OLIGOMERIC BFRS: A POTENITAL SOURCE FOR EMERGING BROMINATED AROMATIC COMPOUNDS

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1- Introduction

In response to the increasing environmental concern of relatively small molecules, such as polybrominated diphenyl ethers (PBDEs), used as additive flame retardants in a vast array of products, manufacturers are now promoting the wider use of brominated polymers. These macromolecules are mainly characterized by a relatively high molecular weight, which prevents their volatilization. Furthermore, they can be considered as virtually embedded in the plastic matrix due to their very large structure. Consequently, their bleeding or blooming from the plastic end products to the atmosphere is eliminated [1]. However, oligomeric BFRs may contain residuals resulting from an incomplete synthesis, a lack of purification, or the breakdown of some parts of the polymer structure. These low molecular weight residuals may be considered as simply blended in the matrix and, so, could be subject to a release to the atmosphere. In a first step, we have demonstrated that this release was effective, mainly under thermal stress [2]. The main objectives of this study were to identify these released compounds and to assess the potential of their environmental concern.

2- Material and Methods

Sample: BC-58 and PBS-64 are a tetrabromobisphenol A carbonate and a bromostyrene oligomers, respectively (Figure 1A and B). Both are produced by the Great Lake Chemical Corporation. FR-1025 is a pentabromobenzyl acrylate oligomer produced by the Dead Sea Bromine Group (Figure 1C). Their molecular weight are comprised between about 3500 and 80000 Da. The three BFR oligomers are mainly used in engineering thermoplastics such as polybutylene or polyethylene terephtalates [3, 4].

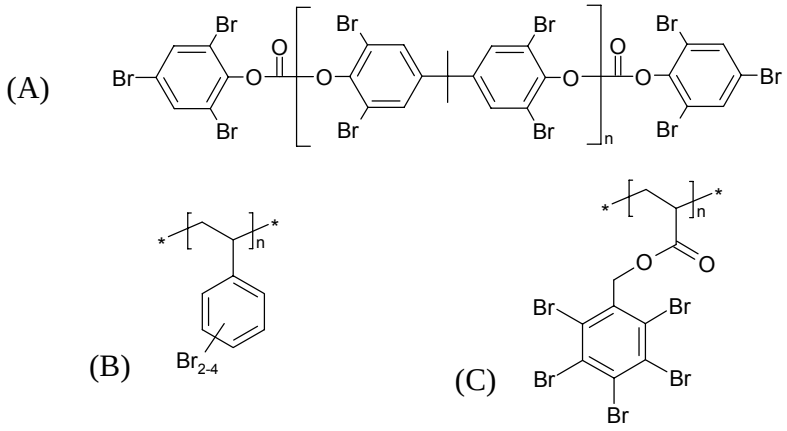


Figure 1: Chemical structure of (A) BC-58, (B) PBS-64, and (C) FR-1025 oligomers.

Thermal stress experiments: Details of the experimental setup and sampling methodology have been already presented elsewhere [2]. Briefly, BFR oligomers were placed in a glass flask and heated up to about 100 °C. A nitrogen flow was maintained trough the system during the experiment and a PUF plug was placed at the exit of the system to collect volatile compounds. PUF plugs were 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 The electron capture negative ion (ECNI) mode was used to monitor selected bromide ions at m/z 79 and 81 (ion source T = 175 ºC, ion source P = 1.0 torr, methane as reagent gas). The electron ionization (EI) mode was used to obtain full scan mass spectra of unknown brominated compounds and authentic materials (ion source T = 175 ºC).

3- Results and discussion

What kind of compounds is released from BFR oligomers?

Released compounds, which were identified, are characterized by an aromatic ring substituted with two to six bromine atoms (Table 1). For PBS-64 and FR-1025 oligomers, some of the most importantly released compounds are monomer molecules; di- or tribromostyrenes and pentabro-mobenzyl acrylate, respectively (Table 1). For BC-58, the monomer unit, tetrabromobisphenol A, was not detected. Other quantitatively important brominated compounds released were tribromophenol and pentabromoethylbenzene (PBEB) for BC-58 and pentabromotoluene (PBT) for FR-1025.

Are these released compounds a matter of environmental concern ?

Computer models EPI SuiteTM [5] and PBT Profiler [6] were used to estimate bioconcentration potential- and environmental persistence-related properties of the brominated compounds released from BFR oligomers (Table 1). Results of these estimations indicate that the most part of these chemicals are expected to bioaccumulate in the food chain (Log K_{ow} > 5 and/or BCF > 5000) and to persist in the environment ($t_{1/2}$air > 2 days or $t_{1/2}$water > 182 days or $t_{1/2}$soil > 182 days or $t_{1/2}$sediments > 365 days) considering the Toxic Substances Management Policy of Canada [7].

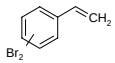
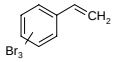
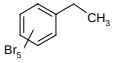
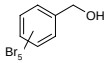
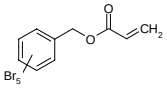
Among the released compounds, four specific compounds (PBT, PBEB, and penta- and hexabromobenzene (PBB and HBB) were of particular interest since they had some of the highest values for all properties and so could be considered as the most susceptible to accumulate in biota and persist in the environment (Table 1).

Are these released compounds already present in the environment ?

A thoughtful review of literature revealed that these compounds have not received much attention from the scientific community until now (Table 2). For example, no data about the PBB environmental dispersion is available even if this compound and HBB have been detected in scrap raw material lots, composed of electric and electronic devices, for an aluminum recycling plant in Finland [8]**.** PBT was reported only as detected in one study on air [9]. Neverthe-less, Wensing in 1999, shown that this compound could be emitted from TV sets at a rate up to 200 pg/unit/hour [10].

More details are available concerning HBB and PBEB. HBB, which is still used as flame retardant in Japan, was occasionally found in some bottom sediment samples collected during a recent survey of chemicals of concern throughout the Japan territory [11]. Levels, up to 43 ng/g dry weight, were higher than levels found for others halogenated organic contaminants, such as DDTs and their derivatives, monitored in the same samples [11]. HBB was also detected in air samples with a detection frequency of more than 70 % and at levels up to 100 pg/m^3 [11]. However, HBB was not detected in surface water or fish.

Table 1: Molecular weights, estimated physical-chemical properties and half-lives in different environmental media of volatile brominated compounds released from PBS-64, BC-58, and FR-1025 oligomers. (Underlined data in bold are equal or exceed thresholds used as criteria by the Toxic Substances Management Policy of Canada to determine if a substance is bioaccumulable and/or persistent [7]).

Compound	Structure	BFR oligomer	MW[a] (g/mol)	Log K_{ow}[b]	BCF[c]	$t_{1/2}$ air[d] (d)	$t_{1/2}$ wat.[e] (d)	$t_{1/2}$ soil[f] (d)	$t_{1/2}$ sed.[g] (d)
Dibromophenol		BC-58 FR-1025	252	3.2[h]	24	**5.4**	38	75	340
Dibromostyrenes		PBS-64	262	4.7	790	0.3	38	75	340
Tribromophenol		BC-58 FR-1025	331	4.1[h]	120	**34**	60	120	**540**
Tribromostyrenes		PBS-64	341	**5.6**	3800	0.3	60	120	**540**
Pentabromobenzene		FR-1025	473	**6.4**	**18 000**	**400**	**180**	**360**	**1 600**
Pentabromotoluene		BC-58 FR-1025	487	**7.0**	**48 000**	**88**	**180**	**360**	**1 600**
Pentabromoethyl Benzene		BC-58 FR-1025	501	**7.5**	**14 000**	**14**	**180**	**360**	**1 600**
Pentabromobenzyl alcohol		FR-1025	503	**5.5**	800	**4.6**	**180**	**360**	**1 600**
Hexabromobenzene		FR-1025	552	**6.1[h]**	**9 400**	**1 400**	**180**	**360**	**1 600**
Pentabromobenzyl acrylate		FR-1025	557	**6.9**	**40 000**	1.2	**180**	**360**	**1 600**

[a] MW = molecular weight; [b] K_{ow} = octanol-water partition coefficient; [c] BCF = bioconcentration factor; [d] $t_{1/2}$air = atmospheric half-life; [e] $t_{1/2}$wat. = water half-life; [f] $t_{1/2}$soil = soil half-life; [g] $t_{1/2}$sed. = sediment half-life; [h] experimental data [12].

Table 2: Worldwide environmental levels of some brominated compounds released by BFR oligomers.

Compound	Air (pg/m^3)	Sediments (ng/g d.w.)	Fish (ng/g w.w.)	Water (µg/L)	Reference
PBT	Chicago (US): d[a]				(9)
PBEB	Chicago (US): 520				(9)
	Chilton (UK): 8.9-90				(13)
HBB	Japan: nd[b]-100	Japan: nd - 43	Japan: nd	Japan: nd	(11)
		Japan: nd - 60			(14)

[a] d = detected but not quantified; [b] nd = non detected

PBEB has been detected in one 2003 summer Chicago air sample at a concentration of 520 pg/m^3 [9]. In comparison, the total PBDE (tri to hexa PBDEs) concentration was only 47 pg/m^3 [9]. PBEB has also been detected in 2001 Chilton (UK) air samples at an average concentration of 30 pg/m^3 (n=45); three times higher than the average concentration of total PBDEs (tri to hepta PBDEs) [13]. Interestingly, Hoh and collaborators were questioning about the source of a very high level of PBEB in the atmosphere at Chicago considering that all available information sustained that PBEB has never been a high volume production chemical in North America [9]. Our work suggests that the production and/or use of BFR oligomers, in particular FR-1025 and BC-58, could be one the source of this compound in the environment.

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5- References

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