Central Lancashire Online Knowledge (CLoK)

Title	Disulfides – Effective radical generators for flame retardancy of polypropylene
Type	Article
URL	https://clok.uclan.ac.uk/id/eprint/13651/
DOI	https://doi.org/10.1016/j.polymdegradstab.2014.09.013
Date	2014
Citation	Pawelec, Weronika, Holappa, Anton, Tirri, Teija, Aubert, Melanie, Hoppe, Holger, Pfaendner, Rudolf and Wilén, Carl-Eric (2014) Disulfides – Effective radical generators for flame retardancy of polypropylene. Polymer Degradation and Stability, 110. pp. 447-456. ISSN 01413910
Creators	Pawelec, Weronika, Holappa, Anton, Tirri, Teija, Aubert, Melanie, Hoppe, Holger, Pfaendner, Rudolf and Wilén, Carl-Eric

It is advisable to refer to the publisher's version if you intend to cite from the work.
https://doi.org/10.1016/j.polymdegradstab.2014.09.013

For information about Research at UCLan please go to http://www.uclan.ac.uk/research/

Disulfides - effective radical generators for flame retardancy

of polypropylene

Weronika Pawelec,[1] Anton Holappa,[1] Teija Tirri,[1] Melanie Aubert,[1] Holger Hoppe,[2] Rudolf Pfaendner,[3] Carl-Eric Wilén[1*]

[1]Laboratory of Polymer Technology, National Center of Excellence for Functional Materials (FUNMAT),

Åbo Akademi University, Biskopsgatan 8, FIN-20500 Åbo, Finland; emails: wpawelec@abo.fi, anton.holappa@abo.fi, teija.tirri@abo.fi, maubert@abo.fi, cwilen@abo.fi

[2]Performance Materials Research, BASF Schweiz AG, Klybeckstr. 141, CH-4057 Basel, Switzerland;

email: holger.hoppe@basf.com

[3]Fraunhofer Institute for Structural Durability and System Reliability LBF, Division Plastics, Schlossgartenstr. 6,

D-64289 Darmstadt, Germany, email: Rudolf.Pfaendner@lbf.fraunhofer.de

* Corresponding author: Tel: +358 2215 4308, Mobile: +358 50 4096406, e-mail: cwilen@abo.fi

Abstract

The potential of thirteen aliphatic, aromatic, thiuram and heterocyclic substituted organic disulfide derivatives of the general formula R-S-S-R' as a new group of halogen-free flame retardants (FR) for polypropylene films have been investigated. According to DIN 4102-1 standard ignitibility test, for the first time it has been demonstrated that many of the disulfides alone can effectively provide flame retardancy and self-extinguishing properties to polypropylene (PP) films at already very low concentrations of 0.5 wt%. In an effort to elucidate the mechanism of the thermal decomposition of disulfide derivatives the fragmentation patterns of the evolved gases from a thermogravimetric analyzer (TGA) have been analyzed by simultaneous mass spectrometry (MS) and Fourier transform infrared spectrometry (FTIR). The main decomposition products initiated by homolytic scission of the S-S bond and/or scission of the C-S bond were identified as thiols, aliphatic and aromatic hydrocarbons, isothiocyanates (depending on the disulfide structures) with further evolution of elemental sulfur and sulfur dioxide at temperatures of above 300 $^{\circ}$C and 450 $^{\circ}$C, respectively. Based on this preliminary study, we have shown that disulfides represented by e.g. diphenyl disulfide (**1**), 5,5'-dithiobis(2-nitrobenzoic acid) (**2**), bis(1-phenyl-1H-tetrazol-5yl)-disulfide (**4**), 2-bisbenzothiazole-2,2'-disulfide (**6**) and N,N-dithiobis-(phtalimide) (**10**) constitute a new halogen-free family of additives for flame retarding of polypropylene.

1. Introduction

Free radical processes play a vital role in many fields of organic chemistry including combustion, auto-oxidation, polymerizations, vulcanizations as well as in living systems, since they are also involved in both biological and even many pathological chain reactions [1,2]. In general, free radicals are chemical species characterized by an odd number of orbital electrons or by pairs of electrons of similar directional spin isolated singly in separate orbitals. In recent years, in order to better understand the principles of free radical chain reactions, their formation, structure, selectivity and reactivity have been the subject of intensive research [3-6]. Free radical reactions frequently occur in gas phase although they can also occur in the liquid phase. They often show an induction period and proceed by a chain reaction, which can be divided into three distinct processes: initiation, propagation and termination. Usually formation of radicals is initiated by radiation (e.g. light) [7], heat [8] (e.g. thermolysis of peroxide or azo compounds) or redox systems [9]. Inhibition of radical processes is possible by derivatives (inhibitors), which react rapidly with free radicals [10] (e.g. hydroquinone). These kinds of radical reactions are rarely acid or base catalyzed and often proceed at a rate independent of the polarity of the medium.

The lifetime for most of the generated free radicals is usually short. However, long-living radicals also exist and can be classified into stable (molecular oxygen), persistent (TEMPO, nitroxyl radicals) and diradicals (atmospheric oxygen). Various radical generators based on different substance classes have had undoubtedly an impact on both polymer chemistry and have played an important role in many different fields of natural sciences. In particular, free radicals are involved in polymer degradation [11-14], controlled free radical polymerization [15], grafting processes [16], cross-linking of polymers and chemical reactions (cyclizations,

additions, decarboxylation) [17] and wide applications in biochemistry [18]. It is well known, that free radicals are also important (and influence ignition, heat release, flame propagation and/or flame quenching) as intermediates in the combustion reactions of various materials and the flammability of a given material is strongly dependent on the concentration of free radicals [19].

More recently, it has been shown that selected radical precursors may also play a significant role as flame retardants for various polymers [20,21]. From the viewpoint of flame retardancy of polymers mainly radical generators triggered by thermolysis or redox systems have been successfully used to suppress and retard the fire response of polymeric materials [21,22]. In the past it has been demonstrated that certain peroxides can be used as synergists to enhance the action of brominated flame retardants (BFR) [23-29], whereas azo compounds [30] and alkoxyamines [12,31] have been shown to provide self-extinguishing properties to polymers even by themselves. Thus, it has been established that radical precursors that are capable of generating various carbon (e.g. azoalkanes and related structures), oxygen (e.g. peroxides, alkoxyamines) and nitrogen (e.g. triazenyl, alkoxyamines) centered radicals can be very useful as flame retardant additives. These additives based on selective radical generators interrupt or delay the combustion process that takes place in the gas phase by terminating the highly reactive radicals OH· and O· produced from the chain-branching reaction of combustion. Otherwise the formed hydroxyl and oxygen radicals would continue to propagate and sustain the combustion process.

As a consequence of this, we have been interested in the further design and application of different free radical generators for use as novel halogen-free flame retardants. Our interest towards disulfides R-S-S-R' stems from the fact that they are a neat source to sulfur centered

thiyl radicals, where the sulfur atom is bonded to only one substituent. As for alkoxyl radicals, thiyl radicals have a plane of symmetry and two electronic structures of similar energy. The unpaired electron lies in an orbital, which is either symmetric or antisymmetric with respect to the plane. Compared to the O-O bond, the S-S bond requires significantly higher temperatures (200 - 300 ºC) than peroxides (80 - 150 ºC) for thermolysis [32]. The higher thermal stability of disulfides is also beneficial from the standpoint of polymer processing, since polypropylene is normally processed at temperatures of ca. 230 °C or above. In contrast to alkoxy radicals they do not undergo β−fragmentation reactions and they only abstract hydrogen with difficulty from saturated hydrocarbons. Moreover the S-S bond possesses a unique character since it is an easily isolable and at the same time is a very labile bond. The chemical structures of disulfides evaluated in this study are depicted in Figure 1.
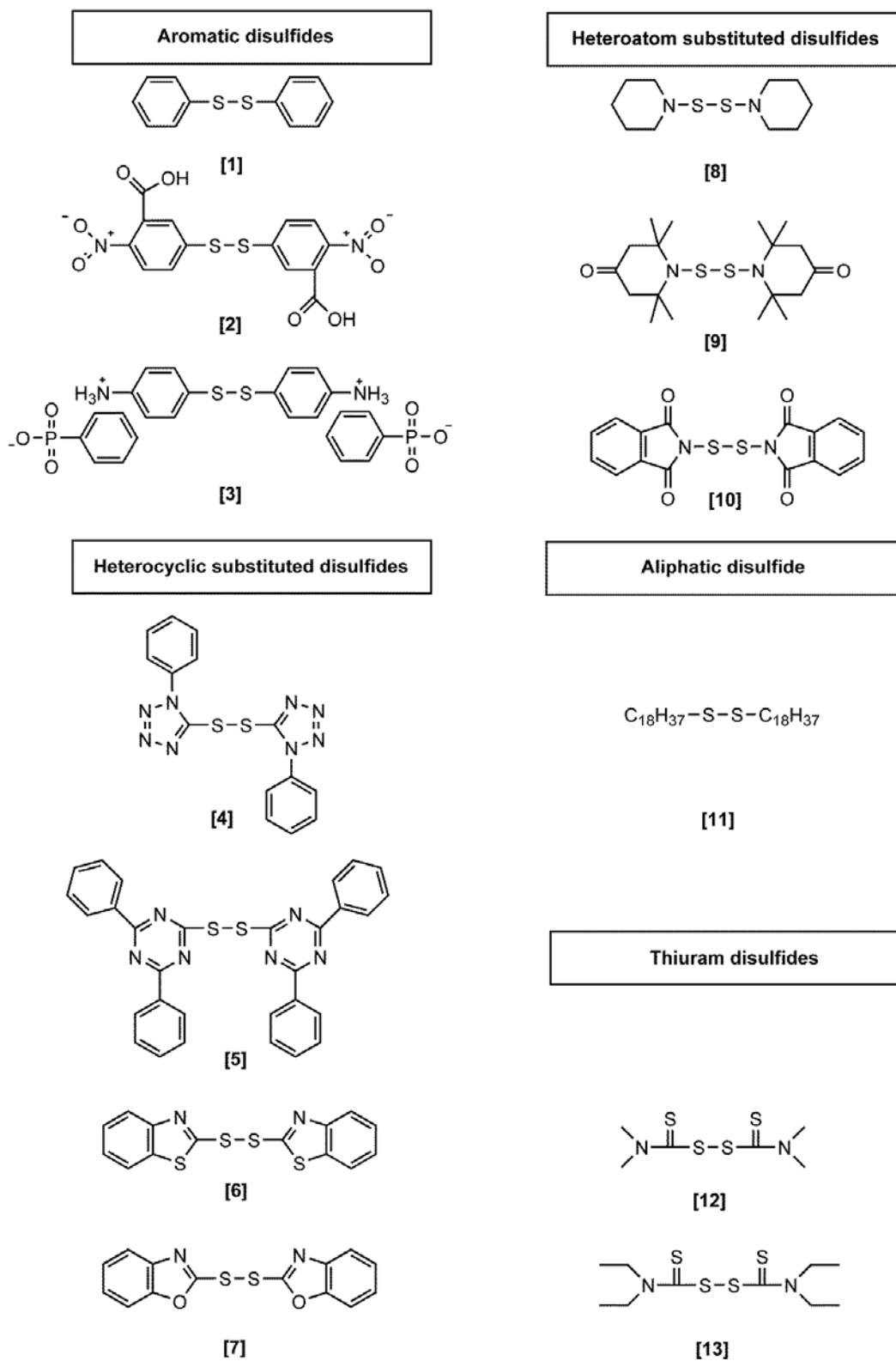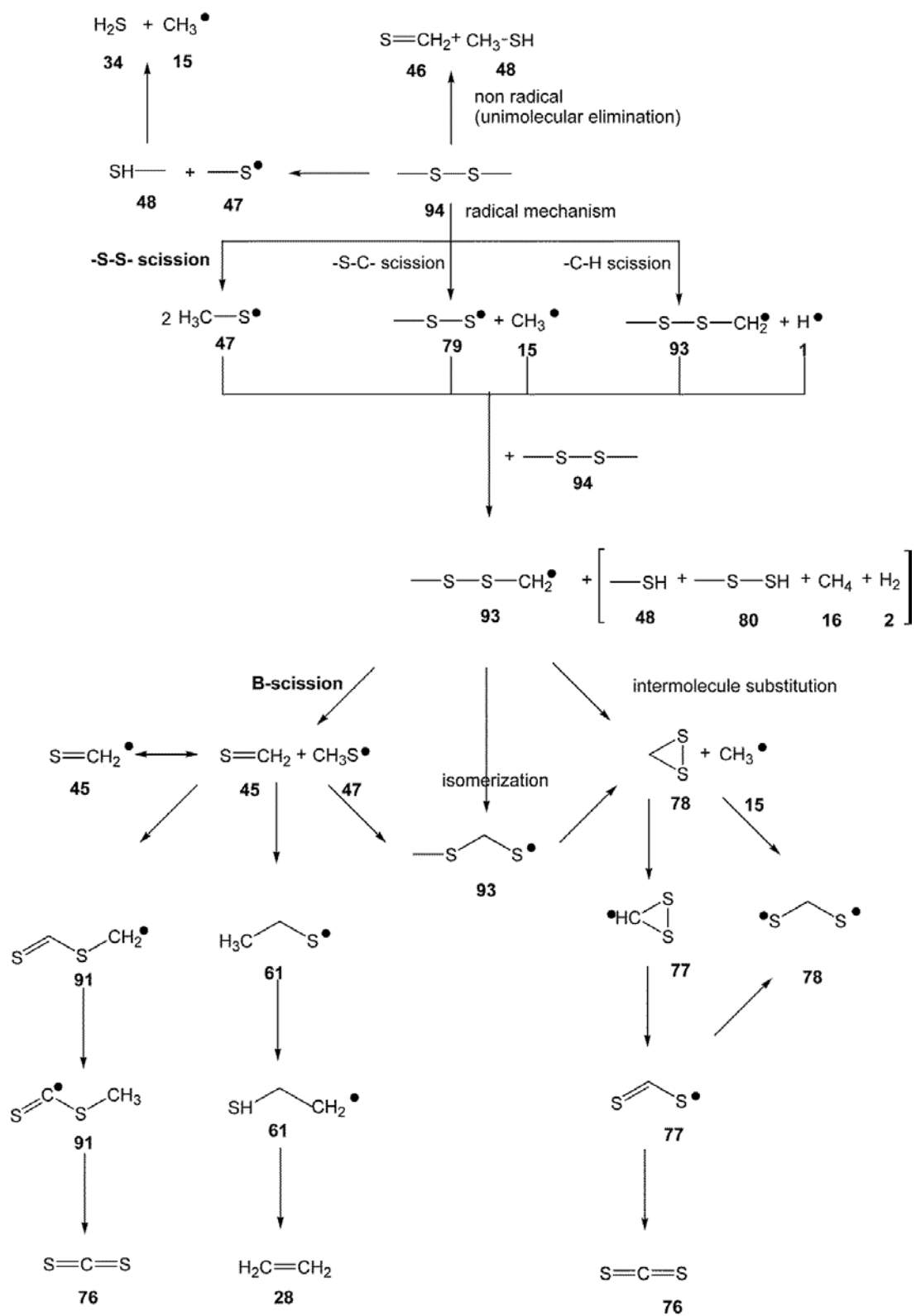
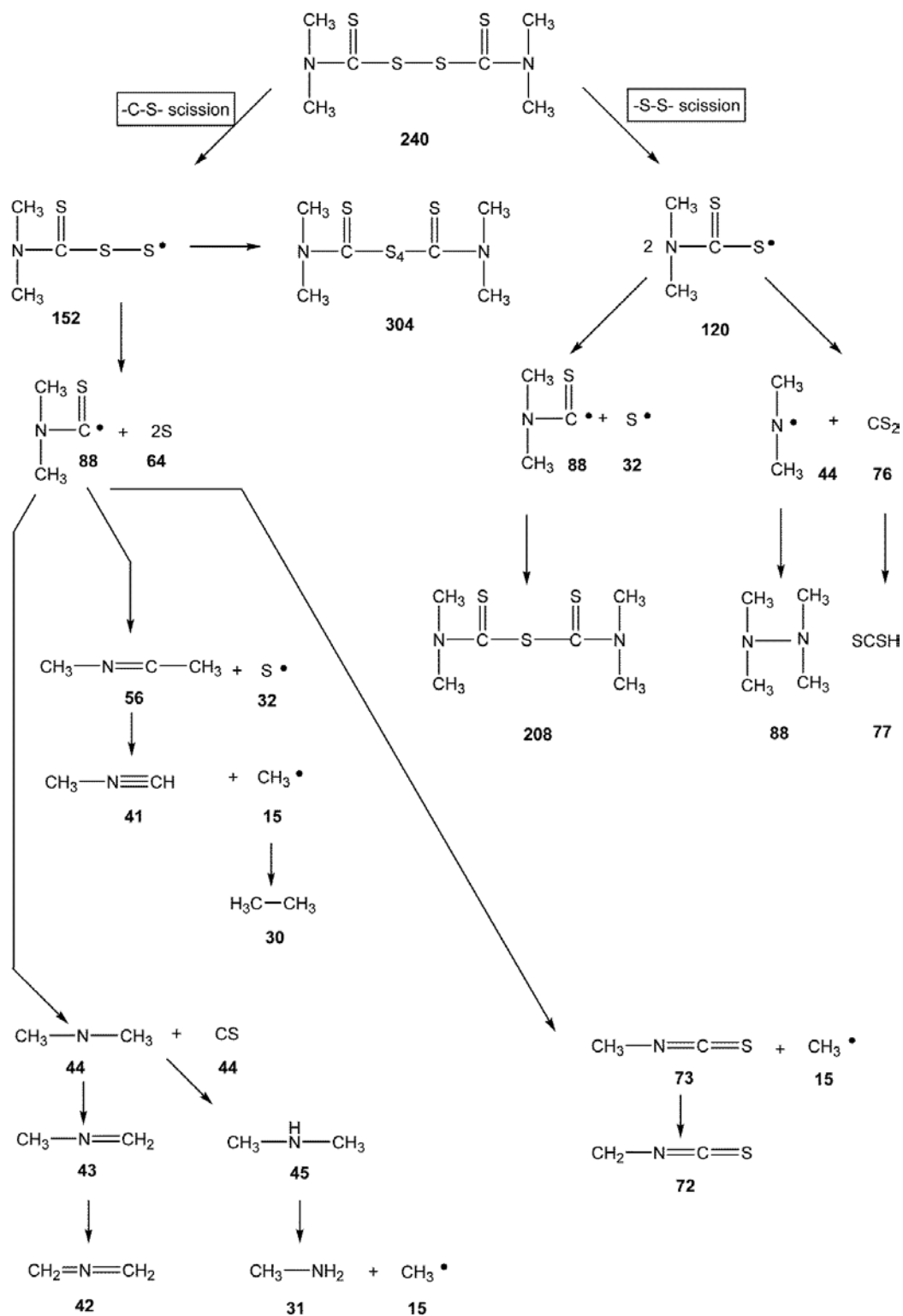**Fig. 1.** Molecular structures of disulfides.

Disulfides represent a class of compounds having the general structure R-S-S-R' where R and R' are either alkyl or aryl groups. They can be prepared in high yields by controlled oxidation of thiols using different reagents and oxidants under a broad range of experimental conditions such as sonication [33,34]. The selected compounds used for this study have found utility as rubber vulcanization accelerators [35] (compounds **6** and **7**), devulcanizators [36] (compound **1**), thermal stabilizers, corrosion inhibitors [37] (compound **6**), agents for determination of thiol groups [38] (compound **2**) and/or initiators of polymerizations [39] (compound **12**). In the past, some combinations of flame retardants based on halogen or metal hydroxides in combination with disulfides as synergists have been claimed [40]. For example some disulfides presented in this paper (e.g. disulfide **6**) are claimed to be effective flame retardant synergists with halogens in polystyrene [23]. Moreover, elemental sulfur and other polysulfides are also known as effective flame retardant components [41-45]. Recently, it has also been reported in the patent literature that disulfides together with halogenated flame retardants enhance the flame retardant properties of engineering plastics such as polyamides and polyesters [46,47]. In the past, a vast number of both experimental and theoretical studies to assess the reaction mechanisms of the thermal decomposition of different disulfide families have been performed. These research efforts have yielded important information of sulfur compounds behavior at elevated temperatures. In general, the S-S bond in disulfides is the weakest bond and there seems to be a consensus that, independently of the structure it first undergoes homolytic cleavage, whereby thiyl radicals are formed, as depicted in reactions Scheme 1 for aromatic[48], aliphatic [49], thiuram [50] and benzothiazole disulfides [51]. The proposed reaction mechanisms for the various families of disulfides relevant for this study have been summarized in Scheme 1.
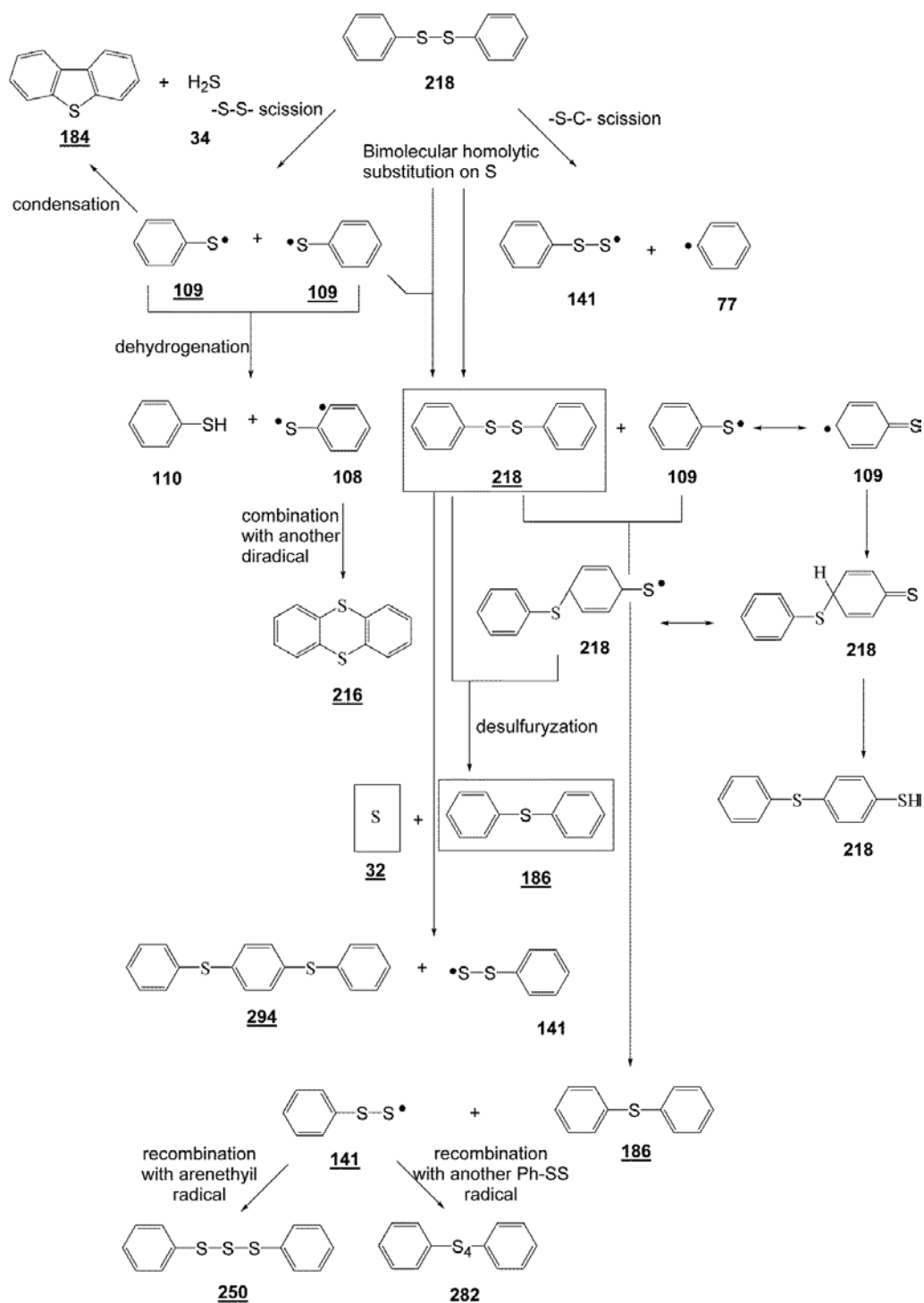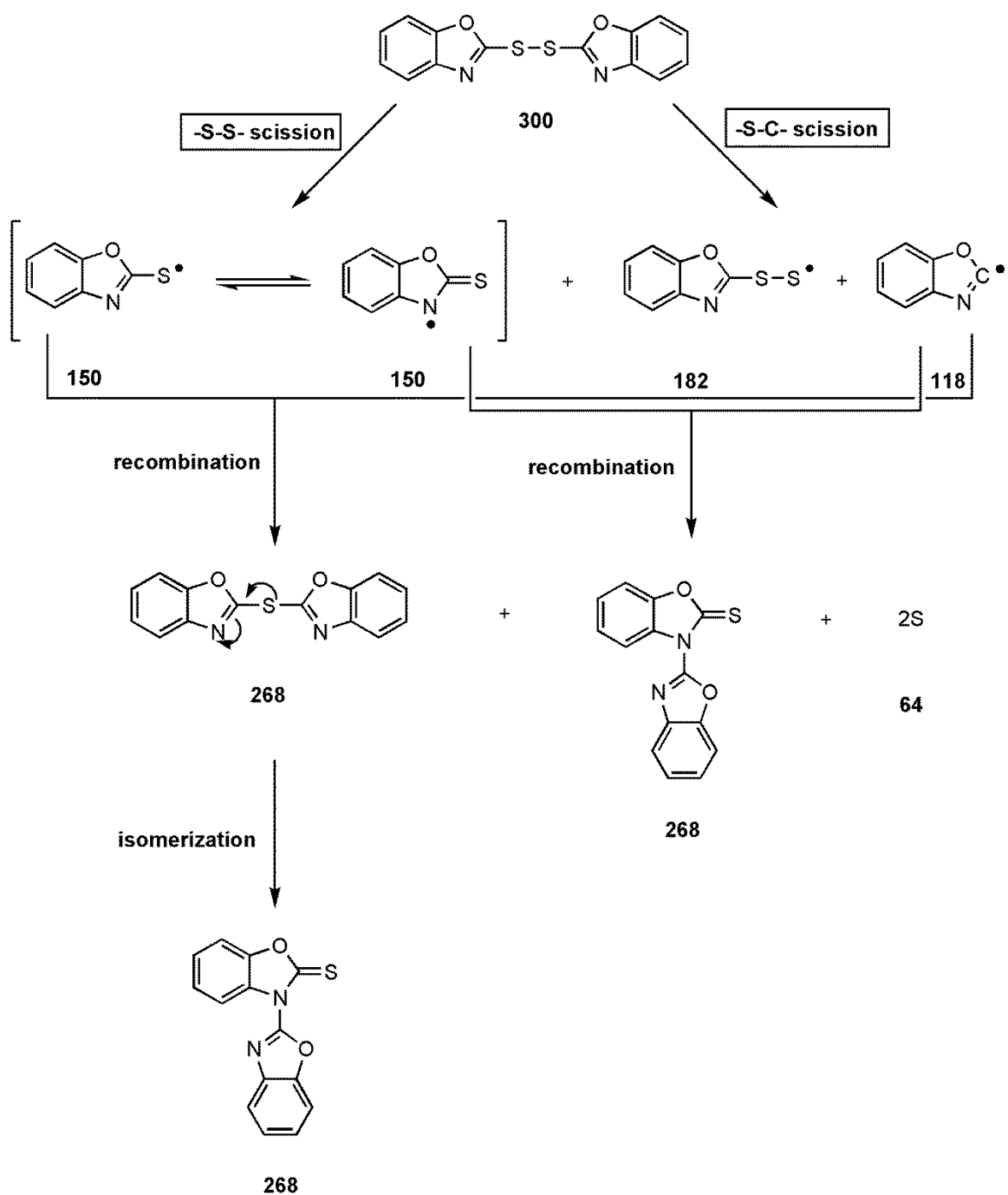
Scheme 1. Thermal dissociation mechanisms for various examples of disulfides: **(a)** aromatic [48], **(b)** aliphatic [49], **(c)** benzothiazole [50,51], thiuram [50].

H_2S + $CH_3^\bullet$

34 **15**

$S{=}CH_2$ + $CH_3{-}SH$

46 **48**

non radical
(unimolecular elimination)

$SH{-}$ + $-S^\bullet$ ← $-S{-}S-$

48 **47** **94** | radical mechanism

-S-S- scission | -S-C- scission | -C-H scission

2 $H_3C{-}S^\bullet$ | $-S{-}S^\bullet$ + $CH_3^\bullet$ | $-S{-}S{-}CH_2^\bullet$ + $H^\bullet$

47 **79** **15** **93** **1**

+ $-S{-}S-$

94

$-S{-}S{-}CH_2^\bullet$ + $\left[-SH + -S{-}SH + CH_4 + H_2 \right]$

93 **48** **80** **16** **2**

B-scission | isomerization | intermolecule substitution

$S{=}CH_2^\bullet$ ↔ $S{=}CH_2$ + $CH_3S^\bullet$

45 **45** **47**

$S{<}{}^{S}_{S}{>}$ + $CH_3^\bullet$

78 **15**

$-S{\diagdown}^{CH_2}{\diagup}S^\bullet$

93

$S{=}{}^{CH}{\diagup}S{\diagdown}CH_2^\bullet$

91

$H_3C{\diagdown}_{S}^{\bullet}$

61

$^\bullet HC{<}^{S}_{S}{>}$

77

$^\bullet S{\diagdown}^{CH_2}{\diagup}S^\bullet$

78

$S{=}{}^{C^\bullet}{\diagdown}S{\diagdown}CH_3$

91

$SH{\diagdown}^{}{\diagup}CH_2^\bullet$

61

$S{=}C{\diagdown}S^\bullet$

77

$S{=}C{=}S$

76

$H_2C{=}CH_2$

28

$S{=}C{=}S$

76

Scheme 1. (continued).

-C-S- scission

-S-S- scission

240

152

304

2

120

88 **64**

88 **32**

44 **76**

208

88 **77**

SCSH

$CH_3-N=C-CH_3$ + S$^\bullet$
56 **32**

$CH_3-N\equiv CH$ + $CH_3{}^\bullet$
41 **15**

H_3C-CH_3
30

CH_3-N-CH_3 + CS
44 **44**

$CH_3-N=CH_2$
43

$CH_3-\overset{H}{N}-CH_3$
45

$CH_2=N=CH_2$
42

CH_3-NH_2 + $CH_3{}^\bullet$
31 **15**

$CH_3-N=C=S$ + $CH_3{}^\bullet$
73 **15**

$CH_2-N=C=S$
72

Scheme 1. (continued).

Scheme 1. (continued).

Scheme 1. (continued).

In this paper, we report that disulfides themselves function as effective flame retardants for polypropylene films at already very low concentrations of 0.5 wt%.

2. Experimental part

General considerations

2.1. Materials

Polypropylene MOPLEN®HF500N (MFR=12g/10min (230 °C/2.16 kg)) and derivatives **3, 11** were supplied by BASF, products **1, 2, 4, 6, 10, 12, 13** were purchased from Sigma Aldrich Corporation and compounds **5** [52], **7** [53], **8** [54], **9** [55] were prepared according to previously described procedures. For comparison a commercial alkoxyamine Flamestab®NOR116 (supplier BASF SE) was used. All starting materials used for synthesis were of reagent grade and purchased from Sigma Aldrich Corporation, BASF or Fluka Chemie.

2.2. Instrumentation

Thermogravimetric analyses (TGA) were performed using a SDT Q600 apparatus from TA Instruments under nitrogen atmosphere at a heating rate of 10 °C/min. FTIR/MS analyses were conducted on a Netsch TG209F1 Iris, Bruker Tensor-27 and Netsch Aeolos QMS 403.

2.3. Evaluation of the Flame Retardancy

DIN 4102-1 flammability test

The disulfide additives were melt compounded in a Brabender mixing chamber at 230 °C together with polypropylene (MOPLEN®HF500N), 0.3 % IRGANOX®B225 (1:1 composition of benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-1,1'-[2,2-bis[[3-[3,5-bis(1,1-

dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]-1,3-propanediyl] ester (CA: 6683-19-8) and phenol, 2,4-bis(1,1-dimethylethyl)-1,1'1''-phosphite (CA: 31570-04-4)) and 0.05 % Ca-stearate. The resulting polymer compounds were prepared by compression molding in a heated press at 230 °C into films of 200 µm thicknesses and sizes of 250 mm × 110 mm. The film was mounted vertically inside a test chamber. The samples were subjected to edge exposure from a gas flame (45° angle, 16 mm away from the film, 40 mm flame length). Noteworthy is that 40 mm flame length was used instead of the 20 mm flame length as described in the DIN 4102-1 standard [56]. In general, we have earlier noticed that 40 mm flame length allows for better differentiation of the flame retardant efficacy than using a 20 mm flame length [22]. In total, three or five samples were ignited for each formulation. From the flammability experiments, the damaged length and burning time were recorded.
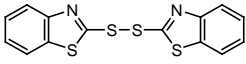
Limiting Oxygen Index test (LOI)

The LOI test was carried out using Oxygen Index Module apparatus from Fire Instrumentations and Research Developments according to ASTM D 2863 standard [57]. According to the test method, specimen's samples of type IV and dimensions of 70 × 6.5 × 3 mm were supported vertically in the center of heat resistant glass chimney containing the oxygen/nitrogen mixture and tested in accordance with test method A.

3. Results and discussions

The reactions of disulfides are of high importance in many areas of chemistry and especially vital in biological systems and they can be divided into three groups: 1) reactions occurring with cleavage of weak S-S bond, 2) reactions occurring with cleavage of C-S bond, 3) reactions leading to an increase in the valence of sulfur [33]. Hence, the most important reaction of disulfide bonds is their cleavage, which can occur by both homolytic (reaction involving free radical intermediates) and heterolytic [58] (reactions involving ionic intermediates) cleavage. Homolytic cleavage of sulfur-sulfur bonds can occur either by direct dissociation or as a result of attack of a free radical of one of the sulfurs.

Although it is known that mostly the S-S bonds in organic disulfides are initially cleaved homolytically by heat or light yielding thiyl radicals, little is known about the detailed complex radical mechanism for the formation of the thermal decomposition products identified experimentally [49,59]. Disulfides undergo transformations during thermal processing (pyrolysis, combustion) which result in release of various types of radicals and sulfur compounds. Understanding these processes is essential for the development of effective radical generators and consequently for effective flame retardation of burnable materials. Interestingly, it is known that already subtle variations in the structures of the disulfides have a tremendous effect on their properties [33]. Thus, thermogravimetric analysis (TGA) associated with Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography-Mass Spectroscopy (GC–MS) analysis were carried out to identify the decomposition products of compounds **(6)** and **(11)** and to elucidate the mechanism associated with thermolysis of benzothiazole and aliphatic disulfides. The principal products found after the thermolysis are summarized in Table 1.

Table 1 Results of TGA-FTIR-MS investigations.

Structure	Observed thermal fragments by MS	IR signals
$C_{18}H_{37}$-S-S-$C_{18}H_{37}$ **(11)**	**Relatively stable until 280 °C** Release of S above 300 ºC m/z = 33 and 34 (isotopes of S) Above 450 ºC release of SO_2 (fragments m/z = 48 and 64)	IR bands between 2600 and 3000 cm^{-1} i.e. release of the C_{17}-alkene chain
  (6)	**Relatively stable until 250 °C** Release of benzene (m/z =51/78) Release of SO_2 above 450 ºC m/z = 48 and 64 from SO_2	1354 and 1378 cm^{-1} from SO_2 and 2073cm^{-1} from N=C=S Isothiocyanate

Interpretation of TGA-FTIR-MS results is not straightforward due to the complexity of reactions taking place. For many kinetically controlled systems, the number of elementary reaction steps is so large that simple analytical solutions are not possible. As an example, the products reported in a theoretical study of the decomposition products for thermal decomposition of a structurally "simple" disulfide, i.e. dimethyl disulfide derivative, amounts to reaction mechanism containing 36 reactions among 25 reaction species that account for the formation of the decomposition products reported in the literature [51]. According to Glotova and coworkers, the thermal induced dissociation of 2,2-dibenzoxazolyl proceed by a radical mechanism with the cleavage of S-S and C-S bonds and the subsequent formation of 2,2´-di(benzoxazolyl) sulfide, 3-(2-benzoxazolyl)benzoaxazoline-2-thione and elemental sulfur [51]. Whereas, the thermodynamic properties of benzyl disulfide has been previously reported and the results show that decomposition of benzyl disulfide proceeded in a one-step decomposition starting at 200 °C to give stable arenethiyl radicals and elemental sulfur [60].

From Table 1 it is clear, that both compounds **6** and **11** are thermally relatively stable and that they start to decompose at 250 °C and 280 °C, respectively. Consequently, in contrast to peroxides, the disulfide compounds can survive polymer processing at 230 °C without thermal decomposition. Their stabilization mechanism is known and it ends with the formation of sulfur dioxide via sulfoxide and sulfon reactions [61].

At very high temperatures of above 450 °C, only SO_2 and elemental sulfur are released as fragments (according to both MS and FTIR analysis) and the other constituents are difficult to fully identify under these experimental settings. The formation of elemental sulfur apparently occurs by successive displacement from disulfide radicals with formation of various sulfur cycles, linear radical species (S_2 and S_n) that with further heating polymerize into longer polymeric sulfur chains which again depolymerize at even higher temperature forming short chains of sulfur atoms [62]. Further dissociation of C-S bond occurs and leads to rearrangement and dislocations of electrons, which finally results in the formation of thiophenyl diradicals. In addition, N=C=S fragments (at 2073 cm^{-1}) could be observed by IR analysis. Unfortunately, any other fragment detection under these conditions has not been possible. From thiophenyl most probably diradical fragments, carbon oxide and dioxide were formed as a result of further cleavages. Similarly, in the case of the aliphatic compound (**11**), only elemental sulfur and SO_2 fragments were detected by MS. IR signals found at 2600 cm^{-1} and 3000 cm^{-1} correspond to the release of alkene chains. The homolytic scission of S-S bonds for diaryl disulfides requires less energy than in the case of alkyl disulfides. This can be explained by the greater stability (resonance stabilization) of aryl thiyl radicals in comparison to alkyl thiyl radicals [49]. Hence, it can be expected that mainly two factors significantly govern the decomposition of disulfides:

destabilization of disulfides and stability of formed thiyl radicals from decomposition of disulfides.

3.1. Flammability

Combustion consists of various radical chain reactions and the flammability of hydrocarbon material is strongly dependent on the concentration of propagating free radicals. However, in case of disulfides their heating doesn't result in any significant equilibrium concentration of RS· [63] which is the one electron spin intermediate between thiols (RSH) and disulfides (RSSR).

DIN 4102-1

 For the evaluation of flame retardancy of polypropylene formulations containing disulfides, the ignitability tests were performed according to DIN 4102-1 standard. The results from these tests are summarized in the Table 2.

Table 2 Flammability results according to DIN 4102-1/B2 test method: edge ignition test, 200 µm pressed PP films.

Formulation	Loading (wt-%)	Average burning length (mm)	Average burning time (s)	T_{dec} by TGA/DTA (ºC)	Classification
REFERENCES					
Blank PP	100	190	38	464	NC[a]
Flamestab®NOR116	0.5	78	11	295	B2
DISULFIDES					
1	0.5	63	17	264	B2
2	0.5	53	10	274	B2
3	0.5	96	32.7	-	B2
4	0.5	85	14.5	-	B2
5	0.5	190	41	281	NC
6	0.5	86	18	321	B2
7	0.5	95	23	276	B2
8	0.5	91	20.3	276	B2
9	0.5	190	35.3	203	NC
10	0.5	85	14.5	-	B2
11	0.5	180	47	-	NC
12	0.5	182	49	225	NC
13	0.5	163	51	215	NC

From the flammability experiments the damaged length and burning time were determined. In general it was found, that most of the tested disulfide compounds themselves provided flame retardancy and self-extinguishing properties to PP films at the loading of 0.5 %wt. The present finding is, to the best of our knowledge, unprecedented in the prior literature. Interestingly, only four compounds (**5**, **9, 12** and **13**) out of thirteen tested disulfides did not show sufficient FR activity to pass the DIN 4102-1 fire test. The efficacy of the various disulfide compound families decreased in the following order: aromatic > heterocyclic substituted disulfides > heteroatom substituted disulfides > benzothiazole disulfides > aliphatic disulfides >> thiuram disulfides. The reason for the low flame retardant activity of **9, 12** and **13** can at least partially be attributed to

their low thermal stabilities of 203 °C, 225 °C and 215 °C respectively. Thus, these disulfide compounds decompose already to a great extent during processing of polypropylene at 230 °C and, therefore, they cannot any longer act as radical generators and flame retardants for PP films during combustion. The lack of flame retardant activity of compound **5** at this low loading of 0.5 wt% is not that surprising when considering that even its azo analog did not either exhibit a significant flame retardant activity under similar conditions [64]. All of the other compounds passed the classification criteria set forth for the DIN 4102-1 test. Noteworthy is, that five compounds (**1**, **2, 4, 6** and **10**) passed the test with average burning times of less than 20 s and damaged lengths of below 85 mm. Thus, all of these compounds exhibited very good fire retardant properties for polypropylene films. A remarkably strong FR effect was recorded for 5,5'-dithiobis(2-nitrobenzoic acid) (**2**) where the very low values for burning length (53 mm) and burning time (10 s) reflect significantly increased fire retardant performance compared to other compounds in this series (even including the commercially available Flamestab®NOR116). This can be attributed to electron withdrawing substituents (nitro and carboxylic acid moieties) at the aromatic rings that remove electrons from the aromatic system and stabilize the disulfide bond. In general, it seems that the flame retardant efficacy of the various types of disulfides mainly depends on: (1) thermal stability (homolysis temperature), (2) products of decomposition and mechanisms thereof, and (3) reactivity of the radicals generated during decomposition.

Hence, our studies have clearly demonstrated that thiyl radicals, generated from selected disulfides, have the ability to interrupt the combustion process of polypropylene. For this reason, disulfides could be considered as an intriguing family of halogen-free flame retardants e.g. for polypropylene that may fulfill the criteria of sustainable products and production.

Limiting Oxygen Index (LOI)

The limited oxygen index (LOI) test is widely recognized as a useful method for numerical assessment of the flammability of polymeric materials. As a consequence of this, we determined the LOI values for the most promising disulfide candidates i.e. flame retardants **1**, **2** and **6** at a loading of 3 wt% in polypropylene, as shown in Figure 2.
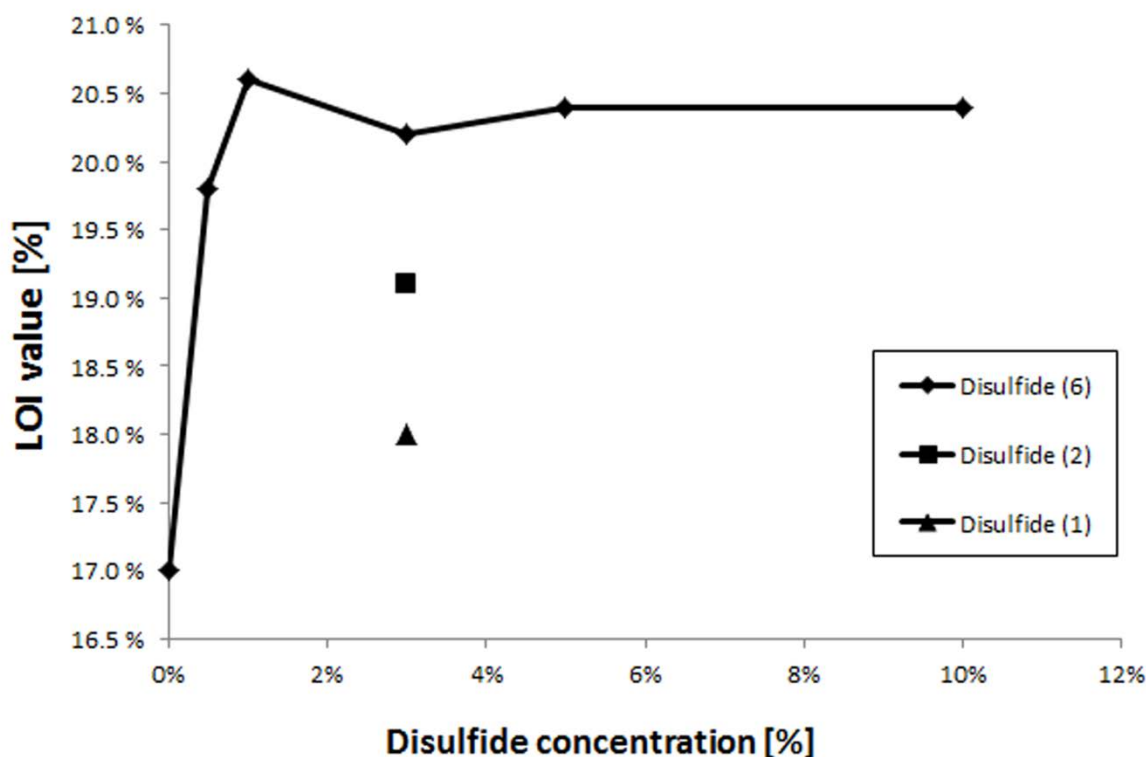

Fig. 2. Limited oxygen index (LOI) of polypropylene (PP) containing disulfides **1, 2, 6** (error LOI ± 0.1).

The recorded LOI values revealed that the various types of disulfides only marginally improved LOI values of virgin polypropylene from 17.0 % to 17.9 %, 19.1 %, 20.3 %, respectively. Since, the highest LOI value of 20.3 % was measured for compound **6**, we investigated the correlation between LOI values and the amount of additive **6**. The results show that LOI values increased

rapidly to 20.6 % at a loading of 1 wt% of **6**, whereas higher flame retardant loadings up to 10 wt% do not improve LOI values any further, as depicted in Figure 2. These findings are in good agreement with previous literature data for flame retardants based on radical generators such as Flamestab®NOR116. Thus, radical generators only marginally improve LOI values of polypropylene, i.e. when 1 wt% of Flamestab®NOR116 is added to polypropylene the LOI values only increase to 22 % [31].

3.2. Thermogravimetry TGA/DTA

The decomposition of virgin polypropylene in an inert atmosphere according to the obtained TGA data starts at around 337 °C and the maximum decomposition peak appears at 464 °C, as shown in Figure 3.
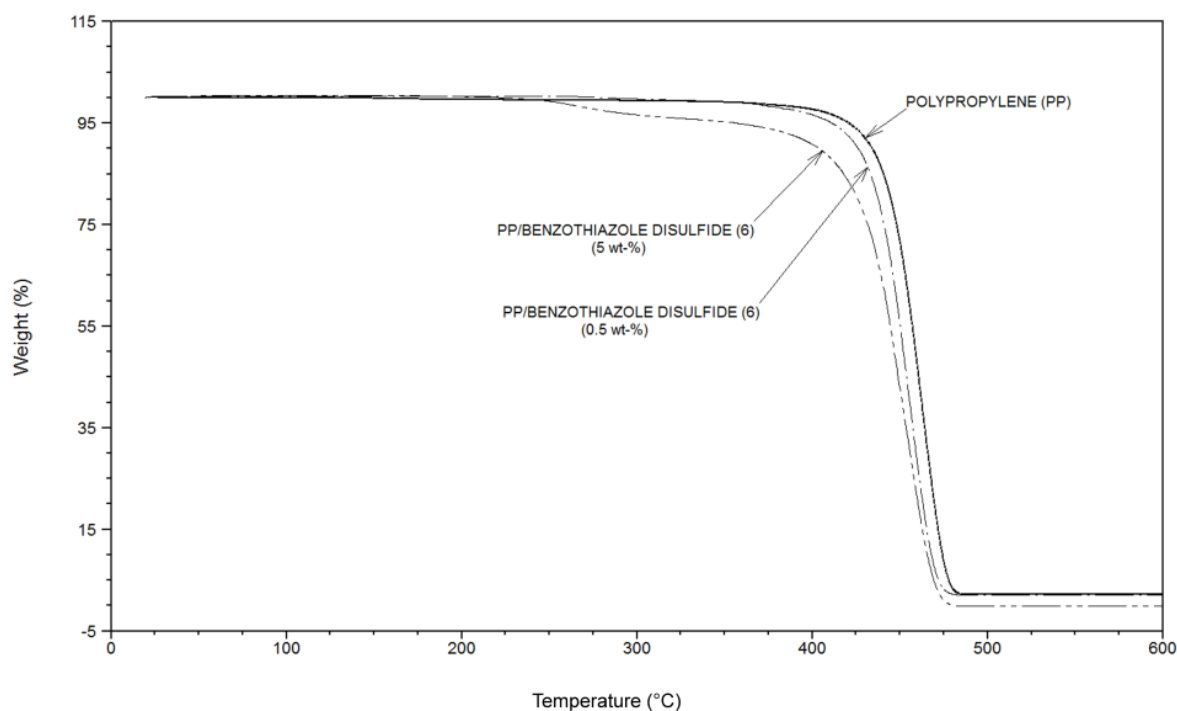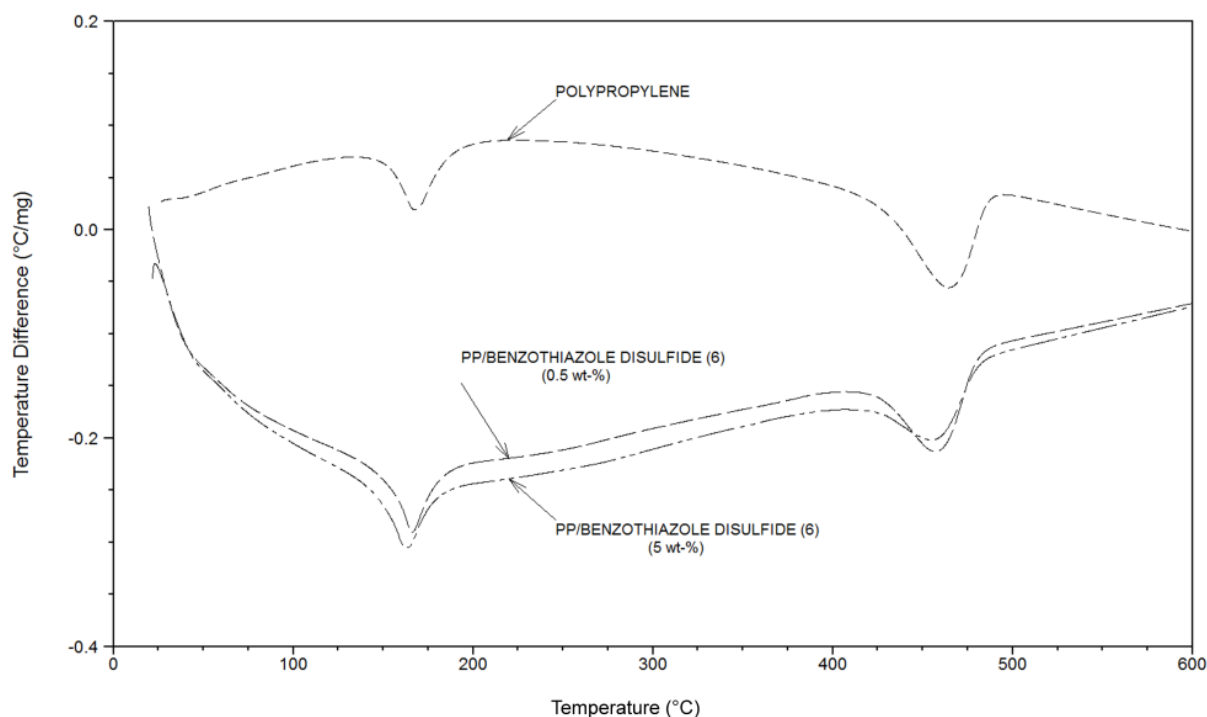
Fig. 3. Thermogravimetry (TG) and (DTA) of PP and PP/ benzothiazole disulfide (**6**) under an inert atmosphere.

Whereas the analysis of the polymer formulations uncovers that the onset of polypropylene decomposition occurs at 40 °C earlier when combined with additive **6**. The thermal decomposition rate of polypropylene is significantly faster when using the higher loading of 5 wt% in comparison to using 0.5 wt% loading of additive **6**. This observation suggests, that additive **6** has the ability to strongly degrade polypropylene when flames impinge on the polymer. This is inline, with previous studies that have observed enhancement of polystyrene degradation by sulfur, i.e. sulfur significantly facilitates polystyrene degradation [65]. Thus, the flame retarding mechanism of disulfides can be partially ascribed to the generation of radicals that induce a fast degradation of the polymer chain and flame retardancy is achieved by

removing the substrate from the flame. In addition, the generated radicals may also be involved in the free radical chemical reactions during the combustion process itself.

4. Conclusion

The development of new halogen-free and efficient flame retardants for polymeric materials remains an important challenge for researchers both in academia and industry. In this study, we demonstrated that certain disulfide based plastic additives can alone be successfully used as efficient flame retardants for polypropylene films. Particularly, 5,5'-Dithiobis(2-nitrobenzoic acid) (**2**) exhibited excellent FR properties in the presented test series. Nevertheless, other tested disulfide compounds used in concentrations of 0.5 wt% only, were also able to provide flame retardancy and self-extinguishing properties to polypropylene films. Research efforts are currently in progress to further develop this new and exciting family of flame retardants. Examination of their structure-property relationship, synergistic effects with conventional flame retardants and additional testing in different polymer systems are in progress.

5. Acknowledgement

6. References:

[1] Alfassi ZB, editor. General aspects of free radical chemistry. New York: Wiley, 1999.

[2] Lazar M, editor. Free radicals in chemistry and biology. Boca Roton: CRC Press, 1989.

[3] Alabugin IV, Manoharan M. Thermodynamic and strain effects in the competition between 5-exo-dig and 6-endo-dig cyclizations of vinyl and aryl radicals. J Am Chem Soc 2005; 127 (36): 12583-12594.

[4] Ingold KU. Kinetic and mechanistic studies of free radical reactions in the 21st century. Pure Appl Chem 1997; 69 (2): 241-243.

[5] Parsons AF, editor. An introduction to free radical chemistry. Cambridge: Wiley-Blackwell, 2000. pp. 44-60.

[6] Nonhebel DC, Walton JC, editors. Free-radical chemistry; structure and mechanism. Cambridge: Cambridge University Press, 1974. pp. 10-21.

[7] Ivanov VL, Aurich J, Eggert L, Kuzmin MG. Dye-photoinitiated chain reaction of halogen substitution by a sulpho group in halogenonaphthols. J Photoch Photobio A 1989; 50 (2): 275-281.

[8] Denisov ET, Denisova TG, Pokidova TS, editors. Handbook of free radical initiators. New Jersey: John Wiley&Sons, 2003. pp. 303-353.

[9] Parsons AF, editor. An introduction to free radical chemistry. Cambridge: Wiley-Blackwell, 2000. pp. 44, 47.

[10] Denisov ET, Azatyan VV, editors. Inhibition of chain reactions. London: Taylor&Francis, 2000. pp. 23-31.

[11] Step EN, Turro NJ, Gande ME, Klemchuk PP. Mechanism of polymer stabilization by hindered-amine light stabilizers (HALS). Model investigations of the interaction of peroxy radicals with HALS amines and amino ethers. Macromolecules 1994; 27 (9): 2529-2539.

[12] Pfaendner R. Nitroxyl radicals and nitroxylethers beyond stabilization: radical generators for efficient polymer modification. CR Chemie 2006; 9 (11-12): 1338-1344.

[13] Pfaendner R. (Photo)oxidative degradation and stabilization of flame retarded polymers. Polym Degrad Stab 2013; 98 (12): 2430-2435.

[14] Wan D, Ma L, Zhang Z, Xing H, Wang L, Jiang Z, Zhang G, Tang T. Controlling degradation and branching reactions of polypropylene by different heteroaromatic ring derivatives. Polym Degrad Stab 2012; 97 (1) 40-48.

[15] Braunecker WA, Matyjaszewski K. Controlled/living radical polymerization: features, developments, and perspectives. Prog Polym Sci 2007; 32 (1): 93-146.

[16] Kaur I, Verma SK. Living radical polymerization and grafting of diethyl (acryloyloxy) ethylthiophosphoramidate onto cotton fabric to impart flame retardancy. Surf Coat Tech 2010; 205 (77): 2082-2090.

[17] Togo H, editor. Advanced free radical reactions for organic synthesis. Oxford: Elsevier, 2004.

[18] Redpath JL. Free radical reactions with simple biochemical systems. J Chem Educ 1981; 58 (2): 131-135.

[19] Furusawa K, Kawamura T, Akutsu Y, Arai M, Tamura M. Reaction of gas-phase radicals from combustion with radical scavengers. Atmos Environ 1997; 31 (20): 3363-3367.

[20] Dufton PW, editor. Flame retardants for plastics, Market report. Shrewsbury: Rapra Technology, 2003.

[21] Camino G, Costa L. Performance and mechanisms of fire retardants in polymers—a review. Polym Degrad Stab 1988; 20 (3–4): 271-294.

[22] Aubert M, Ronan CN, Pawelec W, Wilén C-E, Roth M, Pfaendner R. Azoalkanes-novel flame retardants and their structure-property relationship. Polym Adv Tech 2011; 22 (11): 1529-1538.

[23] Eichorn J. Synergism of free radical initiators with self-extinguishing additives in vinyl aromatic polymers. J Appl Pol Sci 1964; 8 (6): 2497-2524.

[24] Gouinlock EV, Porter JF, Hindersinn RR. Mechanism of the fire-retardance of dripping, thermoplastic compositions. J Fire Flammability 1971; 2 (7): 206-218.

[25] Eichorn J. Method for making self-extinguishing alkenyl aromatic resin compositions comprising incorporating therein an organic bromine-containing compound and an organic peroxide. US 3058926, 1962.

[26] Eichorn J, Stanley BI. Foamed self-extinguishing alkenyl aromatic resin compositions containing an organic bromide and peroxide. US 3058928, 1962.

[27] Vanderhoff JW, Jahn AK. Method of polymerizing a vinyl aromatic monomer in the presence of an organic bromide and an organic peroxide and a self-extinguishing vinyl aromatic polymer containing same. US 3058929, 1962.

[28] Burger H, Daumiller G, Grohmann J, Kastning EG, Weber H, Willersin H. Self-extinguishing thermoplastic compositions. DE 1255302, 1973.

[29] Weber H, Burger H, Daumiller G, Willersin H, Grohmann J. Verfahren zur Herstellung von Schaumstoffbahnen aus schwerentflammbaren Styrolpolymerisaten. DE 1270803, 1976.

[30] Nicolas RC, Wilén C-E, Roth M, Pfaendner R, King RE. Azoalkanes: A novel class of flame retardants. Macromol Rapid Commun 2006; 27 (12): 976-981.

[31] Marney DCO, Russell LJ, Soegeng TM, Dowling VP. Mechanistic analysis of the fire performance of a fire retardant system. J Fire Sci 2007; 25 (6): 471-497.

[32] Chatgilialoglu C, Asmus KD, editors. Sulfur-centered reactive intermediates in chemistry and bilogy. New York: Plenum Press, 1990.

[33] Koval IV. The chemistry of disulfides. Russ Chem Rev 1994; 63 (9): 735-750.

[34] Garcia-Ruano JL, Parra A, Alemán J. Efficient synthesis of disulfides by air oxidation of thiols under sonication. Green Chem 2008; 10 (6): 706–711.

[35] Mak AM, Steudel R, Wong MW. Homolytic S-S bond dissociation of 11 bis(thiocarbonyl)disulfides R-C(=S)-S-S-C(=S)R and prediction of a novel rubber vulcanization accelerator. Chem Asian J 2008; 3 (6): 1026-1034.

[36] Vega B, Montero L, Lincoln S, Agulló N, Borrós S. Control of vulcanizing/devulcanizing behavior of diphenyl disulfide with microwaves as the heating source. J Appl Polym Sci 2008; 108 (3): 1969-1975.

[37] Abdeli M, Ahmadi NP, Khosroshahi RA. Influence of bis-(2-benzothiazolyl)-disulfide on corrosion inhibition of mild steel in hydrochloric acid media. J Solid State Electrochem 2011; 15 (9): 1867-1873.

[38] Riddles PW, Blakeley RL, Zerner B. Ellman's reagent: 5,5'-dithiobis(2-nitrobenzoic acid)-a reexamination. Anal Biochem 1979; 94 (1): 75-81.

[39] Xu W, Zhu X, Cheng Z, Chen G, Zhu J. Polymerization of styrene with tetramethylthiuram disulfide as an initiator in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy. J Polym Sci A 2005; 43 (3): 543-551.

[40] Eichhorn J. Self-extinguishing alkenyl aromatic polymers. US 3271333 (Dow), 1966.

[41] Sunpor Kunststoff. Flammgeschützte expandierbare polymerisate. AT 508303, 2010.

[42] Sunpor Kunststoff. Flammgeschützte expandierbare polymerisate. AT 508304, 2010.

[43] Bellin I, Denecke H. Flame-retardant polymer foams with halogen-free flame-retardant agents containing phosphorous on a sugar basis. EP 2574614, 2013.

[44] Bellin I, Spies P. Flame retardant system. WO 2012089667, 2012.

[45] Hahn K, Fuchs S. Bellin I, Spies P, Hofmann M, Deglmann P, Massonne K, Denecke H, Fleckenstein Ch, Janssens G. Flame retardant. WO 2011121001, 2011.

[46] Rim YS, Nudenberg W. N-(o- or p-thiophenyl) substituted polyhalo-5-norbornene-2,3-dicarboximide flame retardants and polymers containing said imides. US 4026963, 1977.

[47] Eichhorn J, Mich M. Polysulfide flameproofing agents for self-extinguishing resins. US 3284544, 1966.

[48] Chandrasiri JA, Wilkie CA. Thermal degradation of diphenyl disulfide and a blend of diphenyl disulfide with poly(methyl methacrylate). Polym Degrad Stab 1994; 46 (2): 275-284

[49] Vandeputte AG, Reyniers MF, Marin GB. Theoretical study of the thermal decomposition of dimethyl disulfide. J Phys Chem A 2010; 114 (39): 10531-10549.

[50] Štaudner E, Beniska J, Kyselá G. Study of thermal decomposition of tetramethylthiuram disulfide. Chem. Zvesti 1976; 30 (3): 336-341.

[51] Glotova TE, Nakhmanovich AS, Lopyrev VA. Thermal decomposition and isomerization of 2,2'-di(benzoxazolyl)disulfide. Russ Chem B 1993; 42 (10): 1753-1755.

[52] Leino R, Lönnqvist JE. A very simple method for the preparation of symmetrical disulfides. Tetrahedron Lett 2004; 45 (46): 8489-8491.

[53] Montazerozohori M, Joohari S, Karami B, Haghighat N. Fast and highly efficient solid state oxidation of thiols. Molecules 2007; 12 (3): 694-702.

[54] Beerheide W, Sim MM, Tan YJ, Bernard HU, Ting AE. Inactivation of the human papillomavirus-16 E6 oncoprotein by organic disulfides. Bioorgan Med Chem 2000; 8 (11): 2549-2560.

[55] Bennett JE, Sieper H, Tavs P. 2,2,6,6-Tertramethylpiperidyl-1-thiyl: A stable new radical. Tetrahedron 1967; 23 (4): 1697-1699.

[56] German Standard DIN 4102-1: 'Fire behavior of building materials and building components-Part 1: Building materials, concepts, requirements and tests' 1998.

[57] ASTM, Standard test method for measuring the minimum oxygen concentration to support candle-like combustion of plastics (oxygen index). Standard D2863. American Society for Testing Materials, Philadelphia, PA.

[58] Parker AJ, Kharasch N. Derivatives of sulfenic acids. XXXVI. The ionic scission of the sulfur-sulfur bond. Part 1. J Am Chem Soc 1960; 82 (12): 3071-3075.

[59] Miyashita T, Matsuda M, Iino M. Kinetics of the thermal decompositions of diaryl and dialkyl disulfides. B Chem Soc Jpn 1975; 48 (11): 3230-3235.

[60] Wang SX, Tan ZC, Li YS, Li Y, Shi Q, Tong B. Heat capacity and thermodynamic properties of benzyl disulfide ($C_{14}H_{14}S_2$). Thermochim Acta 2007; 463 (1-2): 21-25.

[61] Zweifel H, editor. Plastic additives handbook. Munich: Hanser Publishers, 2009. p. 15, 112.

[62] Tobolsky AV. Polymeric sulfur and related polymers. J Polym Sci, Part C: Polymer Symposia 1966; 12 (1): 71-78.

[63] Muth OH, Oldfield JE. Symposium: Sulfur in nutrition, Oregon State University: 1969. pp. 6-30.

[64] Tirri, T, Aubert M, Pawelec W, Wilén C-E, Pfaendner R, Hoppe H, Roth M, Sinkkonen J. Preparation and characterization of bis-[1,3,5] triazinyl diazenes and their utilization as flame retardants in polypropylene films. J Appl Pol Sci 2014; http://dx.doi.org./10.1002/app.40413.

[65] Beach MW, Rondan NG, Froese RD, Gerhard BB, Green JG, Stobby BG, Shmakov AG, Shvartsberg VM, Korobeinivhev OP. Studies of degradation enhancement of polystyrene by flame retardant additives. Polym Degrad Stab 2008; 93 (9): 1664-1673.