

Flame retardant polyester by combination of organophosphorus compounds and an NOR radical forming agent

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ABSTRACT: Polymer materials with different surface to volume ratios require different mechanisms of flame retardants regarding condensed phase and gas phase activity. The flame retardant formulations in poly(ethylene terephthalate) (PET) are investigated regarding a condensed phase and gas phase activity by using thermogravimetric analysis (TGA), TG mass spectrometry (MS), TG Fourier transform infrared (FTIR), UL94, cone calorimeter and scanning electron microscopy energy dispersive X ray spectrometer measurements. The flame retardant formulations containing phosphates, phosphonates, and phosphinates as flame retardants are analyzed by using a simultaneous analysis consisting of a differential thermal analysis TGA device which is *in situ* coupled to FTIR and MS. All analysis methods show a gas phase activity for the phosphonate (PCO 910), a condensed phase activity for the phosphate (3,9 bis(phenoxy) 2,4,8,10 tetraoxa 3,9 diphosphaspiro 5,5 undecane 3,9 dioxide, (SPDPP) and a mixed condensed and gas phase activity for the new synthesized phosphate and 9,10 dihydro 9 oxa 10 phosphaphenanthrene 10 oxide containing flame retardant 3,9 bis(phenoxy) 2,4,8,10 tetraoxa 3,9 diphosphaspiro 5,5 undecane 3,9 dioxide (SPDPDOM). The fire behavior of PCO 910 can be improved by adding O,O' Terephthaloyl bis N,N' naphthalimide ester as NOR radical forming agent (NOR RF) reaching a total amount of 3 wt % of both active agents for a UL94 V 0 classification in PET. © 2019 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2020**, *137*, 47876.

KEYWORDS: phosphorus-containing flame retardants; poly(ethylene terephthalate); radical forming agent; synergism

INTRODUCTION

Poly(ethylene terephthalate) (PET) offers a broad portfolio of applications for thin walled or bulk materials and is a combustible material which requires tailor made flame retardant solutions. Thin walled applications like foils, fibers, and foams are very sensitive to changes of the melt viscosity by additives like flame retardants restricting their use. For this purpose, it is preferable to choose low loadings of flame retardants resulting in lower impairments of the melt viscosity, foamability, or mechanical

properties of the finished product. In this work, the total amount of flame retardants was kept as low as possible. High processing temperatures of PET (max 300 °C) call for flame retardant agents which have an adequate thermostability.¹ Some phosphorus containing flame retardants like AFLAMMIT PCO 910 or Exolit OP 950 satisfy these requirements. There are very few radical forming (RF) agents which meet this requirement. NOR RF agents include Flamestab NOR 116 and ester of *N* hydroxyimides.^{2,3} The selected NOR RF agent thereof has a suitable thermostability

for an extrusion process with PET. The development of non halogenated as well as nonvolatile flame retardants is getting more important due to bans of certain toxic flame retardants.⁴⁻⁶

Phosphorus based flame retardants can be active in the gas phase and/or condensed phase depending on the chemical environment of the phosphorus atom and the structural characteristics of the matrix polymer. The increasing oxygen environment of the phosphorus atom in flame retardants results in an increasing charring effect. On the other hand, an increasing carbon or hydrogen environment of the phosphorus atom in flame retardants result in a predominantly gas phase activity as mentioned in many studies before.^{7,8} During the combustion process of organic polymeric materials highly reactive H* and OH* radicals are generated as flame propagating species. Phosphorus based flame retardants which decompose with evolution of phosphorus based radicals decrease the concentration of H* and OH* radicals thus being not able to maintain the combustion process (flame poisoning).⁸⁻¹⁵

We examined the flame retardant efficiency and the thermal properties of different phosphorus based flame retardants such as phosphonates, phosphates, and phosphinates individually and in combination with a NOR RF agent (Figure 1). The phosphate based flame retardants are all derivatives of a spirocyclic pentaerythritol compound. The spirobis(pentaerythritol chlorophosphate) (SPDPC) can be used easily for esterification. Pentaerythritol spirobis(methylphosphonate) (PCO 910) is commercial available and used among other things as flame retardant for polyesters. By the esterification of 6 oxide 6 H dibenz[*c,e*][1,2]oxaphosphorin 6 methanol (DOPO MeOH) with SPDPC we synthesized a new flame retardant unifying a phosphate and a DOPO moiety and thus gas phase and condensed phase activity in one molecule. DOPO based polymers realized in Heim by TOBOYO are intrinsically flame retardant fibers.¹⁶ PO* radicals were detected for flame retardants indicating a gas phase activity using a thermogravimetric analysis (TGA)/differential thermal analysis (DTA)

device which is *in situ* coupled to Fourier transform infrared (FTIR) and MS. In this work, a combination of a flame retardant with gas phase activity was combined with NOR RF agent characterized by its high thermostability enhancing the flame retardancy with only a total loading of 3% of active agents.

EXPERIMENTAL

Material

PET (BISNEINEX) was provided by Equipolymers in Italy. AFLAMMIT PCO 910 was provided by Thor (Speyer, Germany). Unless stated otherwise, solvents and chemicals were obtained from Acros Organics (Fisher Scientific in Schwerte, Germany) and used without further purification. DOPO MeOH was supplied by Metadynea Austria GmbH (Krems, Österreich).

General Procedure

All experiments were carried out under nitrogen atmosphere and dry solvents were used. Nuclear magnetic resonance (NMR) data were obtained on a Bruker NanoBay 300 spectrometer. Chemical shifts are reported as δ values relative to the solvent peak in ppm. Trimethylsilane was used as a standard.

Single crystals of C₁₇H₁₈O₈P₂ [SPDPP] were obtained through precipitation from water/methanol. Diffraction data of a suitable crystal were collected on a STOE STADIVARI diffractometer. The crystal was kept at 150.15 K during data collection. Using Olex2,¹⁷ the structure was solved with the ShelXS¹⁸ structure solution program using direct methods and refined with the ShelXL¹⁹ refinement package using least squares minimization. Structural data are in agreement with those published by Heinemann *et al.*²⁰

The phosphorus content was determined using an SEM (JEOL JSM 6400, 20 kV acceleration voltage and 40 \times magnification) equipped with an energy dispersive X ray spectrometer (EDX, EDAX Apollo).

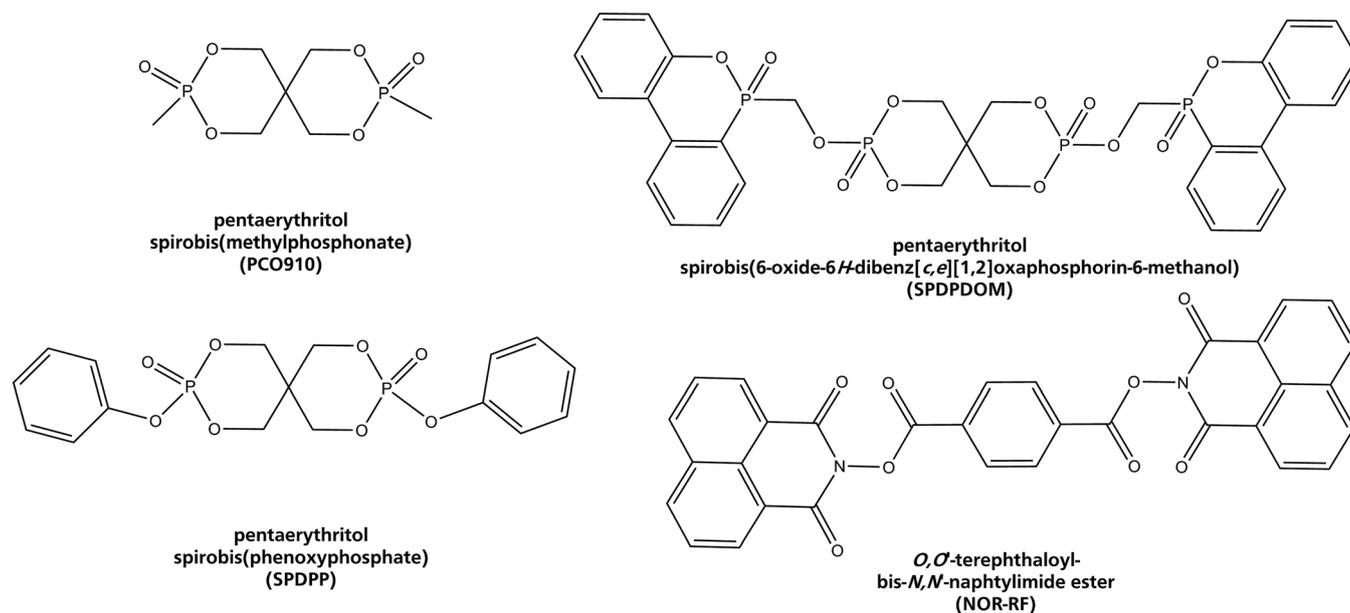


Figure 1. Molecular structures of the phosphonate based (PCO910), phosphate based (SPDPP), DOPO /phosphate based (SPDPDOM) flame retardants as well as the NOR RF agent.

Thermodesorption MS experiments were made using a Finnigan MAT 95 with a constant heating rate of 25 K min⁻¹ in a temperature range of 40–400 °C.

TGA was carried out using a TGA Q500 from TA Instruments, Inc. (New Castle, DE, USA) with a heating rate of 10 K min⁻¹ under constant nitrogen or air atmosphere.

The simultaneous thermal analysis was carried out using a TGA/DTA (STA 449C Jupiter; NETZSCH Gerätebau GmbH, Selb, Germany) coupled to FTIR (Bruker TENSOR 27) and MS (QMS 403C Aeolos) at a constant heating rate of 10 K min⁻¹ in a temperature range of 35–600 °C.

Compounding was carried out using a corotating twin screw extruder (Thermo Scientific Process 11 from Fisher Scientific (Schwerte, Germany), screw diameter: 11 mm) with a screw rotation speed of 150 rpm. The first temperature zone was set as 240 °C, all other temperature zones were set as 270 °C. The melt strand was cooled with a water bath and pelletized in a pelletizing system (VariCut Granulator).

The UL94 samples were obtained by hot pressing (Collin) of the compounds at 270 °C and 5 bar for 5 min. The UL 94 vertical burning test setup was done using a WAZAU burning chamber according to DIN IEC 60,695 11 10 with a 50 W burner flame.

The cone calorimeter tests were carried out according to ISO 5660 on a cone calorimeter from Fire Testing Technology (35 kW m⁻² heat flux orientation of the samples) according to ASTM E 1354, on 10 × 10 cm² plaques (2 mm thickness). All samples were tested in triplicate.

Synthesis of 3,9 Dichloro 2,4,8,10 Tetraoxa

3,9 Diphosphaspiro 5,5 Undecane 3,9 Dioxide (SPDPC)

A flame dried three necked round bottom glass flask was equipped with a reflux condenser and a magnetic stirrer. A total of 60 g (441 mmol, 1.0 aq.) of pentaerythritol and 189.11 g (1233 mmol, 2.8 aq.) of phosphoroychloride were added and heated to 75 °C for 4 h. The reaction mixture was heated to 105 °C for 6 h and cooled to room temperature (RT). The colorless residue was filtered off and washed with chloroform. The obtained solid was dried *in vacuo* for 24 h. Yield: 81% ¹H NMR (300.38 MHz, 298 K, CDCl₃): δ = 4.59 (ddd, 1H; J = 28.5 Hz, 12.4 Hz, 2.8 Hz); 4.44–4.27 (m, 1H); 4.19–3.88 (m, 2H) ppm. ³¹P NMR (121.60 MHz/298 K/CDCl₃): δ = -3.09 ppm.^{21,22}

Synthesis of 3,9 Bis(phenoxy) 2,4,8,10 Tetraoxa

3,9 Diphosphaspiro 5,5 Undecane 3,9 Dioxide (SPDPP)

A flame dried 250 mL three necked round bottom glass flask was equipped with a reflux condenser and a magnetic stirrer. A total of 40 g (134.7 mmol, 1.0 aq.) SPDPC, 28 g (297.5 mmol, 2.2 aq.) phenol, and 380 mL acetonitrile were added. Under vigorous stirring 42 mL (298.8 mmol, 2.2 aq.) triethylamine was added drop by drop. After 6 h, the precipitated white solid was collected by filtration and washed with water and dried *in vacuo* at 60 °C. Yield: 53% ¹H NMR [300.38 MHz, 298 K, hexadeuterated dimethyl sulfoxide (DMSO *d*₆)]: δ = 7.50–7.26 (m, 10 H); 4.85–4.41 (m, 8H) ppm. ³¹P NMR (121.60 MHz/298 K/DMSO *d*₆): δ = -13.60 ppm. TGA: T₉₈ = 405 °C, T₀ = 530 °C.

Crystal data for C₁₇H₁₈O₈P₂ (*M* = 412.25 g mol⁻¹): orthorhombic, space group Pna2₁ (no. 33), *a* = 11.4710 (3) Å, *b* = 6.1955 (2) Å, *c* = 25.7028 (7) Å, *V* = 1826.66 (9) Å³, *Z* = 4, *T* = 150.15 K, μ(GaKα) = 1.663 mm⁻¹, *D*_{calc} = 1.499 g cm⁻³, 11,487 reflections measured (5.984° ≤ 2θ ≤ 114.982°), 3743 unique (*R*_{int} = 0.0328, *R*_{sigma} = 0.0237) which were used in all calculations. The final *R*₁ was 0.0498 [*I* > 2σ(*I*)] and *wR*₂ was 0.1407 (all data).^{21,22}

Synthesis of 3,9 Bis(phenoxy) 2,4,8,10 Tetraoxa

3,9 Diphosphaspiro 5,5 Undecane 3,9 Dioxide (SPDPDOM)

A flame dried 500 mL three necked round bottom glass flask was equipped with a reflux condenser and a magnetic stirrer. A total of 12.16 g (40.94 mmol, 1 aq.) SPDPC, 21.17 g (85.99 mmol, 2.1 aq.) DOPO MeOH, and 200 mL acetonitrile were added. Under vigorous stirring 12 mL (86.10 mmol, 2.1 aq.) Triethylamine was added drop by drop. After 12 h at 80 °C, the precipitated white solid was collected by filtration and washed with water and dried *in vacuo*. Yield: 89% ¹H NMR (300.38 MHz, 298 K, DMSO *d*₆): δ = 8.34–8.25 (dd, *J* = 21.96; 7.75 Hz, 4 H); 8.09–8.06 (m, 2H); 7.93–7.87 (td, *J* = 8.22; 7.52; 1.41 Hz, 2H); 7.72–7.67 (t, *J* = 7.50; 7.50 Hz, 2H); 7.52–7.47 (m, 2H); 7.39–7.35 (m, 4H); 4.94–4.72 (m, 4H); 4.26–4.16 (m, 2H); 3.86–3.82 (d, *J* = 12.12 Hz, 2H); 3.64–3.59 (dd, *J* = 11.72; 2.22 Hz, 2H); 3.30–3.26 (d, *J* = 11.89 Hz, 2H). ³¹P NMR (121.60 MHz/298 K/DMSO *d*₆): δ = -8.47 ppm (d; *J* = 31.75 Hz); 27.29 ppm (d; *J* = 31.75 Hz). TGA: T₁ = 293 °C, T₉₅ = 357 °C.

Synthesis of *N* Hydroxynaphthalimide

A flame dried 1000 mL three necked round bottom glass flask is equipped with a magnetic stirrer. A total of 42.08 g (605.51 mmol, 1.5 aq.) hydroxylamine hydrochloride was dissolved in 600 mL pyridine. Then, 80.00 g (403.67 mmol, 1.0 aq.) 1,8 naphthalic acid anhydride were added and the reaction mixture is stirred for 20 h at RT. The precipitate is filtered off and washed with water. Yield: 79% ¹H NMR (300.38 MHz, 298 K, DMSO *d*₆): δ = 10.76 (s, 1 H), 8.52–8.45 (dd, 4H), 7.91–7.86 (m, 2H).²³

Synthesis of *O,O'* Terephthaloyl Bis *N,N'* Naphthalimide Ester (NOR RF)

A flame dried 2000 mL three necked round bottom glass flask is equipped with a reflux condenser and a magnetic stirrer. A total of 50.00 g (234.54 mmol, 2.5 aq.) *N* hydroxynaphthalimide was dissolved in 1500 mL pyridine at 45 °C. Then, 19.05 g (93.82 mmol, 1.0 aq.) terephthalic acid dichloride was added and the reaction mixture is stirred at 45 °C for 1 h and then stirred at RT for 20 h. The precipitate is filtered off and washed with water. Yield: 75% MS *m/z*: 556.24 u. TGA: T₁ = 237 °C, T₉₅ = 349 °C.²³

RESULTS AND DISCUSSION

SPDPC was synthesized according to the literature^{21,22} from pentaerythritol and phosphorus oxychloride. AFLAMMIT PCO 910 is a commercial available phosphonate from Thor. The flame retardants SPDPP and SPDPDOM are synthesized from SPDPC and phenol respectively DOPO MeOH.

Crystal Structure of SPDPP

Single crystals were obtained from SPDPP and the crystal structure was investigated (Figure 2). SPDPP crystallizes in an orthorhombic crystal system with the space group Pna2₁. The planes of the phenol rings are forming an angle of 8.16° and the six membered

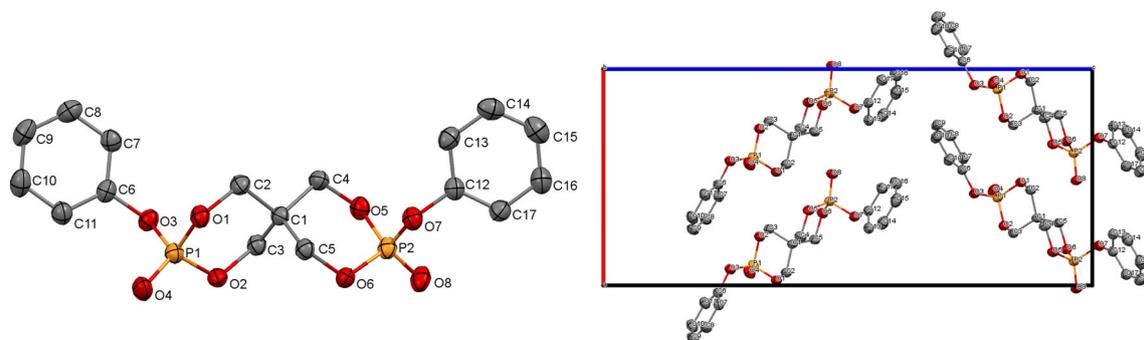


Figure 2. Molecular structure of SPDPP. Crystal packing of SPDPP viewed along the b axis. Hydrogen atoms were omitted for clarity. [Color figure can be viewed at wileyonlinelibrary.com]

rings of the spirobis(phosphate) ring are twisted against one another about 89.12° . The six membered aliphatic rings of the spirobis(phosphonate) adopt a flattened chair confirmation with the P=O group in the equatorial position. The crystal structures of 3,9 dichloro 2,4,8,10 tetraoxa 3,9 diphosphaspiro[5.5]undecane 3,9 dione and 3,9 diphenoxy 2,4,8,10 tetraoxa 3,9 diphosphaspiro [5.5]undecane 3,9 dioxide have been reported by Zhan *et al.*²⁴ and Heinemann *et al.*²⁰ Cyclic phosphate esters like 2 oxo 2 phenoxy 1,3,2 dioxaphosphorinane reported by Geise show very similar O—P—O bonding angles as the corresponding spirobis(phosphate) SPDPP.²⁵ For SPDPPDOM, no crystals were obtained but the crystal structure is expected to be comparable to SPDPP.

Flame Retardant Formulations in PET

Table I summarizes the composition of the flame retardant formulations. The phosphorous atoms of the flame retardants PCO 910, SPDPP, and SPDPPDOM have different chemical environments.

Table I. Investigated Compositions of Flame Retarded PET Formulations Containing Different Phosphorus Compounds and the NOR RF Agent

#	Amount of flame retardants and NOR-RF agent				Calculated phosphorus content (%)
	PCO 910 (%)	SPDPP (%)	SPDPPDOM (%)	NOR-RF (%)	
1	—	—	—	—	—
2	2	—	—	—	0.48
3	3	—	—	—	0.73
4	5	—	—	—	1.29
5	10	—	—	—	2.42
6	—	2	—	—	0.30
7	—	10	—	—	1.50
8	—	—	2	—	0.35
9	—	—	10	—	1.73
10	2	—	—	1	0.48
11	—	2	—	1	0.30
12	—	—	2	1	0.35
13	8	—	—	4	1.93
14	5	5	—	—	2.04
15	—	—	—	5	—

SPDPPDOM includes phosphate as well as DOPO moieties and an overall phosphorus content of 17.32%. PCO 910 has a phosphorous content of 24.18% whereas SPDPP contains 15.02% phosphorus.

In Situ Thermal Analysis of Flame Retardant Formulations

Figure 3 shows TGA curves for the single flame retardant components under nitrogen (left diagram) and under air atmosphere (right diagram). The TGA results indicate a condensed phase activity for SPDPP and a gas phase activity for PCO 910 due to the amount of residues at 600°C . The phosphonate has a residue of 6% at 600°C whereas the corresponding phenoxy phosphate has a residue of 37% at 600°C . Both phosphorous compounds degrade in a single step. The thermal behavior of PCO 910 under air atmosphere is similar to that under nitrogen atmosphere with slightly more residue at 600°C . Neat SPDPP decomposes more rapidly and with less residue at 600°C under air atmosphere due to oxidation processes which is in accordance with the literature.^{22,26} The decomposition of SPDPPDOM starts at lower temperatures under air atmosphere than under inert atmosphere showing a further degradation step starting at 600°C which is also caused by oxidation processes. The TGA curve under air atmosphere of NOR RF shows a further oxidation of the char residue especially at 600°C . No significant differences of the TGA curves of the neat flame retardants can be observed, so further investigations of the thermal behavior were carried out under nitrogen atmosphere.

Table II summarizes the thermal properties of the investigated flame retardants and flame retardant formulations. It can be clearly observed that the incorporation of 10 wt % of SPDPP in PET leads to a char formation of +10.13% at 600°C in comparison to neat PET and the incorporation of the same amount of phosphonate flame retardant. Then, 10% SPDPPDOM as well as 10% SPDPP result in 30% total residue at 600°C . An increasing amount of the remaining residues at 600°C of the flame retardant formulations is an indication for a condensed phase activity. The temperature of the maximum decomposition rate ($T_{\text{max dec rate}}$) is most influenced and decreased by the incorporation of the phosphate into PET. The phosphonate flame retardant in PET leads to an increased temperature of the decomposition maximum (435.444°C) in comparison to neat PET. Also, 5% PCO 910 and 10% SPDPP having comparable phosphorus contents of about 1.3–1.5% show a difference in the remaining residues at 600°C of about 9%.

The neat NOR RF compound as NOR RF agent generates a residue of 42% at 600°C (Table II) due to the high aromatic content

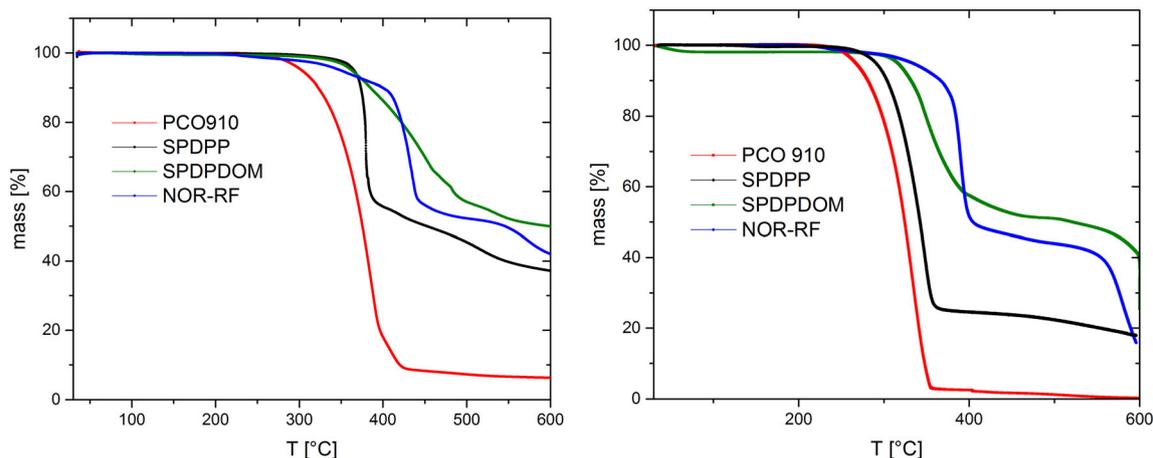


Figure 3. TGA of neat flame retardants PCO 910, SPDPP, SPDPDOM, and the NOR RF agent at 10 K min⁻¹ under nitrogen (left diagram). TGA of neat flame retardants PCO 910, SPDPP, SPDPDOM, and the NOR RF agent at 10 K min⁻¹ under air atmosphere (right diagram). [Color figure can be viewed at wileyonlinelibrary.com]

of the NOR RF that will remain in the condensed phase in case of fire. Figure 4 shows the TGA curves for all flame retardant formulations in PET (upper left diagram). The turning points of the phosphate containing formulations 10% SPDPP and 10% SPDPDOM have lower corresponding temperatures than comparable phosphonate formulations. As expected, the quantities of the remaining residues of the phosphate containing formulations are higher than those of phosphonate containing flame retardant formulations with comparable phosphorus contents. As can be seen in the upper right diagram, a mass loss step of about 5% for the formulation containing 5% NOR RF takes place.

The NOR RF degrades first which also can be observed by the release of carbon dioxide in TG FTIR experiments (Figure 5).

There are two clear and separate CO₂ release steps. The combination of 8% PCO 910 and 4% NOR RF shows also a degradation in two steps, but they are more close and the degradation of the NOR RF starts 15 °C higher than without PCO 910 and has no clear maximum. The formulation 8% PCO 910 + 4% NOR RF was chosen because lower concentrations complicate the analysis of the data due to less pronounced maxima.

The fragmentation of the spirobis(phosphate) and spirobis(phosphonate) flame retardant in TG MS analysis is different. The fragmentation of spirocyclic phosphonates in MS experiments is already investigated and described in the literature.²⁷ Some found fragments of the decomposition of PCO 910 are in accordance with the decomposition pathway described in the literature.

Table II. Thermal Properties of the Flame Retardant Formulations in PET By Simultaneous Thermal Analysis (TGA DTA)

#	Composition	$T_{1\%}$ (°C)	T_m (°C)	$T_{\max \text{ dec rate}}$ (°C)	Residue at 600 °C (%)
0-1	PCO 910	267.05	250.03	386.29	6
0-2	SPDPP	315.54	197.31	379.65	37
0-3	SPDPDOM	293.33	—	457.13	50
0-4	NOR-RF	237.33	—	423.72	42
1	PET	375.58	243.99	429.48	16
2	2% PCO 910	368.35	244.20	443.50	17
3	3% PCO	311.61	243.43	442.15	13
4	5% PCO 910	288.29	242.14	444.15	19
5	10% PCO 910	155.39	239.6	435.29	19
6	2% SPDPP	375.79	244.60	436.46	24
7	10% SPDPP	367.94	241.31	394.24	30
8	2% SPDPDOM	378.76	247.12	440.64	24
9	10% SPDPDOM	370.50	278.05	411.63	30
10	2% PCO 910 + 1% NOR-RF	327.38	244.56	442.89	17
11	2% SPDPP + 1% NOR-RF	353.29	244.51	436.63	23
12	2% SPDPDOM + 1% NOR-RF	358.17	247.79	428.57	18
13	8% PCO 910 + 4% NOR-RF	300.10	240.29	441.92	20
14	5% PCO 910 + 5% SPDPP	278.05	242.20	412.03	22
15	5% NOR-RF	316.59	246.75	440.42	16

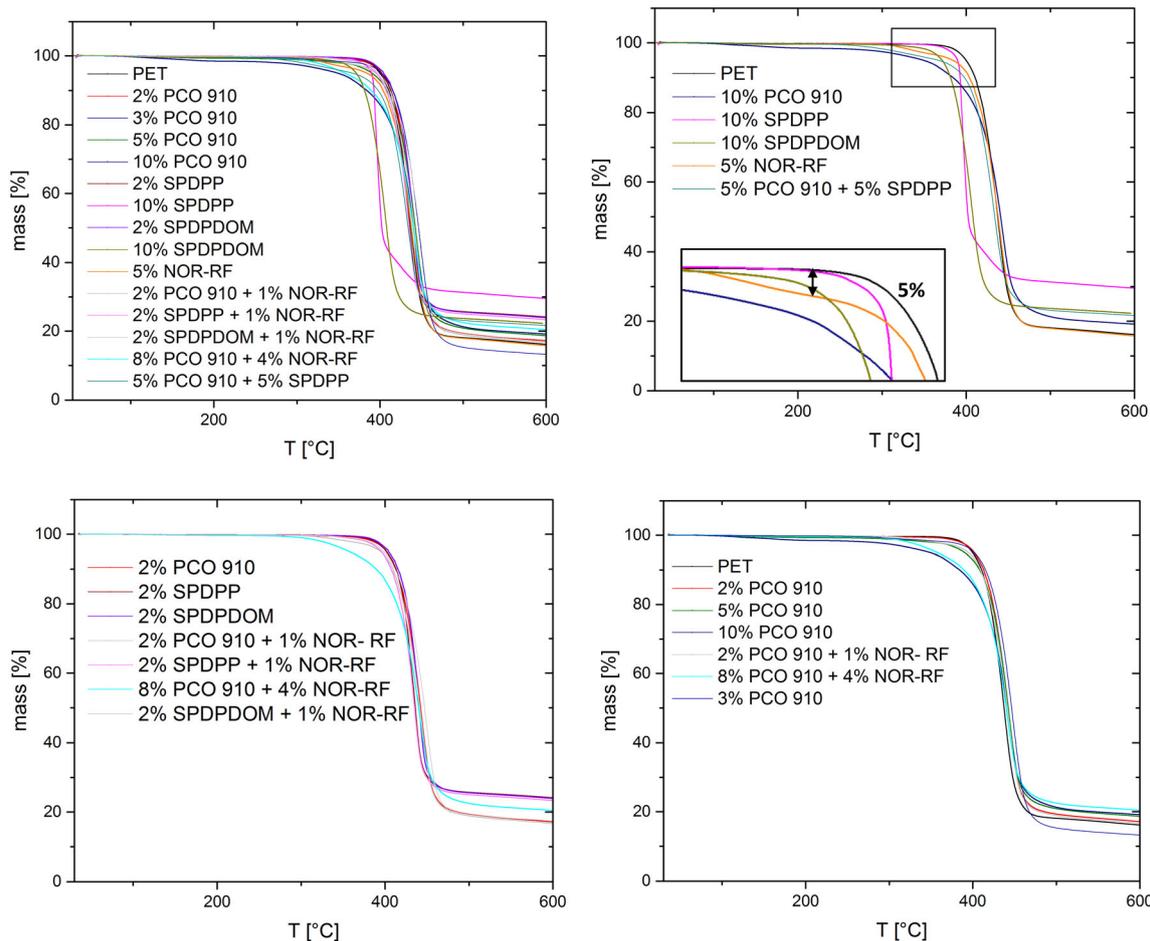


Figure 4. TGA curves of the flame retardant formulations (PET, 2% PCO 910, 3% PCO 910, 5% PCO 910, 10% PCO 910, 2% SPDPP, 10% SPDPP, 2% SPDPDOM, 10% SPDPDOM, 5% NOR RF, 2% PCO 910 + 1% NOR RF, 2% SPDPP + 1% NOR RF, 2% SPDPDOM + 1% NOR RF, 8% PCO 910 + 4% NOR RF, 5% PCO 910 + 5% SPDPP) under nitrogen and a heating rate of 10 K min^{-1} (top left diagram). For reasons of clarity, top right, bottom left, and right diagrams show selected curves of the flame retardant formulations. [Color figure can be viewed at wileyonlinelibrary.com]

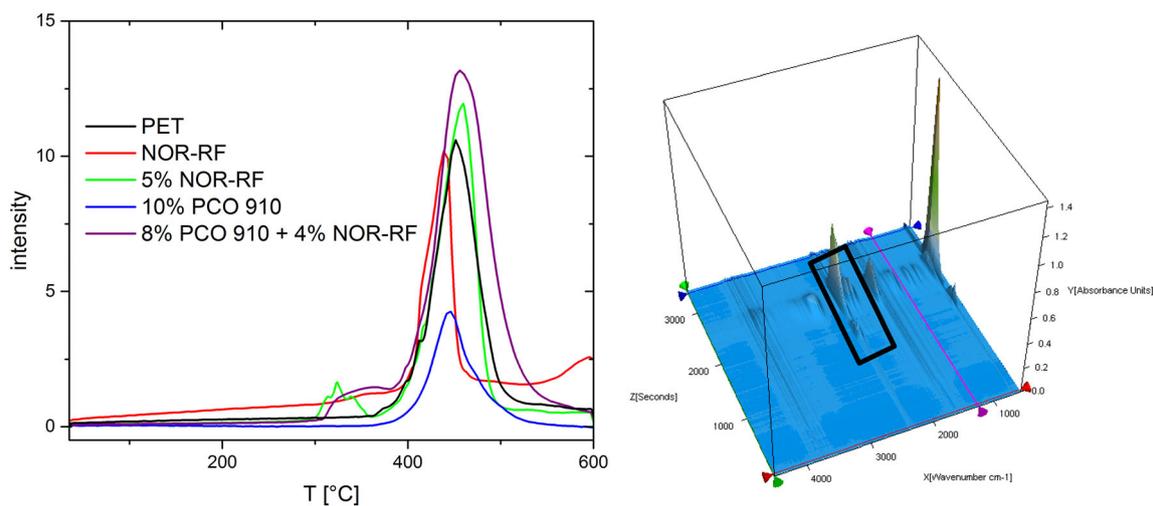


Figure 5. TG FTIR curve (left diagram) showing the CO_2 release intensity of PET flame retardant formulations containing neat PET, neat NOR RF, 5% NOR RF, 10% PCO 910, and 8% PCO 910 + 4% NOR RF in PET (integral traces at $2378 \text{ } 2302 \text{ cm}^{-1}$ [CO_2]). Three dimensional FTIR spectroscopy of PET containing 5% NOR RF (right diagram). [Color figure can be viewed at wileyonlinelibrary.com]

Former experiments showed a more difficult detection with no clear maxima of mass fragments by using relatively low loadings of 5%. For this purpose, the tested phosphorus flame retardants are used in a formulation containing 10% of the phosphorus compound. The decomposition of the phosphonate PCO 910 shows the release of MeOH whereas the phosphate derivative releases phenol and its derivatives during the decomposition process. These two decomposition species can be obtained also by TG FTIR analysis. SPDPP was chosen as corresponding phosphoric compound for the comparison with the phosphonate compound PCO 910 because phenolic decomposition products can be detected by FTIR and be distinguished by the decomposition products of PCO 910. The formulation containing the phosphate in PET leads to no detection of phenol and its derivatives in TG MS experiments which indicate that no release of phenol takes place. As found by simultaneous TG FTIR and TG MS experiments, no release of the PO* fragment could be observed by all phosphorous containing flame retardants as neat substances. Under the same conditions of measurement, the PO* fragment could be detected in flame retardant formulations containing the phosphonate flame retardant PCO 910 in PET. High concentrations of the phosphonate flame retardant

lead to a more pronounced maximum of the PO* fragment release. The detection of the PO* fragment can be observed at concentrations of PCO 910 in the range of 5 and 10% whereas 2% of PCO 910 results in no detection of the PO* fragment. Figure 6 demonstrates the release of PO* fragment for PET containing 10% (top left diagram) phosphonate and the correction line of the corresponding phosphate (top right diagram) demonstrating no detection of the mass fragment $m/z = 47$ u which indicates a condensed phase activity of SPDPP in PET. The TG MS curve for $m/z = 47$ u and $m/z = 63$ u for 10% SPDPPDOM is illustrated in the bottom left diagram. A slight maximum can be obtained for $m/z = 63$ u whereas no clear maximum for $m/z = 47$ u can be monitored. $m/z = 63$ u is referred to the PO₂ fragment²⁸ which also participates in key reactions of radical recombination in the gas phase. The release of PO* fragments in this experiment setup points out the formation of PO* radicals and a gas phase activity during the combustion process. The generation of PO* radicals allows a recombination reaction of the PO* radicals and high reactive H* or OH* radicals formed during the combustion process intervening the decomposition of the polymer. In this case, the detection of $m/z = 47$ u is very specific for the PO* fragment.

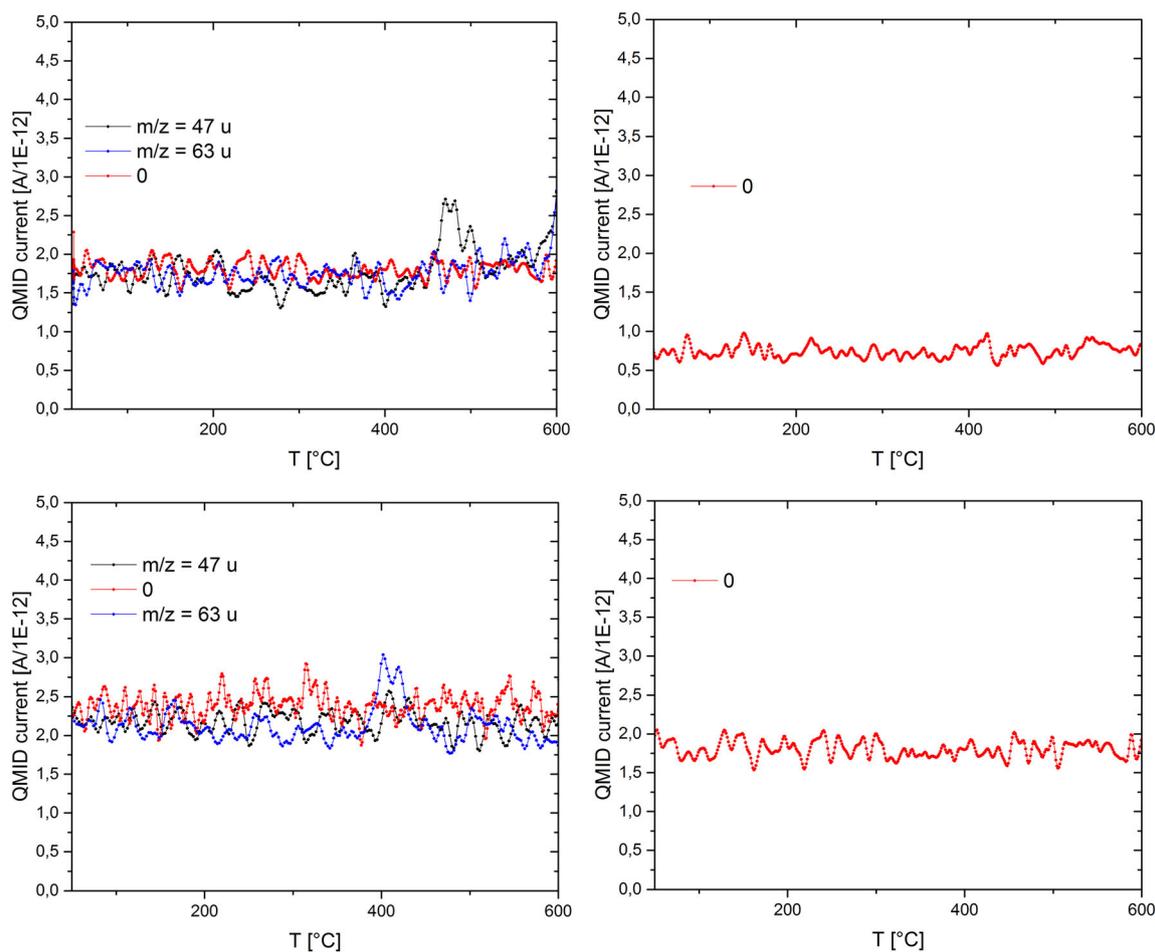


Figure 6. TG MS of 10% PCO 910 (top left diagram), 10% SPDPP (top right diagram), 10% SPDPPDOM (bottom left diagram) in PET, and PET (bottom right diagram) at 10 K min⁻¹ under nitrogen. The correction lines of the measurements are marked with 0. [Color figure can be viewed at wileyonlinelibrary.com]

To enhance the gas phase activity of the phosphonate, a 1,8 naphthalimide ester (NOR RF) as NOR RF agent was combined with the phosphonate providing different sources of radicals during the combustion process. A combination of NOR RF agents with PCO 910 is described in the literature for polypropylene.^{23,29} The expected radical fragment based upon N–O bond cleavage with $m/z = 196$ u cannot be detected by TG MS experiments. The detection of fragments with relatively high molecular weights of more than $m/z = 91$ u is difficult due to possible condensation in the transfer line. In addition, a thermodesorption MS experiment was used for pure NOR RF compound to investigate possible fragmentation reactions. A cleavage mechanism for similar sulfonyl ester of *N* hydroxynaphthalimide is already described in the literature.^{30,31} The most important mass fragments are picked in Figure 7 and are in accordance with the mechanism described in the literature by Malval *et al.*³¹ (Scheme 1). The main fragment of NOR RF is $m/z = 197$ u representing a thermodynamically more stable fragment after a hydrogen rearrangement. The main fragments are in accordance with the fragmentation pattern of 1H benz[de]isoquinoline 1,3(2H) dione ($m/z = 197$ u) described in the literature.³² Due to the experimental setup, the onset temperatures of the decomposition in the TD MS and the TGA DTA FTIR MS experiments are not comparable with each other. The temperatures of the TD MS experiments are measured *in vacuo* and thus are representing no exact temperatures of the pyrolysis process.

Analysis of the Remaining Residue at 600 °C

The residues of selected DTA/TGA MS FTIR experiments are investigated by SEM EDX to analyze the approximate phosphorus content in the remaining residues at 600 °C. Spots and areas of the samples were measured with no significant difference. The determination of the P, C, and O contents by measurements over areas are listed in Table S1 representing an approximately average content of oxygen, carbon, and phosphorus contents of the samples. An exact quantification with SEM EDX is not possible but the relative phosphorus contents of the samples can be

compared to each other. SEM EDX is a very sensitive method and no unburned samples were measured due to possible contaminations by gas evolution or destruction of the samples by heat development. Neat PCO 910 was not investigated in this context due to almost no residue remaining at 600 °C. In accordance with previous investigations of this work compositions containing PCO 910 as flame retardant with gas phase activity, the phosphorus content of the investigated samples is very low which leads to the conclusion that the main part of the flame retardant is released into the gas phase and thus having an effect in the gas phase. For example, 10% of PCO 910 in PET has calculated phosphorus content of 2% in the undecomposed sample whereas 0% as phosphorus content remains in the residue at 600 °C. The same amount of the corresponding phenolic phosphate (SPDPP) in PET has a phosphorus content of 1% in the residue in comparison to predicted 1% phosphorus content in the undecomposed sample. The main part of the phosphorus content remains in the residue acting in the condensed phase during the decomposition. Then, 10% SPDPPDOM results in 1% phosphorus content at 600 °C in comparison to 1.7% calculated phosphorus content in the flame retardant formulation. A decrease of the phosphorus content at 600 °C was expected, because SPDPPDOM has phosphinate and phosphate moieties acting in the gas and condensed phase. The combination of the NOR RF agent and PCO 910 in PET results in no significant change of the phosphorus or carbon content in the residue at 600 °C. The main part of the phosphorus content of SPDPPDOM remains in the condensed phase due to condensed phase active phosphate moieties.

Burning Behavior of Flame Retardant Formulations in PET

A UL94 vertical burning test was performed in order to investigate the fire behavior of the developed flame retardant formulations. The results are presented in Table III. A V 0 classification was reached for samples containing 5% PCO 910, 10% PCO 910, and 5% PCO 910 + 5% SPDPP whereas 2% PCO 910 was

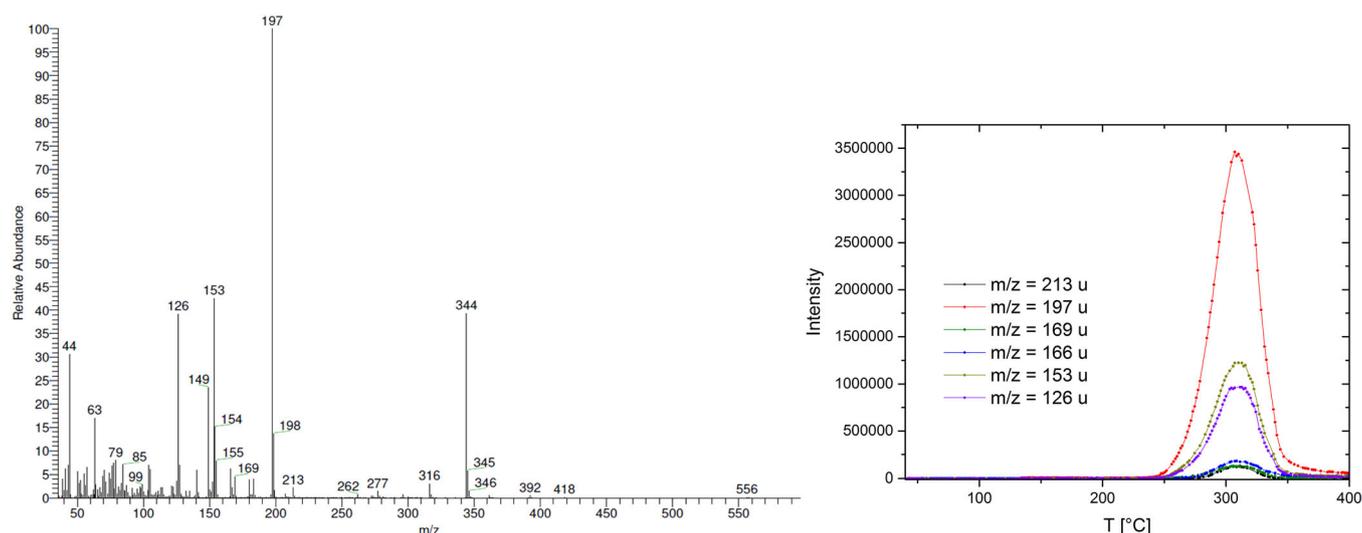
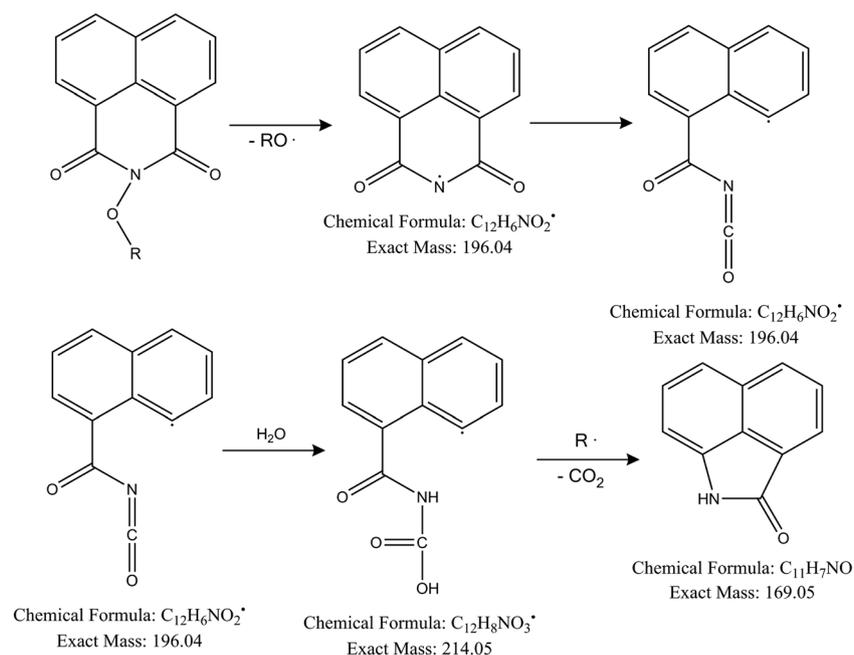


Figure 7. Mass spectrum (left) and corresponding thermodesorption MS diagram (TD MS, right). The samples were measured under vacuum with a heating rate of 25 °C min⁻¹. [Color figure can be viewed at wileyonlinelibrary.com]



Scheme 1. Radical dissociation mechanism of 1,8 naphthalimide esters described by Malval *et al.*³¹

classified V 2. The fire behavior of 2% PCO 910 as gas phase active flame retardant could be improved by adding 1% NOR RF. In comparison to that 2% SPDPP as condensed phase active flame retardant in combination with 1% NOR RF was classified V 2 as well as 2% SPSPDOM + 1% NOR.

Cone calorimetry tests were performed for flame retardant formulations which contain 10% of phosphorus based flame retardants alone and mixtures of them with NOR RF as well as 5% PCO 910 + 5% SPDPP. The results are listed in Table IV and the heat release rate (HRR) curves are compared in Figure 8. The phosphorus content of 5% PCO 910 (1.29%) is comparable to that of 10% SPDPDOM (1.73%) and 10% SPDPP (1.50%), respectively. Phosphorus species with high oxygen content in

the chemical environment of the phosphorus atom show an increased PHRR compared to other phosphorus compounds at a concentration of 10%. The highest reduction in PHRR of 52% can be obtained for the formulation 5% PCO 910 + 5% SPDPP, whereas the reduction of PHRR for 10% SPDPDOM (45%) and 10% PCO 910 (49%) is similar. 10% of SPDPP lowers the reduction of PHRR about 32%. The PHRR of the formulations containing the phosphorus species in combination with NOR RF is very similar for all three formulations, whereas the UL 94 burning test shows a V 0 rating only for 2% PCO 910 + 1% NOR RF. Regarding the three combinations, an increasing total heat released (THR) for 2% SPDPP + 1% NOR RF was observed. Though significant differences still exist regarding the

Table III. UL94 Classifications of Flame Retardant Formulations in PET with a Sample Thickness of 1.6 mm

#	Composition	Average burning time per sample (s)	Dripping behavior	UL94 classification
1	PET	74.46	Burning dripping	n.c.
2	2% PCO 910	0.72	Burning dripping	V-2
3	3% PCO 910	0	Nonburning dripping	V-0
4	5% PCO 910	0	Nonburning dripping	V-0
5	10% PCO 910	0	Nonburning dripping	V-0
6	2% SPDPP	1.12	Burning dripping	V-2
7	10% SPDPP	0	Nonburning dripping	V-0
8	2% SPDPDOM	1.07	Burning dripping	V-2
9	10% SPDPDOM	0	Nonburning dripping	V-0
10	2% PCO 910 + 1% NOR-RF	0.52	Nonburning dripping	V-0
11	2% SPDPP + 1% NOR-RF	0	Burning dripping	V-2
12	2% SPDPDOM + 1% NOR-RF	0.63	Burning dripping	V-2
13	5% PCO 910 + 5% SPDPP	0	Nonburning dripping	V-0
14	5% NOR-RF	20.34	Burning dripping	n.c.

Table IV. Cone Calorimetry (Irradiation 35 kW m^{-2}) Results of Flame Retardant Formulations in PET with a Sample Thickness of 2 mm

Composition	TTI (s)	PHRR (kW m^{-2})	PHRR reduction (%)	THR (MJ m^{-2})	MAHRE (kW m^{-2})
PET	105.33	632.66 ± 37.48	—	51.42	160.56
3% PCO 910	115.67	456.49 ± 46.25	27.85	33.72	100.50
5% PCO 910	117.33	395.11 ± 32.14	37.55	25.01	98.17
10% PCO 910	112.33	317.56 ± 10.86	49.81	21.79	98.23
10% SPDPP	94.00	428.89 ± 4.63	32.21	29.19	119.03
10% SPDPDOM	95.50	344.82 ± 12.89	45.50	31.49	97.20
2% PCO 910 + 1% NOR-RF	106.00	484.86 ± 17.10	23.36	37.03	116.74
2% SPDPP + 1% NOR-RF	97.33	509.41 ± 5.65	19.48	41.51	124.74
2% SPDPDOM + 1% NOR-RF	99.00	514.11 ± 38.13	18.74	37.63	114.75
5% PCO 910 + 5% SPDPP	103.50	301.27 ± 5.77	52.38	29.75	90.51

UL 94 burning test a synergistic behavior of all three phosphorus compounds in combination with NOR RF was monitored in cone calorimeter tests. A clearly decreased THR can be obtained by 10% PCO 910 (21 MJ m^{-2}) whereas 10% SPDPDOM (31 MJ m^{-2}) and 10% SPDPP (29 MJ m^{-2}) have a THR in the range of 5% PCO 910 (25 MJ m^{-2}). The time to ignition was reduced for 10% SPDPP and 10% SPDPDOM and increased by 3% PCO 910, 5% PCO 910, and 10% PCO 910. The maximum average rate of heat emission (MAHRE) was clearly decreased

for all flame retardant formulations. 5% PCO 910 + 5% SPDPP, 10% SPDPDOM, 10% PCO 910, and 3% PCO 910 are just below 100 kW m^{-2} .

CONCLUSIONS

The fire behavior as well as the pyrolysis behavior of different phosphorus species was investigated and compared by *in situ* thermal analyses of TGA/DTA FTIR MS experiments. The PO*

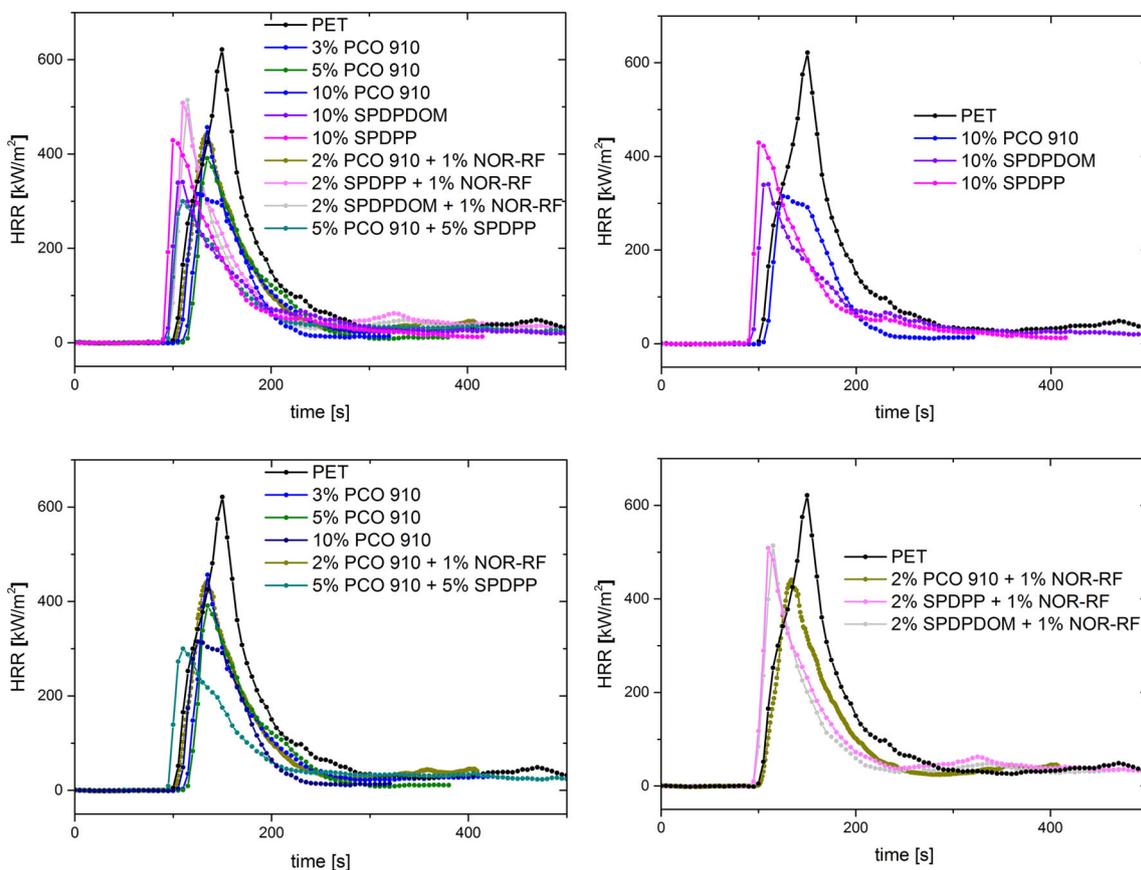


Figure 8. HRR curves (heat flux of 35 kW m^{-2}) for flame retardant formulations (PET, 3% PCO 910, 5% PCO 910, 10% PCO 910, 10% SPDPP, 10% SPDPDOM, 2% PCO 910 + 1% NOR RF, 2% SPDPP + 1% NOR RF, 2% SPDPDOM + 1% NOR RF, 5% PCO 910 + 5% SPDPP). For reasons of clarity, top right, bottom left, and right diagrams show selected curves of the flame retardant formulations. [Color figure can be viewed at wileyonlinelibrary.com]

radical was detected exclusively by compositions containing the phosphonate PCO 910 in PET whereas no PO* radical was detected during the decomposition of the neat flame retardants. The corresponding phenolic phosphate in PET showed a condensed phase activity by TGA/DTA FTIR MS experiments as well as SEM EDX experiments investigating the phosphorus content in the remaining residue at 600 °C. The fire behavior of PCO 910 could be improved by adding an NOR RF agent resulting in a total loading of 3% in PET reaching a V 0 UL94 classification. A new flame retardant SPDPDOM containing phosphate and DOPO moieties was also developed and investigated. A PHRR reduction of 52% could be obtained by the formulation 5% PCO 910 + 5% SPDP.

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AUTHOR CONTRIBUTIONS

Conceptualization was done by M.D. and D.G.; writing original draft preparation was done by D.G. and M.D.; writing, reviewing, and editing were done by D.G. and M.D.; crystal structure determination was done by O.F.; DTA MS FTIR analysis was carried out by C.F. and R.R.; TGA analysis was carried out by D.G.; synthesis and NMR analysis were done by D.G. and D.M.; UL94 by D.G. and L.W.; cone calorimeter tests were done by F.P., J.B., and C.B.; MS analysis was carried out by A.S.; supervision was done by M.D.; project administration by M.D. and V.A.; and finally funding acquisition was done by M.D.

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