



## Development of a new class of brominated polymeric flame retardants based on copolymers of styrene and polybutadiene



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### ABSTRACT

Brominated polymeric flame retardants (FR) have been developed that can provide effective flame retardant performance in polymer systems that previously relied on hexabromocyclododecane (HBCD). This polymeric FR material exhibits a superior environmental profile to that of HBCD and other lower molecular weight FR molecules. The brominated polymer flame retardant is based on a copolymer of styrene and butadiene where the polybutadiene portion is brominated on the 1,2 and 1,4 isomer units to give a brominated polybutadiene. Bromination is best carried out with a quaternary ammonium tri-bromide reagent which provides a selective bromination of just the polybutadiene portion of the copolymer. A styrene-butadiene-styrene (SBS) triblock architecture is utilized where the presence of the styrene enhances the thermal stability and gives the copolymer to better compatibility when blended with polystyrene. The resulting brominated polybutadiene-polystyrene (BrPBPS) polymeric flame retardant contains similar aliphatic bromine as in HBCD but with a higher molecular weight structure. BrPBPS provides similar flame retardant activity as HBCD in polystyrene blends where both release HBr to provide gas phase activity. Both also provide enhanced polymer degradation as another major pathway for condensed FR activity.

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### 1. Introduction

Many polymers require flame retardant (FR) additives to provide improved fire resistance so that the polymers can be used in many commercial applications. Several of the widely-used commercial flame retardants have faced increased regulatory scrutiny because of their PBT impact (Persistence, Bioaccumulation, Toxicity) in the environment. In particular, many of the commercial flame retardants are low molecular weight/small molecules that can readily migrate out of the base polymer and into the environment. One such widely used flame retardant, hexabromocyclododecane (HBCD), is a brominated flame retardant produced in Europe, US and Asia and used in thermal insulation foams and in textile coatings. HBCD is facing a ban from commercial

use in Europe within the next few years [1–4]. As a result, there have been increased research efforts to find a suitable replacement for HBCD in many commercial applications [5–8]. Key criteria for selecting a replacement for HBCD include fire performance, thermal stability, environmental and health profile, as well as complexity and cost of using the new FR in existing processes, polymer systems, and various applications.

Since many polymeric materials are not fire resistant, the safe use of these materials in commercial applications requires that they are formulated with a flame retardant to pass certain 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 [9]. In the case of HBCD and identifying a suitable alternative for its use in polystyrene, a similar FR mechanistic action is desired. Previous

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work has shown that HBCD delivers HBr in the gas phase [10] after degradation. The HBr molecule serves as a radical scavenger of key combustion radicals (OH, H) to effectively shut down the combustion process [11]. HBCD also delivers condensed-phase activity based on the FR interaction with the base polymer polystyrene as it causes enhanced polymer degradation to increase the polymer melt flow during the burning process. This non-flaming drip can effectively pull fuel/polymer from the burning process as well as aid in the mass transfer of gas-phase active HBr through the polymer network and to the flame [12–14].

A new class of brominated polymeric flame retardants has been developed for use in polymer systems that previously relied on HBCD. This polymeric material exhibits a superior environmental profile to that of HBCD and other lower molecular weight FR molecules while still providing excellent fire performance. The higher molecular weight of the polymeric FR prevents migration once embedded (blended) in a plastic resin/blend. In addition, the size of the coiled form for the polymeric FR is of the order of 20–50 times the size of small molecule alternatives such as HBCD, thus hindering its ability to penetrate through biological membranes, which significantly reduces the bioaccumulation and toxicity potential. The polymeric FR is based on a copolymer of styrene and butadiene where the polybutadiene portion has been brominated on the 1,2 and 1,4 isomer units to provide a brominated polybutadiene. A styrene-butadiene-styrene (SBS) triblock architecture was utilized to produce a brominated polybutadiene polystyrene (BrPBPS) FR [15,16]. The styrene block enhances the compatibilization in the case of polystyrene blends as well as improves the overall thermal stability of the polymeric FR. Thus, the resulting brominated polybutadiene-polystyrene (BrPBPS) polymeric flame retardant contains similar aliphatic bromine as in HBCD but with a higher molecular weight structure. The microstructure and other properties of the polymeric FR can be fine-tuned to provide very good thermal stability and effective flame retardant activity in polystyrene that is equivalent to that provided by HBCD.

## 2. Experimental

### 2.1. Chemicals and blending

Pure HBCD was obtained from Albemarle or from Aldrich. Polymeric FR/polymer blends were prepared using a Haake Rheocord 90 Extruder-Mixer 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 the polystyrene (PS) was added under low RPM. After the resin softened, the speed was increased to 40 RPM and the polymeric FR was added. Blending was continued for 8 min.

Polymer/Polymeric FR blends were prepared to ensure uniform mixing of polymeric FR into the polymer by grinding the mixture (Wiley lab grinder and a 3 mm screen size) extensively 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 MPa (MPa)) application time of 5 min. A small band saw was used to cut the molded plaques into strips for fire tests.

### 2.2. Preparation of extruded polystyrene foams

Foaming was conducted using a small-scale proprietary extrusion line that consisted of an extruder. The extruder used a mixing head wherein liquid or supercritical blowing agent could be

injected and two heat exchangers were used to reduce the temperature of the mixture down to the desired foaming temperature [17]. The foam material was characterized through conventional analytical techniques, such as density, cell morphology, mechanical properties and thermal insulation performance as well as fire performance.

### 2.3. FR activity testing of blends of polymeric FR 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.

The FP-7 test has been described as a small scale “resistance to ignition” test [18] 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.

### 2.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using either a TA Instruments 2950, TA Q500 TGA, or 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. Thermogravimetric analysis mass spectrometry

Thermogravimetric analysis mass spectrometry (TGA-MS) was performed using a TA Instruments Q5000IR TGA configured with an Agilent 6890 GC and a Thermo DSQ Mass Spectrometer (MS). Samples (5–20 mg) for TGA analysis were heated at 10 °C/min to 500 or 600 °C under helium. Off-gases from the TGA were transferred to the MS via glass-coated metal capillary tube (Ultra ALLOY Deactivated Tube 0.15 mm I.D. × 0.47 O.D.) through a TA EGA attachment and a heated transfer line (Atmo-Seal Engineering) which were both heated to about 250 °C. Mass spectral measurements used an electron ionization (EI source) along with a detector voltage of 1525 V and spectral scans from  $m/z$  18–450 at 3.4 scans per second. The emission current was 100 µA. The GC oven temperature and the MS transfer line were at 250 °C.

### 2.6. Direct-insertion-probe mass spectrometry

Polymeric FR/PS blends were analyzed by direct insertion probe 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/minute 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.

### 2.7. Transmission electron microscopy

Samples were sectioned into thin membrane slices approximately 50 nm thick by ultramicrotomy at ambient conditions with a diamond knife and floated onto DI water (Milli-Q). No staining was required. Sections were imaged using a JEOL 1230 TEM with a cryo stage.

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