



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Highly efficient multifunctional mono-component flame retardants comprising of sulfenamide and phosphate moieties for polypropylene

Ääritalo, Timo; Brusentsev, Yury; Tirri, Teija; Breton, Lou; Wilen, Carl Eric

Published in: Polymer Degradation and Stability

DOI: 10.1016/j.polymdegradstab.2023.110568

Published: 01/12/2023

Document Version Final published version

Document License CC BY

Link to publication

Please cite the original version:

Ääritalo, T., Brusentsev, Y., Tirri, T., Breton, L., & Wilen, C. E. (2023). Highly efficient multifunctional monocomponent flame retardants comprising of sulfenamide and phosphate moieties for polypropylene. *Polymer Degradation and Stability*, *218*, Article 110568. https://doi.org/10.1016/j.polymdegradstab.2023.110568

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.



Contents lists available at ScienceDirect

Polymer Degradation and Stability



journal homepage: www.journals.elsevier.com/polymer-degradation-and-stability

Highly efficient multifunctional mono-component flame retardants comprising of sulfenamide and phosphate moieties for polypropylene

Timo Ääritalo, Yury Brusentsev, Teija Tirri, Lou Breton, Carl-Eric Wilen

Faculty of Science and Engineering, Åbo Akademi University, Henriksgatan 2, 20500 Åbo, Finland

ARTICLE INFO	A B S T R A C T
A R T I C L E I N F O Keywords: Flame retardant Multifunctional Sulfenamide Phosphate Polypropylene	A strategy to enhance flame retardant properties of polypropylene (PP) has been investigated by the design of six multifunctional mono-component flame retardants denoted from NS1 to NS6, where sulfenamide and phosphate moieties have been integrated into a single molecule. Herein, the synthesis and characterization of six different mono-component flame retardants are presented. Thermal decomposition characteristics of the multifunctional flame retardants were studied by thermogravimetry analysis, and a 5% mass lose was recorded in the temperature range between 220 °C to 267 °C for the samples. Moreover, the flame retardant samples were oven aged up to 260 °C in the presence and absence of 9, 10-dihydroantracene and the formed decomposition products were analyzed using GC/MS, LC/MS, ¹³ C NMR and ³¹ P NMR. The results indicate that the sulfenamide bond dissociates before the phosphorus moiety for samples NS1, NS2, NS3 and NS6. Whereas the phosphorus moiety breaks first in case of NS4 and NS5. The prepared flame retardants were then admixed with polypropylene in a Haake Rheocord melt blender at loadings ranging from 0.5 to 4 wt%. Thereafter, polypropylene films and plaques were prepared by hot pressing and their flame retardant properties were evaluated according to DIN 4102-B2 and UL94V standards, respectively. All the PP film samples containing any of the different multifunctional flame retardants at the low loading of 0.5 wt% passed the DIN4102 B2 test and for NS1film sample no burning dripping nor ignition of paper were recorded. Noteworthy, is that NS2 and NS3 samples reached the UL94V2 classification as standalone flame retardants even at a loading of only 4 wt%. From this standpoint, it seems the multifunctional mono-component flame retardants may exhibit inherently an exceptionally high synergistic effect.

1. Introduction

In recent years, the surge for new flame retardants with better environmental profiles, reprocessability, recyclability and higher efficacies at lower loadings have gained momentum both in academia and industry. To address these key challenges a lot of focus has been placed on development of novel phosphorus, bio- and radical generator-based flame retardants [1–5]. Many of the developed so-called next generation of green flame retardant candidates have shown a lot of promise. However, studies have revealed that the introduction of one single flame retardant element into a polymeric material is rarely optimal and stringent fire standards for many intended end applications cannot be reached [6]. Therefore, to further improve the flame retardancy a current trend has been to incorporate several elements of P, N, S, Si into the flame retardant formulations that exert their individual flame retardant action via different mechanisms [7–9]. The synergistic effect can be finetuned by proper selection of the elements whereby fire-retardant

combinations can be constructed that simultaneously exert fire protection actions in the condensed, meso- and gas-phase. In theory, the plural mode of actions give raise to strong synergistic effects that can be obtained either by using multicomponent flame retardant systems (the conventional method) or by incorporating the various elements in a multifunctional mono-component flame retardant. Thus, there is a distinction between multicomponent and multifunctional mono component flame retardants. There is a plethora of examples of successful multicomponent flame retardant systems that exhibit strong synergistic effects. For instance, various families of radical generators such as alkoxyamines (NOR) [10], azoalkanes (AZO) [11-13], triazene [14], disulfides [15–17], sulfenamides (NS) [18–20], silyamines [21], siloxyamines [22] and oxyimides [23] based flame retardants have been successfully used as synergists with conventional phosphorus and metal oxide-based flame retardants. In contrast, multifunctional mono-component flame retardants have been less explored and still to a large extent at a developmental stage.

E-mail address. Cwilen@abo.ii (C.-E. Wilen).

https://doi.org/10.1016/j.polymdegradstab.2023.110568

Received 28 July 2023; Received in revised form 12 October 2023; Accepted 16 October 2023 Available online 21 October 2023

0141-3910/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

^{*} Corresponding author. *E-mail address:* cwilen@abo.fi (C.-E. Wilen).

One of the most successful commercial multifunctional monocomponent flame retardants are ammonium- and melamine polyphosphates, where the phosphorus group exerts its flame retardancy in the condensed phase and the nitrogen group contributes to fire retardancy by fuel dilution in the gas phase and/or by its action as a blowing agent for the char [24]. Moreover, several examples of efficacious combinations of P-N bonds such phosphoramines or phosphoramidates have been reported [25]. On top of this, many different combinations of phosphor with silicon, boron and sulfur groups as mono-component fire retardants have been recently disclosed [26-40]. For example, alkyl sulfone bridged phosphorus flame retardants have been introduced as mono-component flame retardant for polypropylene [41]. Interestingly, it has also been demonstrated that by combining two different phosphorus flame retardants in a single molecule such as phosphine oxide with phosphate a synergistic effect was observed, since the phosphine group provided gas phase activity whereas the phosphate group was able to partially promote char formation in the condensed phase [42]. Furthermore, we have demonstrated that by combining azoalkanes (AZO) and alkoxyamine (NOR) groups in one molecule (AZO-NOR) a surprisingly high flame retardant efficacy can be reached. Thus, AZO-NOR flame retardant clearly outperformed the classical alkoxyamine (NOR) flame retardants in thin polypropylene plaques, and it also passed more stringent fire standards tests such as UL94 VTM-2 at lower loading of 0.25 to 1 wt% than was possible with the classical alkoxyamines (NOR) or with its mixture with azoalkanes [43]. Therefore, it seems that multifunctional mono-component flame retardants may potentially exhibit a higher synergistic effect at a lower total loading than their multicomponent counterparts blended separately. Another foreseeable advantage is that mono-component flame retardants are easier to blend homogeneously in the polymer matrix than multicomponent additives.

Herein, we report the design, synthesis, and characterization of six unique multifunctional mono-component flame retardants which incorporate sulfenamide and phosphate units; bis(1-((4-((diethoxyphosphoryl)oxy)-phenyl)thio)-2,2,6,6-tetramethylpiperidin-4-yl) carbonate (NS1), bis(1-((4-((diphenoxyphosphoryl)oxy)-phenyl)thio)-2,2,6,6-tetramethylpiperidin-4-yl) carbonate (NS2), bis(1-((4-((bis(2,6dimethylphenoxy)-phosphoryl)-oxy)phenyl)thio)-2,2,6,6-tetramethylpiperidin-4-yl) carbonate (NS3), 1-(benzo[d]thiazol-2-ylthio)-2,2,6,6-tetramethylpiperidin-4-yl diethyl phosphate (NS4), 1-(benzo[d] thiazol-2-vlthio)-2,2,6,6-tetra-methylpiperidin-4-vl diphenyl phosphate (NS5) and tris(1-benzothiazol-3-ylthio)-2,2,6,6-tetra-methylpiperidin-4-vl) phosphate (NS6). The chemical structures of the multifunctional mono-component flame retardants are depicted in Fig. 1. The flame retardant efficacy of the novel flame retardants in polypropylene films and plaques was investigated according to DIN4102-B2 and UL94 V standards, respectively.

2. Experimental

Materials; all chemicals used for the synthesis were of reagent grade. Solvents from Sigma-Aldrich (Finland) were used directly from fresh bottles or in case of THF dried over 3 Å molecular sieves for at least 48 h. The reagents and reactants were used without further purification, i.e., triethyl amine Sigma-Aldrich >99 % reagent grade, sulfuryl chloride Merck >97 %, bis-(2,2,6,6-tetramethylpiperidin-4-yl) carbonate was obtained from Songwon >95 %, 2,2,6,6-tetramethylpiperidin-4-ol from Degussa-Huls >99 %, n-butyl lithium 2.5 M from sigma-Aldrich, sodium hydride from Aldrich 60 % in mineral oil, 4,4'-disulfaneyldiphenol from Sigma-Aldrich >98 %, diethyl chlorophosphate from Sigma-Aldrich >99 %, diphenyl chlorophosphate from Aldrich >99 % and 2,2'-dithiobis(benzothiazole) from Sigma-Aldrich >96 %.

Characterization methods: NMR spectra (¹H, ³¹P and ¹³C) were recorded on a 500 MHz Bruker AVANCE-III NMR-system. Thermal treatment of FR mixtures for ³¹P NMR analysis and radical mechanism

verification study were done in the following manner: 9,10-dihydroanthracene, NS1–6 were weighed into NMR-tubes and sealed under argon atmosphere. Samples were then placed in silicon oil bath set to the target temperature for the time given. Depending on the sample, either dimethylsulfoxide-d₆ or chloroform-d was added to the tubes before the NMR analysis. Mass spectra was analyzed with Waters Aquity RDa LC-MS spectrometer.

Test specimens for fire tests were prepared by mixing the flame retardant with polypropylene in Haake Rheocord melt blender (Waltham, MA, USA) (60 rpm). Thus, molten polypropylene (PP MFR25, MOPLEN HP552R from LyondellBasell, Netherlands, MFR 25 g/10 min (230 °C/2.16 kg)) were mixed with Ca-stearate (Baerlocher, Unterschleißheim, Germany, 0.05 wt%) and Irganox® B 225 (0.3 wt%), first for 1 min at 210 °C in the melt blender. Then flame retardant was added and the mixing was continued for five minutes. Crude polymer was crushed and then pressed with 150 bar hydraulic press at 190 °C, for 1 min without applying pressure followed by 1 min with maximal pressure in a mold. The prepared polypropylene bars containing NS1, NS3 and NS4 were completely white, whereas NS2 bars had a slight yellow tint, whereas bars containing NS5 and NS6 were yellowish. Thermogravimetric (TGA) and differential thermal analysis (DTA) was performed using an SDT Q600 apparatus from TA Instruments under N₂ atmosphere (flow rate 100 mL/min) and at the heating rate of 10 °C/min.

3. Test procedure of flame retardant properties

The flame retardant properties of test specimen were determined in a UL-94 fire chamber based on DIN EN 60,695–11–10. The test specimen was secured in the sample holders of the UL-94 15 fire chamber. The burner upper surface was positioned 1 cm below the lower surface of the test specimen, the flame was positioned in a 45° angle and a heating output of 50 W. The test specimen was exposed to the flame for 10 s, before removing the flame. If the test specimen extinguished by itself within 10 s, the process was repeated. DIN 4102 B2 tests were done in the same UL-94 test chamber, the specimen was attached to a frame so that the lower end of the film was 1 cm above the upper surface of the burner. Specimen were exposed to the flame for 15 s and the burning time and length were measured.

4. Synthesis of multifunctional flame retardants NS1-NS6

4.1. Disulfanediylbis(4,1-phenylene) tetraethyl bis(phosphate) (1)

4,4'-disulfaneyldiphenol (40 g, 0,160 mol) was dissolved in 500 ml THF under argon atmosphere in a three-neck bottle, then NaH (60 % in mineral oil, 14 g, 0,35 mol) was added in portions and the mixture stirred for 60 min. Then diethyl chlorophosphate (60,6 g, 0,35 mol) in 200 ml THF was added dropwise. The mixture was then stirred for 20 h. Reaction mixture was then washed first with 400 ml solution containing 10 to 1 brine and 0.1 M NaOH, and then with brine. Organic fraction was collected, dried with Na₂SO₄ and evaporated to dryness to give slightly brown liquid. The crude product was then filtered through silica with DCM as eluent to give a yellow viscous liquid, 67,4 g, 78 % yield.

¹H NMR (CDCl₃): 7.37 (4H, d), 7.10 (4H, d), 4.14 (8H, m), 1,27 (12H,

t) ³¹P NMR: -6.45 (pentet) ¹³C NMR: 150.5 (d), 133.1, 130.2, 120.8 (d), 64.7 (d), 16.1 (d)

4.2. Disulfanediylbis(4,1-phenylene) tetraphenyl bis(phosphate) (2)

4,4'-disulfaneyldiphenol (10 g, 0,040 mol) with diphenyl chlor-ophosphate (19 ml, 0,088 mol) gave 23,3 g (0,026 mol) product with 65 % yield.

- ¹H NMR (CDCl3): 7.39 (4H, d), 7.05 (16H, m), 2.37 (24H, s) ³¹P NMR: -17.1 (s)
- ¹³C NMR: 150 (d), 148 (d), 133.5, 130.4 (d), 130.0, 129.2 (d), 125.6



Fig. 1. Chemical structures of synthesized multifunctional flame retardants denoted from NS1 to NS6.

(d), 120.8 (d), 17

4.3. Tetrakis(2,6-dimethylphenyl) (disulfanediylbis(4,1-phenylene)) bis (phosphate) (3)

4,4'-disulfaneyldiphenol (3,3 g, 0,013 mol) with bis(2,6-dimethylphenyl) chlorophosphate (10 g, 0,029 mol) gave 6,3 g (0,0076 mol) product with 58 % yield.

¹H NMR (CDCl₃): 7.48 (4H, d), 7.37 (8H, m), 7.26 (8H, t), 7.22 (8H, t)

³¹P NMR: -17.2 (s)

¹³C NMR: 150.35 (d), 150.1 (d), 134, 130 (d), 125.7, 125.6, 121 (d), 120.1

4.4. Diethyl (2,2,6,6-tetramethylpiperidin-4-yl) phosphate (4)

2,2,6,6-tetramethylpiperidin-4-ol (10 g, 0,0636 mol) was dissolved in 100 ml THF under argon atmosphere, mixture was cooled on iceethanol bath and n-BuLi (2.5 M in hexane, 25,4 ml, 0,0636 mol) was added, after 60 min stirring diethyl chlorophosphate (8,7 ml, 0,0604 mol) in 50 ml THF was added. The mixture was then stirred for 14 h at RT. Then 100 ml of water was added and the organic layer separated, and it was further washed with Brine. Organic fraction was collected, dried with Na₂SO₄ and evaporated to dryness to give a yellow liquid, 13,7 g, 66 % yield with impurity deducted, this contains around 10m% impurity.

¹H NMR (CDCl₃): 4.72 (1H, m), 4.09 (4H, p), 2.05 (2H, dd), 1.33 (6H, t), 1.21 (2H, t), 1.20 (6H, s), 1.15 (6H, s)

³¹P NMR: -1.62 (sextet)

¹³C NMR: 73.5 (d), 63,5 (d), 45.8 (d), 34.9, 28.9, 18.7, 16.1 (d)

4.5. Diphenyl (2,2,6,6-tetramethylpiperidin-4-yl) phosphate (5)

2,2,6,6-tetramethylpiperidin-4-ol (10 g, 0,0636 mol) with diphenyl chlorophosphate (12,6 ml, 0,064 mol). Product purified with silica filtration using DCM as eluent, contains around 20wt% impurity. 5,7 g (0,0082 mol), 24 % yield with impurity deducted.

¹H NMR (CDCl₃): 7.35 (4 h, t), 7.24 (4H, d), 7.20 (2H, t), 4.96 (1H, m), 2.05 (2H, dd), 1.28 (2H, t), 1.20 (6H, s), 1.15 (6H, s)

³¹P NMR: –12.6 (duplet)

¹³C NMR: 150, 130, 125, 120, 75.8, 51, 45, 35, 29

4.6. Tris(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl) phosphite (6)

4-hydroxy-TEMPO (60 g, 0,348 mol) and TEA (55 ml) were dissolved in DCM (400 ml) cooled to -16 °C under argon atmosphere. PCl3 (10 ml 0,116 mol) was then slowly added with a syringe. Reaction mixture was then allowed to warm up to RT and stirring was continued overnight. Reaction was quenched with water and rapid stirring, organic phase was then collected and washed with more water and then brine and dried with Na₂SO₄. Solution was filtered and used as such for the next step.

4.7. Tris(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl) phosphate (7)

Ascorbic acid (35 g, 0,232 mol) was dissolved in water/THF mixture (200+200 ml) and added to the solution of **(6)**. Mixture warmed and lost color. Product was extracted with ether, 39,5 g (0,070 mol) pale yellow solid, 70 % purity.

¹H NMR(CDCl₃): 4.45 (1H, m), 1.91 (2H, dd), 1.52 (2H, t), 1.09 (6H, s), 1.05 (6H, s)

 31 P NMR decoupled: -3.16 ppm (quartet)

4.8. Tris(2,2,6,6-tetramethylpiperidin-4-yl) phosphate (8)

Tris(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl) phosphate **(7)** (24 g, 0,044 mol) was dissolved in glacial acetic acid (100 ml) under

rapid stirring. Zinc powder (11,6 g, 0,175 mol) was added in portions to avoid clumping. Mixture heated up almost to boil. After it cooled down, KOH (100 g) in water was added slowly to neutralize the acid and the mixture was then extracted with chloroform (2 \times 200 ml). Organic fractions were combined, dried with Na₂SO₄ and solvent was then removed with rotary evaporator to give 19,3 g of slightly brownish liquid.

¹H NMR (CDCl₃): 4.72 (1H, m), 2.06 (2H, dd), 1.26 (2H, t), 1.22 (6H, s), 1.17 (6H, s)

³¹P NMR decoupled: –2.90 ppm (quartet)

4.9. Bis(1-((4-((diethoxyphosphoryl)oxy)phenyl)thio)-2,2,6,6-tetramethylpiperidin-4-yl)carbonate (NS1)

Disulfanediylbis(4,1-phenylene) tetraethyl bis(phosphate) (1) (67,4 g, 0,129 mol) was dissolved in 100 ml DCM, SO_2Cl_2 (11 ml, 0,135 mol) was added and solution stirred for 15 min. Then it was evaporated slowly to dryness with rotavapor at 40 °C and 650mbar for another 15 min and then completely dried with lower pressure. Then 100 ml DCM was added and the solution was slowly added to 100 ml DCM solution of bis(2,2,6,6-tetramethylpiperidin-4-yl) carbonate (43,9 g, 0,129 mol) under argon atmosphere at -16 °C. After addition, the mixture was stirred overnight at RT. Then the mixture was washed with NaHCO₃ solution and then brine, and organic fraction was collected, dried with Na₂SO₄ and evaporated to dryness under reduced pressure. Residue was filtered through silica with DCM as eluent, after evaporation, the material was further washed with 200 ml hexane, at this stage, white solid was obtained, and it was collected by filtration. 77 g (0,089 mol, 69 % yield), pure product.

¹H NMR (CDCl₃): 7.25 (4H, d), 7.14 (4H, m), 5.02 (2H, tt), 4.23 (8H, m), 2.18 (4H, dd), 1.77 (4H, t), 1.37 (12H, td), 1.34 (12H, s), 1.27 (12H, s) s)

³¹P NMR decoupled: -6.0 ppm (pentet)

¹³C NMR: 154, 148, 142, 123, 120, 70, 65 (d), 61, 46, 32, 26, 16 (d) M/z = 860.3261, calc. 860.32703, error 1.1 ppm

4.10. Bis(1-((4-((diphenoxyphosphoryl)oxy)phenyl)thio)-2,2,6,6-tetramethylpiperidin-4-yl)carbonate (NS2)

23,3 g (0,030 mol) of (2) and piperidinol carbonate 10 g (0,030 mol) gave 14,35 g (0,0136 mol, 45 % yield), pure product.

¹H NMR (CDCl₃): 7.37 (8H, t), 7.26 (8H, d), 7.24 (8H, t), 7.16 (4H, d), 5.02 (2H, tt), 2.18 (4H, dd), 1.77 (4H, t), 1.34 (12H, s), 1.27 (12H, s)

³¹P NMR decoupled: -17.38 ppm ¹¹C NMR: 154.3, 150.5 (d), 147.3 (d), 142.3, 129.9,125.6, 123.0,

120.1 (d), 70.8, 61.1,45.5, 32.2, 25.6

M/z = 1052.32703, calc. 1052.3260, error 1.0 ppm

4.11. Bis(1-((4-((bis(2,6-dimethylphenoxy)phosphoryl)oxy)phenyl) thio)-2,2,6,6-tetramethylpiperidin-4-yl) carbonate (NS3)

6,3 g (0,0076 mol) (2) and piperidinol carbonate 1,95 g (0,0076 mol) gave 4,1 g (0,0035 mol, 46 % yield).

¹H NMR (CDCl₃): 7.19 (4H, d), 7.05 (12H, m), 7.00 (4H, d), 5.02 (2H, tt), 2.18 (4H, dd), 1.77 (4H, t), 1.34 (12H, s), 1.27 (12H, s)

³¹P NMR decoupled: -16.82 ppm ¹¹C NMR (CDCl3): 154.2, 148.2 (d), 147.7(d), 141.78, 130.4(d),

```
129.2 (d), 125.5 (d), 122.63, 120.2 (d), 70.7, 61.0,45.5, 32.2, 25.6, 17.1 M/z = 1164.4529, calc. 1164.45223, error 0.6 ppm
```

4.12. 1-(benzo[d]thiazol-2-ylthio)-2,2,6,6-tetramethylpiperidin-4-yl diethyl phosphate (NS4)

10,8 g (0,0276 mol) of (4) and 4,6 g (0,0138 mol) of bis benzothiazole disulfide gave 5,9 g (0,013 mol, 47 % yield).

¹H NMR (CDCl₃): 7.8 (2H, dd), 7.4 (1H, t), 7.0 (1H, t), 4.7 (2H, m),

4.16 (4H, pentet), 2.26 (2H, dd), 1.90 (2H, t), 1.50 (6H, s), 1.39 (6H, t), 1.36 (6H, s)

³¹P NMR decoupled: -1.5 ppm

¹¹C NMR: 180, 154, 135, 126, 124, 122, 121, 71 (d), 64 (d), 62, 47, 32, 26, 16 (d)

M/z = 458.1460, calc.458.14629, error 0.6 ppm

4.13. 1-(benzo[d]thiazol-2-ylthio)-2,2,6,6-tetramethylpiperidin-4-yl diphenyl phosphate (NS5)

14,9 g (90 % purity, 0,0454 mol) of (5) and 5,7 g (0,0227 mol) of bis benzothiazole disulfide gave 5,7 g (0,013 mol, 24 % yield) of product.

¹H NMR (CDCl3): 7.8 (2H, dd), 7.4 (5H, t), 7.28 (5H, m) 7.24 (2H, td), 4.96 (2H, m), 2.21 (2H, dd), 1.91 (2H, t), 1.47 (6H, s), 1.33 (6H, s) ³¹P NMR decoupled: -12.5 ppm

¹¹C NMR: 180, 154, 150 (d), 135, 130, 126, 125, 124, 121.6, 120.8,



Fig. 2. General synthesis routes to NS1-NS6, where R=Et for (1), (4), NS1 and NS4, R = pH for (2), (5), NS2, and NS5 and R = 2,6-dimethylphenyl for (3) and NS3.

120.1 (d), 73 (d), 62, 47 (d), 33, 26 *M*/*z* = 554,14,472, calc. 554,14,629, error 2.7 ppm

4.14. Tris(1-benzothiazol-3-ylthio) – 2,2,6,6-tetramethylpiperidin-4-yl) phosphate (NS6)

10,0 g (0,0194 mol) of (8) and 12,9 g (0,0388 mol) of bis benzo-thiazole disulfide gave 9,6 g (0,0096 mol, 49 % yield) of product.

¹H NMR (CDCl₃): 7.84 (1H, d), 779 (1H, d), 7.42 (1H, t), 7.30 (1H, t), 4.80 (1H, m), 2.30 (2H, dd), 1.95 (2H, t), 1.54 (6H, s), 1.41 (6H, s)

³¹P NMR decoupled: -2.67 ppm (quartet)

¹¹C NMR: 180, 154, 134.5, 126, 132.7, 121.6, 120.8, 71.0 (d), 62.0, 47.3 (d), 32.7, 25.9

M/*z* = 1010,29,727, calc. 1010,29,727, error 1 ppm

5. Results and discussion

In the design of these novel flame retardants, we wanted to preserve certain structural sulfenamide elements based on our previous work on the optimization of sulfenamide flame retardant structures for polypropylene. On top of this our intention was to incorporate phosphate groups into the sulfenamide structure in order to create multifunctional flame retardants. Thus, firstly to ensure sufficiently high thermal stability of sulfenamides (to survive polypropylene processing at ca. 230 °C) it has been established to be beneficial that the sulfur group (benzothiazole or phenyl sulfur) is connected to a sterically hindered secondary amine such as 2,2,6,6-tetramethylpiperidine or bis(2,2,6,6tertramethyl-4-piperdinyl) carbonate. Moreover, we have noticed that by using sulfenamide as standalone flame retardants it has been difficult to reach UL94 V rating for polypropylene, despite of very short burning times after first ignition. However, after the second ignition the polypropylene plaques burn too long to achieve a UL94 V rating as standalone flame retardant and burning drips ignited the cotton. Our hypothesis of introducing a phosphate group into the sulfenamide flame retardant structure was to investigate whether the burning time after second ignition could be significantly reduced by the tethering a phosphate group onto the sulfenamide based flame retardant. It is well known that phosphate-based flame retardants mainly exert their flame retardant action by charring. Thus, we wanted to explore if the phosphate group could slow down the burning tendency after the second ignition by slight charring. Therefore, we decided to design and synthesize the following six different multifunctional flame retardants NS1 to NS6. The synthesis routes for the preparation of the six multifunctional flame retardants are depicted in Fig. 2 (a, b and c).

The structure of final products was verified by 1 H and 13 C NMR (see supplementary material). In addition, LC-MS was used to confirm the exact masses of each multifunctional flame retardant and to determine the pathway of their fragmentation.

6. Thermal stabilities of multifunctional flame retardants

First, thermogravimetric analysis (TGA) was used to determine the thermal stabilities of the synthesized multifunctional flame retardants under nitrogen atmosphere. The TGA results are depicted in Table 1. The onset degradation temperatures were evaluated using the temperature

Table 1

Decomposition	temperatures	and	char	residue.
---------------	--------------	-----	------	----------

Compound	T _{dec} 5wt% / $^{\circ}$ C	T _{dec} 50wt% / $^{\circ}C$	Char at 600 $^\circ\text{C}$ /%
NS1	250	286	20.0
NS2	254	323	15.4
NS3	265	348	23.1
NS4	250	308	10.3
NS5	220	279	14.3
NS6	248	281	14.5

of 5 mass% loss (Td 5 %) and it varied between 220 °C to 267 °C, while the temperature of mass loss of 50 mass% (Td 50 %) loss ranged from 281 °C to 348 °C. The highest initial stabilities and char formation were measured for the multifunctional flame retardants having the bis (2,2,6,6-tetramethyl-4-piperidinyl) carbonate synthon (NS1, NS2, NS3), whereas the lowest thermal stability was recorded for NS5, as shown in Table 1. NS2 and NS3 exhibited a two-stage decomposition profile, whereas the other NS flame retardants decomposed in one stage.

For NS1–3, phosphate groups having ethyl substituents is slightly less stable than the corresponding flame retardants having either phenyl or 2,6-dimethylphenyl substituents attached to the phosphate moieties when comparing the Tdec 50 wt% values. This is in line with previous studies of showing that phosphate based flame retardants having aromatic substituents P-O-C_{aromatic} have a higher capacity to protective charring in the condensed phase than those with aliphatic substituents P-O-C_{aliphatic}. Furthermore, the thermal stabilities of polypropylene samples containing 4 wt% of the different multifunctional flame retardants were compared in nitrogen atmosphere. The results are shown in Fig. 3. Initial decomposition temperature at 5wt% weight loss occurs ca. 40 °C sooner for PP samples containing either NS2 or NS3 in comparison to the other samples.

7. Combustion behaviors of different multifunctional flame retardants

The flame retardant efficacy of multifunctional flame retardants for polypropylene films and plaques were tested according to DIN4102 B2 and UL94 V fire tests, respectively. The results are summarized in Tables 2 and 3. The DIN4102 B2 test results reveal that all of the NS compounds were able to self-extinguish the polypropylene films at the very low concentration of 0.5 wt%. The high efficacy for PP films is attributed to thermolysis of the sulfenamide bond which leads to the release of sulfur and aminyl radicals that effectively promote the pyrolysis of polypropylene, whereby the flame zone is deprived from fuel since the viscosity drop enables the polymer fragments to retract from the flame zone. In general, it has been reported that radical generators containing sulfur such as sulfur, sulfide, disulfide or sulfenamides may besides promoting polymer fragmentation, enhance crosslinking (excluding PP) and generate sulfur dioxide which acts as a diluent or radical scavenger in the gas phase [44,45].

The UL94 V fire test is a basic and critical parameter to be evaluated for various end applications of polymeric materials. As shown in Table 3, polypropylene samples containing the multifunctional flame retardants denoted NS2 and NS3 passed the UL94 V2 criteria as standalone flame retardants at 4 w% loadings. This is to the best of our knowledge the first example of halogen free flame retardants that can pass UL94 V2 by themselves at this low loading of 4 wt% in polypropylene. The secondbest performance was recorded for sample NS1 followed by NS6, whereas NS5 burned to the clamp.

It is difficult to directly compare the efficacies of the various multifunctional flame retardants due to variations in their sulfur content (e.g., sulfur content decreases from 7,5 % for NS1 to 5,5 % for NS3), phosphorus content, differences in P/S ratios. Moreover, the initial decomposition takes place at the sulfenamide bond or at the phosphorus moiety depending on the flame retardant structure. Therefore, in this article the flame retardant efficacy comparison has been based on weight% of multifunctional flame retardant.

8. Analysis of multifunctional flame retardants decomposition products

The decomposition products are important indicators for elucidating the mechanism of action of the multifunctional flame retardants in a real fire scenario. Therefore, thermal decomposition products formed after oven aging between 220 and 260 $^{\circ}$ C were studied by GC/MS, ¹H NMR, ³¹P NMR and SEM-EDX. In addition, thermal decomposition



Fig. 3. TGA curves of polypropylene samples containing 4 wt% of NS1 to NS6, respectively.

Table 2DIN4102 B2 fire test results for polypropylene films (200 μm).

Test DIN 4201	Sulfenamide	Loading /%	Damage length /cm	Average burning time/ s	Pass / fail
1	NS1	0,5	10,4	0	pass
2	NS2	0,5	10,1	0	Pass
3	NS3	0,5	10,8	0	Pass
4	NS4	0,5	8,6	4,3	Pass
5	NS5	0,5	7,9	0	Pass
6	NS6	0,5	8,1	1,3	Pass

Table 3

Results of UL-94	V	test for	po	lypropy	lene p	laques	(1.6)	o mm)).
------------------	---	----------	----	---------	--------	--------	-------	-------	----

No.	FR	Loading /wt%	UL 94 classification	Burn t	Burn time average/s		
				T ₁	T ₂	Total	
1	NS1	2	NC (4/5 pass)	20	22,7	212	
2	NS1	4	NC (4/5 pass)	12,4	7,8	101	
3	NS2	4	V2	3	12,2	76	
4	NS3	4	V2	2,4	11,6	70	
5	NS4	4	NC (2/5 pass)	17,6	18,7	182	
6	NS5	4	NC, burn to clamp	85	-	-	
7	NS6	4	NC (3/5 pass)	3,5	46,8	2513	

experiments were also conducted in the presence of 9,10-dihydroanthracene as a proton donor to determine whether the sulfenamide part of the multifunctional flame retardants give raise to free aminyl and sulfur radicals that support polypropylene breakdown (melt away mechanism). In addition, the thermal release of these free radicals may also contribute to flame retardancy by interfering with the free radical reactions occurring during the combustion process of polypropylene itself.

Thus, for thermal decomposition experiments all samples were heated for limited times (60 - 90 s) under argon atmosphere, at a temperature range from 220 °C to 260 °C in the presence or absence of 9,10dihydroanthracene. The formed decomposition products were then analyzed by ¹H NMR and ³¹P NMR and the interpretation of obtained spectra reveal that the decomposition starts at the sulfenamide bond for samples NS1-3 and seemingly also for NS6 since no change of phosphorus atom couplings could be recorded and only a minor shift in form of shoulder for phosphorus itself could be observed. Whereas for samples NS4 and NS5 the decomposition started with cleavage of P-O-/-Cbond prior to breaking of the sulfenamide bond as the ${}^{31}P$ couplings and shifts in the spectra changed markedly. Furthermore, ¹H NMR spectra recorded in the presence of 9,10-dihydro-anthracene confirmed the thermolysis of sulfenamides to free radicals because a major portion of 9,10-dihydroanthracene had been converted to anthracene, as exemplified for NS3 in Fig. 4. Decomposition from the NS -bond causes clear shift in piperidine CH2 proton and methyl -signals and only minor shift in the CH-signal connected to phosphorus.

Thus, the ¹H NMR spectra confirms that the sulfenamide part of the multifunctional flame retardant can generate free radicals that exert their flame retardant action via the formation of aminyl and sulfur based free radicals. Moreover, NS3 exhibits fractions that also confirm the thermolysis of sulfenamide bond and in the LC-MS spectra the fragment



Fig. 4. Proton spectra of a) pure NS3, b) NS3 decomposed alone at 260 °C for 90 s and c) NS3 decomposed in the presence 9,10-dihydroanhtracene at 260 °C for 90 s.

assigned to di(2,6-dimethyl)phenyl sulfide phosphate was observed, as shown in Fig. 5.

Whereas in the case of NS4 and NS5, the decomposition took initially place at the phosphorus part by cleaving of the sterically hindered piperidine, as shown Fig. 6. In addition, the 31 P NMR reveal that for NS4, the pentet signal is converted to quartet and for NS5, the duplet to singlet.

Because NS3 sample created the highest yield of char in this series of multifunctional flame retardants and it passed the UL94 V2 criteria in PP, the char composition was further analyzed by SEM-EDX. The

analysis revealed that the char was mostly carbon (polyaromatics, 40,4%), phosphorus (likely phosphate, or polyphosphates, 20,4%) oxygen (28,7%) and nitrogen (aminyl radicals, 7,1%) and only an insignificant amount of sulfur (2,7%) could be detected. Therefore, it can be concluded that the aromatic phosphate moiety is mainly responsible for the charring effect and the sulfenamide function as an efficient radical generator. The combination of these two complementary flame retardant mechanisms within a single multifunctional flame retardant has led to a strong synergistic effect.



Fig. 5. LC-MS spectra of NS3.



Fig. 6. LC-MS spectra of NS4.

9. Conclusions

In this work, six novel multifunctional flame retardants comprising of sulfenamide and phosphate units have been successfully synthesized which display extraordinary high flame retardant efficacy for polypropylene both in thin films and plaques. Two of the prepared multifunctional flame retardants provided UL94 V2 rating for polypropylene plaques of 1.6 mm at 4 wt% loading. The high flame retardant effect has been attributed to the synergistic interplay between the sulfenamide and phosphate moieties. Thus, the sulfenamide unit exerts its fire retarding property by thermal release of aminyl and sulfur radicals that support a faster polymer degradation in which polypropylene fragments are removed from the flame zone and/or they suppress the radical processes in the combustion cycle of polypropylene. Whereas, the role of the phosphorus moiety may be attributed to reinforcement of the gas phase activity, acceleration of the thermal induced degradation of polypropylene. This type of multifunctional flame retardants exhibits inherently a strong synergistic effect in a fire scenario and therefore it has been able to endow polypropylene with a high flame retardant property. In general, it seems that multifunctional flame retardants possessing dual fire retardant functionalities can become a valuable strategy for the development of the next generation flame retardants.

Authors contributions

Timo Ääritalo: He conducted all the synthetic work and characterization of the flame retardants properties. He also participating in flame retardancy testing and in the writing of the manuscript. Yury Brusentsev: He participated in the idea generation and characterized of the decomposition products of the multifunctional flame retardants by NMR. Carl-Eric Wilen: He participated in the original idea generation; formulation and evolution of overarching research goals and aims. He had the oversight and leadership responsibility for the research activity planning and execution, including mentorship external to the core team. He also participated in writing of the manuscript. Teija Tirri: She participated in the idea generation and in overseeing the experimental part. Luo Breton: She participated in polymer blending, preparation of PP specimens and evaluation of flame retardant efficacies and characteristics of thermal properties.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Carl-Eric Wilen and Teija Tirri reports a relationship with Songwon Industrial Co Ltd that includes: funding grants. Carl-Eric Wilen and Teija Tirri has patent #WO2015/067736 issued to Songwon Industrial. no other conflict of interest

Data availability

The authors do not have permission to share data.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2023.110568.

References

- H. Yang, B. Yu, X. Xu, S. Bourbigot, H. Wang, P. Song, Lignin-derived bio-based flame retardants toward high-performance sustainable polymeric materials, Green Chem. 22 (2020) 2129–2161.
- [2] F. Carosio, A. Di Blasio, J. Alongi, G. Malucelli, Green DNA-based flame retardant coatings assembled through Layer by Layer, Polymer (Guildf) 54 (2013) 5148–5153, 407.
- [3] X. Jin, S. Cui, S. Sun, X. Gu, H. Li, X. Liu, W. Tang, J. Sun, S. Bourbigot, S. Zhang, The preparation of a bio-polyelectrolytes based core-shell structure and its application in flame retardant polylactic acid composites, Compos. Part A Appl. Sci. Manuf. 124 (2019), 105485.
- [4] B.P. Chang, S. Thakur, A.K. Mohanty, M. Misra, Novel sustainable biobased flame retardant from functionalized vegetable oil for enhanced flame retardancy of engineering plastic, Sci. Rep. 9 (2019) 15971.
- [5] Z.Y. Chen, P. Xiao, J.M. Zhang, W.G. Tian, R.N. Jia, H.F. Nawaz, K. Jin, J. Zhang, A facile strategy to fabricate cellulose-based, flame-retardant, transparent, and anti-dripping protective coatings, Chem. Engin. J. 379 (2020), 122270.
 [6] T. Sai, S. Ran, Z. Guo, P. Song, Z. Fang, Recent advances in fire-retardant carbon-
- [6] T. Sai, S. Ran, Z. Guo, P. Song, Z. Fang, Recent advances in fire-retardant carbonbased polymeric nanocompoistes through fighting free radicals, SusMat 2 (2023) 411–434.

T. Ääritalo et al.

- [7] C. Wan, H. Duan, C. Zhang, C. Liu, H. Zhao, H. Ma, Synthesis of a multielement flame retardant and its application in epoxy resin, ASC Appl. Polym. Matter 5 (2023) 1775–1785.
- [8] W.-J. Yan, C.-J. Ding, J.-J. Min, S.-C. Liu, J. Jian, J. Hu, S. Xu, Fabrication of green and scalable N/P/S/Mn containing biobased layered double hydroxide as a novel flame retardant and efficient char forming agent for polypropylene, ACS Sustain. Chem. Eng. (2023) 5216–5228.
- [9] W.-J. Jin, X.-W. Cheng, J.-P. Guan, W. Chen, Q.-F. Qian, J.-L. Xu, Investigation on flame retardancy on sulfur/nitrogen-based compounds for polyamide 6 fabric through exhaustion route, Polym. Deg. Sta. 195 (2022), 109779.
- [10] D.W. Horsey, S.M. Andrews, L. Harris, D. Darrel, D. Dyas, R.L. Gray Jr., A. Gupta, B. Vincent, H.J. Steven Puglisi, R. Ravichandran, P. Shields, R. Srinivasan, Flame retardant composition, WO1999000450A1.
- [11] Ronan, N.; Wilen, C.-E.M., "Flame Retardant Compositions", WO 2005030852.
 [12] R.C. Nicolas, C.E. Wilén, M. Roth, R. Pfaendner, R.E. King, Azoalkanes: a novel
- class of flame retardants, Macromol. Rapid Commun. 27 (12) (2006) 976–981.
 M. Aubert, C.N. Ronan, W. Pawelec, C.E. Wilén, M. Roth, R Pfaendner, Azoalkanesnovel flame retardants and their structure-property relationship, Polym. Adv. Tech. 22 (11) (2011) 1529–1538.
- [14] W. Pawelec, M. Aubert, R. Pfaendner, H. Hoppe, C.E. Wilén, Triazene compounds as a novel and effective class of flame retardants for polypropylene, Polym. Degrad. Stab. 97 (6) (2012) 948–954.
- [15] W. Pawelec, A. Holappa, T. Tirri, M. Aubert, H. Hoppe, R. Pfaendner, C.-E Wilén, Disulfides-effective radical generators for flame retardancy of polypropylene, Polym. Degrad. Stab. 110 (2014) 447–456.
- [16] J. Wagner, P. Deglmann, S. Fuchs, M. Ciesielski, C.A. Fleckenstein, M. Döring, A flame retardant synergism of organic disulfides and phosphorus compounds, Polym. Degrad. Stab. 129 (2016) 63–76.
- [17] A. Manfredi, F. Carosio, P.F.J. Alongi, E. Ranucci, Disulfide-containing polyamidoamines with remarkable flame retardant activity for cotton fabrics, Polym. Degrad. Stab. 156 (2018) 1–13.
- [18] C.-E. Wilen, M. Aubert, T. Tirri, W. Pawelec "Sulfenamides as Flame Retardants" WO2015/067736 A1.
- [19] T. Tirri, M. Aubert, W. Pawelec, A. Holappa, C.-E. Wilén, Structure–property studies on a new family of halogen free flame retardants based on sulfenamide and related structures, Polym. (Basel) 8 (2016) 360.
- [20] A. Mountassir, T. Tirri, P. Sund, C.-E. Wilén, Sulfenamides as standalone flame retardants for polystyrene, Polym. Degrad. Stab. 188 (2021), 109588.
- [21] T. Ääritalo, T. Tirri, M. Aubert, C.-E. Wilen, Synthesis of silylamine and siloxyamine compounds: a novel approach to flame retardancy of polypropylene and Epoxy resins, Polym. Degrad. Stab. 211 (2023), 110336.
- [22] Kröller T., Meyer A., Al-Masri M., Piestert F., Wilen C.-E., Aubert M., Tirri T., Ääritalo T., Silyl Functional Compound for Improving Flame Retardant Properties, WO2020212377A1.
- [23] R. Pfaendner, E. Metzsch-Zilligen, M. Stec, Use of Organic Oxy Imides as Flame Retardants for Plastics and Flame-Retardant Plastics Composition and Mouldings Produced Therefrom, WO 2014154636.
- [24] G. Liu, W. Chen, J. Yu, A novel process to prepare ammonium polyphosphate with crystalline form II and its comparison with melamine polyphosphate, Ind. Eng. Chem. Res. 49 (23) (2010) 12148–12155.
- [25] Deng, Z.B. Shao, Y. Tan, M.J. Chen, Y.Z. Wang, Flame retardation of polypropylene via novel intumenscent flame retardant :ethylenediamine modified ammonium polyphosphate Polym. Degrad. Stabil. 106 (2014) 88–89.
- [26] Z.B. Shao, C. Deng, Y. Tan, M.J. Chen, L. Chen, Y.-Z. Wang, An efficient Monocomponent polymeric intumescent flame retardant for polypropylene: preparation and application, ACS Appl. Mat. Interfac. 6 (2014) 7363–7370.
- [27] Q. Lv, J.Q. Huang, M.J. Chen, J. Zhao, Y. Tan, L. Chen, Y.-Z. Wang, An effective flame retardant and smoke suppression oligomer for epoxy resin, Ind. Engin. Chem. Res. 52 (2013) 9397–9404.

- [28] C. Deng, H. Yin, R.-M. Li, S.-C. Huang, B. Schartel, Y.-Z. Wang, Modes of action of a mono-component intumescent flame retardant MAPP in polyethylene-octene elastomer, Polym. Degrad. Stab. 138 (2017) 142–150.
- [29] J.L. Yan, M.J. Xu, Design, synthesis and application of a highly efficient monocomponent intumescent flame retardant for non-charring polyethylene composites, Polym. Bull. 78 (2021) 643–662.
- [30] L.B. Liu, Y. Xu, Y.T. He, M.J. Xu, W. Wang, B. Li, A facile strategy for enhancing the fire safety of unsaturated polyester resins through introducing an efficient monocomponent intumescent flame retardant, Polym. Adv. Technol. 31 (2020) 1218–1230.
- [31] S.Y. Xia, Z.Y. Zhang, Y. Leng, B. Li, M.J. Xu, Synthesis of a novel mono-component intumescent flame retardant and its high efficiency for flame retardant polyethylene, J. Anal. Appl. Pyrolys. 134 (2018) 632–640.
- [32] H. Luo, W. Rao, P. Zhao, L. Wang, Y. Liu, C. Yu, An efficient organic/inorganic phosphorus-nitrogen-silicon flame retardant towards low-flammability epoxy resin, Polym. Deg. Stab 178 (2020), 109195.
- [33] L. Yi, Z. Huang, Y. Cao, Y. Peng, Synthesis of a novel spiro phosphorus-nitrogen concentrated reactive flame retardant curing agent and its application in epoxy resins, Front. Mater. 7 (2020), 293 article.
- [34] L. Yi, Z. Huang, Y. Cao, Y. Peng, Novel phosphorus-nitrogen-silicon flame retardants and their application in cycloaliphatic epoxy systems, Polym. Chem. 6 (2015) 2977–2985.
- [35] Q. Li, P. Jiang, P. Wei, Synthesis, characteristic, and application of new flame retardant containing phosphorus, nitrogen and silicon, Polym. Eng. Sci. (2006), https://doi.org/10.1002/pen.20472.
- [36] S. Zhang, F. Chu, Z. Xu, Y. Zhou, Y. Qiu, L. Qian, Y. Hu, B. Wang, W. Hu, The improvement of fire safety performance of flexible polyurethane foam by highlyefficient P-N-S elemental synergistic flame retardant, J. Colloid Interface Sci. 606 (2022) 768–783.
- [37] Z.-M. Zhu, Y.-J. Xu, W. Liao, S. Xu, Y.-Z. Wang, Highly flame retardant expanded polystyrene foams from phosphorus-nitrogen-silicon synergistic adhesive, Ind. Eng. Chem. Res. 56 (2017) 4649–4658.
- [38] Y. Chen, H. Peng, J. Li, Z. Xia, H. Tan, A novel flame retardant containing phosphorus, nitrogen and sulfur, J. Them. Anal. Calorim. 115 (2014) 1639–1649.
- [39] K. Song, Y. Wang, F. Ruan, J. Liu, N. Li, X. Li, Effects of a macromolecule spirocyclic inflatable flame retardant on the thermal and flame retardant properties of epoxy resin, Polym. (Basel) 12 (2022) 132.
- [40] Z.-B. Shao, C. Deng, Y. Tan, M.-J. Chen, L. Chen, Y.-Z. Wang, An efficient monocomponent polymeric intumescent flame retardant for polypropylene: preparation and application, ACS Appl. Mater. Interface. 6 (2014) 7363–7370.
- [41] R. Nazir, A. Gooneie, S. Lehner, M. Jovic, P. Rupper, N. Ott, R. Hufenus, S. Gaan, Alkyl sulfone bridged phosphorus flame retardants for polypropylene, Mater. Des. 200 (2021), 109459.
- [42] J. Sag, P. Kukla, D. Goedderz, H. Roch, S. Kabasci, M. Döring, F. Schönberge, rSynthesis of novel polymeric acrylate-based flame retardants containing two phosphorus groups in different chemical environments and their influence on the flammability of poly(lactic acid), Polym. (Basel) 12 (2020) 778.
- [43] M. Aubert, C.-E. Wilen, R. Pfaendner, S. Kniesel, H. Hoppe, M. Roth, Bis(1-propyloxy-2,2,6,6-tetramethylpiperidin-4-yl)-diazene An innovative multifunctional radical generator providing flame retardancy to polypropylene even after extended artificial weathering, Polym. Degra. Stabil. 96 (2011) 328–333.
- [44] A. Battig, J.C. Markwart, F.R. Wurm b, B. Schartel, Sulfur's role in the flame retardancy of thio-ether–linked hyperbranched polyphosphoesters in epoxy resins, Eur Polym J 122 (5) (2020), 109390.
- [45] C.-C. Höhne, C. Posern, U. Böhme, F. Eichler, E. Kroke, Dithiocyanuartes and thiocyamelurates: thermal thiyl radical generators as flame retardants in polypropylene, Polym. Deg. Stab 166 (2019) 17–30.