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Photodegradation of brominated flame retardants in polystyrene:  
quantum yields, products and influencing factors

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**Abstract**

1 Brominated flame retardants (BFRs) are widely used as additives in plastics, textiles  
2 and electronics materials. Here, we investigated the photodegradation of four BFRs  
3 including decabromobiphenylether (BDE-209), tetrabromobisphenol A (TBBPA),  
4 tetrabromobisphenol A-bis(2,3-dibromopropylether) (TBBPA-DBPE) and  
5 tetrabromobisphenol A bis (allyl) ether (TBBPA-BAE). Experiments were carried out  
6 in polystyrene (PS) films using monochromatic and polychromatic irradiations. For  
7 comparison, irradiations were also carried in a solvent (tetrahydrofuran: THF).  
8 Monitoring of BFR degradation was performed using bulk and surface infrared (IR)  
9 measurements, as well as by extraction and HPLC-UV. Photoproducts were  
10 characterized using HPLC-high resolution electrospray ionization mass spectrometry  
11 (HPLC-ESI-Orbitrap-MS).

12 All four BFRs underwent photochemical transformation in THF at 290 nm with a  
13 quantum yield ( $\Phi$ ) ranging from 0.05 for TBBPA to 0.27 for BDE-209, indicating an  
14 increase of photoreactivity with the number of Br atoms in BFRs. On the other hand,  
15 no major difference in the  $\Phi$  values was observed when BFRs were embedded in PS  
16 films ( $\Phi$ : 0.82 - 0.89). The higher photoreactivity in PS appears to be associated with  
17 a fast oxidation of PS as revealed by infrared (IR) analysis and yellowing of the films.  
18 Interestingly, the faster the yellowing occurred, the faster the BFR degradation was  
19 inhibited due to light screening effect. Several major photoproducts were identified for  
20 TBBPA and TBBPA-DBPE. Additional photoproducts possibly arising from PS  
21 oxidation and bromination by  $\text{Br}^\bullet$  were observed for the first time. This work provides  
22 a better understanding of the reactivity and fate of BFRs in polymers allowing for a  
23 better assessment of their environmental impacts.

24 **Keywords:** polybrominated diphenyl ethers, tetrabromobisphenol A, kinetic, fate.

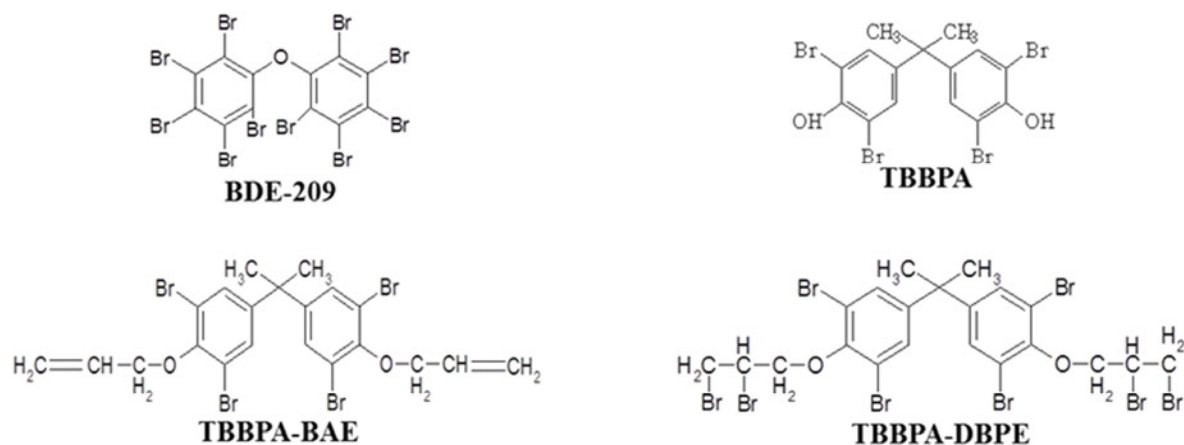
25

## 26 1. Introduction

27 Brominated flame retardants (BFRs) are ubiquitous industrial chemicals that are  
28 commonly used in plastics, textiles and electrical /electronic equipment to improve  
29 their fire resistance (de Wit, 2002; Birnbaum and Staskal, 2004). BFRs include more  
30 than 75 different substances which belong to three main groups: polybrominated  
31 diphenyl ethers and biphenyls (PBDEs and PBBs), hexabromocyclododecanes  
32 (HBCDs), tetrabromobisphenol A (TBBPA) and derivatives (Alaee et al., 2003). Due to  
33 their toxicity and environmental persistence, strict bans on the production and use of  
34 several PBDEs (penta-, octa-, deca-BDE) have been introduced. Furthermore, these  
35 BFRs were listed under the Stockholm convention for persistent organic pollutants  
36 (POPs)(Sindikú et al., 2015). Other emerging BFRs, dubbed as novel BFRs (NBFRs)  
37 have been introduced into the market as alternatives to banned formulations. Some  
38 of the commonly used NBFRs include decabromodiphenyl ethane or 1,2-  
39 bis(pentabromodiphenyl)ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)ethane  
40 (BTBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB or EHTBB), bis(2-  
41 ethylhexyl)-3,4,5,6-tetrabromo-phthalate (TBPH or BEHTBP), tetrabromobisphenol A-  
42 bis(2,3-dibromopropylether) (TBBPA-DBPE) and tetrabromobisphenol A bis (allyl)  
43 ether (TBBPA-BAE). At present, the most widely used BFR is TBBPA (50% of BFRs  
44 currently used) with an estimated annual production volume of 130.000 tons (Han et  
45 al., 2016). TBBPA-containing materials are used in the manufacturing of office and  
46 home electronic equipment, such as computer printed circuit boards, mobile phones,  
47 televisions, washing machines, etc. Due to its extensive use, environmental  
48 contamination of TBBPA has been detected in various matrices such as air, water,  
49 dust and sediments (Morris et al., 2004; Abdallah et al., 2008; Lin, 2015). Moreover, it  
50 has been found in exposed humans and animals and was reported to be neurotoxic

51 and endocrine disruptor (Jakobsson et al., 2002; Cariou et al., 2008; Van der Ven et  
52 al., 2008; Geens et al., 2009; Dourson, 2015; Liu et al., 2016; Gong et al., 2017;  
53 Inthavong et al., 2017). Various studies have investigated the transformation  
54 pathways of TBBPA in the environment, in particularly photodegradation in surface  
55 water (Eriksson et al., 2004b; Wang et al., 2015b; Han et al., 2016). Direct photolysis  
56 of TBBPA under solar irradiation was found to occur in aqueous solution and via  
57 photosensitized reactions with  $\text{OH}^\bullet$  radicals and singlet oxygen generated by  
58 irradiation of humic substances (Eriksson et al., 2004b; Han et al., 2009; Wang et al.,  
59 2015b; Han et al., 2016). The major phototransformation pathways included  
60 debromination and oxidation (Eriksson et al., 2004b; Wang et al., 2015b; Han et al.,  
61 2016). While these studies shed light on the photoreactivity of TBBPA in water, no  
62 data is available to date on the kinetics and photoproducts of TBBPA in solid polymer  
63 matrices as well as on the photodegradation of some of its NBFR derivatives  
64 (TBBPA-DBPE and TBBPA-BAE). This is of great significance since TBBPA and its  
65 NBFRs derivatives are incorporated in plastics, and absorb solar radiation (>290 nm)  
66 which can induce their degradation during use, recycling in landfills or in  
67 microplastics contaminating rivers and oceans (Ballesteros-Gómez et al., 2017). As  
68 an example, we have recently demonstrated that BDE-209 can undergo  
69 photodegradation in car seat fabrics collected from end of life vehicles, leading to the  
70 formation of dibenzofurans and dioxins as well as leachates to air and water (Khaled  
71 et al., 2018). In this study, our aim was to investigate the photoreactivity of TBBPA  
72 and two of its NBFR derivatives (TBBPA-DBPE and TBBPA-BAE) illustrated in Fig. 1.  
73 Experiments were performed in tetrahydrofuran (THF) and in PS films. THF was  
74 selected due to the high solubility of BFRs in this solvent and its relative stability  
75 under UV irradiation. While not all selected BFRs are used in PS materials, we used

76 it as a model target plastic material due to its wide use and ease of preparation and  
 77 analysis. In addition to TBBPA NBFR derivatives, BDE-209 was included in the  
 78 present study as a reference BFR for comparison. This is the first study to examine  
 79 photodegradation of TBBPA and its NBFR derivatives in solid matrices. The results  
 80 will help to better assess the environmental fate and impact of these BFRs.



81 **Fig. 1.** Structures of studied brominated flame retardants (BFRs).

## 82 2. Materials and Methods

### 83 2.1. Materials

84 Bis (pentabromophenyl) ether (BDE-209, 98% purity) was purchased from Sigma  
 85 Aldrich, Germany. The three other flame retardants standards such as  
 86 Tetrabromobisphenol A (TBBPA, >98% purity), 2,2-Bis [3,5-dibromo-4-(2,3-  
 87 dibromopropoxy) phenyl] propane (TBBPA-DBPE >90% purity), and 2,2-Bis (4-  
 88 allyloxy-3,5-dibromophenyl) propane (TBBPA-BAE >99% purity) were obtained from  
 89 Tokyo Chemical Industry (TCI Europe, Belgium). THF and acetonitrile (ACN) were of  
 90 HPLC grade purity (99%) and obtained from Sigma-Aldrich, Germany. The studied  
 91 polymer was PS material without additive ( $M_w=172175 \text{ g mol}^{-1}$ ) in powder form.

## 92 2.2. Samples preparation

93 - **In THF.** The solutions of BDE-209, TBBPA, TBBPA-DBPE and TBBPA-BAE were  
94 prepared at a concentration of  $10^{-4}$  M. All solutions were stored in the dark at room  
95 temperature.

96 - **PS film preparation.** It is important to note that the TBBPA-BAE molecule has not  
97 been studied in PS because of the difficulties of preparing PS films containing  
98 TBBPA-BAE by extrusion at high temperature. The two other brominated additives  
99 (TBBPA and TBBPA-DBPE) in an amount of 2% in weight were incorporated into the  
100 PS matrix by an extrusion process, using a Haake Minilab twin-screw extruder  
101 device. Laboratory experimental conditions were:  $T=180$  °C, with a roller speed of  
102 100 rpm for 5 min. Then films of PS and PS/BFRs (approximately  $\approx 80-85$   $\mu\text{m}$   
103 thickness) were prepared by compression molding between PTFE-coated glass  
104 cloths at 200 bars in an electrically heated laboratory press at 180 °C for 3 min.

## 105 2.3. Extraction of BFRs from PS

106 The BFRs contents in polystyrene samples were extracted and quantified as follows:  
107 0.01g of PS films was dissolved into 2ml THF then mixed by vortex for 1min. Then,  
108 1ml of the extracts was centrifuged for 5 min at 13500 rpm before analysis. Before  
109 irradiation, the recovery efficiency ( $95\pm 5\%$ ) of the extraction procedure was evaluated  
110 by the analysis of three blank PS samples spiked with known amounts of BFRs.

## 111 2.4. Irradiations

112 To determine quantum yield of BFRs, solutions were irradiated in a quartz cuvette in  
113 a parallel beam using a high pressure mercury arc lamp equipped with an oriel  
114 monochromator with a wavelength ( $\lambda$ ) fixed at 290nm for all irradiations experiments

115 in THF. The quartz cuvette was hermetically closed by a stopper to avoid THF losses  
 116 by evaporation. All photodegradation experiments were performed in triplicate. The  
 117 different irradiation parameters are given in Table 1A. For PS/BFR films, irradiation  
 118 was carried out using the same irradiation system cited above (monochromator). The  
 119 different irradiation parameters are given in Table 1.B. The initial and remaining  
 120 BFRs concentrations in PS films were determined by HPLC analysis after extraction  
 121 by THF (as described later in section 2.5.2).

122 The quantum yield values were the average of two independent measurements. The  
 123 quantum yields ( $\Phi$ ) of photodegradation were calculated based on the following  
 124 equations:

$$\Phi = \frac{\Delta n}{\bar{I}_a \times \Delta t}$$

125 where  $\Delta n$  is the number of photodegraded molecules during  $\Delta t$ , the irradiation time,  
 126 and  $\bar{I}_a$ , the average number of absorbed photons during the irradiation time ( $\Delta t$ ).

- 127     ▪ In THF:  $\Delta n = \Delta c \times N$  where  $\Delta c$  is the concentration decrease expressed in  
 128 mole/cm<sup>3</sup> measured by HPLC and  $N$  the Avogadro number,  $\bar{I}_a = \frac{I_a^{t_0} + I_a^t}{2}$ , where  
 129  $I_a^{t_0} = \frac{I_0}{\ell} (1 - 10^{-A_{BFR}^{t_0} \lambda})$  and  $I_a^t = \frac{I_0}{\ell} (1 - 10^{-A_{BFR}^t \lambda})$ , where  $I_0$  is the photon flux  
 130 expressed in photon/cm<sup>2</sup>/s,  $A_{BFR}^{t_0} \lambda$  the initial absorbance at wavelength  $\lambda$  of  
 131 BFR,  $A_{BFR}^t \lambda$  the absorbance of BFR at instant  $t$  after irradiation, and  $\ell$ , the path  
 132 length (1cm) . The contribution of THF to the absorbance of the solution is  
 133 negligible at the irradiation wavelength (290 nm).
- 134     ▪ In PS:  $\Delta n$  is obtained by multiplying  $n_0$ , the initial number of molecules in the  
 135 sample by the percentage of degradation measured by HPLC.  $n_0$  was  
 136 calculated using the volume of the sample (0.0083 cm<sup>3</sup>), a density of 1g cm<sup>-3</sup>



137 and a loading of 2% in weight. Since PS can also contribute to the absorbance  
 138 of the film PS/BFR, we used the following expressions to calculate  $I_a^{t0}$  and  $I_a^t$ :  
 139  $I_a^{t0} = \frac{I_0}{\ell} (1 - 10^{-A_{BFR}^{t0}\lambda})$  where  $I_0$  is the photon flux expressed in photon/cm<sup>2</sup>/s,  $\ell$   
 140 is the film thickness (80-85  $\mu$ m) and  $A_{BFR}^{t0}\lambda$  is the initial absorbance of BFR (at  
 141 2% in weight) in the PS film (for a path length  $\ell$ ) corrected by subtracting the  
 142 contribution of PS initial absorbance at the same  $\lambda$  which was negligible at the  
 143 selected  $\lambda$  for irradiating the PS/BFR films (as shown later in section 3.1,  
 144 Figure 2). After irradiation, the contribution of PS to the total absorbance  
 145 increased due to yellowing (as described later in the results section) and thus  
 146 a correction of the measured absorbance was performed as follows:

147  $I_a^t = \frac{I_0}{\ell} * \frac{A_{BFR}^t}{A_{PS+BFR}^t} (1 - 10^{-A_{BFR}^t\lambda})$ , where  $A_{PS+BFR}^t$  represents the total  
 148 absorbance of irradiated PS/BFR film and  $A_{BFR}^t$  is the absorbance of BFR in  
 149 the PS film after irradiation, as estimated by multiplying the initial absorbance  
 150  $A_{BFR}^{t0}$  by the percentage of remaining BFR in the PS film after irradiation (by  
 151 extracting and analyzing BFR using HPLC as described later in section 2.5.2).

152 For the purpose of photoproducts identification, irradiation of films was carried out  
 153 using a Suntest CPS photosimulator from Atlas equipped with a Xenon arc lamp and  
 154 a special glass filter that restricted the transmission of wavelengths below 290 nm.  
 155 The irradiance was set at 500 Wm<sup>-2</sup>, whereas the emitted wavelengths ranged from  
 156 290 to 800 nm. The temperature within the dishes did not exceed 25 °C thanks to a  
 157 water circulation cooling system maintained at 10 °C. Irradiation of the samples in  
 158 THF was carried out using a polychromatic device equipped with six fluorescent  
 159 tubes TLAD 15W05 Philips (300-450 nm, emission maximum at 365 nm) at room  
 160 temperature. A 20 ml capacity Pyrex-glass cylindrical reactor (1.4 cm, i.d.) was used

161 and closed with a stopper to avoid THF evaporation. For all photolysis experiments,  
162 duplicate samples were irradiated.

## 163 *2.5. Analytical methods*

### 164 *2.5.1. Spectroscopic Analyses*

165 Absorption spectra of BFRs solutions in THF were recorded using a Cary 3 UV-  
166 Visible spectrometer (Varian) in a quartz cuvette. Solid state UV-Visible spectra were  
167 obtained with a UV2600 spectrophotometer equipped with an integrating sphere from  
168 Shimadzu. Infrared (IR) spectra of PS films were recorded in transmission mode  
169 using a Nicolet 760-FTIR spectrophotometer (nominal resolution of  $4\text{cm}^{-1}$ , 32 scan  
170 summations), and also in reflection mode with a Nicolet 380-FTIR spectrophotometer  
171 equipped with a Thunderdome-ATR accessory with a diamond crystal ( $4\text{cm}^{-1}$ , 32  
172 scans). Note that unlike Transmission IR spectroscopy which probes the entire  
173 thickness of the material, ATR-IR technique generates only a few microns depth  
174 penetration of the IR beam in the sample thickness. Therefore it is commonly  
175 considered that IR spectrum obtained using a diamond ATR crystal provides  
176 information regarding the first 3–5  $\mu\text{m}$  superficial layer of solid materials. All  
177 absorbance values presented are an average of at least four samples.

### 178 *2.5.2. HPLC Analysis*

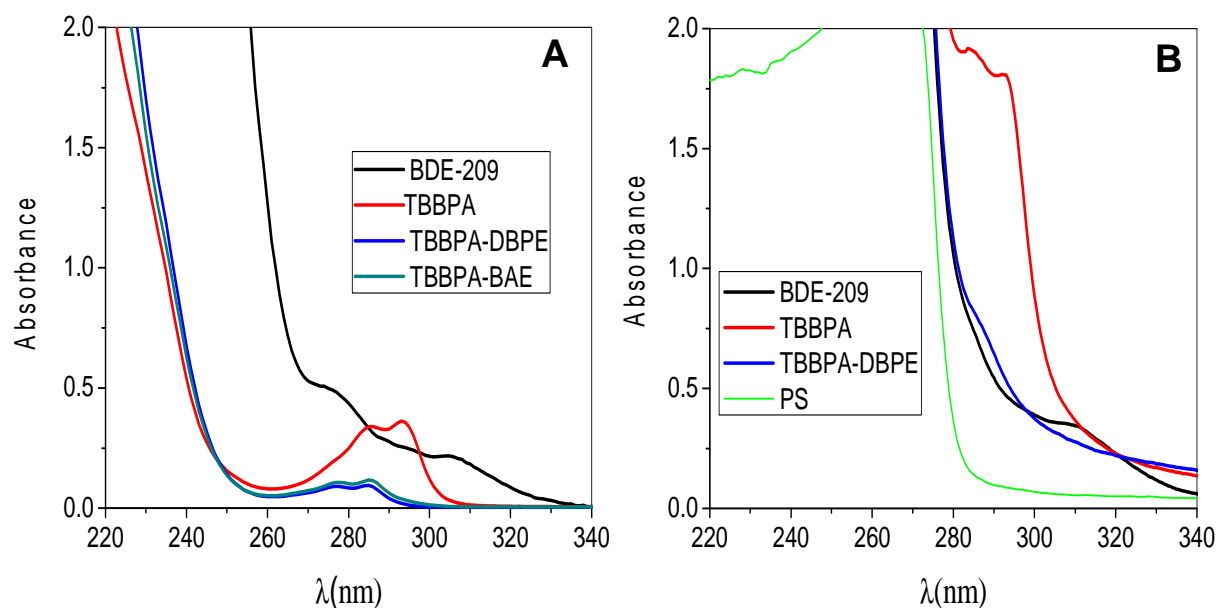
179 All BFRs samples in THF and in PS were analysed using a Shimadzu liquid  
180 chromatography type equipped with a UV-visible absorption detector SPD-M20A. A  
181 10  $\mu\text{l}$  aliquot was injected in a Marchery-Nagel Nucleodur column  $\text{C}_8$  grafted silica of  
182 250 mm length and of 4.6 of particle mm i.d, at a flow rate of  $1\text{ml min}^{-1}$  and the mobile  
183 phase consisted of 100% ACN for BDE-209, TBBPA-DBPE, and 80% ACN-20%  
184 water for TBBPA. The peaks for each compound were identified in the chromatogram

185 by comparing the retention times of the analyte in the liquid sample and in the PS.  
186 Photoproducts in THF and PS were identified using an HP 3000 RSLC high  
187 performance liquid chromatography system (ThermoScientific) equipped with a high  
188 resolution Orbitrap mass spectrometry analyzer. Samples were injected onto a  
189 Kinetex™ C<sub>18</sub> LC column (100 mm × 2.1 mm, 1.7 μm particle sizes). The binary  
190 solvent system used was composed of ACN and water acidified with 0.5% v/v formic  
191 acid. The gradient program was 5% ACN for the 7 first min, followed by a linear  
192 gradient to 99% in 7.5min and kept constant until 20 min. The flow rate was set at  
193 0.45 mL min<sup>-1</sup> and injection volume was 5 μL. Scan parameters were set  
194 from m/z 120 to 1800 amu in full-scan negative ESI ionization mode. To identify  
195 unknown photoproducts, the mass accuracy was set at <5 ppm. Chemical structures  
196 are proposed based on the mass spectra and bromine isotope patterns

### 197 **3. Results and discussion**

#### 198 *3.1. UV-Vis absorption spectra*

199 The absorption spectra of the studied BFRS in THF are presented in Fig. 2A.  
200 Compared to BDE-209, TBBPA derivatives absorb at shorter wavelength. TBBPA  
201 shows an absorption band extending from 260 to 310 with two maxima at 283-  
202 293nm. TBBPA-DBPE and TBBPA-BAE have similar absorption band, but much less  
203 intense than TBBPA and shifted to the blue by about 10 nm. Thus, one can assume  
204 that the addition of side groups to the TBBPA moiety in TBBPA-DBPE and TBBPA-  
205 BAE reduces light absorption and could thus help to reduce photodegradation.  
206 Nevertheless, the band edges around 300 nm make possible solar photons  
207 absorption ( $\lambda > 290$  nm). The absorption of BFRs above 300 nm is more obvious in  
208 the PS samples loaded at 2% in weight (Fig. 2B).



209 **Fig. 2. (A)** UV-vis absorption spectra of BFRs in THF; **(B)** UV-vis absorption spectra  
 210 of BFRs (2% w:w) in PS.

211 This suggests that photodegradation of incorporated BFRs could take place during  
 212 UV exposure of PS. The 2% loading was selected because it is comparable to BFRs  
 213 concentration used in polymers (2-20%) while avoiding to reach absorbance  
 214 saturation at high percentage. Since PS can absorb light  $<280\text{nm}$  as shown in Fig.  
 215 2B, we choose to irradiate BFRs at higher wavelengths ( $\lambda >290\text{nm}$ ) to avoid  
 216 screening effect due to PS light absorption and to mimic solar light.

### 217 3.2. Quantum yields of photodegradation

218 Dark control experiments for each BFR did not show any noticeable degradation  
 219 ( $<2\%$ ). The quantum yields of BFRs degradation in THF upon monochromatic  
 220 excitation at 290nm are presented in Table 1A.

$\Phi$  values ranged between 0.05 for TBBPA and 0.27 for BDE-209. TBBPA-DBPE (0.190) and TBBPA-BAE (0.08) exhibited in-between values. These values are close to those reported for BDE-209 in water (0.28) and in THF (0.38), and for TBBPA

(0.018-0.045) in water depending on pH values (Eriksson et al., 2004b; Kuivikko et al., 2007; Xie et al., 2009). However, this is the first time that quantum yield of photodegradation is reported for TBBPA-DBPE and TBBPA-BAE.

221 **Table 1A.** Quantum yields ( $\Phi$ ) of BFRs ( $10^{-4}$  M) in THF.

BFR	Concentration (M)	Absorbance at 290 nm	Time (min)	loss (%)	$I_0$ (photon/cm <sup>2</sup> /s)	$\Phi$
BDE-209	$10^{-4}$	0.30	5	14%	$2.2 \times 10^{14}$	$0.27 \pm 0.03$
TBBPA	$10^{-4}$	0.64	10	14%	$3.6 \times 10^{14}$	$0.05 \pm 0.02$
TBBPA-DBPE	$10^{-4}$	0.11	5	8%	$3.6 \times 10^{14}$	$0.19 \pm 0.02$
TBBPA-BAE	$10^{-4}$	0.15	30	26%	$3.6 \times 10^{14}$	$0.08 \pm 0.01$

**Table 1B.** Quantum yields ( $\Phi$ ) of BFRs (2% in weight) in PS films (80-85 $\mu$ m)

BFR	$\lambda$ nm	$N_0$ (mole/cm <sup>3</sup> )	Absorbance	Time (h)	loss%	$I_a$ (photon/cm <sup>2</sup> /s)	$\Phi$
BDE-209	310	$2.08 \times 10^{-5}$	0.29	2	20%	$3.9 \times 10^{14}$	$0.89 \pm 0.08$
TBBPA	302	$3.6 \times 10^{-5}$	0.29	8	34%	$3.11 \times 10^{14}$	$0.82 \pm 0.08$
TBBPA-DBPE	285	$2.1 \times 10^{-5}$	0.4	7	21%	$1.25 \times 10^{14}$	$0.84 \pm 0.08$

222 The order of photoreactivity seems to correlate with the number of Br atoms present  
 223 in the molecules. As an example, TBBPA with 4 Br atoms exhibits the lowest  $\Phi$   
 224 followed by TBBPA-BAE (6Br), TBBPA-BDBPE with 8 Br ( $\Phi = 0.19$ ), whereas for  
 225 BDE-209 (10 Br)  $\Phi$  is the highest (0.27). This finding is in agreement with previous  
 226 studies showing that the higher brominated diphenylethers photodegrade faster than  
 227 lower brominated (Eriksson et al., 2004a; Fang et al., 2008; Wang et al., 2015a;  
 228 Staszowska, 2017). Our study reveals that this correlation can be also verified when  
 229 comparing brominated flame retardants which do not share the same core structure  
 230 such as TBBPA and BDE-209. On the other hand, the calculated  $\Phi$  values for the 3

231 BFRs in PS vary in a very narrow range (0.82 - 0.89) as shown in Table 1B,  
232 indicating that the correlation based on the number of Br is not valid in PS.  
233 Surprisingly, these values are much higher than those found in THF. In a previous  
234 study, we have shown that BDE-209 exhibits very high photoreactivity in PS  
235 compared to other polymers such as PET and cellulose (Khaled et al., 2018). While  
236 the reasons for this high photoreactivity in PS are not clear, several assumptions can  
237 be postulated:

238 - a higher hydrogen donor capacity of PS which can promote debromination and thus  
239 accelerate photodegradation (Kajiwara et al., 2008; Khaled et al., 2018). This can be  
240 explained by the lower C-H bond dissociation energy in PS or Ar-C-H (386 kJ/mol)  
241 than in THF (410 kJ/mol) (Agapito et al., 2005). This lower dissociation energy in PS  
242 can facilitate the debromination via formation of HBr.

243 -  $\pi$ - $\pi$  stacking between PS and BFRs (Pan et al., 2013). A recent study has shown  
244 via theoretical calculations that face-to-face  $\pi$ - $\pi$  stacking interaction plays an  
245 important role in the low-lying  $\pi \rightarrow \sigma^*$  transitions of BDE209-toluene  $\pi$ -stacking  
246 complex at around 300 nm in the sunlight region. This leads to notable changes for  
247 the  $\pi \sigma^*$  excited states and promotes the breaking of the C-Br bonds. The  
248 photodegradation reaction via an intermolecular charge-transfer excited state formed  
249 by the electronic transition from a  $\pi$  orbital of toluene to a  $\sigma^*$  orbital of BDE209 was  
250 thus found to be a dominant mechanism. Given the similarity between toluene and  
251 styrene, we hypothesize that a similar  $\pi$ - $\pi$  stacking interaction interaction could  
252 occur in PS/BFR resulting in a favorable condition for C-Br photolysis. Further  
253 investigations are needed to confirm this assumption.

254 - an auto-acceleration effect due to mutual interaction between the PS and Br  
255 radicals released by the photodegradation of BFRs. It is possible that the first Br  
256 radicals released by debromination cause change in PS structure and lead to the  
257 formation of reactive species which can in turn enhance the degradability of BFRs.

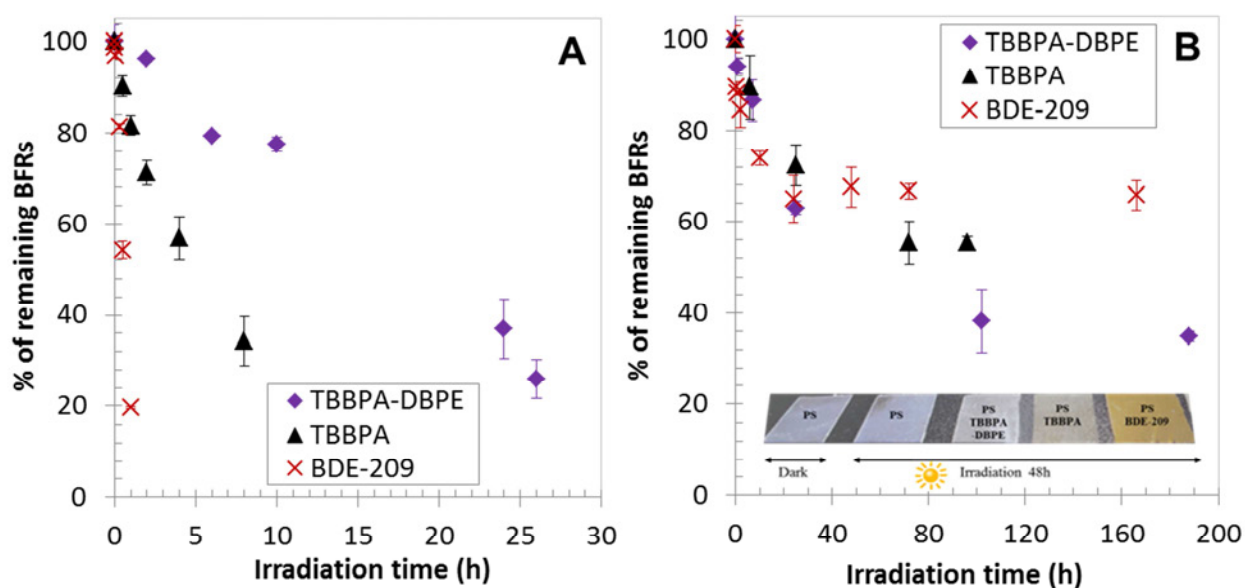
258 It is important to note that the  $\Phi$  values were not calculated at the linear initial stage  
259 of the reaction due to the difficulty to measure very low conversion extents. Thus,  
260 longer irradiation times (2-8 h of exposure compared to 5-30 min of exposure for THF  
261 solution) were required, and secondary reactions (e.g. degradation of primary  
262 photoproducts, oxidation of PS, formation of adducts, etc.) may have taken place. In  
263 particular, a significant yellowing of the films was observed. This yellowing induces a  
264 decrease in  $I_a$  during irradiation due to the competition of absorbance between BFRs  
265 and PS yellowing byproducts which can affect the  $\Phi$  measurement. The other  
266 possible bias is that BFRs concentration measurements were performed after  
267 dissolution of the films in THF. The percentage of conversion obtained is thus an  
268 averaged value inside the film sample and it does not reflect the potential  
269 heterogeneous BFRs photodegradation inside the films due for instance to an  
270 oxidation profile as previously suggested (Torikai et al., 1995; Sinturel et al., 1999).

271 To examine the oxidation profile of BFRs in the PS film, ATR-IR measurements were  
272 carried out on both sides of the irradiated film (the first 3-5  $\mu\text{m}$  surface layer) in  
273 addition to transmission IR analysis (the whole thickness of the film) before film  
274 dissolution and HPLC-UV analysis. The photodegradation occurred more significantly  
275 at the irradiated face of the PS film. After 2h of irradiating PS containing BDE-209,  
276 the average conversion extent measured by HPLC and IR was around 20% while the  
277 measurement by ATR-IR (Fig S1) indicates 33% for the exposed surface (upper) and  
278 23% for the non-exposed surface (lower) as it can be seen in Fig. S1 and Table S2. It

279 can be concluded that the photodegradation of BFRs is indeed heterogeneous in PS  
 280 and thus data presented in Table 1B are consequently only indicative and must be  
 281 taken with care.

### 282 3.3. Kinetics of BFRs photodegradation

283 We measured the decay profiles of BFRs in THF (Fig. 3A) and in the PS films under  
 284 polychromatic irradiation: between 300-450 nm for THF solutions using a  
 285 photoreactor and between 300-800 nm for PS films using the SUNTEST device (Fig.  
 286 3B). In THF, the rate of BFRs photodegradation varied in the order BDE-209 >>  
 287 TBPPA >> TBPPA-DBPE. The rate is related to the product  $I_a\Phi$ . The dominant factor  
 288 here is likely the light absorption that is much more important for BDE-209 and in a  
 289 minor extent for TBPPA than for the TBBPA-DBPE (see Fig. 2A).



290 **Fig. 3. (A)** Decay profiles of BFRs ( $10^{-4}$  M) irradiated in THF (300-450 nm). Error bars  
 291 represent the relative standard deviation obtained from triplicate measurements. **(B)**  
 292 Decay profiles of BFRs in PS irradiated in the Suntest solar simulator (300-800 nm,  
 293  $500 \text{ W m}^{-2}$ ).



294 In PS films, when one considers the early stages of the reactions (the first 10h of  
295 exposure), the highest rate of photodegradation is observed for BDE-209, which is  
296 due to its high absorption in the range 290-365nm. At higher extent of the reaction (>  
297 40h), differences are observed in the plateau values reached. BDE-209 is the BFR  
298 the less photodegraded with a maximum of ~30%. TBPPA reaches 45% of  
299 photodegradation, followed by TBPPA-DBPE (62%). This is almost in the opposite  
300 order of the rate of photodegradation measured in THF and what is measured during  
301 the initial stage of PS films exposure. A plausible explanation is that a low initial rate  
302 of BFRs phototransformation induces a low rate of PS degradation, thus a low  
303 yellowing (see Fig. 3B inset) and therefore a small impact of the polymer matrix on  
304 BFRs photodegradation. On the contrary, a fast rate of BFRs photodegradation  
305 results in a fast rate of PS degradation, an intense yellowing (Fig. 3B) and therefore  
306 an important inhibiting effect of the degraded polymer matrix on the BFRs  
307 photodegradation through a light screening effect. This latter is confirmed by the  
308 increase of absorption of PS films at higher wavelengths (> 300 nm) after 24h of  
309 irradiation as depicted in Fig. S2 (A,B,C). Consequently, despite a lower light  
310 absorption for TBBPA-DBPE than TBBPA, its photodegradation during the lifetime of  
311 the polymer will be more extensive than TBBPA. This finding questions the strategy  
312 of using less absorbing BFR additives as an efficient solution to avoid or minimize  
313 photodegradation. Moreover, it raises the question of the impact of enhanced  
314 photodegradation on the long-term efficiency of BFRs and its environmental impacts.

#### 315 *3.4. Photoproducts of TBBPA and TBBPA-DBPE in THF and PS*

316 Tables 2 and 3 summarize the major photoproducts detected during photolysis of  
317 TBBPA and TBBPA-DBPE respectively in THF and in PS. To obtain a valid  
318 comparison, samples were irradiated for different durations to reach the same level of

319 conversion in both media at about  $45 \pm 5\%$ . Due to experimental constraints, the  
320 photoproducts of TBBPA-BAE were only identified in THF and are presented in Table  
321 S1. Overall, eleven major photoproducts for each BFR were identified, assigned as  
322 products A1-A11 for TBBPA photoproducts and B1-B11 for TBBPA-DBPE. To our  
323 knowledge this is the first study to report on the products of TBBPA-DBPE and  
324 TBBPA-BAE. According to the proposed structures of the photoproducts, products A1  
325 and A2 are formed by debromination of TBBPA, products A3-A5 can result from  
326 debromination and replacement of bromine by OH group. With the exception of A5,  
327 products A1-A4 were detected in both THF and PS under irradiation. The formation  
328 of hydroxylated products of BFRs in PS suggest that oxygen or water vapor present in  
329 the air are involved in the photodegradation mechanisms. Moreover, all these  
330 products have also been reported in previous studies of TBBPA photolysis in water  
331 (Wang et al., 2015b). On the other hand, product A6 appears to be only detected in  
332 PS. While it is not clear how A6 might arise from TBBPA, this product is a derivative  
333 of benzophenone, a well known photosensitizer, it may therefore contribute to PS  
334 oxidation (Lin et al., 1992). A7 has been previously detected during TBBPA  
335 photolysis in water (Eriksson et al., 2004a; Eriksson et al., 2004b; Bao and Niu,  
336 2015). It could result from C-C scission, followed by oxidation (Wang et al., 2015b).  
337 Further oxidation of A7 could lead to product A8 whereas bromination could lead to  
338 tribromophenol (product A9). This latter was commonly detected during TBBPA  
339 photolysis (Bao and Niu, 2015; Wang et al., 2015b). Products A10-A11 are only  
340 observed in PS and thus are likely to be generated by oxidation of PS and  
341 bromination by released  $\text{Br}^\bullet$  radicals. This suggests a new mechanism of degradation  
342 of polymers containing BFRs.

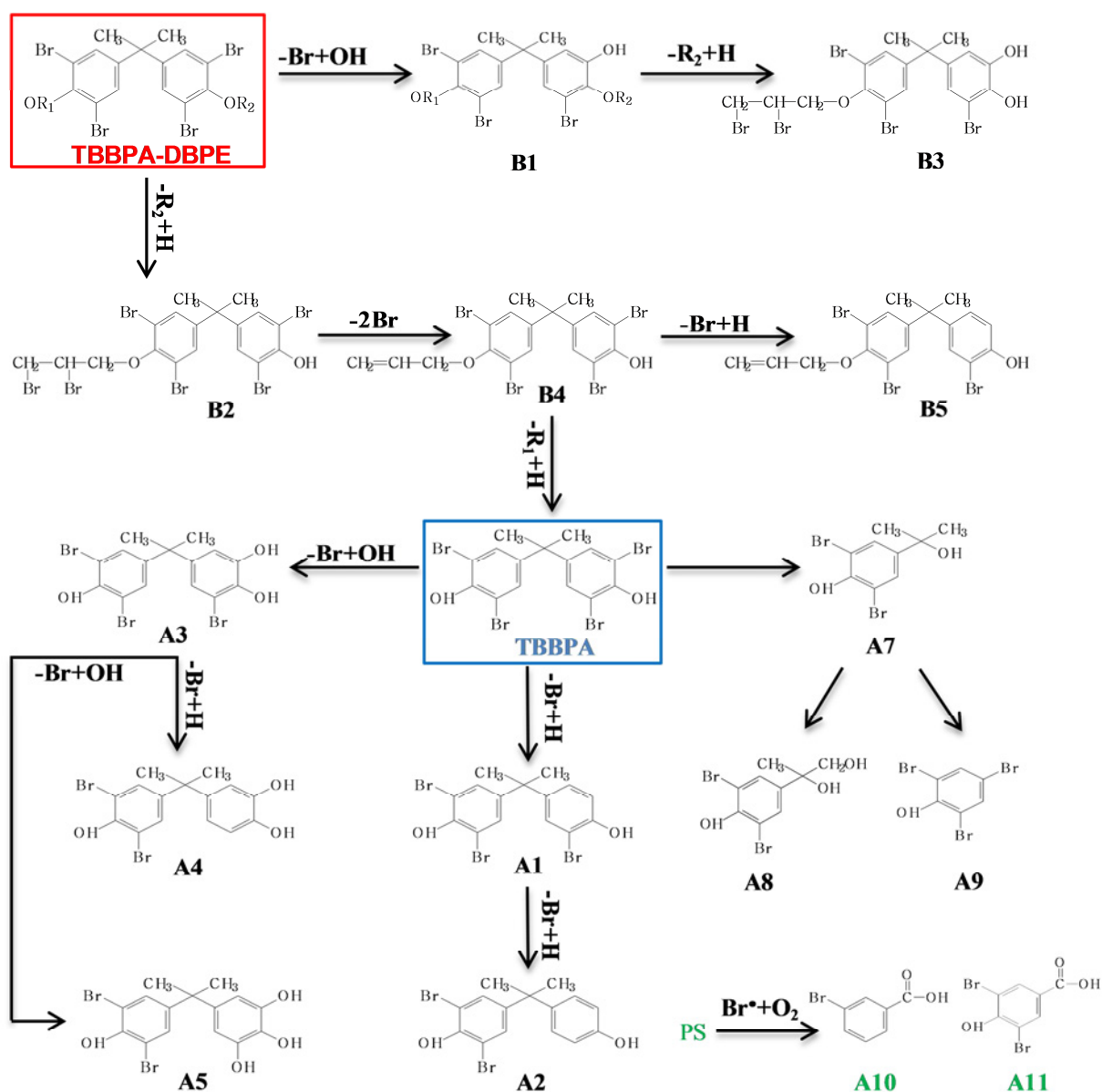
343 **Table 2.** Identified TBBPA photoproducts at 45±5% degradation in THF and in PS. \*THF, +PS. <sup>a</sup>Only the monoisotopic and most intense m/z are  
 344 presented.

Chemical formula	m/z <sup>a</sup>	Structure	Chemical formula	m/z <sup>a</sup>	Structure
<b>A1- C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>Br<sub>3</sub><sup>*+</sup></b> <b>C<sub>15</sub>H<sub>13</sub>O<sub>2</sub><sup>79</sup>Br<sub>2</sub><sup>81</sup>Br</b>	460.8396 462.8374		<b>A7- C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>Br<sub>2</sub><sup>*+</sup></b> <b>C<sub>9</sub>H<sub>10</sub>O<sub>2</sub><sup>79</sup>Br<sup>81</sup>Br</b>	306.8975 308.8955	
<b>A2- C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>Br<sub>2</sub><sup>*+</sup></b> <b>C<sub>15</sub>H<sub>14</sub>O<sub>2</sub><sup>79</sup>Br<sup>81</sup>Br</b>	382.9289 384.9268		<b>A8- C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>Br<sub>2</sub><sup>*+</sup></b> <b>C<sub>9</sub>H<sub>10</sub>O<sub>3</sub><sup>79</sup>Br<sup>81</sup>Br</b>	322.8928 324.8904	
<b>A3- C<sub>15</sub>H<sub>13</sub>O<sub>3</sub>Br<sub>3</sub><sup>*+</sup></b> <b>C<sub>15</sub>H<sub>14</sub>O<sub>3</sub><sup>79</sup>Br<sub>2</sub><sup>81</sup>Br</b>	476.8344 478.8321		<b>A9- C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>Br<sub>2</sub><sup>+</sup></b> <b>C<sub>7</sub>H<sub>4</sub>O<sub>3</sub><sup>79</sup>Br<sup>81</sup>Br</b>	294.8434 294.8457	
<b>A4- C<sub>15</sub>H<sub>14</sub>O<sub>3</sub>Br<sub>2</sub><sup>*+</sup></b> <b>C<sub>15</sub>H<sub>14</sub>O<sub>3</sub><sup>79</sup>Br<sup>81</sup>Br</b>	398.9237 400.9217		<b>A10- C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>Br<sup>+</sup></b>	198.9392 200.9372	
<b>A5- C<sub>15</sub>H<sub>14</sub>O<sub>4</sub>Br<sub>2</sub><sup>*</sup></b> <b>C<sub>15</sub>H<sub>14</sub>O<sub>4</sub><sup>79</sup>Br<sup>81</sup>Br</b>	414.9189 416.9167		<b>A11- C<sub>6</sub>H<sub>3</sub>OBr<sub>3</sub><sup>*+</sup></b> <b>C<sub>6</sub>H<sub>3</sub>O<sup>79</sup>Br<sub>2</sub><sup>81</sup>Br</b>	326.7661 328.7641	
<b>A6- C<sub>13</sub>H<sub>6</sub>O<sub>3</sub>Br<sub>4</sub><sup>+</sup></b> <b>C<sub>13</sub>H<sub>6</sub>O<sub>3</sub><sup>79</sup>Br<sub>2</sub><sup>81</sup>Br<sub>2</sub></b>	528.6942 526.6965				

345 **Table 3.** Identified TBBPA-DBPE photoproducts at (45±5%) degradation in THF and in PS. \*THF, +PS. <sup>a</sup>Only the monoisotopic and most  
 346 intense m/z are presented.

Chemical formula	m/z	Structure	Chemical formula	m/z	Structure
<b>B1- C<sub>21</sub>H<sub>21</sub>O<sub>3</sub>Br<sub>7</sub><sup>*+</sup></b> <b>C<sub>21</sub>H<sub>21</sub>O<sub>3</sub><sup>79</sup>Br<sub>3</sub><sup>81</sup>Br<sub>4</sub></b>	874.5690 878.5642		<b>B7- C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>Br<sub>3</sub><sup>*+</sup></b> <b>C<sub>15</sub>H<sub>13</sub>O<sub>2</sub><sup>79</sup>Br<sub>2</sub><sup>81</sup>Br</b>	460.8398 462.8377	
<b>B2- C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>Br<sub>6</sub><sup>*+</sup></b> <b>C<sub>18</sub>H<sub>16</sub>O<sub>2</sub><sup>79</sup>Br<sub>3</sub><sup>81</sup>Br<sub>3</sub></b>	738.6168 742.6127		<b>B8- C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>Br<sup>+</sup></b>	216.9322 214.9342	
<b>B3- C<sub>18</sub>H<sub>17</sub>O<sub>3</sub>Br<sub>5</sub><sup>*+</sup></b> <b>C<sub>18</sub>H<sub>17</sub>O<sub>4</sub><sup>79</sup>Br<sub>3</sub><sup>81</sup>Br<sub>2</sub></b>	676.6995 678.6975		<b>B9- C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>Br<sub>2</sub><sup>+</sup></b> <b>C<sub>7</sub>H<sub>4</sub>O<sub>3</sub><sup>79</sup>Br<sup>81</sup>Br</b>	294.8434 294.8457	
<b>B4- C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>Br<sub>4</sub><sup>*+</sup></b> <b>C<sub>18</sub>H<sub>16</sub>O<sub>2</sub><sup>79</sup>Br<sub>2</sub><sup>81</sup>Br<sub>2</sub></b>	578.7817 582.7773		<b>B10- C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>Br<sup>+</sup></b>	198.9392 200.9372	
<b>B5- C<sub>18</sub>H<sub>17</sub>O<sub>2</sub>Br<sub>3</sub><sup>*+</sup></b> <b>C<sub>18</sub>H<sub>17</sub>O<sub>2</sub><sup>79</sup>Br<sub>2</sub><sup>81</sup>Br</b>	500.8712 502.8691		<b>B11- C<sub>6</sub>H<sub>3</sub>OBr<sub>3</sub><sup>*+</sup></b> <b>C<sub>6</sub>H<sub>3</sub>O<sup>79</sup>Br<sub>2</sub><sup>81</sup>Br</b>	326.7661 328.7641	
<b>B6- C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>Br<sub>4</sub><sup>*+</sup></b> <b>C<sub>15</sub>H<sub>12</sub>O<sub>2</sub><sup>79</sup>Br<sub>2</sub><sup>81</sup>Br<sub>2</sub></b>	538.7503 542.7459				

347 For TBBPA-DBPE, the primary intermediates arose from debromination followed by  
348 oxidation of the phenyl side to yield the hydroxylated product (B1) and ether bond  
349 cleavage (B2). The formation of these products can occur in the presence of water as  
350 shown in Scheme 1. The mechanism of debromination on the phenyl side was  
351 previously reported during photodegradation of NBFRs such as DPTE (2,3-  
352 dibromopropyl-2,4,6-tribromophenylether)(Zhang et al., 2016). These intermediates  
353 can further degrade to produce photoproducts B3 and B4. B3 could arise from ether  
354 bond cleavage of B1 whereas B4 might be formed by successive debromination and  
355 H-abstraction on the alkyl side of B2 yielding a C=C double bond in B4(Liu et al.,  
356 2017). A subsequent degradation of B4 through debromination on the phenyl moiety  
357 could lead to the formation of B5 or to the generation of B6 (TBBPA) via ether bond  
358 cleavage. Other studies have also found that TBBPA can be a major photoproduct of  
359 NBFR derivatives of TBBPA (Qu et al., 2013; Liu et al., 2017). The remaining  
360 photoproducts (B7-B11) are similar to those found during TBBPA photodegradation,  
361 as discussed above. These photoproducts belong to the group of bromophenols and  
362 bromobenzoic acid derivatives. In a previous study, we have demonstrated the  
363 potential transfer of bromophenols from solid polymeric matrices to water. Hence,  
364 further investigation should be performed to assess the toxicity and risk of these  
365 photoproducts in water. While the main reaction pathways for TBBPA and TBBPA-  
366 DBPE appear to be similar, a competition can occur initially between the reactivity of  
367 the brominated side groups (OR1 and OR2) via ether cleavage and the  
368 debromination of the tetrabromobisphenol moiety. This competition can reduce the  
369 extent of debromination initially as compared to TBBPA and thus a less pronounced  
370 bromination and oxidation of PS by released Br. This seems to be consistent with the  
371 lower yellowing of PS film observed when TBBPA is replaced by TBBPA-DBPE.



372 **Scheme 1.** Proposed TBBPA and TBBPA-DBPE photodegradation pathways in  
 373 polystyrene (PS).

#### 374 4. Conclusion

375 In this study, quantum yields of BFRs photodegradation were determined in solution  
 376 (THF) and in polymer (PS) under monochromatic irradiation. Overall, higher values of  
 377  $\Phi$  were obtained in PS than in THF and a significant yellowing of the irradiated PS  
 378 film was observed. This shows the existence of a mutual accelerating effect. At

379 longer irradiation duration in a solar simulator, the yellowing of PS was found to  
380 inhibit BFRs photodegradation via light screening effect, leading to a stationary state  
381 within 2-3 days of irradiation. Interestingly, the higher the initial absorbance of BFR  
382 above 290 nm, the fastest it degrades initially, causing a yellowing of the PS film  
383 which in turn inhibits BFR from being further degraded.

384 Analysis of TBBPA and TBBPA derivatives showed similar photoproducts in PS and  
385 in THF. Nonetheless, some photoproducts, potentially brominated C7 derivatives  
386 were only detected in PS, these products might be resulting from PS oxidation. In  
387 addition, new BFR photoproducts never reported in the literature were identified for  
388 the first time, thus allowing to complete the mechanisms of their photodegradation.  
389 Further, investigation should be performed to better understand the mechanism of PS  
390 oxidation in the presence of BFRs. Moreover, assessments of environmental  
391 exposure and the resulting health impacts of the transformation products of TBBPA  
392 derivatives warrant further study.

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## Highlights

- Quantum yields of four BFRs were measured in tetrahydrofuran and polystyrene
- Higher photoreactivity of BFRs was observed in polystyrene
- Photodegradation of BFRs induced oxidation and yellowing of polystyrene
- The less absorbing BFR was found to be further degraded during irradiation
- C7-brominated photoproducts of polystyrene oxidation were detected for the first time