Toxicity of degradation products of the commercially used polymeric flame retardant PolyFR following UV irradiation and heat treatment

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Introduction

Flame retardants (FR) are often necessary in order to comply with fire safety requirements. A prominent example for such a chemical has been hexabromocyclododecane (HBCD), which was mainly used in expanded (EPS) and extruded (XPS) polystyrene foams. However, due to its bioaccumulative, persistent, and toxic characteristics, the manufacturing and use of HBCD has been prohibited. The most common substitute for HBCD on a commercial scale is PolyFR a block copolymer of polystyrene and brominated polybutadiene. It was developed with the aim of having a superior environmental profile while still being suitable for the established technical process. Therefore, the bromine-containing polymer is chemically bound to the base material and persistent by design. Additionally, because of its high molecular weight, no bioavailability is expected. However, considering the long life time and various life cycle stages of EPS and XPS, abiotic and biotic environmental factors need to be taken into account. These factors may lead to a degradation of the commercial polymer and could result in smaller molecules with a different mobility and toxic potential. We have thus decided to study the possible degradation of PolyFR following UV irradiation and heat exposure (60 °C) in different media (distilled, rain, and reconstituted water). In addition, we have tested some of the commercially available degradation products regarding their individual and combined toxicity in three different OECD tests.

Materials and methods

In order to compare the degree of degradation and the type of products which are possibly formed during the respective process, pure PolyFR powder was exposed to two different treatments: UV radiation and heat.

A Hoenle UV cube was used for the UV treatment with an irradiance of approximately 500 W/m^2 (covers the UV-ABC and partly VIS spectrum, however, mainly between 290 and 450 nm). The irradiance decreased to approximately 150 W/m^2 on the ground of the Erlenmeyer flasks filled with 150 mL water. The irradiation was started approximately 20 minutes after water addition. Triplicates of 1 mL were taken from each of the 150 mL preparations every 15 minutes up to 180 minutes and stored in 1.5 mL Eppendorf tubes afterwards.

In addition to UV irradiation, samples of PolyFR were exposed to heat using the same Thermo Scientific Heraeus Function Line oven at 60 °C. Within this exposure scenario, 1.17 g PolyFR was either placed in Erlenmeyer flasks filled with 350 mL rain water or reconstituted water (same concentration of 3.33 g/L as for the UV measurements) or was placed without any kind of solvent in a closed glass petri dish. PolyFR in reconstituted water was exposed to heat for up to 36 weeks and in rain water for up to 12 weeks. Furthermore, some powder samples were added to 350 mL reconstituted water after the 24 weeks period. These samples were then exposed to heat for 12 additional weeks (with sampling after 4, 8, and 12 weeks). The maximum exposure of PolyFR in ddH_2O was 2 years at RT.

ICP-MS measurements have been used to detect the degree of degradation and – in combination with pH changes – be able to estimate the amount of organically bound bromine compared to overall bromine. We have also analysed the TOC to understand the ratio between brominated and non-brominated degradation products. LC-qTOF-MS and LC-MS/MS measurements were used to detect and determine individual degradation products. Based on these results and our previous work, we have then used four of the brominated ones with a score above 95, namely 2,4,6-Tribromophenol, 5-Bromosalicylic acid, 2,4,6-Tribromo-3-hydroxybenzoic acid, and 3,5-dibromo-4-hydroxybencoic acid, within the OECD tests no 201 (Algae growth inhibition test), 202 (*Daphnia* acute immobilisation test), and 211 (*Daphnia* reproduction test) to evaluate their individual and combined toxic potential.

Results and discussion:

After treating ddH_2O samples for 180 minutes with UV radiation, LC-qTOF-MS was used to generate a feature list of possible degradation products. Only molecular formulas were taken into account which were identified in both measurements and had a score above 95. Based on this feature analysis, 75 molecular formulas were identified, including eight containing bromine. These eight molecular formulas were selected for further research to obtain more information regarding their molecular structure. Based on our previous research, 5-Bromosalicylic acid ($C_7H_5BrO_3$) was included into the analysis as well. LC-qTOF-MS measurements were carried out again using standards where available to compare spectra and retention time for the selected degradation products. These analyses were performed in samples that were treated with UV radiation, but also with samples which were kept at 60 °C for 36 weeks to determine, if the pattern of brominated degradation products is similar for both degradation scenarios. Additionally, LC-MS/MS measurements were performed in case more data was required regarding the chemical structure.

Table 1: Information about possible degradation products that were found via LC-qTOF-MS and LC-MS/MS after degradation of PolyFR by UV treatment for 180 minutes and heat treatment at 60 °C for 36 weeks. The crosses indicate that the corresponding molecular formula was identified in all samples.

Mass-to-Charge (m/z)	Molecular Formula	Mass present in LC-qTOF-MS measurements		Certain structure confirmed?	
		UV samples	60 °C sam.	UV samples	60 °C samples
214.9349	$C_7H_5BrO_3$	x	x	5-Bromosalicylic acid identified	5-Bromosalicylic acid identified
250.8542	$C_6H_4Br_2O$	x	û	Spectrum not distinct	-
258.9248	$C_8H_5BrO_5$	x	û	Spectrum not distinct	-
294.8440	$C_7H_4Br_2O_3$	x	x	3,5-Dibromo-3-hydroxybenzoic acid identified	Spectrum not distinct
322.8390	$C_8H_4Br_2O_4$	x	û	Possible product: dibromophtalic acid	-
328.7647	$C_6H_3Br_3O$	x	û	Retention time different to 2,4,6-tribromophenol	-
338.8339	$C_8H_4Br_2O_5$	x	û	Possible product: dibromohydroxyisophthalic acid	-
346.7389	C_5HBr3O_3	x	û	Possible product: tribromofuroic acid	-
372.7546	$C_7H_3Br_3O_3$	x	û	2,4,6-Tribomo-3-hydroxybenzoic acid identified	-

Typically, the toxicity of a BFR is evaluated without considering degradation products, even though it was shown that the degradation of a BFR can alter its toxic potential (Chen, Hale, & Letcher, 2015; Chen, Letcher, Gauthier, & Chu, 2013; Martin, Evans, Faust, & Kortenkamp, 2017; Su, Letcher, Farmahin, & Crump, 2018). Especially for polymeric BFRs, which are claimed to be more environmental friendly, degradation products should be considered. In a previous study dealing with PolyFR (Koch et al., 2016), possible structures of such products were listed. Based on these insights, we have used UV radiation as a quick and effective tool for degradation to further improve our knowledge regarding degradation of polymeric BFRs. Among many substances, 75 molecular formulas were identified in a feature analysis with a score above 95, including about 10 % brominated compounds. This proves the previous prediction that only a minor fraction of the degradation products is actually brominated (Koch et al., 2016). Interestingly, some of the identified molecular formulas contain for instance nitrogen, which is also used within the manufacturing process of PolyFR (Beach et al., 2017). However, we have decided to focus only on brominated degradation products, as these might be the toxicological most interesting compounds.

By applying LC-qTOF-MS and LC-MS/MS measurements, we were able to identify 5-bromosalicylic acid, 2,4,6-tribromo-3-hydroxybenzoic acid, and 3,5-dibromo-3-hydroxybenzoic as degradation products following UV irradiation (Table 1). The standard of 2,4,6-tribromophenol showed a different retention time compared to the detected compound with the same mass and spectrum, suggesting that an isomer like 2,4,5-tribromophenol might derive from PolyFR when UV treated. Except 2,4,6-tribromophenol, which has been identified as a degradation product of other BFRs as well (Barontini, Cozzani, Marsanich, Raffa, & Petarca, 2004; Barontini, Marsanich, Petarca, & Cozzani, 2004; Eriksson, Rahm, Green, Bergman, & Jakobsson, 2004), not much is known regarding these compounds. Especially information concerning their effects on biota is largely missing. Again, to our knowledge only 2,4,6-tribromophenol has been the subject of multiple studies until now (Koch & Sures, 2018; Leonetti, Butt, Hoffman, Lynn, & Stapleton, 2016; Nomiyama et al., 2017). Based on the LC-MS/MS measurements, possible structures were suggested for three of the five remaining masses, namely dibromophtalic acid, dibromohydroxyisophthalic acid, and tribromofuroic acid. No structures could be suggested for the last two masses.

Comparing the detected brominated degradation products after UV irradiation and heat treatment, only one chemical (5-bromosalicylic acid) was clearly identified following both scenarios. Different explanations are possible for the fact that almost none of the nine analysed chemicals was detected in the heat treated samples. On the one side it is possible that the concentration of brominated degradation products is simply too low to be detected and give distinct spectra. This explanation is supported by the rather low concentration of total bromine in these samples as explained earlier. Taking into account that these samples were exposed for 36 weeks and concentrated afterwards, it is questionable to which extent degradation products would actually be relevant at such a low concentration. On the other side it is also possible that degradation mechanism following heat treatment is simply different to the one following UV irradiation. In this case, a full feature analysis might be useful for futures studies. In conclusion, it is not clear if the time efficient UV irradiation can be utilized to generate similar brominated degradation products compared to the rather time-consuming heat exposure.

In general, the feature list including 75 possible degradation products might be used as a kind of “fingerprint” in future studies to check if PolyFR contributes in any regard to BFRs found in indoor dust in homes and offices (Abdallah, Bressi, Oluseyi, & Harrad, 2016; Ali et al., 2016; Newton, Sellström, & de Wit, 2015) – which might not be expected at first, but is an important fact for evaluating the claimed superior environmental behaviour compared to previous BFRs.

In order to gain first data on possible effects of such degradation products for biota, we have performed the present study using three different OECD tests. Within those, the acute toxicity seems to be rather limited. If at all, effects can only be found at presumably extremely high concentrations, which are not to be expected following degradation of PolyFR. Nevertheless, data from chronic experiments indicates that the mixture of the four tested possible degradation products had effects, but only at comparable high concentrations as well. However, it has to be considered that the used mixture represents an artificial combination of only four substances of more than 75 that were detected during the degradation experiments. Therefore, tests using a native degradation “cocktail” would be advantageous for a realistic risk assessment as well as testing different groups of organisms.

References:

Abdallah, M. A. E., Bressi, M., Oluseyi, T., & Harrad, S. (2016). Hexabromocyclododecane and tetrabromobisphenol-A in indoor dust from France, Kazakhstan and Nigeria: Implications for human exposure. *Emerging Contaminants*, *2*(2), 73–79. https://doi.org/10.1016/j.emcon.2016.03.006

Ali, N., Eqani, S. A. M. A. S., Ismail, I. M. I., Malarvannan, G., Kadi, M. W., Albar, H. M. S., … Covaci, A. (2016). Brominated and organophosphate flame retardants in indoor dust of Jeddah, Kingdom of Saudi Arabia: Implications for human exposure. *Science of the Total Environment*, *569–570*, 269–277. https://doi.org/10.1016/j.scitotenv.2016.06.093

Barontini, F., Cozzani, V., Marsanich, K., Raffa, V., & Petarca, L. (2004). An experimental investigation of tetrabromobisphenol A decomposition pathways. *Journal of Analytical and Applied Pyrolysis*, *72*, 41–53. https://doi.org/10.1016/j.jaap.2004.02.003

Barontini, F., Marsanich, K., Petarca, L., & Cozzani, V. (2004). The Thermal Degradation Process of Tetrabromobisphenol A. *Industrial & Engineering Chemistry Research*, *43*, 1952–1961. https://doi.org/10.1021/ie034017c

Beach, M. W., Hull, J. W., King, B. A., Beulich, I. I., Stobby, B. G., Kram, S. L., & Gorman, D. B. (2017). Development of a new class of brominated polymeric flame retardants based on copolymers of styrene and polybutadiene. *Polymer Degradation and Stability*, *135*, 99–110. https://doi.org/10.1016/j.polymdegradstab.2016.11.008

Chen, D., Hale, R. C., & Letcher, R. J. (2015). Photochemical and microbial transformation of emerging flame retardants: Cause for concern? *Environmental Toxicology and Chemistry*, *34*, 687–699. https://doi.org/10.1002/etc.2858

Chen, D., Letcher, R. J., Gauthier, L. T., & Chu, S. (2013). Tetradecabromodiphenoxybenzene flame retardant undergoes photolytic debromination. *Environmental Science & Technology*, *47*(3), 1373–1380. https://doi.org/10.1021/es3042252

Eriksson, J., Rahm, S., Green, N., Bergman, Å., & Jakobsson, E. (2004). Photochemical transformations of tetrabromobisphenol A and related phenols in water. *Chemosphere*, *54*, 117–126. https://doi.org/10.1016/S0045-6535(03)00704-5

Koch, C., Dundua, A., Aragon-Gomez, J., Nachev, M., Stephan, S., Willach, S., … Sures, B. (2016). Degradation of Polymeric Brominated Flame Retardants: Development of an Analytical Approach Using PolyFR and UV Irradiation. *Environmental Science & Technology*, *50*, 12912–12920. https://doi.org/10.1021/acs.est.6b04083

Koch, C., & Sures, B. (2018). Environmental concentrations and toxicology of 2,4,6-tribromophenol (TBP). *Environmental Pollution*, *233*, 706–713. https://doi.org/10.1016/j.envpol.2017.10.127

Leonetti, C., Butt, C. M., Hoffman, K., Lynn, M., & Stapleton, H. M. (2016). Concentrations of polybrominated diphenyl ethers (PBDEs) and 2,4,6-tribromophenol in human placental tissues. *Environment International*, *88*, 23–29. https://doi.org/10.1016/j.envint.2015.12.002

Martin, O. V., Evans, R. M., Faust, M., & Kortenkamp, A. (2017). A human mixture risk assessment for neurodevelopmental toxicity associated with polybrominated diphenyl ethers used as flame retardants. *Environmental Health Perspectives*, *125*(8), 1–11. https://doi.org/10.1289/EHP826

Newton, S., Sellström, U., & de Wit, C. A. (2015). Emerging Flame Retardants, PBDEs, and HBCDDs in Indoor and Outdoor Media in Stockholm, Sweden. *Environmental Science & Technology*, *49*(5), 2912–2920. https://doi.org/10.1021/es505946e

Nomiyama, K., Takaguchi, K., Mizukawa, H., Nagano, Y., Oshihoi, T., Nakatsu, S., … Tanabe, S. (2017). Species- and Tissue-Specific Profiles of Polybrominated Diphenyl Ethers and Their Hydroxylated and Methoxylated Derivatives in Cats and Dogs. *Environmental Science & Technology*, *51*, 5811–5819. https://doi.org/10.1021/acs.est.7b01262

Su, G., Letcher, R. J., Farmahin, R., & Crump, D. (2018). Photolysis of highly brominated flame retardants leads to time-dependent dioxin-responsive mRNA expression in chicken embryonic hepatocytes. *Chemosphere*, *194*, 352–359. https://doi.org/10.1016/j.chemosphere.2017.11.153