Åbo Akademi

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Doctoral Thesis
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Academic Dissertation

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Tę pracę dedykuję Tobie

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Abstract

The driving forces for current research of flame retardants are increased fire safety in combination with flame retardant formulations that fulfill the criteria of sustainable production and products. In recent years, important questions about the environmental safety of antimony, and in particular, brominated flame retardants have been raised. As a consequence of this, the current doctoral thesis work describes efforts to develop new halogen-free flame retardants that are based on various radical generators and phosphorous compounds.

The investigation was first focused on compounds that are capable of generating alkyl radicals in order to study their role on flame retardancy of polypropylene. The family of azoalkanes was selected as the cleanest and most convenient source of free alkyl radicals. Therefore, a number of symmetrical and unsymmetrical azoalkanes of the general formula R-N=N-R’ were prepared. The experimental results show that in the series of different sized azocycloalkanes the flame retardant efficacy decreased in the following order: R = R´= cyclohexyl > cyclopentyl > cyclobutyl > cyclooctanyl > cyclododecanyl. However, in the series of aliphatic azoalkanes compounds, the efficacy decreased as followed: R = R´= n-alkyl > tert-butyl > tert-octyl. The most striking difference in flame retardant efficacy was observed in thick polypropylene plaques of 1 mm, e.g. azocyclohexane (AZO) had a much better flame retardant performance than did the commercial reference FR (Flamestab® NOR116) in thick PP sections. In addition, some of the prepared azoalkane flame retardants e.g. 4’4-bis(cyclohexylazocyclohexyl) methane (BISAZO) exhibited non-burning dripping behavior.

Extrusion coating experiments of flame retarded low density polyethylene (LDPE) onto a standard machine finished Kraft paper were carried out in order to investigate the potential of azoalkanes in multilayer facings. The results show that azocyclohexane (AZO) and 4’4-bis (cyclohexylazocyclohexyl) methane (BISAZO) can significantly improve the flame retardant properties of low density polyethylene coated paper already at 0.5 wt.% loadings, provided that the maximum extrusion temperature of 260 ^{o}C is not exceeded and coating weight is kept low at 13 g/m^2.

In addition, various triazene-based flame retardants ($RN_1=N_2-N_3R'R''$) were prepared. For example, polypropylene samples containing a very low concentration of only 0.5 wt.% of bis-4’4’-(3’3’-dimethyltriazene) diphenyl ether and other triazenes passed the DIN 4102-1 test with B2 classification. It is noteworthy that no burning dripping could be detected and the average burning times were very short with exceptionally low weight losses. Therefore, triazene compounds constitute a new and interesting family of radical generators for flame retarding of polymeric materials. The high flame retardant potential of triazenes can be attributed to their ability to generate various types of radicals during their thermal decomposition. According to thermogravimetric analysis/Fourier transform infrared spectroscopy/MS analysis, triazene units are homolytically cleaved into various aminyl, resonance-stabilized aryl radicals, and different CH fragments with simultaneous evolution of elemental nitrogen.

Furthermore, the potential of thirteen aliphatic, aromatic, thiuram and heterocyclic substituted organic disulfide derivatives of the general formula R-S-S-R’ as a new group of halogen-free flame retardants for polypropylene films have been investigated. According to the DIN 4102-1 standard ignitibility test, for the first time it has been demonstrated that many of the disulfides alone can effectively provide flame retardancy and self-extinguishing properties to polypropylene films at already very low concentrations of 0.5 wt.%. For the disulfide family, the highest FR activity was recorded for 5’5’-dithiobis (2-nitrobenzoic acid). Very low values for burning length (53 mm) and burning time (10 s) reflect significantly increased fire retardant performance of this disulfide compared to other compounds in this series as well as to Flamestab® NOR116.

Finally, two new, phosphorus-based flame retardants were synthesized: P’P-diphenyl phosphinic hydrazide (PAH) and melamine phenyl phosphonate (MPhP). The DIN 4102-1 test and the more stringent UL94 vertical burning test (UL94 V) were used to assess the formulations ability to extinguish a flame once ignited. A very strong synergistic effect with azoalkanes was found, i.e. in combination with these radical generators even UL94 V0 rate could be obtained.

Sammanfattning

Ökad brandsäkerhet i kombination med flamskyddsmedel som uppfyller kriterierna för hållbar utveckling är av stor vikt i dagens välfärdssamhälle. Flamskyddsmedel används för att försvåra antändningen av polymera material eller fördröja spridningen av bränder, men de gör inte materialen obrännbara. Under senare år har kritiska frågor om miljösäkerhet av i synnerhet bromerade flamskyddsmedel höjts. Studier har visat att vissa bromerade flamskyddsmedel lagras i människokroppen och i miljön. Enligt många forskare är det möjligt att bromerade flamskyddsmedel skadar foster, har hormonstörande effekter på människan och skadar miljön. Målsättningen med denna doktorsavhandling var att utveckla nya halogenfria flamskyddsmedel, baserade på radikalgeneratorer och fosforföreningar, som uppfyller kraven på hållbar utveckling.

Undersökningen inriktades först på föreningar som kan generera alkylradikaler för att studera deras roll som flamskyddsmedel för polypropen. Azoalkanföreningarna valdes som den renaste och mest lämpliga källan för generering av alkylradikaler. Därför syntetiserades ett antal symmetriska och osymmetriska azoalkaner med den allmänna formeln R-N=N-R'. De experimentella resultaten visar att i serien av olika ringstorlekar hos azocykloalkaner minskar flamskyddseffekten i följande ordning: R = R' = cyklohexyl > cyklopentyl > cyklobutyl > cyclooctanyl > cyclododekanyl. Effektiviteten i serien av alifatiska azoalkanföreningar minskade emellertid enligt följande: R = R' = n-alkyl > tert-butyl > tert-oktyl. Den största skillnaden i flamskyddseffekten observerades vid tester av 1 mm tjocka flamskyddade polypropenskivor, där azocyklohexan (AZO) uppvisade en mycket högre flamskyddseffekt än den kommersiella referensen Flamestab® NOR116. Därtill observerades i brandtester med azoalkaner, till exempel 4,4´-bis(cyklohexylazocyklohexyl)metan (BISAZO), inga brinnande droppar, vilket är en indikation av föreningarnas förmåga att förhindra sekundära bränder.

Flamskyddspotentialen av azoalkaner i flerskiktsbeläggningar av polyeten (LDPE) på papper genomfördes i extrusionsbeläggningsexperiment i en pilotanläggning. Extrusionsbeläggning är en kontinuerlig process där baspapperet på banan beläggs med smält plastfilm i nypet mellan kylvals och motvals. Resultaten visar att AZO och BISAZO kan avsevärt förbättra de flamhämmande egenskaperna hos papper som belagts med polyeten redan vid en tillsats av 0,5 vikt-%, under förutsättning att den maximala extrusionstemperaturen inte överskrider 260 °C och beläggningsvikten hålls låg vid 13 g/m^2.

Den andra gruppen av flamskyddsmedel som studerades var triazener ($RN_1=N_2-N_3R'R''$). Till exempel polypropenprov som innehöll en mycket låg koncentration av endast 0,5 vikt-% av bis-4’4’-(3’3’-dimetyltriazen)difenyleter och andra triazener uppfyllde kraven i DIN 4102-1 B2-flamskyddstestet. Det är anmärkningsvärt att inga brinnande droppar kunde detekteras och den genomsnittliga brinntiden var mycket kort med exceptionellt låga viktförluster. Triazenföreningar utgör en ny och intressant familj av radikalgeneratorer för flamskyddande av polymera material. Den höga flamskyddande effekten kan hänföras till deras förmåga att generera olika typer av radikaler såsom aminyl- och resonansstabiliserade arylradikaler under den termiska nedbrytningen.

Dessutom studerades tretton olika alifatiska, aromatiska och heterocykliska substituerade organiska disulfidderivat med den allmänna formeln R-S-S-R' som en ny grupp av halogenfria flamskyddsmedel för polypropenfilmer. Enligt flamskyddstestet i DIN 4102-1-standarden har man för första gången kunnat visa att många av de syntetiserade disulfiderna effektivt kan ge flamskydd och självsläckande egenskaper till polypropenfilmer vid redan mycket låga koncentrationer av 0,5 vikt-%. Den högsta flamhämmande aktiviteten registrerades för 5’5’-ditiobis (2-nitro-bensoesyra). De mycket låga värden för brandlängden (53 mm) och brinntiden (10 s) återspeglar signifikant ökad brandhämmande prestanda för denna disulfid jämfört med andra föreningar i denna serie eller det kommersiellt tillgängliga flamskyddsmedlet Flamestab® NOR116.

I doktorsavhandlingen presenteras även två nya fosforbaserade flamskyddsmedel: och P'P-difenylfosfinsyra hydrazid (PAH) och melaminfenylfosfonat (MPhP). DIN 4102-1-testet och det mera krävande UL94 vertikala brandtestet (UL94 V) användes för att bedöma föreningarnas förmåga att släcka ett brinnande polypropenprov efter antändning. En mycket stark synergistisk effekt med azoalkaner kunde fastställas i och med att i kombination med dessa nya radikalgeneratorer kunde man även uppnå den högsta UL94 V0-klassificeringen.

List of original publications

The thesis consists of the following Papers I-V, which are referred in the text by their Roman numerals.

I. Aubert, M.; Nicolas, R.; Pawelec, W.; Wilén, C.E.; Roth, M.; Pfaendner, R., ***Azoalkanes-novel flame retardants and their structure-property relationship***, Polymers for Advanced Technologies 2011, 22, (11), 1529-1538.

II. Pawelec, W.; Tirri, T.; Aubert, M.; Häggblom, E.; Lehikoinen, T.; Skåtar, R.; Pfaendner, R.; Wilén, C.E., ***Toward halogen-free flame resistant polyethylene extrusion coated paper facings***, Progress in Organic Coatings 2014, (in press).

III. Pawelec, W.; Aubert, M.; Pfaendner, R.; Hoppe, H.; Wilén, C.E., ***Triazene compounds as a novel and effective class of flame retardants for polypropylene***, Polymer Degradation and Stability 2012, 97, (6), 948-954.

IV. Pawelec, W.; Holappa, A.; Tirri, T.; Aubert, M.; Hoppe, H.; Pfaendner, R.; Wilén, C.E., ***Disulfides-effective radical generators for flame retardancy of polypropylene***, Polymer Degradation and Stability 2014, (in press).

V. Pawelec, W.; Holappa, A.; Wilén, C.E., ***Novel, phosphorus-based flame retardants in combination with other radical generators***, Polymer Degradation and Stability 2014, (submitted).

Contribution of the author

Paper I. The author was responsible for a part of the synthetic work and characterization thereof. She was partially participating in evaluation of the results and in writing the manuscript.

Paper II. The author did a significant part of the synthetic work and was responsible for the evaluation of the results. She was the main author of the paper.

Paper III. The author was involved in the planning of the synthesis and FR testing. She did all the experimental work (besides testing) and evaluation of the results. She was the main author of the paper.

Paper IV. The author was responsible for the planning and performing of all synthetic work with the exception of commercially available compounds. She evaluated the results and was the main author of the paper.

Paper V. The author planned the synthetic work and testing. She did all the experimental work (besides FR testing) and evaluation of the results. She was the main author of the paper.

Supporting publications and conference presentations

Article

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

Patent

- Kniesel, S.; Hoppe, H.; Pfaendner, R.; Xalter, R.; Wilén, C.E.; Pawelec, W.; Aubert, M., ***Phosphinic acid hydrazide flame retardant compositions***, WO2012013565A1, 2012.

Related conference presentations

- Lindholm, J.; Pawelec, W.; Tirri, T.; Aubert, M.; Norouzian, R.; Hupa, M.; Wilén, C.E., ***Design of non-halogenated flame retardants-combustion and polymer scientists join forces***, Sustainable Production and Products, Ketju, 2010, September 7th, Helsinki, Finland, (poster).
- Pawelec, W.; Aubert, M.; Tirri, T.; Wilén, C.E., ***Towards efficient and environmentally friendly flame retardants***, Nordic Polymer Days, 2011, June 15th-17th, Stockholm, Sweden, (poster).
- Pawelec, W.; Aubert, M.; Hoppe, H.; Pfaendner, R.; Wilén, C.E., ***New, highly efficient, halogen-free flame retardants based on triazenes***, FunMat Seminar, 2012, May 23rd, Turku, Finland, (poster).
- Pawelec, W.; Aubert, M.; Hoppe, H.; Pfaendner, R.; Wilén, C.E., ***Triazene based flame retardants***, 2nd International Symposium on Flame Retardant Materials and Technologies (ISFRMT2012), 2012, September 17th-20th, Chengdu, China, (presentation, poster award).

List of abbreviations and symbols

ABBREVIATIONS

APP	Ammonium polyphosphate
ATH	Aluminium trihydroxide
ATO	Antimony trioxide
BRFR	Brominated flame retardant
deca-BDE	Decabromodiphenyl ether
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
FR	Flame retardant
FTIR	Fourier Transform Infrared Spectroscopy
HALS	Hindered amine light stabilizer
HBCD	Hexabromocyclododecane
HFR	Halogen flame retardant
HRR	Heat release rate
LOI	Limiting oxygen index
MDH	Magnesium dihydroxide
MLR	Mass loss rate
NMR	Nuclear Magnetic Resonance
PBDE	Polybrominated diphenyl ether
PE	Polyethylene
PER	Pentaerythritol
PFR	Phosphorus-based flame retardant
POP	Persistent organic pollutant
POSS	Polyhedral oligomeric silsesquioxanes
PP	Polypropylene
SFR-100	Silicon fluid FR
TBBPA	Tetrabromobisphenol A
TBBPA-DBPE	bis 2’3-dibromopropylether of tetrabromobisphenol A
TBBPP	Tris (3-bromo-2’2-bis(bromomethyl)-propyl) phosphate
TGA	Thermogravimetric Analysis
THR	Total heat release
TTI	Time to ignition
UL	Underwriters Laboratory
UV	Ultraviolet radiation
VTES	Vinyltriethoxy silane

SYMBOLS

°C	Degree Celsius
H_c	Heat of combustion
wt.%	Weight percentage
T_d	Decomposition temperature

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ORIGINAL PAPERS

1. Introduction

Polypropylene is a widely applied material in constructions, electronics and transport industries due to its many excellent properties and characteristics [1]. However, due to its carbon rich, organic structure it is also highly combustible and therefore, the material's flammability needs to be reduced by various flame retardants (FRs) that inhibit ignition and reduce the burning rate or the mechanism of its combustion. The increased awareness of fire safety and more stringent legislation have accelerated the development of flame retarded polymeric materials [2,3]. According to a market research, the annual consumption of flame retardants is currently over 1.5 million tons, which is the equivalent of a sales volume of approximately € 1.9 billion [4]. The total flame retardant business is constantly growing due to the fact that the use of plastics by consumers has increased significantly. Consequently, the growth potential in polypropylene is huge and there is a great demand for more efficient flame retardant systems that can fulfill the highest fire safety standards without impairing other properties of polypropylene. This could substantially further widen the range of applications for polypropylene.

Traditionally used, halogen-based FRs have been restricted mostly due to environmental issues [5-9]. Furthermore, their large smoke, high CO generation and corrosivity of formed products during fire retardant action have also reduced their role and significance in recent years. It has been shown, that certain brominated compounds form toxic dioxins and furans during accidental fires, incineration of flame retarded waste and/or postconsumer recycling of such goods. Halogenated flame retardants (HFR) have been identified as widespread contaminants, that can be found in almost every form of household dust [10], foodstuffs [11] and above all in alarmingly high and increasing concentrations in human tissue [12], blood [13] and breast milk [14,15]**.** Certain brominated flame retardants (BRFRs), have been proven to be persistent organic pollutants (POP), bio-accumulative in living organisms (e.g. fish [16], polar bears [17,18]) and/or in the environment. Therefore, the production, marketing and use of some of these additives have already been banned or is in the process of being abolished in several European countries [19,20]. In view of the above, although BRFRs have good balance of performance, cost, properties and processability, concerns regarding their use and consumer preferences has driven industries to voluntarily seek for halogen-free alternatives, that are more ecologically friendly [21,22].

In order to fulfill the criteria of sustainable development in fire protection, it is inevitable that flame retardants need to have a low impact on health and environment during their entire life cycle, i.e. in manufacturing, use, recycling and disposal. Moreover, for commercial reasons, the new flame retardants also need to be cost effective. In view of the above, design and development of halogen-free flame retardants have received attention and significance in recent years [23-26]. However, although numerous effective halogen-free formulations have been developed throughout the years, none of them have been able to fully fulfill all the requirements of the ever more demanding markets and regulations [21]. Therefore, there is still a need for new systems, which are halogen-free, inexpensive, safe and effective at a low loading.

The aim of this work has been to design and synthesize new halogen-free flame retardants in order to improve the flame retardancy of polypropylene. Polypropylene was selected as the material for our investigations due to fact, that it is an important, commonly used polymer in various industrial applications [1]. The synthesis and utilization of novel phosphorous flame retardants and those based on azoalkane, triazene and disulfide type of radical generators for flame retardancy of polypropylene have been described.

This thesis is divided into two parts:

In the theoretical part, a short introduction to the fundamentals of polymer combustion and flame retardation, as well as brief overview of flame retardant systems used through the years in polypropylene is given. An outline of the properties of these FR systems and their mode of actions in polypropylene formulations is presented. Finally, fire test methods, commonly used to assess and classify their performance are described.

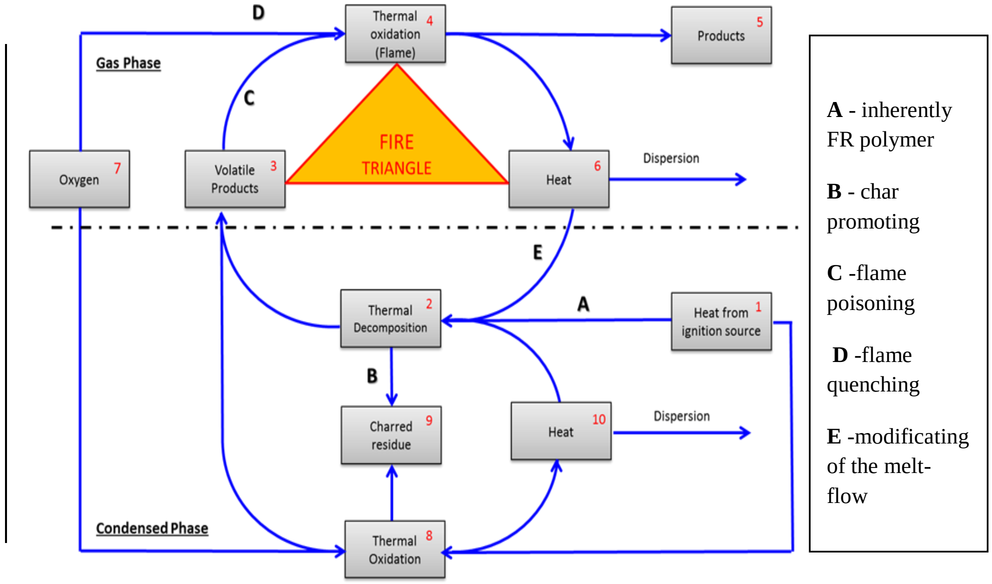
In the experimental part flammability test results, structural and thermal properties of new FR families are discussed. A more detailed description and synthesis of all additives are presented in the five papers attached (I-V). After a short summary, conclusions from performed investigations are presented and possible future work is suggested.

2. Background

Different flame retardant systems function in different ways. To become familiar with the way in which the flame retardants reduce the flammability of polymeric materials, it is necessary to know the mechanisms of polymer combustion.

2.1. Polymer combustion

Scheme 1 represents a basic model of sequential phenomena taking place during the polymer combustion cycle (1-10) and shows the different stages at which the combustion process can be interrupted, through physical or chemical modes of action, by various flame retardants (A,B,C,D,E)



Scheme 1: Polymer combustion cycle [27].

Polymer combustion and flame retardation are closely related with thermal degradation processes that include pyrolysis and thermal-oxidative degradation. In contrast to the combustion of gases, the combustion process of condensed materials such as polymers has a multiphase character that involves various physical and chemical processes and the transformation of initial products. In order to burn, polymers need to initially be broken down and gasified to generate combustible degradation products. Their degradation can be significantly affected by the flame retardant or any other additive present in the polymer, and it depends mostly on chemical structure, composition and physical properties of polymer, which determine decomposition temperature (T_d), rate of thermal degradation, composition of pyrolysis products and finally also the products of combustion. The combustion process due to these factors depends on both the nature of fuel and the burning conditions [28].

In principle, to begin the combustion cycle, an increase in the temperature of the polymeric bulk material, caused by heat from external ignition source (**1**) or thermal feedback (**6**,**10**) is needed. In this initial stage, thermoplastics due to their linear molecular chains tend to soften or melt and they begin to flow [29]. In case of thermosets, their crosslinked structure prevents their melting under the influence of heat [30]. Under further energy supply polymers undergo thermal decomposition (**2**) before vaporization, where high molecular weight molecules start to break up into smaller fragments made up of number of different chemical species with different equilibrium vapor pressures [31]. The lighter the molecular fragments, the faster vaporization they undergo and earlier combustion in the gas phase. The heavier fragments remain in the condensed phase until they undergo further decomposition to lighter fragments which vaporize easily.

Four general mechanisms of conversion of polymeric materials into volatile organic molecules can be distinguished: 1) end chain scission called unzipping (chain releases groups from its end most easily), 2) random chain scission (chain breaks at random points along its length), 3) chain stripping (release groups from the chain attached to the backbone as side chains) and 4) char formation (chains undergo carbonization that result in char at the expense of combustible volatiles) [32]. In terms of flammability, polymers that have a tendency to decompose by random chain scission (polypropylene) or to undergo depolymerization/unzipping (methyl methacrylate, polystyrene) are usually more flammable than the polymers that crosslink and form char (polyacrylonitrile) or remove side pendant groups (polyvinylchloride) [33].

Due to fact that thermal degradation is a result of the action of heat and oxygen, degradation of polymers may be affected by the presence of oxygen, which can catalyze the pyrolysis at low concentration or cause thermal oxidation processes at high concentration. Hence, non-oxidizing (**2**) and oxidizing (**4**) thermal degradation can be distinguished.

In the condensed phase, non-oxidizing thermal degradation (**2**) is usually initiated by inert pyrolysis [34], where chain scission is mainly a result of the effect of temperature. Several factors such as: presence of oxygen in polymer chain, catalyst residues, chemical defects and weak bonds in the polymer chain influence the initial chain scission which may occur in two ways: 1) by formation of free radicals (initiation), which can react further in both oxidizing and non-oxidizing conditions or 2) by migration of hydrogen atoms and creation of two stable molecules, one of which has a reactive C=C double bond. The first mechanisms involve the formation of highly energetic and reactive chemical species called "free radicals", which are responsible for the degradation and production of various decomposition products [35] (**3**,**9**); the second mechanism contributes more to the char formation.

Under thermal oxidizing conditions [36,37] (**4**,**8**), polymer reacts with the oxygen in the air and generates variety of low molecular weight products and reactive radical species ($H^{\cdot}$, $OH^{\cdot}$). Oxidation of these macromolecular radicals may lead to crosslinking through recombination reactions and formation of char; nevertheless still at this point the bond scission is the main reaction. Moreover, thermal oxidation [38] both in the gas and in condensed phase (which is dependent on the amount of oxygen at the polymer surface, preparation and purity of polymer) provides heat (**6,10**) to the polymer matrix and sustains the exothermic pyrolysis process.

In the gas phase, flammable gases (**3**) are mixed with oxygen (**7**) from the air to form an ignitable mixture (**4**). This gaseous mixture ignites at an adequate ratio between these gases and oxygen in the air when the auto-ignition temperature is reached liberating heat (**6**) and combustion products (**5**). Alternatively, the fuel can also ignite at a lower temperature (called the flash point) upon reaction with an external source of intense energy (spark, flame, etc.). The reaction rates within the flame and the heat produced are functions of the concentration and reactivity of $H^{\cdot}$ and $OH^{\cdot}$ radicals, which are the most reactive species in the flame. Heat from thermal oxidation (**6**,**10**) is partially dispersed. Maintenance of the combustion cycle depends on the quantity of heat liberated during the combustion of the fuel. When the amount of heat liberated reaches a certain level, new decomposition reactions are induced in the condensed phase and therefore more combustibles are produced and the combustion cycle is maintained. However, when the energy supplied to the polymer is higher than the energy required for feeding the flame, the reaction may lead to explosion or flashover.

Parallel to the reactions in the gas phase, reactions in the condensed phase also still occur. Since all material (polymer) is not always expected to burn and transformed into fuel vapor, the result of an incomplete combustion gives rise to an inert carbonized material, called char (**9**). Additionally, smoke (results of pyrolysis or incomplete combustion) and soot may be produced. However, in this phase some reactions which volatilization temperature is higher than their combustion temperature proceeds without free flame (non-flaming combustion), under glowing (sufficient oxygen supply) or smoldering conditions (insufficient oxygen supply) and in specific polymer cases some not always take place (e.g. charring and/or thermal oxidation). Polypropylene and poly(methyl methacrylate) for instance burn without significant char, whereas polymers with reactive side groups (such as poly(vinyl chloride) or with aromatic and heterocyclic backbones (such as polycarbonates) belong to the group of char-forming polymers.

Physical characteristics of char such as thickness, density, continuity, coherence, adherence, resistance to oxidation, thermal insulation properties or permeability dictate the rate of further thermal decomposition of polymeric material and continued combustion. For example, when deeper layers of polymeric material continue to decompose, the new volatile fuels must pass through the char that has already been formed in order to reach the surface and be burned. Depending on the char form, it can cause the secondary reactions to occur in the volatiles (pure char) or can slow down further decomposition reactions if it is present as an intumescent layer. While charring of polymers proceeds through various stages (crosslinking, aromatization, fusion of aromatics and graphitization) char is only formed if the cross-linked polymer contains aromatic fragments and/or conjugated double bonds which are prone to aromatization during thermal decomposition [39]. Hence, polymers that tend to crosslink at the early stage of their decomposition do not always form char [40].

2.2. Flame retardation

Scheme 1 depicts how to interrupt and extinguish the fire by function of flame retardants (A,B,C,D,E). The simplest way of preventing polymer from burning is to (**A**) design thermally stable polymer with increased decomposition temperature (T_d) [41]. Polymers such as polyimides, polyphosphonates, phenol formaldehyde resins or fluorinated polymers are less prone to thermally decompose into combustible gases, whereby initiation is delayed [42]. However, due to frequent difficulties in processing, high price and other performance limitations, manufacturers impart the fire retardancy to polymeric materials more easily by use of chemically modified polymers [43] or by adding suitable additives called flame retardants (FRs). Their purpose is to break the combustion cycle (Scheme 1) by affecting chemical or/and physical processes taking place in one or more of the steps of burning, which are heating, ignition, decomposition and/or flame spread [44].

In principle, flame retardant additives in polymer may (**B**) promote char formation and hence diminish the concentration of combustible fuel; (**C**) slow down chain propagation reactions in the flame by flame poisoning; (**D**) decrease the oxygen concentration in the flame of the burning polymer by flame quenching or (**E**) modificate melt-flow characteristics to allow enhanced dripping to take away part of the heat flux delivered to the polymer surface [42]. Generalized, decreased flammability of polymers can be obtained either by altering the products of thermal decomposition in such a way that the amount of non-flammable combustion products is increased at the expense of flammable volatiles (solid phase retardation) or by inhibiting oxidation reactions in the gas phase through trapping of free radical species (gas phase retardation). Most experimental observations reported in the literature can be explained with reference to these two mechanisms or their combinations [43]. Moreover, it should be noted that several principles can simultaneously contribute to the effectiveness of a particular flame retardant system due to the fact that these mechanisms do not contradict each other. Combinations of flame retardant additives may also be deliberately designed to include several modes of action in a given polymer substrate in order to enhance flame retardant efficacy [33].

As described in section 2.1, significant polymer degradation occurs in the condensed phase whereby volatile species are gradually liberated into the gas phase. Accordingly, flame retardants can work either in the gas or in the condensed phase as shown in Figure 1.

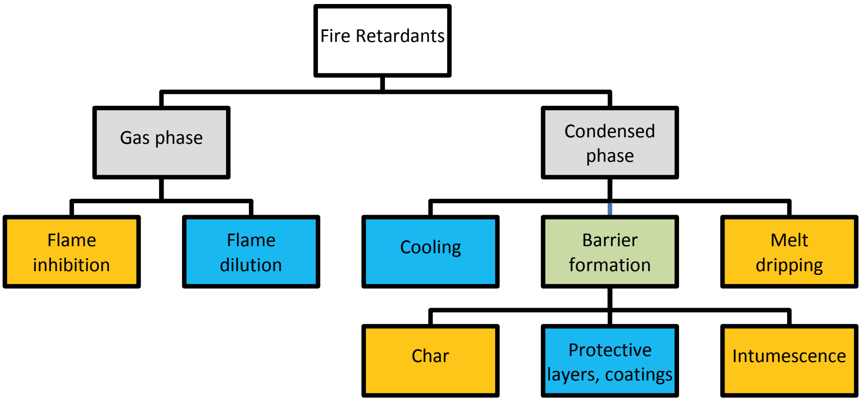


Figure 1: Classification of flame retardant action.

The gas or condensed phase mechanism prevails depending on flame retardant and polymeric system.

Based on their function, flame retardants can be divided into those that block the fire physically by dilution, cooling or formation of protecting layers (marked in blue on Figure 1) and into those that use chemical reactions in gas and condensed phase to stop the material from burning (marked in yellow, Figure 1). Barrier formation (marked in green, Figure 1) includes char and intumescence which work by chemical reactions and protective layers which operate by physical action. Some flame retardants, such as aluminum or magnesium hydroxides, show almost only a physical mode of action; whereas there is no single flame retardant that will operate simply through chemical mode of action. Chemical mechanisms always operate together with several physical mechanisms, usually endothermic dissociation or dilution of fuel.

Different mechanisms and modes of action for flame retardants working within these phases are reported below:

Gas phase flame retardation

Flame inhibition [45] proceeds by action of specific radicals (e.g. Cl·, Br·) which interfere with combustion process by reacting with highly reactive species such as H·, OH· which are responsible for branching of radical chain reactions in the flame. This way less reactive or even inert molecules are formed and the reactive radical concentration in the flame falls below a critical value so the flame goes out. Exothermic processes which occur in the flame are thus stopped, system cools down and the supply of flammable gases is reduced or totally suppressed. Often they are halogen-containing flame retardants which release hydrogen halides effective in quenching free radicals [46].

Flame dilution [47] involves the addition of inert substances (fillers) and FR additives which produce inert gases during decomposition, such as water vapor (metal hydroxides) or carbon dioxide (calcium carbonate), results in dilution of the fuel in solid and reduction in the concentration of decomposition gases in gaseous phase. This way, the lower ignition limit of the gas mixture is not exceeded [48].

Condensed phase flame retardation

C**ooling** of the reaction medium below the polymer combustion temperature influences the energy balance of combustion. In this case, flame retardants such as magnesium and aluminium hydroxide act as a heat sink. They decompose in a highly endothermic process giving non-combustible volatile products, which perform blanketing action in the flame [49,50]. The formed blanket coating removes the formed heat and cool the substrate to a temperature below that required to sustain the combustion process.

Charring [51,52] is the most common condensed phase mode of action in which flame retardant forms on the polymer surface a layer of carbonaceous, porous char for example by removing the side chains and thus generating the double bonds in the polymer, which are precursors of char (either through crosslinking or aromatization). Char functions as a barrier to inhibit further degradation, starves the flame of fuel and protects the polymer surface from heat and air. This usually reduces the formation of smoke and other products of incomplete combustion. Phosphorus-based compounds are usually given as an example of this mode of action, when they are used with polymers containing oxygen and nitrogen.

Alternatively, **intumescent system** [53,54] can cause the formation of an expanded carbonized or vitreous layer at the surface of the polymer by chemical transformation of degrading polymer chains. This layer also acts as a trap for gaseous products of polymer decomposition and consists a barrier to heat, air and pyrolysis products. Usually, intumescent systems are based on tree basic ingredients: a catalyst (acid source), charring agent and spumific (foaming) agent.

The last system of barrier formation is simply creation of **protective layer as coating** [55,56], which happens between the gaseous phase where combustion takes place and the solid phase where thermal degradation occurs. Such a layer (solid or gaseous) cools the solid phase and limits the transfer of combustible volatile gases and oxygen. As a result, the amount of decomposition gases produced is decreased. Ammonium polyphosphates, borates and silicates work this way.

Finally, **melt dripping** mechanism [57] works when flame retardants (e.g. melamine cyanurate) accelerate the breaking of the polymer chains and facilitate melting. In this case, the polymer drips and it moves away a portion of heat and/or fuel (that would contribute to polymer decomposition and volatilization) from the flame action zone. By reducing the release of volatile decomposition products, the reduction in the amount of gaseous products able to feed the flame is obtained. Theoretically this system decreases flammability but it can happen that the burning droplets help to spread the fire.

Flame retardants can be also classified by how they are incorporated into polymer **-** additively or reactively [58]. Additive FRs are incorporated into polymer by physical means prior to, during or more frequently after polymerization. They are mixed with polymer without undergoing any chemical reactions hence they are not chemically bonded to the polymer structure. However, such additives may have shortcomings due to lack of compatibility with polymer matrix, leaching problems and high loadings which can cause negative changes in physical or mechanical properties. To avoid these difficulties in some polymers such as polyesters [59], polyurethanes [60], polymethacrylates [61] or epoxy resins [62,63] reactive FRs are applied. They are introduced into the polymer during synthesis as monomers or precursor polymers or in a post-reaction process. As a result, they have higher effect on chemical and physical properties of polymers than similar admixed flame retardants. Despite that reactive solutions impart permanency of FRs they are not always economically sound due to more complicated manufacturing processes.

3. Flame retardation of polypropylene

Polypropylene offers a great combination of physical, mechanical, thermal, and electrical properties, which determine its wide use for a variety of applications [1]. However, although it is one of the most commonly used polymers today, it is one of the most challenging to flame retard. The highly combustible nature of polypropylene is determined by its organic, hydrocarbon structure containing tertiary carbons which are prone for scission and lead to polymer decomposition. Polypropylene's pyrolysis products are easily combustible and burn rapidly with relatively smoke-free flame and without significant char formation [64]. Additionally, polypropylene ignites readily, melts and drips, increasing the risk of fire propagation [65]. For these reasons flame retarded polypropylene material is highly desirable in many industrial fields in various applications.

In order to enhance flame retardancy of polypropylene, additive manufacturers have developed a variety of products. However, their effectiveness is often reduced due to high crystallinity of polypropylene which makes their homogenous distribution within polymer matrix more difficult [66]. Those additives may also adversely affect other properties of the polymer [67]. For example when aiming for good flame retardancy of polypropylene, usually high loadings of certain additives are required, which impair the mechanical performance of the polymer. Additionally, flame retardants can also reduce processability due to chemical interactions or cause a phase separation between polymer and applied additives.

They are certain difficulties in bringing polypropylene and polypropylene-based materials to pass UL94 V0 standard without affecting its physical properties such as impact strength, light stability and surface appearance for instance. Hence, often UL94 V2 rate (UL94 V2 polypropylene grade represents 75 % of flame retarded polypropylene) is acceptable for various applications such as monitor housings, electrical conductors or polypropylene pipes [68]. Nevertheless, it is obvious that polypropylene could be used in wider range of applications if UL94 V0 rate could be reached without impairing the polymer properties.

In this chapter, past and present efforts to improve flammability of polypropylene by using halogen and halogen-free systems are discussed.

3.1. Halogen-based FR systems

Halogen-based FR compounds contain I, Br, Cl or F elements. Their effectiveness is rated as follows: I > Br > Cl > F [69]. However, in practice iodine compounds are rarely used due to fact that their thermal stabilities are too low, e.g. in many cases they already decompose during polymer processing. In contrast, fluorine derivatives decompose too late making bromine and chlorine formulations the most useful [70]. Bromine possesses a weaker bonding with carbon than chlorine; therefore it is more effective and can interfere at an earlier stage of combustion. Therefore, hydrogen bromine (HBr) is liberated over a narrow temperature range whereby higher concentrations of radical scavengers are liberated into the flame zone than in the case of chlorinated compounds. The thermal stability of halogen-based compounds decreases as follow: brominated aromatic > chlorinated aliphatic > brominated aliphatic.

Chlorinated additives in form of cycloaliphatic compounds such as dodecachloropentacyclooctadeca-7,15-diene (Dechlorane Plus) or chloroparaffins are used in higher loadings (40-70 wt.% is necessary to reach good FR level when used alone) than bromine compounds to flame retard PP [4]. Brominated FRs such as decabromodiphenylether (deca-BDE), bis (2’3-dibromopropyl ether) of tetrabromobisphenol A (TBBPA-DBPE) or stabilized hexabromocyclododecane (HBCD) from a price-performance standpoint are used in combinations with antimony oxide [71,72]. Halogen compounds retard the combustion process by inhibiting the chain branching reactions (R1, R2)

$$\mathrm{H^{\cdot} + O_2 \rightarrow \mathbf{OH^{\cdot}} + O^{\cdot}} \tag{R1}$$

$$\mathrm{O^{\cdot} + H_2 \rightarrow OH^{\cdot} + \mathbf{H^{\cdot}}} \tag{R2}$$

which produce high energy $OH^{\cdot}$ and $H^{\cdot}$ radicals that are responsible for spreading the fire.

Halogenated flame retardants operate by:

a) Releasing of halogen radicals (X may be $Cl^{\cdot}$ or $Br^{\cdot}$) from the flame retardant R-X:

$$\mathrm{RX \rightarrow R^{\cdot} + X^{\cdot}} \tag{R3}$$

b) Formation of hydrogen halides (HX)

$$\mathrm{RH + X \rightarrow HX + R^{\cdot}} \tag{R4}$$

c) Neutralization of energy-rich radicals

$$\mathrm{HX + \mathbf{H^{\cdot}} \rightarrow H_2 + X^{\cdot}} \tag{R5}$$

$$\mathrm{HX + \mathbf{OH^{\cdot}} \rightarrow H_2O + X^{\cdot}} \tag{R6}$$

Scheme 2: Mechanism of action of halogenated FRs [73,74].

Halogen flame retardants RX decompose to form halogen as free radical X·, which reacts with hydrocarbon molecule RH and forms hydrogen halide HX. The FR effect is produced by HX, which eliminates high energy radicals OH· and H· replacing them with low energy X· radicals. Thus, the efficacy of halogen compounds depends on balance between the two competitive reactions, i.e. the formation of OH· and H· radicals and the consumption thereof when they react with HX.

In order to reduce the additive loading and to decrease the content of halogen, synergistic formulation of bromine with antimony [75], zinc [76], tin [77], iron oxides [78], chlorinated paraffins [79,80] and/or intumescent systems [81] based on nitrogen and phosphorus have been developed. Especially antimony trioxide (ATO) is commonly used due to fact that it acts both in the condensed and gas phase. Hydrogen bromine (HX) released during pyrolysis of halogenated FR forms antimony oxide bromide (SbOX) upon reaction with antimony trioxide (Sb_2O_3) which favors the C-X bond scission in the condensed phase.

$$2\,\mathrm{HX} + \mathrm{Sb_2O_3} \xrightarrow{250°\mathrm{C}} 2\,\mathrm{SbOX} + \mathrm{H_2O} \qquad (R7)$$

Scheme 3: Halogen-antimony trioxide synergism [82].

Gaseous antimony tribromide (SbX_3) is formed during further exposure to heat

$$5\,\mathrm{SbOX} \xrightarrow{245-280°\mathrm{C}} \mathrm{Sb_4O_5X_2} + \mathrm{SbX_3} \qquad (R8)$$

$$4\,\mathrm{Sb_4O_5X_2} \xrightarrow{410-475°\mathrm{C}} 5\,\mathrm{Sb_3O_4X} + \mathrm{SbX_3}\uparrow \qquad (R9)$$

$$3\,\mathrm{Sb_3O_4X} \xrightarrow{475-565°\mathrm{C}} 4\,\mathrm{Sb_2O_3} + \mathrm{SbX_3}\uparrow \qquad (R10)$$

Scheme 4: Formation of antimony tribromide [82].

and leads to disruption of flame propagation by reaction with hydrogen radicals as depicted in the scheme below

$$SbX_3 + H^{\cdot} \rightarrow SbX_2 + HX \quad (R11)$$

$$SbX_2 + H^{\cdot} \rightarrow SbX + HX \quad (R12)$$

$$SbX + H^{\cdot} \rightarrow Sb + HX \quad (R13)$$

$$Sb + O^{\cdot} \rightarrow SbO \quad (R14)$$

$$Sb + OH^{\cdot} \rightarrow SbOH \quad (R15)$$

Scheme 5: Antimony halide reactions in flame [53].

Moreover, resulted oxides and hydroxides may also react in flame with reactive radicals

$$SbO + H^{\cdot} \rightarrow SbOH \quad (R16)$$

$$SbOH + H^{\cdot} \rightarrow SbO + HX_2 \quad (R17)$$

$$SbOH + OH^{\cdot} \rightarrow SbO + H_2O \quad (R18)$$

Scheme 6: Antimony oxide and hydroxide reactions in flame [53].

To achieve UL94 V0 rate in PP, decabromodiphenylether (deca-BDE) should be present in at least 20 wt.% together with 7 wt.% of antimony trioxide [83].

Another example showed that UL94 V0 classification can be reached when tetrabromobisphenol A bis (2’3-dibromopropyl ether) (TBBPA-DBPE) is used together with antimony trioxide at 12 wt.% and 4 wt.% respectively [84]. Compared to the formulation where TBBPA-DBPE was used alone, the bromine loading is reduced to ca. 8 wt.%, UV stability is maintained, tensile strength is less affected and melt flow is improved. However, recently antimony trioxide (ATO) has been under scrutiny because its dusty powder has been shown to cause skin or eye irritation. Therefore to avoid these problems and provide protection against ATO dust it is nowadays delivered as a suspension in oil, as pellets or in the form of masterbatch. [49].

Phosphorus can also be used as synergist to reduce the loading and to enhance the FR activity of brominated compounds [80]. However in this case, contrary to antimony trioxide, phosphorus may also exist in the same molecule with bromine. An example is phosphoric acid tris (3-bromo-2,2-bis-bromomethyl-propyl)ester, which is used in polypropylene mostly for external applications due to its UV stability and good processability. UL94 V2 rate can be reached when used alone in 13 wt.% loading.

In order to reach V0 with this phosphorous compound 1 wt.% of N-alkoxy HALS needs to be added [85]. A small addition of N-alkoxy HALS to phosphoric acid tris (3-bromo-2,2-bis-bromomethyl-propyl)ester in polypropylene causes a change in mechanism of action and allows to reach the highest classification in UL94 vertical test. The role of NOR compounds in flame retardancy of PP will be discussed later as they are classified as halogen-free additives.

Although halogen-based FRs are still widely used due to their high effectiveness and low cost, there are some areas where they cannot be applied due to performance limitations and customer preferences. For example, recent emphasis on lower smoke evolution and smoke density, corrosion issues and elimination of potentially harmful by-products generated during decomposition and recycling of halogen compounds have contributed to a steadily growing market for non-halogenated alternatives [86]. Extensive research efforts are currently being conducted to develop highly efficient, halogen-free flame retardants for polypropylene that can even meet the highest fire safety standards [87].

3.2. Halogen-free FR systems

Metal hydroxides

Metal hydroxides are the most commonly used halogen-free flame retardants [74]. However, in order to obtain UL94 V0 rate in polypropylene they need to be used in significant amounts [88-90]. Metal hydroxides such as magnesium dihydroxide (MDH) decompose endothermically according to reaction R19 and release water molecules into the gas phase during the burning process.

$$\mathrm{Mg(OH)_2} \xrightarrow{300-320^{\circ}\mathrm{C}} \mathrm{MgO} + \mathrm{H_2O} \uparrow \qquad \text{(R19)}$$

Scheme 7: Endothermic release of water from MDH [58].

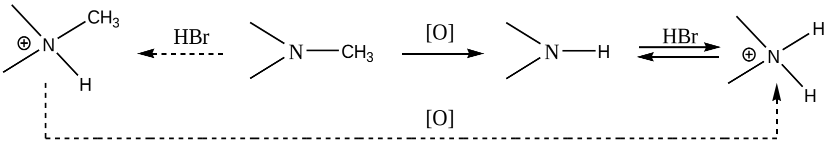
As a consequence of this, dilution of flammable gases and reduction in thermal feedback are achieved and thereby polymer decomposition is also slowed down. Moreover, flame spread and smoke generation are often additionally reduced [91,92].

For example, by using 57 wt.% loading of magnesium dihydroxide in polypropylene a formulation passing UL94 V0 classification was obtained with reduced smoke emission [89]. However, at the same time the flexural and tensile strength of PP/$Mg(OH)_2$ were reduced in comparison to neat polypropylene. In order to retain good material properties and lower the loading level of magnesium dihydroxide of about 10 wt.% a synergists such as transition metal oxides (e.g. nickel oxide) is needed [93]. However, although this solution decreases filler content it at the same time, tends to reduce the viscosity of polymer and thereby increases its tendency to drip. Additionally, color of nickel oxide may limit its application.

The dominant hydrated filler used for flame retardancy is alumina trihydrate (ATH). It has a broader range of applications than MDH due to its lower cost and less smoke production, but it exhibits lower thermal stability and therefore it is less suitable to be processed with polypropylene [94]. In fact, general shortcoming of inorganic hydroxides for polyolefins is their incompatibility with the host polymer. In order to improve the miscibility and positively influence on the mechanical, electrical and FR properties inorganic hydroxides are surface coated with fatty acids such as stearic acid [95,96], silanes [97,98] or titanates [99], PP graft acrylic acid [100] or PP functionalized with vinyltriethoxy silane (VTES) [101]. An alternative solution to the surface treatment is the optimization of its physical characteristics such as particle size, particle size distribution or particle shape by controlled precipitation from alkaline solution [102] or drying of hydroxides [103]. Synergistic combinations of inorganic fillers with red phosphorus [104], silicones [105], nanoclays [106] or charring agents [107] have been also explored to reduce the loading, improve flame retardancy or/and other physical properties. In comparison to halogen-based systems inorganic filler additives are non-volatile, non-toxic and non-corrosive. However, they are effective at much higher concentrations and have an adverse effect on impact strength and melt flow characteristics.

NOR compounds

In general, halogen flame retardants suffer from high specific gravity, insufficient light and UV stability and its tendency to inactivate hindered amine light stabilizers (HALS) [108,109] by salt formation (through protonation and formation of secondary amine salt which prevents conversion of HALS to the active form of nitroxyl radicals necessary in polymer stabilization) as shown on Scheme 8.



(R20)

Scheme 8: Mechanism of formation of secondary amine salts upon photooxidation of fire retarded sample containing HAS-1 [110].

The effect of NOR, as light stabilizer, was initially investigated in the presence of halogens. The results indicated an improvement in UV and long term stability as well as FR synergy with bromine in polypropylene products [111]. Moreover, it has been shown, that Flamestab®NOR116 can replace antimony trioxide as synergist for halogen FRs [112]. The effectiveness of NOR can be partly explained by the earlier release of bromine during interactions of halogen FRs with radicals produced from NOR thermolysis (Scheme 9).

$$\underset{\text{Aminyl radical}}{N^{\cdot}} + \underset{\text{Alkoxy radical}}{OR^{\cdot}} \leftarrow NOR \rightarrow \underset{\text{Nitroxyl radical}}{NO^{\cdot}} + \underset{\text{Alkyl radical}}{R^{\cdot}} \qquad \text{(R21)}$$

Scheme 9: Thermolysis of alkoxyamines (NOR) [113].

For example, UL94 V0 rate can be reached when 0.5 wt.% of Flamestab®NOR116 was used with 14.5 wt.% of Decabromodiphenyl ether (deca-BDE) [114]. This antimony-free system allows to reduce the loading of halogenated FR without impairing the FR properties or polymers light stability due to low basicity of the NOR derivative in comparison to HALS (NOR makes it less prone to react with decomposition products of FR than HALS). This formulation provides polymer with better processability, lower smoke density and good mechanical properties. Flamestab® NOR116 as well as other N-alkoxyamines [115,116] are also very effective alone [113] or can be used in combination with phosphorus (as additive [117] or reactive molecule [113]) showing improved condensed phase efficiency.

Phosphorus compounds

Red phosphorus is very effective (in the absence of halogen or nitrogen FRs) flame retardant for polypropylene. It can be used alone at a loading of 2.5 wt.% to give UL94 V2 rate [118]. In combination with synergistic additives such as those containing nitrogen (spumific agent) or oxygen (carboniphic agent), higher UL94 V0 classification is achieved when red phosphorus is used at higher loadings (20-25 wt.%) [119]. It acts partly in the gas phase via free radical scavenging or in the condensed phase as a char former. The advantages of red phosphorus are its high effectiveness (the highest among P-based compounds), low concentrations required to achieve good FR effect, stability during processing, reduced formation of smoke and negligible effect on mechanical and electrical properties. Although in the past its use was limited due to high flammability and sensitivity to humidity (could liberate toxic phosphine gas) these problems were circumvented by microencapsulation [120,121] together with inorganic (copper acetate) or polymeric materials which lead to dust suppression [122] and stabilization of red phosphorus powder [123]. The major drawback of red phosphorus remains its red-brown color which limits its application. Because of this issue, other phosphorus-based flame retardants (PFRs) or their combinations are being developed.

For example, intumescent systems have received increased attention during the last decades [124]. Several intumescent systems based on a phosphorus-nitrogen combinations are available for polypropylene such as ammonium polyphosphate (APP) + pentaerythritol (PER) [125], APP + melamine + PER [126], APP + triazine [127], diammonium pyrophosphate + PER [128], melamine + intrinsical flame retarded polymer [129], macromolecular char former contained system [130] or melamine phosphate + PER [131]. Among them, ammonium polyphosphate [125] and diammonium pyrophosphate [128] have been extensively used with PER as the most common intumescent system for polypropylene. APP acts both as acid source and blowing agent, whereas PER due to its propensity of dehydration acts as carbonizing agent. Generally, phosphorous compounds used alone in PP are not very effective (except red phosphorus) but phosphorus containing intumescent systems have gained popularity. They are used with co-additives such as cyclic urea-formaldehyde resins [132], hydroxyl ethylcyanurates [133] or piperazine based species [134] that increase char, reduce burning and improve the flammability rates [135]. Typical advantages of intumescent systems are their high thermal stability (ca. 260 °C), high UV stability compared to halogen systems and reduced smoke density during combustion. In contrast to halogen containing formulations where the effect of FR linearly increases with concentration, the effect of intumescent system is more complex [136].

Silicon compounds

Silicon compounds in polypropylene may act both in the gas (trapping of radicals) and condensed phase (char formation) [137]. Compared to halogen FRs, they are considered to be more environmentally friendly, to have better dielectric and gloss properties, improved moldability, anti-dripping properties, processability and impact resistance, thermal stability and non-corrosive smoke evolution. Moreover, recently they have been even considered to be an alternative to phosphorus containing flame retardants [138]. However, only few of them have been used in polypropylene that passed UL94 V0 rate [139]. For example, commercial flame retardant SFR-100 when used alone in PP can reach UL94 V0 rate at a loading of 25 wt.% [140]. When used as a part of intumescent system (SFR- 100+APP+PER) the loadings of SFR-100 can be greatly reduced [141]. Silicones were also used in other PP intumescent systems (e.g. with metal soap or metal stearate), however although they show some FR activity they are not commonly used [142].

Nanocomposites

With the development of nanotechnology, nanocomposites containing nanoparticles such as layered silicate [143,144], carbon nanotubes [145,146] and polyhedral oligomeric silsesquioxanes (POSS) [147] have gained a special attention in flame retardancy of PP. Especially polymer-nanocomposites based on blends of PP (or maleic anhydride-grafted PP [148]) and clays (such as montmorillonite [149,150], sodium bentonite [151], calcium carbonate [152] or boronsiloxanes [153,154]) have been the most studied. Most work to date has been done with montmorillonite due to its small particle size, high aspect ratio and high swelling capacity. However, the high hydrophilicity of the clays requires further modification of such material in order to be more miscible and compatible with the polymer matrix. Modification is usually conducted by ion exchange with long-chain amine, ammonium salt compounds or phosphonium cations which lower the surface energy and improve wettability of the clay making it more hydrophilic. For example sodium ion in the montmorillonite can be exchanged for an amino acid (12-aminododecanoic acid) according to the reaction R22.

$$\mathrm{Na}^{+}\,\mathrm{Clay} + \mathrm{HO_2C-R-NH_3}^{+}\,\mathrm{Cl}^{-} \rightarrow \mathrm{HO_2C-R-NH_3}^{+}\,\mathrm{Clay} + \mathrm{NaCl} \qquad \mathrm{(R22)}$$

Scheme 10: Ion exchange reaction in organophilic modified clay [155].

Organically modified clays are usually melt blended with polypropylene and resulted nanocomposites have an exfoliated structure, which significantly enhance mechanical properties at low filler level and often reduce the flammability of nanocomposites. Noteworthy is that nanocomposites cannot meet UL94 V0 rate when used alone [156]. They usually slow down burning process and enhance charring but they do not reduce tendency to ignite and do not reduce after glowing. Therefore, in order to enhance their efficacy, they have been used in polypropylene with other additives such as intumescent FR systems [157], inorganic hydroxides [158] or halogenated additives [159]. Marosi et all showed that by using boroxosiloxanes in combination with IFR (Na+ grade montmorillonite 1.5 wt.%, and using 10:1 boroxosiloxanes:clay ratio) the UL94 V0 rate is obtained [154]. Other PP/nanocomposites such as PP/titanium dioxide, PP/antimony trioxide, PP/silver, PP/ceramic and PP/zeolites have been reported but none of them improve significantly FR properties of PP [160]. Nanocomposites prevent dripping, promote charring and exhibit synergism with various conventional FRs but the reduced long-term stability of modified clays (due to its huge surface area and presence of ammonium groups that are prone to undergo decomposition already at 180 °C via Hoffman degradation) has led to a slow development and no commercialization of PP/nanocomposite systems.

Based on the above examples it can be stated, that wide variety of FR systems is available for polypropylene. However none of them have ideal overall properties for flame retardancy of polypropylene. Table 1 presents the advantages and drawbacks of commonly used FR systems in polypropylene. New formulations are therefore needed that do not have these shortcomings and can be easily applied in products that successfully face the stricter regulations appearing in flame retardant sectors. Non-halogenated flame retardants have emerged as the obvious choice for the industry even though they still partially suffer from certain technical limitations.

Table 1: Advantages and drawbacks of flame retardants used in PP [161].

Type of additive	**Advantages**	**Drawbacks**
Halogen compounds	• Inexpensive • Commonly used • Efficient at low loadings with synergists • Easy to process	• Emissions of smoke and toxic gases • Low heat and light stability • Corrosive emissions
Metal hydroxides	• No acidic gas emissions • Effective smoke reduction • Non-toxic • Low price	• Very high loading necessary • Decrease mechanical properties
NOR compounds	• Halogen-free • Good FR at low loading in thin PP films • Light stability function	• Effectiveness limited to thin section • Not able to reach UL94 V2 or V0 alone
Red phosphorus	• Effective at low levels • Excellent mechanical properties	• Safety concern • Discoloration of polymer
Intumescent (P,N)	• Halogen-free • Low smoke occurring • Low toxicity	• Poor processability • High price • Volatility problem
Silicon compounds	• Environmentally friendly • Anti-dripping properties • Good processability	• Few structures effective in PP
Nanocomposites	• Synergistic effect with other FRs • Reduce dripping • Improved quality of char • Reduced peak heat release rate	• Poor thermal stability • Difficult to incorporate • High cost

4. Fire testing

The role of fire tests is to demonstrate that the product has a sufficient fire safety performance and compliance with various fire safety laws and standards. Other function may include the study of the nature of the combustion process and determination of the fire risks [162]. Since flammability of polymeric materials is assessed through ignitability, flame spread and heat release, one or more of these criteria should be measured in order to evaluate the fire behavior.

Numerous flammability tests are used in academic and industrial laboratories for either screening the materials during product development or for the testing of manufactured products [163]. These tests range from small-laboratory tests, bench-scale to full-scale tests but none of them cover the whole range of fire scenarios, since there is a wide variability of conditions in a real fire [164] and a single test focuses only on particular fire stage and conditions. Therefore, when possible, evaluation of the fire performance should be done using several methods in order to get a better picture of the fire behavior. In this chapter, few examples of regularly used test methods are described.

4.1. Small-scale laboratory tests

Small-scale flammability tests are very useful tools for initial studies of candidate materials. However, they are not adequate to directly simulate the actual fire conditions. They provide information on the nature of the material itself or on its behavior when subjected to a standardized, controlled ignition source.

4.1.1. DIN 4102-1 test

DIN 4102-1 is a German test standard, which measures the ignitability of various building materials (edge or surface ignition) when exposed to a small flame (20 mm high) [165].

In the edge ignition test, the specimen films (size 190 mm × 90 mm) with a maximum thickness of 60 mm are mounted vertically inside a test chamber and are subjected to a gas flame (45° angle). A filter paper is placed under the specimen to collect burning drips. The flame is applied for 15 s. The specimen successfully passes the test if the flame does not reach the 150 mm reference mark within 20 s after the flame has been removed. The damage length, burning time, burning drips, weight loss and paper ignition are recorded.

4.1.2. Limiting oxygen index

The limiting oxygen index (LOI) test measures the minimum concentration of oxygen [O_2] in the flowing mixture of oxygen and nitrogen [O_2/N_2] that will support the combustion of material [166]. The oxygen concentration is reported as volume percent

$$\mathrm{LOI}\,[\%] = 100\,\frac{[\mathrm{O_2}]}{[\mathrm{O_2}]+[\mathrm{N_2}]} \tag{R23}$$

where O_2 is the minimum volumetric concentration of oxygen which will support combustion and N_2 is the associated nitrogen concentration.

According to ASTM D2863 international standard, LOI is determined on specimens placed vertically in the center of glass tube by passing a mixture of oxygen and nitrogen upstream over a burning sample [166-168]. The sample is ignited with a flame and burns downwards into unheated material. The oxygen/nitrogen ratio is varied reducing the oxygen content until a critical level is reached. More flammable materials continue burning at lower oxygen concentrations than the less flammable materials. Thus, conversely, a higher limiting oxygen concentration (LOI) indicates more flame resistant material [168]. Examples of selected polymers with their LOI indexes are listed in the Table 2.

Table 2: LOI, flash-ignition and self-ignition temperature for selected polymers [21].

Polymer	Flash-ignition temperature (°C)	Self-ignition temperature (°C)	LOI (%)
Polyethylene	340	350	18
Polypropylene	320	350	18
Polystyrene	350	490	18
Poly(vinyl chloride)	390	450	42
Poly(tetrafluoroethylene)	560	580	95
Poly(methyl methacrylate)	300	430	18
Poly(acrylonitrile)	480	560	27
Polyamide 6’6	490	530	24

The LOI value is considered as a basic property of the plastic, but it necessarily does not tell us how the plastic will react to fire in an open atmosphere. Due to the fact that this test is simple, cheap, repeatable [169], requires small samples and is one of the most accurate of the lab-scale flammability tests it has been extensively used for a wide range of materials [170,171]. Literature shows, that certain modifications in the test methodology have been made [172,116] and correlations with other test were attempted to find [173,174] in order to indicate and/or assess the flammability of materials.

4.1.3. UL94 vertical test

The UL94 vertical test is one out of six UL94 flame tests which are divided into: vertical (94 V, 94 VTM, 94 5V) and horizontal (94 HB, 94 HBF, 94 HF) [175]. All methods use standard specimens, controlled heat source and conditioning of specimen prior to the test.

For UL94 V, the standard specimen (125±5 mm × 13±5 mm) with a maximum thickness of 13 mm is mounted vertically in a test chamber and held from the top. A thin layer of cotton is placed 30 cm below the sample. A 20 mm methane gas flame is applied 10 mm from the bottom edge of specimen for 10 s and then removed. The after flame time t_1 (flame time required for the fire to extinguish) is noted. The second flame application takes place immediately when the flame caused by the first application extinguishes. The after flame time t_2 with the afterglow time t_3 (time required for the fire glow to disappear) is noted. Moreover, the presence of burning drops and ignition of the cotton located under the sample is observed. The specimen is classified according to the criteria listed in the Table 3.

Table 3: UL94 vertical burning test classification [176].

Criteria conditions	V0	V1	V2
Afterflame time for each individual specimen $\mathbf{t_1}$ **or** $\mathbf{t_2}$	$\leq$ 10 s	$\leq$ 30 s	$\leq$ 30 s
Total afterflame time for any conditions set $\mathbf{t_1 + t_2}$ **for 5 specimens**	$\leq$ 50 s	$\leq$ 250 s	$\leq$ 250 s
Afterflame and afterglow time for each individual specimen after the second flame application $\mathbf{t_2 + t_3}$ **for any specimen**	$\leq$ 30 s	$\leq$ 60 s	$\leq$ 60 s
Flame or glowing up to the clamp	No	No	No
Cotton ignition	No	No	Yes

Material assigned with the V0 rate is considered to be the least flammable. Nevertheless, V2 rate is also commonly accepted in many applications.

4.2. Bench-scale tests

Bench tests simulate how the material would burn in a certain specific fire scenario. They produce precise analytical data used in fire safety engineering to predict full-scale fire performance. However, contrary to the full-scale tests, they do not require a finished product (instead plates, strips or films of various dimensions are used).

The cone calorimeter is considered as the most significant bench-scale instrument in fire testing and is the most advanced and effective method for assessing various materials reaction to fire [177,178]. It is a standardized method [179,180] used worldwide, which can produce large amounts of data and measure the fire properties of the material being tested under well specified and controlled conditions. In the cone calorimeter test the surface of the test specimen (100 mm × 100 mm specimen, maximum thickness of 50 mm) is exposed horizontally to a constant level of heat irradiance from a conical heater [181]. The heat flux from the heater can be adjusted in the range of 10-100 kW/m^2. Volatile gases from the heated specimen are ignited by an electrical spark igniter. Air, pyrolysis and combustion gases are collected by an exhaust hood and analyzed. The temperature, pressure, velocity, opacity and gas concentrations (O_2, CO and CO_2) as well as smoke density are measured in the exhaust duct. Data such as heat release rate (HRR), heat of combustion (H_C), time to ignition (TTI), total smoke release, time of combustion and mass loss rate (MLR) during combustion can be obtained and evaluated from the cone calorimeter test. Calculations of cone calorimeter measurements are based on oxygen consumption principle, which assumes that quantity of heat released from the material is proportional to quantity of oxygen consumed when burning (13.1 MJ of heat is released per kg of oxygen consumed) [181].

4.3. Full-scale tests

Full-scale tests are intended to simulate the actual performance of product in real fire. They include furniture calorimeter tests and room tests [182]. These tests are often very expensive because large amounts of materials are consumed, they take long time to set up and run and their reproducibility is uncertain. However, they give a real measure on the degree of fire protection of the final product. During these tests, fire properties such as heat release, mass loss and optical smoke density are measured as a function of time.

Room corner fire test is a test method designed to evaluate the burning behavior of construction products in a room scenario i.e. combustible wall and ceiling materials [183,184]. Similarly to cone calorimeter, the oxygen consumption principle is utilized and the primary output of this test is the occurrence and time to flashover. The results may also include heat release rate, smoke production rate, temperature of the gas layers, flame spread and heat fluxes.

During the test, a specimen is mounted inside the room (typically 3.6 m × 2.4 m × 2.4 m with a doorway of dimension 0.8 m × 2.0 m) on the ceiling and/or on the walls. A propane gas burner is placed in one of the corners and produces a specified heat release rate (i.e. 100 kW during the first 10 minutes, and then 300 kW the following 10 minutes). Combustion gases are collected through the hood where heat release rate and the smoke production are measured. Additionally flame spread along the walls and ceiling is observed. The test is terminated when flashover occurs during the 20-minutes test period. The product is classified according to euroclasses presented in the table below:

Table 4: Euroclass classification in room corner fire test ISO 9705 [47].

Euroclass	Expected burning behavior in the test
A2	No flashover
B	No flashover
C	No flashover at 100 kW
D	No flashover before 2 mins at 100 kW
E	Flashover before 2 mins

5. Experimental

5.1. General considerations

All chemicals used were of reagent grade and purchased from Aldrich or Fluka except for Flamestab® NOR116 which was supplied by BASF. Nuclear magnetic resonance (NMR) spectra were recorded at 298 K using a Bruker Avance 600 (^{1}H NMR 600 MHz, ^{13}C NMR 150.9 MHz). Differential scanning calorimetry (DSC) analyses were performed using Q1000 equipment from TA instruments under N_2 atmosphere at a heating rate of 10 °C/min using sealed pressure capsules. Thermogravimetric analyses (TGA) were performed using a SDT Q600 apparatus from TA instruments under N_2 atmosphere at a heating rate of 10 °C/min. FTIR/MS analyses were conducted with a Netsch TG209F1 Iris, Bruker Tensor-27, Netsch Aeolos QMS 403.

5.2. Flame retardancy tests

Polypropylene films of 200 µm and/or plaques of 1.3 mm thicknesses were prepared by first melt-compounding in a Brabender or Haake mixing chamber at 230 °C or 210 °C respectively and then pressed (Fontje TP200, p_{max} = 50 kN, 1 min) into films/plaques at the same temperatures. 1.6 mm thick plaques were prepared by compounding the additives with polypropylene in a twin screw extruder operating at 230 ºC and then injection molding using an Arburg 370S apparatus at 230 ºC.

5.2.1. DIN 4102-1 test

For the DIN 4102-1 test, the 200 µm and 1 mm thick films were cut into 230 mm × 100 mm specimens. For better differentiation of the flame retardant efficacy of the FR candidates, a 40 mm flame length was used instead of a 20 mm flame length as described in the DIN 4102-1 standard (20 mm flame length was used for 1 mm thick plaques). Five or three samples were ignited for each formulation.

5.2.2. UL94 V test

For the UL94 V test the 1.3 and 1.6 mm thick plaques (specimen size 127 mm × 12.7 mm size specimens) were prepared. Specimen flammability classifications were made according to the Table 3.

5.2.3. Limiting oxygen index test (LOI)

The LOI test was carried out using Oxygen Index Module apparatus from Fire Instrumentations and Research Developments according to ASTM D2863 standard [166]. According to the test method, specimen’s samples of type IV and dimensions of 70 mm × 6.5 mm × 3 mm were supported vertically in the center of heat resistant glass chimney containing the oxygen/nitrogen mixture and tested in accordance with test method A.

6. Results and discussion

The starting point of our investigations was the appearance of a new FR additive called Flamestab® NOR116 on polypropylene market. This commercial product based on alkoxyamine was introduced in 2000 by Ciba (nowadays BASF) as halogen-free flame retardant for polypropylene fibers, nonwovens and films, and was seen in the industry as an alternative to conventional halogen-based FR systems mainly due to very high efficacy at low loadings and more environmental friendly characteristics [185]. Flamestab® NOR116 decomposes creating various types of radicals (see Scheme 9) i.e. aminyl, alkoxy, nitroxyl and alkyl, which differ in their stabilities and reactivities [113]. Hence, in this light, we started to investigate various derivatives which could be a source of different radicals (radical generators) to find the most effective in disturbing the combustion process.

The following chapter summarizes the results obtained in the experimental part of this thesis. The new families of halogen-free flame retardants developed during the thesis work are depicted in the Figure 2.

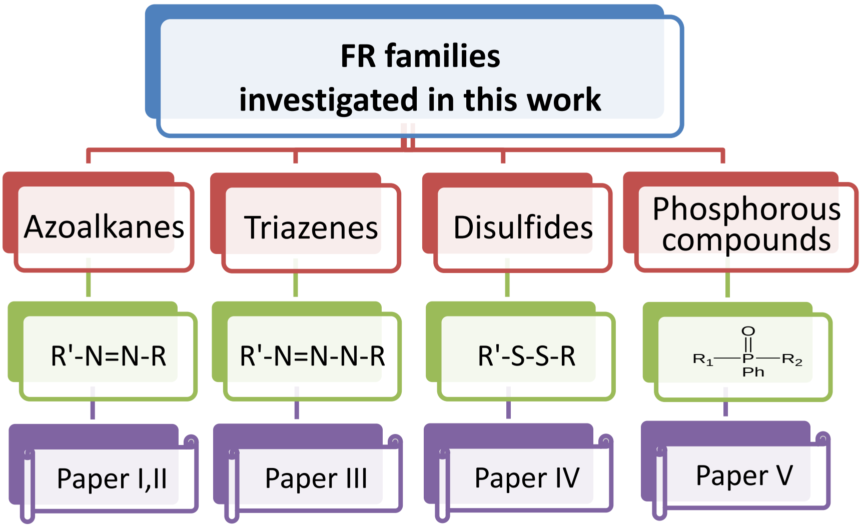


Figure 2: Flame retardants investigated in this work.

6.1. Flame retardant activity of azoalkanes/diazenes (paper I)

Azoalkanes represent a clean source of alkyl radicals and were the first group of flame retardant compounds that we started to study during our attempts to better understand the mechanism of action of the commercial flame retardant Flamestab® NOR116.

Azoalkanes have not been claimed in the literature to be effective flame retardants when applied alone. However, certain flame retardant activity of these compounds has been shown in some papers i.e. to exhibit synergy with halogen flame retardants [186,187]. Azoalkane compounds were believed to work by triggering the thermal decomposition of halogen compounds and hence increasing their activity.

In 2006, we published an article which demonstrated that certain aliphatic azo compounds (such as azocyclohexane or 4’4-bis(cyclohexylazocyclohexyl) methane) function as flame retardants when used alone and they possess self-extinguishing properties in polypropylene films already at very low concentrations of 0.5 wt.% [188]. The flammability test DIN 4102-1 was successfully passed with the B2 classification and the obtained results inspired us to continue along this pathway. Therefore, we started to study more in detail this interesting family and related compounds in order to find the relation between their chemical structure, thermal stability and FR performance.

Previous literature studies showed that the thermal stability of azoalkanes is closely related to their chemical structures and depends on ground-state energy, stability of the incipient radicals and factors related to orbital symmetry [189]. In our next paper, marked in this thesis as paper I, we wanted to study how structural factors such as electronic and/or steric hindrance or ring size variations can influence the flame retardant properties of diazenes. Therefore, a series of symmetrical and unsymmetrical, cyclic and aliphatic azoalkanes were synthesized. Examples of molecular structures evaluated in this work are shown in the Figure 3.

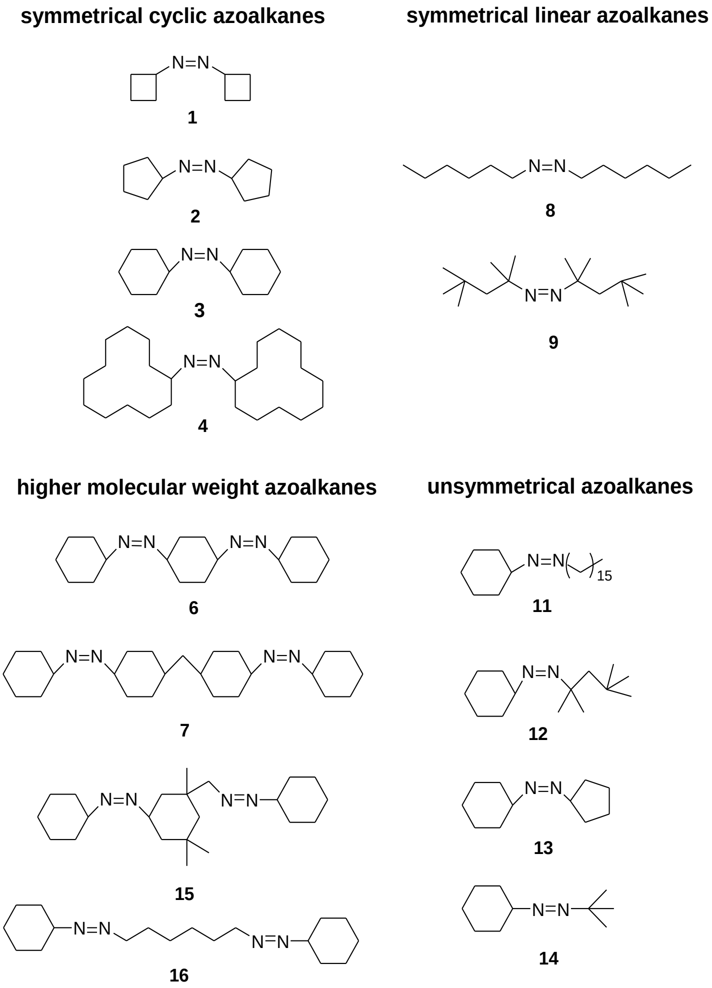


Figure 3: Azoalkanes-molecular structures investigated in paper I.

Flame retardant efficacy of azoalkanes in polypropylene was investigated according to DIN 4102-1 flammability test by using two slightly different methods, A and B. Method A was the standard DIN 4102-1 procedure [165], whereas in method B the applied flame length has been changed from 20 mm flame (method A) to 40 mm flame in order to better differentiate the flame retardant performance of various formulations. Additionally, the test specimens in method B were directly molded without fiber spinning, whereas in method A fiber spinning was included in sample preparation. Flammability results of the tested azoalkane additives are shown in Table 5.

Table 5: Flammability results of azoalkanes according to DIN 4102-1.

Azoalkane	Loading (wt.%)	Burning length (mm)	Weight loss (%)	T_{dec} (°C)	Method (A/B)
Blank PP	100	190 150	100 100	-	A B
Symmetrical azoalkanes					
1	0.5	115	12	510	B
2	0.5	100	n.d.	n.d	B
3	0.5	92	3.8	280	B
4	0.5	165	46	180	A
6	0.5	85	8.2	230	B
7	0.5	86	1.9	316	B
8	0.25	58	5.8	n.d.	A
9	0.5	72	8.4	n.d.	A
Unsymmetrical azoalkanes					
11	0.5	108	7.2	307	B
12	0.25	78	2.5	245	A
13	0.25	80	5.0	170	B
14	0.5	82	5.1	190	B
15	0.5	130	14	178/242	B
16	0.5	107	2.8	n.d.	B

* n.d. - not determined

Flammability results for **symmetrical cyclic** azoalkanes showed a strong correlation between their thermal stabilities and flame retardant activities. For example compound **3** (cyclohexylazo) possess higher decomposition temperature and lower ring strain than compound **4** (1’1-biscycloazo) and therefore perform better as a flame retardant. However, although decomposition temperature is very important criteria, it is not enough to predict the FR activity of new compounds. For instance, volatility and low boiling point of compound **1** are probably responsible for its lower FR activity because it is partially evaporated during polypropylene processing.

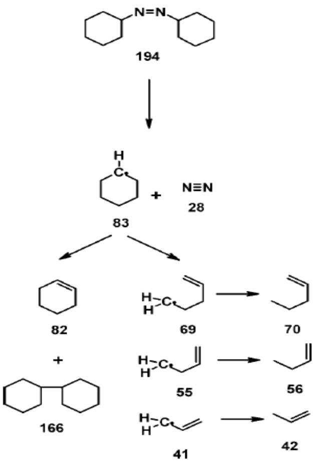
In order to reduce volatility problems, **higher molecular weight compounds** such as bisazo derivatives **6,7,15** and **16** (analogues of the best performing compound **3**) were synthesized. In this series, compound **7** performed the best. When comparing to compound **3** it has reduced weight loss and non-dripping behavior. The non-dripping was also noted for compound **16**, whereas for some reasons it could not be reached for compound **3**.

Some FR activity was also recorded for **symmetrical linear** azoalkanes **8** and **9**. These additives exhibited relatively short burning time but their efficacy was poorer compared to compound **7** or **16** due to fact that their burning was not homogenous.

Furthermore, it was of interest for us to study if and how the flame retardant efficacy will be affected in case of **unsymmetrical azoalkanes** which decomposition mechanism is believed to be different than in case of symmetrical azos. In the case of unsymmetrical compounds, the correlation between decomposition temperature and flame retardant efficacy was not so obvious. Surprisingly, compound **11**, which exhibits appropriate decomposition temperature, did not show a good FR efficacy whereas additives **12**, **13** and **14** showed opposite trend even if their burning behavior was not homogenous and weigh loss was high. Compounds **15** and **16** did not perform well.

Compound **3** was further tested in thick PP sections and as a synergist with commonly used flame retardants. When comparing additive **3** to commercial Flamestab® NOR116 it was noticed that undeniably it exhibits excellent FR efficacy in 1 mm polypropylene plaques in a way of homogenous burning and average burning time of 45 mm. Mechanisms of action for these compounds could be an actual reason of such difference and possible explanation of better performance of compound **3**. Flamestab® NOR116 is believed to work mainly in the condensed phase via the liberation of alkoxy radicals which trigger polypropylene chain scission and accelerate withdrawal of the polymer from the flame. In thick section, due to higher amount of polymer, the activity of Flamestab® NOR116 is not sufficient hence most of the polymer remains intact and can be burned. As compound **3** is active in thick section too, it may indicate that besides condensed phase activity its mechanism of action is located also in the gas phase and alkyl radicals can act as flame inhibitors.

Decomposition products of **3** were studied by TGA/FTIR/MS analysis. The TGA/FTIR spectra show that **3** is rather volatile and boils at around 200 °C. The main products of thermolysis of **3** found by MS are shown on Scheme 11.



Scheme 11: Decomposition products of azoalkane **3**.

As soon as nitrogen is liberated, cyclohexyl radicals are produced. These radicals can undergo disproportionation to yield cyclohexene or react via bimolecular attack on azocyclohexyl with subsequent unimolecular B(C-H) splitting to cause further decomposition reactions [190]. In addition, cyclohexyl radical can also decompose to smaller fragments [191] such as resonance stabilized 5-hexenyl-, propyl and allyl radicals as well as bi-cyclic hydrocarbons. However, in oxygen rich atmosphere the range of decomposition products may vary and be slightly different.

Finally, combinations of compound **3** with commercially available flame retardants such as aluminum trihydroxide (ATH), decabromodiphenyl ether (deca-BDE) as well as tris(3-bromo-2'2-bis(bromomethyl)-propyl)phosphate (TBBPP) were investigated for synergistic or antagonistic effect. Table 6 contains the results of these investigations.

Table 6: Combinations of azo **3**, Flamestab®NOR116 and conventional FRs. UL94 V test.

Formulation	UL94 V
Reference (PP)	NC
PP + 15 wt.% TBBPP	NC
PP + 0.5 wt.% **3** + 14 wt.% TBBPP	NC
PP + 0.5 wt.% NOR116 + 14 wt.% TBBPP	V0
PP + 5 wt.% deca-BDE	NC
PP + 0.5 wt.% **3** + 5 wt.% deca-BDE	V2
PP + 0.5 wt.% NOR116 + 5 wt.% deca-BDE	V2
PP + 60 wt.% ATH	V2
PP + 1 wt.% **3** + 25 wt.% ATH	V2
PP + 1 wt.% NOR116 + 25 wt.% ATH	V2

*NC – not classified

Good synergistic effect was obtained and UL94 V2 rate was reached for formulations containing additive **3** together with deca-BDE or ATH. Compared to single systems the quantity of conventional flame retardants was significantly reduced, e.g. in case of ATH from 60 wt.% to 25 wt.%. For deca-BDE, although the loading stays on the same level, the FR properties were drastically improved so V2 rate could be obtained. In UL94 vertical test no synergistic effect was observed for compound **3** together with TBBPP. Nevertheless, according to DIN 4102-1 test, some FR activity of this formulation can be noticed when TBBPP loading is lower than 3 wt.% but not at higher concentrations.

To explain this issue, thermogravimetric analysis for tree different polypropylene samples containing 3.5 wt.% TBBPP, 3.5 wt.% TBBPP + 0.5 wt.% of Flamestab® NOR116 and 3.5 wt.% TBBPP + 0.5 wt.% additive **3** were performed in order to find the differences in their thermal decomposition temperatures. It has been found that nitroxyl radicals from thermolysis of Flamestab® NOR116 cause more effective decomposition of TBBPP at lower temperature than alkyl radicals from azoalkane **3** and thus accelerate the decomposition of the polymer more effectively [85]. Therefore, the effect of azo at higher concentration of TBBPP is less pronounced compared to low loading of brominate phosphate ester.

We concluded that symmetrical and unsymmetrical, cyclic and aliphatic azoalkanes are effective flame retardants when used at low loading of 0.5 wt.% in thin PP films. In the series of different-sized azocycloalkanes, the flame retardant efficacy decreased in the following order: R = R´= cyclohexyl > cyclopentyl > cyclobutyl > cyclooctanyl > cyclododecanyl whereas in the series of aliphatic azoalkanes their efficacy is rated as follow: R = R´= n-alkyl > tert-butyl > tert-octyl [192]. Especially compound **7** shows excellent FR characteristics together with non-dripping behavior. Furthermore, compound **3** exhibited a significant FR efficacy in thick section what makes it better in comparison to commercial Flamestab®NOR116. As Flamestab® NOR116, most of azoalkanes are characterized by effectiveness at very low concentrations and no problem with affecting polymer mechanical properties. However, unlike this commercial product, they do not contribute to light stability and do not cause significant polymer discoloration.

6.1.1. Flame retardant activity of azoalkanes in LDPE (paper II)

Next we decided to investigate the potential of azoalkanes as flame retardants for fire resistant paper coating applications. We wanted to explore the possibility of using azoalkanes as halogen-free flame retardants for low density polyethylene (LDPE) extrusion-coated paper. We selected azocyclohexane (AZO) and 4’4-bis(cyclohexylazocyclohexyl) methane (BISAZO) (compound **3** and **7** in paper I) for these experiments due to the following reasons: they could be easily synthesized in a substantial quantity, they exhibited high flame retardant activity at low concentrations, they possess fairly high thermal stabilities and they do not alter the rheological properties of low density polyethylene.

Before running the trial tests, the FR behaviors of compounds **3**, **7** and other commercial flame retardants (including Flamestab® NOR116, magnesium dihydroxide (MDH) and brominated additive Luvogard MB81/PE) were evaluated according to DIN 4102-1 fire test in LDPE. Table 7 shows the results obtained from these investigations.

Table 7: Flammability results of FR compounds in LDPE. DIN 4102-1 fire test.

Composition	Burning length (mm)	Burning time (s)	Burning drips (Yes/No)	Td by DSC (° C)	DIN 4102-1 B2 (Pass/Fail)
Control (LDPE)	190	21.5	Yes	-	Fail
AZO (0.5 wt.%)	122.3	9.2	Yes	280	Pass
BISAZO (0.5 wt.%)	103	10.3	Yes	306	Pass
Flamestab® NOR116 (0.5 wt.%)	92	11.1	Yes	284	Pass
Flamestab® NOR116 (1.0 wt.%)	92	9.6	Yes	-	Pass
$Mg(OH)_2$ (50 wt.%)	90	33.0	Yes	300	Pass
Luvogard MB81/PE (5 wt.%)	68	6.8	Yes	-	Pass
Luvogard MB81/PE (10 wt.%)	79	0.0	Yes	-	Pass
Luvogard MB81/PE (5 wt.%) + Flamestab® NOR116 (0.5 wt.%)	60	0.6	Yes	-	Pass

The preliminary data demonstrated that all tested additives provide good flame retardancy to LDPE films. All compounds passed mentioned test and showed increased flame retardant efficacy compared to virgin LDPE polymer in the following order:

$Mg(OH)_2$ (50 wt.%) < AZO (0.5 wt.%) < BisAzo (0.5 wt.%) < Flamestab® NOR116 (0.5 wt.%) < Flamestab® NOR116 (1 wt.%) < Luvogard MB81/PE (5 wt.%) < Luvogard MB81/PE (10 wt.%) < Luvogard MB81/PE (5 wt.%)/Flamestab® NOR116 (0.5 wt.%). The best performance in terms of fire retardancy was seen for LDPE/Luvogard MB81/PE (5 wt.%)/Flamestab® NOR116 (0.5 wt.%). The quality of films was also checked in order to avoid foreseeable problems with coating line runnability [193]. For example, the film quality of magnesium dihydroxide $Mg(OH)_2$ was too bad to be used for further testing of multilayer facings since it contains number of white aggregates which could present runnability problems.

Extrusion coating experiments of flame retarded low density polyethylene (LDPE) onto a standard machine finished Kraft paper have been carried out on a pilot extrusion coating line. Apart from azoalkane compounds **3** and **7**, brominated additive Luvogard MB81/PE and Flamestab® NOR116 have been tested for comparison as commercial flame retardant additives. The concentration of azoalkane compound was 0.5 wt.% for compound **3** and 1 wt.% for compound **7**. The maximum extrusion temperatures varied between 260-290 ^{o}C and the coating layer weight differs from 12.9 to 25.0 g/m^2. The fire retardant properties of produced LDPE-coated papers were evaluated by conducting a small-scale laboratory fire test for multilayer facings using three samples of 190 mm × 90 mm dimensions which have been classified according to the following classification.

Table 8: Classification of fire performance for multilayer facings fire test.

Class	Burning
Class I	**Fast burning.** Sample burns completely < 5 seconds
Class II	**Easy burning.** Sample burns completely < 20 seconds
Class III	**Moderate burning.** Sample burns completely > 20 seconds
Class IV	**Minor burning.** Sample burns < 20 seconds and extinguishes before the flame reaches the borderline at 150 mm
Class V	**Non-flammable.** Sample does not ignite nor char.

The adhesion strength between LDPE and the paper sheet was assessed visually and by manual peeling. The results of these investigations are summarized in the Table 9.

Table 9: Flammability and adhesion results for LDPE-extrusion coated papers.

Composition	Coating weight (g/m^2)	Pilot processing temperature (°C)	Evaluation of adhesion by manual pealing of layers	Flame class
MF60/LDPE/Azo (0.5 wt.%)	12.9	260	Fair to poor	IV (Minor burning)
MF60/LDPE/Azo (0.5 wt.%)	12.9	280	Fair to poor	I (Fast burning)
MF60/LDPE/Azo (0.5 wt.%)	20	260	Poor	III (Moderate burning)
MF60/LDPE/BisAzo (1 wt.%)	20	280	Good	II (Easy burning)
MF60/LDPE/BisAzo (1 wt.%)	15	290	Poor	II (Easy burning)
MF60/LDPE/BisAzo (1 wt.%)	20	290	Good	II (Easy burning)
MF60/LDPE/ Flamestab® NOR116 (0.5 wt.%)	12.9	260	Poor	I (Fast burning)
MF60/LDPE/ Flamestab® NOR116 (0.5 wt.%)	25	290	Good	I (Fast burning)
MF60/LDPE/ Flamestab® NOR116 (1 wt.%)	25	290	Good	I (Fast burning)
MF60/LDPE/ Luvogard MB81/PE (5 wt.%)	25	290	Good	I (Fast burning)
MF60/LDPE/ Luvogard MB81/PE (10 wt.%)	25	290	Good	I (Fast burning)

The results showed some difficulties in simultaneously obtaining high FR properties of tested multilayers together with good adhesion between polymer and the paper surface [194].

It was seen that the extrusion coating temperature of 290 °C was too high for the investigated additives to provide good flame retardancy. Some additives, such as brominated FR Luvogard MB81/PE and Flamestab® NOR116 started to decompose already during processing and created strong odor. From the other side, this temperature was high enough to promote adhesion by causing melt oxidation of polyethylene.

As could be anticipated, also the coating thickness affected the flame retardant properties and adhesion [195]. Higher coating thicknesses enhanced adhesion since the higher amount of molten polymer more easily penetrates into the pores and enhances physical bonds. For thinner coatings faster cooling reduces adhesion [196].

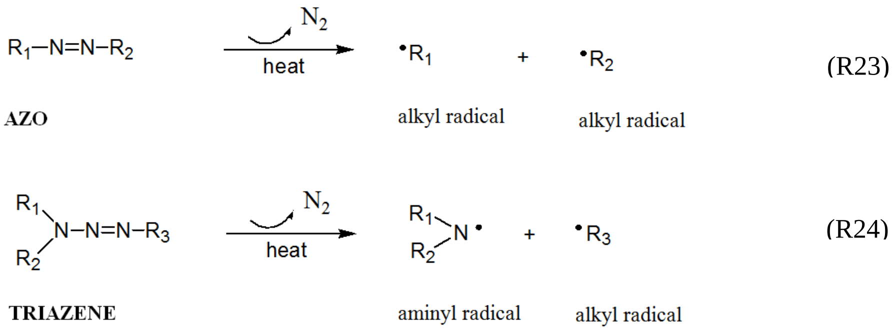
Multilayer facings containing azocyclohexane showed improved flame retardant properties when lower temperature of 260 °C and lower coating weight of 12.9 g/m^2 were used. When using higher extrusion temperatures and higher coating thicknesses the flame retardant properties started to decrease whereas the adhesion between polymer layer and the porous paper substrate was enhanced. Therefore, to fully reach the objectives of polyolefin extrusion coated paper and to be able to achieve both high flame retardant properties and good interfacial adhesion, azoalkane such as compound **7** (used at 1 wt.%) with higher thermal stability than azocyclohexane **3** should be tested at lower coating weight and lower extrusion temperatures.

Nevertheless, for both azoalkane formulations the flame retardant properties were better than for multilayer facings containing the commercial Flamestab® NOR116 and Luvogard MB81/PE. Moreover, under all experimental conditions the runnability in the pilot line was flawless for azoalkanes.

6.2. Flame retardant activity of triazenes (paper III)

Results obtained with azoalkanes (paper I, II and other related publications) proved, that diazene based flame retardants constitute a real potential and can be a good alternative to conventional flame retardants. Therefore, it was interesting for us to extend the field of investigations and consider another group of compounds containing azo moiety as possible effective radical generator [197].

In the previous paper we have demonstrated, that during thermolysis azoalkanes form free radical species (alkyl radicals) which affect the burning process of polypropylene advantageously and reduce its flammability [188]. As a consequence, we envisioned that triazenes, having general formula $R_1\text{-}N_1=N_2\text{-}N_3R_2R_3$ (where R_1 and R_2 are either alkyl or aryl groups and R_3 is hydrogen, alkyl, aryl or acyl group) might also be effective as flame retardants since similarly to azoalkanes they contain diazoamino group which undergoes thermal dissociation into free radicals with subsequent liberation of nitrogen [57]. Thermolysis reactions of both azoalkanes and triazenes are shown in the Scheme 12.



Scheme 12: Thermolysis of azoalkanes and triazenes.

Noteworthy, when azo compounds allowed us to evaluate the FR activity of alkyl radicals, triazenes gave us the possibility to study the FR activity of aminyl radicals. Figure 4 shows the set of triazene compounds synthesized and investigated in this paper.

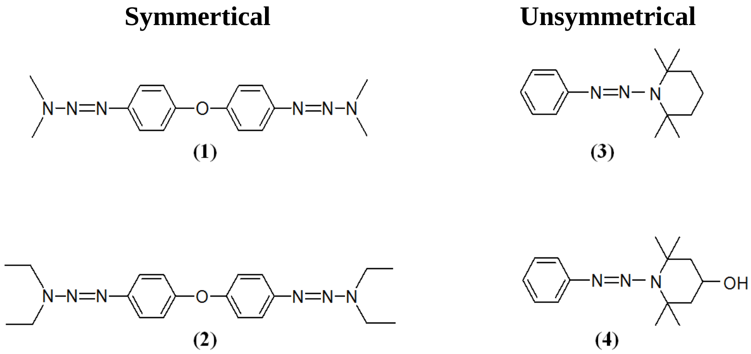
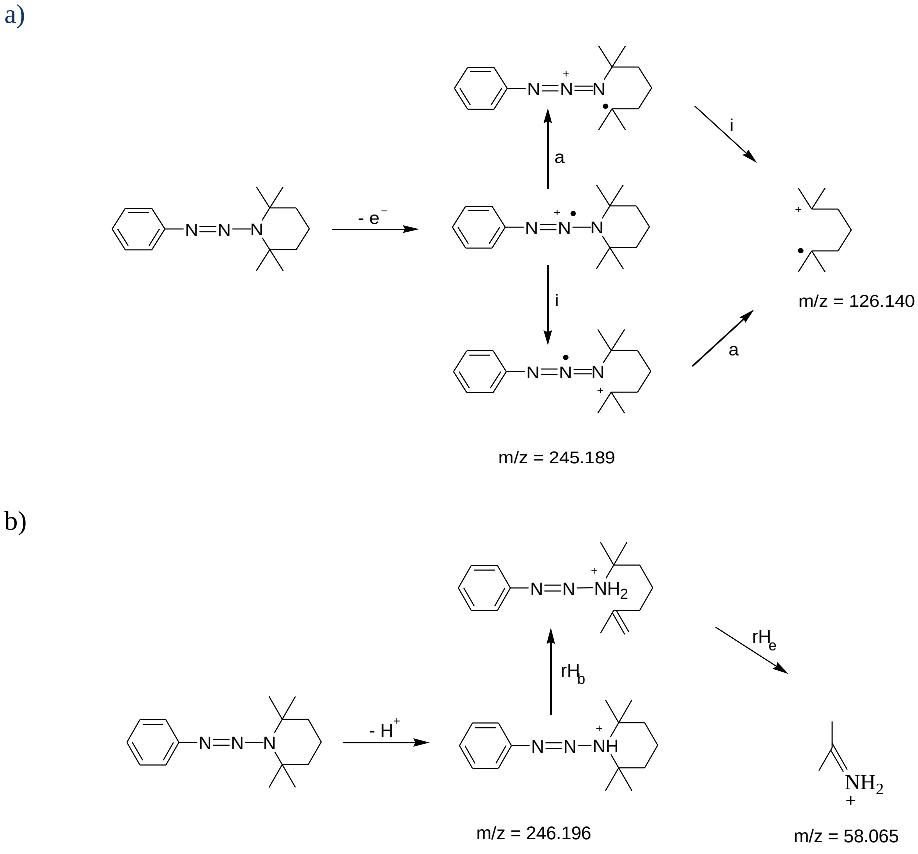


Figure 4: Molecular structures of triazenes.

Similarly to azos, triazenes may have high thermal stability which can be easily tuned over a broad temperature range by selection of substituents both on the aromatic ring and on the amino group. In the literature it has been reported that the rate constants of thermal dissociation of different bistriazenes depend mostly on the nature of R_1 and R_2 groups and to lesser extend on the character of X of the central aryl segment (-Ph-X-Ph-) [198,199]. For example, when methyl groups have been used as R_1, R_2 (compound **1**), the decomposition temperature was 260 °C whereas when changing the R_1, R_2 groups to ethyl substituents (compound **2**) decomposition temperature increases of about 100 °C.

Interesting for us was the fact that the thermal stability of triazenes was not reported in case when alkyl group has been changed to aliphatic cyclic group. We already knew from investigations concerning azoalkanes that in their case at least one cyclohexyl group connected to azo function was needed for imparting good flame retardancy in polypropylene. Hence, we wanted to evaluate how the thermal stability of triazenes, their decomposition pattern and above all flame retardant action will be affected when methyl or dimethyl groups will be replaced by aliphatic cyclic group such as 2’2’6’6-tetramethylpiperidine or 2’2’6’6 tetramethylpiperidin-1-ol. For this reason two triazene compounds **1**, **2** which showed high thermal stability and two new molecules **3**, **4** possessing aliphatic cyclic group were synthesized and tested as flame retardants. All prepared compounds were expected to be sufficiently stable not to break down to any significant extent at normal processing temperature of polypropylene. The thermal properties of **1 - 4** were determined and confirmed to have suitable onset of decomposition temperatures which is between 230 ^{o}C to 280 ^{o}C [200].

The fragmentation patterns and decomposition products of compound **3** were analyzed by simultaneous mass spectrometry (MS) and Fourier transform infrared (FTIR) spectrometry of off-gases from a thermogravimetric analyser (TGA). In agreement with earlier reports [196], it was found that the decomposition of triazenes involves homolytic bond breaking of the N_2 and N_3 atoms and generation of two radicals, i.e. diazyl and aminyl radical. The aminyl radical is more stable than diazyl radical that continues to decompose by elimination of nitrogen and thereby create $R^{\cdot}$ species which have been detected by electron paramagnetic resonance (EPR) [201]. For 2'2'6'6-tetramethyl-1-phenylazopiperidin **3** we observed early decomposition of material starting partially already at 150 °C under release of benzene (probably due to its high volatility) and continuing further above 230 °C with release of tetramethylpiperidine fragments. Tentative routes to the detected products are shown in Scheme 13.



Scheme 13: Proposed decomposition mechanisms for triazenes.

First possible mechanism **(a)** includes loss of one electron from the structure what contributes to creation of radical cation on -N_2- in triazene moiety. This radical cation, depending on the delocalization of the charge, can exist in two forms. In the first form isopropyl radical is created on one of the piperidinyl carbons. Knowing that the durability of the radicals is depending on the substitution pattern (the more substituted radical, the more durable it is) it is right to assume that this resonance structure is more thermodynamically stable than the second form. Moreover, N-C bond is weaker than two double N=N bonds and can undergo further deionization or breakage leading to the final product. Another proposed structure is created firstly by making carbocation on piperidine moiety, breaking N-C bond and finally producing less stable radical on nitrogen. Both possible structures can decompose further and produce carbocation radical on piperidine moiety.

The second mechanism **(b)** includes protonation of -N_3- which initiates decomposition. In the presence of ions H^+, cation form of tetramethylpiperidine is created. This form can further undergo transformations to the final decomposition product. However, these proposed mechanisms are investigated under nitrogen conditions and therefore it is important to notice that the range of decomposition products may be different in the real fire conditions.

Finally, the flame retardant potential of investigated triazene compounds was evaluated according to the DIN 4102-1 standard flammability test. Method B with 40 mm high flame, used in evaluation of azoalkanes, was also adopted for triazene compounds. Polypropylene films were prepared by using a low additive loading of 0.5 wt.%. No alteration of the physical or esthetic properties of polymer (except the color) was observed during the blending. From flammability test the damaged length, burning time and weight loss were measured. Moreover, it was also recorded whether the paper ignited or not due to burning dripping. Table 10 contains the flammability results together with thermal investigations of triazene compounds.

Table 10: Flammability results according to DIN 4102-1 test method: edge ignition test of 250 mm × 110 mm samples (flame length 40 mm, DELA).

Formulation	Loading (wt.%)	Ave. burning length (mm)	Ave. burning time (s)	Weight loss (%)	Drips (yes/no)	Paper ignition (yes/no)	T_{dec} by TGA/DSC (°C)	Classification
Blank PP	100	190	33.3	100	Yes	Yes	224-493	NC
NOR116	0.50	78	11	6.0	Yes	Yes	-	B2
1	0.50	80	8.7	6.2	Yes	No	230-300	B2
2	0.50	77	7.0	4.4	Yes	No	240-316	B2
3	0.50	85	7.3	5.6	Yes	No	233-292	B2
4	0.50	89	8.3	3.7	Yes	No	134-262	B2

*NC-not classified

All of the tested triazene formulations passed the DIN 4102-1 standard with B2 classification and their average burning times were short (less than 9 s for all compounds) with exceptionally low weight losses that varied between 3.7 % to 6.2 %. For example compound **2** provides polypropylene with very good flame retardant properties and shows the best overall performance among the all tested molecules.

Somehow, for **symmetrical** compounds, it was not surprising that compound **2** outperforms its analogue bistriazene with methyl substituents **1**. Compound **2** has broader decomposition range according to DSC and its onset of decomposition temperature is closer to PP burning temperature when compared to compound **1**. Hence, its FR performance was expected to be better. Moreover compared to compound **3**, which was also performing very well, **2** has shorter average burning time and length as well as lower weight loss. This can be explained in terms of volatility and decomposition issues. The low molecular weight triazene **3** evaporates before the decomposition temperature is reached hence part of its activity is lost during processing, whereas for the less volatile triazene, compound **2**, the decomposition temperature and onset of weight loss temperature are very similar and are well contained within the desired range.

In the series of **unsymmetrical** triazenes better performance was noticed for compound **3**. It was surprising for us, since compound **4** has higher onset of decomposition temperature and is less volatile. However, from the other side these results were in agreement with flammability results of unsymmetrical azoalkanes investigated in the first paper [202]. In fact, additive **3** shows shorter burning time and burning length than **4** even if its burning was not homogenous. This may be explained by faster decomposition of **3** and increased dripping behavior for this additive suggested by higher weight loss, which in turns causes a faster extinction of the flame.

Similarly as in the case of azoalkanes, the great performance of triazenes (especially **2** and **3)** was also related to the action of commercial flame retardant Flamestab® NOR116 at the same loading of 0.5 wt.%. Both additives **2** and **3** have the same 4 s shorter average burning times when compared to Flamestab® NOR116, whereas their average burning length is 1mm shorter for bis-4’4’-(3’3’-diethyltriazene) diphenyl ether **2** and 7 mm longer for 2’2’6’6-tetramethyl-1-phenylazo-piperidine **3**. Longer burning length for compound **3** when comparing to Flamestab® NOR116 can be attributed to smaller amount of active species within the flame. It is also noteworthy that in contrast to reference flame retardant Flamestab® NOR116, all triazene additives have shorter burning times, none of the tested formulations ignited the paper and no burning dripping could be detected. Thus, all of the prepared compounds exhibited excellent flame retardant properties for polypropylene films and show a very high FR effect at low concentrations of 0.5 wt.%.

We concluded that triazenes have excellent FR effect and high potential to constitute a new family of radical generators for flame retarding of polypropylene and perhaps other polymeric materials.

6.3. Flame retardant activity of disulfides (paper IV)

In the course of our chemical approach towards finding new type of radical generators, we started to investigate the potential of disulfides as a source of sulfur radicals (thiyl radicals). To the best of our knowledge, the use of disulfides alone as flame retardants is unprecedented in the literature [203] whereas, as other sulfur compounds, they are claimed in certain patents to be effective synergists and exhibit good flame retardant effect with halogen additives and metal hydroxides [204-206].

Disulfides represent a class of compounds having the general structure R-S-S-R', where R and R' are either alkyl or aryl groups and they can be prepared in high yields by controlled oxidation of thiols using different reagents and oxidants under a broad range of experimental conditions [207]. Chemical structures of compounds investigated in this work are depicted on the Figure 5.

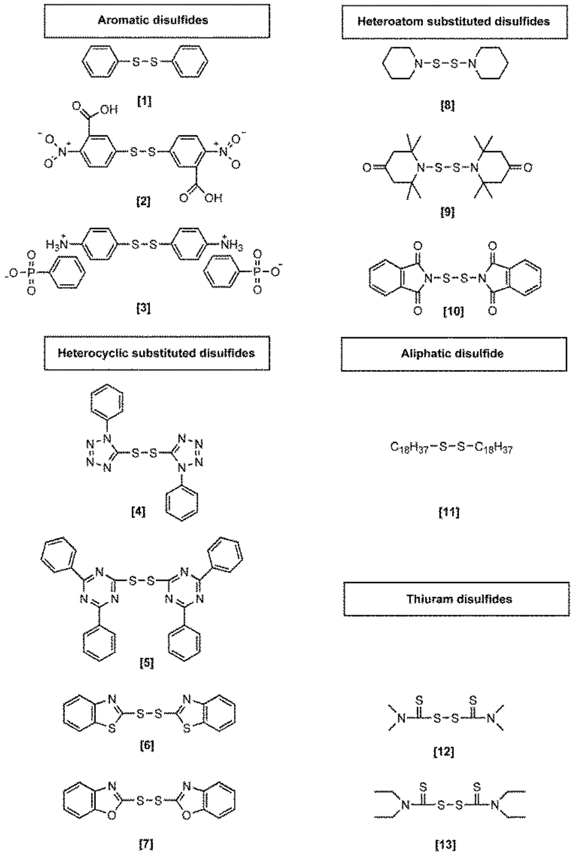


Figure 5: Chemical structures of investigated disulfides.

Flame retardancy of polypropylene formulations containing disulfides was evaluated by performing the ignitability tests according to DIN 4102-1 standard. The results are summarized in the Table 11.

Table 11: Flammability results according to DIN 4102-1 test method: edge ignition test of 250 mm × 110 mm samples (flame length 40 mm, DELA).

Formulation	**Loading (wt.%)**	**Average burning length (mm)**	**Average burning time (s)**	**T_{dec} by TGA/DTA (°C)**	**DIN 4102-1 classification**
			REFERENCES		
Blank PP	100	190	38	464	NC
Flamestab®NOR116	0.5	78	11	295	B2
			DISULFIDES		
1	0.5	63	17	264	B2
2	0.5	53	10	274	B2
3	0.5	96	32.7	-	B2
4	0.5	85	14.5	-	B2
5	0.5	190	41	281	NC
6	0.5	86	18	321	B2
7	0.5	95	23	276	B2
8	0.5	91	20.3	276	B2
9	0.5	190	35.3	203	NC
10	0.5	85	14.5	-	B2
11	0.5	180	47	-	NC
12	0.5	182	49	225	NC
13	0.5	163	51	215	NC

*NC – not classified

It was found that majority of the tested disulfides provided flame retardancy and self-extinguishing properties to polypropylene films by themselves at very low loading of 0.5 wt.%. The highest efficacy has been observed for aromatic > heterocyclic substituted disulfides > heteroatom substituted disulfides > benzothiazole and benzoxazole disulfides >

aliphatic disulfides >> thiuram disulfides. From the range of tested structures only five compounds (**5**,**9**,**11**,**12**,**13**) did not show sufficient fire retardant performance to pass the mentioned test. All the other compounds passed the DIN 4102-1 test and showed very good FR activities. Especially compound **2**, 5'5-dithiobis (2-nitrobenzoic acid), showed a remarkable strong performance in terms of very low burning length (53 mm) and burning time (10 s) compared with other compounds in this series and even with the commercially available Flamestab® NOR116. Higher performance of compound **2** can be attributed to stronger stabilization of disulfide bond by the electron withdrawing substituents (nitro and carboxylic acid moieties) at the aromatic ring.

In addition, the limiting oxygen index test was used for the most promising disulfide candidates i.e. flame retardants **1**, **2** and **6** used at a loading of 3 wt.% in order to investigate their LOI values in polypropylene. The results are depicted on the Figure 6.

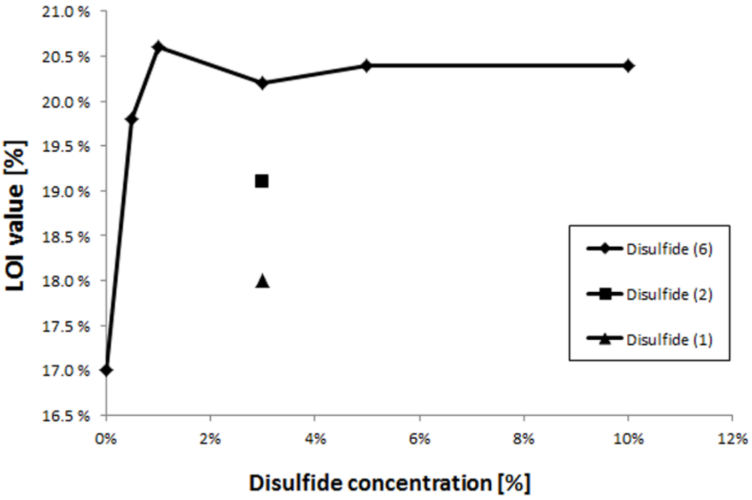


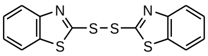
Figure 6: Limited oxygen index of polypropylene containing disulfides **1**, **2** and **6**.

It was showed that the addition of disulfides to polypropylene only slightly improves the LOI value of the pure polymer. For example, when additives **1**, **2**, **6** were incorporated, the LOI value of polypropylene increased from 17 % to 17.9 %, 19.1 % and 20.3 % respectively. These findings correlate well with the previous literature data for flame retardants based on radical generators such as Flamestab® NOR116, where 1 wt.% of Flamestab® NOR116 raise the LOI value of polypropylene to 22 % [116].

Next, we wanted to evaluate the correlation between the amount of best performing in this test additive **6** and the LOI value. For compound **6** the highest LOI number (20.6 %) was recorded at the loading of 1 wt.%, whereas when the loading increased up to 10 wt.% no further improvement in LOI was observed.

Furthermore, the mechanism of thermal decomposition of disulfides **6** and **11** was also investigated and the decomposition patterns of the evolved gases from a thermogravimetric analyzer (TGA) have been analyzed by simultaneous mass spectrometry (MS) and Fourier transform infrared spectrometry (FTIR) as shown in Table 12.

Table 12: Results of TGA-FTIR-MS investigations of disulfide **6** and **11**.

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

According to the data both compounds were quite stable and started to decompose at 250 ºC (compound **6**) and 280 ºC (compound **11**). Thiols, aliphatic and aromatic hydrocarbons as well as isothiocyanates (in case of compound **6**) were identified as the main decomposition products. For compound **6** only SO_2 is released at the temperature above 450 ºC whereas for the compound **11** at the same temperature SO_2 is released together with elemental sulfur (detected already above 300 ºC according to both MS and FTIR analysis).

The interpretation of the obtained results was not easy and straightforward. It is known that disulfides undergo transformations during thermal treatment (pyrolysis, combustion) that produce various types of radicals and sulfur compounds depending on their structures [208]. The S-S bond in disulfides is the weakest and it first undergoes homolytic cleavage, independently of the structure, forming thiyl radicals [209-212]. These released radicals have a big effect on the properties and performance of disulfides [207]. Aryl disulfide **6**, which is less resonance stabilized and requires less energy than alkyl disulfide **11** to be broken up, undergoes therefore faster homolytic scission of S-S bond and releases earlier the thiyl radicals. Therefore, the decomposition of disulfides is mainly influenced by two factors: destabilization of disulfides and stability of the formed thiyl radicals from their decomposition.

Performed additional thermogravimetrical studies (TGA/DTA) revealed that disulfide **6** has the ability to cause faster degradation of polymer. Moreover, decomposition of polypropylene starts earlier when using higher loading of additive **6** (e.g. at 5 wt.% loading the 5 % weight loss ($T_{5\%}$) is observed at T=355 °C whereas for 0.5 wt.% $T_{5\%}$=412 °C). Observed results were not very surprising since they stayed in line with the previous literature data, where enhancement of polystyrene degradation by sulfur was reported [213]. Based on this fact, the flame retardant mechanism of disulfides is expected to work by generation of thiyl radicals that induce faster degradation of polypropylene chain and remove substrate from the flame. In addition, some of these radicals can be partly involved in the free radical chemical reactions during the combustion process itself.

It was concluded that thiyl radicals, generated from certain disulfides have the ability to interrupt the combustion process of polypropylene and affect the burning process advantageously. The flame retardant efficacy of these compounds depends on: (1) thermal stability (homolysis temperature), (2) products of decomposition and mechanisms thereof, and (3) reactivity of the radicals generated during decomposition. Especially disulfides represented by 5’5’-dithiobis (2-nitrobenzoic acid) **2**, diphenyl disulfide **1**, bis(1-phenyl-1H-tetrazol-5yl)-disulfide **4**, 2-bisbenzothiazole-2’2’-disulfide **6** and N,N-dithiobis-(phtalimide) **10** have shown high FR effect even when compared to commercial flame retardant Flamestab® NOR116. For this reason, disulfide compounds are considered as an intriguing family, which can be successfully used as halogen-free flame retardants. Further research efforts within these compounds are definitely warranted.

6.4. Flame retardant activity of phosphorus-based formulations (paper V)

Finally, the potential of two new phosphorous flame retardants, i.e. P’P-diphenyl phosphinic hydrazide (PAH) and melamine phenyl phosphonate (MPhP) was investigated in polypropylene films and plaques using various flammability tests. These compounds were tested alone (according to DIN 4102-1, UL94 V, LOI) or in case of MPhP in combination with other radical generators based on azoalkane and disulfide structures (UL94 V, LOI). The structures of all compounds used in these studies are depicted in Figure 7.

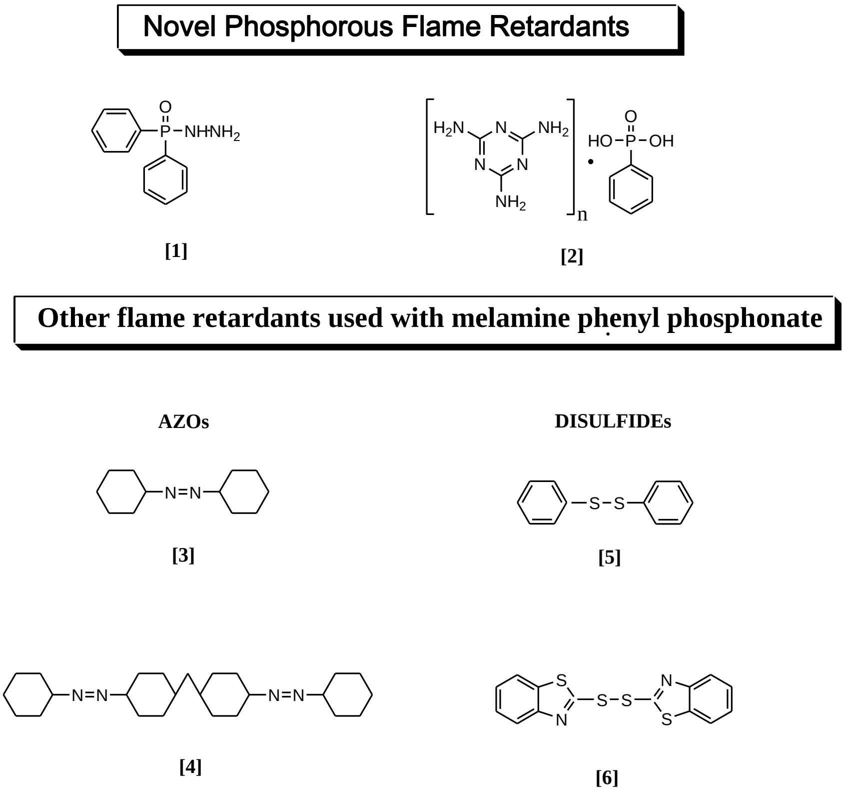


Figure 7: Molecular structures of P’P-diphenyl phosphinic hydrazide (**1**), melamine phenyl phosphonate (**2**), azocyclohexane (**3**), 4’4-bis(cyclohexylazocyclohexyl) methane (**4**) diphenyl disulfide **(5)** and 2’2’-dithiobis-benzothiazole (**6**).

First we compared the FR efficacy of phosphorous compounds, P’P-diphenyl phosphinic hydrazide (**1**) and melamine phenyl phosphonate (**2**) in DIN 4102-1 flammability test with previously reported flame retardants **(3**,**4**,**5** and **6**) tested by us in polypropylene films according to the same test procedure. The results are summarized in the Table 13.

Table 13. Flammability results according to DIN 4102-1/B2 test method: edge ignition test, 200 µm pressed PP films of size 190 mm × 90 mm (flame length 40 mm).

Formulation	**Loading of FR (wt.%)**	**Average burning length (mm)**	**Average burning time (s)**	**Melt dripping/ paper ignition, (Y/N)**	**Test rate**
PP	100	190	33	Y,Y	NC
PP + **1**	0.5	116	10.7	Y,Y	B2
PP + **2**	0.5	190	38	Y,Y	NC
PP + **2**	6.5	71	3	Y,Y	B2
PP + **3**	0.5	65	9.8	Y,Y	B2
PP + **4**	0.5	63	9.5	N,N	B2
PP + **5**	0.5	63	17	Y,Y	B2
PP + **6**	0.5	86	18	Y,Y	B2

*NC – not classified

It was found that there is a difference in flame retardant efficacy between these two compounds. P'P-diphenyl phosphinic hydrazide **1** passed the B2 classification at very low loading of 0.5 wt.% whereas melamine phenyl phosphonate **2** required higher concentration of 6.5 wt.% in order to reach the same rate. It has been suggested that additive **1** displays higher gas phase activity and may operate by withdrawal of the fuel from the flame zone by accelerating polypropylene degradation and causing pronounced melt dripping. In contrast, melamine phenyl phosphonate **2** which is more thermally stable than P'P-diphenyl phosphinic hydrazide **1** has a less pronounced gas phase activity and its thermal decomposition is less well synchronized with the initiation of the degradation of the host polymer. Therefore in this test it performs better when used at higher loadings. As expected, all other radical generators from azoalkane and disulfide families show much higher flame retardant efficacy in polypropylene films compared to phosphorous compounds.

Encouraged by good DIN 4102-1 test results we started to evaluate the phosphorous compounds according to UL94 vertical burning test [175]. The results from these investigations are contained within the Table 14.

Table 14. UL94 vertical test results for PP blends containing **1** or **2**, samples thickness 1.3 [mm].

Formulation	Burning time (s)	Dripping ignition (x/4)	UL94 V rate	LOI (%)
PP	58	4/4	NC	17
PP + 1 (10 wt.%)	1.1	4/4	V2	21.5
PP + 1 (20 wt.%)	5.5	4/4	V2	n.d.
PP + 2 (10 wt.%)	11	4/4	V2	19.3
PP + 2 (20 wt.%)	0	4/4	V2	20.7
Investigation of synergistic effects				
PP + 1 (10 wt.%) + **3** (1 wt.%)	0.5	4/4	V2	21.5
PP + 1 (20 wt.%) + **3** (1 wt.%)	0.5	4/4	V2	21.8
PP + 2 (10 wt.%) + **3** (1 wt.%)	0	2/4	V2	21.0
PP + 2 (20 wt.%) + **3** (1 wt.%)	0	0/4	V0	22.8
PP + 2 (20 wt.%) + **3** (0.5 wt.%)	0	3/4	V2	-
PP + 2 (17 wt.%) + **3** (1 wt.%)	0	0/4	V0	-
PP + 2 (15 wt.%) + **3** (1 wt.%)	0.1	1/4	V2	-
PP + 2 (10 wt.%) + **3** (1 wt.%)	0	2/4	V2	-
PP + 2 (20 wt.%) + **4** (1 wt.%)	0	0/4	V0	-
PP + 2 (20 wt.%) + **5** (1 wt.%)	0.1	4/4	V2	-
PP + 2 (20 wt.%) + **6** (1 wt.%)	0	4/4	V2	-

*NC – not classified
*n.d. – not defined

In UL94 V tests, both phosphorous compounds reached UL94 V2 rate when used alone at 10 wt.% and/or 20 wt.%. Nevertheless due to their high tendency to drip the better V0 rate was not obtained even at 20 wt.% loadings.

In order to reach better classification in UL94 V test, potential synergism between melamine phenyl phosphonate **2** and other radical generators from azoalkane and disulfide families were investigated. Especially strong synergistic effect was observed between melamine phenyl phosphonate **2** and azoalkanes **3** and **4**. Thus, in these cases, the high dripping tendency was reduced and the formulations of PP + 2 (20 wt.%) + 3 (1 wt.%) (or 4 (1 wt.%)) were easily assigned with UL94 V0 rate.

Furthermore, some efforts to minimize the loading of phosphorous flame retardant **2**, while still meeting the UL94 V0 classification were made through the use of azoalkane synergist **3**. It was found that in order to keep UL94 V0 rate at least 1 wt.% of azoalkane **3** together with 17 wt.% of MPhP is acquired. Besides, in all cases where azoalkanes were used together with melamine phenyl phosphonate **2** the improved in UL94 rate from V2 to V0 was observed. Noteworthly, the disulfide synergists were unable to enhance UL94 V test classification.
Additionally, performed LOI investigations indicated that the phosphorous compounds increased the LOI numbers of polypropylene from 17 % up to 21.5 %. Higher LOI value of 21.5 % for additive **1** in comparison to 19.3 % for **2** is noted, what is in agreement with the proposed higher gas phase activity of compound **1**. It is also in accordance to the literature, where higher sensitivity to flame inhibition in LOI test was observed [214].

When azoalkane **3** was used together with melamine phenyl phosphonate **2**, the LOI value was increased by 2 units from 20.7 % (PP+2 (20 wt.%)) to 22.8 % for PP+2 (20 wt.%) + 3 (1 wt.%). In contrast, no significant increase in LOI or improvement of UL94 V classification could be recorded for P’P-diphenyl phosphinic hydrazide **1** and azoalkanes under the same experimental conditions.

Based on DIN 4102-1, UL94 V and LOI flame retardant tests it was concluded that both phosphorous compounds may be successfully utilized as halogen-free flame retardants in polypropylene. One of them, melamine phenyl phosphonate **2**, exhibited strong synergistic effect with azoalkanes such as azocyclohexane **3** and/or 4’4-bis (cyclohexylazocyclohexyl) methane **4**. Further work with these compounds is definitely needed to understand and optimize their performance.

7. Conclusions

The main objective of this work was to design and synthesize new and efficient halogen-free flame retardants for polypropylene and to better understand the interplay between flame retardant molecular structure and its efficacy as a flame retardant. With regard to flame retardant structures, the flame retardants were selected to contain molecules capable of generating free radicals during their thermal decomposition. A series of new radical generators based on azoalkanes, triazenes and disulfides was successfully prepared and its flame retardant efficacy was examined using standard fire tests. In the present work, we also report our successful experiments of preparing flame retarded LDPE-coated paper by extruding low density polyethylene containing azoalkanes as flame retardant additives onto a high-density paper surface. Furthermore, we wanted to explore the potential of new phosphorus-based flame retardants, as viable alternatives to halogen flame retardants, that could act in both the condensed phase by enhancing char formation and in the gas phase by flame inhibition through radical trapping. The prepared phosphorous compounds such as P’P-diphenylphosphinic acid hydrazide (PAH) and melamine phenyl phosphonate (MPhP) exhibited flame retardant activity alone and showed an especially strong synergistic effect with the other radical generators presented in this thesis work. Detailed achievements obtained in papers I-V are listed below in chronological order:

Paper I-

A number of symmetrical and unsymmetrical azoalkanes of the general formula R-N=N-R’ were prepared. The experimental results show that in the series of different-sized azocycloalkanes, the flame retardant efficacy in polypropylene films decreased in the following order: R = R’ = cyclohexyl > cyclopentyl > cyclobutyl > cyclooctanyl > cyclododecanyl. However, in the series of aliphatic azoalkanes compounds, the efficacy decreased in the following order: R = R’ = n-alkyl > tert-butyl > tert-octyl. Whereas, in general, the unsymmetrical azoalkanes were less effective than symmetrical azoalkanes used as flame retardants. Noteworthy is that a striking difference to other halogen-free radical generators such as Flamestab® NOR116 was that the azoalkanes exhibited also very high flame retardant efficacy in thick polypropylene plaques of 1 mm. In addition, selected azoalkanes additives showed less discoloration and even non-burning dripping behavior. Interestingly, it was found that azocyclohexane shows a strong synergistic effect with ATH.

Thus, in the presence of 0.5 wt.% of azoalkane **3** the ATH loading could be reduced from 60 wt.% to 25 wt.% and still UL94 V2 rate could be reached.

Paper II-

Halogen-free azocyclohexane flame retardant can improve the FR properties of LDPE coated paper already at low loading of 0.5 wt.% provided that the extrusion temperature do not exceed 260 °C and coating weight is kept low (12.9 g/m^2). At higher extrusion temperatures and coating weights, adhesion to paper is significantly enhanced but at the expense of flame retardancy. Moreover, the multilayer facings containing the Flamestab® NOR116, Luvogard MB81/PE or mixtures thereof, showed inferior flame retardant properties compared to azoalkane based facings. Under all of the used experimental conditions, the runnability on the pilot line was flawless for azoalkane formulations.

Paper III-

Various triazene-based ($R\text{-}N_1{=}N_2\text{-}N_3\text{-}R'R''$) flame retardants were prepared. For example, polypropylene samples containing a very low concentration of only 0.5 wt.% of bis-4’4-(3’3-dimethyltriazene) diphenyl ether **2** passed the test with B2 classification. It is noteworthy that no burning dripping could be detected and the average burning times were very short with exceptionally low weight losses. The high flame retardant potential of triazenes can be attributed to their ability to generate various types of radicals during their thermal decomposition. According to thermogravimetric analysis/Fourier transform infrared spectrometry/MS analysis, triazene units are homolytically cleaved into various aminyl, resonance-stabilized aryl radicals, and different CH fragments with simultaneous evolution of elemental nitrogen. For the first time it was demonstrated that triazenes constitute a new and effective family of FR additives.

Paper IV-

The potential of thirteen aliphatic, aromatic, thiuram and heterocyclic substituted organic disulfide derivatives of the general formula R-S-S-R’ as a new group of halogen-free flame retardants for polypropylene films were examined. The efficacy of the various disulfide compound families decreased in the following order: aromatic > heterocyclic substituted disulfides > heteroatom substituted disulfides > benzothiazole disulfides > aliphatic disulfides >> thiuram disulfides. Especially 5’5-dithiobis (2-nitrobenzoic acid) exhibited excellent FR properties and it outperformed all other compounds in this series, including the reference Flamestab® NOR116. Also, increased limiting oxygen index (LOI) values were recorded for the PP/disulfide formulations compared to neat polypropylene. The study has clearly demonstrated that thiyl radicals, generated from selected disulfides, have the ability to effectively interrupt the combustion process of polypropylene.

Paper V-

Two new, phosphorus-based FR additives were successfully synthesized: P’P-diphenyl phosphinic hydrazide (PAH) and melamine phenyl phosphonate (MPhP). Higher FR activity of PAH was shown according to DIN 4102-1 flammability test. Nevertheless, in UL94 vertical burning test (UL94 V) very strong synergistic effect of MPhP with azoalkanes was found and gave UL94 V0 rate in this test classification. It was concluded that both phosphorous-based compounds have very good FR activity although operate by different FR mechanisms.

Different halogen-free flame retardants based on radical generators such azoalkanes, triazenes, disulfides and phosphorus-based additives (P’P-diphenyl phosphinic hydrazide, melamine phenyl phopshonate) have been developed and their versatility and usefulness as flame retardants for polypropylene (or polyethylene) has been demonstrated. Besides providing self-extinguishing properties already at low concentrations alone, many of them also provide valuable synergistic abilities with conventional flame retardants. Thus, the developed new “green” flame retardants show considerable promise and they have already awoken some interest from both academia and industry.

8. Remarks and future directions

The burning characteristics of various plastic materials are polymer specific and still not fully understood due to the complexity of the physicochemical properties of polymers that all have an influence on their burning behavior. It is important to realize that the actual fire behavior cannot be simply computed from knowing some basic chemical properties of the polymer. Equally complex methods are needed to prevent and/or retard burning of polymers and thereby making the development of more efficient FRs very challenging. In general, flame retardants work by interrupting the combustion process at one or more of its complex stages chemically or physically by inhibiting ignition, reducing burning rate and/or changing the mechanism of combustion. Nowadays, viable FR alternatives should, besides controlling the flame, also not produce any toxic, dense or noxious smoke or fumes and have no negative life-cycle impacts associated with their production, use, recycling or disposal. Thus, future viable halogen-free FR candidates need to combine high fire safety benefits with minimal adverse impact on human health and environment. Despite that nitrogen, sulfur or phosphorous compounds have been globally widely investigated (not only for FR applications) still in each group there may be plenty of effective molecules to be discovered as new, green FR families. Therefore, continued research efforts and refining of FR structures are definitely warranted. Future research related to performed work calls for:

- Verification and assessment of the nontoxicity of new FR compounds and their decomposition products (performing epidemiological and environmental studies).
- Preparation of larger quantities of best performing additives and their extensive testing in a variety of polymers and applications. In addition, further studies are needed to assess their synergistic effect with conventional FR additives (e.g. nanocomposites).
- Perform single burning item (SBI) tests in order to obtain more fire characteristics and to evaluate the polymer products behavior more closely in real fire situations.
- Perform detailed investigations of decomposition pathways and interactions occurring during pyrolysis of polymers. Identification of intermediate products, monitoring their concentrations and their mechanisms of action during polymer combustion.
- Study of structure and reactivity at the molecular level of these types of flame retardant molecules by computer-aided molecular design.

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