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Recent advances in flame retardant polymers via thiol-ene click chemistry

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ABSTRACT

Within the toolbox of click chemistry, the utilization of thiol-ene reactions for polymer synthesis and modification is a current area of intense attention. Thiol-ene click reactions are used for a broad range of applications. One main area that needs particular attention, where thiol-ene click reactions are immensely employed, is the fabrication of coatings. Especially, when light is used to trigger the thiol-ene reactions, coatings can be prepared within seconds. This method is known as thiol-ene photopolymerization (TEP) and it is a marvelous advancement among light-induced crosslinking systems. TEP is a powerful tool for the preparation of coatings. The synthesis of phosphorous monomers for TEP has prominent importance for improved thermal properties and flame retardancy. Here, the existing literature on flame retardant TEP systems and reactive phosphorous monomers used in TEP are summarized. This review mainly highlights the studies on thermosets yet some linear polymer examples are also included. While this mini-review focuses mostly on TEP, relevant works involving other thiol-ene polymerization routes (i.e. thermal thiol-ene polymerization) rather than photopolymerization are presented. Finally, studies that utilize thiol-ene click reactions to synthesize phosphorous monomers and flame retardants are also given.

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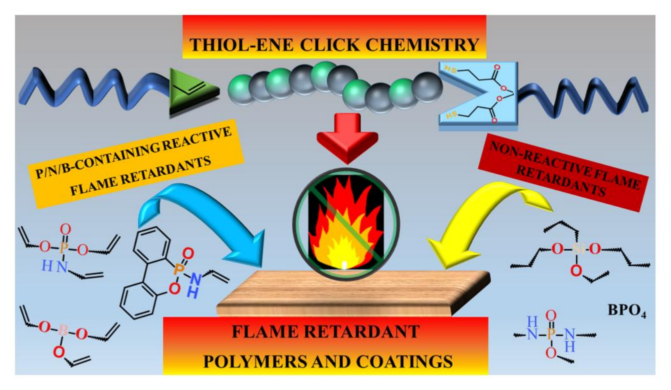
Thiol-ene click; thiol-ene photopolymerization; flame retardant; phosphorus; nitrogen

GRAPHICAL ABSTRACT



1. Introduction

Sharpless and coworkers took inspiration from nature and developed a revolutionary concept; "Click chemistry" in 2001.[1] According to this concept, a click reaction must be modular, wide in scope, solvent-free (if possible), and give very high yields. Additionally, the product must be easily purified without using chromatographic methods. Diels Alder reaction, copper catalyzed-alkyne azide cycloaddition (CuAAC), and thiol-X reactions are the most widely studied click reaction examples.

Among click reactions, thiol-X click reactions are powerful and versatile tools for polymer synthesis and modification. The applications of thiol-X click chemistry span a wide range of disciplines including chemistry, engineering, physics, biology, and medicine. Thiol-X click chemistry reactions include thiol-Michael, thiol-ene, thiol-yne, thiol-epoxy, thiol-bromo, thiol-isocyanate, and thiol-para-fluoro reactions.[2–4] Within the framework of thiol-X click routes, thiol-ene (TE) click reactions are highly preferred for polymer synthesis, polymer post-modification, and coating manufacturing due to the readily available starting materials, mild reaction conditions, degradability, atom economy, etc. The first report for the thiol-ene reaction dates back to 1905, yet its potential in material science was recognized only after 2010.[5–7]

In the case of thermoset coatings, TE click reactions offer a smart and elegant way to prepare coatings with tailorable features. Often in the literature, UV irradiation is used to initiate the TE click reactions polymerization and therefore, the term thiol-ene photopolymerization (TEP) is used. TEP follows a radical-induced step-growth mechanism that brings properties such as low shrinkage, delayed gelation,

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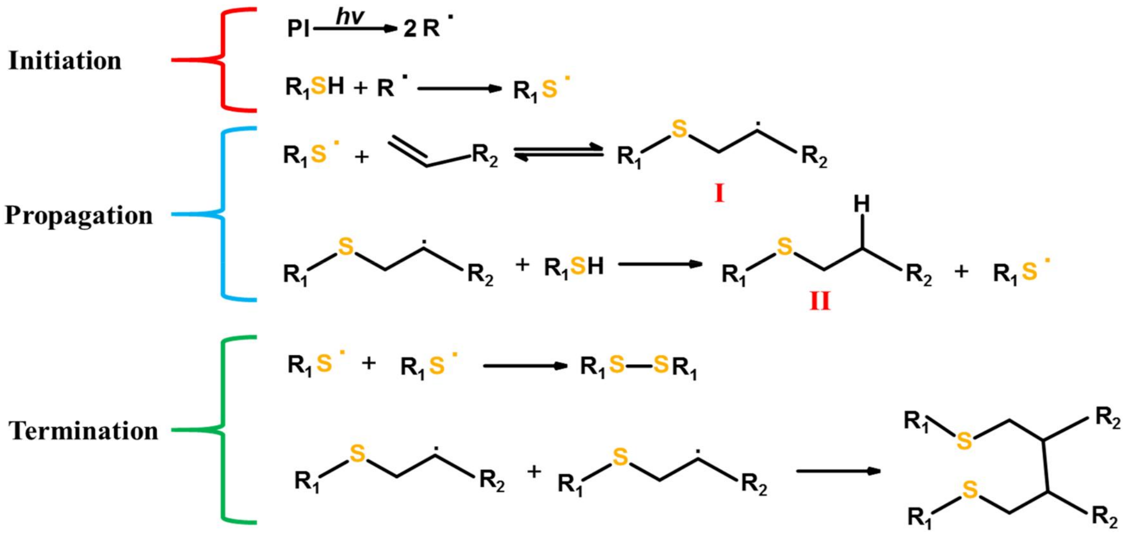


Figure 1. Mechanism of thiol-ene photopolymerization.

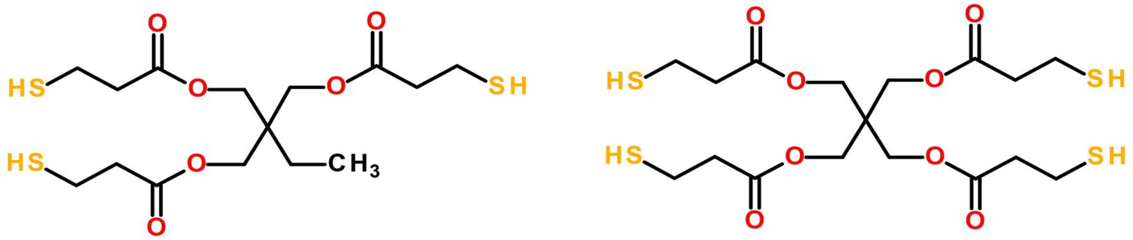
spatial and temporal control, high conversion percentages, and homogeneous networks.[6,7] These features of TEP make it superior to classical free-radical photopolymerization. Furthermore, oxygen inhibition; a huge problem in classical photopolymerization when coatings are considered, is not a problem in TEP.

Photopolymerization is the process of the rapid transformation of liquid monomer and oligomer mixtures into solid 3D networks with the aid of photoinitiators and light irradiation.[8–11] Whilst acrylate- or methacrylate-functional monomers/oligomers are the most widely used species in photopolymerization, vinyl-, allyl, epoxy, or oxetane-functional monomers are also utilized. Photopolymerization follows a free-radical addition polymerization mechanism with the double bond-containing species while photoinitiated cationic ring opening polymerization occurs when oxetanes or epoxy-functional monomers are used. In addition to the term photopolymerization, several terms like photo-crosslinking, light-induced crosslinking, photocuring, etc. are also used. Photopolymerization has several applications such as coatings, 3D printing, printing inks, dentistry, enzyme immobilization, lithium-ion batteries, adhesives, varnishes, photoresists, electronics, etc.[12–23] Photopolymerization is versatile, VOC-free, and displays 5E properties (efficient, enabling, economical, energy-saving, and environment-friendly).[9,24–26] These features make photopolymerization a preferable method over conventional thermal curing processes.[27,28] TEP is a unique technique in the plethora of photopolymerization systems.

Several reviews have been published on the mechanism, kinetics, applications, and features of TE click reactions.[3,6,7,29,30] Herein, the mechanism of TEP is briefly summarized to give an insight to the reduced oxygen inhibition in TEP. The mechanism of TEP is presented in Figure 1. Under UV irradiation the photoinitiator produces radical species which abstract hydrogens from thiols to generate thiyl radicals (RS·). Next, these thiyl radicals react with an –ene to give a new radical (I). The propagation step is completed with a hydrogen transfer from another thiol molecule to give an anti-Markovnikov product (II). In the termination step, any radical specie can react with another radical. It is not depicted in Figure 1 for simplicity, but another thiyl radical (RS·) can also react with I. When multifunctional thiols and multifunctional enes are used, networks are obtained. Structures of some of the common multifunctional –enes and thiols are illustrated in Figure 2.

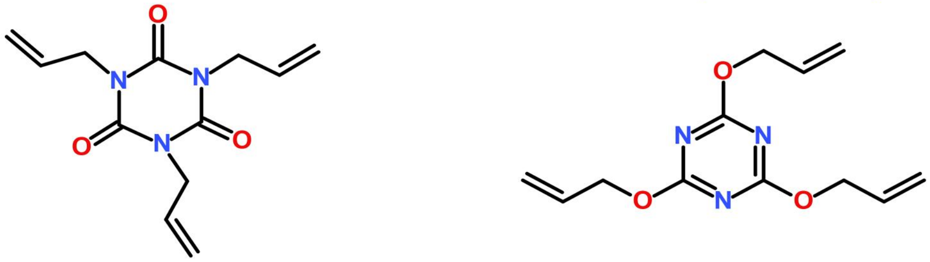
In classical free radical polymerization, after the generation of free radicals from the photoinitiator, they rapidly react with monomers (M) to give high molecular weight propagating polymer radicals (P·). In the presence of air, these propagating chains react with oxygen to give peroxide radicals (POO·) which are incapable of proceeding the monomer addition and polymerization.[31] POO· radicals often react with another propagating chain (P·) or abstract hydrogen and the polymerization is terminated (Figure 3a). On the other hand, in the case of TEP, the hydrogen abstraction from a thiol compound by the peroxide radical leads to the generation of another thiyl radical which can continue to add to the bonds, and thus, the polymerization is not inhibited (Figure 3b). This leads to very high conversions in TEP even in the presence of air.

Another unique feature of TEP is that almost any type of –ene (acrylate, methacrylate, allyl, vinyl, maleimide, etc.) can react with any thiol compound. Moreover, TE click reactions can be conducted in the absence of a photoinitiator in TEP. Generally, TEP is performed with –enes that are incapable of homopolymerization. When homopolymerizable enes such as acrylates or methacrylates are used in TEP, mixed modes of photopolymerization systems occur. Binary (multifunctional thiols + acrylate/methacrylate) or ternary (multifunctional thiols + acrylate/methacrylate + non-homopolymerizable ene) modes of polymerizations are possible in TEP which can be modulated to give thermoset networks with improved thermal and mechanical properties.[32,33] TEP has been used for several applications such as enzyme immobilization,[34] hydrophobic coatings,[35] dental resins,[36] organogels,[37]



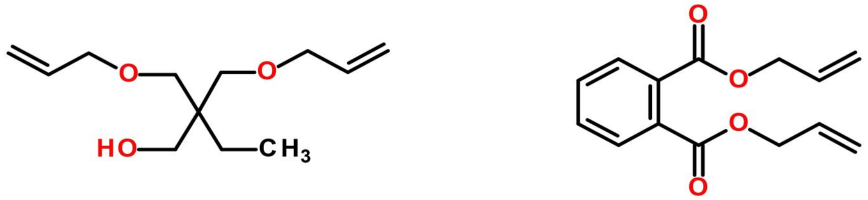
Trimethylolpropane tris(3-mercaptopropionate) (3SH or TMPTMP)

Pentaerythritol tetrakis(3-mercaptopropionate) (4SH or PETMP)



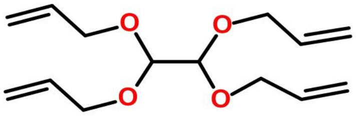
1,3,5-Triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT or TATAO)

2,4,6-Triallyloxy-1,3,5-triazine (TAT)



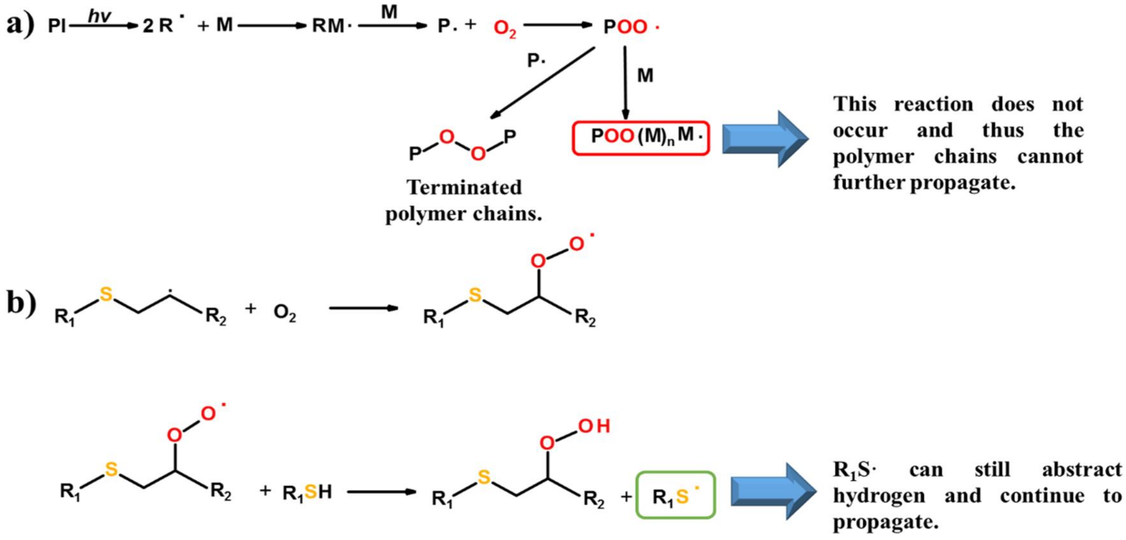
Trimethylolpropane diallyl ether (TMPDE)

Diallyl phthalate (DAP)



Glyoxal bis(diallyl acetal) (GBDA)

Figure 2. Structures of common thiols and –enes used in TEP.



Terminated polymer chains.

This reaction does not occur and thus the polymer chains cannot further propagate.

R₁S· can still abstract hydrogen and continue to propagate.

Figure 3. Oxygen inhibition in classical free-radical polymerization (a) and reduced oxygen inhibition effect in TEP (b).

antibacterial networks,[38] 3D printing,[39] metal recovery,[40] etc.

Despite all these exclusive features of TEP, the polymers obtained *via* TE click reactions are composed of mostly C, H, O, and S, and thus they are flammable. Therefore, in recent years several approaches have been made to prepare TE networks with enhanced thermal properties and flame retardancy.

Flame retardant photocurable materials and P-containing polymers have been previously highlighted in many reviews[41–45] and in books and book chapters[46,47]. Some of these sources touch upon thiol-ene systems but to the author's best knowledge an exclusive review on the flame retardancy of thiol-ene photocured networks has not yet been published.

Often phosphorus-, silicon-, boron, and/or nitrogen-containing monomers with reactive groups (allyl, acrylate, methacrylate, etc.) are synthesized and used in photopolymerization to impart flame resistance (Figure 4). Besides reactive monomers, the incorporation of various non-reactive flame retardant additives is another widely applied strategy to prepare flame retardant photocured networks.

Herein, the existing literature on flame retardant TEP systems and reactive flame retardant monomers used in TEP are summarized. This review mainly focuses on thiol-ene photocured flame retardant thermosets. However, some relevant examples are also presented where thermal thiol-ene polymerization was utilized, or phosphorus-modified linear polymers are synthesized. Additionally, studies that report the use of thiol-ene reactions for flame retardant monomer/additive synthesis are also included in this review.

The flame retardancy of polymeric materials is evaluated with tests such as limiting oxygen index (LOI), UL-94, thermogravimetric analysis (TGA), thermogravimetric analysis coupled to Fourier transform infrared spectroscopy (TGA-FTIR), cone calorimeter, etc. Here, though it was tried to summarize studies involving at least some of these tests and studies that mention flame retardant properties, some works which report the synthesis of phosphorous monomers and utilize thiol-ene click reactions are also discussed.

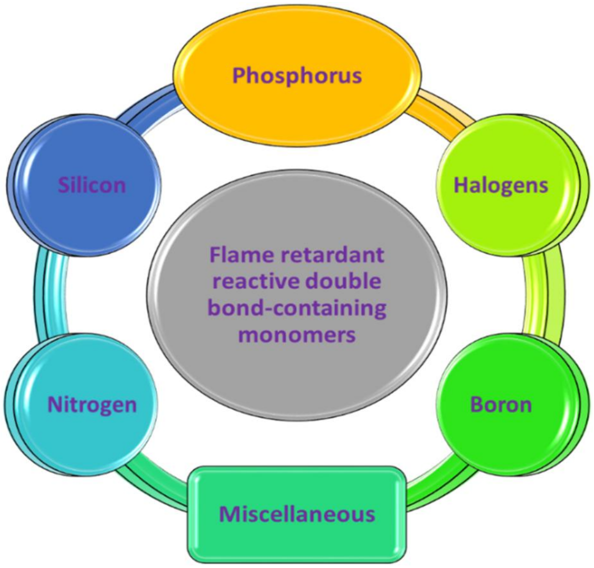


Figure 4. Common elements used for the synthesis of reactive flame retardant monomers.

2. P-containing reactive monomers in TEP

As noted above, the design and synthesis of P-containing monomers for TEP is an important area of research. It is evident from a review of the literature that many phosphorus monomers have been synthesized for TEP. Kahraman and coworkers reported one of the earliest examples of a phosphorus monomer used for thiol-ene photocured coatings.[48] The authors synthesized a mono allyl-functional monomer; allyldiphenyl phosphine oxide (ADPPO). In a previous study by the same groups, the same monomer was used in a classical photopolymerization system containing an epoxy acrylate resin, but it was found that ADPPO did not participate in copolymerization, formed intramolecular dimers and thus the gel contents of the prepared coatings were found to be low.[49] When ADPPO was used in a thiol-ene system (Figure 5), the gel contents increased and the double bond conversions were found to be over 90%. It must be noted that actually in this study, a binary system containing an acrylate oligomer, an ally compound (ADPPO), and a multifunctional thiol, was used. According to the TGA results (under air atmosphere), the char yields were found to increase with increasing amounts of ADPPO. The LOI value for the ADPPO-free coating material was found as 19.5% while it was 27.5% for the polymeric film containing the highest phosphorus content (4.4%).

In another work, cardanol; a bio-based phenol, obtained from cashew nutshell liquid (CNSL), was utilized.[50] Cardanol was reacted with PCl_3 to give a tricardanolic phosphite with a yield of 65.3%. Tricardanolic phosphite was mixed with 4,4′-di(mercaptomethyl) benzophenone and spin-coated on a glass plate. Finally, the resin was cured under UV light. 4,4′-di(mercaptomethyl)benzophenone was functioned as dithiol and as a photoinitiator. The authors stated that it could be expected from this resin to display good flame-retardancy.

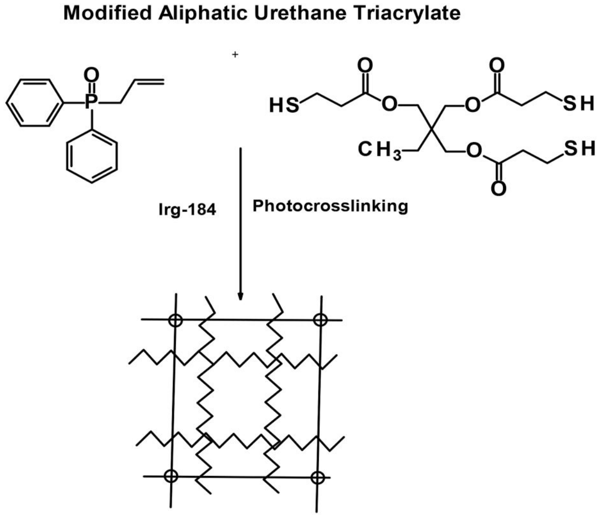


Figure 5. ADPPO-containing binary thiol-ene/acrylate photocured thermosets. Redrawn with permission from ref. 48, copyright ©2011, Elsevier.

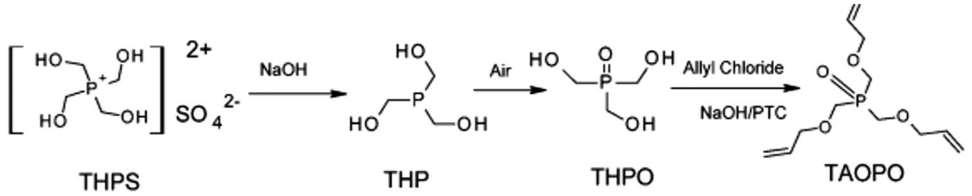


Figure 6. Synthesis of TAOPO. Redrawn with permission from ref. 51, copyright ©2014, Royal Society of chemistry.

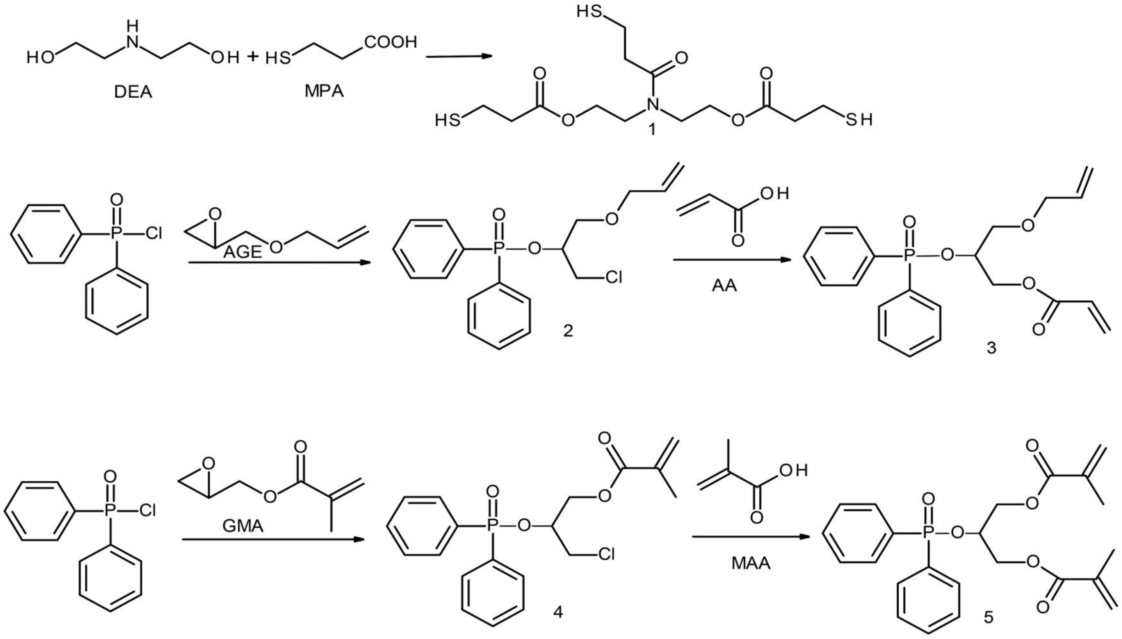


Figure 7. Synthesis of a N-containing multifunctional thiol (1) and two different P-containing monomers (3 and 5). Redrawn with permission from ref. 52, copyright ©2016, Elsevier.

Tan *et al.* prepared a tri-allyl functional phosphorus monomer by using an environmental friendly monomer; tetrakis(hydroxymethyl)phosphonium sulfate (THPS).[51] THPS was converted to tris(hydroxymethyl)phosphine oxide (THPO) by reacting it with an aqueous solution of NaOH (Figure 6). Next, THPO was reacted with allyl chloride in the presence of NaOH and benzyltriethylammonium chloride to give tris(allyloxymethyl)phosphine oxide (TAOPO) as a light yellow liquid with a yield of 80%. TAOPO was mixed with 2,3-bis[(2-mercaptoethyl)thio]-1-propanethiol (tri-thiol) or 4SH and a photoinitiator. After curing under UV irradiation, the obtained coatings displayed good optical properties; excellent transparency and high refractive index values. When a 1:1 thiol to ene ratio was employed the coatings displayed almost 100% gel content values. According to the TGA, results, the coatings prepared with tri-thiol (1:1 thiol:ene) exhibited a char yield of 14.26% whereas the coatings prepared with 4SH produced 14.72% char yield at 850 °C. LOI values were estimated from TGA data and determined as ~23% for both formulations.

Zhang and coworkers prepared a N-containing multifunctional thiol (1) and two different P-containing monomers (3 and 5) as illustrated in Figure 7.[52] One of the phosphorus monomer was designed to have both allyl and acrylate groups (3) and the other had methacrylate groups (5). When these monomers were separately blended with the synthesized trithiol compound (1) at 1:1 thiol to ene ratio, the double bond conversion percentages were found to reach to ~96%. The thiol conversion percentages were found to be lower (60–75%), and this situation was attributed to the simultaneous homopolymerization of the acrylic and methacrylic double bonds. The thermal degradation profiles under nitrogen atmosphere displayed that the films produce 11 ± 2% char yields at 800 °C. Later, the monomer 3 was used to prepare shape memory polymers (SMPs).[53] 3 was crosslinked with thiol-tethered hyperbranched polyimides (BTMP) *via* photocuring. These SMPs displayed good thermomechanical properties and excellent shape memory behavior, with a shape recovery ratio above 90%. Owing to the thermally stable imide rings and phosphorous groups these SMPs were found to be stable up to 300 °C and displayed over 30% char yields at 700 °C under nitrogen atmosphere.

Guo and coworkers prepared flame retardant coatings for wood substrates by using triallyl orthophosphate (TAP), 4SH, N, N-dimethylacrylamide (DMAA), and pentaerythritol triacrylate (PET3A) (Figure 8).[54] The percentages of TAP and DMAA were varied in the formulations. The presence of P and N elements led to a synergistic effect and LOI values of the coating formulations reached up to ~27%. Additionally, the formulations which contained 30 molar % TAP or 20 molar % TAP and 10 molar % DMAA were classified as V-0 according to UL-94 test. Thermogravimetric analysis under nitrogen atmosphere revealed that the

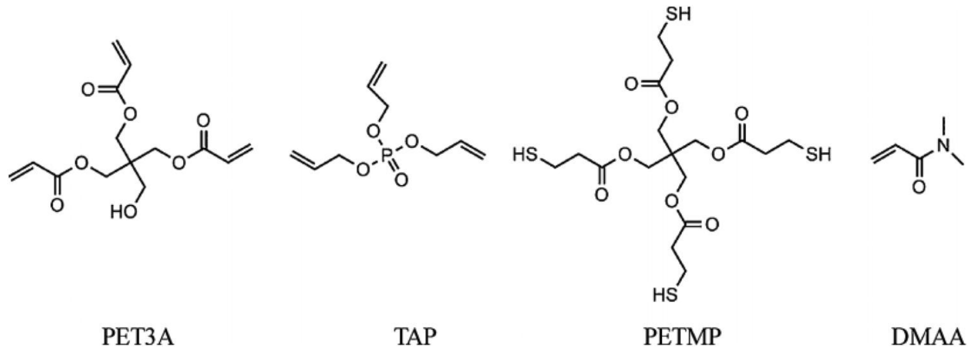


Figure 8. Chemical structures of TAP, DMAA and PET3A. Reused with permission from ref. 54, copyright ©2018, Elsevier.

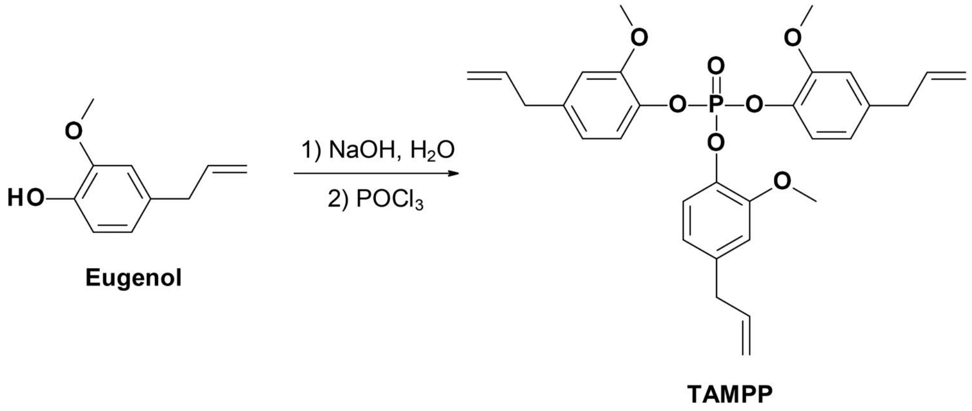


Figure 9. Aqueous synthesis of TAMPP from eugenol. Redrawn with permission from ref. 55, copyright ©2018, American Chemical Society.

coatings containing relatively higher P and N, exhibit as high as 27% char yield at 600 °C. The pyrolysis products of the coatings were investigated *via* TGA-FTIR. The TGA-FTIR results revealed that large amounts of CO_2 and NH_3 gases were released, diluting the oxygen concentration in the gas phase and leading to improved flame retardancy.

Miao *et al.* demonstrated an elegant way for the synthesis of a phosphorus monomer.[55] The authors synthesized a tri-functional biobased allyl compound (tris(4-allyl-2-methoxyphenyl) phosphate (TAMPP)) with 100% renewable carbon content, by using a bio-based monomer; eugenol and performing the reaction in water (Figure 9).

The inherently present ally-group in eugenol makes it a beneficial monomer for the fabrication of thiol-ene photocured coatings and thus several thiol-ene photocured materials were prepared by using eugenol in the literature.[56–58] TAMPP was cured with di, tri, or tetra functional thiols. Dynamic mechanical analysis (DMA) results showed that the networks were homogeneous and both the storage modulus, crosslinking density, and the tanδ values increased with the increase in the thiol functionality as expected. Similarly, DSC results also displayed that the T_g values of the thermosets to escalate as the thiol functionality was increased from 2 to 4. Finally, the TGA results displayed that the films produced from TAMPP and 4SH generate ~34% char yield at 800 °C under a nitrogen atmosphere (Figure 10).

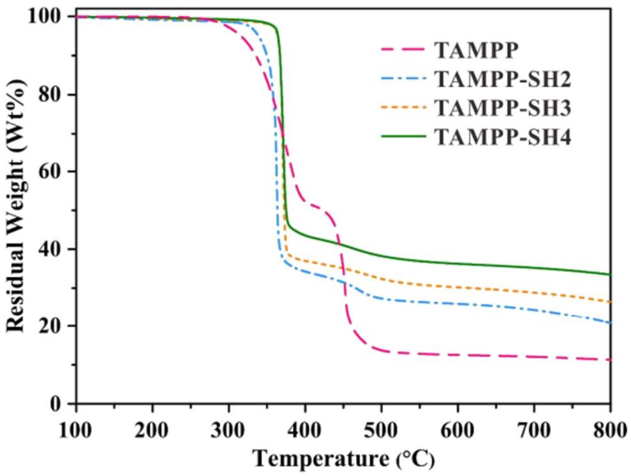


Figure 10. TGA thermograms of TAMPP-based thermosets. Reused with permission from ref. 55, copyright ©2018, American Chemical Society.

The group of Guo reported the synthesis of a 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-containing diallyl compound.[59,60] DOPO is a widely used P-containing compound for the synthesis various flame retardant monomers. The authors prepared a DOPO-based diallyl compound by reacting a DOPO derivative ([(6-Oxido-6H-dibenz [c,e][1,2] oxaphosphorin-6-yl) methyl] butanedioic acid (DDP) with allylglycidyl ether. Next, castor oil was reacted 3-mercaptopropionic acid (MPA) to produce a multifunctional mercaptan molecule (CO-SH). 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane (TTC) was also used as N- and Si-containing monomer to enhance flame retardancy. Finally, DDP, CO-SH, and TTC were mixed in different ratios to prepare a series of formulations which were coated on wood substrates, followed by UV curing (Figure 11).[60] The flame retardant effect of

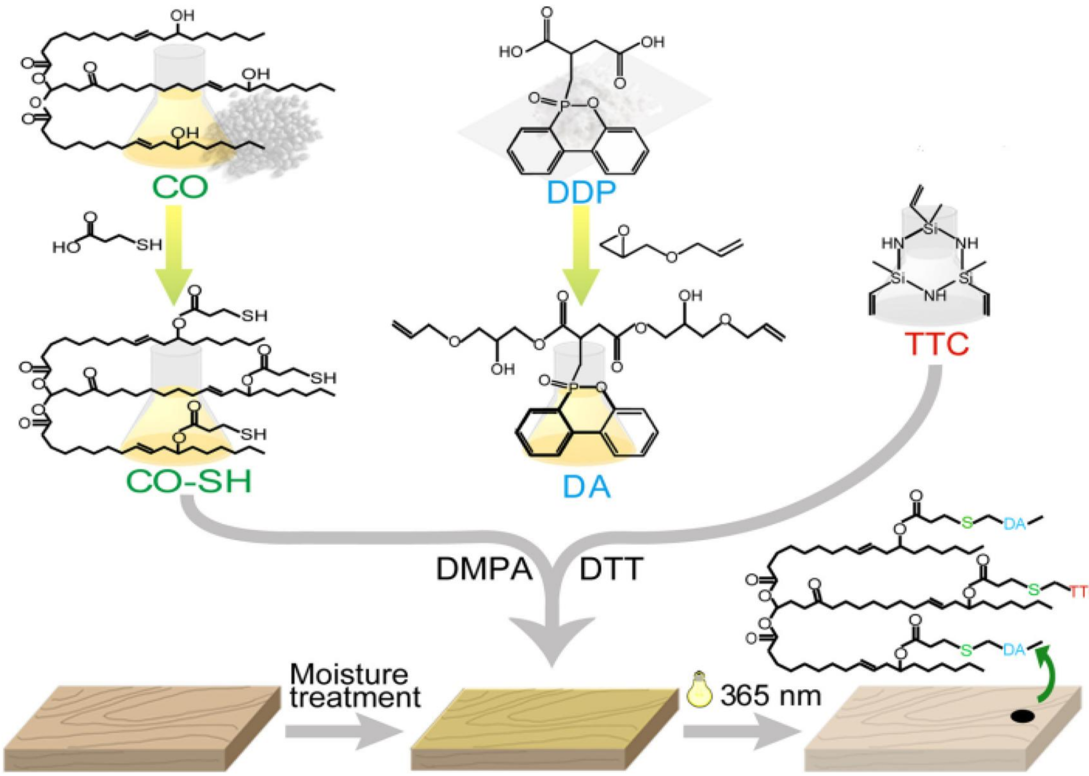


Figure 11. Structures of CO-SH, TTC, and DDP and the preparation coatings on wood substrates. Reused with permission from ref. 60, copyright ©2019, Elsevier.

these systems was assessed by means of a cone calorimetry test. The formulation containing equal moles of DDP and TTC (encoded as F4 in the article) displayed the best results according to the cone test. The peak of heat release rate and the total heat release (THR) of the F4 formulation were found to be lower than the other formulations, indicating a good flame retardancy owing to the P/N/Si synergistic flame retardant effect. The LOI value and UL-94 rating of F4 were 27.52% and V0, respectively.

Li *et al.* reported the fabrication of intumescent flame retardant fiber composite materials.[61] The flax fiber, kenaf fiber, and polypropylene fiber were blended (1:1:2 by mass) and hot-pressed into fiber composites at 180 °C and 8 MPa. 4SH, triallyl cyanurate (TAC), and 2-hydroxyethyl methacrylate phosphate (PM-2) were used to prepare the intumescent flame retardant coating compositions. Phenylbis (2,4,6-trimethylbenzoyl) phosphineoxide (BAPO) was used as the photoinitiator. The best formulation that exhibited the highest LOI value (28.6%) and the lowest total smoke production (2.18 m^2) was obtained when the molar ratio of N:P was 3:2.

Guo *et al.* reported the synthesis of a phosphorus-containing bio-based monomer (MBDPP) from renewable magnolol which is obtained from the Magnolia officinalis plant.[62] Magnolol is an aromatic compound with two allyl groups and two phenolic hydroxyl groups. The presence of allyl groups makes it a suitable material for TEP. Magnolol-derived bis(diphenyl phosphate) (MBDPP) was prepared by reacting magnolol with two moles of diphenyl phosphoryl chloride. MBDPP was cured with either 3SH or 4SH (Figure 12).

The calculated LOI values for MBDPP-3SH and MBDPP-4SH networks were 25.4 and 27.2%, respectively. Cone calorimetry results of MBDPP-3SH and MBDPP-4SH thermosets displayed similar TSP and THR values for both networks. Moreover, as can be seen from Figure 13, both networks produced a large amount of intumescent char. An XPS analysis of these chars revealed the presence of P, C, and O elements. The authors also recorded the Raman spectra of these chars. In Raman spectroscopy, the bands at 1351 and 1598 cm^{-1} are known as D and G bands, respectively. The ratio of the intensity of these bands (I_D/I_G) is recognized as the graphitization degree and the lower I_D/I_G values indicate a higher graphitization degree and higher flame retardancy. The I_D/I_G values for MBDPP-3SH and MBDPP-4SH were found as 3.48 and 3.24, respectively.

Recently, Ozukanar *et al.* utilized from Atherton–Todd reaction and synthesized a phosphorus reactive monomer from DOPO and eugenol.[63] The newly synthesized monomer was named E-DOPO (Figure 14). Another eugenol monomer containing piperazine units was also synthesized (BEECH). E-DOPO and BEECH were blended with other monomers (both allyl and thiol) to prepare a series of flame retardant formulations. The P/N synergistic effect led to improved thermal properties.

3. P-and N-containing monomers in TEP

In the previous section, a selection of P-containing monomers previously used for TEP was presented. Yet, in many works, these phosphorus monomers were blended with N- or Si-containing monomers to take advantage of the

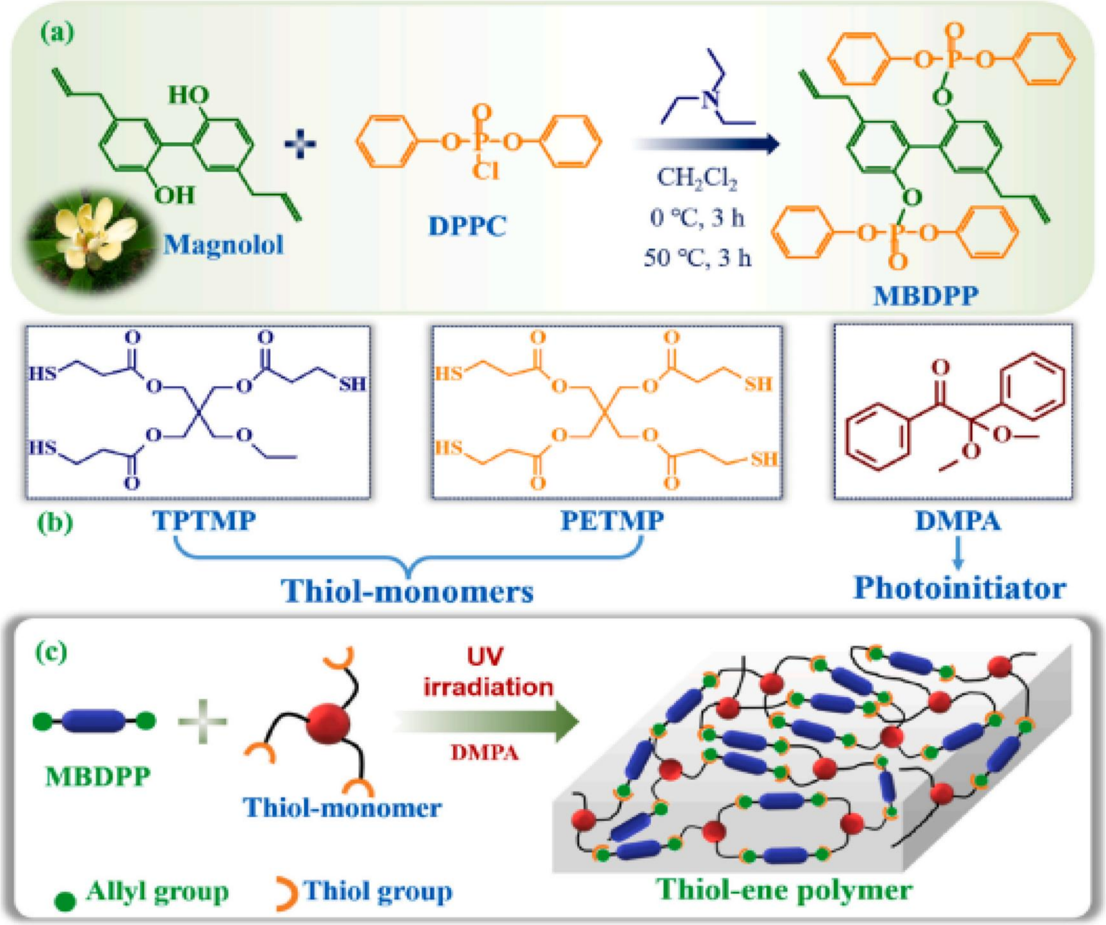


Figure 12. (a) Synthesis of MBDPP, (b) chemical structures of 3SH, 4SH, and DMPA; (c) illustration of the photocured thermosets. Reused with permission from ref. 62, copyright ©2022, Elsevier.

synergistic effect of these elements. A much more elegant approach for exploiting the synergistic effect of N and P is the direct synthesis of compounds having both N and P. Several studies have been devoted to finding smart synthetic pathways to combine P and N in a single flame retardant. In addition to P and N, elements such as B and Si are also beneficial for enhanced flame retardancy, and studies that describe the synthesis of flame retardant monomers that combine three or four of these elements were reported in the literature. Synthesizing compounds bearing P, N, and Si (or B) is challenging. However, the challenge is not to combine these elements into a single molecule but to do it in fewer, preferably in a single step.

Hexachlorophosphazene (HCCP), which is a cyclic compound having alternating phosphorus and nitrogen is another widely used starting compound for flame retardant synthesis. Recently, HCCP was reacted with eugenol,[64] and allyl 4-hydroxybenzoic (AHB)[65] to prepare P- and N-containing flame retardant monomers to be used for TEP. Liu *et al.* synthesized hexa(4-allyl-2-methoxyphenyl) phosphazene (HEP) from the reaction of HCCP and eugenol.[64] HEP was photocured *via* the thiol-ene mechanism by using thiol compounds having different thiol functionality and structures (Figure 15). A range of glass transition temperatures was obtained (20.9–65.1 °C) depending on the type of the thiol used. Generally, thiol-ene networks are characterized by low T_g values due to the nature of the flexible thioether linkages. Here, the highest T_g value (65.1 °C) was observed when 4SH was used and this can be attributed to the presence of increased crosslinking due to the hexa functionality of HEP and the tetrafunctional 4SH. While this network (HEP + 4SH) was classified as V-0 according to the UL-94 test, its LOI value was determined to be 29.7%, which is also higher than the other formulations. The HEP-based networks produced large amounts of intumescent chars after cone calorimeter tests.

Ma *et al.* also utilized HCCP and reacted it with AHB to synthesize a hexa-allyl functional monomer, namely HABP.[65] HABP was mixed with 3SH and 1H,1H,2H,2H-perfluorodecanethiol (PFDT) in different amounts. PFDT was used to impart hydrophobicity. Coating formulations were applied onto wood and glass surfaces. All coatings on glass substrates were transparent but the transparency decreased with increasing amounts of PFDT. The coatings with the highest amount of PFDT displayed a water contact angle of 129°, indicating a good level of hydrophobicity and this formulation also passed the UL-94 test (V-0).

Recently, metal-free click reactions of activated alkynes were used to synthesize novel monomers for TEP.[66,67] The electron-deficient nature of the activated triple bonds makes

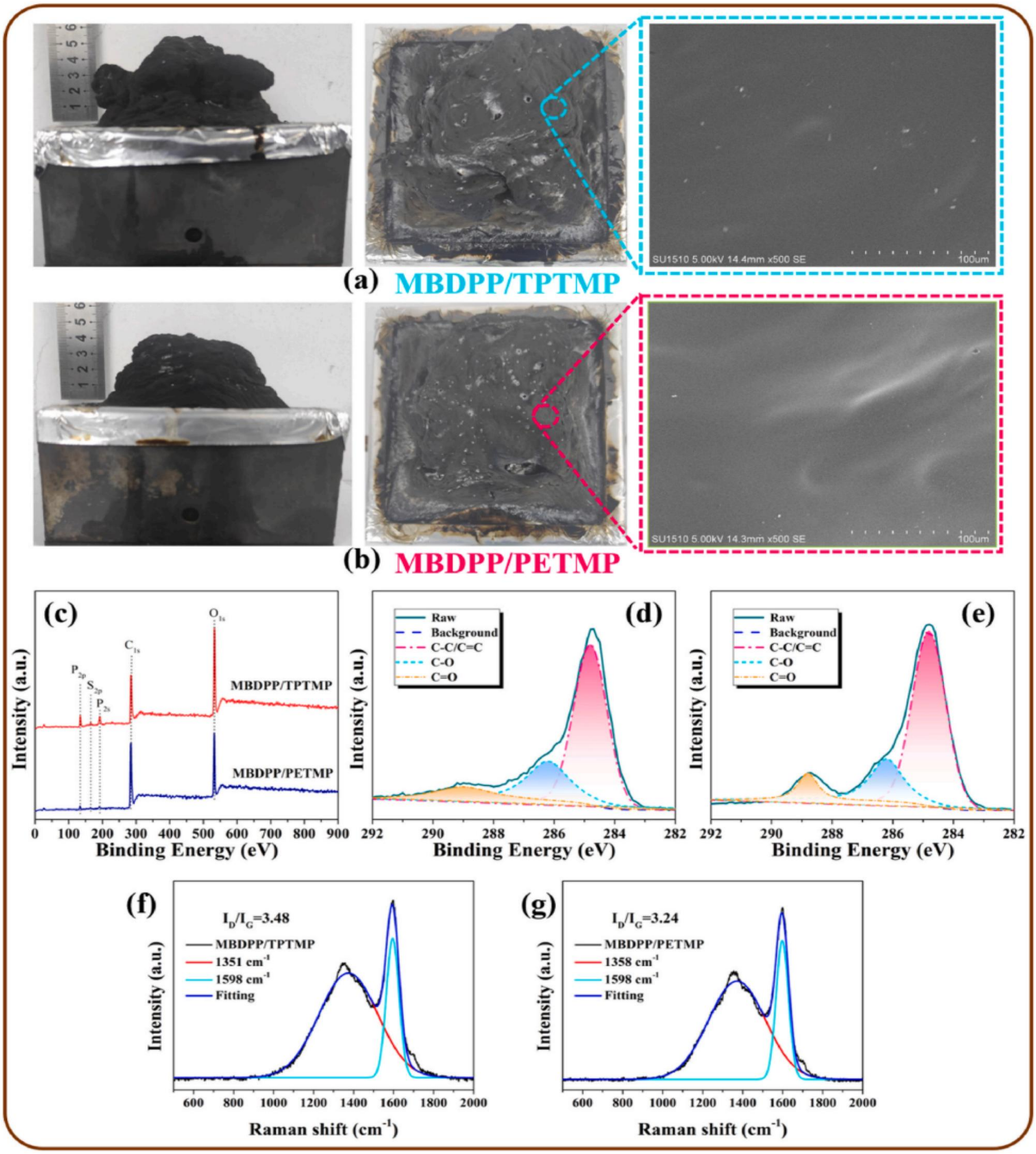


Figure 13. Photographs of the char residues of MBDPP-based networks (a, b). The XPS spectra of the char residues (c, d, and e). The Raman spectra of the char residues. Reused with permission from ref. 62, copyright ©2022, Elsevier.

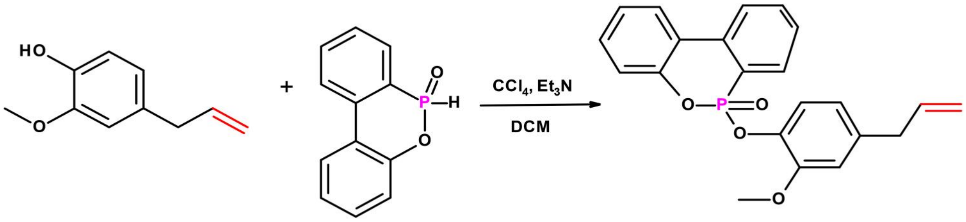


Figure 14. Synthesis of E-DOPO. Redrawn with permission from ref. 63, copyright ©2023, Springer.

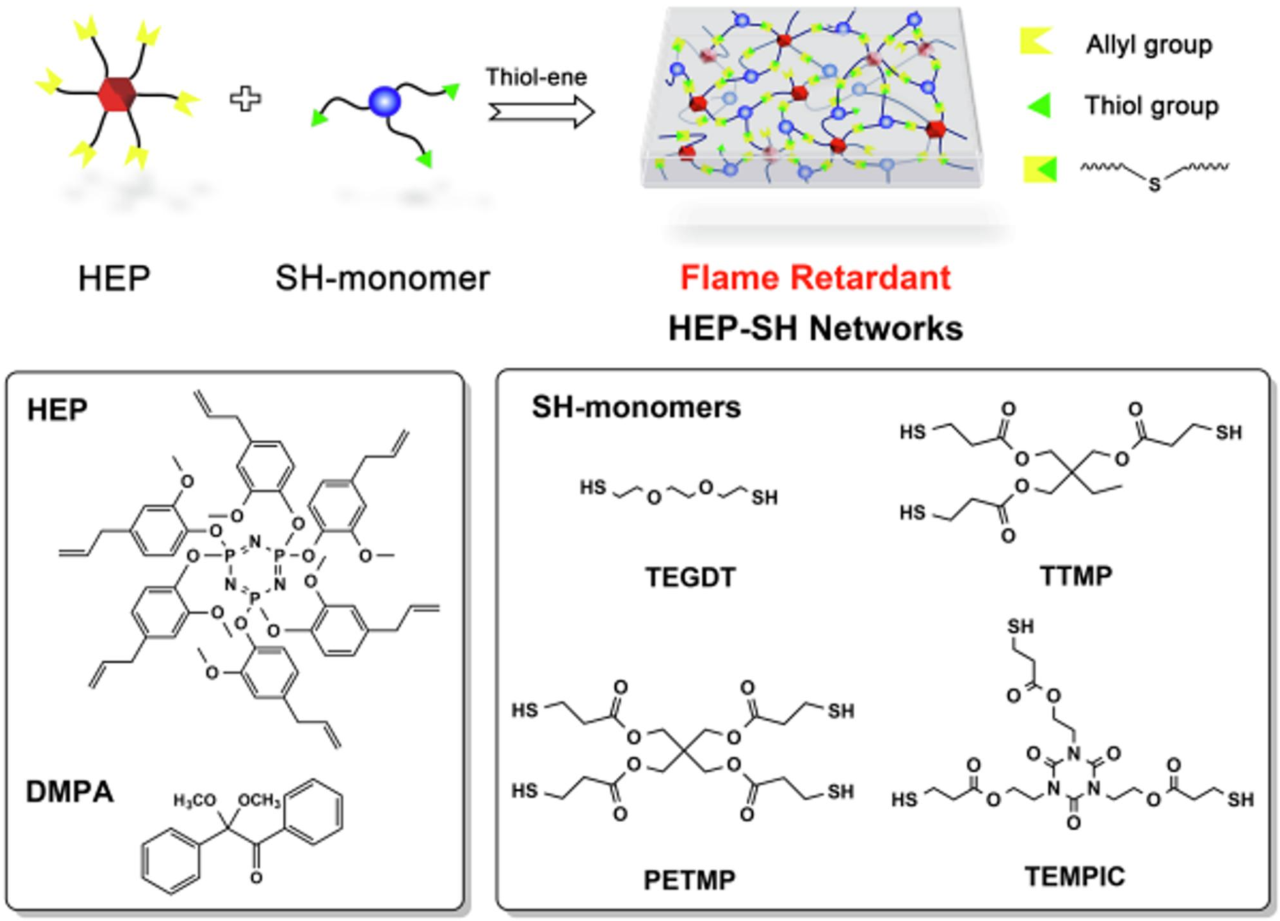


Figure 15. HEP-based thiol-ene photocured networks. Reused with permission from ref. 64, copyright ©2019, Elsevier.

them highly reactive toward organic amines, thiols, and azides. Aza-Michael, thiol-Michael, Diels Alder, and azide-alkyne click reactions can be easily performed on activated alkynes.[68,69] Indeed, in one study three different monomers were prepared by using acetylene dicarboxylic acid diallyl ester (ACDAE) and applying aza-Michael, thiol-Michael, and azide-alkyne click reactions.[66] Figure 16 illustrates the structures of the monomers synthesized *via* the aforementioned routes. The allyl groups of ACDAE did not interfere during these reactions. A P- and N- containing monomer (PTA) was prepared from the azide-alkyne click reaction of ACDAE with bis(2-azidoethyl) phenyl phosphate. This reaction generated two triazole units that are also preferred N-containing rings for synergism and intumescent behavior. Several formulations were prepared and cured under UV light. The formulations composed of only PTA and 4SH produced 17.5% char yield at 600 °C under a nitrogen atmosphere, displayed an LOI value of 23.2%, and rated as V1 according to the UL-94 test.

Later on, the same group of authors synthesized a liquid, DOPO-based, P-and N-containing reactive flame retardant monomer (DTDAE).[67] As can be seen from Figure 17, DTAE was synthesized from the metal-free click reaction of azide-functionalized DOPO and ACDAE. DTDAE was added at different ratios to a mixture of diallyl phthalate (DAP) with 4SH and after UV curing flame retardant thiol-ene photocured thermosets were obtained. When DTDAE was mixed with 4SH and cured (without DAP), the resulting thermosets displayed an LOI value of 27.8% and were classified as V-0 according to UL-94 tests. The authors stated that there is much more potential for metal-free click reactions in material science and flame retardant synthesis.

Yang and coworkers prepared a piperazine-containing phosphorus tetra-functional acrylate monomer (POPHA).[70] POPHA was mixed with thiol-containing silicone hyperbranched polymers (HBPSHs). HBPSHs were prepared from condensation of (3-mercaptopropyl)trimethoxysilane with neopentyl glycol, 1,4-butanediol, ethylene glycol, and diethylene glycol. After curing, transparent, flexible, and self-extinguishing flame retardant materials were obtained owing to the synergism of N, P, and Si elements (Figure 18).

Very recently, Durmaz and coworkers developed a novel, straightforward, robust, fast, and organocatalyst-mediated phospha-Michael reaction (OCPMR) which allows the double-phosphorylation of activated alkynes in one-step.[71] ACDAE was modified with three different phosphorous species (see Figure 19) and novel double-phosphorylated monomers were prepared. These P-containing diallyl compounds were then used to prepare linear or crosslinked polymers *via* TEP. The photocrosslinked networks displayed LOI values in the range of 22.6–26.4% depending on the composition and the type of the phosphorous monomer used.

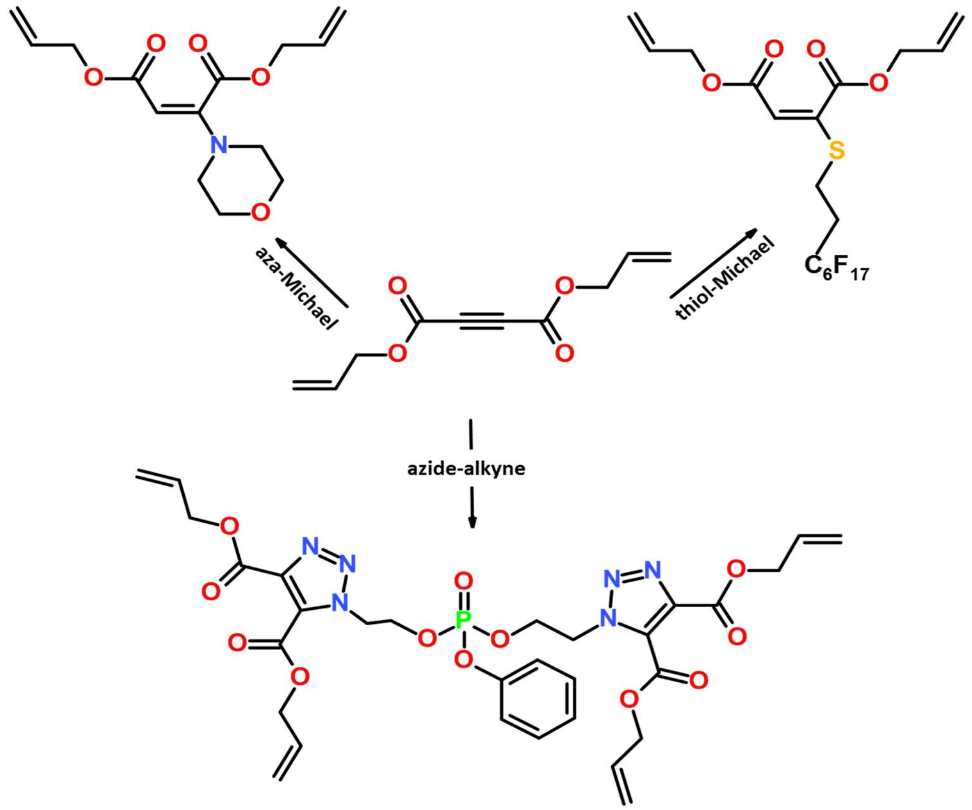


Figure 16. ACDAE-based monomers *via* three different click reactions. Redrawn with permission from ref. 66, copyright ©2021, Wiley.

4. Miscellaneous additives in TEP

In the previous sections, some of the previously reported studies on reactive phosphorus monomers were summarized. In this section, some other strategies to impart flame retardancy to thiol-ene networks will be presented.

Baştürk *et al.* synthesized a P- and N-containing sol–gel coupling agent (BESPPA) and utilized the sol-gel technique to prepare thiol-ene photocured coatings.[72] Sol–gel is a widely employed route to improve both the mechanical and thermal properties of photocurable coatings.[73–78] Figure 20 illustrates the synthetic pathway for BESPPA.

Methacryloxypropyltrimethoxysilane (MAPTMS) was hydrolyzed in an ethyl alcohol/water mixture and then this hydrolyzed MAPTMS was mixed with glyoxal bis diallyl acetal and 4SH. Finally, different amounts of BESPPA were added. The highest amount of BESPPA-containing formulation displayed an LOI value of 26.5%. It must be noted here that BESPPA can be regarded as a reactive phosphorous compound yet, it is preferred to be included in this section since it does not have double/triple bonds that can react with thiols. Herein, it is treated as a sol-gel additive.

Sen and Kahraman suggested a dual-curable route to obtain flame retardant thiol-ene photocured composites.[79] The authors first synthesized 2,2′-diallylbisphenol A dicyanate ester (DA-BADCy) and then mixed it with 3SH, 3-mercaptopropyltrimethoxysilane (MPTMS), and photoinitiators. To further improve the thermal and flame retardancy properties, different amounts of BPO_4 were added to this mixture. Formulations were first cured *via* UV light and then post-cured thermally *via* sequential heating from 120 to 250 °C. In the first stage of the photocuring process, classical TE click reactions take place and in the second step, the cyanate groups undergo thermal cyclotrimerization, and highly crosslinked networks are obtained (Figure 21). The formulation having the highest amount of BPO_4 (∼17%) displayed a T_g of 223 °C, 30.31% char yield at 750 °C (under nitrogen atmosphere), and an LOI value of 33%. The enhanced flame retardancy and the thermal properties stem from the unique combination of aromatic groups, B, P, N, and Si elements, and the thermally stable cyanurate rings.

In another study, phosphorous-modified reactive silica nanoparticles were incorporated into a bismaleimide-containing thiol-ene photocurable formulation.[80] The authors first prepared amine-functional silica nanoparticles. Next, these particles were reacted with furfural. Finally, the imine bonds-containing silica nanoparticles were reacted with DOPO to produce P-and N-containing silica nanoparticles having furfural groups (DDAS) (Figure 22). Furfural was used to introduce furan groups to silica nanoparticles so that the silica nanoparticles would be covalently attached to the polymer matrix *via* maleimide-furan Diels Alder click reactions. The char yields of the 5% DDAS-containing resins were measured as 3.36 and 15.0% at 750 °C under air and nitrogen atmospheres, respectively.

DOPO, which was used to synthesize reactive flame retardant monomers, was also used as an additive without any modification in a thiol-ene photocurable formulation composed of 3SH and pentaerythritol allyl ether (TAE).[81] DOPO was added at 5%. According to the cone calorimetry test, compared to the neat formulation (DOPO-free) the peak heat release rate (PHRR) and total heat release (THR)

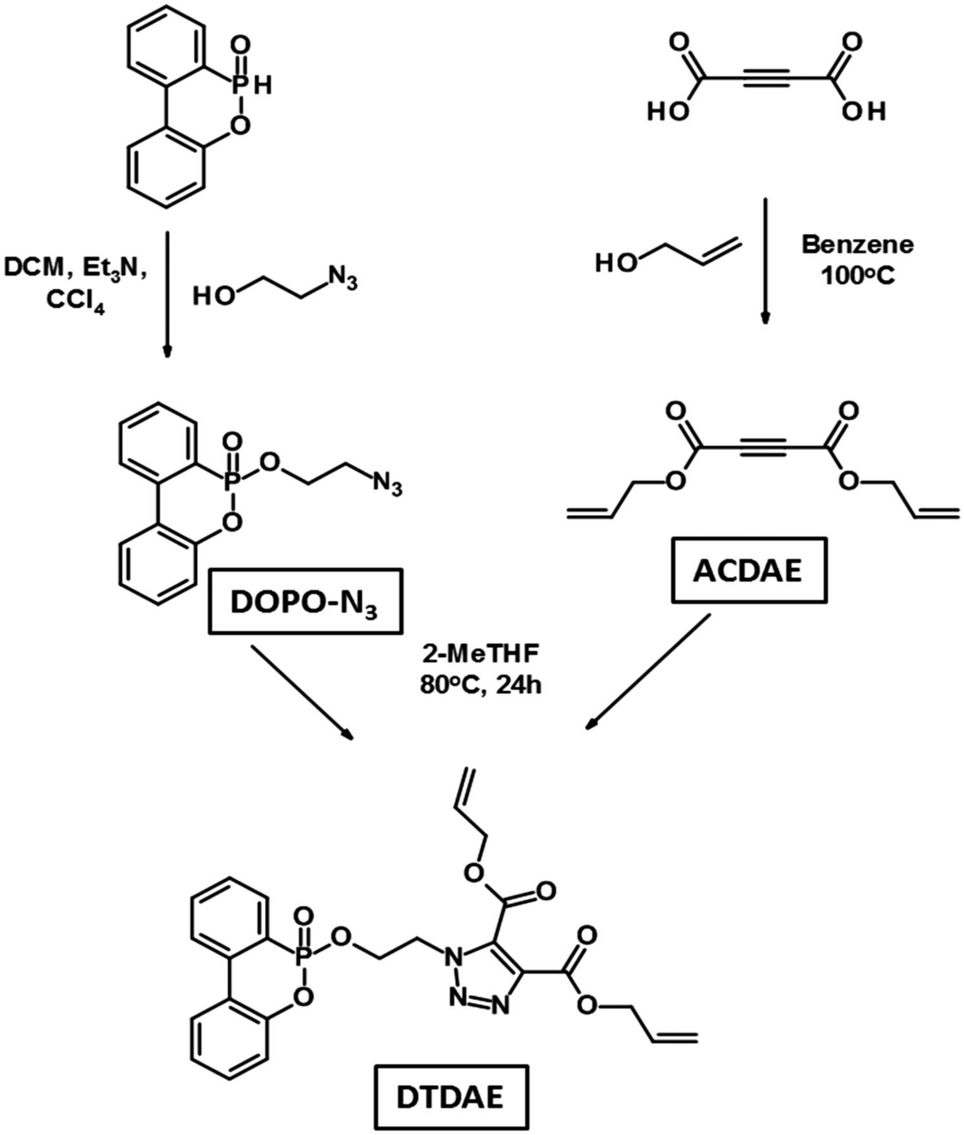


Figure 17. DOPO-based liquid reactive monomer. Redrawn with permission from ref. 67, copyright ©2022, Elsevier.

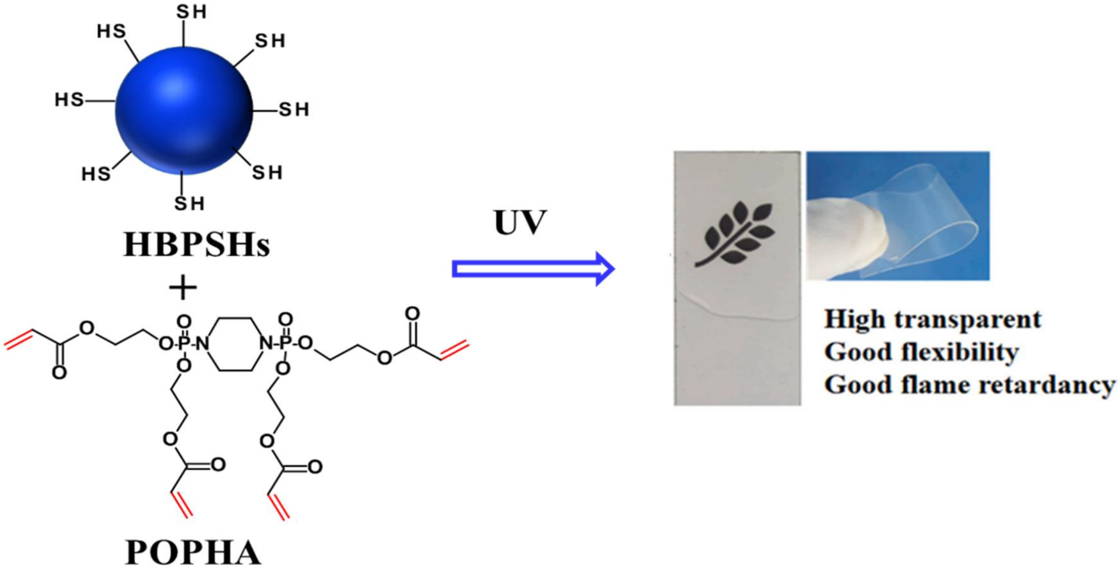


Figure 18. DOPO-based liquid reactive monomer. Reproduced with permission from ref. 70, copyright ©2022, Elsevier.

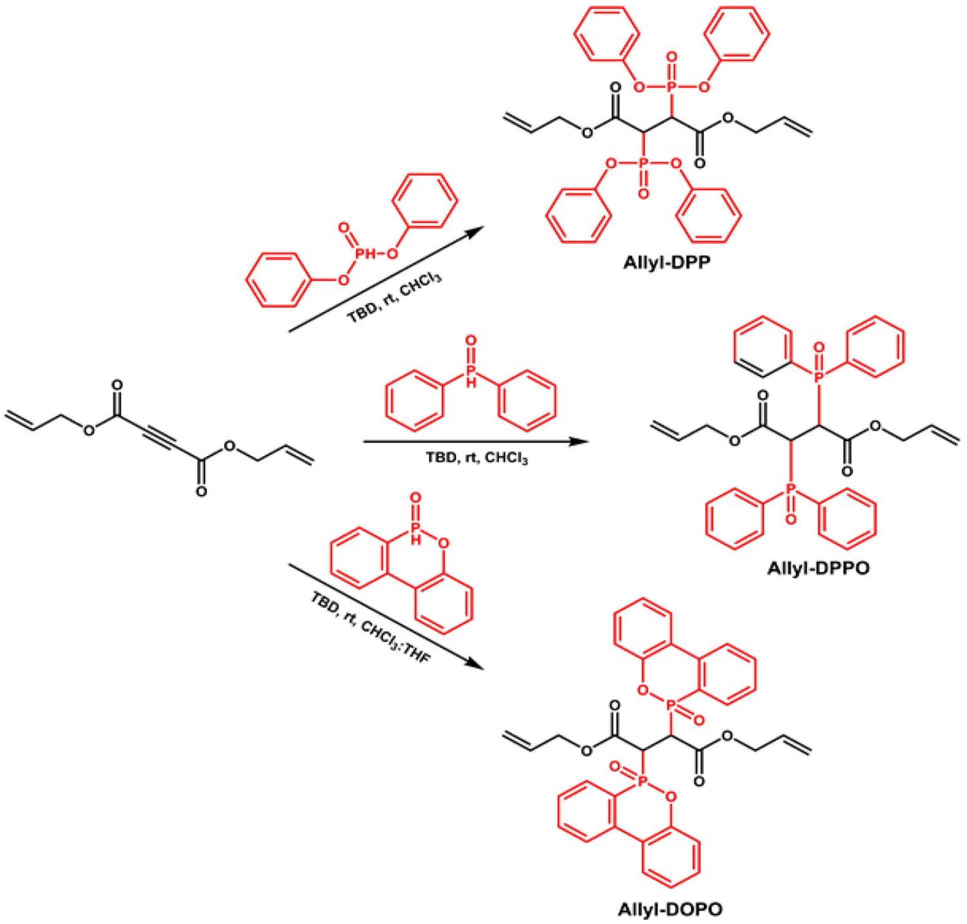


Figure 19. Organocatalyst-mediated phospha-Michael reaction (OCPMR) for the synthesis of double-phosphorylated diallyl monomers. Reproduced with permission from ref. 71, copyright ©2022, American Chemical Society.

of the DOPO-containing thermosets were reduced by 40.9 and 21.8%, respectively.

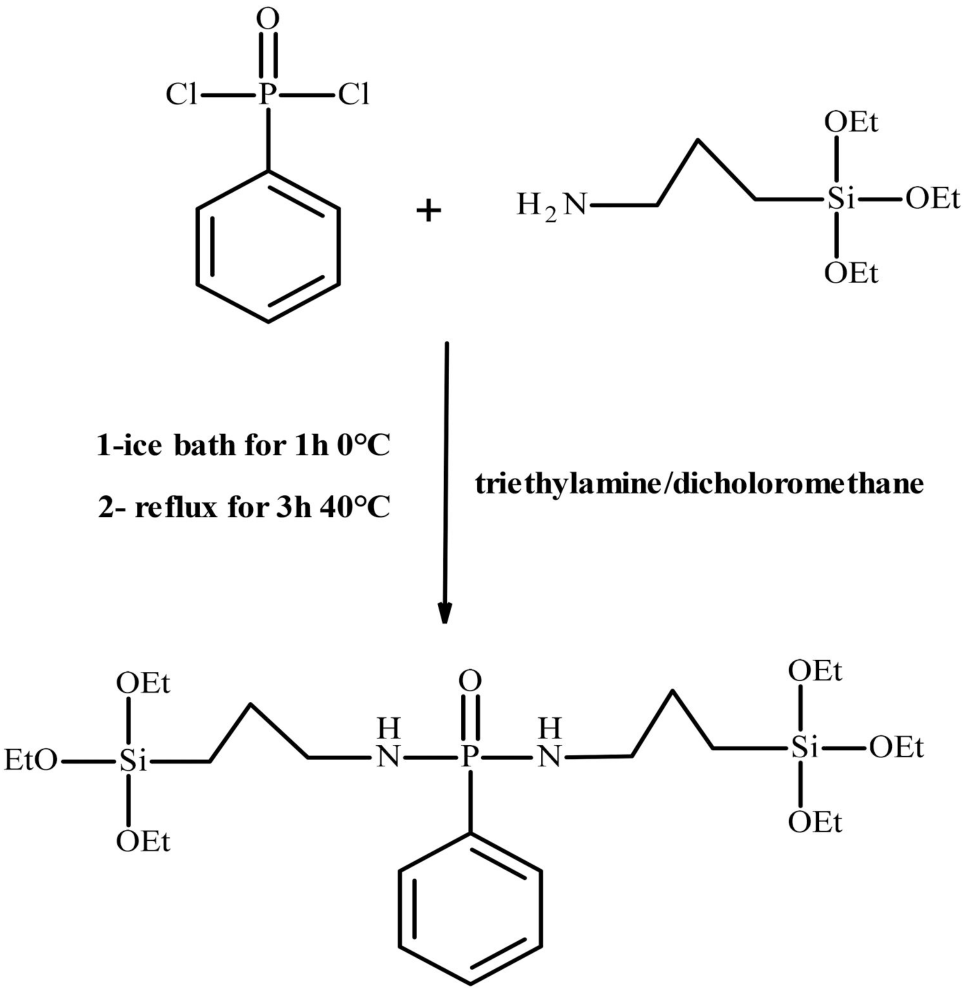
Wang reported the use of a siloxane resin for the preparation of flame retardant thiol-ene photocured resins.[82–84] Phenyltriethoxysilane (PTES) and 3-aminopropyltriethoxysilane (APS) were reacted in an ethanol/water mixture in the presence of tetramethylammonium hydroxide (TMAOH) to produce a siloxane resin (PA).[82] Then, this resin was added (5%) to a base formulation composed of pentaerythritol allyl ether (TAE), 3SH, and a photoinitiator. The siloxane-containing thermosets were found to be thermally stable and more resistant to fire when compared to the thermosets prepared from only TAE and 3SH. To further improve the flame retardancy of the thiol-ene photocured thermosets, in one study Wang modified carbon nanotubes (CNTs) with PA[83] and in another one, Wang and coworkers, used a DOPO-containing silane precursor (DOPO-V) to prepare a siloxane resin as described above.[84] DOPO-V was prepared by reacting DOPO and vinyltrimethoxysilane (VTMS). In each case, the flame retardancy of the composite networks was found to be higher than the pristine thermosets.

Boron-based flame retardants such as zinc borates are widely used in thermoplastics while boron-containing compounds were also used in thermoset materials such as flame retardant epoxy resins[85] and photocurable coatings.[86] In the area of TEP, the use of boron for flame retardancy is very limited. In one study, vinyl boronic acid was used in a thiol-ene/acrylate binary system.[87] Thermosets containing 1.44% B produced 5% char yield at 750 °C (under air atmosphere) and the LOI value of this thermoset was found as 24.2%.

5. Phosphorous monomers and other thiol-ene polymerization routes

In this section, a couple of examples of thermally stable phosphorous-containing polymers that are synthesized *via* TE click reactions initiated by other methods rather than photoinitiation will be given. Instead of photoinitiation, thermal or redox initiation methods can be used for performing TE reactions. Furthermore, thiol-Michael reactions are often conducted in the presence of a base catalyst.

Battig *et al.* prepared hyperbranched phosphorus flame retardants (hb-FRs) for epoxy resins.[88] The hb-FRs (hb-polyphosphoramide (1), hb-polyphosphorodiamidate (2), hb-polyphosphoramidate (3), and hb-polyphosphate (4)) were synthesized from the reaction of three allyl-functional phosphorous monomers (B_3-monomer) and 1,2-ethanedithiol (A_2) *via* thermally initiated thiol-ene radical polymerization (Figure 23). Azobisisobutyronitrile (AIBN) was used as the thermal initiator while N, N-dimethylformamide, or toluene was used as the solvent and the reactions were



BESPPA

Figure 20. P- and N-containing sol-gel additive. Redrawn with permission from ref. 72, copyright ©2013, Elsevier.

conducted at 100 °C for 24 h. The hb-FRs were blended with an epoxy resin and the thermal properties of the cured epoxy networks were characterized. The hb-FRs with a higher N-content were found to be thermally more stable than those with a higher O-content.

Later, the same group of authors prepared hb-FRs similarly but by using an AB_2 monomer instead of utilizing $A_2 + B_3$ polymerization.[89] The AB_2 monomer was synthesized in four steps (Figure 24). First, one mole of $POCl_3$ was reacted with a mole of 4-bromo-1-butanol, followed by two moles of 5-hexen-1-ol. Next, the bromine group was converted to –SH functionality in two steps. The hb-FR synthesized from an AB_2 monomer exhibited a slightly higher flame retardant performance compared to a similar hb-FR which was prepared *via* the $A_2 + B_3$ route. This situation was attributed to the higher phosphorus content in the AB_2 monomer route.

Steinmann and Wurm prepared water-soluble and degradable, linear polyphosphorodiamidates (PPDAs) and polyphosphates (PPEs) (M_w: 2000–13000 g/mol) by using thermal TE click reactions (Figure 25).[90] First, P-containing diallyl monomers were prepared and then reacted with a dithiol (2,2′-(ethylenedioxy)diethanethiol) in the presence of a thermal initiator (AIBN) at 65 °C. Next, the obtained polythioethers were oxidized to polysulfones *via* H_2O_2 and H_3BO_3. This last step increased the polarity of the polymers and rendered them water-soluble. The authors stated that these polymers could be used as flame retardants.

6. TE click reactions for P-containing flame retardant materials

TE click reactions were also used for the synthesis of flame retardants or attaching flame retardants onto different surfaces rather than preparing linear polymers or networks.

El Khatib *et al.* prepared flame retardant polyurethane elastomers (PUE) by using a phosphorous diol compound synthesized *via* TE click reactions.[91] Two different P-containing diols were prepared *via* free-radical thiol-ene reactions with the aid of thermal initiator (AIBN) at 80 °C as depicted in Figure 25. Different ratios of these phosphorylated diols were used to prepare PUEs. The char yields of the PUEs increased with increasing amounts of the phosphorous diols and the LOI increased from 17.2% (for neat

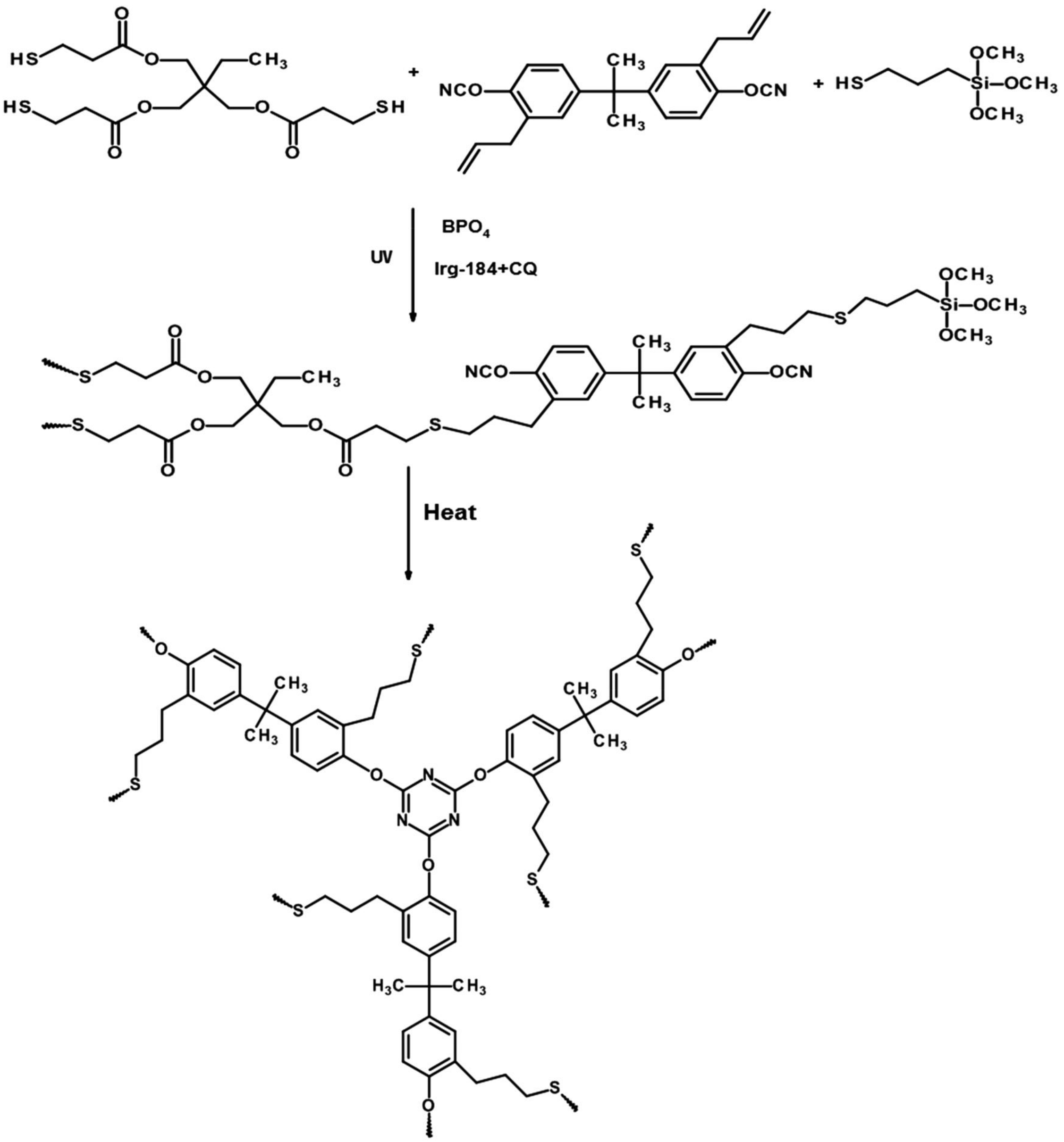


Figure 21. BPO_4-containing dual-cure coatings. Redrawn with permission from ref. 79, copyright ©2014, Elsevier.

PUE) to 23.2% when 3% phosphorous diol, I (see Figure 26) was used.

Gupta and coworkers prepared the above-mentioned phosphorous diol compound (I, Figure 26) but used photoinitiation instead of thermal initiation.[92] The synthesized reactive flame retardant diol was used to fabricate polyurethane foams (PUFs) that were prepared from bio-based polyols. Different amounts of flame retardant diol-containing PUFs were prepared. The cone calorimeter results revealed a significant reduction in peak heat release rate, total heat release, total smoke release, and overall smoke production rate for PUFs containing 1.5 wt% P compared to foam without flame retardant.

In another study, Gupta and coworkers continued their work on flame retardant PUFs.[93] The researchers reacted mercaptenized castor oil (MCO) with diethyl allyl phosphonate (DEAP) using the thiol–ene reaction to prepare P-containing bio-based polyols (Figure 27). MCO, DEAP, and 2-hydroxy-2-methylpropiophenone (photoinitiator) were mixed in a beaker and exposed to ultraviolet radiation for 3 h at room temperature. Foams containing 1.5 wt% P showed a 50% reduction in the peak HRR and a 55% reduction in the total heat release compared to neat PUFs.

Yu and coworkers used TEP for the functionalization of cotton surfaces and to make flame retardant fabrics.[94] The authors synthesized dimethyl-[1,3,5-(3,5-triacryloylhexahydro)triazinyl]-3-oxopropylphosphonate (DHTP) *via* the phospha-Michael reaction of 1,3,5-triacryloylhexahydro-1,3,5-triazine and dimethyl phosphite. Cotton fabrics were coated with MPTMS and finally, they were functionalized with DHTP *via* TE click reactions (Figure 28). 8% DHTP-treated fabrics produced 48.1% char yield at 600 °C under a nitrogen atmosphere. The LOI value of the untreated cotton fabric was determined as 18.3%, whereas the LOI value of the 8% DHTP-treated fabrics treated fabrics was found to be 27.2%.

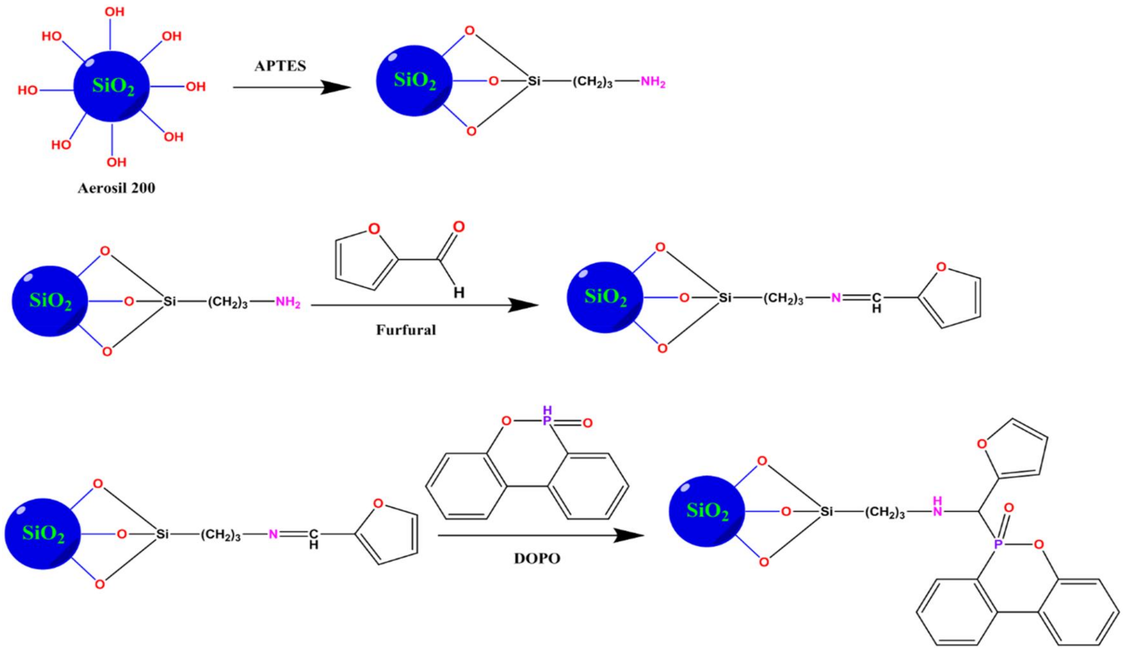


Figure 22. Furan- and DOPO-containing silica nanoparticles. Redrawn with permission from ref. 80, copyright ©2017, Elsevier.

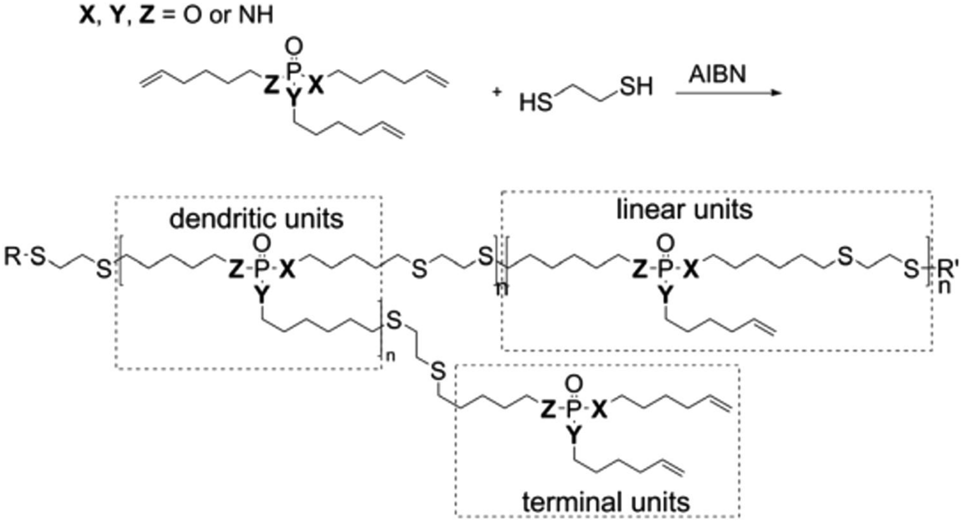


Figure 23. Hyperbranched flame retardant *via* thermal TE click reactions. Reused with permission from ref. 88, copyright ©2019, Royal Society of chemistry.

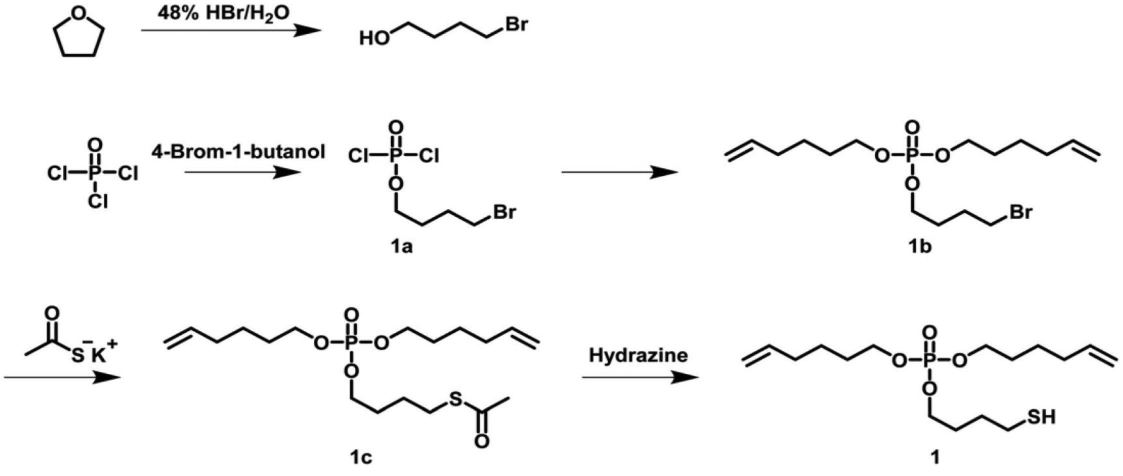


Figure 24. Hyperbranched flame retardant *via* thermal TE click reactions. Reused with permission from ref. 89, copyright ©2019, Royal Society of chemistry.

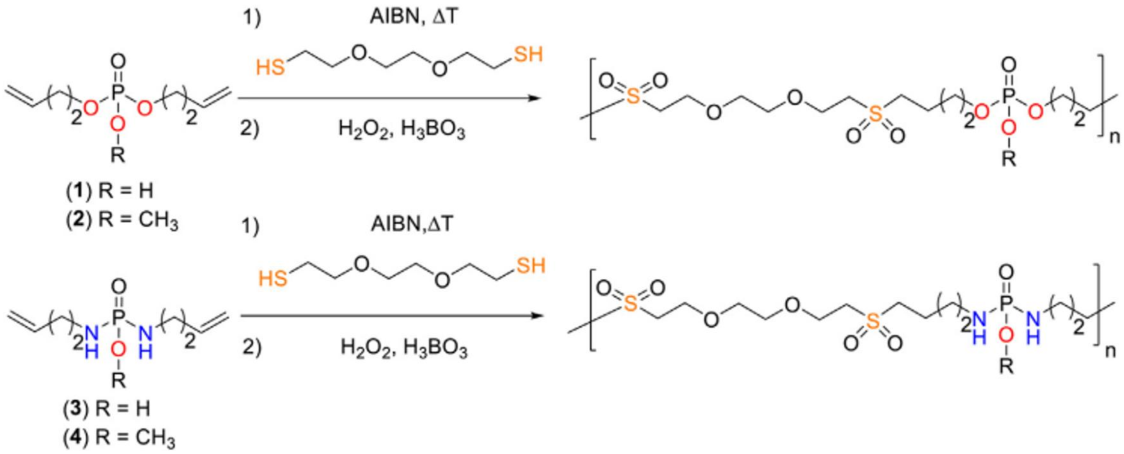


Figure 25. Polyphosphorodiamidates and polyphosphates *via* thermal TE click reactions and their subsequent oxidation. Reused with permission from ref. 90, copyright ©2020, Elsevier.

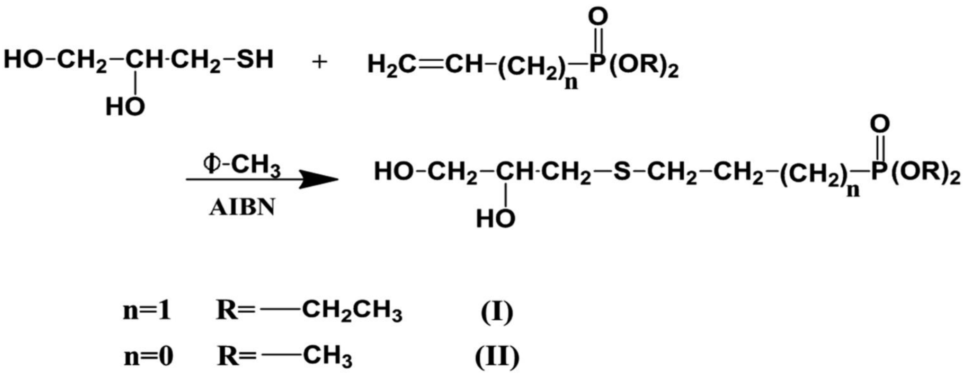


Figure 26. P-containing diols for flame retardant polyurethane elastomers. Redrawn with permission from ref. 91, copyright ©2003, Wiley.

7. Thiol-yne systems

The fabrication of P-containing flame retardant additives or polymers by using TE click reactions is widely studied as can be seen from the examples given herein. On the other hand, there is less number of examples where thiol-yne systems are used.

Durmaz and his coworkers recently reported the synthesis of phosphorus-containing polythioethers *via* 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)-catalyzed thiol-yne Micheal reactions.[95] The authors used several alkynes having electron-withdrawing groups. Owing to the electron-deficient nature of these activated alkynes, they reacted very rapidly with P-containing dithiol compounds, and polythioethers (M_w: 12–29 kDa) were obtained in high yields within 1 min. The general scheme for the suggested route for P-containing polythioethers is given in Figure 29.

The P-containing dithiol compounds were prepared by taking excess amounts of a dithiol (1,6-hexanedithiol or 2,2′-(ethylenedioxy)diethanethiol) and reacting it with phenyl dichlorophosphate. These P-containing polythioethers have the potential to be used as non-migratory polymeric flame retardants for various polymers such as epoxy resins, unsaturated polyester resins, polyurethanes, etc.

Haudum *et al.* reported the synthesis of degradable amino acid-based polyphosphorodiamidate (APdA) monomers.[96] Next, these monomers were photocured with 3SH. In addition to the APdA monomers; 1 and 2, another similar monomer (3) was also synthesized by using propargyl amine (Figure 30).

While monomers 1 and 2 were easily degraded at pH = 7.4, monomer 3 was found to be resistant to degradation. Yet, monomer 3 was completely decomposed to phosphoric acid within 35 days. 3D-printed objects were fabricated by using these monomers. The photocured networks were found to be non–toxic. The authors suggested that these materials could be used for the development of 3D-printable biological scaffolds due to their low cytotoxicity and degradability. The significant feature of this study in terms of flame retardant monomer design is that it shows the hydrolytic instability of phosphoramidate-like molecules. The hydrolytic stability of flame retardants is a highly desirable property and is very important so that the flame retardant does not easily degrade and migrate, thus leading to the loss of flame retardancy.

8. Conclusions and outlook

In this review, the recent advancements in flame retardant TEP systems are summarized. TEP is an advantageous method in many ways, exhibits diverse superior features, and has great potential to be exploited in many application areas.

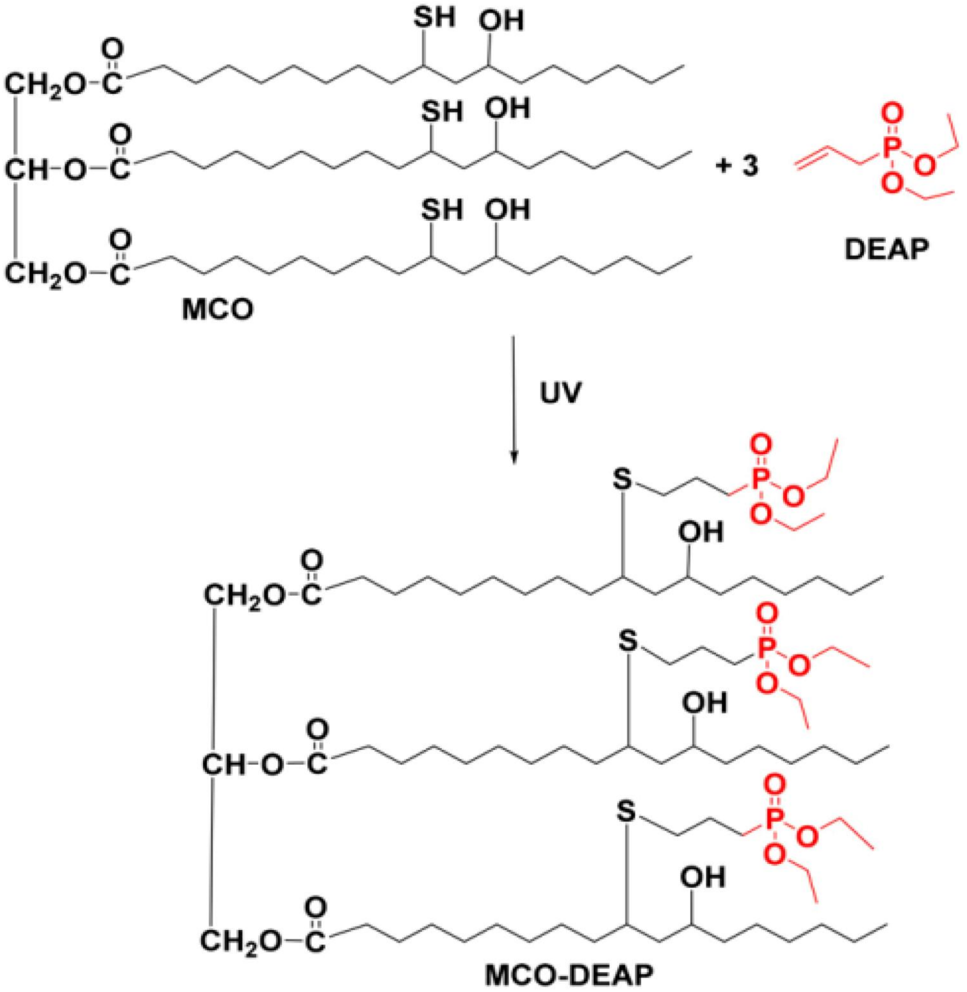


Figure 27. P-containing vegetable oil-based polyol for flame retardant polyurethane foams. Reused with permission from ref. 93, copyright ©2019, Wiley.

Researchers have synthesized several promising reactive P- or P/N-containing monomers for TEP. Besides, a vast range of approaches have been suggested in the literature such as adding flame retardant additives (BPO_4, unmodified DOPO, etc.). In addition, sol-gel routes were also utilized to improve the resistance to flammability.

From the studies presented in the open literature, it can be seen that thermal thiol-ene reactions were used more often than the photoinitiated thiol-ene reactions to prepare linear or hyperbranched P-containing polymers. Moreover, the literature reports examples of the use of TE click reactions for the fabrication of flame retardant monomers for various polymers such as polyurethane foams. TE click reactions were also used for flame retardant surface-treatment applications. Finally, a few examples of thiol-yne reactions are also presented here.

When all these studies are evaluated, a few important details need to be mentioned. First, the use of Cl-containing phosphorous compounds that are used as the starting monomers for the synthesis of flame retardant monomers is not atom-economic and sustainable. As can be seen from the examples given here, generally, phosphoryl chloride (phosphorus oxychloride, $POCl_3$) and its derivatives are used as the starting compounds for the design and synthesis of phosphorous monomers to be used in flame retardant TEP systems. Among similar starting phosphorus compounds; phenyl dichlorophosphate, phenylphosphonic dichloride, diphenyl phosphoryl chloride, methyl dichlorophosphate, HCCP, DOPO, triphenyl phosphine, and methylphosphonic dichloride can be counted. Acrylate, methacrylate or allyl groups can be attached to these precursors by using commercially available monomers such as 2-hydroxyethylacrylate (HEA), 2-hydroxyethylmethacrylate (HEMA), allyl alcohol, allyl monomer, etc. Aside from these petroleum-derived double bond-containing compounds, biophenols such as eugenol and cardanol are also used.

The synthesis of phosphate esters by using these starting compounds and the above-mentioned –OH-functional monomers is straightforward and generally gives high yields. However, the reactions performed by using these halogen-containing phosphorus precursors are not atom-economic due to the release of toxic $HCl_{(g)}$ (often precipitated as triethylammonium chloride salt) and therefore, in terms of Green Chemistry, alternative strategies need to be considered. In recent years, due to the increase in concerns about environmental issues and the rise of the Green Chemistry

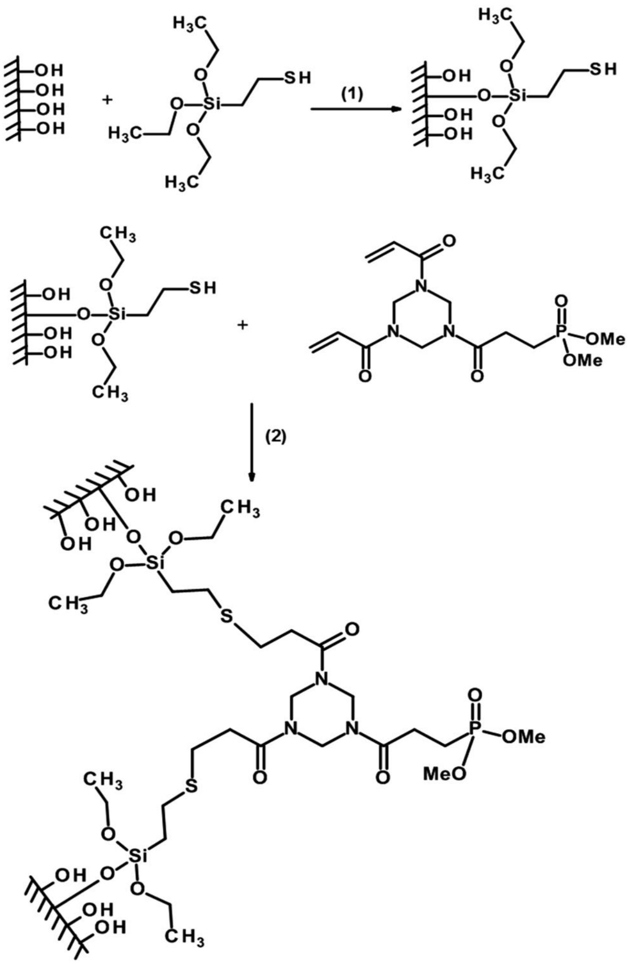


Figure 28. Flame retardant cotton fabrics *via* TE click reaction.[92] Redrawn with permission from ref. 94, copyright ©2017, Elsevier.

concept, researchers started to synthesize P-containing bio-based flame retardants. Nevertheless, PCl_3 or its derivatives are still widely used as the P source.

Recently, Hong *et al.* reviewed phosphorus trichloride-free routes that can be used for the synthesis of P-containing polymers.[97] PH_3, elemental phosphorus (P_4), H_3PO_2, THPS, and tetrakis(hydroxymethyl)phosphonium chloride (THPC) are recommended in that review instead of the Cl-containing phosphorus starting compounds. Phytic acid, which is a bio-based, environmentally friendly substance, is also another useful building block for phosphorous flame retardant monomers. Therefore, it is necessary to find suitable chemical pathways to combine monomers like eugenol or cardanol with the above-mentioned Cl-free phosphorous compounds such as phytic acid or THPS to prepare more sustainable and green flame retardant monomers for TEP. Click chemistry protocols could be useful for this purpose.

The second issue that needs to be mentioned is the lower hydrolytic stability of the phosphate esters or phosphoamidates. The study by Haudum *et al.*[96] and others[98,99] clearly demonstrate the low hydrolytic stability of these types of monomers. Several studies reported the presence of toxic bromine- or P-containing metabolites in human blood or urine.[100] Therefore, the use of non-migratory flame retardant monomers is of great importance to prevent these substances to be released into the environment. This issue not only leads to pollution and adverse health effects, but it also leads to the loss of flame resistant properties. For cross-linked systems such as TEP-based networks, the overall hydrolytic resistance is higher compared to linear polymer matrices. Yet increasing the hydrolytic stability of the flame retardant monomers ensures their safety. Therefore, when

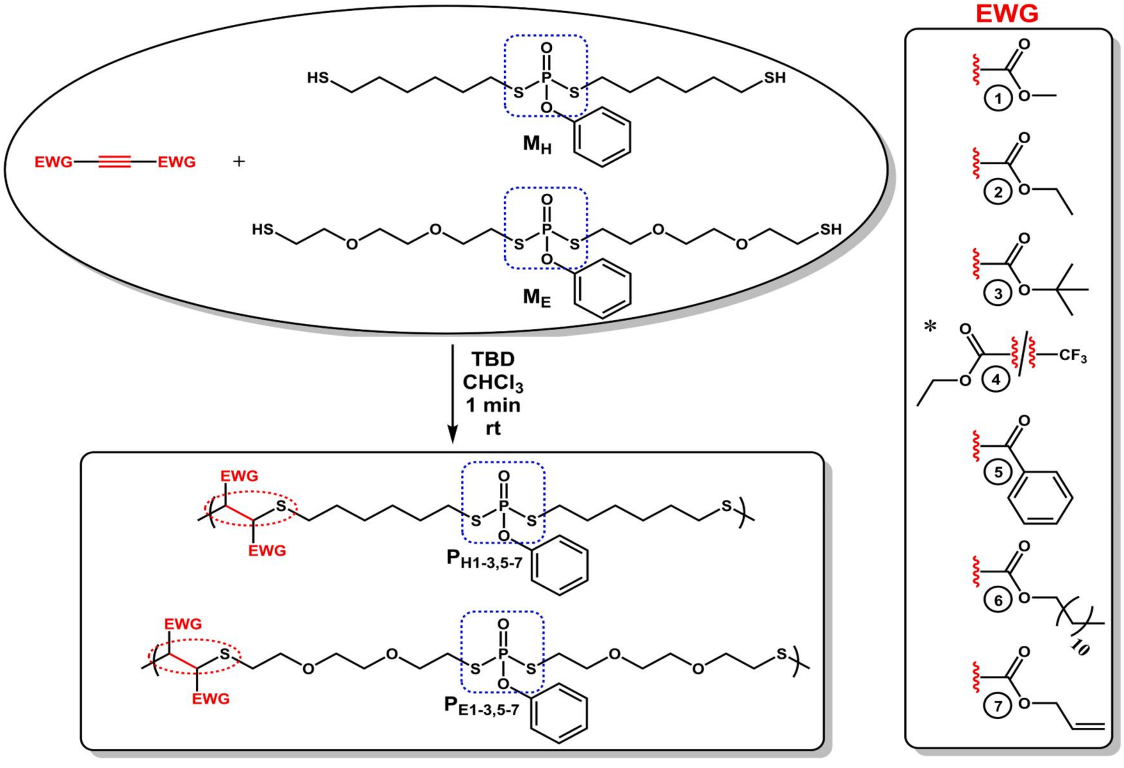


Figure 29. Synthesis of polythioethers from activated alkynes *via* thiol-yne Michael reactions. Reused with permission from ref. 95, copyright ©2022, Elsevier.

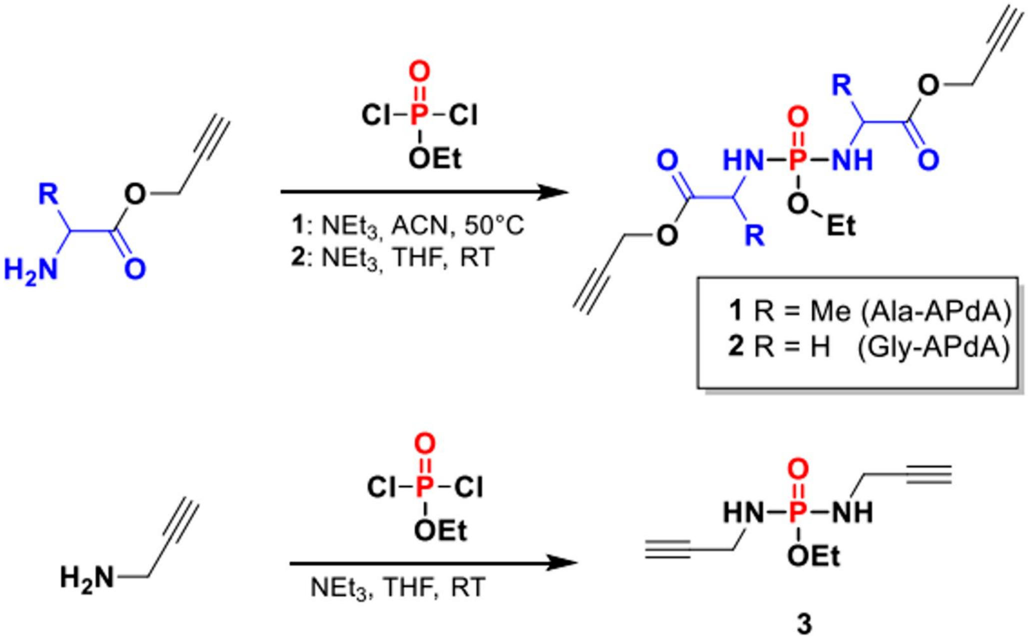


Figure 30. Synthesis of phosphorodiamidate monomers for thiol-yne photopolymerization. Reused with permission from ref. 96, copyright ©2023, American Chemical Society.

designing P- or P/N-containing flame retardants, the hydrolytic resistance also needs to be considered in addition to the utilization of the above-stated Cl-free phosphorous compounds and bio-based building blocks.

Finally, I would like to mention an eye-opening development in the design of flame-retardants. A recent advancement within the framework of flame retardants is the use of machine learning (ML) techniques.[101–103] ML can be used to properly design flame retardant monomers suitable for TEP as well as for other photocurable systems. ML methods analyze the existing literature data and suggest synthetic parameters for an efficient flame retardant. ML methods can answer questions like; What should be the valence state of phosphorus for an efficient flame retardant for TEP?, Should the flame retardant contain aromatic units?, Should the flame retardant contain nitrogen?, or Should the flame retardant be a phosphate, phosphoramidate or phosphodiamidate?, etc. ML methods can bring new horizons to this area.

To prevent or minimize the hazardous effects of fires, the use of flame retardants is necessary. However, we still need to find sustainable, efficient, low-smoke-generating, and nontoxic flame retardants. We need atom economic, preferably one-step, and solvent-free synthetic procedures. While meeting all these requirements, we must not forget that we need to find a cost-effective way.

In conclusion, TE click reactions will continue to be used for the development of flame retardant materials. Thanks to TEP's versatile nature and unique features, its applications are expected to multiply in the future. The studies summarized herein project that there is much more work needed in the area of flame retardant thiol-ene photocurable polymers and coatings. With the development of efficient, sustainable, and innovative flame retardants, flame retardant thiol-ene photocurable materials will find uses in many areas in the future and contribute to the quality of life and people's safety.

Acknowledgments

This paper is dedicated to the memory of Prof. Atilla GÜNGÖR. The author would like to thank all colleagues and group members who have contributed over the years.

Disclosure Statement

The author declares no conflict of interest.

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