speciation of sulfur vapor can involve several species of the form S_n [33]. Scheme 4 provides a simplification by using formation of the S_8 di-radical which gives a BDE of 131 kJ/mol. Sulfur homolytic cleavage would occur at a lower temperature than either the HBCD homolytic cleavage or the degradation of polystyrene. This is confirmed by the TGA curves in Fig. 9. The subsequent FR abstraction reactions (reaction 2 and 3 in Scheme 4) of the hydrogen off polystyrene are less favorable compared with similar reactions for HBCD (reaction 2 and 3 in Scheme 3). The higher energy barrier suggests that the abstraction reactions are less favorable for sulfur than HBCD. Thus, a lower level of polystyrene degradation is expected in the case of sulfur relative to HBCD, which agrees with the quantitative heat studies in Fig. 8.

Initiation reactions to form radicals by homolytic cleavage for phosphorous-containing FRs are shown in Scheme 5. In each case, the BDE is high for homolytic cleavage of the P–C (TPPO and TPPS) and the P–O bond for TPP. The BDE for each of the phosphorous FRs is greater than 273 kJ/mol estimated for pure polystyrene degradation and the formation of an FR radical will not occur until after the initiation of polystyrene degradation (above 340 °C). Thus,
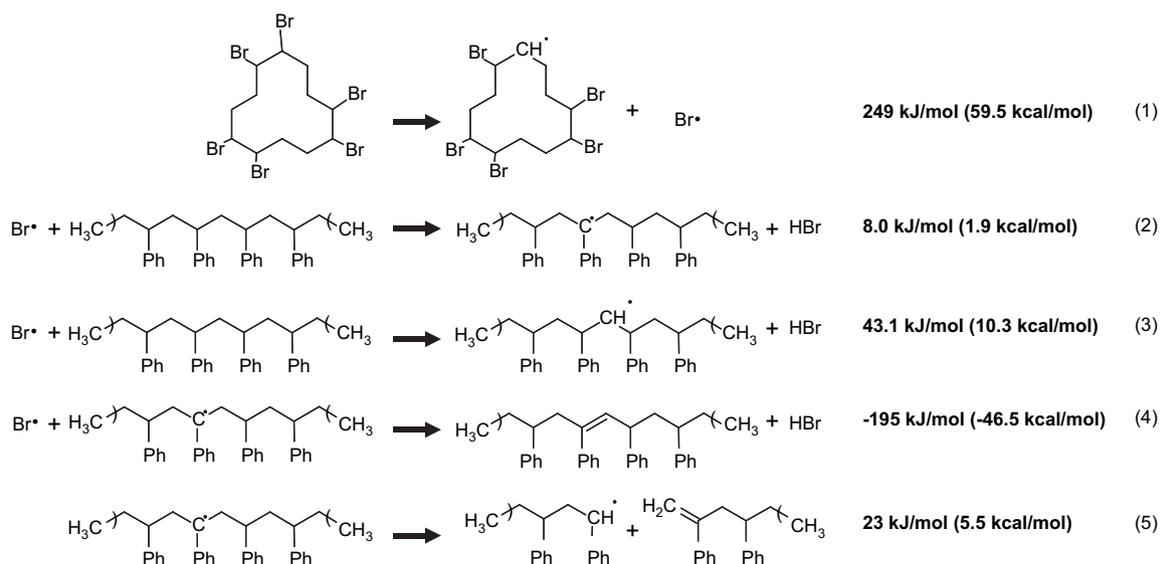
Scheme 3. HBCD enhanced degradation of PS.

	131 kJ/mol (31.3 kcal/mol)	(1)
	76.2 kJ/mol (18.2 kcal/mol)	(2)
	111 kJ/mol (26.6 kcal/mol)	(3)
	128 kJ/mol (-30.5 kcal/mol)	(4)
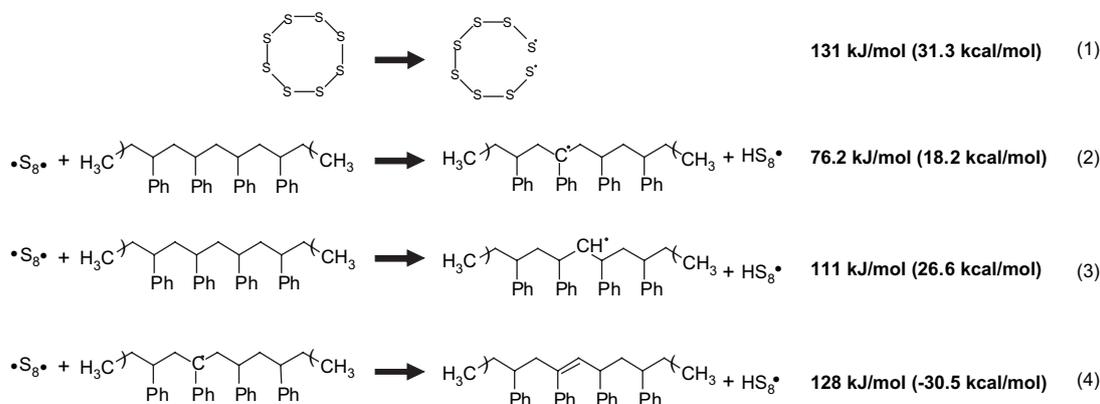
Scheme 4. Sulfur enhanced degradation of PS.

formation of an FR radical and subsequent enhanced polystyrene degradation by H abstraction are not favorable. Instead, the lower molecular weight of the phosphorous-based FRs and higher BDE favor FR volatization and not degradation. TGA curves in Fig. 10 for the pure phosphorous FRs show a low temperature loss of each FR. As mentioned in the experimental polystyrene degradation studies, TPP, TPPO, and TPPS showed negligible enhanced polystyrene and a very low degree of FR degradation (formation of lower FR species versus FR parent). For phosphorous-based FRs, the lower temperature TGA mass-loss and lack of significant formation of FR degradation species all confirm FR vaporization as the primary path for FR loss at higher temperatures. The lack of condensed-phase FR-enhanced degradation of polystyrene exhibited for the phosphorous FRs is caused by an unfavorable formation of the initiator radical due to the very strong bonds associated with each FR.

3.6. Possible synergy between phosphorous and sulfur

Fire testing data listed in Table 1 showed a clear boost in fire performance (lower FP-7 and higher LOI) when both TPP and sulfur were blended together with polystyrene compared with polystyrene blends of only TPP or sulfur. There are several possible explanations for this apparent synergy for the sulfur–TPP combination. These could include some type of interaction between the two molecules – TPP and sulfur. For example, sulfur degrades first and could facilitate TPP degradation or formation of some type of P–S species that could provide a high level of FR activity and scavenge key combustion radicals in the flame. No previous known studies have proposed or shown evidence for P–S species as active flame inhibitors. PyGCMS experiments of pure TPP, sulfur, as well as a mixture are shown in Fig. 11. Pure sulfur degradation shows formation of SO_2 and various S_n species as denoted by m/z 32 and 64. Pure TPP shows the parent TPP and a minor amount of phenol. The mixture test (Fig. 11c) gives the same species observed in the pure tests and shows no evidence for any P–S species. Fig. 11d shows profiles for sulfur species based on fragments m/z 32 and 64. Only SO_2 and a broad sulfur degradation peak at about 30 min are observed and no unique sulfur or P–S species are evident. Although unstable P–S species could still form in the flame, no current evidence exists for such species.

Two previous studies have also looked at enhanced polymer degradation of polystyrene by bromine FR additives. A study by Gouinlock et al. suggested that enhanced polymer degradation leads to removal of fuel/heat from the fire to provide more effective fire performance [34]. Another study by Eichhorn suggests synergistic action between a radical initiator and polymer

	322 kJ/mol (77.0 kcal/mol)	(1)
	352 kJ/mol (84.0 kcal/mol)	(2)
	314 kJ/mol (74.9 kcal/mol)	(3)

Scheme 5. Homolytic cleavage of TPP, TPPO, and TPPS.

Fig. 10. TGA curves of pure TPP, TPPS, and TPPO.

a high amount of non-flaming drip which effectively pulls heat/fuel away from the fire, which is similar to the explanation proposed by Gouinlock [34].

4. Conclusions

Effective flame retarding of polystyrene can best be achieved through a combination of gas-phase and condensed-phase activity. Effective gas-phase activity typically is achieved through flame inhibition chemistry of radical scavenging of OH and H radicals. The MBMS technique provides an understanding of the potential for fundamental gas-phase activity by FRs. MBMS experiments confirm that HBCD, TPP, and TPPO are active in the gas phase whereas sulfur provides a lower level of activity. MBMS also confirms the gas-phase activity as flame inhibition chemistry based on the reduction of OH and H radicals in the flame.

Condensed-phase activity is also a key area of FR activity for HBCD and sulfur based on the enhanced degradation of polystyrene. In contrast, the phosphorous FRs TPP, TPPO, and TPPS provide no enhanced degradation. The enhanced degradation of polystyrene proceeds by hydrogen abstraction off the polystyrene backbone to form a weak polystyrene radical, which then degrades by β scission. The most favorable hydrogen abstraction based on molecular modeling is the hydrogen on the 3° carbon of polystyrene. The key step in the overall FR-enhanced mechanism is the formation of the radical initiator. For HBCD and sulfur, the homolytic cleavage is favorable based on the BDE calculation. In contrast, TPP, TPPO, and TPPS are not favorable below 341 °C, which is the approximate onset for polystyrene degradation.

FR-enhanced degradation of polystyrene is a key condensed-phase mechanism that loosens the polymer network to allow enhanced mass-transfer of gas-phase species to the surface as well as fire resistant melt flow to pull fuel away from the fire. Based on evidence to date, the synergistic action observed for the TPP/sulfur polystyrene blend is likely caused by the enhanced degradation of polystyrene by sulfur. Sulfur degrades polystyrene to loosen the polymer polystyrene network for improved mass-transfer of TPP to the surface of the polymer and the flame region. This facilitates the delivery of TPP, which has a very high level of potential gas-phase activity as determined from MBMS experiments. This "condensed-phase enhanced gas-phase activity" provides high FR activity for non-charring polystyrene to provide good overall fire resistant performance. Sulfur also provides fire resistant melt drip as the increased level of polystyrene degradation leads to a high level of drip which helps to pull fuel and heat away from the fire.

degradation fragments leads to delayed loss of the halogen and more efficient use of the halogen [30]. The boost in fire performance from the TPP–sulfur mixture is clearly related to the high degree of condensed activity observed for sulfur. Based on the MBMS studies, sulfur provides only a low-level potential for gas-phase activity. In contrast, sulfur provided a high degree of condensed-phase activity and early occurrence of condensed-phase polystyrene degradation. Both gas and condensed-phase activity are required for the effective fire performance of FR-polystyrene blends as exhibited with the HBCD-polystyrene blend. The enhanced degradation of polystyrene by sulfur loosens up the polymer network and facilitates the mass-transfer of gas-phase active species, TPP, to the surface and to the fire. Such activity would be beneficial in both the flame and pre-flame zone to help suppress flame spreading and inhibit the fire. The combination of high melt flow and an active gas-phase FR (TPP) must also lead to

Fig. 11. PyGCMS studies and total ion chromatogram (TIC) plots of (a) pure sulfur, (b) pure TPP, and a (c) mixture of TPP/sulfur at 5:1. (d) Mass fragments for m/z 32 and 64 for sulfur species for PyGCMS of the TPP/sulfur mixture test.

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