FORMATION OF POLYBROMINATED DIBENZO-p-DIOXINS AND -DIBENZOFURANS DURING PYROLYSIS OF POLYBROMINATED DIPHENYLETHERS AND HIGH IMPACT POLYSTYRENE

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ABSTRACT

During pyrolysis of high impact polystyrene (HIPS) containing the flame retardant system decabroomdiphenylether ($D_{10}BrDPO$)/antimony oxide (Sb_2O_3) mainly polybrominated dibenzofurans are formed. In an open flow system the optimum PBDF formation temperature lies at the depolymerization temperature of the polymermatrix HIPS (350-400°C).

INTRODUCTION

During pyrolysis of some widely used brominated flame retardants pure or blended in plastic matrices, polybrominated dibenzo-p-dioxins (PBDD's) and -dibenzofurans (PBDF's) are formed [1,2,3,6,7,8]. Since polybrominated diphenylethers produce the highest yield of these toxic compounds more insight in the formation mechanism is necessary. The work described here involves a comparison of the formation of PBDD's and PBDF's from:

1. pure polybrominated diphenylethers (PBDPO's) in a micro-pyrolysis system according to the method of Buser [1]
2. HIPS containing $D_{10}BrDPO/Sb_2O_3$ (HIPS FR) in a macro-pyrolysis system according to the method of Hutzinger [2].

The influence of the polymermatrix HIPS and the temperature on the formation of PBDF's are discussed. The influence of temperature on PBDF formation in the macro-pyrolysis experiments is studied with two different test systems.

EXPERIMENTAL PART

The micro-pyrolysis experiments were performed in quartz mini-vials (sample size 100 µg, air atmosphere, residence time in the furnace after reaching the established temperature 10 s, clean-up with pasteur pipet columns containing 33% NaOH silica and Al_2O_3).

The macro-pyrolysis experiments were performed in a quartz tube reactor (30 cm x 3 cm I.D.) which was placed in a furnace (2000 W, Heraeus ROK/A 4/30). The temperature was controlled by a Cr/V thermocouple connected to a digital controller (48x96 din series D, Ascon, Spa). In the first system the HIPS FR sample was placed in a quartz basket in the middle of the tube reactor. The whole reactor system was placed in the furnace and the temperature profile of the reactor was registrated by an extra thermocouple. In the second

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*To whom correspondence should be adressed system the HIPS FR sample was placed in a quartz basket and inserted in the tube reactor by a hollow pin. This contained the second thermocouple to registrate the temperature profile of the sample inside the tube reactor. In both systems the sample size was 1 g and nitrogen was used as carriergas. The flow rate was 10 ml/s in the first system and 5 ml/s in the second. The pyrolysis products were trapped in two empty cold traps (liquid N_2) and a washing bottle connected in series. After collecting the pyrolysis products in the washing bottle with 25 mL hexane and 25 mL ethanol, the water- and organic phases were separated. The water phase was titrated with 0.1 N NaOH to measure the inorganic bromide content. The organic fraction was evaporated to small volume and cleaned up according to the method of Donnelly et.al. [3]. The HIPS FR sample at 275°C was dissolved in toluene and the HIPS polymer matrix was precipitated with isopropylalcohol.

The analytical GC-MS conditions were:

GC-MS	HP 5980, HP MSD 5970B (SIM mode, 70 eV EI mode)
Carriergas	Helium, 20-30 cm^3/s
Capillary Column	DB5 20-60m, 0.25 μm film density, 0.32 mm i.d.
Injection	1-3 μL on-column
T-program	140°C (40°C/min) $\longrightarrow$ 200°C (8°C/min) $\longrightarrow$ 325°C

The samples were technical products of BASF and Broomchemie BV. The reagents for the PBDD and PBDF clean-up were similar to those for the PCDD/PCDF clean-up [4].

RESULTS AND DISCUSSION

The flame retardant activity of $D_{10}BrDPO/Sb_2O_3$ in HIPS FR is based on the emission of antimony bromide ($SbBr_3$) which acts as a radical scavenger for the propagation radicals formed during the degradation of HIPS in a real fire situation. In water, $SbBr_3$ is converted back to Sb_2O_3 and HBr.

The results of the acid-base titration show that in all macro-pyrolysis experiments 70-80% of the original bromine content in HIPS FR is emitted as inorganic bromine. This means that 20-30% of the bromine percentage remains organically bound and directly available for PBDF formation during pyrolysis of HIPS FR.

The results of the micro- and macro-pyrolysis studies are listed in Tables 1 and 2.

Table 1. The formation of PBDD's and PBDF's during thermal decomposition of pure PBDPO's in a closed micro-pyrolysis system in ppm ($\mu g/g$)

Sample	Temp.	Atm.	T4BDD	T4BDF	P5BDD	P5BDF	H6BDD	H6BDF
P5BrDPO	500	air	5300	6200	220	80	n.d.	n.d.
P5BrDPO	600	air	41000	65000	13000	150000	1000	3800
O8BrDPO	600	air	4100	700	20000	4600	23000	22000
D10BrDPO	600	air	110	80	360	160	380	570

Table 2. The formation of PBDF's during macro-pyrolysis of HIPS FR in an open flow system

Test system I in ppm (μg/g) relative to HIPS FR sample:

SAMPLE	ATM.	TEMP	D2BDF	T3BDF	T4BDF	P5BDF	H6BDF
HIPS FR	nitrogen	500	41	193	366	259	128
HIPS FR	nitrogen	625	41	240	513	338	173
HIPS FR	nitrogen	695	92	201	264	171	41
HIPS FR	nitrogen	780	47	239	618	398	133
HIPS FR	nitrogen	860	60	131	202	87	3
HIPS FR	air	500	8	19	66	61	24
HIPS FR	air	700	26	130	307	187	46

Test system II in ppb (ng/g) relative to HIPS FR sample:

SAMPLE	ATM.	TEMP	D2BDF	T3BDF	T4BDF	P5BDF	H6BDF	H7BDF	O8BDF
HIPS FR	nitrogen	275	0	0	305	9640	260587	713392	3304493
HIPS FR	nitrogen	360	61365	128866	131987	560201	253764	59288	54338
HIPS FR	nitrogen	450	45228	32304	45850	89256	125410	41200	13868
HIPS FR	nitrogen	560	48338	22840	21262	21644	16320	4134	3220
HIPS FR	nitrogen	640	2100	692	316	242	302	32	0
HIPS FR	nitrogen	720	121	41	27	20	23	0	0
HIPS FR	nitrogen	825	34	34	32	19	9	0	0

Tabel 1. shows that the micro-pyrolysis of lower brominated PBDPO's gives a much higher yield of PBDD's and PBDF's. This phenomena has been explained by Buser for the corresponding chlorinated species due to the energetically more favourable emission of HCl compared with the emission of Cl_2 [5]. D_{10}BrDPO with two ortho bromine atoms has to eliminate Br_2 for the ring-closure reaction to O_8BDF. It is assumed that the elimination of Br_2 is less favourable than the elimination of HBr.

The highest yield of PBDF's is found at 600°C, which was also the highest test temperature in the closed system micro-pyrolysis study. These results are comparable with those of Buser and Hutzinger [1,6].

In Table 2. it can be seen that during macro-pyrolysis of HIPS FR in an open flow system PBDF's are mainly formed. The maximum overall yield of PBDF's is about 1-2% relative to the original bromine content. The influence of the polymer matrix on the formation of PBDF's consists of an enhancement of the yield of PBDF's and a shift to lower optimal formation temperature compared to the closed micro-pyrolysis system. This phenomena was also shown for the polybutyleneterephtalate/D_{10}BrDPO/Sb_2O_3 system [7]. The HIPS FR sample pyrolyzed at 275°C did not depolymerize. The formation of lower brominated diphenylethers and predominantly higher brominated dibenzofurans at this relatively low temperature is explained by the exchange of bromine and hydrogen in D_{10}BrDPO [8]. At this temperature PBDPO's as well as polystyrene may, to a certain extend, undergo thermal decomposition and form lower brominated PBDPO's. The lower brominated diphenylethers are more reactive towards ring closure by elimination of HBr. These phenomena, i.e. the exchange of H and Br to form lower brominated PBDPO's and the formation of PBDF's, have also been shown during extrusion of HIPS FR [8].

The influence of the established furnace temperature on the yield of PBDF's is dependant on the chosen test system. In test system I there is no significant influence. Because of the low heating capacity of the furnace the pyrolysis products pass a reactor zone with a temperature just above the depolymerization temperature of HIPS (350-400°C). The residence time is about 10 s. In test system II HIPS FR also degrades at 350-400°C, but the pyrolysis products pass a reactor zone with the established furnace temperature with a residence time of about 20 s. In Table 2 it can be seen that the optimum yield of PBDF's during pyrolysis of HIPS FR in test system II lies at the lowest temperature (T=360°C). This means that PBDF's are formed during radical depolymerization of the HIPS polymer matrix. During reactor residence time (in test system II) at higher temperature, the formed PBDF's start to debrominate and the total yield of PBDF's decreases drastically. Although test system II is a good model to describe a real fire situation [7], the reactor residence time of 20 s is too long to simulate the conditions in a municipal waste incinerator.

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