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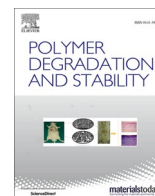
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# Highly efficient multifunctional mono-component flame retardants comprising of sulfenamide and phosphate moieties for polypropylene

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## ABSTRACT

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 loss 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-dihydroanthracene and the formed decomposition products were analyzed using GC/MS, LC/MS, <sup>13</sup>C NMR and <sup>31</sup>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 NS1 film 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 efficiencies 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 rise 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], triazines [14], disulfides [15–17], sulfenamides (NS) [18–20], silylamines [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.

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One of the most successful commercial multifunctional mono-component 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 as phosphoramines or phosphoramidates have been reported [25]. On top of this, many different combinations of phosphorus 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(2,6-dimethylphenoxy)-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-ylthio)-2,2,6,6-tetra-methylpiperidin-4-yl diphenyl phosphate (NS5) and tris(1-benzothiazol-3-ylthio)-2,2,6,6-tetra-methylpiperidin-4-yl 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, sulfuric 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 >97 %, bis-(2,6-dimethylphenyl) chlorophosphate TCI Europe >99 %, diphenyl chlorophosphate from Aldrich >99 % and 2,2'-dithiobis(benzothiazole) from Sigma-Aldrich >96 %.

**Characterization methods:** NMR spectra ( $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$ ) were recorded on a 500 MHz Bruker AVANCE-III NMR-system. Thermal treatment of FR mixtures for  $^{31}\text{P}$  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- $d_6$  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  $\text{N}_2$  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. Disulfaneyldibis(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  $\text{Na}_2\text{SO}_4$  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.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.37 (4H, d), 7.10 (4H, d), 4.14 (8H, m), 1,27 (12H, t)

$^{31}\text{P}$  NMR: –6.45 (pentet)

$^{13}\text{C}$  NMR: 150.5 (d), 133.1, 130.2, 120.8 (d), 64.7 (d), 16.1 (d)

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

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

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.39 (4H, d), 7.05 (16H, m), 2.37 (24H, s)

$^{31}\text{P}$  NMR: –17.1 (s)

$^{13}\text{C}$  NMR: 150 (d), 148 (d), 133.5, 130.4 (d), 130.0, 129.2 (d), 125.6

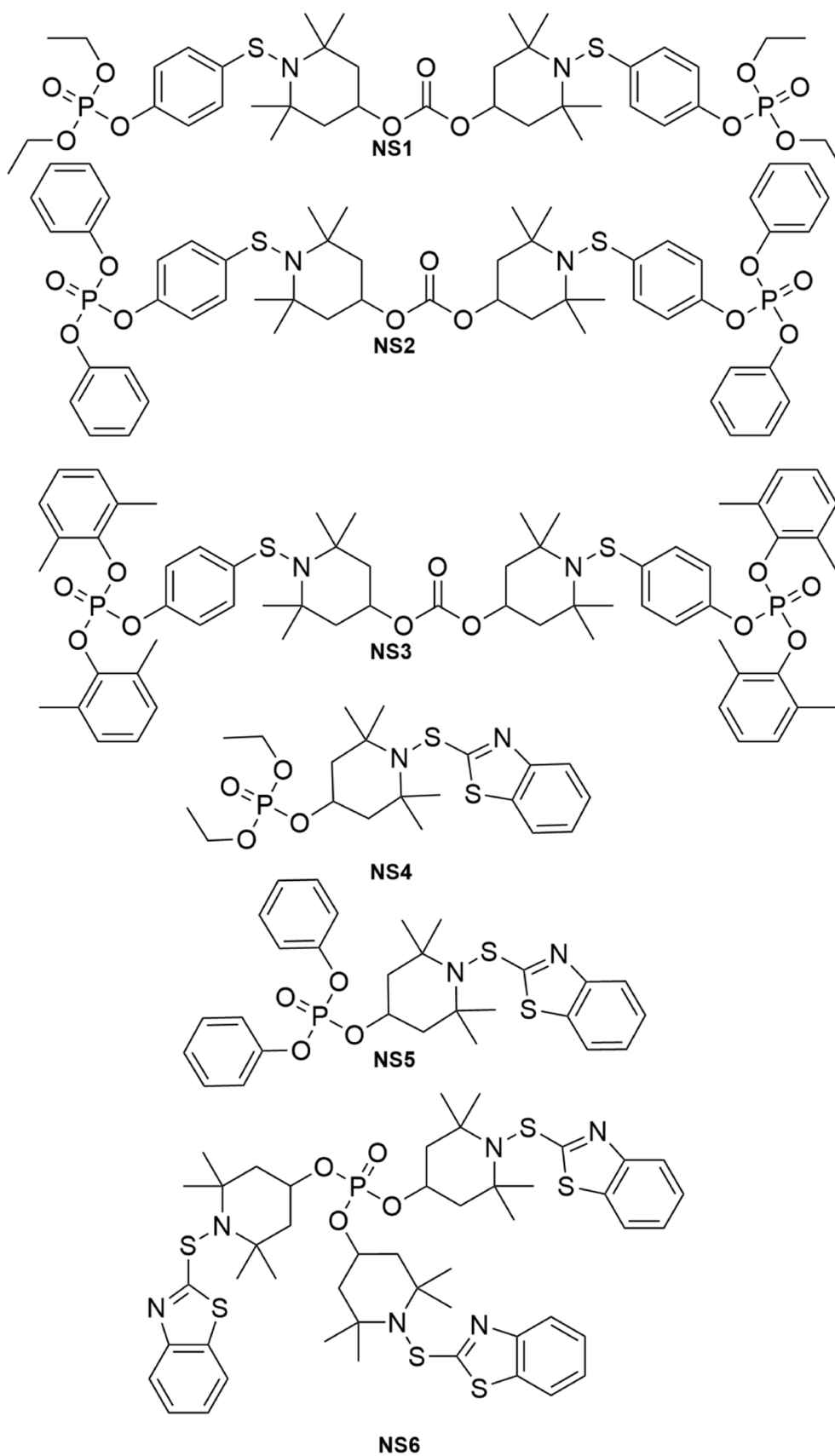


Fig. 1. Chemical structures of synthesized multifunctional flame retardants denoted from NS1 to NS6.

(d), 120.8 (d), 17

#### 4.3. Tetrakis(2,6-dimethylphenyl) (disulfanediybis(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.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 7.48 (4H, d), 7.37 (8H, m), 7.26 (8H, t), 7.22 (8H, t)

$^{31}\text{P NMR}$ : -17.2 (s)

$^{13}\text{C NMR}$ : 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 ice-ethanol 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  $\text{Na}_2\text{SO}_4$  and evaporated to dryness to give a yellow liquid, 13,7 g, 66 % yield with impurity deducted, this contains around 10m% impurity.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 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)

$^{31}\text{P NMR}$ : -1.62 (sextet)

$^{13}\text{C NMR}$ : 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.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 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)

$^{31}\text{P NMR}$ : -12.6 (duplet)

$^{13}\text{C NMR}$ : 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  $-16^\circ\text{C}$  under argon atmosphere.  $\text{PCl}_3$  (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  $\text{Na}_2\text{SO}_4$ . 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.

$^1\text{H NMR}$ ( $\text{CDCl}_3$ ): 4.45 (1H, m), 1.91 (2H, dd), 1.52 (2H, t), 1.09 (6H, s), 1.05 (6H, s)

$^{31}\text{P NMR}$  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  $\text{Na}_2\text{SO}_4$  and solvent was then removed with rotary evaporator to give 19,3 g of slightly brownish liquid.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 4.72 (1H, m), 2.06 (2H, dd), 1.26 (2H, t), 1.22 (6H, s), 1.17 (6H, s)

$^{31}\text{P NMR}$  decoupled: -2.90 ppm (quartet)

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

Disulfanediybis(4,1-phenylene) tetraethyl bis(phosphate) (1) (67,4 g, 0,129 mol) was dissolved in 100 ml DCM,  $\text{SO}_2\text{Cl}_2$  (11 ml, 0,135 mol) was added and solution stirred for 15 min. Then it was evaporated slowly to dryness with rotavapor at  $40^\circ\text{C}$  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  $-16^\circ\text{C}$ . After addition, the mixture was stirred overnight at RT. Then the mixture was washed with  $\text{NaHCO}_3$  solution and then brine, and organic fraction was collected, dried with  $\text{Na}_2\text{SO}_4$  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.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 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)

$^{31}\text{P NMR}$  decoupled: -6.0 ppm (pentet)

$^{13}\text{C NMR}$ : 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.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 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)

$^{31}\text{P NMR}$  decoupled: -17.38 ppm

$^{13}\text{C NMR}$ : 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).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 7.19 (4H, d), 7.05 (12H, m), 7.00 (4H, d), 5.02 (2H, t), 2.18 (4H, dd), 1.77 (4H, t), 1.34 (12H, s), 1.27 (12H, s)

$^{31}\text{P NMR}$  decoupled: -16.82 ppm

$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ): 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 benzo-thiazole disulfide gave 5,9 g (0,013 mol, 47 % yield).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 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)

$^{31}\text{P}$  NMR decoupled:  $-1.5$  ppm

$^{13}\text{C}$  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.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 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)

$^{31}\text{P}$  NMR decoupled:  $-12.5$  ppm

$^{13}\text{C}$  NMR: 180, 154, 150 (d), 135, 130, 126, 125, 124, 121.6, 120.8,

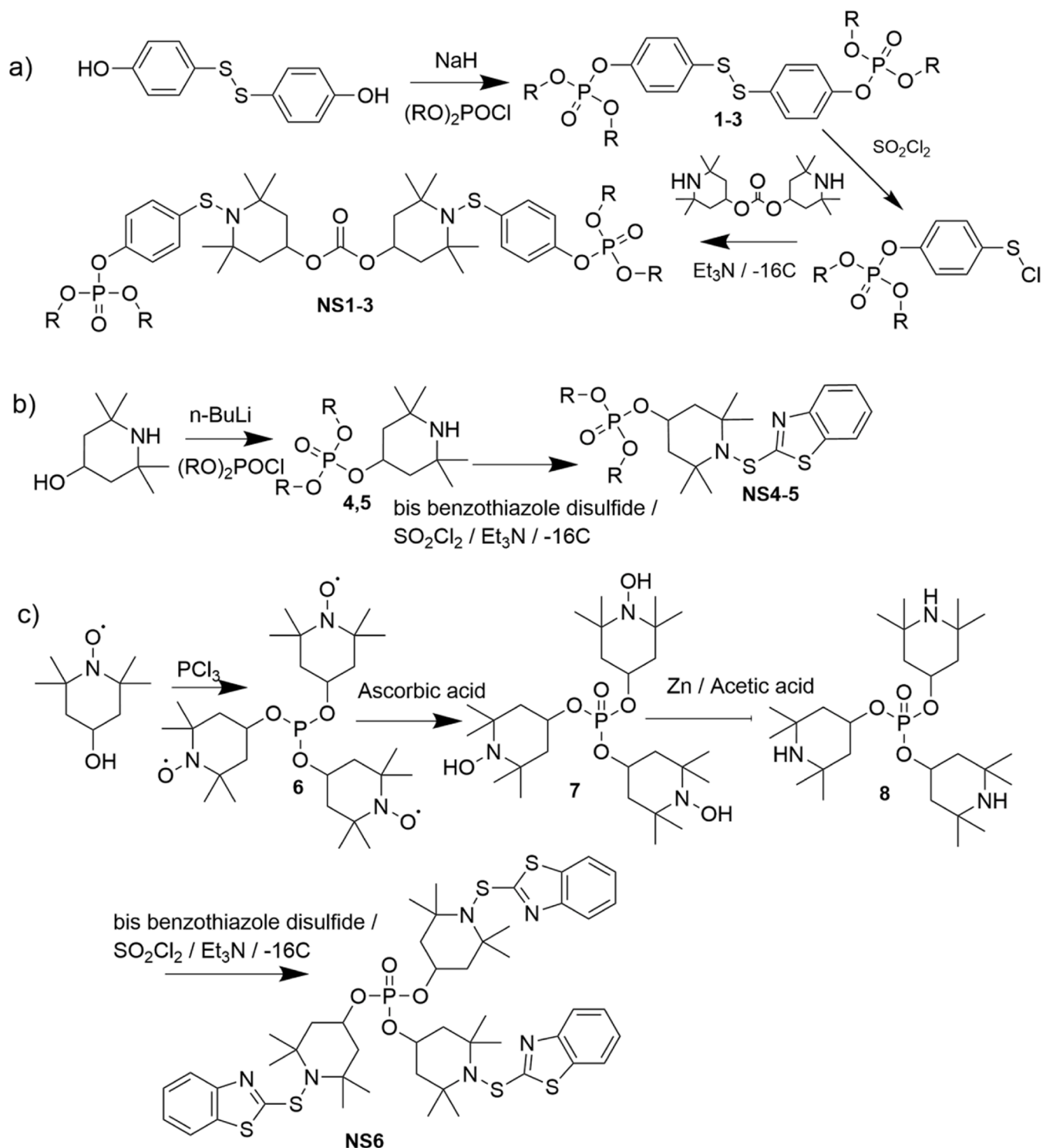


Fig. 2. General synthesis routes to NS1-NS6, where  $R=\text{Et}$  for (1), (4), NS1 and NS4,  $R = \text{pH}$  for (2), (5), NS2, and NS5 and  $R = 2,6\text{-dimethylphenyl}$  for (3) and NS3.



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 benzothiazole disulfide gave 9,6 g (0,0096 mol, 49 % yield) of product.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 7.84 (1H, d), 7.79 (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)

$^{31}\text{P NMR}$  decoupled:  $-2.67$  ppm (quartet)

$^{13}\text{C NMR}$ : 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(2,2,6,6-tetramethyl-4-piperidinyl) 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  $^1\text{H}$  and  $^{13}\text{C}$  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	$T_{\text{dec}} 5\text{wt\%} / ^\circ\text{C}$	$T_{\text{dec}} 50\text{wt\%} / ^\circ\text{C}$	Char at 600 °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 ( $T_d 5\%$ ) and it varied between 220 °C to 267 °C, while the temperature of mass loss of 50 mass% ( $T_d 50\%$ ) 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  $T_{\text{dec}} 50\text{ wt\%}$  values. This is in line with previous studies of showing that phosphate based flame retardants having aromatic substituents P-O-C<sub>aromatic</sub> have a higher capacity to protective charring in the condensed phase than those with aliphatic substituents P-O-C<sub>aliphatic</sub>. 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 second-best 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 °C were studied by GC/MS,  $^1\text{H NMR}$ ,  $^{31}\text{P NMR}$  and SEM-EDX. In addition, thermal decomposition

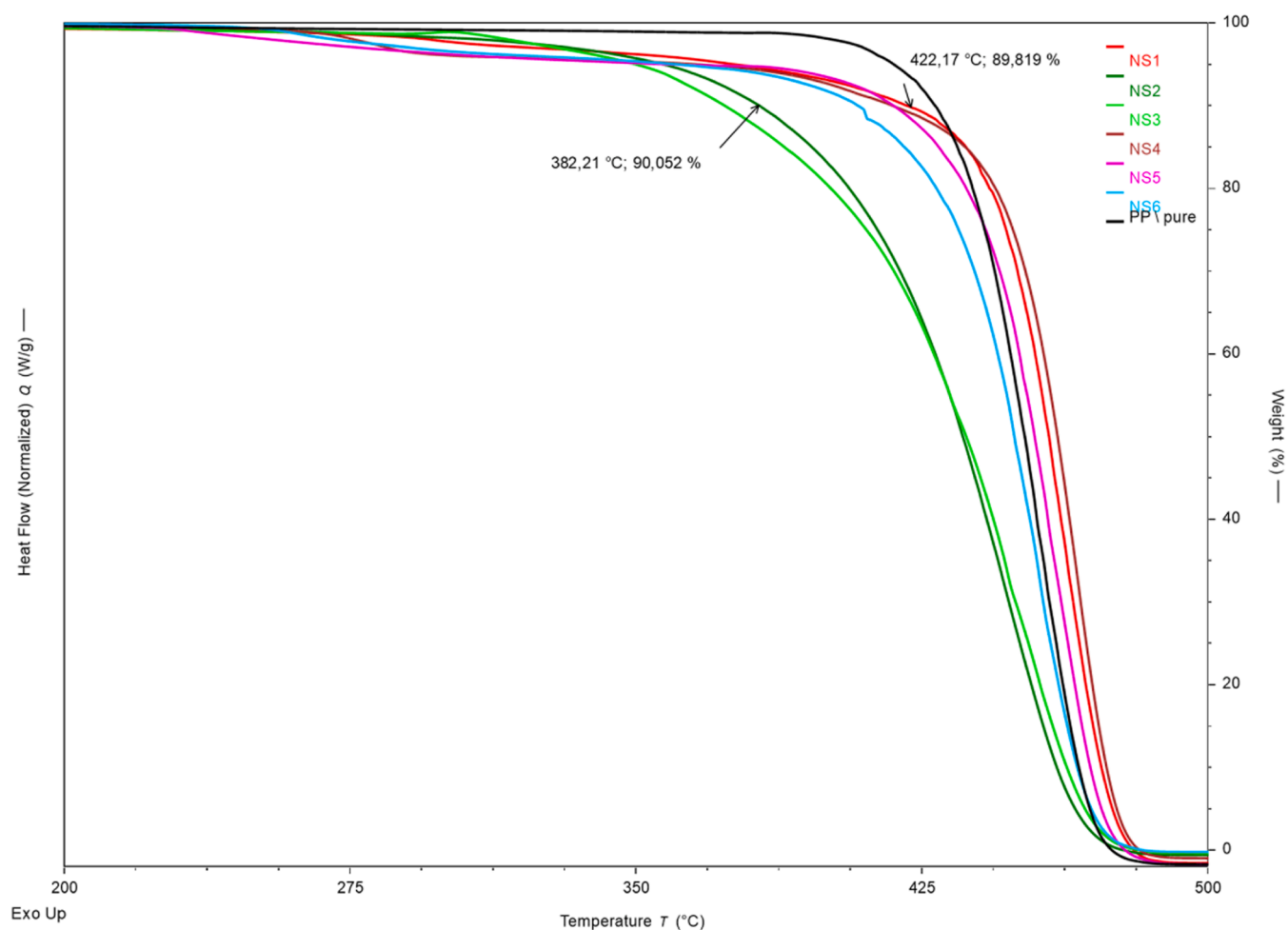


Fig. 3. TGA curves of polypropylene samples containing 4 wt% of NS1 to NS6, respectively.

**Table 2**  
DIN4102 B2 fire test results for polypropylene films (200  $\mu\text{m}$ ).

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 polypropylene plaques (1.6 mm).

No.	FR	Loading /wt%	UL 94 classification	Burn time average/s		
				T <sub>1</sub>	T <sub>2</sub>	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 9,10-dihydroanthracene. The formed decomposition products were then analyzed by <sup>1</sup>H NMR and <sup>31</sup>P 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-/C-bond prior to breaking of the sulfenamide bond as the <sup>31</sup>P couplings and shifts in the spectra changed markedly. Furthermore, <sup>1</sup>H 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 CH<sub>2</sub> proton and methyl -signals and only minor shift in the CH-signal connected to phosphorus.

Thus, the <sup>1</sup>H 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



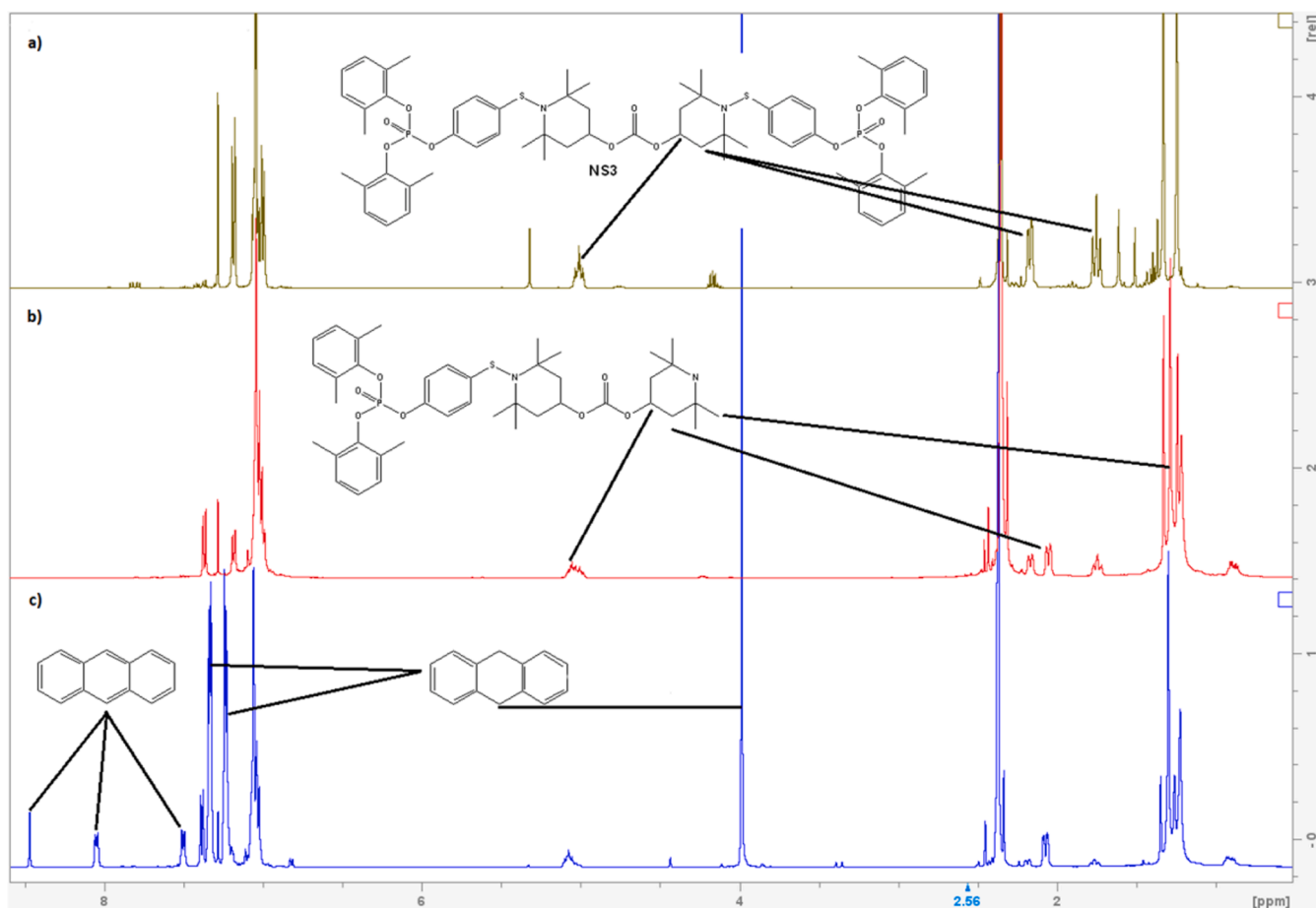


Fig. 4. Proton spectra of a) pure NS3, b) NS3 decomposed alone at 260 °C for 90 s and c) NS3 decomposed in the presence 9,10-dihydroanthracene at 260 °C for 90 s.

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  $^{31}\text{P}$  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.

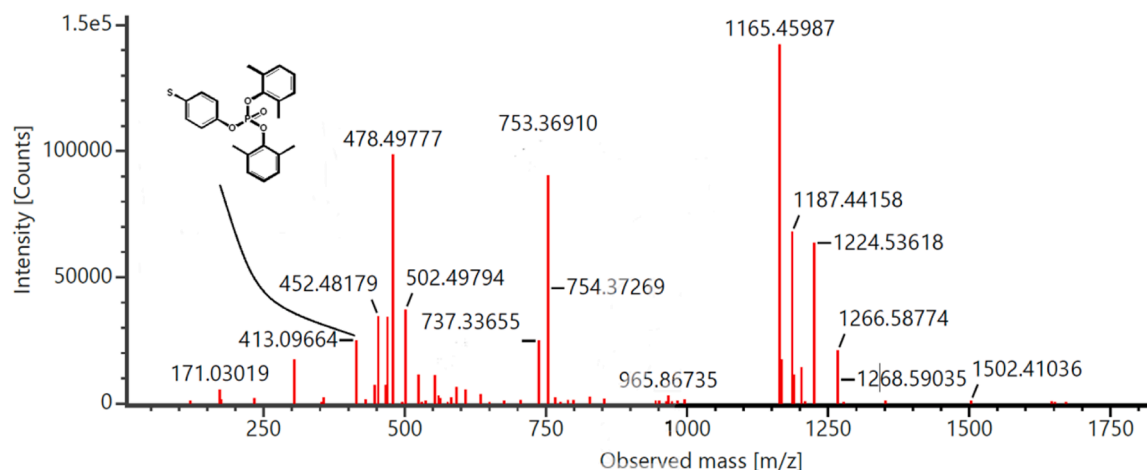


Fig. 5. LC-MS spectra of NS3.

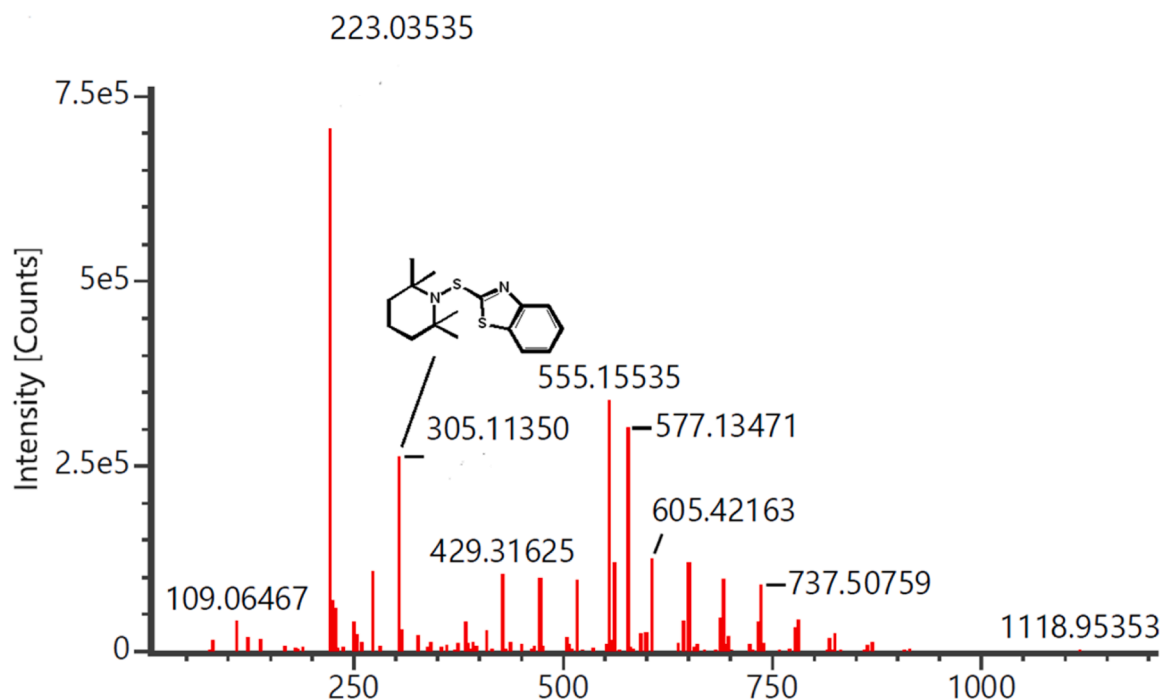


Fig. 6. LC-MS spectra of NS4.

## 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](https://doi.org/10.1016/j.polymdegradstab.2023.110568).

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