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Low Flammability Polymers Based on Phosphorus-Containing Methacrylates

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Abstract—To reduce the flammability of polymers, functional flame retardants have become widespread, among which phosphorus-containing methacrylates occupy a special place. Despite the well-developed issues of their synthesis and use, the search for new monomers of this class remains a demanding task due to their efficiency, environmental friendliness, and a number of other reasons. This review systematizes the results of recent research concerning phosphorus-containing polymerizable monomers of the methacrylate series, the use of which makes it possible to reduce the flammability of the resulting materials and composites.

Currently, high demands are placed on polymers in relation to fire resistance [1]. In this regard, there is a need to create materials that not only will meet all modern standards, but also surpass existing analogues in properties. The relevance of this line of research is confirmed by a large number of scientific papers [2–4] devoted to this topic.

Depending on their chemical structure, fire retardants can prevent and/or suppress combustion processes through chemical, physical, or combined effects in the gas or condensed phase. They can influence individual stages of high-temperature pyrolysis, ignition, and flame propagation during the combustion process [8–10].

The most common way to reduce the flammability of a polymer material is the introduction of fire retardants during the manufacturing process of polymer materials. Fire retardants are subdivided into inert, chemically active (reactive), and additive (that are mechanically combined with polymers to form a homogeneous physical mixture and do not react with them). When chemically active fire retardants interact with a polymer, a new polymer is formed, which differs from the pristine one in composition and chemical structure. Inert flame retardants do not react with a polymer, but they form a physically homogeneous mixture with it; in addition, this can affect the physical structure of the polymer material [10–13].

One of the effective methods for reducing flammability is the synthesis of polymers based on phosphorus-containing (meth)acrylates, which are used as both modifiers and polymer binders [6–12]. The presence of chemical bonds between flame retardant molecules and the polymer matrix not only leads to the improvement of important properties of the parent high-molecular compounds, such as fire resistance, hydrophilicity, and thermal stability, but also makes it possible to obtain polymer materials capable of ion exchange or sorption of transition metal ions from solutions and to synthesize polymers with redox properties and biological activity [15]. Furthermore, the processes of migration, exudation, or leaching of flame retardants are excluded in this case and their content in the material remains constant during its whole life cycle [16]. In addition, phosphorus-containing flame retardants can have a synergistic effect in polymer materials in the presence of other flame retardants, with their impact on the environment being negligible [17–22]. This fact has increased interest in the study of the synthesis and (co)polymerization of phosphorus- and halogen-containing monomers, especially derivatives of acrylic and methacrylic acids. Work in the field of synthesis of copolymers of phosphorus-containing (meth)acrylates has shown that monomers of this class actively enter into a copolymerization reaction to form macromolecular compounds. Most of the research is applied in nature and aims to obtain copolymers with reduced flammability based on unsaturated compounds that are widely used in industry: styrene, alkyl acrylates, vinyl acetate, unsaturated polyesters, etc.

An analysis of the literature on the copolymerization of organophosphorus monomers, including derivatives of (meth)acrylic acids, shows that the syn-

thesis of polymers by a radical mechanism is carried out in the presence of conventional initiators: 2-hydroxy-2-methyl-1-phenylpropanone, benzoyl and di-*tert*-butyl peroxides, AIBN, potassium or ammonium persulfate, and redox systems. Homopolymers and copolymers of (meth)acrylic phosphorus-containing monomers are glassy or rubbery substances that generally swell only to a limited extent in polar solvents. The physical and thermomechanical properties of (co)polymers of phosphorus-containing (meth)acrylates significantly depend on the structure of the monomers. With an increase in the number of alkyl substituents at the phosphorus atom, the glass transition temperature of polymers naturally decreases in the studied groups of monomers. Polymers obtained from derivatives of trivalent phosphorus have a higher glass transition temperature than the corresponding polymers of unsaturated derivatives of pentavalent phosphorus [23]. With an increase in the proportion of phosphorus-containing monomethacrylate units in the macromolecules of copolymers with styrene and methyl methacrylate, the glass transition temperature, heat resistance and thermal stability, and mechanical characteristics of polymers decrease [1, 24].

G.-A. Wang et al. [25] found that the copolymer of 2-methacryloxyethyl phenyl phosphate with methyl methacrylate can effectively inhibit combustion only in the case of phosphorus content of ≥2.17 wt %. C.P. Reghunadhan Nair et al. [26], studying the properties of phosphorus-functionalized polymers including those obtained by statistical copolymerization of methyl methacrylate and styrene with organophosphorus acrylic monomers, showed that their limiting oxygen index increases with an increase in the phosphorus content in the copolymers; the oxygen index achieved a value of 36 vol % at a phosphorus amount of 10.6% in the polymer.

A series of new phosphorus-containing methacrylate monomers based on hydroxyethyl acrylate were synthesized by L. Song and X. Cheng and co-workers. By reacting phenyl dichlorophosphate with ethylenediamine and hydroxyethyl acrylate, a monomer was synthesized [27], whose copolymerization with epoxy acrylate in various ratios gave materials characterized by reduced flammability due to increased charring and denser char layers. The monomer of the formula
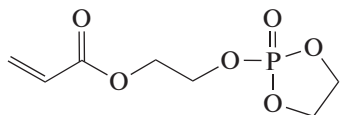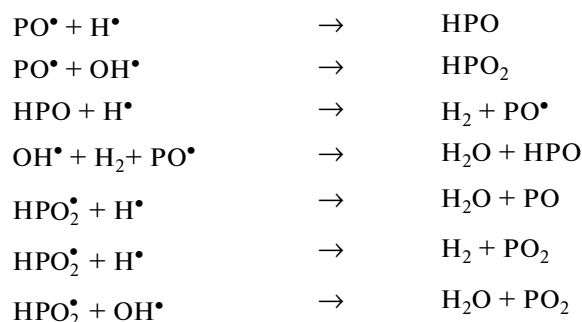

obtained in [28] was copolymerized with unsaturated vinyl ester resins. The polymer had a limiting oxygen index of 26 vol % with a fire retardant content of 15 wt %. By polymerization of the reaction products of epoxyacrylate and the compound presented below
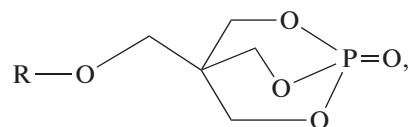
(R is the diisocyanate [29] or di(2-acryloxy-1-ethoxy)phosphonate [30] group), polymers with a limiting oxygen index of 29.5 vol % and a phosphorus content of 2.31 wt % were obtained, having the onset degradation temperature above 280°C and char residue at 700°C up to 36.7 wt %. In all cases, the cited authors explain the successful flame-retarding effect of the developed additives by the presence of P−O−C groups, which have a lower decomposition temperature than C−C bonds and form a char layer as a result of degradation.

There is a relatively large amount of information in the literature about the fire-extinguishing effect of phosphorus, which manifests itself in the gas phase. It has been established that this phenomenon occurs in the presence of P−C bonds. It leads to the formation of phosphorus-containing products: $HPO_2^\bullet$, $PO^\bullet$, $PO_2^\bullet$, and $HPO^\bullet$, which absorb reactive radicals $H^\bullet$ and $OH^\bullet$ in accordance with the following reactions [31−39]:

$$PO^\bullet + H^\bullet \rightarrow HPO$$
$$PO^\bullet + OH^\bullet \rightarrow HPO_2$$
$$HPO + H^\bullet \rightarrow H_2 + PO^\bullet$$
$$OH^\bullet + H_2 + PO^\bullet \rightarrow H_2O + HPO$$
$$HPO_2^\bullet + H^\bullet \rightarrow H_2O + PO$$
$$HPO_2^\bullet + H^\bullet \rightarrow H_2 + PO_2$$
$$HPO_2^\bullet + OH^\bullet \rightarrow H_2O + PO_2$$

Volatile phosphorus compounds are among the best fire inhibitors. S. Levchik [32] reported that phosphorus is on average five times more effective than bromine and ten times more effective than chlorine radicals at the same molar concentration.

It should be noted that the specific mechanism of action of phosphorus-containing flame retardants depends on the polymer structure characteristics, the chemical nature and degree of oxidation of the phosphorus atom, the valence state of phosphorus, and chemical structures of its surrounding groups [40]. In was shown in [42, 43] that the chemical nature of the phosphorus atom that has a saturated bond with carbon/hydrogen increases its activity in the gas phase and phosphorus−oxygen chemical bonds enhance its effect in the condensed phase.

It was found [44−46] that phosphine oxides are weak charring promoters, but they are more active in the gas phase than other phosphorus-containing functional groups with higher phosphorus oxidation states,

since the influence of charring increases with increasing valence and has a higher value in the case of using phosphates.

A. Lorenzetti and coworkers [47], studying the effect of oxidation of phosphinates, phosphonates, and phosphates, came to the conclusion that the oxidation state becomes an important characteristic when the decomposition temperature of fire retardants is in the same temperature range as the polymer network degradation temperature.

It is generally accepted that phosphorus-containing flame retardants are more effective in oxygen-containing or nitrogen-containing polymers, which can be either heteropolymers or polymers with these elements in the side groups. For certain polymeric materials, flame retardants based on phosphorus compounds are more specific than those based on halogen-containing compounds. This refers to the mechanism of action in the condensed phase, where a phosphorus-containing fire retardant reacts with the polymer and participates in its charring [48, 49].

The incorporation of phosphorus-containing moieties into the structure of polymers is effective not only in reducing their flammability, but also in enhancing adhesion, corrosion resistance, and other useful properties. Only phosphorus-based additives prevent smoldering, since fire retardants act at the initial stages of the combustion process in this case, preventing heating and causing dehydration of the polymer and accelerating its charring, so they are more suitable for the pyrolysis zone. The characteristics of phosphorus-containing additives can be improved by synthesizing new multifunctional intumescent systems based on phosphorus-, boron-, nitrogen-, and halogen-containing compounds, whose joint introduction into polymer results in a synergistic effect consisting of the effects of swelling and the formation of a protective char layer with increased strength properties [48, 50, 51].

Oligoester methacrylates (OEMs) are among the most common and commercially important polymerization-curing oligomers. They are used in many fields, such as construction, transportation, aerospace, and home appliance industries; electronics; thermal management systems; adhesives; paints; coatings; and industrial tools. However, OEM polymers have a number of disadvantages, namely, flammability, insufficient thermal stability, and brittleness, which partially limits their use.

There are phosphorus-containing oligoester methacrylates (POEMs) synthesized using glycidyl methacrylate and phosphonic acid dichloride [52]. The product is di-(1-methacryloxy-3-chloro-2-propoxy)methyl phosphonate, known as FOM-II, which is a light brown to red-brown viscous homogeneous liquid and is used to produce polymeric materials with reduced flammability. The product is also used for targeted regulation of the structure and properties of epoxy compounds via chemical interaction with an epoxy oligomer, ensuring the formation of a polymer structure with increased elasticity and resistance to impact loads.

However, it should be noted that the use of FOM-II is problematic due to the fact that there are severe restrictions on the use of phosphonic acid dichloride.

There are products of the reaction of phosphorus trichloride and glycidyl methacrylate, including those obtained using diepoxide oligomers, which are capable of being "incorporated" into the chain [48, 53–57]. In scientific and technical information sources, the term "spacer" is accepted for such "built-in" molecular moieties between (meth)acrylate groups. The generalized structural formula of phosphorus-containing polymerizable compounds with and without a spacer, obtained on the basis of trivalent phosphorus, bioxiranes (E-181 and ED-20), and glycidyl methacrylate can be represented by the scheme
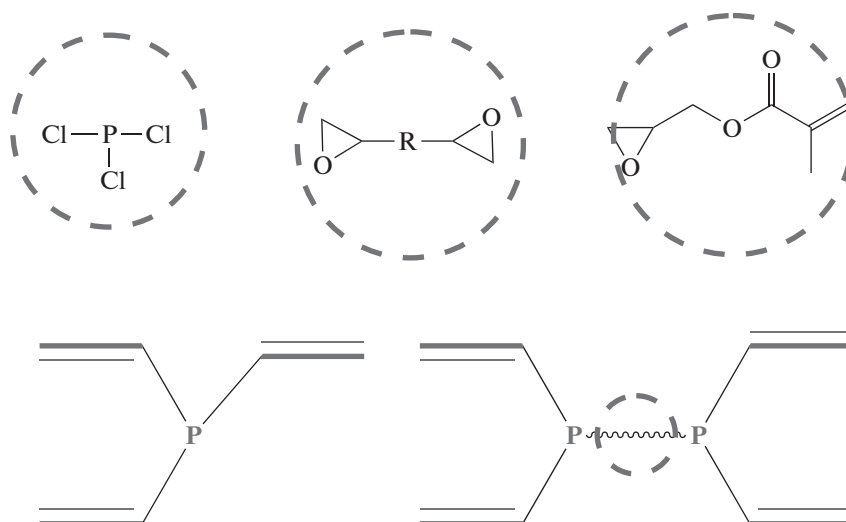
Phosphorus-containing oligoester methacrylates of the aforementioned type are capable of polymerization curing under conditions of photochemical initiation to form three-dimensionally crosslinked polymers with reduced flammability.

Differential thermal analysis studies have established that an aliphatic spacer in the structure of phosphorus-containing polymerizable compounds, including those with trivalent phosphorus, increases the 5% mass loss temperature by 7°C and an aromatic spacer elevates it by 49°C, increasing the char residue from 29 to 34 and 44 wt %, respectively. The limiting oxygen index of crosslinked polymers containing an aromatic spacer is 27 vol %.

However, as was shown in [58], curing of trivalent phosphorus-containing compounds with the use of peroxide initiators is difficult even in the presence of redox systems.

The aforementioned circumstances triggered the development of approach to creation of new phosphorus-containing polymerizable oligoester (meth)acrylate binders with a spacer that are capable of curing by the radical polymerization mechanism under conditions of both UV and peroxide initiation.

Based on the results obtained in [48, 56, 58–61], methods for producing phosphorus-containing compounds using phosphoryl trichloride, glycidyl methacrylate, and bisoxiranes E-181 and ED-20 were developed. The synthesis was carried out in bulk phosphoryl trichloride by the slow addition of oxiranes in the presence of an addition catalyst and a homopolymerization inhibitor.

A trifunctional compound was obtained by reacting glycidyl methacrylate with phosphoryl trichloride in a ratio of 3 : 1, respectively [62]. The monomer, which does not contain a spacer in its structure and has the abbreviated name FOEM-1, was synthesized at temperatures up to 60°C. The reaction scheme for the addition of oxirane compounds to phosphoryl trichloride can be presented as follows:
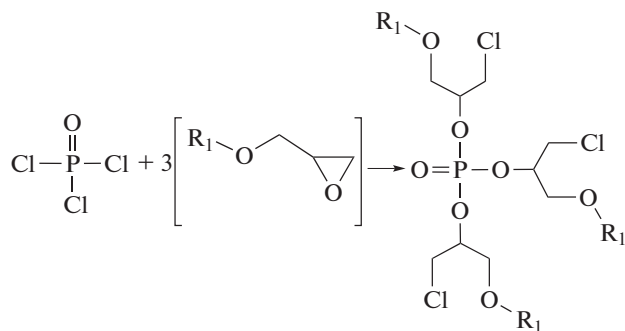
(R_1 is methacryloyl).

A process for synthesizing oligomers FOEM-2 and FOEM-3 containing a spacer in their structure was also patented [59, 60]. The synthesis was carried out in the presence of homopolymerization inhibitors by adding glycidyl methacrylate to phosphoryl trichloride at two chlorine atoms, obtaining a partial substitution intermediate, and subsequent replacing the residual chlorine atom with bifunctional epoxy compound (bioxirane) E-181 or ED-20, which link two phosphorus atoms and provide spatial separation of bis[phosphorus-diether (meth)acrylate]s. The general structure of the synthesized compounds is presented below.
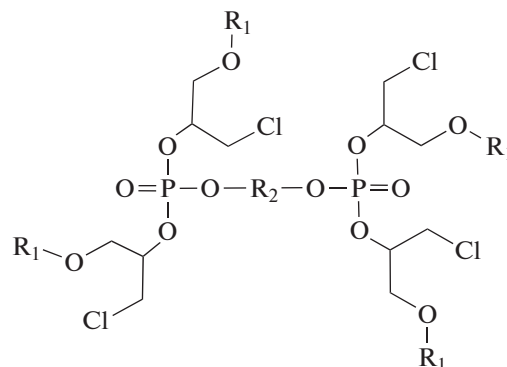
Here R_1 is methacryloyl and R_2 is the residue of the addition structure of the corresponding bioxirane E-181 (FOEM-2) or ED-20 (FOEM-3).

The reaction mixture composition and the physical properties and structure of the products were determined using IR and NMR spectroscopy, gas chromatography, mass spectrometry, and other techniques. The polymerization ability of the resulting compounds was studied using DSC, and the dynamics of photocuring in the bulk was assessed by changes in the dielectric characteristics of the reaction mixture under the influence of UV radiation. The dynamic mechanical properties and heat resistance of the polymers were assessed by the DMA method, the thermal stability of the polymers was characterized by the results of thermogravimetric and STA studies, the mechanical properties were determined using bending strength test, and the resistance to impact loads was additionally examined. The flammability was assessed by determining the limiting oxygen index. The resulting polymers are characterized by reduced flammability with an oxygen index reaching 34 vol %. Cured POEM samples containing an aliphatic and aromatic spacer have an advantage in impact strength. Depending on the nature of the spacer, the impact strength of the polymers reaches 11.0 (FOEM-2) and 4.5 (FOEM-3) kJ/m^2, which is higher by factors of 5 and 2, respectively, than the value characteristic of the FOEM-1 sample without a spacer. The use of synthesized compounds as a binder makes it possible to obtain fiberglass-reinforced plastics with a limiting oxygen index of about 40 vol %. In terms of smoke extinction area in flaming combustion with a standard of no more than 200 m^2/kg, the polymers FOEM-1, FOEM-2, and FOEM-3 are ranked at 113, 100, and 148 m^2/kg, respectively. Smoke generation in pyrolysis made 75, 58, and 85 m^2/kg, respectively. By heat release, the performance of the phosphorus-containing oligoether methacrylates under consideration is 1.5–2 times lower than that of fiberglass plastics with an epoxy binder based on ED-20.

Using DSC and dielectric analysis (DEA), it was established that the resulting POEMs can be cured by photo- and peroxide initiation. The presence and structure of the spacer influences the rate and thermal effects of both initiation methods. DEA studies have established that the presence of an aliphatic spacer in the structure of the compound has a slight effect on the rate of photocuring of the material in bulk ($v_{0.2}^{\text{FOEM-1}} = 8.2 \times 10^{-4}$, $v_{0.2}^{\text{FOEM-2}} 2 = 6.8 \times 10^{-4}$); however, the spacer with an aromatic structure increases the rate of curing ($v_{0.2}^{\text{FOEM-3}} = 2 \times 10^{-3}$).

The resulting new POEMs meet aviation requirements (AP 25 Appendix F, parts IV and V) and can be recommended for the manufacture of passenger cabin floor panels, as well as wall and ceiling panels outside the places of permanent residence of passengers (corridor, kitchen, cockpit, luggage and cargo compartments). In addition, they can be used for the structures of the aircraft external contour (fuselage, fin, wing, elevators and rudder, etc.).

I.A. Novakov et al. [63] reported the results of a study on the radical copolymerization of styrene and epoxy vinyl ester resin with chlorophosphorus- and silicon-containing methacrylates and the influence of the composition of the copolymers on their properties. It has been shown that the copolymers possess reduced flammability and have heat resistance, hardness, and resistance to thermo-oxidative degradation at the levels of a polymer of unmodified vinyl ester resin, but have inferior water resistance.

A study by K. Qin et al. [64] is devoted to imparting inflammability to poly(methyl methacrylate)-based materials via the free radical copolymerization of methyl methacrylate with the phosphorus-containing monomer diethyl-2-(methacryloyloxy) ethyl phosphorothioate. The resulting copolymers are more thermally stable than methyl methacrylate homopolymers and are also characterized by significantly lower flammability, which is due to a high amount of char residue formed during the combustion process.

S. Jiang et al. [65] managed to create optically transparent materials with reduced flammability by copolymerizing methyl methacrylate with a phosphorus-containing acrylic monomer of an aromatic nature, which has the following structure:
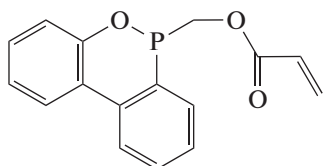
The resulting linear copolymer has the oxygen index exceeding that of PMMA by 12%, already at a fire retardant content of 5 wt %, and the maximum heat release during degradation is reduced by 33%.

It was shown in [61, 66, 67] that chlorinated phosphorus-containing di(meth)acrylates with the structure

$$R-P(OCHCH_2OC-C=CH_2)_2,$$
$$\quad\ \ \overset{\|}{O}\ \ \overset{|}{CH_2Cl}\ \ \overset{\|}{O}\ \ \overset{|}{CH_3}$$
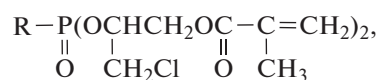
(R is CH_3, CH_2Cl, or OC_6H_5) can copolymerize with styrene-free unsaturated polyester and vinyl ester resins to create a binder composition for fire-resistant fiberglass plastics used in shipbuilding. In terms of mechanical, thermophysical, and water absorption properties, materials of this kind are practically not inferior to fiberglass plastics obtained on the basis of an unmodified binder, but they have a limiting oxygen index of up to 33 vol %. In particular, according to the regulatory and technical documents, the abbreviation FOM-II has been adopted for an organophosphorus monomer with $R = CH_3$, which has double bond functionality of two. However, it should be noted that such a product is a viscous homogeneous liquid from light brown to red-brown in color according to the description. Consequently, there are certain restrictions on its use for optically transparent polymers. The chlorinated phosphorus-containing methacrylate obtained according to the process disclosed in [52] does not have this drawback.

In a number of works [68−72], polymerizable casting compositions containing FOM-II as a flame retardant additive were developed. In the research, the team of authors focused specifically on creating compositions intended for the manufacture of fireproof double-glazed windows for various functional purposes and low-flammability organic glasses. As a result, it was found that by bulk polymerization of compositions including a chlorinated phosphorus-containing dimethacrylate, it is possible to obtain an uncolored, optically transparent polymer with reduced flammability. Glass−polymer structures made from the specified material are able to withstand exposure to flame for 60 min without loss of integrity.

Z. Yildiz et al. [73] developed UV-curable acrylic oligomeric adhesives based on epoxy resin containing vinylphosphonic acid. It has been shown that fire retardant properties increase significantly and the peel strength between the cord fabric and rubber surfaces reaches 50.8 N/cm when the acid is in an amount of 10 wt %.

S. Salman et al. [74] obtained new methacrylate monomers containing phosphonic acid by reacting *tert*-butyl-α-bromomethyl acrylate with triethyl phosphite, followed by selective hydrolysis of phosphonate or *tert*-butyl ester groups with trimethylsilyl bromide and trifluoroacetic acid. A strong influence of monomer structure on the rate of polymerization was observed. The activity of the monomers increased as the spatial hindrance decreased and the ability to form hydrogen bonds increased.

W. Xie et al. [75] managed to enhance the flame resistance of PMMA with maintaining its inherent high transparency. The phosphorus-containing monomer synthesized by the research team was incorporated into PMMA through radical copolymerization.
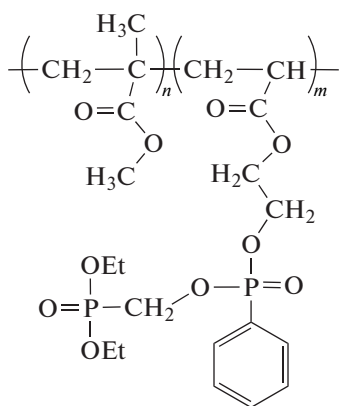
At a phosphorus-containing monomer content of 15 mol %, the copolymer retains good transparency with a light transmission coefficient of 88% in the wavelength range of 600−800 nm and its limiting oxygen index reaches 27.5% to classify it as UL-94 V-0 material.

H. Liu et al. [76] studied the effect of methyl methacrylate on the properties of a transparent fire-retardant copolymer of unsaturated phosphate ester (poly[UPE−co−MMA]), which was obtained by bulk polymerization:
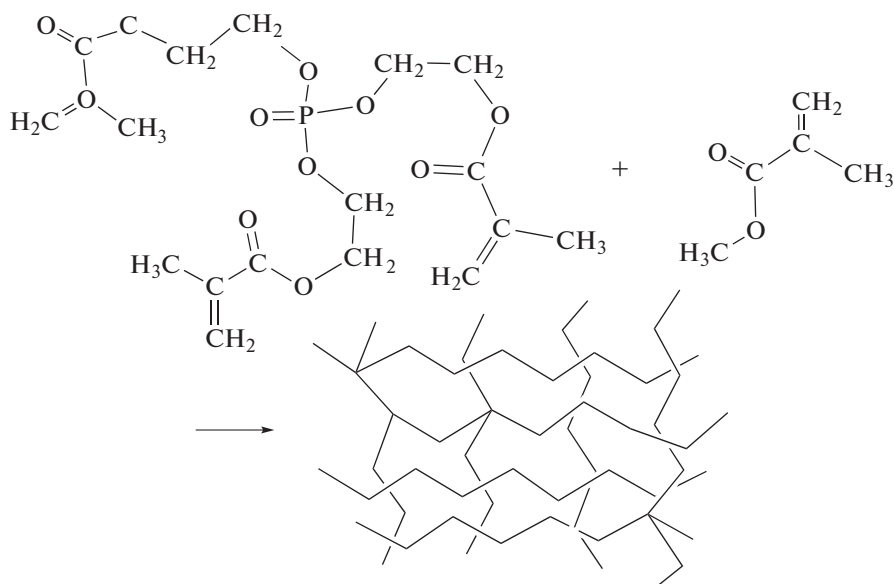
As the MMA content increased from 0 to 50%, the amount of the crosslinked phase increased from 78.46 to 88.93% and the tensile strength increased from 14.62 to 26.5 MPa. Thermogravimetric analysis data showed that the char residue was up to 21.18 wt % at 600°C; as a result of the decomposition of phosphate groups, a layer rich in phosphorus was formed, providing increased thermal stability.

A new type of poly(methyl methacrylate) copolymer was obtained at the College of Chemical Engineering and Materials Science (Hangzhou, China) [77]. Phosphated 2-hydroxyethyl-2-methyl-2-propenoate was chosen as a fire retardant. The phosphine group included in the composition imparts fire resistance, and hydrophilic acrylic phosphate groups provide an antistatic effect. The limiting oxygen index increased from 17.8 to 24.5 vol %. After testing copolymers of methyl methacrylate with the studied phosphated methacrylate using a cone calorimeter, it was found that the latter monomer degrades during combustion to form polyphosphoric acid, which promotes dehydration and carbonization of the polymer matrix with the formation of crosslinks, leading to the formation of a char layer that prevents the spread of fire.

B. Yang et al. [78] obtained by radical copolymerization a material based on phosphorus-containing acrylic monomer (BDPA) and methyl methacrylate:
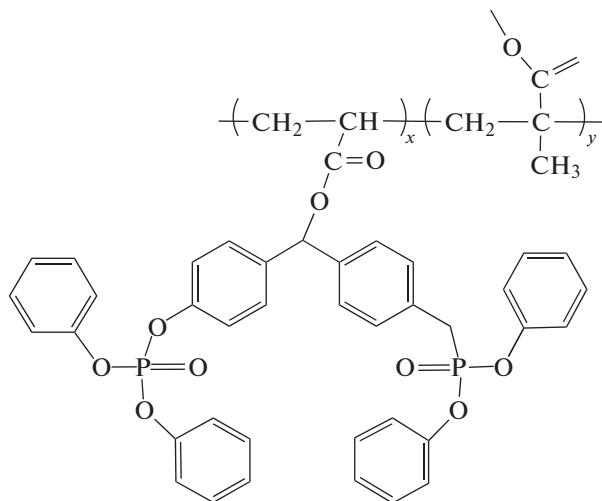
Cone calorimeter testing showed that the peak heat release rate of the MMA−BDPA copolymer was reduced by 29.2% compared to pure PMMA and the char residue in combustion increased.

Acrylates containing pendant phosphonate groups were synthesized by two different routes in [79]. One method involved the reaction of ethyl chloromethyl acrylate and *tert*-butyl bromomethyl acrylate with diethylphosphonoacetic acid. The monomers were polymerized in bulk and solution at 56−64°C using 2,2'-azobisisobutyronitrile. The ethyl ester monomer showed a high tendency to crosslink under these conditions. Selective hydrolysis of the ethyl ester−phosphonic ester compound was carried out with trimethylsilyl bromide to produce the phosphonic acid monomer. In the other method, ethyl hydroxymethyl acrylate and *tert*-butyl hydroxymethyl acrylate reacted with diethyl chlorophosphate. Homopolymerization and copolymerization of these monomers with methyl methacrylate and 2,2'-azobisisobutyronitrile in bulk produced soluble polymers.

Phosphorus-containing acrylates and (di)methacrylates based on 3-(acryloyloxy)-2-hydroxypropyl methacrylate were obtained in [80] by two different methods. One method involved the reaction of 3-(acryloyloxy)-2-hydroxypropyl methacrylate with diethyl chlorophosphate to produce a phosphate-containing (meth)acrylate monomer followed by coupling of this monomer with dihexylamine. In the other method, hydroxyl-containing dimethacrylate monomer was prepared by adding ethanolamine to 3-(acryloyloxy)-2-hydroxypropyl methacrylate followed by reaction with diethyl chlorophosphate. The possibility of including several pendant groups (up to three in this case, but more are possible) suggests use in adhesives and fire retardants where high local concentrations of active groups are desired.

S. Zhu and W. Shi [81] used methacrylate phosphate as reactive flame retardants and additives in epoxy acrylate prepolymer EB600 to compare the difference in their flame retardancy. The results of cone calorimetry show that the sample with cured methacrylate phosphate as an additive flame retardant has higher fire resistance (oxygen index 28 vol %) than the sample with MAP as a reactive flame retardant. The methacrylate phosphate sample of the additive type has lower combustion intensity than the reactive methacrylate phosphate because the degradation of methacrylate phosphate will not contribute to the degradation of EB600 polymer chains.

S. Jiang et al. [82] were the first to synthesize the phosphorus-containing monomer (6-oxido-6H-dibenzo[c,e] [1, 2]oxaphosphinin-6yl)methyl acrylate, which was in situ copolymerized with MMA. The resulting copolymers not only kept relatively high transparency due to good compatibility between monomers, but also exhibited enhanced flame retardancy and heat resistance. In this case, the monomer (6-oxido-6H-dibenzo[c,e] [1, 2]oxaphosphinin-6-yl)methyl acrylate plays the charring function, slowing down the diffusion of heat, oxygen, and gaseous pyrolysis products.

K. Dai et al. [83] prepared a reactive cyclic phosphorus-containing acrylate, which was copolymerized with an unsaturated polyester resin by radical polymerization. Due to the high phosphorus content in the cyclic monomer, its introduction into the formulation led to a noticeable increase in the oxygen index and the formation of char residue during combustion.

Silicon-based acrylate (SHEA) was synthesized by the reaction between 2-hydroxyethyl acrylate and dimethyldichlorosilane [84]. SHEA was mixed with tri(acryloyloxyethyl) phosphate in various ratios to produce a series of UV-curable flame retardant resins. Among TAEP/SHEA resins, the one in 1 : 1 ratio has the highest onset degradation temperature and leaves the largest amount of char residue at 800°C.

A series of UV-curable flame retardant resins was obtained by blending phosphate acrylate (BTP) in different ratios with epoxy acrylate (EA) resin [85]. Materials studies have shown that fire retardant efficiency increases with the addition of BTP. The combustion heat release rate is significantly reduced when BTP is added. Thermogravimetric analysis data shows a decrease in the initial decomposition temperature and an increase in char residue with increasing BTP content compared to the pure epoxy acrylate resin.

C. Alter et al. [86] obtained novel tetrafluorophenylphosphonic acid-functionalized acrylate polymers by free radical polymerization of phosphonic ester acrylate monomers. Dealkylation was accomplished by ester cleavage with bromotrimethylsilane and the subsequent hydrolysis with methanol.

W. Xie et al. [87] proposed a hybrid strategy for producing fireproof PMMA with satisfactory thermal resistance, mechanical properties, and transparency. A new reactive phosphorus-containing monomer is copolymerized with methyl methacrylate to provide the flame retardant function, and an octavinyl polyhedral oligomeric silsesquioxane chemically bonded to the copolymer is used as an enhancer. In addition to maintaining the good optical properties characteristic of PMMA, the resulting material has improved mechanical properties, oxygen index, and a reduced heat release rate.
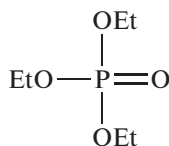
D. Price et al. [88] analyzed both reactive and additive approaches to improving the flame retardancy of (meth)acrylate polymers. In the case of the first approach, MMA was copolymerized with diethyl((meth)acryloxyalkyl) phosphonates of the following structures:
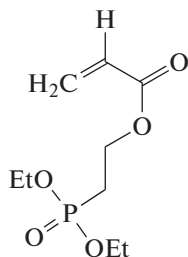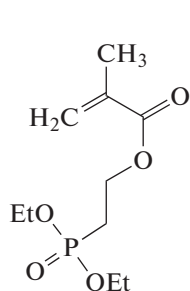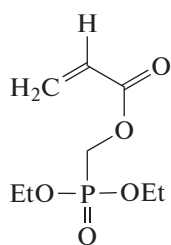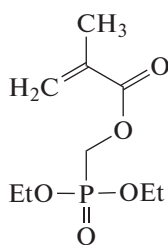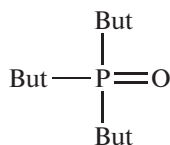
To increase fire resistance, according to the additive approach, the synthesized poly(methyl methacrylate) was modified with phosphorus-containing additives
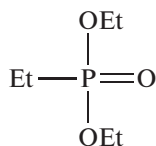
Diethyl ethylphosphonate   Triethyl phosphonate

Tri-*n*-butylphosphine oxide

It was found that the introduction of 3.5 wt % phosphorus increases the limiting oxygen index of PMMA from 17.8 to more than 21 vol % in both reactive and additive approaches. However, cone calorimetry data show that phosphorus-containing copolymers by their nature have greater fire resistance than neat PMMA or PMMA modified with phosphorus-containing additives. All the copolymers tested showed improved flame retardancy compared to the PMMA homopolymer. This means that chemical modification of PMMA is a more effective method for reducing the flammability of PMMA than physical doping with additives.

Thus, contemporary research in the field of phosphorus-containing methacrylates is focused on studying the structural features of molecules, polymerization mechanisms, and interactions with other components of polymer systems. Particular attention is paid to their modification to create materials with improved characteristics, such as thermal stability, fire resistance, and optical transparency. Accumulated scientific knowledge is of great importance in the development of materials with reduced flammability. In general, scientific and technical literature data on the copolymerization of phosphorus-containing methacrylates with industrial monomers indicate that they are capable of actively entering into radical copolymerization reactions with unsaturated compounds. A positive point is that phosphorus-containing units are part of the chemical structure of macromolecular chains. As the proportion of phosphorus-containing units in copolymers increases, their fire resistance increases.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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