SUPPLEMENTARY INFORMATION

Direct Mass Spectrometric Analysis of Brominated Flame Retardants in Synthetic Polymers

*Krista Grönlund[1], Ville H. Nissinen[1], Ilkka Rytöluoto[2], Milad Mosallaei[2], Joonas Mikkonen[2], Kirsi Korpijärvi[3], Paavo Auvinen[1], Mika Suvanto[1], Jarkko J. Saarinen[1] and Janne Jänis[1]**

[1]Department of Chemistry, University of Eastern Finland, Yliopistokatu 7, 80130 Joensuu, Finland

[2]VTT Technical Research Centre of Finland Ltd., Visiokatu 4, 33101 Tampere, Finland

[3]VTT Technical Research Centre of Finland Ltd., Koivurannantie 1, 40400 Jyväskylä, Finland

*Corresponding author: janne.janis@uef.fi

Table S1. Model compound formulations.

	Br target concentration	Experimental Br concentration (XRF)	Ratio	Target formulation		
Sample	**[ppm]**	**[ppm]**	**Exp. vs target**	**Polymer [mg]**	**BFR [mg]**	**Sb_2O_3 [mg]**
ABS-0	0	0 ± 2	–	10000.00	0.00	0.00
ABS-HBCD-1000	1,000	675 ± 10	0.71	9979.92	13.38	6.69
ABS-HBCD-2500	2,500	1,982 ± 20	0.81	9949.81	33.46	16.73
ABS-HBCD-5000	5,000	4,395 ± 39	0.89	9899.61	66.92	33.46
ABS-HBCD-10000	10,000	8,610 ± 73	0.86	9799.23	133.85	66.92
ABS-TBBPA-1000	1,000	982 ± 12	0.98	9974.48	17.02	8.51
ABS-TBBPA-2500	2,500	2,251 ± 22	0.89	9936.19	42.54	21.27
ABS-TBBPA-5000	5,000	4,484 ± 39	0.90	9872.38	85.08	42.54
ABS-TBBPA-10000	10,000	8,914 ± 77	0.89	9744.76	170.16	85.08
ABS-decaBDE-1000	1,000	916 ± 12	0.92	9981.99	12.00	6.00
ABS-decaBDE-2500	2,500	2,109 ± 21	0.84	9954.99	30.01	15.00
ABS-decaBDE-5000	5,000	4,311 ± 38	0.86	9909.97	60.02	30.01
ABS-decaBDE-10000	10,000	8,750 ± 75	0.87	9819.94	120.04	60.02
HIPS-0	0	9 ± 2	–	10000.00	0.00	0.00
HIPS-HBCD-1000	1,000	656 ± 10	0.66	9979.92	13.38	6.69
HIPS-HBCD-2500	2,500	1,688 ± 18	0.68	9949.81	33.46	16.73
HIPS-HBCD-5000	5,000	3,860 ± 34	0.78	9899.61	66.92	33.46
HIPS-HBCD-10000	10,000	8,282 ± 71	0.83	9799.23	133.85	66.92
HIPS-TBBPA-1000	1,000	877 ± 11	0.88	9974.48	17.02	8.51
HIPS-TBBPA-2500	2,500	2,033 ± 20	0.81	9936.19	42.54	21.27
HIPS-TBBPA-5000	5,000	4,334 ± 38	0.87	9872.38	85.08	42.54
HIPS-TBBPA-10000	10,000	8,609 ± 75	0.86	9744.76	170.16	85.08
HIPS-decaBDE-1000	1,000	793 ± 11	0.79	9981.99	12.00	6.00
HIPS-decaBDE-2500	2,500	2,043 ± 21	0.82	9954.99	30.01	15.00
HIPS-decaBDE-5000	5,000	4,148 ± 37	0.83	9909.97	60.02	30.01
HIPS-decaBDE-10000	10,000	8,773 ± 74	0.88	9819.94	120.04	60.02

Table S2. Utilized parameters in DIP-APCI-MS analysis.

Ion source	
End plate offset	500 V
Capillary	4000 V
Corona	4000 nA
Nebulizer	2.0 Bar
Dry gas	5.0 L/min
Dry temperature	200 °C
Vaporizer temperature	150-450 °C
Transfer	
Deflection 1 Delta	40.0 V
Funnel 1 RF	300.0 V_{pp}
Funnel 2 RF	400.0 V_{pp}
Multipole RF	250.0 V_{pp}
Quadrupole	
Ion energy	5.0 eV
Low mass	100.00 m/z

Collision cell	
Collision energy	10.0 eV
Collision RF	600.0 V_{pp}
Transfer time	140.0 µs
Pre pulse storage	12.0 µs
Flight tube	
Flight tube	9900.0 V
Reflector	
Decelerator	882.0 V
Reflector	2500.0 V
Detector	
TOF	2268.9 V
Corrector	
Fill	64.7 V
Extract	-611.1 V
Lens	-6454.3 V

Table S3. Utilized calibration lists for HIPS and ABS samples.

HIPS		ABS	
Ion formula	m/z	Ion formula	m/z
$C_{13}H_9$	165.069877	$C_{11}H_{12}N$	158.096426
$C_{14}H_{10}$	178.077702	$C_{14}H_{15}N_2$	211.122975
$C_{16}H_{15}$	207.116827	$C_{19}H_{20}N$	262.159026
$C_{24}H_{24}$	312.187252	$C_{22}H_{23}N_2$	315.185575
$C_{25}H_{24}$	324.187252	$C_{25}H_{26}N_3$	368.212124
$C_{32}H_{31}$	415.242027	$C_{30}H_{31}N_2$	419.248175
$C_{33}H_{32}$	428.249852	$C_{33}H_{34}N_3$	472.274725
$C_{41}H_{40}$	532.312453	$C_{36}H_{37}N_4$	525.301274
$C_{49}H_{48}$	636.375053	$C_{41}H_{42}N_3$	576.337325
$C_{57}H_{56}$	740.437653	$C_{44}H_{45}N_4$	629.363874
$C_{65}H_{64}$	844.500253	$C_{47}H_{48}N_5$	682.390423
$C_{73}H_{72}$	948.562854	$C_{52}H_{53}N_4$	733.426474
		$C_{55}H_{56}N_5$	786.453023
		$C_{58}H_{59}N_6$	839.479572
		$C_{63}H_{64}N_5$	890.515624

Table S4. Summary of selected signals observed in DIP-MS analysis of ABS-decaBDE sample (Br concentration of 1,000 ppm).

Experimental m/z	Theoretical m/z	Error (ppm)	Observed ion	Ion formula	Proposed compound**	Observation time frame (min)***
881.259062*	881.257073	2.26	$M^{+\bullet}$	$C_{12}HBr_9O$	nonaBDE	5.5–7.0
959.170006*	959.167571	2.54	$M^{+\bullet}$	$C_{12}Br_{10}O$	decaBDE	5.5–7.0
270.234020	270.234202	-0.67	$M^{+\bullet}$	$C_{20}H_{30}$	B_5	7.0–8.5
324.281936	324.281153	2.41	$M^{+\bullet}$	$C_{24}H_{36}$	B_6	7.0–8.5
378.328252	378.328103	0.39	$M^{+\bullet}$	$C_{28}H_{42}$	B_7	7.0–8.5
432.375130	432.375053	0.18	$M^{+\bullet}$	$C_{32}H_{48}$	B_8	7.0–8.5
486.421991	486.422003	-0.02	$M^{+\bullet}$	$C_{36}H_{54}$	B_9	7.0–8.5
540.469117	540.468953	0.30	$M^{+\bullet}$	$C_{40}H_{60}$	B_{10}	7.0–8.5
156.080700	156.080776	-0.49	$[M + H]^+$	$C_{11}H_{10}N$	AS	8.5–10.0
210.115029	210.115150	-0.58	$M^{+\bullet}$	$C_{14}H_{14}N_2$	A_2S	8.5–10.0
261.151354	261.151201	0.59	$M^{+\bullet}$	$C_{19}H_{19}N$	AS_2	8.5–10.0
314.178076	314.177750	1.04	$M^{+\bullet}$	$C_{22}H_{22}N_2$	A_2S_2	8.5–10.0
365.213930	365.213801	0.35	$M^{+\bullet}$	$C_{27}H_{27}N$	AS_3	8.5–10.0
418.240289	418.240350	-0.15	$M^{+\bullet}$	$C_{30}H_{30}N_2$	A_2S_3	8.5–10.0
471.266989	471.266899	0.19	$M^{+\bullet}$	$C_{33}H_{33}N_3$	A_3S_3	8.5–10.0
522.302608	522.302951	-0.66	$M^{+\bullet}$	$C_{38}H_{38}N_2$	A_2S_4	8.5–10.0

* Instead of monoisotopic peak, the most abundant signal is reported in the table.

** The observed polymer fragments were marked with abbrevition $A_aB_bS_s$, in which a, b, and s corresponds to the number of acrylonitrile, butadiene, and styrene monomers, respectively.

*** The observation time frame refers to temperature ramp program utilized in the DIP-MS analyses: time frames 5.5–7.0 min, 7.0–8.5 min and 8.5–10.0 min correspond to approximately 350, 400 and 450 °C, respectively.

Table S5. Summary of signals observed in HIPS-decaBDE sample (Br concentration of 1,000 ppm) during the DIP-MS analysis.

Experimental m/z	Theoretical m/z	Error (ppm)	Observed ion	Ion formula	Proposed compound**	Observation time frame(min)***
530.469526	530.469347	0.34	$M^{+\bullet}$	$C_{35}H_{62}O_3$	Irganox 1076	5.5–7.0
662.446238	662.445849	0.59	$M^{+\bullet}$	$C_{42}H_{63}O_4P$	Irgafos 168 oxide	5.5–7.0
881.257641*	881.257073	0.64	$M^{+\bullet}$	$C_{12}HBr_9O$	nonaBDE	5.5–7.0
959.167551*	959.167571	-0.02	$M^{+\bullet}$	$C_{12}Br_{10}O$	decaBDE	5.5–7.0
270.233973	270.234202	-0.85	$M^{+\bullet}$	$C_{20}H_{30}$	B_5	7.0–8.5
324.281062	324.281153	-0.28	$M^{+\bullet}$	$C_{24}H_{36}$	B_6	7.0–8.5
378.328110	378.328103	0.02	$M^{+\bullet}$	$C_{28}H_{42}$	B_7	7.0–8.5
432.374988	432.375053	-0.15	$M^{+\bullet}$	$C_{32}H_{48}$	B_8	7.0–8.5
486.421913	486.422003	-0.19	$M^{+\bullet}$	$C_{36}H_{54}$	B_9	7.0–8.5
207.116834	207.116827	0.03	$[M + H]^+$	$C_{16}H_{15}$	S_2	8.5–10.0
312.187281	312.187252	0.09	$M^{+\bullet}$	$C_{24}H_{24}$	S_3	8.5–10.0
415.241766	415.242027	-0.63	$[M + H]^+$	$C_{32}H_{31}$	S_4	8.5–10.0
520.312282	520.312453	-0.33	$M^{+\bullet}$	$C_{40}H_{40}$	S_5	8.5–10.0

* Instead of monoisotopic peak, the most abundant signal is reported in the table.

** The observed polymer fragments were marked with abbrevitions B_b and S_s, in which b and s corresponds to the number of butadiene and styrene monomers, respectively.

*** The observation time frame refers to temperature ramp program utilized in the DIP-MS analyses: time frames 5.5–7.0 min, 7.0–8.5 min and 8.5–10.0 min correspond to approximately 350, 400 and 450 °C, respectively.

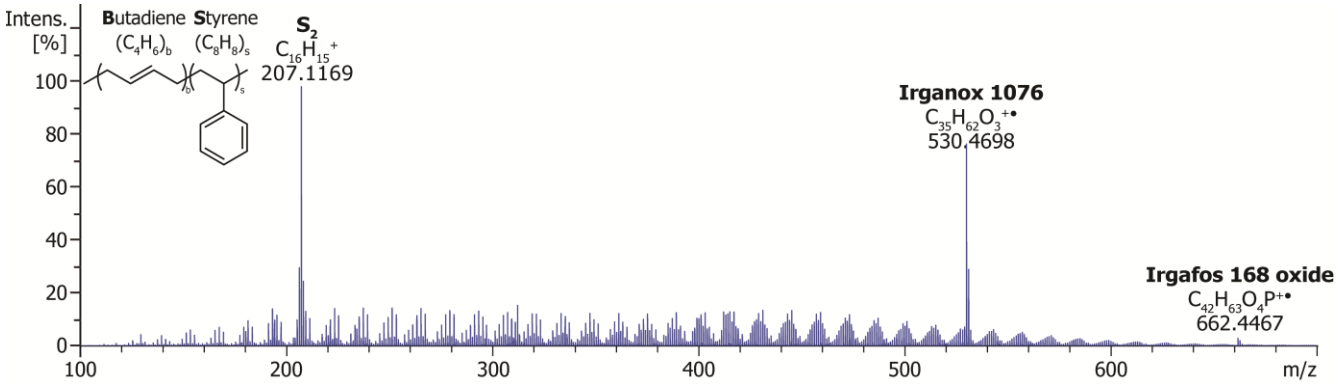

Figure S1. Averaged mass spectrum (time frame of 5.5–7.0 min) from DIP-MS measurement of HIPS sample without any BFRs.

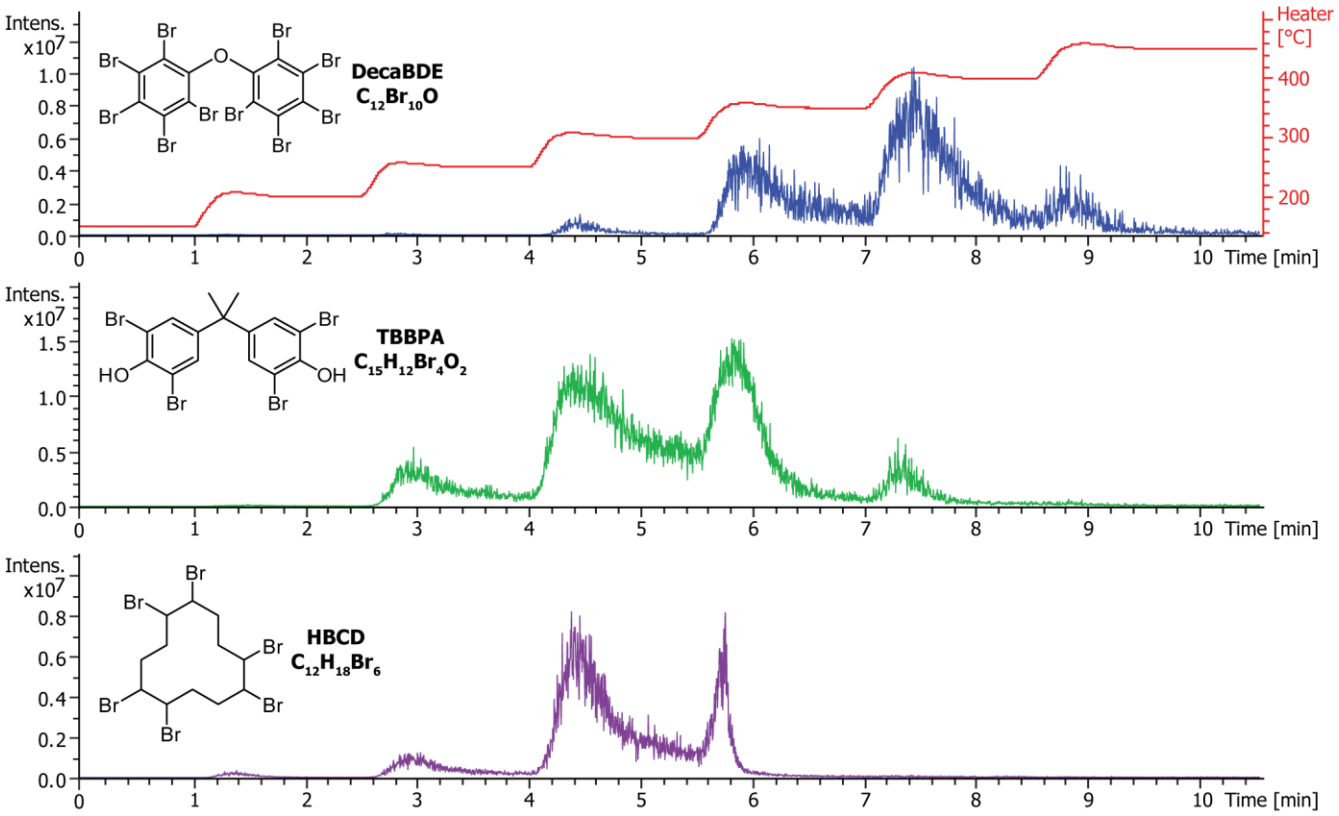

Figure S2. Total ion chromatograms from DIP-MS analysis of decaBDE (top), TBBPA (middle) and HBCD (bottom). The utilized APCI vaporizer temperature program is presented as a red line in the upmost chromatogram.

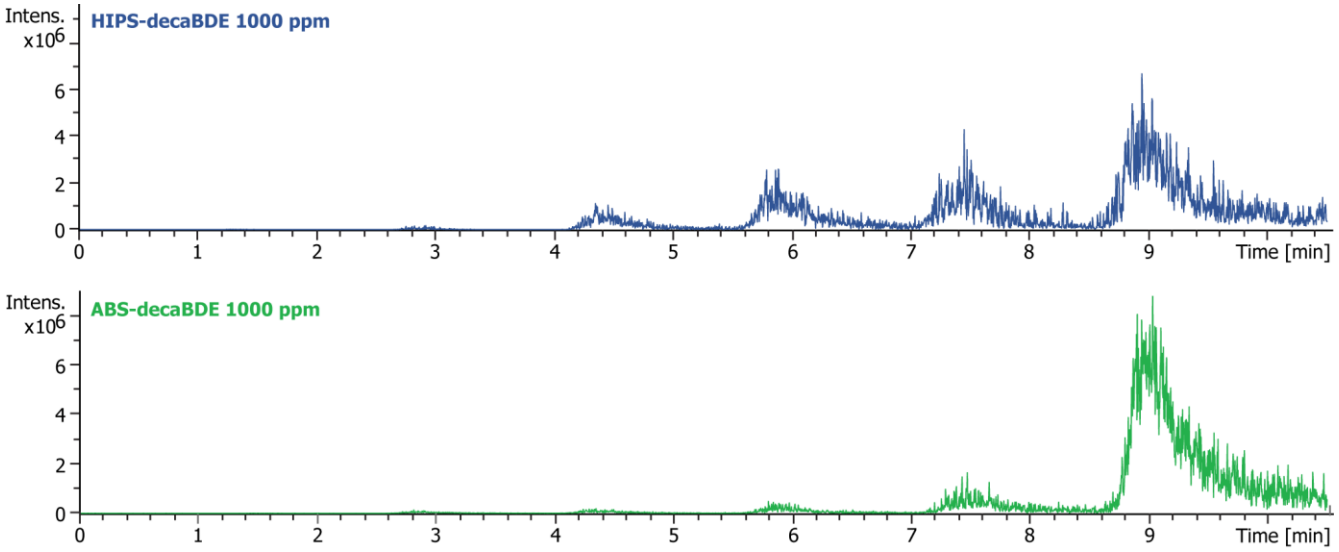

Figure S3. Total ion chromatograms from DIP-MS analysis of HIPS-decaBDE and ABS-decaBDE samples having Br concentrations of 1,000 ppm.

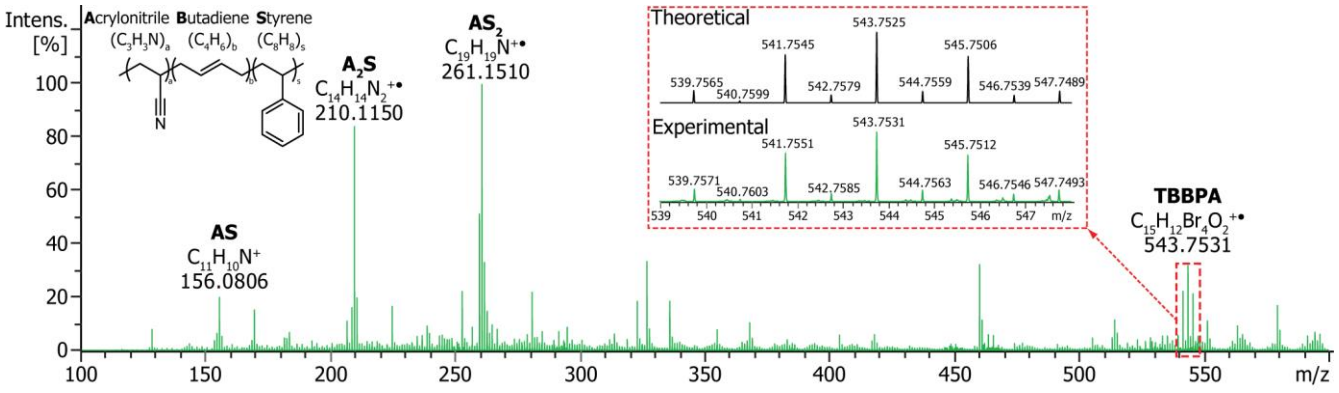

Figure S4. Averaged mass spectrum (time frame of 5.5–7.0 min) from DIP-MS measurement of ABS-TBBPA sample (Br concentration 1,000 ppm).

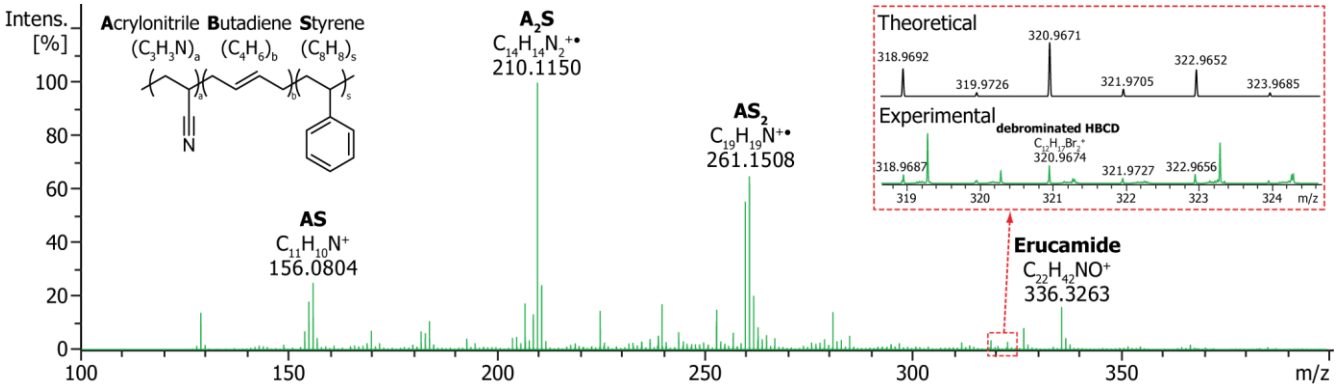

Figure S5. Averaged mass spectrum (time frame of 5.5–7.0 min) from DIP-MS measurement of ABS-HBCD sample (Br concentration 1,000 ppm).

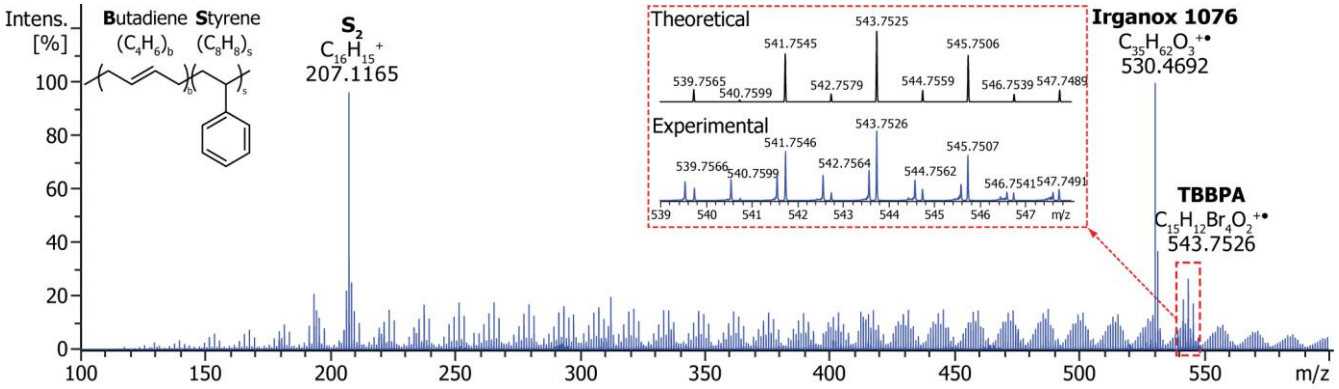

Figure S6. Averaged mass spectrum (time frame of 5.5–7.0 min) from DIP-MS measurement of HIPS-TBBPA sample (Br concentration 1,000 ppm).

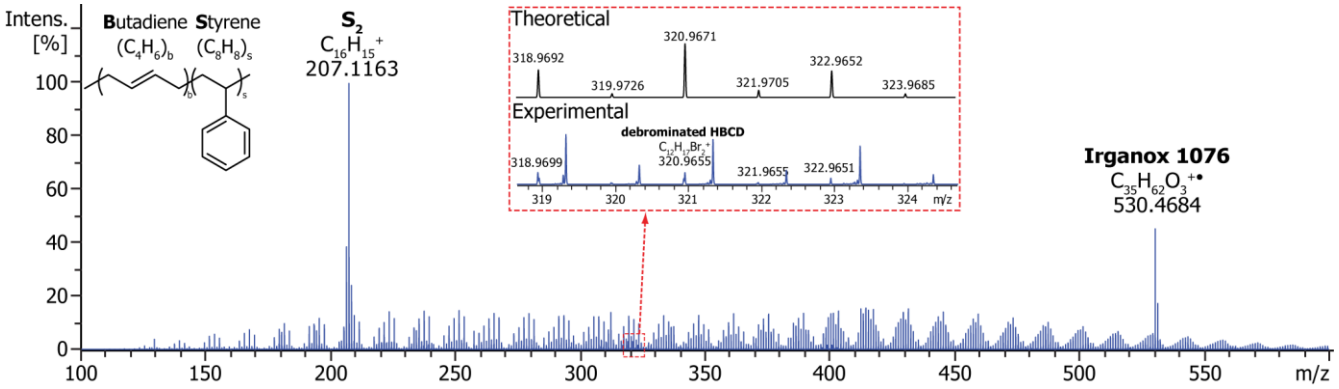

Figure S7. Averaged mass spectrum (time frame of 5.5–7.0 min) from DIP-MS measurement of HIPS-HBCD sample (Br concentration of 1,000 ppm).

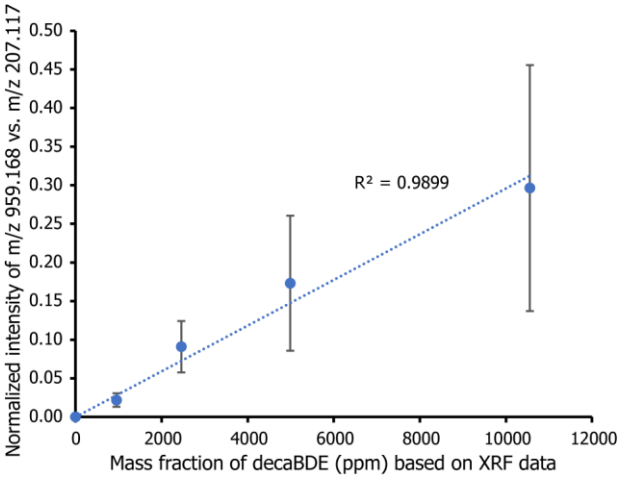

Figure S8. Normalized intensity of *m/z* 959.168 (decaBDE) versus *m/z* 207.117 (styrene dimer) compared to the mass fraction of decaBDE based on XRF data. The MS data was collected using a small sample size (<0.1 mg) and the error bars represent standard deviation of the mean between five parallel measurements.