



## Impact of brominated flame retardants on the thermal degradation of high-impact polystyrene

Guido Grause<sup>a</sup>, Daiki Karakita<sup>a</sup>, Jun Ishibashi<sup>a</sup>, Tomohito Kameda<sup>a</sup>, Thallada Bhaskar<sup>b</sup>, Toshiaki Yoshioka<sup>a,\*</sup>

<sup>a</sup> Graduate School of Environmental Studies, Tohoku University, Aramaki Aza Aoba 6-6-07, Aoba-ku Sendai 980-8579, Japan

<sup>b</sup> Bio-Fuels Division (BFD), CSIR – Indian Institute of Petroleum (IIP), Dehradun 248005, India

### ARTICLE INFO

#### Article history:

Received 10 July 2012

Received in revised form

22 August 2012

Accepted 18 September 2012

Available online 26 September 2012

#### Keywords:

Thermal degradation

Radical induced degradation

Cage-effect

Macro radicals

### ABSTRACT

The degradation of flame retarded high impact polystyrene (HIPS) was examined by thermogravimetry coupled with mass spectroscopy (TG-MS) and compared with that of polystyrene (PS). While the fate of the flame retardant draws a lot of attention, its impact on polymer degradation has been the focus of very little investigation. Temperature change was shown not to affect the product distribution of the thermal induced PS degradation. However, the presence of a brominated flame retardant resulted in changes in the HIPS degradation mechanism, with a larger variation of by-products formed and changes in the product distribution over the investigated temperature range. The early release of a large quantity of bromine radicals from the flame retardant caused the polymer backbone to break at various points (radical induced degradation). While the thermal degradation of PS was inhibited by the recombination of macro radicals (the cage-effect), the recombination of macro radicals induced by bromine radicals was prevented by the fast diffusion of HBr. Pure PS produced mainly styrene by the depolymerisation of the polymer chain after the formation of macro radicals and some oligomers from backbiting/ $\beta$ -scission. Flame retarded HIPS produced various oligomers, many of which were not produced from pure PS. It is assumed that after backbiting, the tertiary radical was terminated by recombination with other radicals, and dimers and trimers were formed from styrene during secondary reactions. One important source of hydrogen for this process was the formation of aromatic compounds, which kept the residual char small.

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### 1. Introduction

The electronics industry is the world's largest and fastest growing manufacturing industry. Rapid growth, combined with rapid product obsolescence and discarded electronics has made electronics the fastest growing waste fraction in this age. The success of this industry over the last decade in developing mass consumer market for computers, cell phones, and other personal electronic equipment has been phenomenal. Society must now find ways for the safe recovery of materials (precious and non-precious metals, plastics, etc.) in an economical way. It is estimated that ca. 315 million computers had become obsolete by 2005, resulting in 1.8 Mt of waste plastics containing at least 159 000 tons of brominated flame-retardants from monitors [1]. Considering the present growth rate, a further rise in the quantity of flame-retarded e-waste is inevitable.

The degradation of flame-retarded plastics from e-waste became a point of interest due to the increasing awareness of the need to recycle plastic waste. There is a plethora of work on the thermal behaviour of brominated flame-retardants [2–9], but little has been done on the impact of the flame retardant on backbone polymer degradation [10,11]. In the present work, we investigated the impact brominated flame-retardants would have on the HIPS degradation. Due to their importance, decabromodiphenyl ether (decaBDE) and decabromodiphenyl ethane (DBDPE) were chosen as examples for the large number of brominated flame-retardants in use. It could be shown that DBPE and DDB have a very similar degradation behaviour [12], which might also be true for others. The use of DBPE is prohibited in several parts of the world; in Europe since 2008 by the European directive 2002/95/EC (Restriction of Hazardous Substances – RoHS) [13]. However, some electronic and electric equipment is used for decades. Therefore, both flame-retardants will have relevance also in the future.

The thermal degradation of PS is a radical process, including an initiation stage, a propagation stage, and a termination stage. The

\* Corresponding author. Tel./fax: +81 22 795 7211.

E-mail address: [yoshioka@env.che.tohoku.ac.jp](mailto:yoshioka@env.che.tohoku.ac.jp) (T. Yoshioka).

degradation of pure PS depends on the polymerisation method and the end groups of the polymer chain. The starting temperature of the degradation is about 300 °C for radical polymerised PS, while anionic polymerised PS shows higher thermal stability. At lower temperatures, the high viscosity of the polymer melt reduces the diffusion velocity of the products, causing high recombination rates of macro radicals, which is known as “the cage effect” [14,15]. Furthermore, olefinic products undergo repolymerisation at low temperature, preventing the escape of degradation products and causing the branching of the polymer [16].

It is widely accepted that the initial step is the fission of the main chain. Radical polymerised PS is degraded by the fission of weak head-to-head links [17], while anionic polymerised PS prefers random fission as the initiation step, which results in higher thermal stability [18]. Guaita et al. [19] reported a zip length of about 50 units for the depolymerisation. However, unzipping as a dominant process was not observed during a MALDI-TOF investigation. It was assumed that depolymerisation was a high-energy process and backbiting/ $\beta$ -scission was the dominant degradation pathway [20]. Polce et al. [21] used a similar technique and reached the conclusion that the energy requirements for depolymerisation and backbiting/ $\beta$ -scission are similar, but that depolymerisation is the faster process at higher energy levels. While depolymerisation results in monomeric styrene units, backbiting/ $\beta$ -scission leads to oligomers, which can also be formed as secondary products by the recombination of styrene. Ohtani et al. [22] found mainly homodimers and trimers by the degradation of styrene/styrene- $D_8$  block-copolymers, and suggested backbiting/ $\beta$ -scission is the main process for the formation of oligomers. Dean et al. [23] found evidence in their investigation for the formation of oligomers by the recombination of styrene. These results suggest that the degradation process is strongly influenced by the methods and conditions used. Termination is simply achieved by the evaporation of small radicals [15].

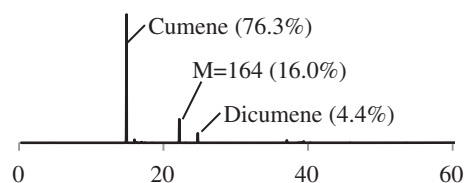
The degradation of brominated PS has also been extensively investigated [24–28]. Ring brominated PS has been shown to have a higher thermal stability than unmodified PS. Since its degradation mainly results in monomers, it is assumed that the degradation behaviour of both brominated PS and PS are the same. The bromination of the backbone significantly reduces the thermal stability of the polymer. The degradation behaviour of chain-brominated PS was shown to be similar to that of poly(vinyl chloride). HBr was eliminated at a low degradation temperature and polyene structures were formed. The backbone was degraded at higher temperatures. It has to be noted that chain scission was observed during the bromination of PS, which might have influenced the thermal stability of the polymer as well. In any case, the degradation of brominated PS did not show any similarities with the degradation of HIPS in the presence of brominated flame retardants [12].

In the present investigation, we report the degradation mechanism of the polystyrene matrix, reflecting the role of flame retardant and synergist ( $Sb_2O_3$ ) on the formation of non-

**Table 1**

Composition of the HIPS samples used.

Sample	Flame retardant		Synergist	
	Abbreviation	Compound	Content (wt.%)	Compound
PS	–	–	–	–
DPE-Sb(5)	–	Decabromodiphenyl ether	13	$Sb_2O_3$
DPE-Sb(0)	–	Decabromodiphenyl ether	13	–
DDB-Sb(5)	–	Decabromodibenzyl	13	$Sb_2O_3$
DDB-Sb(0)	–	Decabromodibenzyl	13	–

**Fig. 1.** Example for the verification of the purity of an ion count for tracing a certain compound:  $m/z = 120$  of DDB-Sb(0).

brominated compounds. The focus of earlier investigations on flame retarded HIPS has almost exclusively been on the degradation of the flame retardant and its environmental impact. The issue of changes in the degradation behaviour of the polymer matrix,

**Table 2**

Identified products from the quartz glass reactor experiment. Bold crosses mark products with a peak area of at least 1/10 of that of styrene.

No.	Compound	$m/z$	$t_r$ [min]	PS	DDB-Sb(0)	DDB-Sb(5)	DPE-Sb(0)	DPE-Sb(5)
1	Toluene	92	9.2	×	×	×	×	×
2	Ethylbenzene	106	12.5	×	×	×	×	×
3	Styrene	104	13.8	×	×	×	×	×
4	Cumene	120	14.9	×	×	×	×	×
5	$\alpha$ -Methylstyrene	118	17.0	×	×	×	×	×
6	Propenylbenzene	118	18.6			×	×	
7	$M = 164$	164	22.2		×	×	×	
8	Bromoethylenebenzene	184	22.8		×		×	
9	Dicumene	238	24.8		×	×		
10	1,3-Diphenylpropane	196	36.5	×	×	×	×	×
11	Diphenylpentene	222	36.6		×	×		×
12	Dimer	208	36.9	×	×	×	×	
13	1,3-Diphenylbutane	210	37.0		×	×	×	×
14	Diphenylpentene	222	37.4					×
15	Dimer	208	37.5		×		×	
16	Diphenylpentene	222	37.7		×	×	×	
17	Dimer	208	38.0	×	×	×	×	×
18	Diphenylpentene	222	38.1			×		
19	Diphenylpropene	194	38.3	×				×
20	Diphenylpentadiene	220	38.3		×	×	×	
21	1,4-Diphenylbutane	210	38.7		×		×	×
22	Dimer	208	39.2	×	×	×	×	×
23	Diphenylpentadiene	220	39.3		×			
24	Methyl-phenyl-indene	130	39.3		×	×	×	
25	Diphenylhexene	236	39.5					×
26	Dimer	208	39.7	×	×		×	×
27	Dimer	208	40.2	×	×			
28	Diphenylpentene	222	40.2					×
29	Diphenylpentadiene	220	40.9		×	×	×	
30	1-Phenyl-naphthalene	204	41.0		×		×	
31	Diphenylpentadiene	220	42.2	×	×	×	×	×
32	Diphenylpentene	222	42.4		×			
33	2-Phenyl-naphthalene	204	43.5		×	×		
34	Diphenylpentadiene	220	43.6		×			
35	Diphenylhexadiene	234	44.0		×			
36	Methyl-phenyl-naphthalene	218	45.9	×	×	×	×	×
37	Trimer	312	50.3	×	×	×	×	×
38	1,3,5-Triphenylpentane	300	51.4		×	×	×	
39	Trimer	312	51.6	×				×
40	Trimer	312	53.1					×
41	Trimer	312	53.3	×	×	×	×	×
42	Trimer	312	54.3	×				
43	Triphenylhexadiene	310	54.6		×			
44	Quaterphenyl	306	55.4		×			
45	Trimer	312	55.8	×	×			
46	Trimer	312	56.4	×	×	×		
47	Quaterphenyl	306	58.9	×	×			×
48	Tetraphenylheptane	404	61.5		×		×	×
49	1,3,5,7-Tetraphenylheptane	404	61.6		×	×	×	×
50	Pentaphenylnonane/tetramer	508/416	62.3				×	×

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