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Influence of brominated flame retardant thermal decomposition products on HALS

K. Antoš [a], J. Sedlář [b,*]

[a] Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
[b] Polymer Institute Brno, spol. s.r.o., Tkalcovská 36/2, 656 49 Brno, Czech Republic

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Abstract

Brominated flame retardants may undergo thermal decomposition at temperatures lower than those of polymer combustion. Decabromodiphenyl ether, which was the main subject of this study, exhibits a threshold decomposition temperature that is close to polypropylene processing temperatures. In the presence of hydrocarbon polymer the loss of bromine leads to the formation of lower brominated by-products and hydrobromic acid. The latter attacks stabiliser package components, HALS in particular. The aminium hydrobromide salt thus formed is well known to be inefficient as a stabiliser. Moreover, it has been found in this work that it is less thermally stable than the parent amine. In the case of polypropylene it has been demonstrated that excessive processing temperature of polymer containing polybrominated aromatic flame retardant and HALS results in an irreversible loss of the light stabiliser from the very beginning of material service life.

Keywords: HALS; Polypropylene; Decabromodiphenyl ether; Brominated flame retardant; Thermal decomposition; Hydrobromic acid

1. Introduction

Highly brominated organic compounds are still among the most widely used flame retardants for plastics although there has recently been some concern about them, namely in connection with health and environmental issues [1,2]. Their function is based upon hydrobromic acid (HBr) evolution through the thermal decomposition of the retardant in the course of combustion (often at more than 1000 °C) [3]. The HBr then interrupts the combustion chemistry of the fire in the gas phase. It can be assumed that also at lower temperatures, e.g. at those used during plastics processing, the decomposition of flame retardant can take place to a certain extent. It follows from the values of dissociation energies (see Table 1) [4] that the C−Br bond is often the weakest one in the flame retardant molecule and its splitting thus represents the primary reaction step.

The mechanism of thermal decomposition of brominated flame retardants will depend on their structure, namely on the availability of hydrogen. Thus, aliphatic bromo-compounds undergo thermally initiated dehydrobromination involving intramolecular hydrogen abstraction [5]. This gives rise to HBr and unsaturated lower brominated derivatives while the aromatic bromo-compounds undergo radical debromination [6]. In the presence of hydrogen donors (polymer, impurities, etc.) the bromine radical forms HBr. The debromination leads to aromatic lower brominated congeners derived

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* Corresponding author. Tel.: +420 545 211 398; fax: +420 545 211 141.

E-mail address: sedlar@polymer.cz (J. Sedlář).

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Table 1
Selected bond dissociation energies [4]

Bond type	Bond dissociation energy (kJ mol^{-1})	Bond type	Bond dissociation energy (kJ mol^{-1})
H–Br	366	$C_6H_5O–C_6H_5$	368
Br–Br	194	$C_6H_5O–C_2H_5$	268
C_2H_5–Br	285	C_2H_5–H	410
i-C_3H_7–Br	285	*i*-C_3H_7–H	398
tert-Bu–Br	280	$CH_3–CH_3$	368
C_6H_5–Br	313	$CH_3–C_6H_5$	418
$C_6H_5CH_2$–Br	230		

from the parent structure [6]. Beside that, formation of some other compounds, such as polybrominated dioxins (PBDD) and dibenzofurans (PBDF) has also been reported [6–8]. From the viewpoint of polyolefin stabilisation the HBr is the most important product in both cases.

In this study we have examined the HBr formation in the course of thermal decomposition of some brominated flame retardants with a special accent placed on aromatic compounds, decabromodiphenyl ether in particular.

2. Experimental

2.1. Chemicals

- Decabromodiphenyl ether (FR-1): CAS: 1163-19-15, Albemarle Corporation, USA, purity ca 98% (2% nonabromodiphenylether).
- Hexabromocyclododecane (FR-2): CAS: 25637-99-4, Great Lakes Chemical Corporation, USA.
- Tris(tribromoneopentyl)phosphate (FR-3): CAS: 19186-97-1, FMC Corporation, UK.
- Tetrabromobisphenol-A-bis(2,3-dibromopropyl ether)(FR-4): CAS: 21850-44-2, Albemarle Corporation, USA.
- Tribromoneopentylalcohol (FR-5): CAS: 36483-57-5, Dead Sea Bromine Group, Israel.
- Antimony trioxide (Sb_2O_3): TIMONOX® Blue Star, Cookson Ltd., UK.
- OCTA: Defined mixture of lower brominated diphenyl ethers, (HPLC standard), Dead Sea Bromine Group, Israel.
- Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidinyl) imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidinyl)imino]], (STAB-1): CAS: 71878-19-8, 500, Ciba Specialty Chemicals, Chimassorb® 944.
- Decanedioic acid, bis(2,2,6,6-tetramethyl-4-piperidinyl)ester (STAB-2): CAS: 52829-07-9, Ciba Specialty Chemicals, Tinuvin® 770.
- Irganox® B 225, Ciba Specialty Chemicals.
- Diethylamine (DEA): Fluka, (p.a.).
- Decahydronaphthalene: (98%) (*cis* + *trans*), Sigma–Aldrich.
- Triethyl phosphite: Fluka (p.a.).
- Docosane (C_{22}): Fluka.
- Polypropylene (PP): Mosten PH-6 (unstabilised fluff stored under an inert atmosphere), homopolymer, MFI = 5–6 dg min^{-1}, Chemopetrol a.s., CZ.
- Tetrahydrofuran (THF): Loba (p.a.).
- Calcium stearate (CaSt): Polyolefin grade, FACI SpA.

2.2. Experimental procedure and analytical methods

Comparison of thermal stability of a series of selected compounds was done by thermogravimetric analysis (TGA) under a nitrogen atmosphere with the programme rate 10 °C min^{-1}, t_{max} = 600 °C, using a TGA-2950 Thermogravimetric Analyser, Texas Instruments, USA.

Thermal decomposition of FR-1 supplemented with the analysis of products was carried out in a Pyrex capillary filled with solid sample. The capillary was placed in an oven and heated up to the selected temperature (heating rate 10 °C min^{-1}, t_{max} = 400 °C). Once the temperature was reached, the sample was exposed for additional 10 min then taken out and rapidly cooled down to ambient temperature. The capillary was broken either under toluene (to analyse parent retardant and organic products) or in NaOH solution (to analyse HBr evolved).

The concentration of residual FRs was determined by HPLC on a Hewlett-Packard 1050 instrument (mobile phase acetonitrile/water, 70/30, isocratic mode, Nucleosil 120-5C18 CC125/3 column, UV detection at 225 nm) employing the external standard method. The products of FR-1 decomposition, lower brominated by-products, were determined by comparative HPLC under the above described conditions using the OCTA standard whose HPLC chromatogram is presented in Fig. 1.

HBr was determined in the form of NaBr via argentometric titration (0.002 N $AgNO_3$, pH = 2) employing potentiometric detection and standard addition method (KBr) on an E436 D Metrohm Herisau instrument fitted with an E436 Potentiograph Metrom Herisau detector.

The concentration of STAB-1 was determined in form of piperidinium sulphate salt. Prior to analysis, the stabiliser was extracted from polymer matrix with decahydronaphthalene (containing DEA). After dissolving, diluted sulphuric acid was added and the aminium salt was extracted into the aqueous layer. The extract was then subjected to UV spectrometric analysis using the external calibration method. A Lambda 900 UV/VIS/NIR Perkin–Elmer Spectrometer was used in the 200–300 nm region.