Formation of polybrominated dibenzofurans during extrusion of high-impact polystyrene/decabromodiphenyl ether/antimony(III) oxide

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Introduction

Polybrominated flame retardants are widely used in synthetic polymers to reduce inflammability. Due to their universality and minor influence on mechanical properties, polybrominated aromatic compounds have a broad application area. Despite technical advantages in applications, the use of polybrominated compounds in polymers has two disadvantages: First, formation of corrosive HBr during compounding (T = 190-225 °C) and second, but more important, formation of polybrominated dibenzo-p-dioxins (PBDDs) and dibenzofurans (PBDFs) during thermal degradation (T = 350-800 °C). The formation of PBDDs and PBDFs has been shown during pyrolysis of pure brominated flame retardants (1-9) and during pyrolysis of polymers with brominated flame retardant additives (4, 5). Especially brominated diphenyl ethers (PBDEs) are reactive precursors in the formation of PBDDs and PBDFs (6, 7). Equation 1 shows the structural similarity of PBDEs and PBDFs/PBDDs. Formation of PBDFs consists of a ring-closure reaction with the elimination of a small molecule (Br2, HBr, or H2). An extra oxidation reaction is needed for the formation of PBDDs.

\[
\begin{align*}
\text{PBDEs} & \rightarrow \text{PBDFs} + \text{Br}_2 \\
\text{PBDFs} & \rightarrow \text{PBDDs} + \text{HBr}
\end{align*}
\]

In this study the thermal behavior of PBDDs during extrusion (melt compounding) of high-impact polystyrene (HIPS) was examined. HIPS is a blend of polystyrene and polybutadiene (6-12 wt %, dispersed in the polystyrene matrix) of which inflammability is reduced by the flame retardant system decabromodiphényl ether/antimony(III) oxide (Br10DPO/Sb2O3). From pyrolysis studies, it is known that mainly PBDFs are formed from PBDDs during thermal degradation of HIPS/Br10DPO/Sb2O3. The formation of PBDFs occurs during polymer degradation (T = 350-400 °C) (8). Recently, formation of PBDDs during compounding of polymers with polybrominated flame retardants has been shown (9-11). Brenner et al. (12) measured PBDDs in the workplace area during compounding of poly(butylene terephthalate) (PBT)/glass fiber/Br10DPO/Sb2O3 polymer blends. They reported total amounts of 34 ng/m3 tetrabromobenzofurans (Br4DFs), 143 ng/m3 pentabromobenzofurans (Br5DFs), 554 ng/m3 hexabromobenzofurans (Br6DFs), and about 200 ng/m3 heptabromobenzofurans (Br7DFs). PBDDs were also found but at much lower concentrations than PBDFs. Around the extruder head the amount of 2,3,7,8-substituted PBDD congeners was tentatively determined at 1.3 ng/m3 for Br4DFs and 2.6 ng/m3 for Br5DFs. Assuming equal toxicity of bromine- and chlorine-substituted dioxins and furans (13, 14), one can estimate the contribution of 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents (toxic equivalents or TEQs) using the toxic equivalence factor method (15). The amount of TEQs in the surroundings of the extruder head during extrusion of PBTP/glass fiber/Br10DPO/Sb2O3 was estimated at 330-910 pg/m3 (12).
intake (TDI), recently established at 10 pg of TEQ kg\(^{-1}\) day\(^{-1}\) in The Netherlands (16), can be converted into a proposed occupational exposure limit (OEL) concentration for toxic equivalents in the workplace area:

\[
\text{OEL} = \frac{\text{TDI} \times \text{body weight}}{\text{breath volume}} = \frac{10 \text{ pg kg}\(^{-1}\) day\(^{-1}\) \times 70 \text{ kg}}{10 \text{ m}^3/\text{day}} = 70 \text{ pg/m}^3
\] (2)

The factors of 70 kg of body weight for an average worker and a 10-m\(^3\) breath volume in an 8-h working day are taken from the method of Leung et al. (17). During extrusion of PBTP/glass fiber/Br\(_{10}\)DPO/Sb\(_2\)O\(_3\), the proposed OEL for toxic equivalents is thus exceeded by at least a factor of 5.

This study focuses in detail on processes which occur during compounding of Br\(_{10}\)DPO/Sb\(_2\)O\(_3\) into the HIPS polymer matrix. A better understanding of extrusion processes will give a probable explanation for the formation of PBDFs at relatively low temperatures. During compounding HIPS is melted in an extruder with barrel temperatures of 190–220 °C. Br\(_{10}\)DPO/Sb\(_2\)O\(_3\) is mixed homogeneously into the polymer matrix. The processes taking place during compounding of HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_3\) were studied by using the following experiments: (1) Formation of PBDFs was studied off-line through RP-HPLC analysis as a function of the number of extrusion cycles \((n = 1-4)\) at \(T = 275 \, ^\circ\text{C}\). (2) Temperature development in a standard extruder was modeled using a computer simulation program. (3) Thermal stability of polystyrene chains was studied by measuring the relative number-average molar mass \((M_n)\), the relative mass-average molar mass \((M_m)\), and the breadth of the molar mass distribution \((M_m/M_n\) or dispersivity index). After repeated extrusion cycles, these quantities were measured with gel permeation chromatography (GPC).

The formation of PBDFs will be described as a logical consequence of polymer degradation processes in HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_3\) under extrusion conditions. It is the flame retardant activity of decabromodiphenyl ether that will give an explanation for formation of PBDFs at relatively low temperatures.

**Experimental Section**

**Materials.** These materials were used: HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_3\) (Dow Chemical Co., Terneuzen, The Netherlands); decabromodiphenyl ether, octabromodiphenyl ether, and pentabromodiphenyl ether (Broomchemie B.V., Terneuzen, The Netherlands); homopolymer polystyrene \(M_n = 100\,000\) (BDH Chemicals Ltd., Poole, England); homopolymer polystyrene (Shell Chemie Nederland B.V., Rotterdam, The Netherlands); \(^{13}\)C-labeled 2,3,7,8-Br\(_4\)DD, 1,2,3,7,8-Br\(_5\)DD, 1,2,3,7,8,9-Br\(_6\)DD, and 1,2,3,4,7,8,9-Br\(_7\)DD, and \(^{13}\)C-labeled 2,3,7,8-Br\(_4\)DF, 1,2,3,7,8,9-Br\(_6\)DF, 1,2,3,4,7,8,9-Br\(_7\)DF, 1,2,3,7,8-Br\(_5\)DF, 1,2,3,7,8,9-Br\(_6\)DF, 1,2,3,4,7,8,9-Br\(_7\)DF, 1,2,3,7,8,9-Br\(_8\)DF, and their chlorinated analogues (Cambridge Isotope Laboratories, Woburn, MA). Reagents which were used in PBDD and PBDF cleanup procedures were similar to those used in PCDD and PCDF cleanup procedures (18).

**Extraction Conditions and Processing Equipment.** Repeated extrusion cycles of homopolymer PS and HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_3\) (1–4 cycles) were performed on a Bersdorff ZE25 corotating twin-screw extruder (screw diameter 25 mm, screw speed 100 rpm). Temperature settings were \(T_1 = 180 \, ^\circ\text{C}\), \(T_2 = 200 \, ^\circ\text{C}\), \(T_3 - T_7 = 220 \, ^\circ\text{C}\) for a barrel temperature of 220 °C and \(T_1 = 180 \, ^\circ\text{C}, T_2 = 240 \, ^\circ\text{C}\), \(T_3 - T_7 = 275 \, ^\circ\text{C}\) for a barrel temperature of 275 °C (see Figure 1). The throughput was 2.1 kg/h. After each extrusion cycle a sample has been collected.

**Formation of PBDFs during Extrusion of HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_3\), Cleanup Method: Extraction and Extract Cleanup.** The extraction and cleanup method to isolate PBDFs in HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_3\) consisted of an extraction/precipitation of the HIPS polymer matrix (19), a carbon column [ACM method (20)], an acid–base column, and preparative RP-HPLC. In order to perform the analysis of PBDFs in polymer samples containing 5–15% decabromodiphenyl ether, two complex processes of separation have to be dealt with: (i) removal of high-molecular polymer chains from low-molecular polybrominated diphenyl ethers (PBDEs) and probably formed PBDFs by precipitation and (ii) separation at ppm levels of PBDFs from PBDEs on RP-HPLC or carbon columns. Precipitation of HIPS was achieved by slowly adding a hot tolue solution of HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_3\) (1:100 w/w) in 10-fold excess of 2-propanol. After filtration of the precipitate, the 2-propanol fraction was concentrated to small volume. PBDEs cannot be separated from PBDFs by a single carbon column while significant amounts of octa-, nona-, and decabromodiphenyl ether elute in the PBDF fraction (in the reverse direction eluate). Donnelly et al. (9) suggested the use of a second carbon column to obtain further separation. However, each carbon column gives rather low recoveries for highly brominated compounds such as heptabromobifenzo[21] and octabromobifenzo[21] dioxin (22) in the order of 30–40%, resulting in final recoveries of approximately 10%. Therefore, we suggest an alternative removal of the remaining PBDEs by RP-HPLC. A direct quantification of PBDFs in the RP-HPLC step will minimize the losses. Differences in retention behavior of PBDEs and PBDFs are explained by their differences in polarity. The relatively high polarity of PBDFs results in an elution sequence shown in Figure 2. The assignment of PBDEs and PBDFs is based upon available standards and prediction of the retention behavior of PBDFs as described in the section Characterization Techniques: RP-HPLC Analysis Used for Prediction of Retention Behavior of PBDFs.

**RP-HPLC offers an adequate method to remove PBDEs from hexa- to octabromobifenzo[21]. It also offers analytical possibilities which will be discussed in the next section. The method is not suitable for tetra- and pentabromobifenzo[21]s because they elute in the same fraction as PBDEs.**

**Characterization Techniques: Semipreparative RP-HPLC Analysis.** During relatively mild thermal degradation processes in the HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_3\) polymer melt, one would expect predominantly hexa-, hepta-, and octabromobifenzo[21]s to be formed from decabromodiphenyl ether. There are no internal \(^{13}\)C-la-
Table 1. log $k'$ of Halogenated Dibenzo-p-dioxins and Dibenzofurans

<table>
<thead>
<tr>
<th>Halogenated compd</th>
<th>log $k'$</th>
<th>Chlorinated compd</th>
<th>log $k'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dibenzo-p-dioxins</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3,7,8-Br$_n$DF</td>
<td>0.442</td>
<td>2,3,7,8-C$_n$DF</td>
<td>0.292</td>
</tr>
<tr>
<td>1,2,3,7,8-Br$_n$DF</td>
<td>0.766</td>
<td>1,2,3,7,8-Cl$_n$DF</td>
<td>0.638</td>
</tr>
<tr>
<td>1,2,3,4,7,8-Br$_n$DF</td>
<td>0.859</td>
<td>1,2,3,4,7,8-Cl$_n$DF</td>
<td>0.804</td>
</tr>
<tr>
<td>Dibenzofurans</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3,7,8-BrDD</td>
<td>0.574</td>
<td>2,3,7,8-ClDD</td>
<td>0.422</td>
</tr>
<tr>
<td>1,2,3,7,8-Br,DD</td>
<td>0.711</td>
<td>1,2,3,7,8-Cl,DD</td>
<td>0.556</td>
</tr>
<tr>
<td>1,2,3,6,7,8-Br,DD</td>
<td>0.855</td>
<td>1,2,3,6,7,8-Cl,DD</td>
<td>0.697</td>
</tr>
<tr>
<td>BrDD</td>
<td>1.09</td>
<td>ClDD</td>
<td>0.934</td>
</tr>
</tbody>
</table>

Column, Zorbax ODS (150 mm x 2.1 mm); eluent, MeOH; flow rate, 1 mL/min; detector, Beckman 160 absorbance detector (254 nm); precolumn, Chrompack (6 cm x 3.8 mm).

column, Zorbax ODS (C18, 5 mm, 25 cm x 9.4 mm); $T = 30^\circ$C. The eluent was collected in three fractions (0–55.5, 35.5–40.0, 40.0–90.0 min) in order to get a confirmation of PBDF assignment with GC/MS. The conditions of GC/MS confirmation analysis were described elsewhere (8).

Characterization Techniques: RP-HPLC Analysis Used for Prediction of Retention Behavior of PBDFs. Assignment of PBDFs in RP-HPLC analysis has been developed by extrapolating simple linear relationships between retention behavior and chemical structure. In prediction models for GC retention behavior of poly-chlorinated dibenzodioxins and dibenzofurans based upon chemical structure, the number of chlorine substituents is often used as a model parameter (25, 26). In a similar way, correlation has been made between RP-HPLC capacity factor $k'$ and the number of halogen substituents (X = Cl, Br). Because there are many more chlorinated compounds available, correlation between brominated and corresponding chlorinated compounds is also of use in predicting retention behavior of unavailable brominated compounds.

The reversed-phase HPLC experiments were performed in triplicate with a Kratos Spectroflow 400 solvent delivery system, a Kratos Spectroflow 787 UV absorbance detector ($\lambda = 225$ nm), and a Rhodyne Type 7125 injector. The capacity factor $k'$ of chlorinated and brominated aromatic compounds was measured on a reversed-phase C$_18$ column (Hypersil ODS, 5 mm, length 20 cm, $N = 3100$). The eluent was methanol/water (95:5 v/v). The flow rate was 1 mL/min. The dead volume or $t_d$ was measured with uracil. The logarithm of capacity factors [log $k' = log (t_r - t_o/t_d)$] of halogenated dibenzodioxins and dibenzofurans are listed in Table 1.

Linear relationships between retention behavior and the number of halogen substituents are

dibenzo-p-dioxins

$$
\log k'_{Br} = -0.354 + 0.209n_{Br}
$$

$n = 3$ $R^2 = 0.907$ SER = 0.094

$$
\log k'_{Cl} = -0.702 + 0.256n_{Cl}
$$

$n = 3$ $R^2 = 0.960$ SER = 0.073

dibenzo-p-dioxins

$$
\log k'_{Br} = 0.066 + 0.129n_{Br}
$$

$n = 4$ $R^2 = 0.998$ SER = 0.013

$$
\log k'_{Cl} = -0.084 + 0.128n_{Cl}
$$

$n = 4$ $R^2 = 0.998$ SER = 0.011

Linear relationships in RP-HPLC retention characteristics of brominated and chlorinated compounds are
dibenzofurans

\[ \log k'_{BR} = 0.207 + 0.833 \log k'_{CL} \quad (7) \]
\[ n = 3 \quad R^2 = 0.988 \quad \text{SER} = 0.034 \]

dibenzo-p-dioxins

\[ \log k'_{BR} = 0.150 + 1.01 \log k'_{CL} \quad (8) \]
\[ n = 4 \quad R^2 = 0.999 \quad \text{SER} = 0.002 \]

Although there are a few standards available, the retention behavior of brominated dibenzo-p-dioxins and dibenzofurans showed rather high correlation with the number of halogen substituents (eqs 3-6). The retention behavior of PBDFs in semipreparative RP-HPLC analysis showed a similar linearity with the number of bromine substituents. In addition, a mixture of PBDFs from electrophilic aromatic bromination of dibenzofuran was used as a control (27). Therefore, we have extrapolated eq 3 to assign hepta- and octabromodibenzo-furan. Although there are four heptabromodibenzo-furan isomers, only one peak was detected. In the GC/MS confirmation analysis also, one main peak was detected for heptabromodibenzo-furan. Linear relationships between the retention behavior of brominated and chlorinated compounds, shown in eqs 7 and 8, offer the possibility to predict capacity factors of brominated compounds. This is under further investigation.

2. Modeling Temperature Development in an Extruder. Modeling of the overall temperature profile of a single-screw devolatilization extruder was carried out by Dr. P. Elemans from DSM Research, Geleen, The Netherlands. The computer simulation model is based upon extruder geometries and rheological characterization of extruded polymers (28). Flow curves of HIPS/Br\(_{p,PO}/Sb_2O_3\) were measured on a Goffert Rheograph 2002, L/D ratio of the capillary was 30:1. Test temperatures were 180, 200, and 220 °C. The shear rate varied between \( \gamma = 100 \) and 1000 (1/s). The consistency index \( \gamma_0 \) was measured on a Rheometrics plate/cone viscometer.

3. Thermal Stability of HIPS/Br\(_{p,PO}/Sb_2O_3\), Characterization Techniques. Gel Permeation Chromatography. Gel permeation chromatography (GPC) was used to determine the relative number-average molar mass \((M_n)\), the mass-average molar mass \((M_w)\), and the breadth of the molar mass distribution \((M_w/M_n)\). HIPS/Br\(_{p,PO}/Sb_2O_3\) were measured after each extrusion cycle (see above) a sample was collected. GPC was performed by using a Waters apparatus composed of a pump, Model 510; injector, WISP 711; UV detector, 254 nm Model 440; column, 10^6, 10^4, or 10^2 \( \mu \)-Styragel (40 °C); columns, calibrated with monodisperse PS standards; and using tetrahydrofuran (THF) 0.6 mL/min as eluent. The polymer samples were dissolved in THF, filtered, and injected on columns. The thermal stability of polystyrene chains in homopolymer PS and in HIPS/Br\(_{p,PO}/Sb_2O_3\) was determined by measurement of the breadth of the molar mass distribution (or dispersivity index \( M_w/M_n \)).

\[ k = \frac{273}{T} + 0.0055 \quad (31) \]

Results and Discussion

1. Formation of PBDFs during Extrusion of HIPS/Br\(_{p,PO}/Sb_2O_3\). Figures 3 and 4 show the relative yield of heptabromodibenzo-furan (Br\(_{7DF}\)) and octabromodibenzo-furan (Br\(_{8DF}\)) during repeated extrusion cycles \((n = 1-4)\) of HIPS/Br\(_{p,PO}/Sb_2O_3\) at 275 °C. The yields of both Br\(_{7DF}\) and Br\(_{8DF}\) show a significant increase as a function of the number of extrusion cycles. The yield of Br\(_{7DF}\) increases with factor 6 and that of octabromodibenzo-furan with factor 10, from 0-1 to 2-4 extrusion cycles. Large error bars in the duplicate analysis are explained by inaccuracy of extraction and extract cleanup procedures. The results indicate a ceiling level of PBDFs after repeated extrusion cycles. This may be explained as an equilibrium between formation and de-bromination of PBDFs. Tentative quantification of the yield of PBDFs based upon comparison with RP-HPLC peak area of a known quantity of octabromodibenzo-p-dioxin resulted in concentrations of octabromodibenzo-furan ranging from 4.5 to 45 ppm and heptabromodibenzo-furan ranging from 1.5 to 9 ppm. In this quantification, it is assumed that overall recoveries for Br\(_{7DF}\) and Br\(_{8DF}\) in extraction and extract cleanup procedures are 50%. The RP-HPLC chromatogram showed only one heptabromodibenzo-furan peak. This was confirmed by GC/MS analysis where again only one hexabromodibenzo-furan was detected. These results indicate that selective debromination processes of PBDFs and PBDFs take place in the polymer melt during extrusion.

The starting material already contained small amounts of Br\(_{7DF}\) and Br\(_{8DF}\). Most probably they are formed during industrial compounding of the flame retardant system Br\(_{p,PO}/Sb_2O_3\) into the matrix of the HIPS polymer blend. Alternatively, the presence of PBDFs in the starting material may have been a background pollution of Br\(_{p,PO}\) (29, 30).

In the RP-HPLC chromatogram, decabromodiphenyl ether and less brominated diphenyl ethers were present. These less brominated diphenyl ethers are formed by the exchange of bromine and hydrogen in Br\(_{p,PO}\) (31).
Hydrogen most probably is abstracted from the polymer backbone. The exchange reaction of bromine and hydrogen in PBDPOs plays a key role in explaining formation of PBDFs at relatively low extrusion temperatures and will be discussed further in sections 2 and 3.

From micropyrolysis of pure polybrominated diphenyl ethers it is known that reactivity toward formation of PBDDs and PBDFs depends on the degree of bromination (I, 8). Less brominated diphenyl ethers like Br,DPO give rise to a much higher yield of PBDDs and PBDFs than Br, 3DPO does. This phenomenon is explained by energetically favorable elimination of HBr in the ring-closure reaction shown in eq 1. During pyrolysis of pure PBDPOs in a gas-phase reaction, the optimum PBDD/PBDF formation temperature is 600–700 °C. During macropyrolysis of HIPS/Br,DPO/Sb2O3 only PBDFs are formed. The HIPS matrix decreases the optimum PBDF formation temperature from 600–700 to 350–400 °C and enhances the yield of PBDFs by a factor of 7 (8). Molecular processes taking place during thermal degradation of the HIPS/Br,DPO/Sb2O3 polymer blend are debromination of the flame retardant Br3DPO forming less brominated diphenyl ethers; depolymerization of polystyrene by β-scission forming mainly styrene monomers, dimers, and trimers; bromination of polystyrene; and formation of antimony(III) bromides and antimony(III) phenoxylbromides (31). It has been shown that formation of PBDFs takes place during degradation of the HIPS polymer blend by a condensed-phase mechanism (8).

To explain the formation of PBDFs during extrusion of HIPS/Br,DPO/Sb2O3 at relatively low temperatures, more insight in temperature development in the extruder and in the thermal stability of polymer chains during extrusion processes is needed. In the next section temperature development in a model-type extruder will be discussed.

2. Modeling Temperature Development in an Extruder

The temperature (T) development in model-type extruders can be calculated with a computer simulation program which is based mainly on extruder geometrics and rheological characterization of extruded polymer systems. This computer model is developed by Meijer and Elemans (28). The temperature development of HIPS/Br,DPO/Sb2O3 is calculated in a single-screw extruder. It is supposed that this extruder is a good model system to simulate conditions during industrial compounding of the flame retardant system Br3DPO/Sb2O3 into an HIPS polymer matrix.

Rheological parameters like the power law index n, the consistency index ηo, and the temperature b (Arrhenius constant) were used in the computer model to calculate the power consumption and the temperature development in the pumping zone of the extruder, i.e., the part filled with the melt. The extruder throughput was set on 75 kg / h with a screw speed of 200 rpm. The temperature and shear rate dependent viscosity η (Pa s) is described using a power law

\[ \eta = \eta_0 \exp \left( -\frac{b(T - T_0)}{T_0} \right) \gamma^{n-1} \]  

where \( n \) is the power law index, \( \eta_0 \) is the consistency index (Pa s), \( b \) is the temperature index (Arrhenius constant) \( \left( \text{°C}^{-1} \right) \), \( T_0 \) is the reference temperature (°C), and \( \gamma \) is the shear rate (s^-1). The flow curve in Figure 5 shows the viscosity (log \( \eta \)) of HIPS/Br,DPO/Sb2O3 as a function of shear rate (log \( \gamma \)). In the range 100 < \( \gamma \) < 1000 it follows readily that the power law index \( n \) is given by

\[ n = \frac{d(\log \eta)}{d(\log \gamma)} + 1 \]  

For HIPS/Br,DPO/Sb2O3 the power law index \( n \) is 0.26.
Optimum polymerization temperature \( T_p \) and ceiling temperature \( T_c \) of polystyrene are shown in Figure 7. While the ceiling temperature is 300 °C, polystyrene already starts to depolymerize at 200 °C. Under given extrusion conditions, the temperature in HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_5\), as discussed in the previous section, locally rises to 400 °C. Therefore, radical (de)polymerization processes occur during extrusion of polystyrene blends.

To get a better understanding of the thermal stability of polystyrene, the homopolymer PS and HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_5\) have been repeatedly extruded \((n = 1-4)\) under normal temperature conditions \((T_{\text{ambient}} = 220 °C)\) and above practical temperature conditions \((T_{\text{extrud}} = 275 °C)\). The thermal stability of polystyrene in homopolymer PS and in HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_5\) was compared using the breadth of the molar mass distribution (or dispersivity index \(M_w/M_n\)) \((36)\). The value of the dispersivity index is a measure for the chain length distribution. In contrast to the relative number-average molar mass \(M_n\), where all polymer chains are of equal weight, the relative mass-average molar mass \(M_w\) outweighs the contribution of longer polymer chains. Therefore, a change in dispersivity index indicates formation or degradation of polymer chains.

Table III shows that the polymer chain length distribution in homopolymer PS and in HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_5\) remain unchanged during extrusion at 220 and 275 °C. After repeated extrusion of the homopolymer PS at 220 °C, \(M_w\) and \(M_n\) show a slight decrease of 5%. After repeated extrusion of homopolymer PS at 275 °C, both \(M_w\) and \(M_n\) show a significant decrease of 20%. This indicates that polystyrene depolymerizes during extrusion at 275 °C and that styrene oligomers are formed. HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_5\) shows a relatively smaller decrease in \(M_w\) and \(M_n\) of 5-8% after extrusion at 275 °C. Depolymerization of polystyrene is stabilized in HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_5\). An explanation for the stabilizing activity of Br\(_{10}\)DPO/Sb\(_2\)O\(_5\) is found in its flame retardant activity based on scavenging the H\(^+\) and OH\(^-\) propagation radicals in a real fire situation. During extrusion a nearly identical radical stabilization of HIPS degradation products is expected to occur. Radicals which start the unzipping of polystyrene chains are scavenged by Br\(_{10}\)DPO/Sb\(_2\)O\(_5\). The radical stabilizing activity of Br\(_{10}\)DPO is accompanied by debromination of Br\(_{10}\)DPO and formation of more stable Br radicals. This mechanism forming less brominated diphenyl ethers is in good agreement with the observation of Brauman and Chen \((37)\), who found that degradation of the HIPS polymer matrix initiates the autocatalytic debromination of Br\(_{10}\)DPO. Debromination of Br\(_{10}\)DPO, initialized by depolymerizing polystyrene chains, is the first step to PBDF formation. Therefore, incorporation of Br\(_{10}\)DPO into a thermally degrading polymer matrix is necessary for the low-temperature formation of PBDFs.

Conclusions and Recommendations

After repeated extrusion cycles of HIPS/Br\(_{10}\)DPO/Sb\(_2\)O\(_5\), a significant increase in the yield of PBDFs was shown. A RP-HPLC analysis method was used to describe the relative increase of hepta- and octabromodibenzo-furan. After four extrusion cycles at 275 °C, the yield of octabromodibenzo-furan increases by a factor of 10 (tentatively quantified as an increase from 4.5 to 45 ppm). The yield of heptabromodibenzo-furan increases by a factor of 6 (tentatively quantified as an increase from 1.5 to 9.0 ppm). The presence of PBDFs in the starting material most probably is explained by the formation of PBDFs during extrusion.
The formation of PBDFs is initiated by radical degradation of polystyrene. Therefore, optimum temperature for formation of PBDFs is increased because debromination of decabromodiphenyl ether in the HIPS matrix. Another explanation may be contamination of decabromodiphenyl ether. Reactive radicals are transformed into less reactive bromine radicals. However, the reactivity of decabromodiphenyl ether in organic solvents, a large injection volume is necessary. Great differences in polarity give rise to a complete separation of hexa- to octabromodibenzo- furans from PBDFs. It is worthwhile to apply a nondestructive detection method to determine recoveries of hepta- and octabromofuran in the RP-HPLC step. As long as there are no 13C-labeled internal PBDF standards available, RP-HPLC is preferable to GC/MS analysis.

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**Registry No.** Br, DPO, 1163-19-5; Sb2O3, 1309-64-4; Br,DF, 62994-32-5; Br,DF, 103582-29-2; polystyrene, 9003-53-8; polybutadiene, 9009-17-2.

**Literature Cited**

Transformation of Carbon Tetrachloride in the Presence of Sulfide, Biotite, and Vermiculite

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Carbon tetrachloride is transformed in aqueous solutions containing dissolved hydrogen sulfide more rapidly in the presence of the minerals biotite and vermiculite than in homogeneous systems. Approximately 80-86% of the CCl₄ was transformed to CO₂ via the measured intermediate, CH₂OCl₂. Chloroform comprised 5-15% of the products. The remaining 5% of the products were unidentified nonvolatile compound and CO. At 25 °C, the half-life of CCl₄ with 1 mM HS⁻ was calculated to be 2600, 160, and 50 days for the homogeneous, vermiculite (114 m²/L), and biotite (55.8 m²/L) systems, respectively. The CCl₄ transformation rate was found to be dependent on the type and quantity of the solid and the temperature, but was independent of pH and HS⁻ concentration above a critical HS⁻ concentration. The activation energies were 13.3 ± 2.0 kJ/mol for the homogeneous, vermiculite, and biotite systems, respectively. The CCl₄ transformation rate was independent of HS⁻ concentration when [HS⁻] > 0.5-4 mM and SCbiotite = 55.8 m²/L. Below [HS⁻] = 0.5 mM, the rate law was dependent on HS⁻ concentration.

Introduction

Abiotic transformations, such as reductive dehalogenation and nucleophilic substitution, can influence the fate of halogenated aliphatic compounds in aqueous environments. Sulfide, commonly found in hypoxic environments such as landfill leachate, hazardous waste plumes, and salt marshes at levels ranging from 0.2 μM to 5 mM, can act as electron donor (3-9) or as a nucleophile (4-6) to promote transformation of halogenated organics. In subsurface environments, the transformation rates of halogenated organic compounds in aqueous solution may be influenced by mineral surfaces (1, 2, 7, 8).

We investigated the effect of mineral surfaces in the presence of dissolved sulfide on the transformation rate of carbon tetrachloride. CCl₄ was chosen as the compound of interest because it is a contaminant which is frequently found in groundwater, it is a suspected human carcinogen (9), it causes ozone depletion, and it is a greenhouse gas (10). Laboratory studies were conducted to identify and quantify the environmental parameters that govern the transformation rate of CCl₄ in a heterogeneous aqueous environment containing sulfide and sheet silicates (biotite and vermiculite). The parameters studied were temperature, pH, mineral surface area, and sulfide concentration. The reaction rate was hypothesized to be a function of surface area because the reactions have been shown to be faster in the presence of mineral surfaces (2). Sulfide was also expected to play a role in the kinetics because it could act as either an electron donor or a nucleophile. Data are presented in terms of [HS⁻] instead of total sulfide because HS⁻ is a much stronger nucleophile than H₂S (5, 11) and HS⁻ is a stronger reducer than H₂S (12). Lastly, pH dependence was studied because it affects the surface properties of the minerals, the aqueous speciation of sulfide, and probably the surface speciation of sulfide.

In these systems, sheet silicates and sulfide were hypothesized to influence the mechanism of CCl₄ transformation in the following three ways (2): (1) CCl₄ can undergo electron transfer with ferrous iron in the sheet sil-