Phosphorus fire retardants for polystyrene

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Polystyrene, despite its high flammability, is widely used as a thermal insulation material for buildings, for food packaging, in electrical and automotive industries, etc. A number of modification routes have been explored to improve the fire retardance and boost the thermal stability of commercially important styrene-based polymeric products. The earlier strategies mostly involved the use of halogenated fire retardants. Nowadays, these compounds are considered to be persistent pollutants that are hazardous to public and environmental health. Many well-known halogen-based fire retardants, regardless of their chemical structures and modes of action, have been withdrawn from built environments in the European Union, USA, and Canada. This had triggered a growing research interest in, and an industrial demand for, halogen-free alternatives, which not only will reduce the flammability but also address toxicity and bioaccumulation issues. Among the possible options, phosphorus-containing compounds have received greater attention due to their excellent fire-retarding efficiencies and environmentally friendly attributes. Numerous reports were also published on reactive and additive modifications of polystyrene in different forms, particularly in the last decade; hence, the current article aims to provide a critical review of these publications. The authors mainly intend to focus on the chemistries of phosphorous compounds, with the P atom being in different chemical environments, used either as reactive, or additive, fire retardants in styrene-based materials. The chemical pathways and possible mechanisms behind the fire retardance are discussed in this review.

styrenic polymers phosphorus containing fire retardants fire retardance thermal stability

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Polystyrene, despite its high flammability, is widely used as a thermal insulation material for buildings, for food packaging, in electrical and automotive industries, etc. A number of modification routes have been explored to improve the fire retardance and boost the thermal stability of commercially important styrene-based polymeric products. The earlier strategies mostly involved the use of halogenated fire retardants. Nowadays, these compounds are considered to be persistent pollutants that are hazardous to public and environmental health. Many well-known halogen-based fire retardants, regardless of their chemical structures and modes of action, have been withdrawn from built environments in the European Union, USA, and Canada. This had triggered a growing research interest in, and an industrial demand for, halogen-free alternatives, which not only will reduce the flammability but also address toxicity and bioaccumulation issues. Among the possible options, phosphorus-containing compounds have received greater attention due to their excellent fire-retarding efficiencies and environmentally friendly attributes. Numerous reports were also published on reactive and additive modifications of polystyrene in different forms, particularly in the last decade.

1. Introduction

Whilst many synthetic commodity plastics have excellent properties, such as light weight, good weatherability, and can be easily manufactured and/or processed into a variety of products with a range of useful applications, they also possess some obvious disadvantages [1][2][3][4]. One of them is high flammability, which often restricts their wider applicability, especially as the building materials, or as the components used in the transport sector [5]. Some chain-growth polymers can be easily ignited, leading to a fast and uncontrolled fire spread. Therefore, it is essential to improve the fire-retardant properties of these materials to warrant their safer and wider use in the construction and transport industries. This is often achieved by treating a polymeric material through a suitable methodology, where an appropriate combustion inhibitory reagent, a fire retardant (FR), is incorporated into the final product. A large number of FRs have been used for many years to protect polymers from the hazards of fire [6][7][8]. These compounds can be incorporated by physical means in the form of additives to the polymer matrix. Another way of improving fire retardance is to prepare the inherently less flammable polymers through *co-* or *ter-* polymerisations of relevant monomers with unsaturated compounds that can impart fire resistance [9].

Polystyrene (PS) is a well-known thermoplastic polymer that is used worldwide for various applications owing to its low costs, ease of processing, excellent chemical resistance, low density, electrical/thermal insulation, etc. [10]. The styrenic polymers fall into different sub-classes [10][11][12][13][14]. Firstly, it is a homopolymer of styrene, which is also known as a general purpose polystyrene (GPPS) [7]. Secondly, the styrene monomer can be polymerised with other monomers to produce *co-* and/or *ter-* polymers, often having improved mechanical properties (Figure 1). The examples from this sub-class include styrene-acrylonitrile (SAN), acrylonitrile–butadiene-styrene (ABS), styrene–butadiene rubber (SBR), etc.

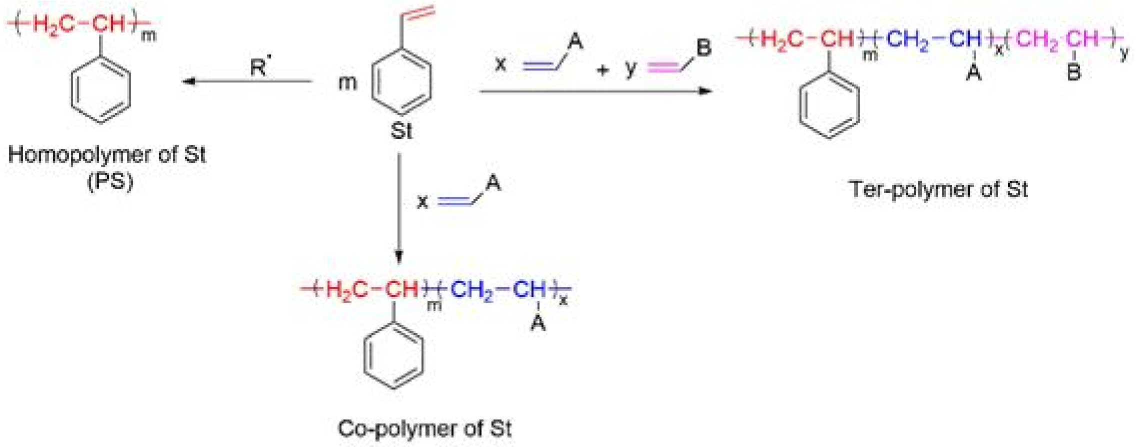

Figure 1. A general scheme of *homo*-, *co-,* and *ter-* polymerisation of styrene (R: is an initiator).

Furthermore, there are two types of polystyrene foams that are available commercially: expanded polystyrene (EPS) and extruded polystyrene (XPS) [8–10,14]. The EPS is a rigid closed-cell foam used for food packaging and thermal insulation [11][14]. The building sector also utilises the XPS, which is a closed-cell foam with higher density, better surface toughness, lower thermal conductivity, and higher stiffness compared to the EPS. The XPS foam is more suitable for weather exposure owing to its better water diffusion resistance compared to the EPS. The EPS is typically manufactured from polystyrene beads with the aid of a blowing agent such as steam, or a low boiling point aliphatic hydrocarbon, e.g., *n*-pentane or *iso*-pentane. The grain-shaped beads are expanded up to 50 times of their original size to produce a rigid foam [14]. Meanwhile, the XPS is prepared through the expansion of a melt, containing a blowing agent and other additives including fire retardants (FRs), to improve the characteristics of the foam . High-impact polystyrene (HIPS) has gained great industrial attention because of its good impact strength, high rigidity, and heat distortion resistance . The HIPS, representing a two-phase system with rubber dispersed in a continuous PS matrix, is prepared by the polymerisation of styrene in the presence of rubber latex materials.

As mentioned earlier, even though styrene-based materials are used in various fields such as thermal insulation for buildings, in electrical and automotive industries, the high flammability of styrenic polymers limits their wider uses. When these polymers are exposed to an external heat source, they depolymerise easily with the release of numerous volatile products such as styrene monomers, dimers, trimers, and other hydrocarbons [14]. In addition, the styrenic polymers burn very rapidly, generating a significant amount of smoke [14]. Furthermore, they have a tendency to undergo a combustion process associated with a low char production, frequently resulting in the melt flow and melt dripping phenomena [14]. The various styrene-based products have to meet a set of stringent fire safety requirements prior to the use within buildings, and, thus, it became necessary to develop the efficient fire-retardant systems for their fire protection.

Over the last 40 years, a wide range of halogenated products were developed and successfully used for different forms of polystyrene. The high effectiveness of halogenated FRs, especially those containing bromine (Br) and chlorine (Cl), and their relatively low costs, made these materials very attractive fire-protective solutions [14][15]. These FRs dominated the polymer industry in the past, but recently, their application became closely monitored, and it is regulated in many countries due to their toxicity, persistence, and bioaccumulation issues. For instance, the study conducted by Wemken et al. (2020) discovered the presence of different brominated FRs in the breast milk of first-time mothers living in Ireland [16][17][18]. Another work reported the high levels of brominated compounds found in the urban soils from the city of Melbourne, Australia [19]. Moreover, halogenated FRs can cause severe health and environmental problems owing to the release of dioxins and furans in the post-fire situations. As a result, in recent years, the wider use of halogen-based FRs has been very severely criticized, and several formulations were banned completely in the European Union (EU), USA, and Canada [20]. Meanwhile, a positive response to the regulatory rules applied to this class of FRs is evident. For example, the ban on the use of hexabromocyclododecane (HBCD) and penta-bromodiphenyl ether (BDE) resulted in the lower concentrations of these compounds detected in the breast milk .

In the last decade, numerous attempts have been made to develop the environmentally benign fire-retardant formulations suitable for polymeric products [17][18][21][22]. Among the proposed FR solutions, the compounds containing phosphorus (P) atom(s) are considered to be less toxic than the corresponding halogen-containing formulations . Despite a wealth of P-containing formulations being developed to reduce the flammability of the chain-growth polymers, it remains challenging to design non-toxic, environmentally friendly yet efficient FRs for PS. The majority of the proposed halogen-free alternatives work, predominantly, in the condensed phase, which is a less useful mode of fire retardance for the polymers with a poor ability to generate char. Nevertheless, the P-bearing FRs can be very powerful in controlling combustion phenomena, at least the processes arising from the vapour phase inhibitory action [17][18]. A comprehensive review of FRs for styrenic polymers was carried out by Weil and Levchik more than 10 years ago, and it was largely dedicated to the halogenated options. The current review focusses on the phosphorus-containing FRs, used either as the additive or reactive modifications, for styrene-based materials. The different classes of phosphorous FRs and their chemical interactions with PS chains are critically analysed. The mechanisms behind the fire retardance are also discussed in detail in this paper, when/if the relevant publications report on this aspect.

2. Combustion and Fire Retardance of Polymeric Materials: General Considerations

Generally, polymer combustion processes can occur in the condensed phase, in the gaseous phase, and at the interphase [2] according to the combustion cycle shown in Figure 2. During the exposure to an external heat flux, a polymer can pyrolyse, generating the increased volumes of flammable volatiles released to the gaseous phase. Then, these volatile products mix with the atmospheric oxygen, forming a fuel source that is consequently ignited, leading to a flaming combustion. The heat generated during this process is fed back to the condensed phase of the polymer system, thus sustaining the burning process. Moreover, a tendency of the polymeric materials to melt and flow, forming a pool of flammable degradation products, can constitute a very serious secondary fire hazard, as it often can result in further ignition or the burning of surrounding fuel loads [23].

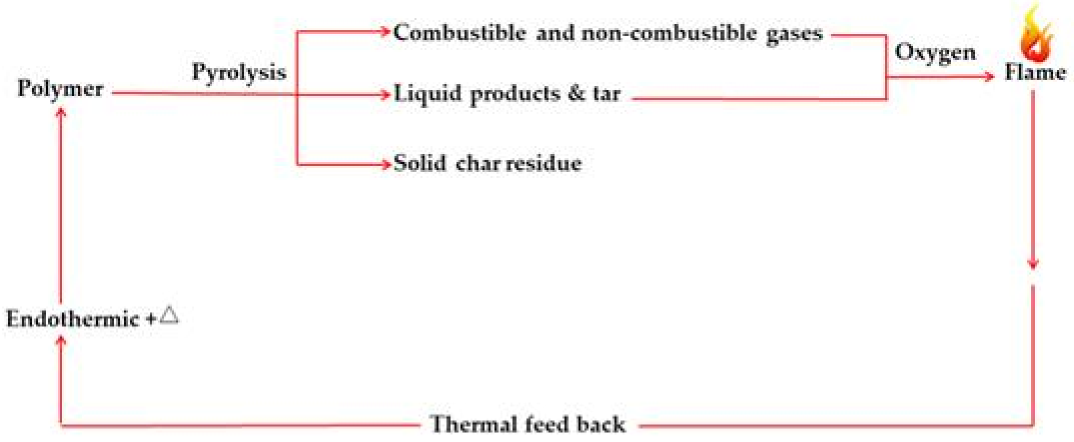

Figure 2. A diagram representation of a polymer combustion cycle.

The commercial polymers exhibit a wide range of propensities to ignite. Generally, they require a temperature range of around 270–470 °C to undergo the ignition [24]. However, the EPS or XPS are highly ignitable even in the presence of low-intensity sources for piloted ignition, and they can initially go through a smouldering phase of combustion. The main reason behind this is a relatively high ignitability/flammability attributed to their porous structure[25][26][27][28][29].

The thermal decomposition pathways of the individual polymers are largely governed by their chemical structures . Typical degradation patterns involve hydrogen transfer to α- or β-carbon atoms, oxygen or nitrogen atoms; cyclisation; side-chain reactions; molecular rearrangements; unzipping to a monomer; and the elimination of small molecules such as carbon dioxide, sulphur dioxide, or hydrogen sulphide [29][30]. Aromatic backbone-containing polymers may involve cross-linking and side-chain reactions leading to carbonaceous char residues [30]. In addition, the heat transfer to the condensed phase and the rate, at which the thermal energy is stored, are the important factors as they determine the time to ignition and the combustion rates of polymers [30]. Furthermore, the burning of solid polymer fuels generally depends on other environmental parameters such as pressure, temperature, an extent of oxygen ingression, as well as on the innate material properties associated with molecular, thermo-physical, thermo-chemical, and degradation characteristics.

The introduction of a FR into a polymer system can hinder certain stages of combustion, either in the condensed phase or in the gaseous phase (Figure 3).

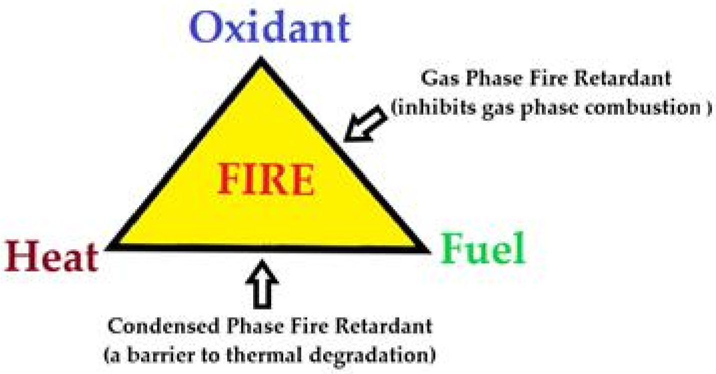

Figure 3. A diagram representation of fire-retardant (FR) actions interrupting a polymer combustion cycle.

In the condensed phase mechanism, the FR compound usually assists the formation of a carbonaceous char and/or an in situ production of water, while undergoing thermal decomposition. The char residue often generates a thick coating layer on a polymer surface, which prevents the release of flammable volatiles into the gaseous phase, thus obstructing this pyrolysis pathway. The intumescent coatings work by this principle as well [31][32]. It also helps protecting the underlying polymeric substrate from further thermal damages [33][34][35].

It is known that the combustion of a gaseous fuel mixture is facilitated by certain free radicals [33]. Most burning polymers generate free radicals, which then combine with the atmospheric oxygen [34][35]. Generally, $H^{\bullet}$ and $HO^{\bullet}$-centred radicals are the predominant intermediates that are responsible for the chain propagation reactions [33]. The $HO^{\bullet}$ species are also responsible for the secondary oxidation of carbon monoxide CO to carbon dioxide CO_2 [34]. In most cases, the free radicals, formed by the burning polymer and released to the gaseous phase, are scavenged by the FRs, or by their degradation fragments, subsequently converting them into more stable species [34][35]. In turn, this interrupts the exothermic processes, leading to a less efficient combustion and a fire suppression. Most of the halogen-based flame retardants follow this mechanism of fire retardance .

The FRs can interact with the polymers physically and/or chemically depending on their inherent nature and the associated properties [34][35]. The predominant physical mechanisms include the following:

- A formation of a protective coating. This involves the formation of a carbonaceous char upon combustion, which then acts as a physical barrier between the polymeric substrate and the surrounding atmosphere. This limits the fuel supply to the system, thus hindering the combustion process. Such coatings also help to prevent the release of flammable volatiles/gases into the atmosphere.
- Cooling. During combustion, this type of FR activates certain endothermic reactions, which absorb the surrounding heat, thereby cooling the system below the temperature that is required to sustain the combustion process.
- Dilution. Flame spread can be hindered by adding certain inert additives, or fillers, to the polymer system. During flaming combustion, these additives liberate inert gases, which then dilute the system, making it less favourable for further burning in the gaseous phase.

Some FRs also control and limit the unwanted phenomena of melt-flowing and the melt-dripping in the polymeric systems [23,34].

3. Thermal Decomposition and Flammability of Styrenic Polymers

When ignited, PS and its copolymers can burn very fast with a visible flame, releasing volatiles into the environment including styrene monomer and the associated oligomers, benzene and lower alkylbenzenes, etc. [36][37][38]. During the burning process, PS can also melt flow and drip, which can lead to an increased fuel load, feeding into the enhanced flame spread [37]. Generally, styrenic polymers generate the minimal amounts of char residues, especially in oxygen-enriched atmospheres.

Generally, the styrene homopolymer starts decomposing at a temperature of around 270 °C and continues degrading until 425 °C under the normal conditions in the air [39]. Through the random main-chain cleavages and associated mechanisms, PS may form the varying amounts of styrene, benzaldehyde, styrene oxide, acetophenone, α-methyl styrene, and l-phenylethanol (Figure 4) [39][40]. Styrene and benzaldehyde are found to be the prominent fractions among all the degradation products [41][42].

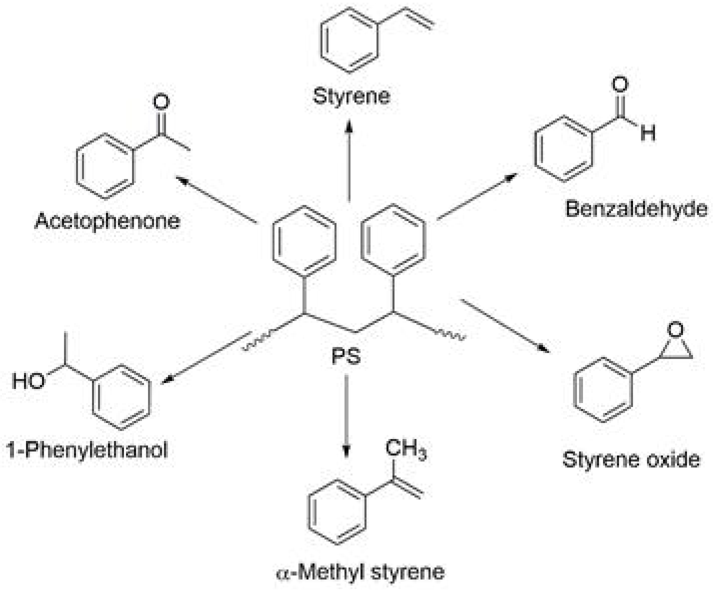

Figure 4. Thermal degradation products generated by burning polystyrene (PS) [38][39][40][41][42].

Similar to the majority of main-chain carbon polymers, the thermal degradation of PS generally occurs in three steps: initiation, propagation, and termination, which follows a free-radical chain mechanism [42].

- Initiation

The degradation of PS can take place via two routes, either through a random chain scission, or by a chain-end scission (Figure 5). In the case of the random chain scission, two radicals are formed, a primary radical (R_p) and a secondary benzyl radical (R_{sb}) with a strong benzylic resonance. In the chain-end scission mechanism, one secondary benzyl radical (R_{sb}) and the resonantly stabilised allyl benzene radical (R_a) are formed, as shown in Figure 5.

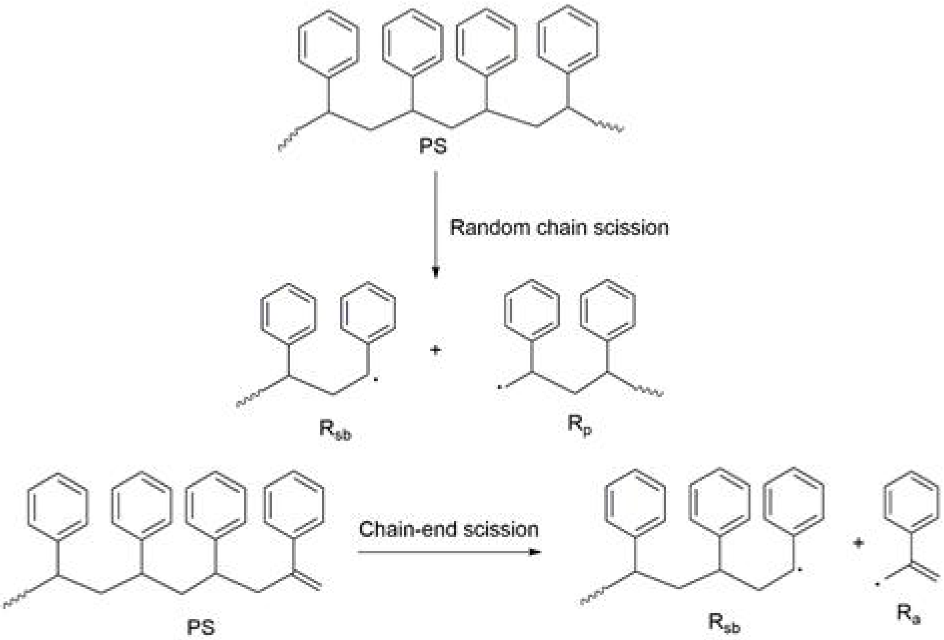

Figure 5. A schematic representation of initiation during the thermal decomposition of PS [42].

- Propagation

The generated free radicals are propagated through hydrogen abstraction and unzipping reactions. There are two types of hydrogen abstraction reactions: intermolecular and intramolecular abstractions.

- Termination

Termination can occur either by recombination or by the disproportionation mechanisms of various active radical fragments.

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