Chemical Composition of Nanoparticles Released from Thermal Cutting of Polystyrene Foams and the Associated Isomerization of Hexabromocyclododecane (HBCD) Diastereomers

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ABSTRACT

Polystyrene foams have various applications, and cutting of them is usually performed with a heated metal wire. However, it has recently been reported that micro- and nanoparticles are released by such thermal cutting at a rate of a few billion particles per second, and these particles have a high likelihood of getting into the respiratory system of the operator. HBCD, as the additive flame retardant, can also be released and is mostly incorporated into the emitted particles.

The chemical composition of the emitted particles was investigated in more detail in this study. Samples were collected by a cascade impactor during the thermal cutting of expanded (EPS) and extruded (XPS) polystyrene foam. Samples from three impactor stages were analyzed by GC-MS for their overall chemical compositions. Both particulate and gaseous samples were analyzed by LC-MS/MS for the amount of HBCD diastereomers. It was found that larger particles contain a significantly higher percentage of compounds with high boiling points. The comparison of the HBCD diastereomer patterns in EPS foam and the emitted particles revealed that isomerization occurred among the HBCD diastereomers. The average α-HBCD fractions were 14% and 60% in the EPS foam and emitted particles, respectively. In contrast, the corresponding average γ-HBCD fractions were 83% and 30%. Thermal cutting led to the conversion of a large fraction of γ-HBCD to α-HBCD, which is relatively stable and bio-accumulative. The diastereomer conversion was much more significant in the particles than in the gas emitted from EPS thermal cutting.

Keywords: HBCD; Diastereomer isomerization; Polystyrene; Aerosol; Nanoparticle emission.

INTRODUCTION

Polystyrene foam is used in numerous applications including building insulation materials, packing materials, and architectural models (Wünsch, 2000; Levchik and Weil, 2008) with the well-known advantages such as low cost, light weight, resistance to moisture and heat transfer. The annual global production exceeded 10^7 tons per year in 2000 and the number has been increasing since then. Thermal cutting is one of the most common processes for shaping or trimming polystyrene foam (Ahn *et al.*, 2003). However, we have shown recently that this process does release particles in the micro- and nanometer range (Zhang *et al.*, 2012). More than one billion particles were emitted per second from the thermal cutting process and the local particle concentration increased to a few trillions #/m^3. These particles mainly constituted of ketone-containing aromatics in addition to some polymer monomers and polymer additives. The emitted aerosol could be taken up by the breathing system of operators, and thus cause negative effects to human health. In addition, mechanical cutting, drilling and abrasion may lead to emission of micro- and nanoparticles from polymer-based materials and are attracting significant research interests (Kuhlbusch *et al.*, 2011; Schlagenhauf *et al.*, 2012).

Hexabromocyclododecane (HBCD) is a brominated flame retardant, which is intensively used in the production of flame-proofed polystyrene (Alaee *et al.*, 2003; BSEF, 2006). Nevertheless, it has been listed on the 2010 Environmental Protection Agency action plans (EPA, 2010), because it fulfills regulatory thresholds for a persistent organic pollutant (POP). During the thermal cutting of polystyrene foams, HBCD can be accumulated on the released particles by a

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factor of 10 compared to polystyrene foam boards (Zhang *et al.*, 2012) and, thus, the released HBCD by thermal cutting is of potential concern.

By the technical production of HBCD via bromination of cyclododeca-1,5,9-triene isomers, three diastereomers are formed, which are called α-, β-, and γ-HBCD. A typical technical HBCD contains 10–13%, 1–12%, and 75–89% of α-, β-, and γ-HBCD, respectively (Heeb *et al.*, 2005; Covaci *et al.*, 2006). However, the isomer patterns of HBCD in biotic and abiotic environmental samples differ significantly from the technical formula. The α-HBCD is usually the dominant isomer in the biological samples and environmental matrix (Gerecke *et al.*, 2003; Marvin *et al.*, 2011). Regarding the toxicity, genes of the chicken xenobiotic-sensing orphan receptor (CXR) can be activated by α-HBCD but not γ-HBCD, and then up-regulate the phase I metabolizing enzymes CYP2H1 and CYP3A37. Moreover, α-HBCD can be more easily accumulated by the biota than β- and γ-HBCD (Gerecke *et al.*, 2006; Eljarrat *et al.*, 2009; Marvin *et al.*, 2011).

HBCD diastereomer interconversion is a known process (Morris *et al.*, 2004; Heeb *et al.*, 2010). Under some conditions, it can be faster than degradation. Photodegradation in dust does not only decay the total HBCD concentration, each diastereomer can isomerize to produce different proportions of the other diastereomers (Harrad *et al.*, 2009). In experiments exposing fishes to only α- or γ-HBCD, significant concentrations of the other isomers were detected afterwards. In a kinetic control thermal treatment above 100°C, γ- to α-HBCD isomerization and β-HBCD racemization can be noticed after half an hour of treatment at 130°C, while no indication for α-HBCD rearrangement to the other HBCD diastereomers was found for the same conditions (Heeb *et al.*, 2008a, b). A specific mixture of diastereomers (78 ± 2% α-HBCD, 13 ± 1% β-HBCD, and 9 ± 1% γ-HBCD) is obtained when thermal equilibrium is reached (Peled *et al.*, 1995; Heeb *et al.*, 2010). We lately reported a substantial transformation of γ-HBCD to α-HBCD induced by the thermal cutting, especially in experiments with expanded polystyrene (EPS) (Zhang *et al.*, 2012). The condensation of pre-existing and freshly formed α-HBCD on the micro and nanoparticles emitted from this process might cause additional emission of the most bioaccumulative HBCD diastereomer.

Herein, we report further chemical details of the thermal cutting experiment, including the detailed fractions of the HBCD diastereomers in the emitted particles of 15 different size ranges and in the gas phase emission. It was found that the diastereomer conversion is much more significant in the particles than in the gas emitted from EPS thermal cutting. The different chemical compositions of particles in three different size ranges were analyzed and the relation of the chemicals' boiling points to the particle size was revealed. High particle emission has been observed during thermal treatment of polymer-based pellets (Wang *et al.*, 2011) and during thermal seal of plastic bags (Wang *et al.*, 2012). The obtained results are helpful for the better understanding of the formation mechanism of aerosols from the thermal treatment of plastics.

METHODS

Experimental Approach

Two kinds of polystyrene foams were thermally cut separately by a polystyrene cutter (Steinel Styrofix, Germany) at 150–200°C in a closed glove box (total volume: 0.28 m³). The cutting process was conducted for 1 h. The temperature in the glove box was 19–21°C, and the relative humidity (RH) was 32%–36%. Aerosols were continually collected during the cutting process and an additional 10 min after stopping the cutting process. The sampling nozzle was fixed at the side of the glove box with a distance of 0.3–0.5 m from the cutting point. The gas stream was pumped through a cascade impactor (Mode 122-NR NanoMoudi, MSP Corporation) at a flow rate of 30 L/min. The cascade impactor had 13 stages. The 50% cutoff diameters for the 13 impactor stages were 10000, 5600, 3200, 1800, 1000, 560, 320, 180, 100, 56, 32, 18 and 10 nm. Uncoated aluminum foils were used as the impaction substrates to collect the particles on the impactor plates, and a back filter (glass filter, id. 90 mm) was installed after the final impactor stage to collect very small particles that were not captured previously. In addition, a piece of polyurethane foam (PUF) was placed under the back filter to collect HBCD in gas phase.

The deposited particle mass on each stage and on the glass filter was obtained gravimetrically by weighing the substrate before and after exposure on a microbalance (METILER TOLEDO, Switzerland, precision is ± 1 µg) at constant temperature and relative humidity condition (20°C and RH 46%). After sampling, the aluminum foils and the glass filter were then stored in the microbalance room for one hour to achieve a constant weight. The weight of each impaction substrate was measured three times and subsequently averaged. The average values were calculated for all data pairs. The relative deviations of particle masses on each stage and back filter were in the range of 4.5%–24.7%, and the relative deviations of the total collected particle masses were smaller than 10%.

Sample Preparation

After weight measurement, the aluminum foils and glass filter with particles were put into glass tubes for chemical analysis. Ultrasonic extraction was conducted three times using 30 mL of dichloromethane. HBCD in the PUF were also extracted using dichloromethane in a Soxhlet extractor for 16 h. Prior to the extraction, $^{13}C_{12}$-labelled HBCD internal standards (from Cambridge Isotope Laboratories, U.S.) were spiked. Chromatography columns were filled (from bottom) with a piece of cotton, 0.5 g activated silica gel (Kieselgel KG 60, Merck, Switzerland, previously activated at 130°C for 12 h), and about 0.5 g anhydrous sodium sulphate. The concentrated extract (1.0 mL) was transferred to the column. Elution was done by 5 mL of hexane followed by 2 mL of a 1:1 mixture of hexane/dichloromethane. The collected solution was concentrated, transferred to a vial, and then evaporated to dryness by a gentle stream of nitrogen. Finally, 10 µL of $^{2}H_{18}$-labelled γ-HBCD recovery standard was spiked and the volume was adjusted to 100 µL using methanol.

LC-MS Analysis of HBCD Diastereomers

The injection volume was 2 μL. HBCD diastereomers were quantified by LC-MS/MS (LC-MS Agilent 6460 Triple Quadrupole). A Zorbax SB-C18 analytical column (50 mm × 3.0 mm i.d., 1.8 μm particle size; Agilent) was used, applying a methanol/water/acetonitrile gradient (starting with 47.5% (v/v) methanol, increased to 57% in 1 min, 57–90% in 5 min, 90–85.5% in 1 min, and 57% in 1 min. 5% acetonitrile, isocratic) at a flow rate of 0.4 mL/min. MS analysis was operated in the negative ESI mode.

The MS was operated in the negative ESI mode with the selection of $[M–H]^-$-ion as parent ion. The transitions 638.7→79.9 m/z and 640.7→79.9 m/z were chosen for the quantification and identification of native HBCD, the transitions 650.7→79.9 m/z and 652.7→79.9 m/z were chosen for the quantification and identification of $^{13}C_{12}$-labeled HBCD, and the transitions 655.7→79.9 m/z and 657.7→79.9 m/z were chosen for the quantification and identification of $^{2}H_{18}$-labeled HBCD, respectively. The ESI-source parameters were as follows: gas temperature, 325°C; gas flow, 8 L/min; nebulizer, 45 psi; sheath gas temperature, 340°C; sheath gas flow, 12 L/min; capillary, 3000 V; nozzle voltage, 1500 V. The limit of detection (LOD) of the instrument was 0.2 pg for all three HBCD isomers (three times signal-to-noise ratio). The recoveries of $^{13}C_{12}$-labelled α-, β- and γ-HBCD isomers were in the range of 51.4%–95.6%, 54.3%–102.1% and 68.9%–118.7%, respectively. The average masses of HBCD collected by each stage, back filter and PUF were respectively calculated for the two measurements. The relative deviations of HBCD masses for all data pairs were in the range of 5.2%–18.9%, and the relative deviations of the total collected HBCD masses were smaller than 9%.

GC-MS Analysis of Chemical Components

The chemical components of particles collected on each of the stages were analyzed by a Hewlett-Packard HP 6890 gas chromatograph coupled to a HP 5973 quadrupole detector (GC-MS). A fused silica column (DB5-MS, 30 m × i.d. 0.25 mm, 0.25 μm film) was employed to separate organic mixtures. 1 μL of each methanol solution sample was injected to the GC column at a split ratio of 3:1. GC separation was performed with the following program: starting oven temperature 40°C, with 2 min hold time, then to 280°C at 10 °C/min and 1 min of final hold time. The temperature of the GC to MS transfer line was set at 280°C. The carrier gas was helium. The chromatographic separation was performed in constant flow mode at 1.5 mL/min. The chromatograms were collected in full scan mode. The electron impact, EI, spectra were recorded from 29 to 421 m/z, with 70 eV ionization energy.

RESULTS AND DISCUSSION

Release of HBCD

The emission of particles and chemicals compounds was assessed for the thermal cutting of expanded polystyrene foam (EPS) and extruded polystyrene foam (XPS). One hour cutting experiments resulted in the emission of totally 5.2 and 4.5 mg of particles for EPS and XPS, respectively, which contained 160 and 250 μg of HBCD isomers. Particles smaller than 1 μm had higher HBCD concentrations than the raw foams, whereas particles larger than 3 μm had lower concentrations than the raw foams. Details are shown in Fig. 1 and are described further by Zhang *et al.* (2012). Occupational exposure assessment using the lung deposition model indicated more than 60% of HBCD deposited in the lung of the cutting operator would be allotted to the alveolar region (Zhang *et al.*, 2012). The subchronic (or chronic) toxic effects jointly caused by the ultrafine particles and HBCD should be concerned for cutting operator in view of the high level exposure to these pollutants.

Isomer Fractions of HBCD

In addition to the shifts in concentration, the thermal cutting process also affected the diastereomer distribution (α-, β-, and γ-HBCD) in the EPS experiments. In the raw EPS board, the γ-HBCD fraction was 83%, which is a characteristic fraction for technical HBCD (Heeb *et al.*, 2005). On the other hand, the main diastereoisomer in the released particles was α-HBCD, which accounted for 60% of the total HBCD in the released particles. The fraction of γ-HBCD decreased to 29% in the released particles. The diastereomer pattern was very similar for all particle samples collected on the impactor stages and the back-up filter of the NanoMoudi (Fig. 2(a)). It is interesting that the diastereomer pattern was independent of the particle size
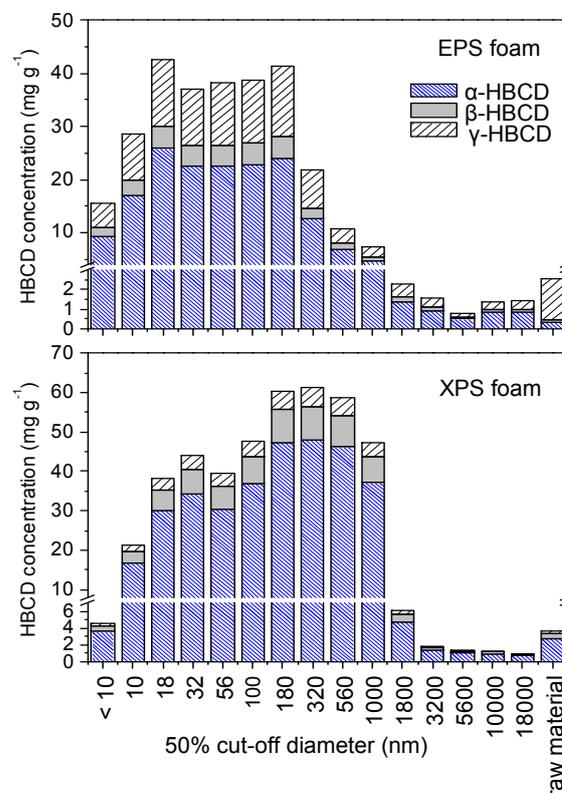

Fig. 1. HBCD concentrations in raw foams and in size separated particles (collected by NanoMoudi) from thermal cutting of polystyrene foams.

and, therefore, of their formation history, whereas the total HBCD-concentrations in particles of different sizes varied by a factor of 20–35. The diastereomer fractions in the gas phase during thermal cutting were 24%, 12% and 64% for α-, β-, and γ-HBCD, respectively. These fractions were different from both raw foam and released particles. The γ-HBCD fraction in the gas phase was more like the raw foam than the particles (see Table 1).

These differences can be partially explained by isomerization reactions shifting the diastereomer pattern toward its thermal equilibrium at the time scales of seconds to hours at temperatures above 100°C. The thermal equilibrium is dominated by α-HBCD, followed by γ-HBCD and β-HBCD. Starting with technical HBCD, the conversion from γ-HBCD to α-HBCD is the most important isomerization process. A very minor fraction of β-HBCD can also be converted to δ-HBCD (Heeb *et al.*, 2008a, b). The α-HBCD to γ-HBCD ratio observed in the particles resembles the ratio of the α-HBCD to γ-HBCD ratio reported by Peled *et al.* (1995) and Heeb *et al.* (2010). The β-HBCD fraction increased, which was also reported by Peled *et al.* (1995) and Heeb *et al.* (2010). It can be assumed that isomer rearrangement is faster in the liquid phase than in the gas phase. Within the short time after the raw board was melted by the hot metal cutter and before HBCD isomers were evaporated, some isomerization took place, which resulted in a shifted diastereomer pattern in the gas phase. The

temperature of the gas phase decreased with increasing distance from the cutting device. The colder temperature facilitated the condensation of HBCD molecules onto the particles, which consisted of semivolatile polymer thermolysis products. However, temperatures of the forming particles apparently were sufficiently high to enable further isomerization, especially with the catalytic help of the polymer fragments and free bromide ion released by the degradation of some HBCD (Peled *et al.*, 1995; Heeb *et al.*, 2008b) in particles. Because of the higher toxicity and more likely bioaccumulation of α-HBCD, the increased fraction of α-HBCD due to the isomer rearrangement during thermal cutting process should result in bigger adverse impact of the released HBCD on the workers and the environment.

In contrast to EPS foam, extruded polystyrene (XPS) foam is exposed to relatively high temperatures during production (up to 180°C for XPS and 100–110°C for EPS) (Andersen, 2011). Exposure to high temperature shifts the HBCD diastereomers pattern in XPS board away from the technical product pattern and becomes 75% α-HBCD, 16% β-HBCD, and 9% γ-HBCD (Fig. 2(b)). Once the XPS board was heat-cut by a hot wire, HBCD diastereomers changed a little to 78%, 13%, and 9% for α-, β-, and γ-HBCD, respectively, which is close to thermal equilibrium (Peled *et al.*, 1995; Barontini *et al.*, 2001). Overall, compared to EPS, thermal cutting of XPS did not cause significant HBCD diastereoisomer conversion.
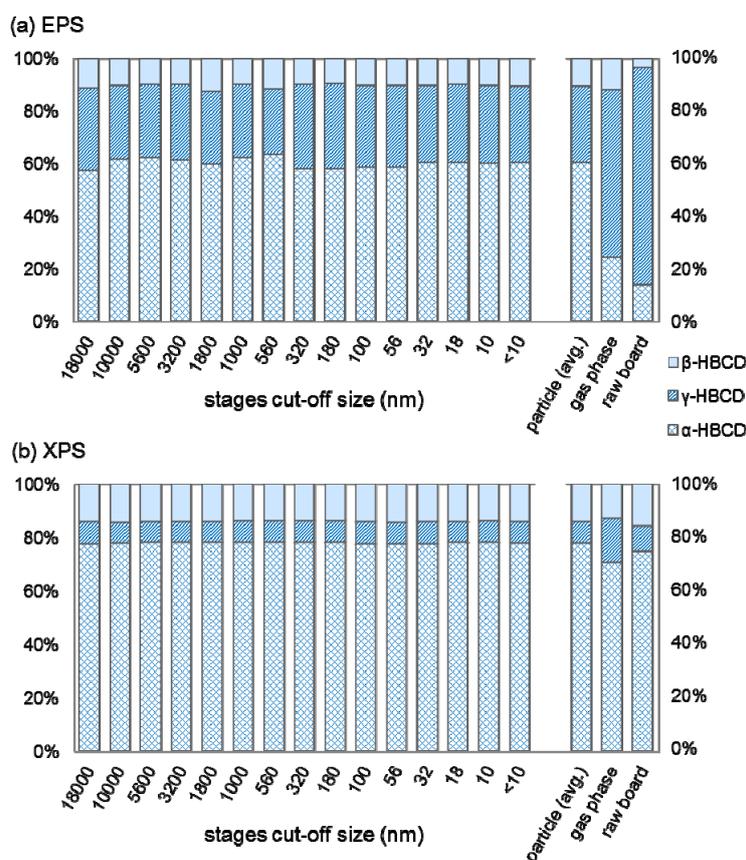
Fig. 2. HBCD diastereomer fractions in the raw board as well as released particles and the gas phase during thermal cutting of EPS foam (a) and XPS foam (b).

Table 1. Comparison of HBCD diastereomer fractions in various phases of different experiments.

	Average in particles	Gas phase	Raw board
EPS			
α-HBCD	60%	24%	14%
β-HBCD	10%	12%	3%
γ-HBCD	30%	64%	83%
XPS			
α-HBCD	78%	70%	75%
β-HBCD	14%	13%	16%
γ-HBCD	8%	17%	9%

Chemical Composition Analysis for the Released Particles

The composition of aerosol particles has strong effect on their properties, such as the solubility in water and the sorption of volatile chemicals. It eventually affects also the lifetime of the aerosols and their impact on the environment. To get a better understanding of the chemical composition, extracts of size separated particles collected by the cascade impactor NanoMoudi were studied by GC-MS analysis. (Fig. 3)

In the present study, attention is focused on the boiling points of the chemical components in the particles of different sizes, which gives indication of the particle formation process we attempted in our recent paper (Zhang *et al.*, 2012). High and low boiling-point chemicals were simultaneously released into the air because of the short contact time of the hot wire. But only compounds with high boiling points condensed in the early stage and nucleated to become liquid droplets. During the progressive cooling of the organic vapors, chemicals that remained in the gas phase had a chance either to undergo homogeneous condensation themselves, or to condense onto existing nuclei of high-boiling-point compounds. Based on this mechanism, high-boiling-point chemicals are enriched in large particles due to the longer time for growing, compared to the later nucleation of the low-boiling-point chemicals. When coagulation was also included in consideration, heterogeneous coagulation would give larger contribution to the particles in the larger size range. Smaller low-boiling-point droplets formed in the later nucleation process were less likely to coagulate to form large particles due to the lack of large interactive surface. The general trend of the enrichment of high-boiling-point chemicals in large particles would still be true.

Based on GC-MS analysis, particles with larger aerodynamic diameters (on stages 8 and 9) contained more molecules with longer retention time (t_R) than smaller particles (on stage 12). That is an indication that aerosol particles were formed by the condensation of cooling vapors. If the particles would have been formed mechanically, no change would be expected. In order to show this argument in a more quantitative way, we separate the chemicals shown in the spectra (Fig. 3) into three groups, which differ by their retention time: group A corresponds to t_R = 6–13 min. The group A includes chemicals such as short cyclo-siloxane rings and acetophenone, which comes from the oxidization of styrene monomer. In the time zone of group B (t_R = 12–20 min), only one significant compound was found, which is dibutylphenol (t_R = 15.2 min). There are a number

of peaks in group C (t_R = 20–27 min). Their MS-spectra match well with 1,3-diphenyl-2-propenone, 3-cyclopentenyl-2-methyl-1,1-diphenyl-propene, and numerous long-alkyl and alkene chain esters. The background was also checked by analyzing a blank dichloromethane sample. No distinguishable peak was found in the blank test. The contributions of chemicals in groups A-C were normalized by the total signal from the GC spectra integration, and arranged into the three tested stages with different particle sizes (see Table 2).

Since less particle mass was collected on stage 12, the spectrum of the extract of stage 12 had a relatively high signal to noise ratio. The contributions from each of the three retention time groups were similar on stage 12. Compared to stage 12, the 10 times larger particles on stage 8 had large differences between groups. On stage 8, the fraction of chemicals from group A was about half of that on stage 12. The contribution of group B was also decreased. Over 70% of the chemicals were detected in Group C on stage 8, which demonstrated that the fraction of higher-boiling-point molecules (t_R > 20 min) in 320–180 nm particles was higher than that in 32–18 nm particles. Stage 9 showed a pattern between the other two stages. However, since it collected particles with similar size as on stage 8, the contribution of the three groups was closer to values on stage 8.
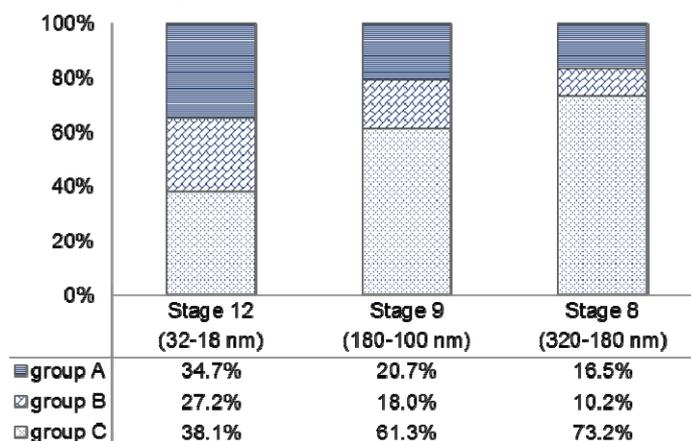
CONCLUSIONS

The particles and gas released by thermal cutting of both EPS and XPS foams were collected by NanoMoudi and analyzed for their chemical composition. It is found that HBCD underwent isomerization during this process, especially for the EPS experiments. The average fraction of the more bio-accumulative α-HBCD increased from 14% in the EPS foam to 60% in the particles phase. In contrast, the average γ-HBCD was 83% and 30% in the EPS foam and emitted particles, respectively. Thermal cutting of XPS foam board did not cause such substantial rearrangements since the foam had experienced thermal treatment during the manufacture of the foam.

Based on the GC-MS overall scanning, particles in a few hundred nanometers size range were mainly composed of high-boiling-point chemicals. The fraction of these was twice as much as that for particles 10 times smaller in size. This result indicates that particles were formed by condensing chemical vapors which evolved from the contact of polystyrene foam with the heated cutter. This particle
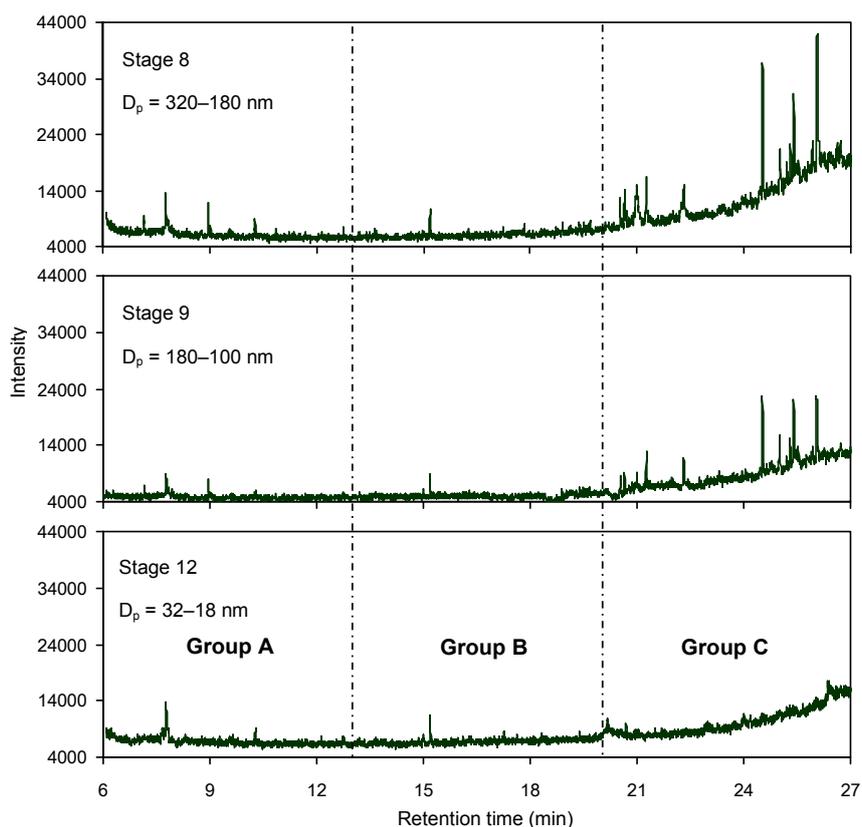
Fig. 3. GC-MS analysis of organic extracts from particles on three impactor stages.

Table 2. Chemical contribution from the groups with different retention time to the particles on 3 NanoMoudi stages.

	Stage 12 (32-18 nm)	Stage 9 (180-100 nm)	Stage 8 (320-180 nm)
group A	34.7%	20.7%	16.5%
group B	27.2%	18.0%	10.2%
group C	38.1%	61.3%	73.2%

forming mechanism did not cause significant variation of the fraction of the three main HBCD diastereomers in different particle sizes, because the HBCD diastereomers had very close boiling points and thus share similar condensation behaviors.

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