

POLYSTYRENE/- AND EXTRUDED POLYSTYRENE FOAM (XPS)/-HEXABROMO-CYCLODODECANE-BLENDS UNDER THERMOLYTIC STRESS; PBDF & PBDD-DETERMINATION.

Karl S. Brenner

BASF AG, ZAX, Trace Lab., Bldg. D216; P.O.Box, D 67056 Ludwigshafen, FRG

ABSTRACT

Test experiments with hexabromo-cyclododecane (HBCD), polystyrene (PS) and polystyrene insulation foam (XPS) blended with HBCD have demonstrated a very low potential for the formation of PBDFs and PBDDs under thermolytic stress. At the worst case, at "optimum" reaction temperatures of about 700 °C, the total amounts of PBDFs/Ds formed in XPS were in the region of 1 to 100 ppb (Table 2). The only detected 2,3,7,8-substituted species was, with all the still inherent analytical uncertainties the 1,2,3,4,6,7,8-heptabromo-dibenzofuran (21 ppb); all the other 2,3,7,8-congeners were not detected (det. limit 0.02 to 2.5 ppb, Table 2). The experimental results can serve as basis of a first risk estimation for the production and use of the mentioned polymer products, and for formation during their disposal by incineration.

INTRODUCTION

Our test experiments have led us to a pragmatic classification of brominated flame retardants (BFRs) with respect to their potential to form brominated dibenzofurans and -dioxins (PBDFs, PBDDs). Depending on the behaviour of the BFRs tested under different thermolytic stress conditions we have grouped these BFRs roughly into groups; A (high degree of PBDF/D-formation), B (middle) and C (low). In the same way we have tested polystyrene (PS) and extruded polystyrene foam (XPS) blended with hexabromo-cyclododecane (HBCD) in order to define the potential of PBDF/D-formation under thermal stress during production or incineration. The test conditions, a brief description of the experimental methods and the results obtained will be given below.

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EXPERIMENTAL

Materials Tested

HBCD. The HBCD-powder tested was of technical grade, used for production of the blended PS and XPS.

PS and XPS. The tested PS-granulate was taken from the production line after extrusion-blending with HBCD. The XPS-sample was an insulating board, as it is used for building insulation (STYRODUR^R, Reg.Tr.M. BASF AG; $\rho \approx 32 \text{ kg/m}^3$).

Test Apparatus, Test Conditions

The test apparatus is shown in Fig.1. The reaction/absorption tube consists of a small quartz tube with a narrow (3 mm i.d., L:110 mm) top part which widens to about 9.5 mm (L:90 mm). A small test crucible (stainless steel, quartz or glass, 2.5 mm x 5 mm) which fits into the top part of the tube is introduced into the heated zone, heated by a micro-oven and held there for the desired test time. The flush and thermolysis gases (air, oxygen, helium, nitrogen ecc.) are introduced via an inlet which also serves for the introduction and removal of the test crucibles (see Fig.1)[1]. The thermolyses gases (products) are absorbed in the wide part of the quartz tube in a series of absorptive layers. In these test experiments we used NaHCO_3 and polyurethane foam (PUF)-micro-plugs (2x 45 mm length) as ab-/adsorbants for the HBr and the organic products formed. The thermolysis tube is fixed in a metal support plate and connected to a large PUF/active carbon (double layers) end-absorber for safety reasons. The test conditions are summarized in Table 1.

The multiple thermolysis of 10 or more crucibles per sample allows a larger accumulation of pyrolysis products which lowers the detection limits. As a result one obtains a statistical mean of the single thermolysis "shots". It also allows sampling of several points on a XPS-board or from the granulate grains in a batch; and the yield of the decomposition products (PBDFs/Ds) of the HBCD, PS or XPS is more realistic.

Table 1. Test Conditions for Thermolysis Tests.

Sample	Temperature	Thermolysis Time	no. of crucibles; Test Gas total amount of sample (mg)
HBCD*	700 °C	2 min.	6; ca. 110 air
PS	700 °C	"	8; ca. 50 "
XPS	700 °C	"	20; ca. 110 "

* for the analysis of the original, technical HBCD-material see below.

Sample Preparation, Clean Up

The crucibles, which are removed from the thermolysis tube after each "shot", are collected separately and crushed before extraction. The thermolysis tubes are changed after every 10th test crucible and stored for extraction as a whole. Depending on the experimental objective, the residuals (in the crucibles) can be extracted separately from the absorber tubes (distinction between "residuals" and "volatiles"). The extraction is done by placing the tubes and crucibles in quartz fibre Soxhlet cartridges and extracting with toluene (benzene) for 24 hrs. Because of the many different interfering organic thermolysis products formed, a special clean-up combination must be used. This includes inverse active carbon/glass fibre clean up [2], and a HPLC-procedure in order to remove the sublimated HBCD. The latter can produce high amounts of PBDFs/Ds in the GC-injection block, leading to entirely wrong positive results. The analysis of the original untreated HBCD was performed with a special procedure, which will be described elsewhere [3].

Determination of PBDFs/PBDDs, GC/MS

The determination of the PBDFs and PBDDs was performed by GC/MSD (mass selective detector) or GC/HRMS (VG Autospec), using a non-polar DB5(dimethyl-diphenyl(5%))-quartz capillary column (15 m). The MS-SIM-procedure was performed with a 3-isotope cluster-confirmation for PBDFs/Ds as far as possible. COBr-split-off was also used for additional identification. The most important check was for absence of HBCD-residues in order to avoid false-positive results.

RESULTS

HBCD. The original untreated technical HBCD contained 20 ppb tetra- and 30 ppb pentabromo-dibenzofuran isomers and no detectable PBDDs. The thermolysis at 700 °C produced Tri- to Hexa-BDFs in a range of 30 to 100 ppb and Tri- and TetraBDDs in a range around 15 ppb (Tab.2).

PS/HBCD. The thermolysis at 700°C, the optimum temperature range for PBDF/D-formation, produced PBDF-values of about 20 to 60 ppb (related to the polymer product). This does not take into account the low percentage of HBCD blended in (Tab.2). For HBCD and PS/HBCD only the volatile compounds were analyzed. The crucibles were empty because of evaporation/sublimation of the samples into the absorption layers.

XPS/HBCD. The thermolysis of this insulating PS-foam (furnished with about 1 to 5 % HBCD) showed very low yields of PBDFs and PBDDs even after a 2 minute long thermal stress on the material. The volatile compounds plus the residues in the crucibles were analyzed in toto. In this case we used a high

FORM

resolution/high sensitivity MS-instrument, and we could show, that only minor amounts of PBDFs/PBDDs are formed at 700°C. The amount of 2,3,7,8-substituted congeners is almost negligible, as far as the toxic isomers can be determined accurately.

Table 2. Results of Thermolysis Tests with HBCD, PS and XPS, Compared to Technical HBCD without Thermal Stress. PBDF and PBDD-Congeners Formed.

	HBCD RT# ppb	HBCD 700°C ppb	PS 700°C ppb	XPS* 700°C ppb	XPS* 700°C ppb	PS inject.moldg. ppb
				Σ	2,3,7,8- subst.congen.	
Di- BDFs	<10	<10	trace?	38	-	1
Tri- "	<10	50	<20	2.3	-	0.2
Tetra-"	20	100	34	1	<0.3	<0.1
Penta-"	30	65	20	1.0	<0.1	<0.1
Hexa- "	<10	30	60	10	<2.5;n.ref. ^β	<0.1
Hepta-"	<10	<10	<20	28	21;n.ref. ^β	n.ref.
Octa- "	n.d. ^α	n.d.	n.d.	~300		n.d.
Di- BDDs	<10	20	<20	0.2	-	<0.1
Tri- "	"	16	"	0.1	-	<0.1
Tetra-"	"	13	"	<0.02	<0.02	1.5 ^γ
Penta-"	"	<10	"	<0.1	<0.1	<0.1
Hexa- "	"	<10	"	<0.3	<0.3	<0.1
Hepta-"	"	<10	"	<1	n.ref.	<0.1
Octa- "	n.d.	n.d.	n.d.	<125		n.d.

* Styrodur[®], BASF; # Room temperature; ^αn.d.: not detected because of interference or inadequate sensitivity of instrument (MSD); ^βn. ref.: no reference standard available; ^γtwo isomers, not identical with 2,3,7,8-TBDD, see text (rel.RT calc.)

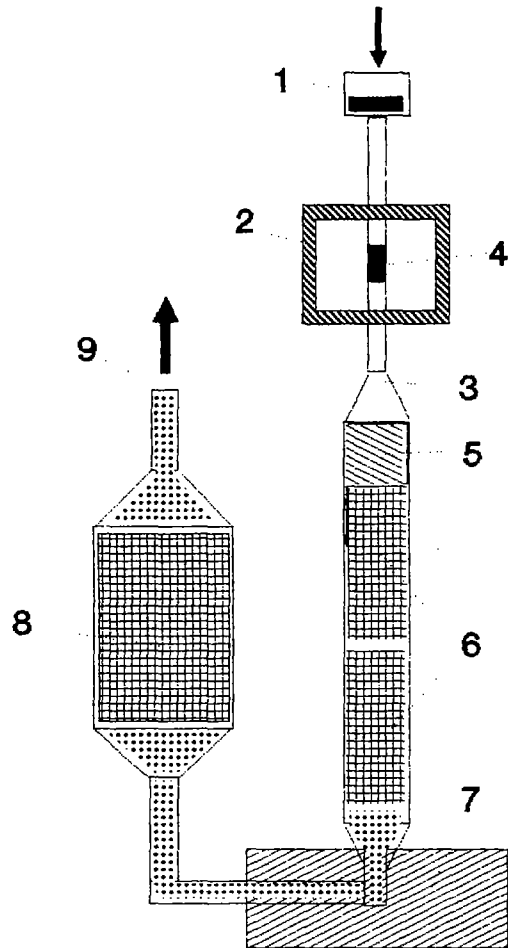
DISCUSSION OF RESULTS

HBCD and HBCD-blended PS and XPS form about 4 to 5 orders of magnitude less PBDFs and PBDDs under thermolytic stress than products containing polybrominated diphenylethers (PBDPEs) [4]. The formation of 2,3,7,8-substituted congeners is, except for one case (Tab.2, column 5), not detectable (det. lim. 0.02 to 2.5 ppb) and even HBCD technical grade forms only very low amounts of tri- and tetra-bromo-dibenzodioxins and tri- to penta-bromo-dibenzofurans. We classify HBCD in our system (see Introduction, for groups A, B, C) as a group C (low potential of PBDF/PBDD-formation) BFR. The close inspection of the GC/MS-diagrams shows at least 8 dibromo-, 6 tribromo-, 5 tetrabromo-, 2 pentabromo-, 1 hexabromo-, 2 heptabromo- and the octabromofuran-isomer compounds for XPS. Preliminary tests at the workplace during injection molding of HBCD-blended PS showed very low traces of about 2.5 ng/m³ ΣTetra-BDDs (ΣPenta- to ΣHepta-BDDs < 0.2 ng/m³) and of about

0.2 ng/m³ ΣTetra- and 1 ng/m³ ΣPentaBDFs (ΣHexa- and ΣHepta-BDFs <0.2 ng/m³) in the workplace air (for more information on the workplace measurement technique see [5]). The detected tetrabromo-dioxin compounds were two isomers; according to a relative retention time (rel.RT) calculation, they are not identical with 2,3,7,8-TBDD.

REFERENCES

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- 1 Inlet with Septum
- 2 Oven, removable
- 3 Quartz Tube
- 4 Crucible, Quartz, Glass or SS
- 5 $\text{NaHCO}_3/\text{Na}_2\text{SO}_4$ -Layer
- 6 PUF-Plugs
- 7 Stainless Steel Block (Support)
- 8 PUF-Absorber + NaHCO_3
- 9 Outlet to Hood Exhaust

Fig.1
Thermolysis (Pyrolysis) Tube for Fire Simulation Tests