Brominated flame retardant polymers as a potential source of volatile brominated compounds

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1- Introduction

The blooming potential of brominated flame retardants (BFRs) is defined as the diffusion of BFRs in materials to the outer surface after curing **(1)**. Relatively low molecular weight brominated BFRs, such as polybrominateddiphenylethers (PBDEs), may be not chemically bound to the polymer backbone (additives), and so, are likely to be released out of them. To lessen this environmental concern, several voices including regulatory authorities and industries have promoted the development of BFR polymers of much larger molecular weights such as brominated polystyrenes **(2,3)**. Even if used also as additive, it is generally considered that BFR polymers will have a lower potential for blooming than PBDEs, for example, since their larger structure will become more entangled in the final material. BFR polymer molecules are also considered relatively harmless since these large molecules are less likely to penetrate the cell membranes of living tissues or to bioaccumulate efficiently **(4)**. However, low molecular weight residuals, which can be monomers, by products, and/or impurities, may be present in commercial BFR polymers. These compounds may have a high potential for blooming if they are not chemically bound to the backbone of the material. Since BFR polymers are predicted to gain increasing market shares in the next future, an experimental approach was developed to investigate if the potential loss of brominated compounds from BFR polymers occurs, in particular under thermal stress.

2- Material and Methods

Sample:Firemaster ® PBS-64, a homopolymer of a dibromo/ tribromo styrene monomer containing 64-65% bromine, was obtained from Great Lakes Chemical Corporation. This BFR polymer is mainly used in engineering thermoplastic polymers such as polyamides or polybutyleneterephthalate (PBT).

Thermal stress experiments: About 400 mg of PBS-64^{TM} were introduced in the gas flask of the sampling system shown in Figure 1. A first experiment was conducted at room temperature (T ≈ 22 ºC) and nitrogen was purged through the system for 20 min. A second experiment was made in the same way, excepted that the heating mantle was started after the introduction of the sample. A maximal temperature of 100 °C was reached at the end of the experiment. PUF plugs were then Soxhlet extracted with a mixture of dichloromethane (DCM) and hexane (50/50 v/v) for about 20 hours. In parallel, all glass parts of the sampling system were rinsed with DCM. Soxhlet and rinse extracts were then evaporated to obtain a similar final volume in isooctane.

GC-MS analyses: An HP 5890 Series II gas chromatograph coupled to an HP 5989AB mass spectrometer was employed for the examination of the extracts. GC was performed on a 30 m x 0.25 mm i.d. HP-5MS capillary column with helium as the carrier gas and the following operating conditions: injector port at 280 ºC, GC oven at 90 ºC for 1.5 min, then to 240 ºC at 20 ºC min^{-1}, then to 310 ºC at 8 ºC min^{-1}, and hold for 5 min. Measurements in electron capture negative ion (ECNI) mode were carried out at an ion source temperature of 175 ºC and an ion source pressure of 1.0 torr using methane as reagent gas. Electron impact (EI) ionization mode measurements were made at 70 eV and 175 ºC ion source temperature.

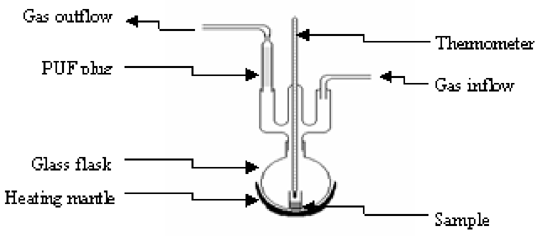

Figure 1: Schematic diagram of the sampling system adapted from Wolf et al. (2000) **(5)**.

3- Results and discussion

Assessment of the release of brominated compounds from the PBS-64^{TM} polymer: At room temperature, the GC-ECNIMS selected ion chromatogram (m/z 79+81) shows a few peaks (labeled a to e in Figures 2) of low intensity indicating that the PBS-64^{TM}oligomer weakly release volatile brominated compounds (Figure 2A). The thermal stress applied to the sample results in a drastic increase of the brominated compound release as shown by the augmentation, as much as 7 000-fold, of peak a to e heights (Figure 2B).

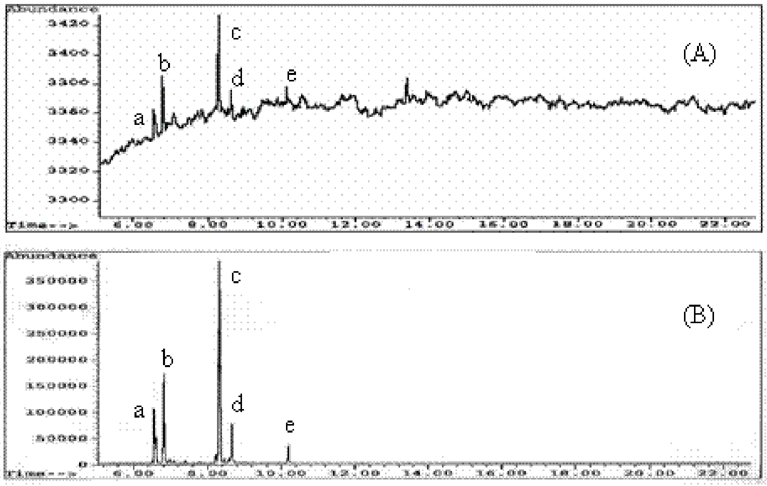

Figure 2: GC-ECNIMS (m/z=79+81) chromatograms of extracts obtained from the rinse of the sampling system glass parts after experiments at A) room temperature and B) increasing temperature up to 100 ºC. Peaks a and c present evidence of co-elution.

Identification of brominated compounds released from PBS-64^{TM}: As the quantity of material obtained during experiments was insufficient to conduct full-scan mass spectrometric investigations in EIMS mode, PBS-64^{TM} was extracted with isooctane. The GC-ECNIMS chromatogram of this extract presented in Figure 3 appears to be similar to the one presented in Figure 2B. Five main peaks, identified a' to e' in Figure 3, were detected at similar retention times (± 0.05 min) than peaks identified a to e in Figure 2B. Furthermore, the shape of peaks a' and c' indicates co-elution of two brominated compounds as peaks a and c in Figure 2B. However, several relatively weak chromatographic peaks, for the most part not resolved, were also present at retention times between 15 and 22 min.

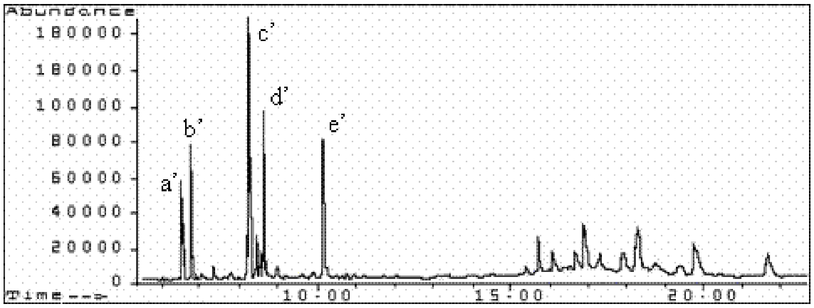

Figure 3: GC-ECNIMS (m/z=79+81) chromatogram of the solution obtained by extraction of PBS-64^{TM} with isooctane. Peaks a' and c' present evidence of co-elution.

The EI mass spectra of brominated compounds were recorded within a mass range of m/z 50-550. Figures 4A and 4B show the EI mass spectra obtained for peaks b' and d', respectively. These mass spectrum were similar to those obtained for the co-eluting brominated compounds in peaks a' and c', respectively. These mass spectra matched with those of dibromostyrene and tribromostyrene monomers, respectively **(8)**.

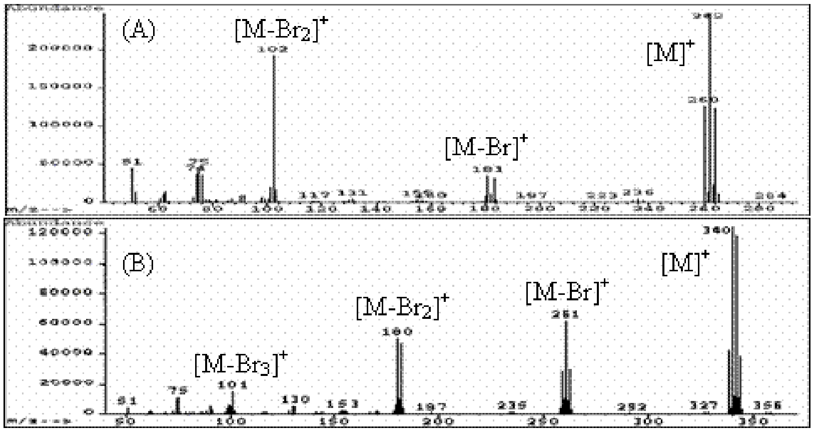

Figure 4: Full-scan EI mass spectra of brominated compounds associated to A) peak b' and B) peak d'.

The fragmentation pattern obtained for the brominated compound eluting at 10.30 min (peak e' in Figure 3) was somewhat different from those obtained for dibromo and tribromostyrenes as shown in Figure 5. In addition to the successive loss of bromine atoms from molecular ion, the mass spectrum indicated the loss of a CH_2Br group from the molecular ion and another successive loss of bromine atoms from the $[M\text{-}CH_2Br]^+$ fragment. Based on this information, this brominated compound is believed to be a (2-bromoethenyl) tribromobenzene

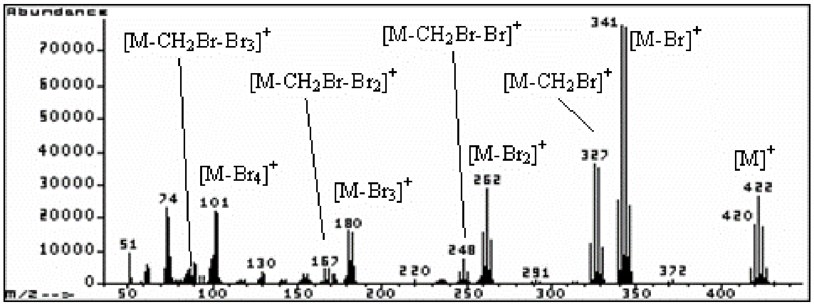

Figure 5: Full-scan EI mass spectra of brominated compound associated to peak e'.

Finally, the extract obtained from the rinse of the sampling system glass parts after the experiment at increasing temperature was analyzed using single-ion monitoring (SIM) in EIMS mode. $[M]^+$ ions were monitored for dibromostyrenes (m/z=262+264) and tribromostyrenes (m/z=340+342). $[M\text{-}Br]^+$ ion was monitored for (2-bromoethenyl) tribromobenzene (m/z=341+343). Peaks were detected at the same retention times (± 0.05 min) than peaks a' to e', confirming that dibromostyrenes, tribromostyrenes, and (2-bromoethenyl) tribromobenzene were really emitted by the PBS-64^{TM} polymer mainly, under thermal stress.

Reference:

(1) National Industrial Chemicals Notification and Assessment Scheme. 2001. Polybrominated Flame Retardants (PBFRs). Priority Existing Chemical Assessment Report No 20, 81 page + Appendix.

(2) Weil, E.D. 2003. Flame retardant workshop. SP Swedish National Testing and Research Institute, May 27-28th, Boras, Sweden.

(3) Moss, K. 2003. Flame retardant workshop. SP Swedish National Testing and Research Institute, May 27-28th, Boras, Sweden.

(4) Borms, R. and P. Georlette. 2004. Kunststoffeplast Europe, 9: 1-4.

(5) Wolf, M.; Riess, M.; Heitmann, D.; Schreiner, M.; Thom, H.; Vierle, O. and R. van Eldik. 2000. Chemosphere, 41: 693-699.

(6) Wolkoff, P. Atmospheric Environment, 32: 2659-2668.

(7) Hahn, O.; Kemmlein, S.; Jann, O.; Kalus, S. and D. Stolle. 2004. Flame Retardants 2004, 27-28th January 2004, London, UK.

(8) Blazsó, M.; Czégény, Zs. and Cs. Csoma. 2002. Journal of Analytical and Applied Pyrolysis, 64: 249-261.