

# Degradation of Polymeric Brominated Flame Retardants: Development of an Analytical Approach Using PolyFR and UV Irradiation

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## 1. Introduction

Since 2014, PolyFR is used as a substitute for HBCD on a commercial scale. Different to HBCD, it is chemically bonded to the base material and a persistent polymer by design. Thus, PolyFR is claimed to be more environmental friendly. However, almost all governmental risk evaluations focus only on the polymer itself and leave potential degradation products disregarded. 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 toxic potential. An environmental factor that is well known for altering the structure of brominated flame retardants (BFR) is ultraviolet (UV) radiation [<sup>1-3</sup>] and heat.

The goal of this study was to establish an adequate procedure to investigate the possible degradation of bulk PolyFR and PolyFR incorporated in EPS under UV irradiation and heat. Besides the search for a suitable marker with regard to the level of decomposition, it was also of interest to determine the structure of water soluble molecules that may derive from the insoluble PolyFR during degradation. Due to the polymeric structure and the fact that PolyFR is a reactive FR, well-tried methods that were applicable when working with BFRs, had to be exchanged in order to accomplish this goal. Afterwards, the developed methods were applied after heat treatment.

## 2. Material and methods

A broad overview of the applied methods and intentions for using them is given in Figure 1.

## 3. Results

Measurements using ICP-MS showed that UV irradiation caused the bromine concentration to increase over time in the 150 mL samples containing 3.33 g EPS with PolyFR per litre. After irradiating for 60 minutes, the bromine concentration raised to 69.21 µg/g EPS of which 2.48 µg/g were bromine that leaches out without UV treatment. Treating the 150 mL samples containing bulk PolyFR (3.33 g/L) caused an almost linear increase of the bromine concentration as well, but to a much higher extent. After 60 minutes, the concentration increased to 17,300 µg/g PolyFR including 57 µg/g bromine that can be detected without previous UV treatment.

Analyses of the adsorbable organically bound bromine in the 350 mL PolyFR samples via CIC, revealed comparably low concentrations of organically bound bromine in contrast with the total bromine concentrations. The adsorbable organically bound bromine accounted on average only for 0.96 % of the total bromine measured with ICP-MS.

After irradiating the samples for 60 minutes, different degradation products were detectable via LC-MS.

The mean contact angle flattens with increasing duration of UV treatment (78.95 ° to 22.23 °).

After 60 minutes of UV treatment, the mean molecular mass of the solid fraction, measured via GPC, stays almost the same compared to untreated bulk PolyFR (untreated: 127,300 g/mol; treated: 125,900 g/mol). The density of PolyFR did not significantly change after UV treatment.

After irradiating the samples for 60 minutes, changes can be analysed using <sup>1</sup>H-NMR in the solid fraction of the polymer, mainly within the signals with the chemical shift in the range of 0.5 to 2.5 ppm. These signals correspond to protons in the polymer main chain without adjacent bromine atoms and broaden after UV treatment for 60 minutes. Similar tests were performed after heat exposure.

## 4. Discussion

Bromine has been chosen as a marker for a possible degradation of PolyFR, because, different to the AObR, it is time efficient and convenient to measure. The bromine concentration raises to over 17,000 µg/g bulk PolyFR. This equates to 2.84 % of the bromine content of 1 g bulk PolyFR (where the bromine content is 61 %). To account for possible free, thus unreacted bromine during industrial manufacturing, experiments were carried out without UV treatment. As a result of these, it was

calculated, that only 0.33 % of the total bromine concentration leaches out of bulk PolyFR without UV irradiation.

EPS, thus the final insulation product and arguably more realistic scenario, around 1 % per mass PolyFR. After UV treatment for 60 minutes, the bromine concentration rose to almost 70 µg/g EPS, which is much lower compared to bulk PolyFR. However, when taking the PolyFR content of 1 % into account, the bromine concentration gets much closer (40 %) to the observed bromine concentration in the bulk PolyFR experiments. The remaining difference might be due to the thicker layer in the EPS experiments.

Although UV irradiation does not seem to change the mean molecular mass distribution or density of the solid fraction of PolyFR, changes are observable via <sup>1</sup>H-NMR. Broadening within the signals with the chemical shift in the range of 0.5 to 2.5 ppm indicate a degradation of the main chain. Possible explanations are changes in aromatic compounds or abstraction of bromine containing fragments, which would be in line with the increasing bromine concentration and the typical stepwise reductive debromination that BFRs undergo when exposed to UV radiation [<sup>1,3</sup>].

As mentioned previously, these changes are reflected in the alteration of the contact angle. The smaller the contact angle with water, the more hydrophilic a surface is [<sup>4</sup>]. Thus, PolyFR becomes more hydrophilic when exposed to UV radiation. This is especially important when considering other environmental factors, like biodegradation.

All of the detected degradation products were brominated. Taking into account that the parent compound PolyFR does not have brominated aromatic structures, bromine needs to be added to these structures. Based on the fact, that only brominated molecules were found in the samples, this addition might either occur to the aromatic structure while still attached to the polymer itself or very rapidly in solution.

This study gives a first approach for studying the environmental degradation of BFRs, particularly polymeric ones, as an effect of exposure to UV radiation and heat. However, further studies should be conducted to use this approach in an environmentally more relevant scenario, because possible degradation caused by UV irradiance and heat is important to take into account when assessing the risk at all life cycle stages of bulk PolyFR and products that contain this BFR.

## 5. References

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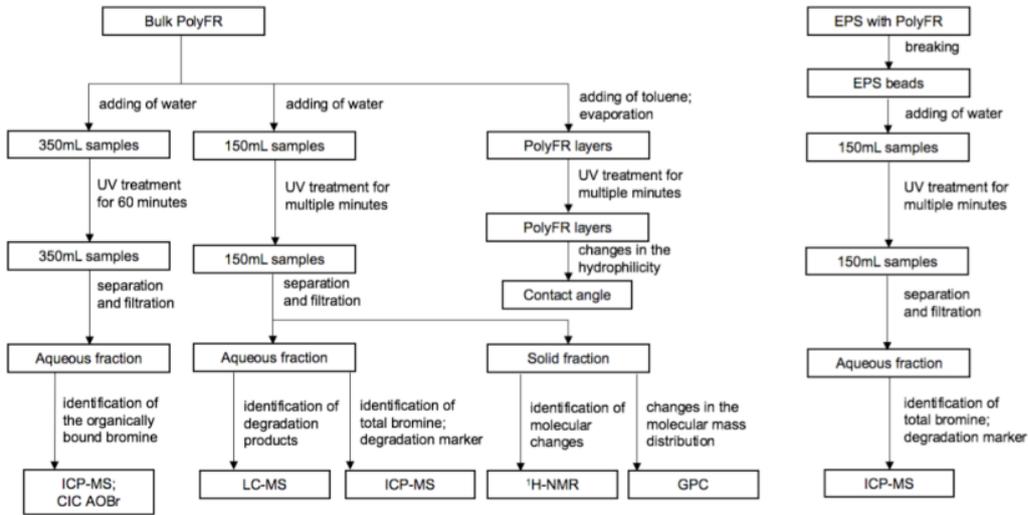


Figure 1: Overview of the applied methods and procedures