

PHOTOLYTIC DEBROMINATION OF DECABROMODIPHENYL ETHER (DecaBDE) AND ETHANE (DBDPE) IN FLAME-RETARDED PLASTICS

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Abstract

Photodebromination of the technical decabromodiphenyl ether (DecaBDE) and ethane (DBDPE) incorporated into high impact polystyrene (HIPS) or in TV casing was investigated under natural sunlight condition. After 112 days of exposure, BDE209 in HIPS+DecaBDE samples degraded with a half-life of 31 days. In contrast, no significant loss of DBDPE occurred throughout the experimental period. During BDE209 photolysis in HIPS+DecaBDE samples, the hepta-, octa-, and nona-BDE congeners increased after one week exposure, indicating debromination of BDE209 resulted in the formation of lower brominated congeners. The formations of polybrominated dibenzofurans (PBDFs) were also observed in the flame-retarded plastics investigated in this study. In the case of HIPS+DecaBDE samples, the concentrations of PBDFs showed approximately 20 times increase after 7 days of exposure with concomitant decrease of BDE209. In TV casing, tetra- to octa-BDF congeners showed a continuous increase during the experiment. Even though the concentrations of PBDFs found in the plastic matrices tested were one to four orders of magnitude lower than those of PBDEs, the fact that PBDFs are formed by sunlight exposure should not be disregarded from the viewpoint of risk assessment during normal use as well as disposal/recycling process of the flame-retarded products.

Introduction

Pollution by polybrominated diphenyl ethers (PBDEs), the popular brominated flame retardants (BFRs) are now a worldwide problem even in remote areas.^{1,2} They have been found to bioaccumulate and there are concerns over the health effects of animals by exposure to PBDEs. They also have potential endocrine disrupting properties.^{3,4} Growth in interest on PBDE has been as exponential as their apparent increase in the environment over the past 20-25 years in various regions, in contrast to the declining trends observed in organochlorine compounds. Another social concern is that PBDEs have the potential to form polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs) when burnt, and toxicity of the resultant compounds was estimated to be similar to chlorinated dioxins.⁵

Higher brominated BDE congeners have the potential to be photolytically debrominated in the environment. Previous studies have reported the photolytic decomposition of deca-BDE (BDE209), the dominant congener found in the commercial mixture known as DecaBDE, in various matrices such as solvents, sediment, soil, and house dust.⁶⁻⁸ However, no study to date has examined the potential for photodegradation of BFRs in the flame-retardant product itself. Risk assessment of plastic additives including BFRs is imperative not only for the sake of harmonious recycling as polymer recourses but also from the viewpoint of possible human intake of BFRs transferred onto dust from electric appliances.^{9,10} Furthermore, BFRs leached out from e-waste dumped outside in developing countries became pivotal issues for the international community.¹¹ From such background, it is important to determine the extent of debromination that may occur in plastic materials under daily usage and also after disposal.

This study was designed to examine photolytic debromination of BFRs including the technical DecaBDE and decabromodiphenyl ethane (DBDPE) in plastic matrices. DBDPE, another BFR which has a similar structure with BDE209, has been used in polystyrene and polyolefin-based thermoplastic formulations as an alternative to PBDEs since the early 1990's. We performed a detailed study of the photolytic debromination of the major components of these BFRs in plastics under natural sunlight conditions to evaluate if this was a potential source for lower brominated congeners and PBDD/Fs in the environment.

Materials and Methods

Sample preparation

Four different plastic powder samples including pure high impact polystyrene (HIPS), HIPS with the technical

DecaBDE (about 0.15% by weight), HIPS with the technical DBDPE (about 0.10% by weight), and used TV casing were prepared for this study. TV casing was selected as a typical flame-retarded product familiar with the public. Pure HIPS pellets were dissolved in toluene, DecaBDE or DBDPE toluene solution and shaken overnight to be completely mixed. The toluene was subsequently removed by air-drying in the dark. After drying, solid materials including TV casing were pulverized in liquid nitrogen chamber. Then using a vibrating stainless steel sieve apparatus, the resultant material was screened in two steps, first through a 300 μm sieve and then a 106 μm sieve. The plastic powder collected between two sieves (106 μm -300 μm) was used in the irradiation experiment. Aliquots of the plastic powder (0.3 g) prepared in this manner was then transferred to clean quartz tubes and sealed with Teflon plugs and laboratory tape. Tubes were kept inside the laboratory in the dark until the following sunlight irradiation experiment.

Experimental Setup

The sunlight irradiation experiment was performed from September 2006 to January 2007 at the NIES campus in Tsukuba, Japan, with sampling occurring at 0, 7, 14, 28, 56, and 112 days. Sample tubes were placed in a temperature-controlled glass room. Dark control samples covered with aluminum foil were prepared and simultaneously exposed to sunlight to establish that only the sunlight exposure affected the samples, not time or elevated temperatures. At each sampling time triplicate tubes were removed from light exposure, wrapped in aluminum foil and stored at room temperature in the laboratory until analysis.

Chemical analysis

PBDEs, DBDPE, and PBDD/Fs were analyzed following the method reported¹² with modification. Briefly, each of the pulverized plastic samples in quartz tube was completely dissolved in toluene. The suspensions were further treated in an ultrasonic bath for 30 min. A portion of toluene solution was added to hexane drop by drop to precipitate the previously dissolved polymer matrix. To analyze high concentration PBDE congeners and DBDPE, an aliquot of supernatant solution spiked with ¹³C₁₂-labeled PBDE and ¹³C₁₄-labeled DBDPE as internal standards was passed through a multilayer column (ML column) which consisted of 22% (w/w)-H₂SO₄ impregnated silica gel and Florisil. For low concentration PBDE congeners and PBDD/Fs analysis, the remaining solution after precipitating polymer was used. After the addition of ¹³C₁₂-labeled PBDE and PBDD/Fs as internal standards, the resulting precipitates were separated by filtration and the remaining solution were further cleaned-up by ML column and an activated carbon dispersed silica gel column. Each eluate was concentrated and analyzed by a HRGC-HRMS with selected ion monitoring (SIM) mode after adding ¹³C₁₂-labeled BDE138 or 1,2,3,7,8-PeBDF as a syringe spike. All the congeners were quantified using the isotope dilution method to the corresponding ¹³C₁₂-labeled congener.

Results and Discussion

The initial concentrations of PBDEs, DBDPE, and PBDD/Fs in each plastic sample prepared in this study were summarized in Table 1. No target compounds were detected in the pure HIPS samples. In HIPS+DBDPE samples, PBDEs and PBDD/Fs were not found, indicating the technical DBDPE does not contain these brominated compounds as impurities. On the other hand, hepta- to nonaBDEs as well as PBDF congeners were found in HIPS+DecaBDE samples which might be due to their presence in the technical DecaBDE. TV casing used in this study contained approximately 10% of BDE209 with smaller amount of di- to nona-BDEs, PBDD/Fs, and DBDPE.

Photodegradation of BDE209 and DBDPE

HIPS+DecaBDE samples showed straightforward results with a gradual disappearance of BDE209 when

Table 1. The initial concentrations ($\mu\text{g/g}$) of PBDEs, DBDPE, and PBDD/Fs in each plastic sample prepared

	HIPS	+DecaBDE	+DBDPE	TV casing
BDE209	nd	1,500 \pm 300	nd	100,000 \pm 7,400
PBDEs	-	1,600 \pm 310	-	110,000 \pm 7,100
DBDPE	nd	nd	980 \pm 110	140 \pm 5.7
PBDDs	nd	nd	nd	0.095 \pm 0.014
PBDFs	nd	0.6 \pm 0.12	nd	21 \pm 0.46
PBDD/Fs	-	0.6 \pm 0.12	-	21 \pm 0.47

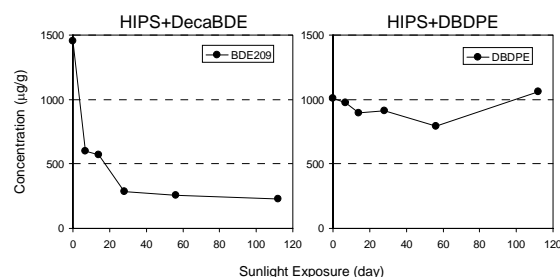


Fig. 1. Photodegradation of BDE209 and DBDPE

exposed to sunlight (Fig. 1). No degradation was seen in the unexposed samples. After one week exposure to sunlight, the concentration of BDE209 was found to decrease to approximately 40% of the initial level, indicating the prompt photodegradation in plastic matrix. In contrast, there was no significant loss of DBDPE incorporated in HIPS during sunlight exposure for 112 days, suggesting that DBDPE has more resistance to UV irradiation compare to BDE209. Assuming a first-order reaction, the calculated half-life of BDE209 in HIPS was 31 days. Previous studies have examined the degradation of BDE209 in various matrices using both UV lamps and sunlight exposures. The half-life reported here in plastic is longer than those measured in sand, sediments and soils,⁶ but equivalent to half-lives measured in house dust.⁸ The half-lives of BDE209 sorbed on clay minerals such as montmorillonite and kaolinite were reported to be 261 and 408 days, respectively,⁷ which are much longer than in plastic observed in this study.

BDE209 Debromination and Photolytes

During BDE209 photolysis in HIPS+DecaBDE samples, the hepta-, octa-, and nona-BDE congeners were observed to increase after one week exposure (Fig. 2), indicating debromination of BDE209 resulted in the formation of lower brominated BDE congeners. Then, however, the amount of these congeners stayed constant throughout the 112 day exposure despite the continuous decline of BDE209. Although a stepwise debromination process previously reported in the cases of silica gel and sand matrices⁶ was not clearly observed in the present study, a similar debromination process is supposed to occur in plastic within one week of exposure. In contrast, TV casing samples showed no clear disappearance of BDE209 and formation of lower BDE congeners throughout 112 day of sunlight irradiation (Fig. 2). In both cases, the formation of BDE47 and BDE99, which are the dominant PBDE congeners detected in biota and humans, were not observed.

As shown in Fig. 3, the formation of PBDFs was observed in the flame-retarded plastics investigated in this study. In the case of HIPS+DecaBDE samples, concentrations of PBDFs showed approximately 20 times

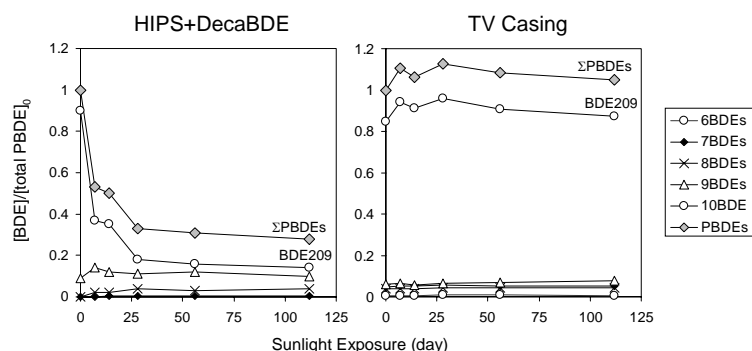


Fig. 2. Degradation and formation of PBDEs of different bromination degrees for HIPS+DecaBDE and TV casing samples, normalized to [total PBDE] at t_0 .

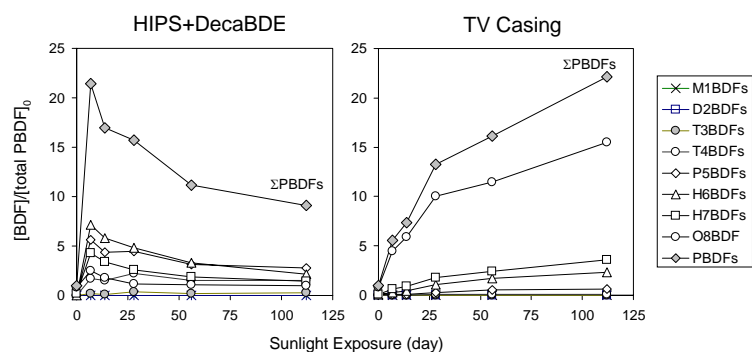


Fig. 3. Degradation and formation of PBDFs of different bromination degrees for HIPS+DecaBDE and TV casing samples, normalized to [total PBDF] at t_0 .

increase on the seventh day of exposure with concomitant decrease of BDE209 (Fig. 2), but since then PBDFs appeared to decrease gradually. This result indicates that tri- to octa-BDF congeners originated from BDE209 were also photodegraded in a phased manner, as PBDFs are also photolytically unstable.¹⁵ On the other hand, in TV casing, tetra- to octa-BDF congeners showed a continuous increase during the experimental period although significant loss of BDE209 was not observed (Fig. 2). In the case of TV casing, amount of BDE209 was too high reaching up to 10% by weight to observe marginal decrease of BDE209, however, it is supposed that BDE209 indeed photodegraded and contributed to the synthesis of PBDFs. Total PBDF concentrations in TV casing after the 112 day exposure were more than 20 times the initial levels, suggesting that formation of PBDFs exceeded their photodegradation, unlike in the case of HIPS+DecaBDE samples. Since the continuous PBDF formation will occur as long as BDE209 remains, the products flame-retarded by the technical DecaBDE will keep producing PBDFs for a fairly long period, probably throughout the life cycle of the products.

Fig. 4 shows the mass balance of PBDEs and PBDFs in HIPS+DecaBDE and TV casing samples. Over the 112 day sunlight exposure, more than 80% of BDE209 in HIPS+DecaBDE samples was degraded, but the accumulation of lower brominated BDE congeners accounted for only 5% of the BDE209 loss. The PBDF composition was fairly small. Therefore, most of the BDE209 in HIPS+DecaBDE was lost to unknown pathways/products. As for TV casing, the mass balance of PBDEs and PBDFs indicated more or less the same throughout the experiment, and the increment of PBDFs shown in Fig. 3 was hidden by overwhelmingly high levels of BDE209. Even though the concentrations of PBDFs found in the plastic matrices tested were one to four orders of magnitude lower than those of PBDEs, the fact that PBDFs are formed by sunlight exposure should not be disregarded from the viewpoint of risk assessment during normal use as well as disposal/recycling process of the flame-retarded products.

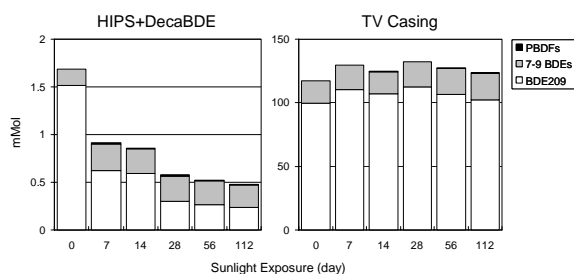


Fig. 4. Mass balance of PBDEs and PBDFs detected in HIPS+DecaBDE and TV casing samples, respectively

Acknowledgements

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