Analysis of the Recently Detected Environmental Contaminant Bis-(4-chlorophenyl)sulfone in Temperature Resistant Polymers

Peter Haglund, Olof Leander and Douglas Zook†

Institute of Environmental Chemistry, Umeå University, SE- 901 87 Umeå, Sweden.

Introduction

Recently, a new environmental contaminant, bis-(4-chlorophenyl)sulfone (BCPS), was detected in Baltic Sea fish and wildlife at levels comparable to major PCB congeners (1). The sources of this contaminant are currently unknown. However, it is well known that BCPS is used in large quantities as feedstock in the production of temperature resistant polymers, such as polysulfones and polyethersulfones. BCPS emissions may arise from the synthesis, handling or storage of the feedstock as well as from the manufacturing of the polymer. Emissions may also stem from the finished plastic itself during the product life cycle. However, reports on such emissions have yet to be published.

In this study we have searched for free BCPS monomer in polysulfone and polyethersulfone granulates as well as finished plastics.

Experimental

Nine polymer samples were obtained from BASF (Ludwigshafen, Germany), five as granulates and four as finished plastics. These are manufactured under the trademark Ultrason. The granulate samples included both polysulfones (Ultrason E1010 and S3010) and polyethersulfones (Ultrason E1010, E2010, and E3010). The corresponding finished plastics are denoted with a suffix "P", e.g., Ultrason E1010P.

The Ultrason polymers are almost insoluble in most common solvents, but slightly soluble in aprotic polar solvents. Five milligram of each plastic sample were therefore dissolved in 2 mL of dimethyl formamide (DMF), and 60 nanogram of $^{13}C_{12}$-2,2',4,5,5'-pentachlorobiphenyl (Cambridge Isotope Laboratories, Woburn, MI, USA) was added as an internal standard. The polymeric material was removed by high-performance gel permeation chromatography (HR-GPC) on two serially connected 7.8 × 300 mm HR-GPC columns (5μm, 50Å, polystyrene-divinyl benzene copolymer, Polymer Laboratories, Church Stetton, UK). DMF was used as the

† Present address: Astra Pain Control, Södertälje, Sweden.

mobile phase at a flow rate of 0.70 mL/min. Repetitive injections of 500 µL aliquots were necessary since the capacity of the HR-GPC columns was not high enough to allow the whole sample to be injected in a single injection. Following each injection the BCPS and the internal standard was recovered by collection of the effluent between 22 and 44 minutes. The corresponding fractions were combined, diluted 1/3 (v/v) with 10% aqueous sodium chloride, and were extracted with 3 x 10 mL iso-octane. The organic phases were combined and dried with potassium carbonate. Finally, the samples were evaporated to a volume appropriate for gas chromatography - mass spectrometry (GC-MS) analyses, i.e. 50 to 100 µL.

Two microliter aliquots of the purified samples were splitless injected onto a 60 m x 0.32 mm 5%-phenyl methylsilicone capillary GC column which was directly interfaced to the ion source of a Fisons MD800 MS. The MS was operating in the electron impact mode at an electron energy of 70 eV. Selected ion monitoring was employed for target analyte and internal standard detection. Four ions were monitored for BCPS (*m/z* 181, 183, 286, 288) and two for the internal standard (*m/z* 336 and 338). The quantifications were performed using the internal standard technique.

Results and discussion

The results of the BCPS analyses are complied in Table 1. All results are within a narrow range of 37 to 170 µg/g. Examination of the results reveal no obvious difference between granulate and finished plastic samples, and no strong correlation is observed between the degree of polymerisation and the BCPS levels. Eventually, the BCPS levels in soft polymers, E1010(P)/S1010(P), are slightly elevated as compared to the hard polymers, E3010(P)/S3010(P), with an exception for the S1010/S3010 pair. However, all samples stem from different batches and it is therefore impossible to draw any definite conclusions based on the few samples analysed in this study.

Table 1: Levels of BCPS in the polysulfone and polyethersulfone samples

Polymer sample	µg BCPS/ g of polymer
E1010	110
E2010	60
E3010	80
S1010	37
S3010	67
E1010P	100
E3010P	80
S1010P	170
S3010P	75

The worldwide annual production of polysulfones and polyethersulfones is in the order of 10 000 tonnes (2). Assuming an average BCPS level of 100μg/g this quantity of polymers would contain 1 000 kg of BCPS residues. This is a substantial amount – but is it enough to explain the environmental levels of BCPS? The levels of BCPS and total PCBs in perch (*Perca fluviatilis*) from the Baltic are 40-100 and 400- 2 000 ng/g lipids (1), respectively, i.e. the levels of PCBs is 10-fold higher. As a comparison, the estimated average annual production of PCBs during the period 1930 to 1980, 25 000 tonnes (3), exceeds the amount of BCPS residue in polysulfones and polyethersulfones with 25 000 times. Further, the BCPS monomers have a very slow migration rate in the polymer (4).

Our result does thus not indicate that polysulfone and polyethersulfone products are large contributors to the environmental burden of BCPS. That does however not exclude that significant quantities of BCPS might be emitted during production, handling, or storage of BCPS monomer, polysulfone, or polyethersulfone polymers.

Acknowledgements

Drs Ahlers, Eichenauer, and Neufeld at BASF Ludwigshafen are all acknowledged for providing us with the polymer samples, and for valuable discussions. The project was sponsored by the Swedish Environmental Protection Agency "Persistent Organic Pollutants" scientific program.

References

1. Olsson A and Bergman Å; *Ambio*. **1995**, 24, 119.
2. Dr. Eichenauer, BASF, Ludwigshafen, *personal communication.*
3. Erickson M; *Analytical chemistry of PCBs*, 2ed. CRC Press, Boca Raton, USA, **1997**, 35.
4. Tice P; *Food Add. Contam.* **1988**, 5, 373.