REVIEW

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Recent advances in fire-retardant carbon-based polymeric nanocomposites through fighting free radicals

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Abstract

Polymeric materials are ubiquitously utilized in modern society and continuously improve quality of life. Unfortunately, most of them suffer from intrinsic flammability, significantly limiting their practical applications. Fundamentally, free-radical reaction is a critical "trigger" for their thermal pyrolysis and following combustion process regardless of the anaerobic thermal pyrolysis in the condensed phase or aerobic combustion of polymers in the gaseous phase. The addition of free radical scavengers represents a promising and effective means to enhance the fire safety of polymeric materials. This review aims to offer a state-of-the-art overview on the creation of fire-retardant polymeric nanocomposites by adding fire retardants with an ability to trap free radicals. Their specific modes of action (condensed-phase action, gaseous-phase action, and dual-phases action) and performances in some typical polymers are reviewed and discussed in detail. Following this, some key challenges associated with these free-radical capturers are discussed, and design strategies are also proposed. This review provides some insights into the modes of action of free radical capturing agents and paves the avenue for the design of advanced fire-retardant polymeric nanocomposites for expanded real-world applications in industries.

KEYWORDS
fire retardants, free radical capturers, polymer nanocomposites, thermal stability

1 | INTRODUCTION

Nowadays, polymeric materials are proliferating in modern society and continuing to improve quality of life. Unfortunately, the majority of them suffer from intrinsic extreme flammability, significantly limiting their practical applications. The statistics has shown that ca. 4 million fires per year across the world caused by polymers directly or indirectly, causing enormous loss of life and property (www.firechina.cn). As typical examples, the tragic London Grenfell Tower catastrophe in 2017 and the Paris Notre-Dame Cathedral fire in 2019 have strongly highlighted the importance of creating fire-safe polymeric materials.

Fire-retardant polymeric nanocomposite has recently become an important branch of polymer nanocomposites. The concept of nanocomposites to capture free-radicals in the flame retardant field was first posited by Wilkie as far back as 2001.[1] Thereafter, the polystyrene/graphite[2] and nylon-6/nano-clay[3] composites were developed as a kind of fire-retardant polymer nanocomposites. Since then, fire-retardant polymeric nanocomposites have been developed rapidly and become a "hot spot" in the international fire-retardancy community.[4–7] Up to date, the discovery and construction of nanomaterials affords many new opportunities and applications for fire retardant community. Compared with the traditional flame retardants, such as halogen-, phosphorous-, organic-, and intumescent-flame retardants, polymer nanocomposites have shown dramatic improvements in the mechanical, thermal, electrical, energy storage, and barrier performances at a relative low loading level of micron/nano-scale additives.[8]

Based on currently acceptable combustion theories,[9] the free radical chain reactions are an essential factor for initialing a pyrolysis and sustaining a fire. The highly active free radicals are easily to overflow out of the polymeric matrix. Therefore, the conventional flame retardants (e.g., halogenated compounds and hindered amines/phenols) improve flame retardancy of polymers mainly by inhibiting free radical chain reactions in the gaseous phase during burning.[10] Although the high efficiency of this action mode, it often leads to incomplete combustion, thus increasing the production of unwanted corrosive gases and even toxic smoke. The fire-retardancy academia has gradually realized that this issue can be avoided by moving this action from the gas phase to the condensed phase, because the radical scavengers are starving the flame zone of combustion, reducing the amount of heat available to further degrade the polymer.[10,11] This has stimulated the development of a series of pristine or modified carbon-based and metal-derived nanomaterials as flame retardants,[13–15] all of which can enhance the flame retardancy of polymers by scavenging free radicals mainly in the condensed phase and generating less smoke and gases. However, to date there remains an urgent lack of pivotal and insightful review on the design and performances of flame retardant polymeric nanocomposites based on free radical fighting agents.

For this reason, this work aims to review recent advances in the creation of flame-retardant polymeric nanocomposites by adding flame retardants with the ability to fight free radicals. Their modes of action (gaseous-phase action, condensed-phase action, and dual-phase action) and performances in some typical polymers will be discussed. Following this, key challenges will be summarized, and corresponding design strategies are proposed. This review will significantly advance a fundamental understanding and the use the free-radical-trapping strategy for the design of advanced fire-retardant polymeric nanocomposites, and greatly interest the international fire-retardancy community by creating a fire-safe society.

2 | PYROLYSIS AND COMBUSTION OF POLYMERIC MATERIALS

2.1 | Pyrolysis of polymeric materials

Upon exposure to an external heat source, the combustion of polymers usually starts from thermal pyrolysis. Generally, the thermal decomposition of polymers that are synthesized via free radical polymerization (e.g., polypropylene [PP], PE, poly-methyl methacrylate [PMMA], PS, and PVC) is dominated by a random free radical chain scission mechanism.[16] In comparison, the pyrolysis of polymers via condensation polymerization (e.g., PC, polyamides, polyesters, and thermosetting resins) is often through the rearrangement or branching reactions. Noted that a slight chain scission reaction initiated by highly active free radicals can still significantly accelerate the pyrolysis of the polymer. Thus, for almost all polymers, reactive free radicals play a crucial role in the entire pyrolysis process. In addition, the presence of oxygen often further accelerates random or end-chain scission (dehydrogenation, hydrogen transfer, etc.).

The thermal oxidative degradation of polymers generally proceeds according to free radical chain reactions (Figure 1), mainly including three-stage elementary reactions[17]: chain initiation, chain propagation and chain termination. With the inducing effect of oxygen, highly active hydrogen radicals ($\cdot$H) and hydroxyl radicals ($\cdot$OH) and accompanying hydrocarbon-oxygen free radicals are the root cause of polymer decomposition. Hence, the pyrolysis of polymers can be disturbed and retarded by capturing or eliminating these free radicals from the degradation process. These series pyrolysis reactions are
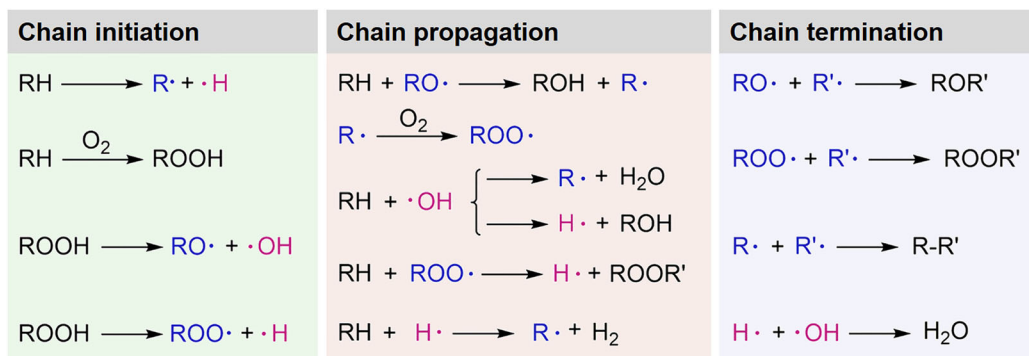
Chain initiation	Chain propagation	Chain termination
RH ⟶ R· + ·H	RH + RO· ⟶ ROH + R·	RO· + R'· ⟶ ROR'
RH $\xrightarrow{O_2}$ ROOH	R· $\xrightarrow{O_2}$ ROO·	ROO· + R'· ⟶ ROOR'
ROOH ⟶ RO· + ·OH	RH + ·OH $\begin{cases} \longrightarrow R· + H_2O \\ \longrightarrow H· + ROH \end{cases}$	R· + R'· ⟶ R-R'
ROOH ⟶ ROO· + ·H	RH + ROO· ⟶ H· + ROOR'	H· + ·OH ⟶ H₂O
	RH + H· ⟶ R· + H₂	

FIGURE 1 Random or end-chain scission reactions of polymeric materials caused by highly active free radicals in oxidative atmosphere
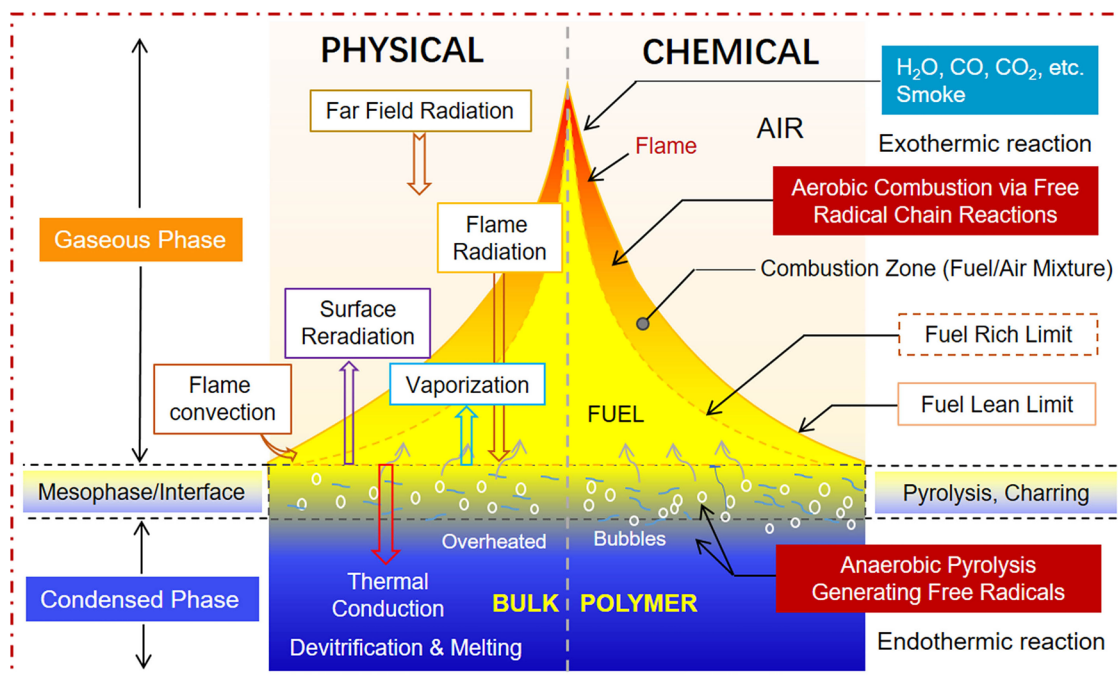

FIGURE 2 Illustration of the typical combustion process and burning partition of polymeric materials

mainly occurred in the gaseous phase where oxygen is sufficient. If the anaerobic thermal pyrolysis of polymers is confined to the condensed phase or mesophase, the free radical reactions can be suppressed effectively, because the chain initiation and chain propagation reactions caused by oxygen can weaken this reaction compared with aerobic pyrolysis.

2.2 | Combustion of polymeric materials

The combustion of polymeric materials is a very complicated process comprising many physical and chemical reactions (Figure 2).[9] Generally, four essential elements, namely heat, fuel, oxygen, and free radical chain reac-

tions are required for sustaining a fire. Reactive free radicals play a vital part in the entire combustion process.[8] In general, the combustion process can be divided into five stages: thermal pyrolysis, ignition, flame propagation and spread, completed combustion, and flame attenuation. While the burning zone in polymeric materials can be divided as the intact bulk zone, melted pyrolysis layer, gaseous degradation layer, flame layer, and oxidation product layer.

Overall, the intact bulk zone and melted pyrolysis layer belong to the condensed phase, while gaseous degradation layer, flame layer and oxidation product layer belong to the gaseous phase, and the interface between them is considered as the mesophase. Because of the heat source, the polymeric matrix generates pyrolysis volatiles through

the foregoing random or end-chain scission free radical reactions. Then, these volatile fragments and highly active free radicals diffuse into hot air (heat and oxygen) to generate fuel mixtures for sustaining the spark or flame. Meanwhile, a large amount of heat generated by the combustion of polymers can also be radiated back to the intact bulk zone and intensify the combustion. Essentially, it is crucial to interfere the generation or action mode of •H and •OH in the combustion process.

3 | MODES OF ACTION FOR FREE RADICAL CAPTURERS

3.1 | Gaseous-phase action

The gaseous-phase action of free radical capturers refers to the substances that scavenge highly active free radicals (H•, HO•, ROO•, etc.) in flames and volatile degradation products, thereby interrupting or interfering the combustion. These capturers mainly include volatile phosphorous- and halogen-containing compounds (i.e., Sb_2O_3-Br system), etc. The low-activity free radicals (Cl•, Br•, PO•, HPO•, etc.) created by their pyrolysis collide with highly active free radicals to generate more sSupplementary Table Species, and a large amount of nonflammable gas, which can dilute the fuel concentration in the gaseous-phase. However, most of the low-reactivity free radicals, stable compounds, and inert gases still exist or suspend in the surrounding gaseous phase but cannot suppress the emission of toxic smokes during combustion.

3.2 | Condensed-phase action

The condensed-phase action of free radical captures stands for those compounds that can trap macromolecular free radicals generated by polymer decomposition at the initial stage of combustion in the melted pyrolysis layer and mesophase.[18] Almost no macromolecular free radicals diffuse into the gaseous phase. It mainly contains some carbon nanomaterials (e.g., fullerenes, graphene oxide, carbon nanotubes [CNTs], carbon black etc.), rare earth compounds, etc. In the condensed-phase, these free radical capturers can inhibit the initial thermal-oxidative degradation and increase the initial degradation temperature of the polymer. This action mode can prevent the volatilization of highly reactive free radicals into the gaseous phase to varying degrees, but some of them are still be released in the later stage of violent combustion. Therefore, some free radical capturers with lamellar morphologies,[19] porosity,[20] and/or catalytic charring capacity[21] have been successfully developed to move the free-radical trapping mechanism from the gaseous to the condensed phase.

3.3 | Determination of free radicals

To date many direct and indirect methods have been developed to detect free radicals in many fields, such as agriculture, biomedicine, organic chemistry, etc.[22] The tools that are applicable to the flame retardancy include electron spin/paramagnetic resonance (ESR or EPR), fluorescence spectrophotometry, high performance liquid chromatography (HPLC) and chemiluminescence (CL). Among them, ESR/EPR and fluorescence spectroscopy are the two most used techniques.[23,24]

The principle of ESR[25] is to use a diamagnetic spin trapping agent to react with unstable free radicals to generate a Supplementary Table Spin-adduct that can be detected by the ESR. Hence, the ESR constant of spin-adducts can be used to study the hyperfine structure of free radicals. The free radical capturing capacity can be quantitatively characterized by monitoring the intensity of ESR signals for spin-adducts. There are some commonly used spin-trapping agents, including 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), 2,2-Diphenyl-1-picrylhydrazyl (DPPH), 3,3,5,5-tetramethyl-1-pyrroline-N-oxide (TEMPO), and 2-carbethoxy-2-methyl-1-pyrroline-N-oxide (EMPO). For instance, the ESR method has been successfully employed to unveil the correlation between the antioxidant performance and free-radical trapping mechanism of CNTs to PE; the antioxidant capacity of the three kinds of CNTs (carbon nanotubes) is MWCNTs-OH > MWCNTs > SWCNTs (Figure 3A).[23]

In comparison, fluorescence spectrophotometry is another powerful tool to stabilize free radicals with a trapping agent.[26] After the capturing process is completed, the concentration of free radicals can be quantitatively computed by calculating the variation value of fluorescence absorbance, and one of the extensively used in fire-retardant field is ultraviolet-visible spectroscopy (UV-Vis). As provided the UV-Vis spectra in Figure 3B,[24] the stronger of the free radical trapping effect, the more significant reduction in the heat release rate of the EP (epoxy resin) nanocomposites in the cone calorimetry testing.

HPLC is a common approach that is mainly used to determine hydroxyl radicals (HO•).[27] Because of a high separation efficiency, HPLC is often combined with various monitoring methods, such as ultraviolet detection, electrochemical detection, and mass spectrometry (MS), and this combined tool can detect a trace of free radicals in a complex system. Meanwhile, CL is another sensitive technique for free radicals detection.[28] During testing, a luminescent reagent is normally used to directly emit light after reacting with free radicals, which allows the calculation of the number of free radicals according to the fluorescence intensity variation. For this reason, the CL
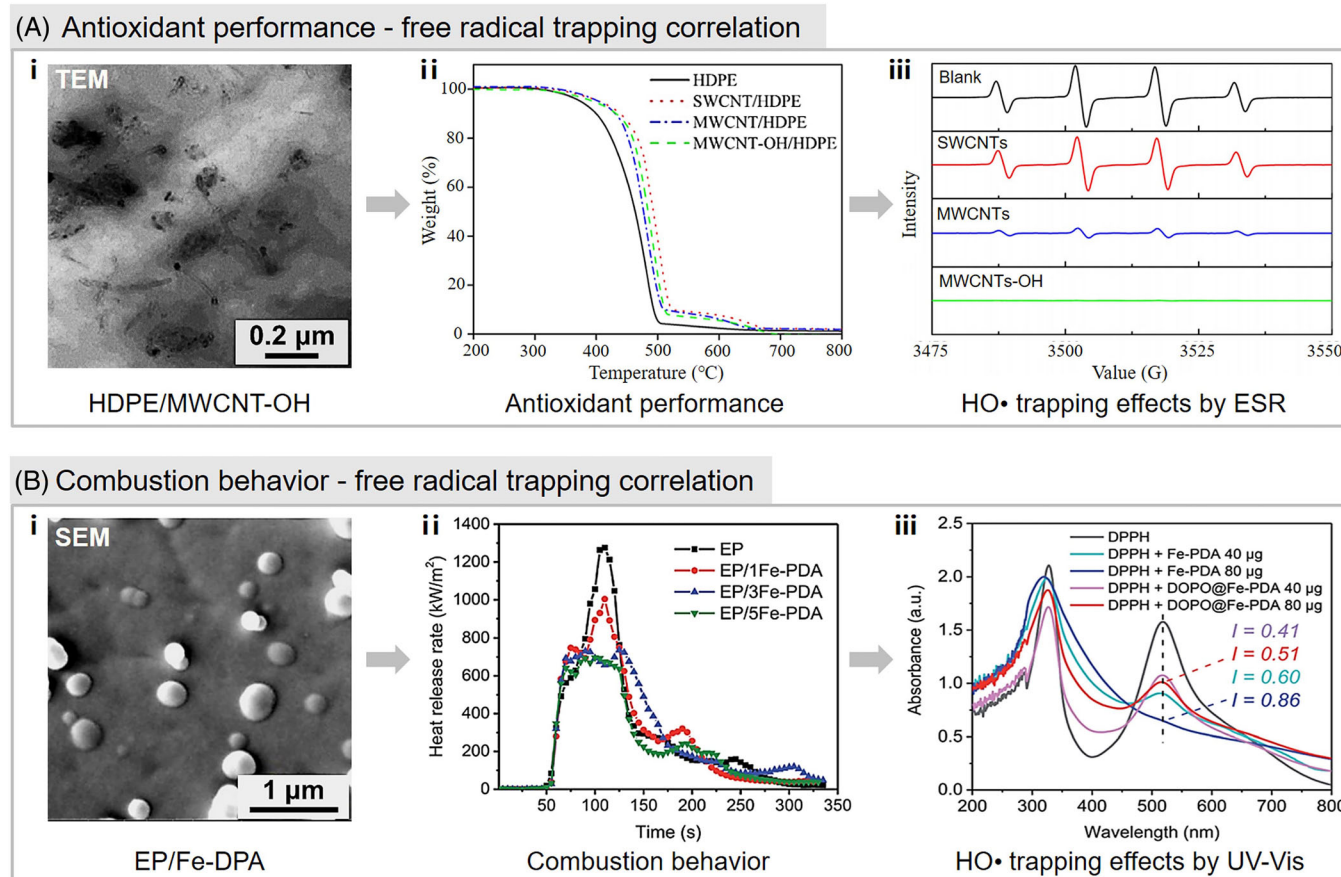
FIGURE 3 Typical free-radical trapping mechanism related to the (A) antioxidant and (B) flame retardant performance of polymeric nanocomposites: (A–i) TEM (transmission electron microscopy) image of high-density polyethylene (HDPE)/MWCNT-OH nanocomposite, (A-i) TGA (thermogravimetric analysis) curves of HDPE nanocomposites under air, (A-ii) generation of hydroxyl radicals by the Fenton reaction in the presence of SWCNTs (single-walled carbon nanotubes), MWCNTs (multi-walled carbon nanotubes), and MWCNTs-OH. Reproduced with permission.[24] Copyright 2012, Elsevier. (B-i) SEM (scanning electron microscopy) image of EP/Fe-PDA (PDA refers to polydopamine) nanocomposite, (B-ii) HRR (heat release rate) curves of EP nanocomposites in cone calorimetry, (B-iii) ultraviolet-visible spectroscopy (UV-Vis) spectral change upon addition of Fe-PDA and DOPO@Fe-PDA. Reproduced with permission.[24] Copyright 2020, The Royal Society of Chemistry

method is widely used to assess the antioxidant capacity of free radical capturers and even the polymeric composites. For instance, Geschwindner et al.[29] has successfully monitored the free radical trapping effect of flame retardants (FRs) during the thermal degradation of polypropylene (PP) using high-speed planar laser-induced fluorescence technology.

In addition to characterizing free radicals, there are some methods for evaluating the thermal and flame retardancy of polymeric materials, such as thermogravimetric analysis and its combination with infrared (TG) or MS (TG-MS),[30] pyrolysis-gas chromatography/mass spectroscopy (py-GC/MS),[31] UL-94 testing,[32] limiting oxygen index (LOI) testing,[33] cone calorimetric testing,[34] and some larger scale combustion testing.[9,35]

4 | FIRE-RETARDANT POLYMERIC NANOCOMPOSITES THROUGH FIGHTING FREE RADICALS

According to modes of action of free radical capturers, fire-retardant polymeric nanocomposites can be categorized into fighting free radicals in the condensed-phase, gas-phase, and dual-phase in which they play a dominant role. The concept of nanocomposites to capture free-radicals in a fire was first posited by Wilkie as far back as 2001. Thereafter, researchers have started to create fire-retardant polymer materials by developing free radical trappers that function mainly in the condensed phase, with some landmark points shown in Figure 4.
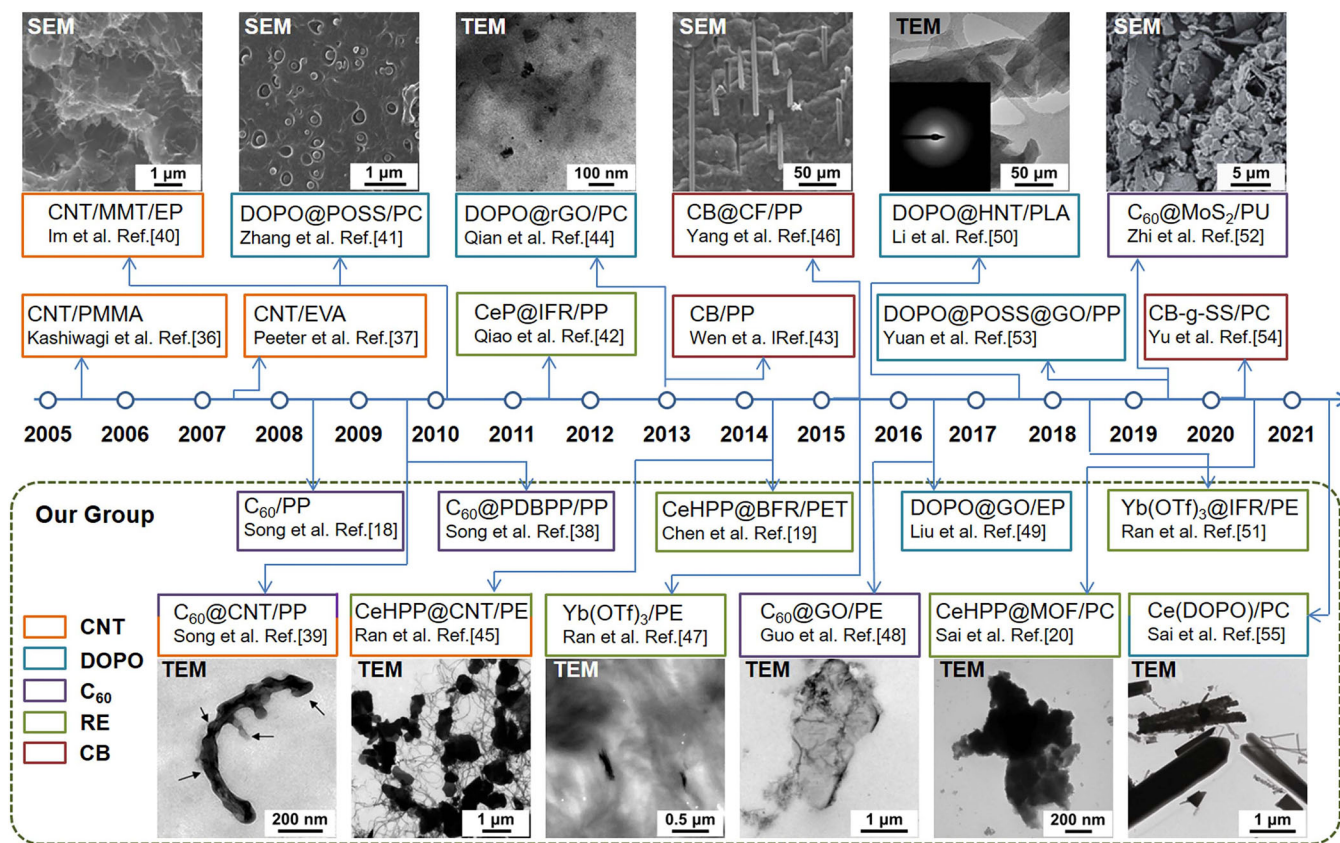
FIGURE 4 Roadmap for in the fire-retardant polymeric nanocomposites enabled by the free-radical fighters acted mainly in condensed-phase.[18–20,36–55] Reproduced with permission.[20] Copyright 2020, Elsevier. Reproduced with permission.[39] Copyright 2009, The Royal Society of Chemistry. Reproduced with permission.[40,41] Copyright 2010, Elsevier. Reproduced with permission.[42] Copyright 2013, The Royal Society of Chemistry. Reproduced with permission.[45] Copyright 2014, The Royal Society of Chemistry. Reproduced with permission.[46,47] Copyright 2015, Elsevier. Reproduced with permission.[48] Copyright 2016, Elsevier. Reproduced with permission.[50] Copyright 2017, Elsevier. Reproduced with permission.[52] Copyright 2019, IOP Publishing. Reproduced with permission.[55] Copyright 2021, Elsevier

## 4.1 | Fighting free radicals in the condensed phase

Over the past 15 years, the fire-retardant researchers have published a series of free radical trapping studies based on C_{60} and rare earth compounds. Condensed-phase free radical capturers mainly include four kinds of carbon-based nanomaterials and rare earth compounds, as shown in Figure 5. The dispersive states of these flame retardants in the polymer matrix are mainly at micro/nano scales.

Carbon-based nanomaterials are a huge family including many different allotropic members. The rise in carbon-based nanomaterials affords many new opportunities to create fire-retardant polymeric materials in the context of nanotechnology.[13] Their unique free radical trapping and antioxidant effects in the condensed phase at the initial stage of polymer degradation have attracted great attention in the fire retardancy community.[14] The understanding of free radical fighting mechanism is vital for the design of advanced fire-retardant polymeric materials.

4.1.1 | Fullerene

Fullerene (typically refers to C_{60}) is the third allotrope of carbon element after diamond and graphite.[58] A C_{60} molecule is full of π-electrons on its surface and thus capable of quenching more than 34 free radicals, thereby termed a "radical sponge."[59] In 2008, Fang et al. pioneered the use of C_{60} as a capturer or scavenger for free radicals to reduce the flammability of PP.[15] As powerful condensed-phase free radical fighters, the inclusion of C_{60} or its derivatives have shown to increase thermal stability and flame retardancy of polymeric materials, as summarized in Table S1.

Song et al.[18,60] first explored the impact of C_{60} on the thermal stability and flame retardancy of PP. The C_{60} can be dispersed uniformly within the PP matrix with a phase domain size of $\sim$200 nm. The addition of C_{60} (less than 2.0 wt%) slightly increases the thermal stability of PP in N_2 atmosphere, but noticeably augments the thermo-oxidative stability of PP in air. For instance, the initial
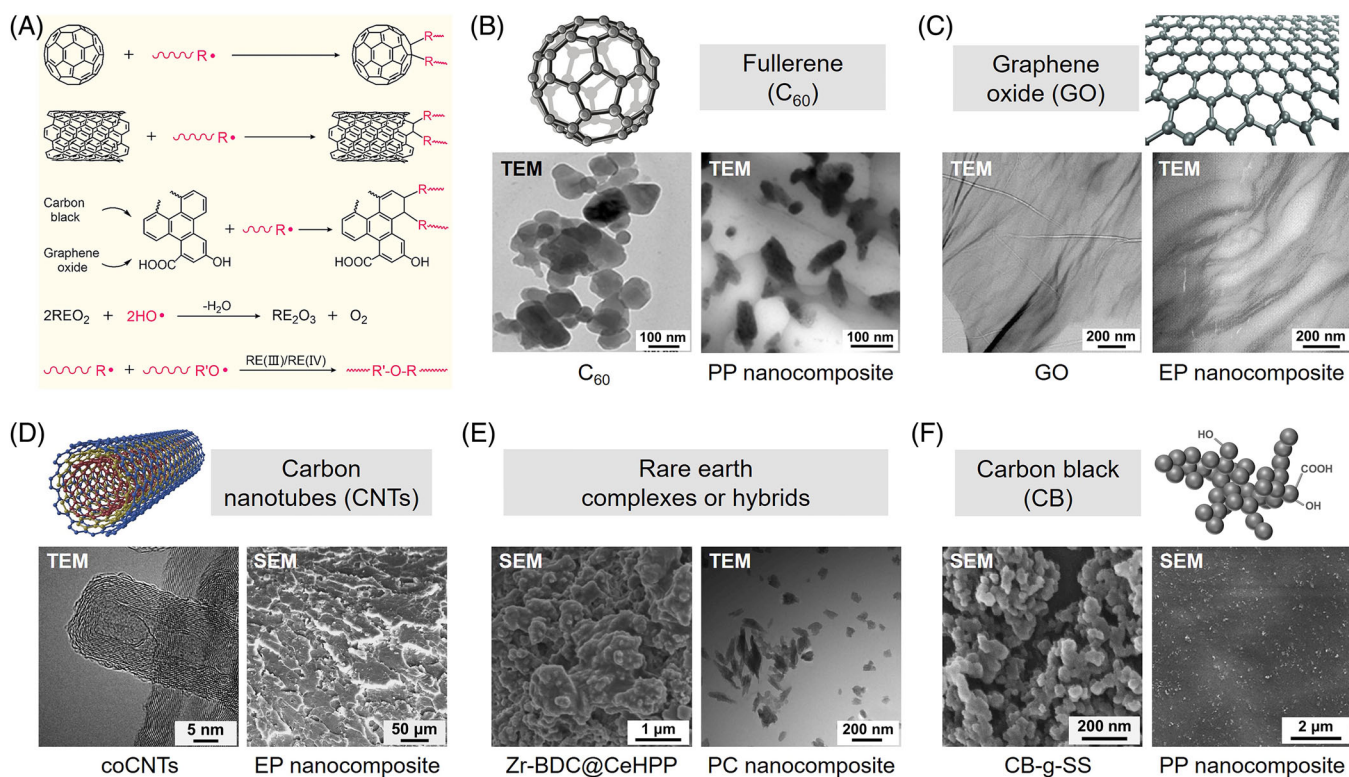
FIGURE 5 (A) Proposed radical reactions of condensed-phase capturers. (B–F) SEM/TEM images of FRs and their polymeric nanocomposites related to the condensed phase free-radical quenching literatures. (B) Fullerene (C_{60}): C_{60} and PP nanocomposite. Reproduced with permission.[18] Copyright 2008, IOP Publishing. (C) graphene oxide (GO): GO and EP nanocomposite. Reproduced with permission.[56] Copyright 2011, American Chemical Society. (D) Carbon nanotubes (CNTs): coCNT and EP nanocomposite. Reproduced with permission.[57] Copyright 2020, American Chemical Society. (E) Rare earth compounds: Zr-BDC@CeHPP and PC nanocomposite. Reproduced with permission.[20] Copyright 2020, Elsevier. (F) Carbon black (CB): CB-g-SS and PP nanocomposite. Reproduced with permission.[54] Copyright 2020, Elsevier

and maximum decomposition temperatures (T_{onset} and T_{max}) of PP nanocomposite containing only 1.0 wt% C_{60} are 15 and 54°C higher than those of virgin PP. Besides, the thermo-oxidative stability of PP becomes better as the content of C_{60} increases.

As for the fire resistance, the time to ignition (TTI) and time to PHRR (peak heat release rate) are significantly prolonged upon the addition of 1.0 wt% C_{60}, and meanwhile the PHRR value of the resultant PP nanocomposite is reduced by 42% relative to pure PP. The results have revealed that increased thermal stability and fire retardancy is mainly attributed to the in situ formation of a gelled-ball cross-linking network by C_{60} molecules or clusters via capturing macromolecular free radicals created by the polymer pyrolysis in the condensed phase. This cross-linking can dramatically increase the melt viscosity the heated polymer matrix and slow down the thermal decomposition of polymers to generate small combustible products (Figure 6A). By comparing the atomic force microscopic (AFM) images of PP and its nanocomposites containing 2.0 wt% of C_{60} (PF2) before and after heat treatment (Figure 6B), one can see no obvious change

in the surface roughness for PP. In sharp contrast, a significant reduction in the roughness is observed for PF2 after heat treatment, further suggesting a chemical cross-linking reaction occurring between the PP matrix and C_{60} during heat treatment.

Subsequently, chemical modifications of C_{60} have been utilized to promote its dispersion within the polymer matrix and to create synergistic fire-retardant systems, with some representative work shown in Figure 7. As a typical example, a functionalized C_{60} (C_{60}-d-PDBPP) was synthesized by reacting C_{60} molecules with a P/N-containing intumescent flame retardant (PDBPP).[38] This surface modification effectively promotes the dispersion of C_{60} in the PP matrix. Thanks to an improved dispersion of C_{60}-d-PDBPP, the thermal pyrolysis process is remarkably delayed, and the time to PHRR (t-PHRR) is prolonged to 102 s, and the PHRR value is decreased by 59%, which is superior to the unmodified C_{60} at the same concentration. The improved fire retardancy is due to the free-radical trapping effect of C_{60} and the char-formation capacity of PDBPP during burning in the condensed phase. Interestingly, it is found that only when the content of C_{60} and
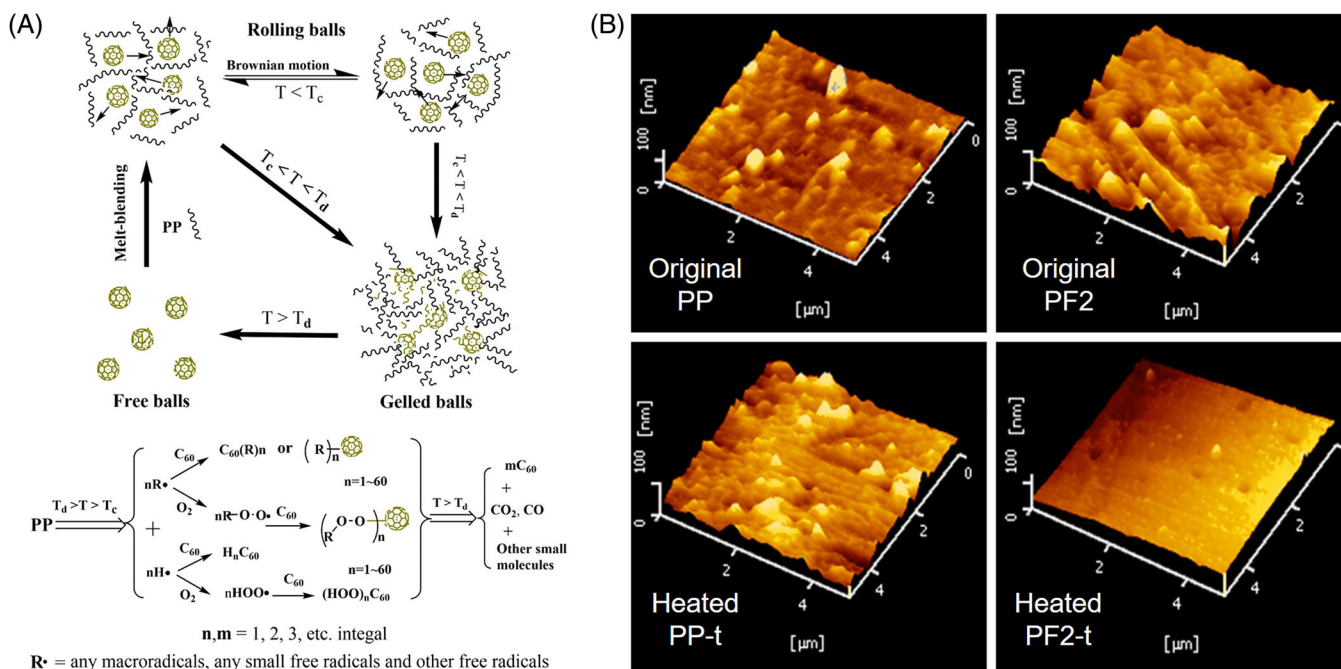
FIGURE 6 (A) Flame retardation mechanism of C_{60} on polymers by in situ forming a gelled-ball network. (B) 3D AFM images for original PP, PF2 composite, and their corresponding heat-treated samples: heated PP-t and heated PF2-t (heat treatment was performed at 260°C for 20 min). Reproduced with permission.[18] Copyright 2008, IOP Publishing

its derivatives are higher than 2.0 wt%, the melt viscosity of the matrix polymer and the quality of the carbonaceous layer can be high enough to support the free radical trapping effect of C_{60} in the condensed phase and to avoid the diffusion of the pyrolysis volatiles into the gaseous phase.

Afterwards, a C_{60}-decorated CNTs (C_{60}-d-CNTs) nano-hybrid was developed by chemically grafting C_{60} molecules onto the CNTs surface.[39] The synthesized C_{60}-d-CNTs exhibited a much better dispersibility than neat CNTs and C_{60}, as reflected by the individual CNTs in the PP matrix. The addition of only 1.0 wt% of C_{60}-d-CNTs prolongs the TTI and reduces the PHRR by 71%. Meanwhile, the T_{onset} and T_{max} of the resultant PP composite in air are increased by 68 and 75°C, respectively. It is noteworthy that the C_{60}-d-CNTs performs better than C_{60} or CNTs alone in terms of enhancing the oxidation resistance of PP. The combination of the radical quenching effect of C_{60} and the barrier effect of CNTs network allows for a more sufficient time for C_{60} and even CNTs to capture free radicals in the condensed phase.

Thereafter, Zhao et al.[16,61] examined the fire-retardant efficiency of C_{60} in a variety of polymers such as high-density polyethylene (HDPE), poly-methyl methacrylate (PMMA) and PC. The results show that C_{60} can only reduce the flammability and enhance the thermos-oxidative stability of these polymers via a free-radical degradation mechanism (HDPE, PP, and PMMA). To

expand fire-retardant applications of C_{60} and reduce the production cost, C_{60} is then used in combination with traditional flame retardants, including brominated flame retardants (BFR),[62] aluminum hydroxide (ATH),[63,64] respectively. Afterwards, several C_{60}-based hybrids (e.g., C_{60}-Si-MMT,[65] C_{60}-Fe,[66] PMPS-d-C_{60},[67] C_{60}@Graphene,[68] MoS_2-C_{60}[52]) are also reported, and likewise the decomposition temperatures and oxidation induction time (OIT) of the resultant polymeric composites in air are found to be appreciably increased. In addition, it should be noted that C_{60} molecules trap free radicals, which is prevented by the restriction effect of the hybrid components (e.g., metal ions, montmorillonite, etc.) on the movement of macromolecular chain in the polymer matrix.

In brief, above modification and combination strategies contribute to the free radical trapping effect of C_{60} in the condensed phase to some extent. However, the addition of C_{60} alone and most of its hybrids fail to make the polymer achieve high LOI values and desired UL-94 ratings (i.e., V-0). This is mainly because of their low concentrations due to the cost restrictions. An exciting result is the combination of 3.0 wt% of C_{60} and 53 wt% of ATH, which is reported to enable SBS (styrene-butadiene-styrene block copolymer) to reach a UL-94 V-0 rating and an LOI of 26.6 %.[63] Given the high cost of C_{60} materials, it should be promising strategy by combining it with traditional inexpensive fire retardants (e.g., ATH, ammonia polyphosphate).[69] Another strategy is to use more effective
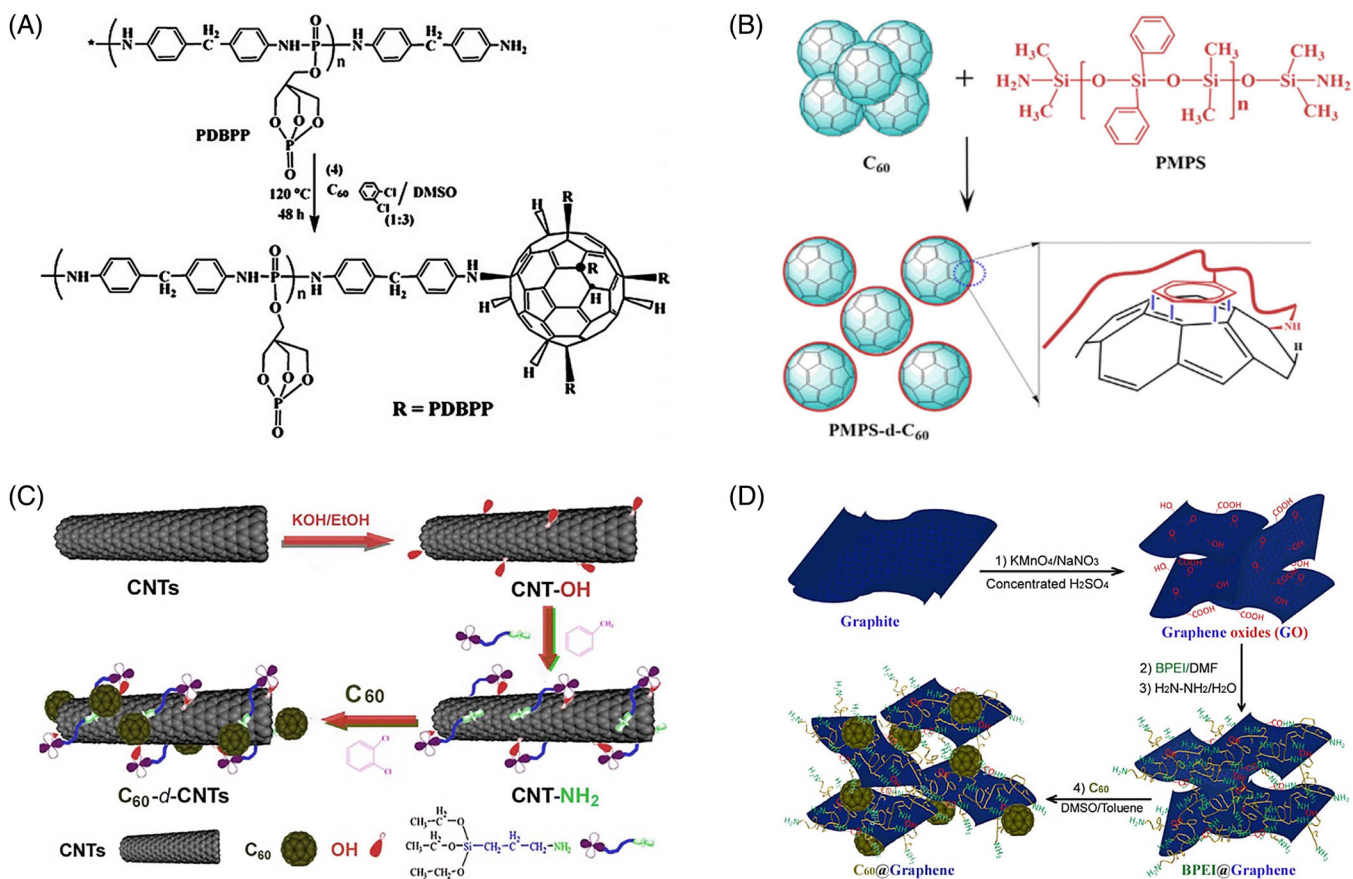
FIGURE 7 Typical work of chemical modifications for C_{60}: (A) C_{60}-d-PDBPP. Reproduced with permission.[38] Copyright 2009, The Royal Society of Chemistry. (B) PMPS-d-C_{60}. Reproduced with permission.[67] Copyright 2018, Elsevier. (C) C_{60}-d-CNTs. Reproduced with permission.[39] Copyright 2009, The Royal Society of Chemistry. (D) C_{60}@Graphene. Reproduced with permission.[68] Copyright 2013, IOP Publishing

fire-retardant elements (e.g., rare earth metals) or groups as functional modifiers or synergists for C_{60}.

4.1.2 | CNTs

CNTs are a typical one-dimensional nanomaterial with a high length-to-diameter ratio and thermostability as well as high electrical and thermal conductivities.[70] Along the longitudinal axis, CNT has an extraordinary mechanical strength while it possesses considerable flexibility as well. Generally, CNTs can be divided into single-walled carbon nanotubes (SWNTs, diameters of 1–2 nm) and multi-walled carbon nanotubes (MWNTs, diameters of 10–100 nm). As early as 2008, Galano A et al., first reported the free radical scavenging effect of SWNTs based on density functional theory calculations.[71] Six different high-energy free radicals were studied and compared, showing a relative reactivity sequence of •OH > •CH$_3$ > •CHO > CH$_3$O• > •OOH > CH$_3$OO•. Given that •OH radicals are the most reactive and dan-

gerous free radical in the combustion process, CNTs have emerged as a potential flame retardant for polymers by capturing free radicals, in addition to its physical networking effect.

Pristine CNTs was first used as a potential flame retardant for PMMA by Kashiwagi et al.,[36] and they found that only well-dispersed SWNT (0.5 wt%) could endow a signification reduction in PHRR and mass loss rate (MSR) of PMMA during cone testing. The uniform dispersion and sufficient concentrations are two key factors for the formation of a continuous network-structure in the polymer matrix.[72] Thereafter, a series of studies further confirmed that the fire resistance of CNTs strongly relies on its dispersion state and loading levels in the polymer matrix, with some representative CNTs-based flame retardants based on free radical trapping effects are listed in Supplementary Table S2. Given the prolonged TTI and elevated decomposition temperatures, Dubois et al.[73] proposed that crushing MWNTs possessed a chemical reactivity, that is, it reacts with the macromolecular free radicals generated by the pyrolysis of ethylene-vinyl acetate copolymer (EVA).
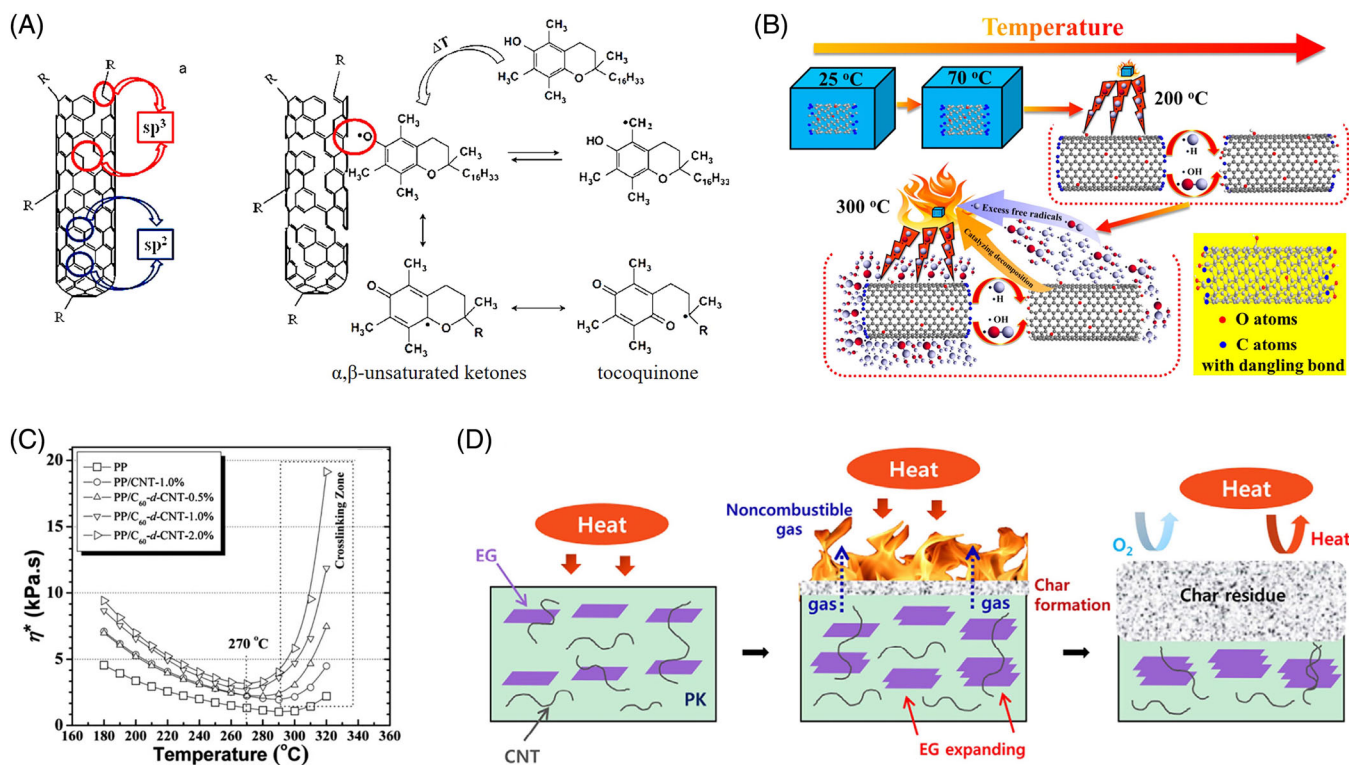
FIGURE 8 (A) The free radical fighting mechanism of CNTs. Reproduced with permission.[74] Copyright 2014, Elsevier. (B) Free radical scavenging effect of the coCNTs during the thermal decomposition of EP composite. Reproduced with permission.[57] Copyright 2020, American Chemical Society. (C) Temperature dependence of the complex viscosity of PP and its nanocomposites. Reproduced with permission.[39] Copyright 2013, The Royal Society of Chemistry. (D) A schematic illustration of the flame retardant and self-extinguish mechanism of EG and MWCNT reinforced polyketone nanocomposite. Reproduced with permission.[76] Copyright 2019, Elsevier

In 2004, Dintcheva et al.[74] proposed the hybridization of the carbon atoms onto the CNT surface without and with surface defects, and modes of action of CNTs on typical radical intermediates (Figure 8A). Meanwhile, Wang et al.[57] reported a CNTs with abundant carbon-centered free radicals (Figure 8B). The special CNTs were found to delay the flame spread at the initial stage of combustion for EP. The in situ ESR study confirmed the free radical scavenging effect during thermal decomposition. The correlation of flame retardancy of the composite and the free radical content in CNTs revealed that the improved fire safety was attributed to the free radical scavenging effect of the numerous dangling bonds on the carbon-centered free radical-rich CNTs. Chiang et al.[75] utilized the free radical reactivity of CNTs to synthesize vinyltriethoxysilane decorated CNTs (VTES-CNT) and blended it with EP. Results indicated that the EP/VTES-CNT composites exhibited improved the thermal stability and flame retardancy relative to pure resin.

Lee et al.[40] claimed that the combination of montmorillonite (MMT) and MWNTs can improve the oxidative resistance, LOI value and char-forming capacity of EP. The results of relationship between the char yield and LOI confirmed that the progress in the anti-oxidation perfor-

mance for EP is related to the free radical fighting effect. Wang et al.[23] reported that the SWNT or functionalized MWNT (MWNT-OH) could obviously enhance the antioxidant and mechanical performances of HDPE, and the free radical trapping effect of those CNTs was confirmed by ESR and Raman spectra. Dintcheva et al.[74] reported that α-tocopherol was capable of inducing the scavenging activity of CNTs in UHMWPE. Similarly, thanks to the free radical fighting effect, expandable graphite (EG) and MWNTs exhibit a synergistic effect in enhancing the flame retardant properties of polyketone (Figure 8D).[76] Gashti et al.[77] anchored CNTs on the cotton surface using vinylphosphonic acid monomer as a crosslinking agent and benzophenone as a catalyst. They found that the combustion rate of the resultant cellulose fiber was reduced by 85%, in addition to significantly delayed the thermal decomposition.

Although the free radical scavenging effect of CNTs has been confirmed by the theory of quantum chemistry and some experiments, there have been limited reports on the use of its free radical trapping mechanism for creating flame-retardant CNTs/polymer nanocomposites. In practice, the addition of CNTs often only reduces the PHRR and MSR of the resultant polymeric nanocomposites because

of the formation of CNTs network within the polymer. For this reason, a critical loading level or threshold value for CNTs is required to create a so-called three-dimensional physical network in the polymeric nanocomposites, which is often reflected by a "second plateau" at the low frequency during rheological or electrical tests. This threshold CNTs content is also essential to allow for sufficient time for its free radical trapping effect and to produce a compact char layer in the condensed phase after burning. However, a high CNTs content does not contribute to a further improved fire-retardant effect in polymers, particularly the LOI values and UL-94 rating, which in turn can deteriorate the melt-processability of the matrix polymer because of a remarkably increased melt viscosity. Likewise, a feasible strategy to use CNTs as a fire retardant or synergist is its combination with traditional fire retardants, which can help reduce the required loading level of the latter while augmenting mechanical properties of the polymer.

4.1.3 | Graphene oxide

As an emerging member of carbon materials family and the thinnest material in the world, graphene has garnered an explosion of research since it was first isolated from graphite in the past decade. Graphene oxide (GO) is often produced by the chemical exfoliation of graphite, thus leaving a large fraction of defects on the graphene plane. As a result, GO has a larger content of free radicals compared with graphene. Meanwhile, both GO and graphene have been extensively used to create fire-retardant polymeric materials, and Supplementary Table S3 summarizes some applications of GO in the flame-retardant polymer materials.

In 2011, Hu et al.[56] for the first time reported organic phosphate functionalized graphite oxides (FGO) which were incorporated into EP via in situ polymerization to prepare EP based composites. This study represented a new approach to prepare functionalized GO with flame retardant elements to improve the flame retardancy of polymer and opened many opportunities for graphene to enhance thermal stability of polymers. For instance, Song et al. fabricated C_{60} decorated graphene oxide (C_{60}-d-GO) for flame-retarding HDPE[48] and PP.[68] Surprisingly, the micron/nano-dispersed C_{60}-d-GO can significantly enhance the flame retardancy, thermal stability and mechanical performances of the resultant flame-retardant polymer nanocomposites, which is attributed to the cooperative effect of the radical scavenging effect of C_{60} and the multiple effects (physical barrier, protection, and reinforcement) of GO (Figure 7D).

Likewise, Huang et al.[78] covalently grafted poly(piperazine spirocyclic pentaerythritol bisphosphonate) (PPSPB) onto the GO surface to synthesize a new GO-based fire retardant nanohybrid, GO-PPSPB for EVA. The physical barrier effect of GO and the charring capacity of PPSPB enable an ideal free-radical trapping condition for P-containing radicals in the condensed phase during combustion. In 2017, Li et al.[79] confirmed the free radical trapping ability of GO. Similarly, the MPP/graphene/PVA composites still exhibited excellent flame retardancy and thermal stability.[80] To date, there has been much research focusing on the flame retardant modifications of GO, especially by using phosphorus-containing flame retardants with a free radical trapping ability, which will be discussed in the following "dual-phases free radical capturers" section.

4.1.4 | Carbon black

Nanoscale carbon black (CB) is one of the most widely used nanofillers because of its abundant source, low density, permanent conductivity, and low cost. It is widely accepted that CB is a strong radical scavenger due to its polycondensed aromatic rings, and thus has been extensively used as fire retardants or synergists for many different polymer matrices, with typical results listed in Supplementary Table S4. For example, Tang et al.[43] first adopted CB as a flame retardant of PP and the resultant PP nanocomposites displayed dramatically enhanced thermal stability in air and slightly improved flame retardancy. The results revealed that CB nanoparticles can trap peroxy radicals at elevated temperatures to form a gelled-ball cross-linked network. To boost the flame retardant efficiency, CB is used in combination with some traditional flame retardants for different polymers including PE,[81] PP,[46,82] PU,[83] PC,[54] and POE.[84] The polycondensed aromatic rings in CB have been confirmed to play a key role by acting as free-radical capturers during thermal decomposition of polymers, which leads to improved fire retardancy for the final polymer nanocomposites.

Tang et al.[85] employed active carbon spheres (AC) with Ni_2O_3 as a flame retardant for PP, and the resultant PP composite containing 7.5 wt% AC exhibits 70% and 38% reductions in PHRR and THR relative to neat PP, respectively. Besides, the thermo-oxidative stability of the PP composite is also greatly improved. With the aid of the catalytic effect of Ni_2O_3, AC can convert PP fragment radicals into hydrocarbons and eventually aromatic compounds via dehydrogenation and aromatization reactions.

In addition to the carbon allotropes discussed above, carbon nitride (g-C_3N_4) has also been reported to show a free radical fighting effect in some polymers. A typical

example is that Shi et al.[86] reported the hypophosphite/g-C_3N_4 hybrid as a flame retardant system for thermoplastic polyurethane (TPU), and they attributed the enhanced fire safety to the induction effect of g-C_3N_4 on hypophosphite to generate more free radical capturers at the mesophase upon exposure to flame.

4.1.5 | Rare earth metal-based compounds

Rare earth (RE) elements contain 15 lanthanides (from La to Lu), yttrium (Y) and scandium (Sc),[87] and their compounds have demonstrated to be able to further improve the fire retardancy of fire retardant polymer materials because of their catalytic effect on dehydrogenation, oxidation, crosslinking, carbonization.[88] Li et al.[89] first reported the synergistic effect of rare earth oxide (La_2O_3) in the fire-retarding PP with an intumescent flame retardant (IFR) composite. The La_2O_3 and IFR exhibits a good synergistic fire-retardant effect. This has driven the following reports on the synergistic effect of rare earth oxides in flame-retardant polymer materials.

It was not until 2014 that the free radical quenching mechanism of rare earth compounds for fire-retardant polymeric materials was proved, with typical work summarized in Supplementary Table S5. Ran et al.[47,51] reported the use of ytterbium trifluoromethanesulfonate ($Yb(OTf)_3$) as a flame retardant for HDPE, the resultant composite containing only 0.5 wt% $Yb(OTf)_3$ can increase the initial degradation temperature in air from 334 to 407°C and prolong the OIT from 11 to 24 min. The authors revealed the free radicals-trapping capacity of $Yb(OTf)_3$ that is mainly responsible for the improved thermal and thermo-oxidative stability by combining ESR, TG-IR and py-GC/MS measurements. Subsequently, various rare earth complexes (La-BDC,[90] MRP/LaPP,[91] Ce(DOPO)$_3$,[55] CeHPP@Zr-BDC[20]) are applied in different types of polymers (e.g., PC, HDPE, PET).

In summary, the specific empty 4f orbitals and variable valences of some rare earth elements, e.g., Ce, Yb, Nb, enables them and their oxides to exhibit exceptional antioxidant and catalytic activities in polymers because of their free radicals trapping effect through redox cycling between different valence states. Notably, whether it is a polymer with a random free radical scission mechanism (PE) or a branching reaction decomposition mechanism (PC, PET), rare earth compounds can have a varied effect in reducing their fire hazards. To date, rare earth compounds have become a promising halogen-free friendly fire retardant. This is because the designability and diversity of their chemical compositions and micro-morphologies afford many possible opportunities for the conversion of free radical fighting effect from the gaseous phase to the condensed phase. It should be noted that RE has been primarily used as a synergist for other traditional fire-retardant systems to enable the polymer to achieve a satisfactory fire-retardance.

## 4.2 | Fighting free radicals in the gaseous phase

Traditionally, halogenated compounds are one of the earliest and most effective fire retardants for polymeric materials via interfering or fighting free radicals in the gas phase. Other similar gas-phase fire retardants or free-radical capturers include hindered amines & phenols, sulfonamides. Figure 9 illustrates their typical free-radical fighting mechanism by which they improve the flame retardancy of the polymer host.

4.2.1 | Halogenated compounds

Halogenated compounds[96] almost act in the gaseous phase by a free-radical mechanism by which they inhibit or suppress the exothermic chain scission. Among them, BFRs have demonstrated the highest flame retardant efficiency, especially in combination with antimony trioxide (Sb_2O_3) to create a synergistic effect, with a well-accepted mode of action shown in the Figure 9B.[94] In general, at elevated temperatures halogenated compounds are decomposed into halogen hydrides (HX), and the created HX can further react with vaporized Sb_2O_3 to generate antimony halides and its oxides, which are further pyrolyzed to generate halogen-containing radicals. Meanwhile, both antimony halides and halogen-containing radicals are capable of quenching high-energy free radicals (e.g., •H, •OOH and CH$_3$•) and thus effectively interrupt the combustion process.

4.2.2 | Organophosphorus

Many phosphorous-containing fire retardants (P-containing FRs) have been developed for a variety of thermoplastic[97] and thermosetting polymers.[95] The phosphorus can exist in the valance of −3, 0, +1, +3, and +5. Previous work has revealed that the free radical quenching action of P-containing FRs usually relies on their oxidation states in the compounds.[98] In general, the gaseous-phase free radical capturing effect of P-containing FRs increases with a decrease in the oxidation state of P element in the FR. Therefore, the volatile P-containing compounds primarily possess lower oxidation states (−3, 0, +1, +3) and thus exert a free radical fighting effect in
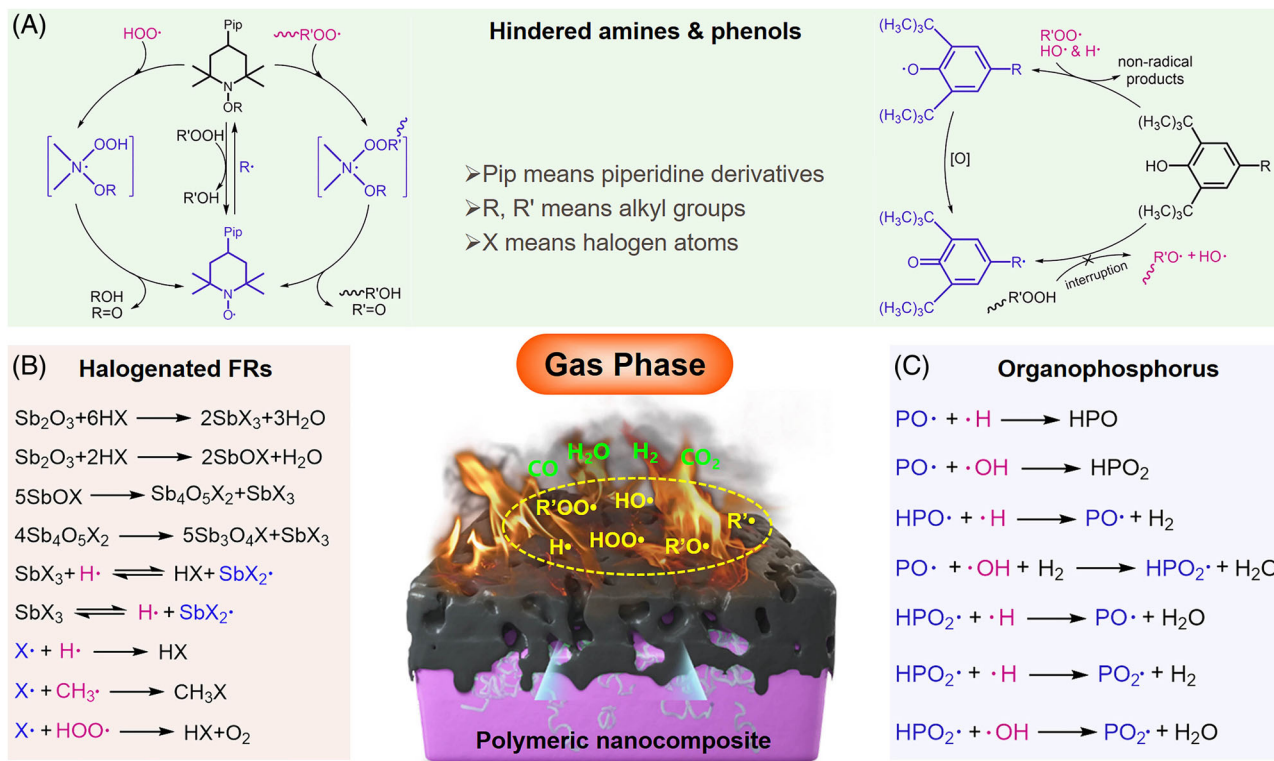
FIGURE 9 Typical gaseous phase free-radical reaction mechanisms related to (A) hindered amines[92] and hindered phenols,[93] (B) halogenated FRs,[94] and (C) organophosphorus FRs in polymeric nanocomposites.[95]

the gaseous phase. Supplementary Table S6 summarized the volatile organophosphorus as the gaseous-phase free radical fighters for polymeric (nano)composites based on DOPO derivatives and other lower oxidation state P-containing compounds.

9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives are an important kind of organophosphorus compounds. Thanks to its highly reactive P-H bond, DOPO has been extensively used as a functional modifier for nanomaterials to prepare fire-retardant polymeric nanocomposites through taking advantage of the free-radical trapping effect of DOPO groups in the gaseous phase.[99] For example, Yang et al. molecularly combined the polyhedral oligomeric silsesquioxane (POSS) with DOPO and the modified POSS can be well-dispersed in PC[100] and EP[41] matrix. The TG-IR and TG-MS results indicate that the OP^+-, O_2P^+- and $P-O-C_{Ph}$-containing fragments are detected in the pyrolysis volatiles, which are mainly from the PO•/HPO• free radicals created by the decomposition of DOPO. These less reactive radicals are capable of quenching or scavenging highly reactive free radicals (•H, •OH, etc.) in the gaseous phase, thus suppressing the burning of polymers.

Li et al.[50] reported a DOPO-functionalized halloysite nanotube (HNT@MAH@DOPO) for the flame retardation

of PLA. The inclusion of 5 wt% of HNT@MAH@DOPO leads to a UL-94 V-0 rating, an LOI of 38.0% and significant reductions in PHRR of the final PLA nanocomposite. The mechanism studies revealed that the stepwise decomposition of DOPO suppressed the flame through the quenching effect of PO• radicals in the gaseous phase, thus resulting in decreased PHRR and delayed TTI. Later on, cellulose nanofiber (CNF) was adopted as a reinforcing component to fabricate a core-shell nanofiber (PN-FR@CNF) by in-situ chemically grafting P/N-based FR on the surface of CNF.[101] Even 10 wt% of PN-FR@CNF could homogeneous dispersed in PLA and enabled nanocomposite to achieve a UL-94 V-0 rating with a reduction in both PHRR (31%) and THR (8%). The R-PO•, PO• and -NH• free radicals are found to fight with H• and HO• free radicals in the gaseous phase to terminate the chain scission degradation reactions of PLA. Up to date, there have been many studies that combine DOPO-based derivatives with nanomaterials in various polymers including PP, PU, EP, PLA, PC, etc.[53,102–105] Meanwhile, research has shown that a subsequent reaction of HPO• with H• and OH• radicals can lead to the regeneration of PO• species, and thus the low-energy P-containing free radicals also contributes to cooling down the flame.

In addition to DOPO, other fire retardants with lower oxidation state P also possess a similar gaseous-phase free

radical capture effect. For instance, Lai et al.[106] reported a functionalized ZrP nanosheet (RQZrP) with a free-radical quenching capability, which shows improved flame retardancy for PP when combined with the IFR. Similarly, Xing et al.[107] constructed an ionic liquid (IL) modified black phosphorus (BP) nanosheet (IL-BP) by self-assembly for flame retardancy of PU, and the final PU nanocomposite containing 2 wt% IL-BP achieved 38% and 20% reductions in PHRR and THR, respectively, as well as a 18°C increase in the T_{onset} compared with pure PU. The authors attributed the increased flame resistance to the physical barrier effect of the 2D lamella and free radical quenching effect of black phosphorus in the condensed phase. In addition, above free-radical trapping effect was well utilized in some EP and biocomposite systems.[108–112] All of them reported that the free radical fighting mechanism in the gaseous phase was related with low-energy P-containing free radicals decomposed from organophosphorus ligands and their derived incombustible components (water, phosphorous acid, etc.).

In brief, the P-containing FRs decompose to release many P-containing radicals under high temperatures that can terminate active free radicals (•H and •OH). Consequently, the combustion of polymers is interrupted and even prevented. The free radical fighting circulation of volatile organophosphorus-containing compounds in the gaseous-phase is summarized in Figure 9C.

4.2.3 | Dopamine and its derivatives

Because of a high content of N element and a strong ability to scavenge free radicals, dopamine and its derivatives have recently been used for creating fire-retardant polymers. Generally, they are almost intrinsically fire-retardant polymeric materials or fire-retardant nano-coatings, and some representative studies based on dopamine and its derivatives as gas-phase free-radical fighters are summarized in Supplementary Table S7. For instance, polydopamine-aramid nanofiber (PANF) is applied as a host to confine a unique phase change guest material (deep eutectic solvent, namely DES) to fabricate PANF-DES host-guest flame-retardant cryogenic phase change films (Figure 10A).[113] The as-prepared films with a phase transition temperature of −21°C and a melting enthalpy of 225 J·g⁻¹ can withstand fire for 60 s without naked flame, and the PHRR is as low as 26.0 MJ·kg⁻¹.

Based on bio-inspired dopamine methacrylamide (DMA) co-monomer, Nam et al.[114] reported an intrinsic fire-retardant polyacrylonitrile (PAN) copolymer, P(AN-*co*-DMA), that was synthesized via free radical polymerization of AN and ADMA monomers (Figure 10B). Because of the radical scavenging capability of DMA in

the gaseous phase and the formation of a carbonaceous layer on the polymer surface, the final PAN exhibits a low heat-release capacity of 58 J·g⁻¹·K⁻¹ and a high LOI value of 37%, even if without introducing any other fire-retardant additives. The proposed reaction mechanism between dopamine and typical free radicals (ROO•, HOO•) is provided in Figure 10C.[115]

In addition to the intrinsic fire-resistant polymers, dopamine derivatives can be used alone or in combination with other FRs to prepare flame-retardant coatings for cellulose,[116] PU,[117–119] EP,[120] and UHMWPE.[121] These studies have further highlighted that it is the free-radical scavenging effect and a good charring capability of dopamine-derived molecules (e.g., catechol units) that are responsible for the excellent fire retardancy of the coatings.

4.2.4 | Hindered amines and phenols, sulfonamides

Hindered amines are initially used as UV stabilizers while hindered phenols are developed as antioxidants for polymeric materials. Because the free-radical quenching capacity, they have also been reported to serve as flame retardants for polymers. The addition of hindered amines or hindered phenols can appreciably enhance the thermo-oxidative stability and prolong the TTI of polymers. As shown in Figure 9A, the decomposed hindered amines generate NO• radicals, which can trap highly active free radicals and cut off the chain scission reactions.[92] In addition, high concentration of NO• radicals can remove and dilute some combustibles and the oxygen concentration in the combustion zone. The mode of action of hindered phenols is analogous to hindered amines, and these hindered phenols also have an additional antioxidant effect by interrupting chain scission of oxidized macromolecules (Figure 9A).[93] However, both hindered amines and hindered phenols are not efficient enough for polymers when used as flame retardants alone. For this reason, they are often used in combination with IFR and P-containing flame retardants.

In addition, Carl-EricWilén et al.[122] reported some sulfonamide flame retardants for polymers because of their strong free-radical trapping capability. More interestingly, some sulfonamide-based fire retardants having a nitrogen-sulfur core can be used alone to provide sufficient flame retardancy for PP, PE and PS.[123]

4.3 | Fighting free radicals in the dual phase

To enhance the fire-retardant efficiency, researchers have developed some multi-component flame retardant
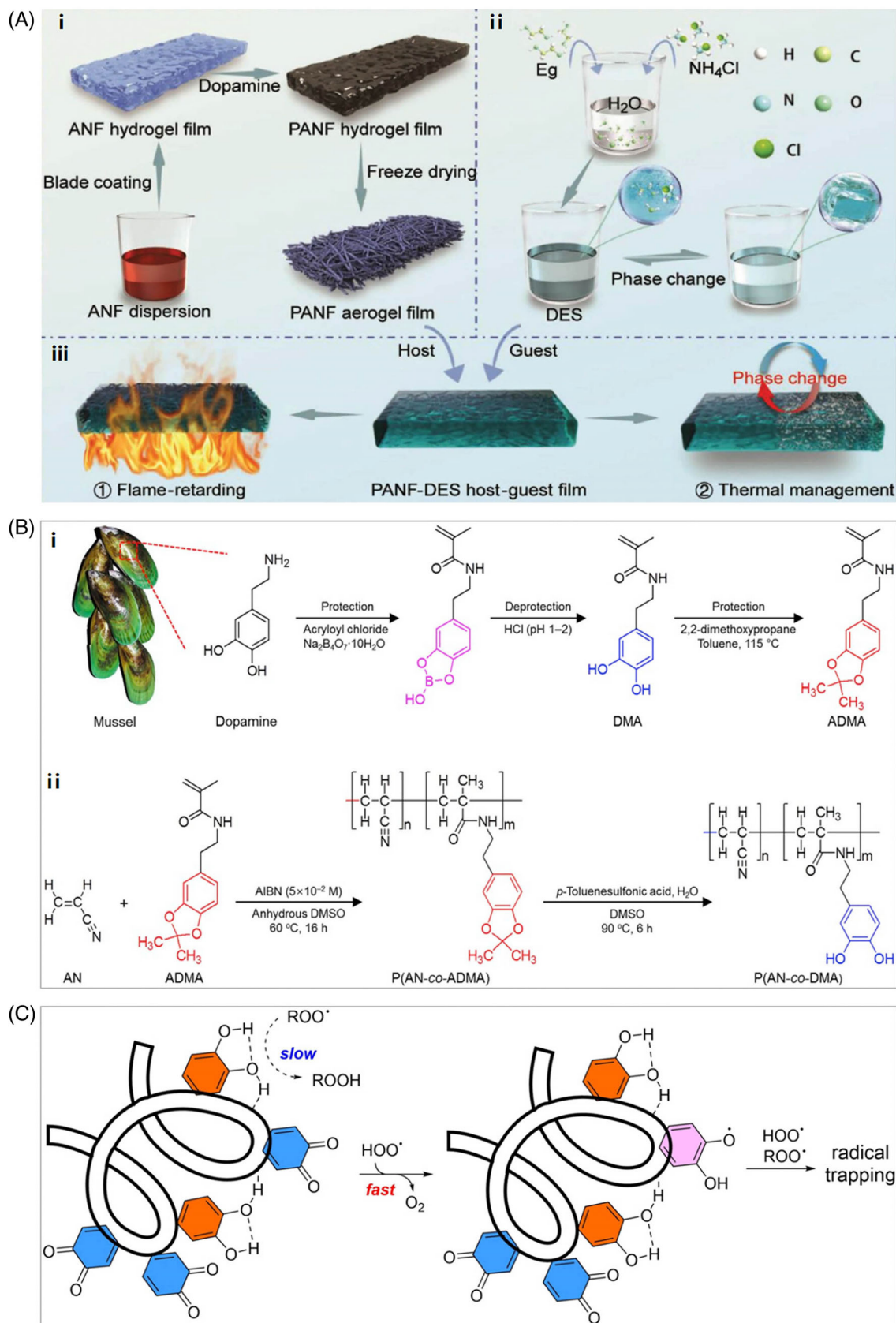
FIGURE 10 (A) Schematic description of the PANF-DES host-guest film and its functionality: fabrication of (A-i) PANF host film and (A-ii) ternary DES guest, (A-iii) thermal management and flame retarding performances of PANF-DES host-guest film. Reproduced with permission.[113] Copyright 2021, Wiley VCH. (B) The synthesis routs of (B-i) DMA and ADMA monomers, and (B-ii) P(AN-*co*-DMA) copolymer. Reproduced with permission.[114] Copyright 2020, Elsevier. (C) Radical reactions between dopamine and typical free radicals (ROO•, HOO•).[115]
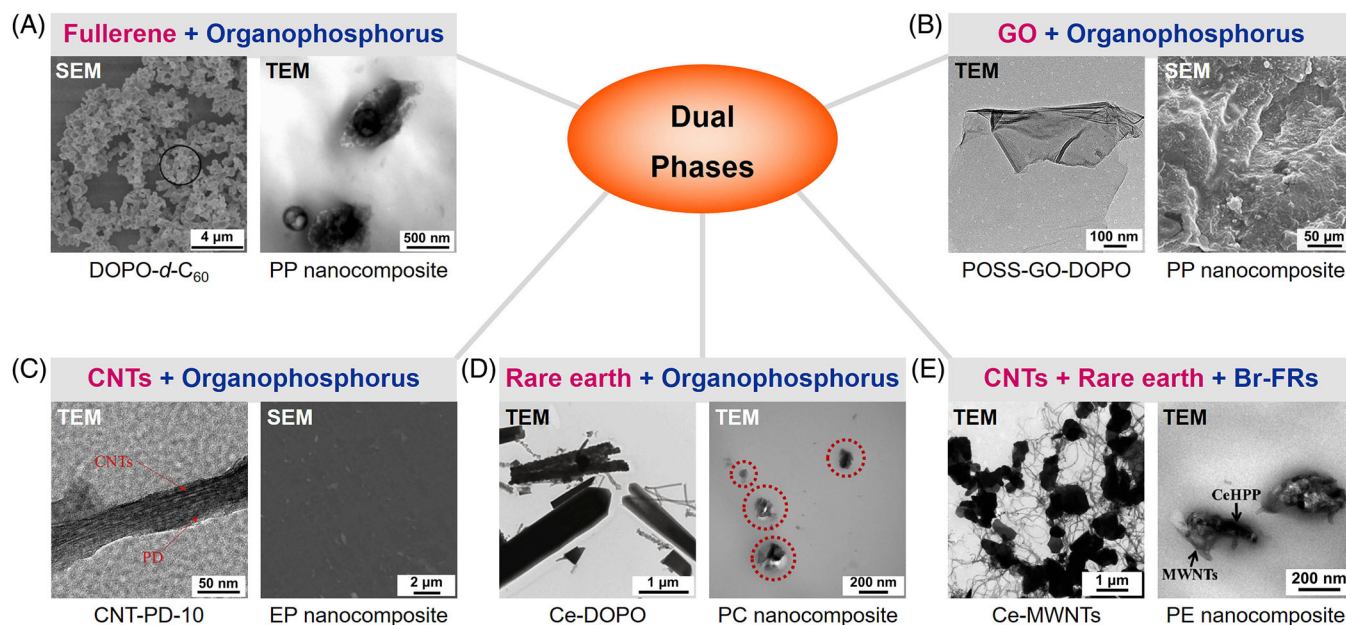
FIGURE 11 Typical SEM/TEM images of FRs and their polymeric nanocomposites related to the dual phases free-radical quenching literatures. (A) Fullerene + organophosphorus: DOPO-d-C$_{60}$ and PP nanocomposite. Reproduced with permission.[124] Copyright 2020, Elsevier. (B) GO + organophosphorus: POSS-GO-DOPO and PP nanocomposite. Reproduced with permission.[53] Copyright 2019, Elsevier. (C) CNTs + organophosphorus: CNT-PD-10 and EP nanocomposite. Reproduced with permission.[125] Copyright 2016, Elsevier. (D) rare earth + organophosphorus: Ce-DOPO and PC nanocomposite. Reproduced with permission.[55] Copyright 2021, Elsevier. (E) CNTs + rare earth + Br-FRs: Ce-MWNTs and PE nanocomposite. Reproduced with permission.[45] Copyright 2014, The Royal Society of Chemistry

systems through physical blending or chemical modifications, which can capture free radicals in both gaseous and condensed phases, namely dual-phase free-radical fighters. For example, some P/Br-containing flame retardants are combined with other synergists, such as carbonization agents, CNTs, graphene oxide and its derivatives, lamellar nanomaterials. This combination can considerably increase the melt viscosity of heated polymer matrices, and even improve the quality of char residues during fire. As a result, most of the highly active free radicals are confined at the condensed-phase or mesophase and then quenched by these combined fire-retardant systems, thus effectively inhibiting the combustion. In general, flame retardants that act in the dual phase can be categorized into carbon nanomaterials modified by organophosphorus flame retardants, and the combination of rare earth compounds and traditional flame retardants, as shown in Figure 11.

Supplementary Table S8 summarizes some representative dual-phase free-radical fighters for flame-resistant polymeric nanocomposites. For example, Chen et al.[19] studied the synergistic flame retardancy effect between cerium phenylphosphonate (CeHPP) and decabromodiphenyl oxide (DBDPO) for PET. They found that once a compact and continuous char layer formed, the rare earth metal ions (Ce) promoted the oxidation and cross-linking reactions in the condensed phase by absorbing the macromolecular free radicals. Fang et al.

reported a DOPO chemically decorated C$_{60}$ (DOPO-d-C$_{60}$) (Figure 11D) and then a rare earth based complexe (CeP$_n$) (Figure 12D) by using DOPO as a gaseous phase component and C$_{60}$[124] and Ce^{3+} ion[55] as the condensed phase component, respectively. They found that DOPO-d-C$_{60}$ was very effective in enhancing the thermo-oxidative stability and fire-retardancy of PP that exhibits a typical polymer experiencing a free radical degradation process when heated.

As for polymers, such as PC, that do not undergo a free-radical degradation process, no significant changes in the thermal degradation are observed. However, the rare earth complexes (CeP$_n$) having a free radical trapping effect in the dual phase was found to exhibit a desired flame retardancy for PC.[55] For instance, with the inclusion of 4 wt% of CeP$_n$, the PHRR and TSR of bulk PC are respectively reduced by 46% and 26%, and a desired V-0 rating is also achieved. Moreover, the as-prepared PC/CeP$_n$ composite shows a marked improvement in the thermal decomposition temperatures in air atmosphere. It is worth noting that some hindered phenols and amines were also used as the gaseous phase trapping component in dual-phase systems,[126] which exhibited satisfactory fire-retardant and smoke suppression efficiencies in some polymer matrices.[126,127]

The combination of radical-reactive CNTs and volatile organophosphorus has also been reported as dual-phase
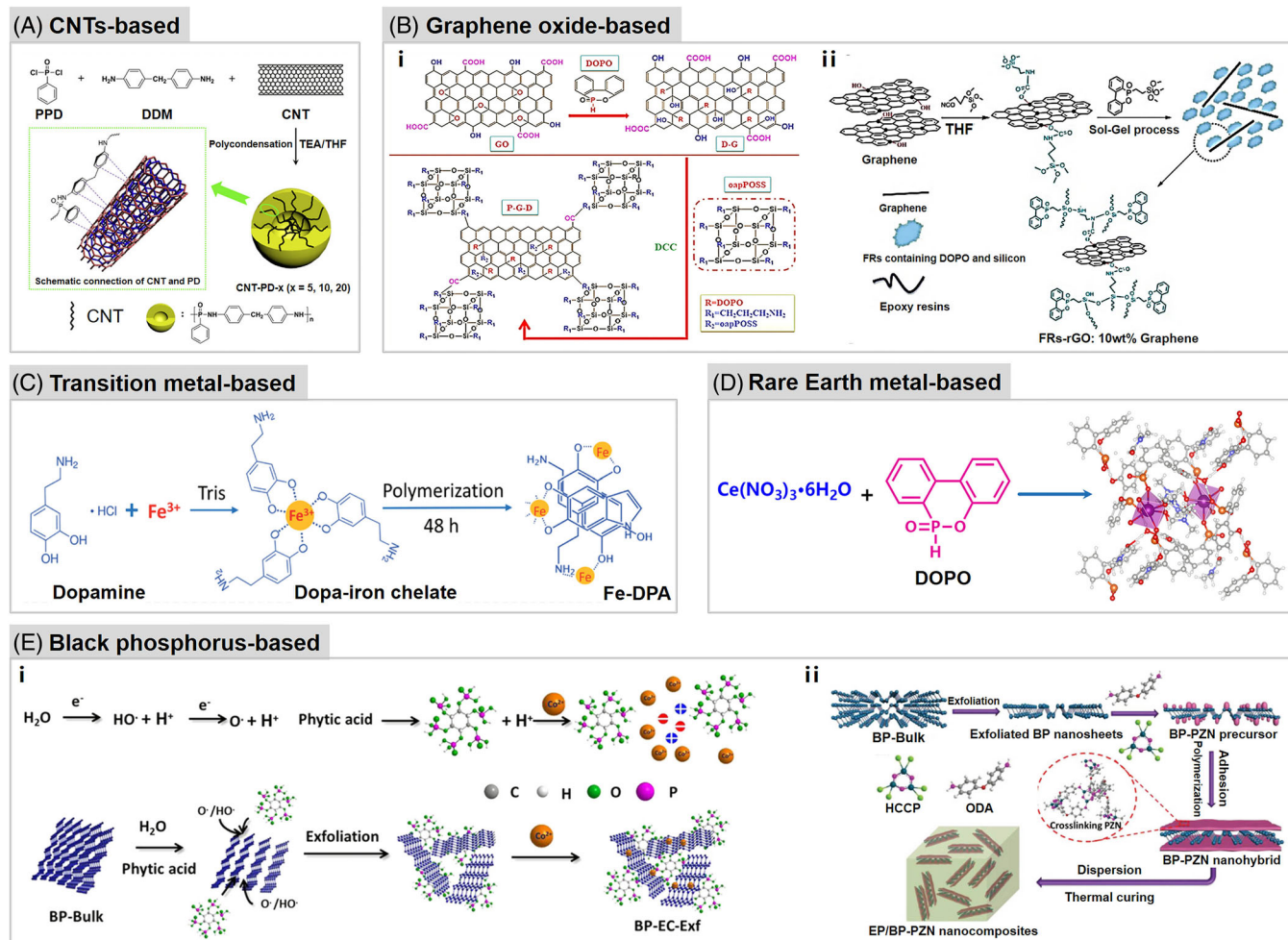
FIGURE 12 Typical synthesis procedure of dual phase free-radical fighters: (A) CNT-PD-*x*. Reproduced with permission.[125] Copyright 2016, Elsevier. (B-i) POSS-GO-DOPO. Reproduced with permission.[53] Copyright 2019, Elsevier. (B-ii) FRs-rGO and EP nanocomposites. Reproduced with permission.[44] Copyright 2013, The Royal Society of Chemistry. (C) Fe-PDA. Reproduced with permission.[24] Copyright 2020, The Royal Society of Chemistry. (D) Ce-DOPO. Reproduced with permission.[55] Copyright 2021, Elsevier. (E-i) BP-EC-Exf (electrochemically exfoliated black phosphorus). Reproduced with permission.[140] Copyright 2019, American Chemical Society. (E-ii) BP-PZN nanohybrid and EP nanocomposites. Reproduced with permission.[141] Copyright 2019, Wiley VCH

free radical scavengers for the creation of fire-retardant polymeric nanocomposites. For instance, Yan et al.[128] combined a phenethyl-bridged DOPO (DiDOPO) compound and MWNT to improve the fire safety of EP. The final EP nanocomposite exhibited 55% and 33% reductions in the PHRR and THR, respectively, and passed a UL-94 V-0 rating. Meanwhile, both the T_{onset} and T_{max} in N_2 were enhanced to varied extent as well. After that, a similar combination was used for preparing PA6 / hexachlorocyclotriphosphazene modified MWNT (MWNT-HCTP) nanocomposites by Zhang and co-workers.[129] Yang et al. used a series of P-containing agents with different oxidation states of P element to modify amino-CNTs, producing DPP(O_x)-A-CNTs and decorated MWNTs (DPPA-WMCNT), which were then used as flame retardants for PET[130] and PS,[131] respectively. Xin et al.[125] introduced

2 wt% of polymer wrapped carbon nanotubes (CNT-PD-10) into EP (Figure 12A), and found that the PHRR and THR of the as-prepared EP composite were reduced by 47% and 29%, with its LOI value reaching 32%. This is because the good charring capacity of CNT-PD-10 limits the diffusion of degraded fragments from the condensed to the gaseous phase.

In addition, the combination of 2D graphene derivatives with polyphosphates or P, N-containing compounds have also been reported to prepare fire-retardant polymeric nanocomposites, including PLA/BPPT/MGO,[132] EP/PN-rGO,[133] EP/DPP-GO,[134] EP/FRGO,[135] PU/PND-GO.[136] These fire-retardant systems mainly function in the condensed phase through a free-radical trapping mechanism. Yu et al. designed a functionalized graphene oxide decorated with DOPO derivatives (FRs-rGO) for EP[44,137]

(Figure 12B). Interestingly, they found that a subsequent reaction of HPO• with H• and OH• radicals led to the regeneration of PO• species, and thus the low-energy P-containing free radicals can further act with the GO. By using this mechanism, a finely-tailored graphene oxide (FGO) grafted by piperazine and phosphonate-containing hyper-branched flame retardant was synthesized to reduce the flammability and toxicity of polystyrene (PS).[138]

Likewise, Chen et al.[139] adopted DOPO decorated GO (PMGO) as a synergist for IFR-fire-retardant PP. The resultant PP composite shows 62% and 40% decreases in the PHRR and THR in addition to a desired UL-94 V-0 rating. However, at high loading levels of IFR, the presence of PMGO does not contribute to the thermal stability of PP in air condition. Similarly, there were huge amount of efficient flame-retardant nanocomposites fabricated by dual-phase free-radical capturers successfully.[140–149] Therefore, these dual-phase hybrid free-radical capturers often possess a higher fire-retardant efficiency than the condensed-phase ones.

5 | CONCLUSIONS AND OUTLOOK

5.1 | Conclusions

In summary, most of the gaseous-phase free-radical scavengers are single-component systems, and they show satisfactory efficiencies in thermo-oxidative degradation and flame-retardancy but often produce large amounts of toxic and dense smokes during combustion. In comparison, the condensed-phase free radical scavengers reduce the smoke release during combustion and improve the thermo-oxidative stability of polymeric nanocomposites more significantly. However, to achieve a satisfactory fire-resistant effect in a polymer, they need to be combined with traditional flame retardants or chemically modified with flame-retardant elements.[150–153] By contrast, the dual-phase free-radical scavengers have demonstrated desired fire-retardant, smoke-suppressant, and anti-oxidation properties of polymers.

In general, there are three major free-radical scavenging reactions for inhibiting the combustion of polymers[154]: (1) addition reactions (e.g., addition and deactivation of the double bond on C_{60}); (2) redox reactions (e.g., variable rare earth metal ions); and (3) coupling or disproportionation reactions to generate neutral, stable and non-flammable molecules (e.g., reactions between highly active H• and HO• and low-active free radicals generated by organophosphorus, hindered amines, hindered phenols and sulfonamides). Besides, it is worth noting that the type of free radical scavenging reactions strongly depends on the features of the fire retardants, and thus there is no direct one-to-one correspondence between the above scavenging mechanisms and the phases (gas phase or condensed phase or dual phases) where they play a dominant role.

5.2 | Outlook

Up to date, although free-radical fighting effects have been extensively applied to the flame retardancy of many different polymeric matrices.[155] Their use often fails to enable the final polymeric (nano)composites to achieve desired fire-retardant ratings, such as a UL-94 V-0 rating and/or an LOI value higher than 26% unless after functionalization or in combination with traditional fire retardants. For this reason, much work needs to be carried out in the future from the following aspects.[156–158]

(i) For the condensed-phase or dual-phases free-radical scavengers, it is essential to further unveil the correlation between flame retardancy and free-radical scavenging capability to resolve the lack of efficiency optimization, because it is prerequisite for the molecular design of high-efficient free-radical scavengers. Moreover, the interfacial compatibility of free-radical scavengers with the polymers determines the flame retardant efficiency, which is normally neglected during the design of free-radical capturers.

(ii) Also, free-radical capturers are found to show a polymer matrix-dependent characteristic. This means that free-radical capturers should match to the polymer matrix when one chooses a fire retardant for a specific polymer matrix. This is particularly important for the polymers, such as EP, PET, PC, PU, UP etc. that do not experience a free-radical pyrolysis process.[159–162] In particular, free radical capturers can be designed by integrating the gas and condensed phase mechanisms. For example, regarding EP and polyesters, the scavengers are more efficient for the LOI and UL-94 tests but will only lead to limited heat release reductions. Hence, the combination of nanomaterials with this class of scavengers represents a promising strategy for the non-radical pyrolysis polymers. Another example is polyolefin or PVC that obey the mechanism of radical pyrolysis, where the combination of free-radical scavengers and nanocomposites is promising because this combination can both promote the formation of carbonaceous char layer created by the thermal barrier effect of nanomaterials in the condensed phase.

(iii) Furthermore, most free-radical scavengers are generally expensive or produced through complicated chemical synthesis. Therefore, a green sustainable route is highly desirable to create free-radical

fighters using inexpensive starting materials. Also, their synthesis often involves the abundant use of organic solvents, which can lead to high production costs and potential environmental issues, thus restricting their practical applications in industry. Finally, the environmental and human toxicity of free-radical scavengers needs to be carefully evaluated.

(iv) The equally important is a good understanding of the structure-composition-performance relationship of fire-retardant polymeric composites, which is conducive to the creation of advanced fire-retardant polymeric nanocomposites with optimized performances.

In brief, the next-generation free-radical fighters for advanced fire-retardant polymeric nanocomposites are expected to be more efficient, affordable, sustainable, and even renewable.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.