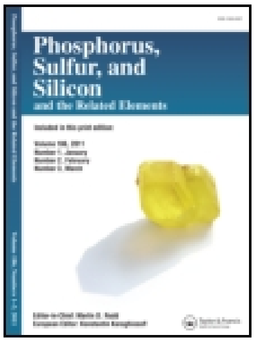

Phosphorus, Sulfur, and Silicon and the Related Elements

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# SYNTHETIC STRATEGY AND PERFORMANCES OF A UV-CURABLE POLY ACRYLOYL PHOSPHINATE FLAME RETARDANT BY CARBENE POLYMERIZATION

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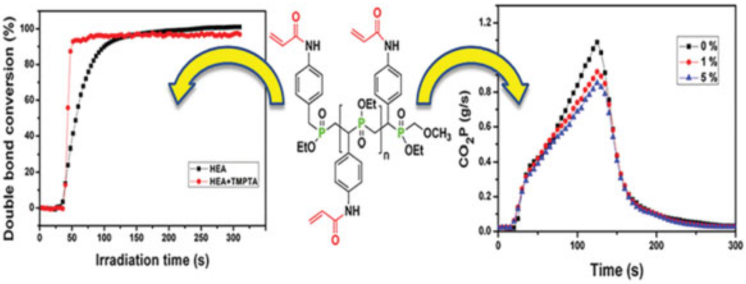
## GRAPHICAL ABSTRACT



*A route to synthesize poly ethyl (4-acrylamidebenzyl) phosphinate (PPAC) was discussed and the optimal route was determined. Diethyl benzylphosphonate was synthesized by Arbuzov reaction, then, a nitryl was introduced onto the aromatic ring by the nitration reaction of ethyl benzylphosphonate. Subsequently the carbene polymerization of the product was carried out. Finally, the nitryls were reduced and amidated to introduce the acryloyl group into the prepolymer to obtain the target product (PPAC). PPAC can rapidly photopolymerize under UV light irradiation. The addition of PPAC decreased the smoke production rate (SPR), $CO_2$ production ($CO_2P$), and CO production (COP) of the UV-cured resin.*

**Keywords** Carbene polymerization; photopolymerization; flame retardant

## INTRODUCTION

In recent years, UV polymerization technology has received more and more attention because of its advantages of energy-saving and environmentally protection. Accordingly,

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UV-curable materials have been developed rapidly and become a significant part of the green industry movement. They are widely used in various fields, such as paints, coating, ink and films.[1] Although UV-curable materials are known as "environmental-friendly materials," UV-curable resins are usually flammable, which limits the application of the resins in fields of fiber paints, wood paints and plastic coatings. Therefore, it is of great importance to develop flame retardants for UV-curable materials. In the 1980s, UV-curable flame retardants drew researchers attention. Specially, phosphine-containing flame retardants gained popularity because their flame-retardant mechanism[2] involves condensed phase or condensed phase and gaseous phase, and less gas and smoke are generated during their combustion. A phosphine-containing polyfunctional monomer (TGMAP) was synthesized by Chen[3] et al., which was introduced into polymer chains by photopolymerization technology to obtain a UV-cured film with flame-retardant effect. The flame retardant significantly improved the formation of carbon residue (carbon residue $> 36.3\%$) by catalyzing the formation of polyphosphoric acid structure in the condensed phase. A phosphorous polyester acrylate oligomer (BEPPPO) containing aromatic ring was synthesized by İnan[4] et al., and some related performance tests on the UV-cured film were carried out. The results indicated that the char yield of the UV-cured film containing the oligomer at 600°C reached 24.5% and the average self-extinguishing time was 32 s. Wang[5] et al. synthesized a difunctional phosphate methacrylate (DMPE), and discussed the thermal degradation process of systems with different additive amounts in detail. The temperature of weight loss 10% of all the systems was above 300°C and the char yield was above 12.5%.

Compared with traditional polymerization methods, carbene polymerization has the advantage of high stereoregularity. The stereoregularity can offer polymers some special structures and performances that are impossible to obtain by using other polymerizations. For example, Hetterscheid[6] synthesized poly (ethyl 2-ylidene-acetate) with a high syndiotactic structure by carbene polymerization. The polymer had a high crystallinity due to its high syndiotactic structure. Doulut[7] studied the effect of isotacticity on the $\alpha$ delay process of poly methyl methacrylate (PMMA). Nevertheless, the synthesis of UV-curable poly acryloyl phosphinate flame retardant by carbene polymerization is seldom reported. The carbene polymerization would endow the UV-curable poly acryloyl phosphinate flame unique structures, resulting in the improvement of performances of the UV-curable materials.

We have already reported the synthetic method and some performances of poly ethyl (4-acrylamidebenzyl) phosphinate (PPAC)[8].

However, the design and synthetic route of PPAC have not been discussed in detail. In addition, during the combustion process, the effect of PPAC on the smoke release of the resin, an important parameter in evaluating the flame resistance, has not been investigated.

In this paper, the route to synthesize PPAC by carbene polymerization was discussed in detail. The optimal route and conditions of the synthesis were determined, and the structures of reaction intermediates and the target product were characterized. The effect of PPAC on the flame resistance of UV-cured resins was further investigated by measuring CO and $CO_2$ productions as well as the smoke production rate (SPR) during the combustion process.

## RESULTS AND DISCUSSION

The synthesis of the target prepolymer involved two main reaction steps, namely carbene photopolymerization reaction and introduction of photopolymerizable groups.

Therefore, we designed two synthetic strategies: first, introducing the photopolymerizable groups to the target compound before carbene polymerization; second, introducing the photopolymerizable groups to the target compound after carbene polymerization. Two synthetic strategies were discussed in detail.

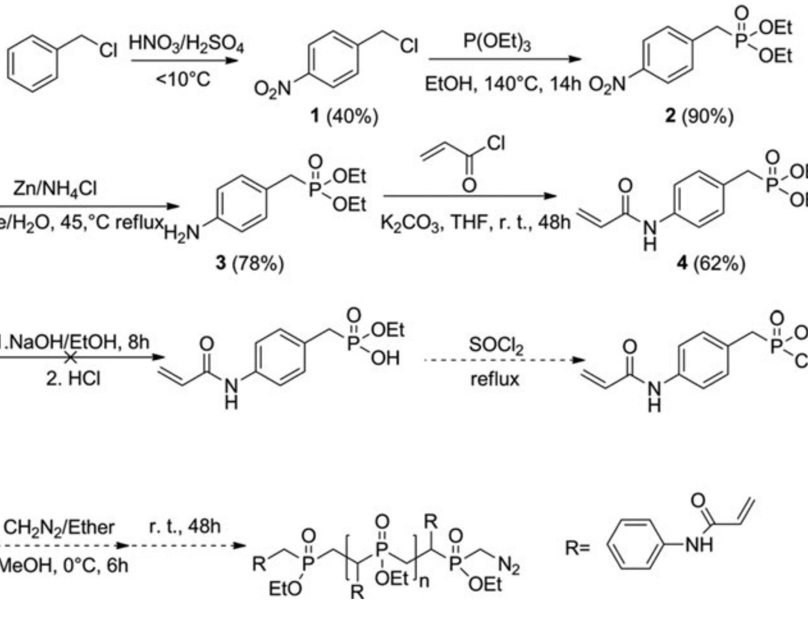
## Introducing Photopolymerizable Groups before Carbene Polymerization

**Route 1.** This design ideal is that the propylene acyl group, which is a photopolymerizable group, is first introduced into benzyl phosphoryl chloride, then the carbene polymerization of the benzyl phosphoryl chloride with propylene acyl group is carried out to synthesize the target product, propylene acyl poly benzyl phosphinate.

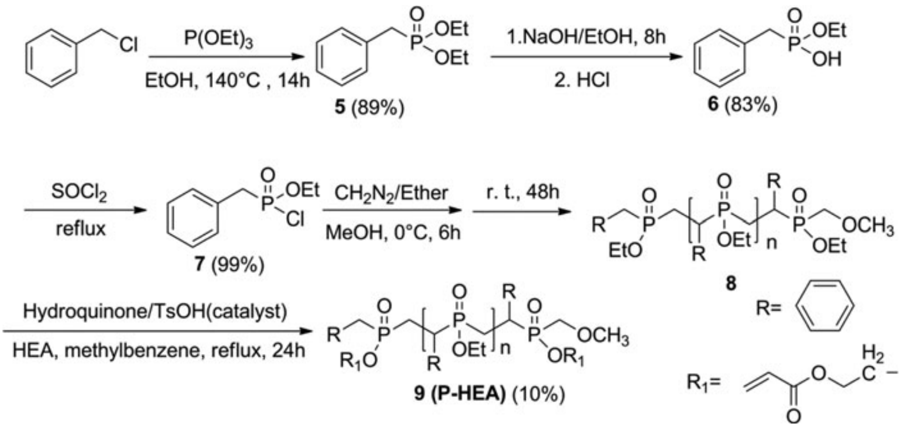
Introducing acryloyl into monoethyl benzylphosphonate directly by Friedel-Crafts acylation[9,10] may induce side reactions. Therefore, Route 1 was designed to introduce the acryloyl by amidation reaction. First, the amino group was introduced into diethyl benzylphosphonate, then, acryloyl ethyl benzylphosphonate was obtained by amidation reaction and hydrolysis reaction. Finally, the target product was synthesized by carbene polymerization. Scheme 1 shows the particular synthetic route.

The $^1$H NMR spectra of intermediate products (1)–(4) were shown in Figures S1–S4 (Supplemental Materials). The hydrolysis reactions of diethyl (4-acrylamidobenzyl) phosphonate under different conditions were investigated by $^1$H NMR. The results indicated that the phosphonate group did not hydrolyze in 2 mol/L NaOH aqueous solution at room temperature or under reflux condition, or even in the NaOH alcoholic solution under reflux condition.

As reported[11,12] before, the phosphonate group can be hydrolyzed in 2 mol/L aqueous solution at room temperature, while the acylamido group cannot, because acylamido group



**Scheme 1** Scheme of synthetic route 1.



**Scheme 2** Scheme of synthetic route 2.

is more stable than the phosphonate group in theory. However, in the experiment, it was found that the acryloyl group was hydrolyzed, whereas the phosphonate group did not. We considered the reason causing the result to be the carbon–carbon double bond in the acryloyl group, which makes acryloyl group less stable, resulting in the hydrolyzation of acryloyl.

## Introducing Photopolymerizable Groups after Carbene Polymerization

Because the aforementioned route was unfeasible, we designed a new strategy whereby poly phosphinate was obtained by the carbene polymerization of benzylphosphoryl chloride, then, photopolymerizable group was introduced into the target product. Two synthetic routes were investigated in detail.

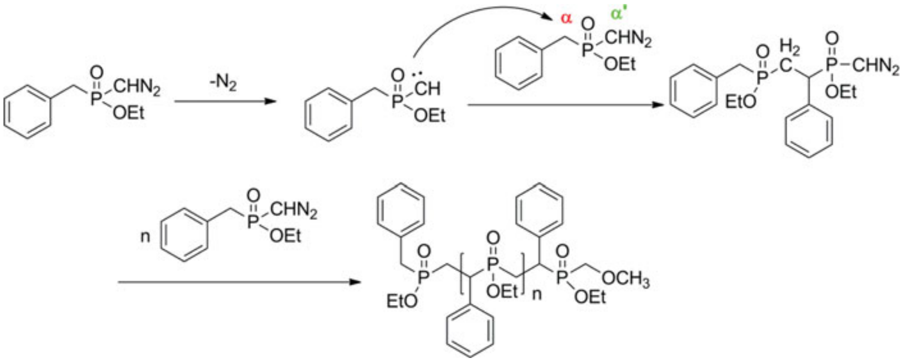
**Route 2.** As shown in Scheme 2, the main idea of route 2 is that the carbene polymerization of benzylphosphoryl chloride was carried out first, and then the photopolymerizable groups, acryloyl groups, were introduced by transesterification of oxethyl in branched chains of poly ethyl hydrogen (4-acryloylbenzyl) phosphinate and 2-hydroxyethyl acrylate (HEA).

The $^1H$ NMR spectra of intermediate products (5)–(7) were shown in Figures S5–S7 (Supplemental Materials).

Two products were obtained by the carbene polymerization of benzylphosphoryl chloride, one was solid; the other was liquid. The solid product was considered to be polymer with extremely high molecular weight and could not further react with HEA because of its poor solubility. Therefore, the liquid product, poly phenylethyl phosphinate (8) that further reacted with HEA, was characterized. Its IR and $^{13}C$ NMR spectra are shown in Figures S8 and S9. Figure S10 and Table 1 show the GPC result of the compound (8).

**Table 1** Molecular weight and molecular weight distribution of poly phenylethyl phosphinate (8)

| Mn | Mw | Polydispersity |
|---|---|---|
| 1070 | 1425 | 1.33 |



**Scheme 3** Mechanism of phosphoryl carbene insertion.

The number-average molecular weight (Mn) and weight-average molecular weight (Mw) of the prepolymer were 1070 and 1425, respectively. The degree of polymerization of the prepolymer was about 5 according to its structure. Meanwhile, there were a small number of polymers with a higher molecular weight and small molecules which did not polymerize.

As shown in Scheme 3, the phosphoryl carbene inserted at $\alpha$-C because of the steric hindrance, thus, compound (8) presented a linear structure.[13] Figure 1 is $^{31}$P NMR spectrum of the compound (8). There are two peaks at 28.0 and 29.0 ppm in the $^{31}$P NMR spectrum because the compound (8) has two chiral centers and a pair of epimers. It is further demonstrated that compound (8) possesses a syndiotactic structure.[13]

Figure S11 shows the $^1$H NMR result of the product purified by column chromatography. The $^1$H NMR result indicated that the molecule already contained aryl and acryloyl units.

Because intermediate product (8) and the product P-HEA were both prepolymers, they are very difficult to purify, thereby resulting in a very low yield of the transesterification (about 10%), According to route 2, the total yield of the target product was less than 1%

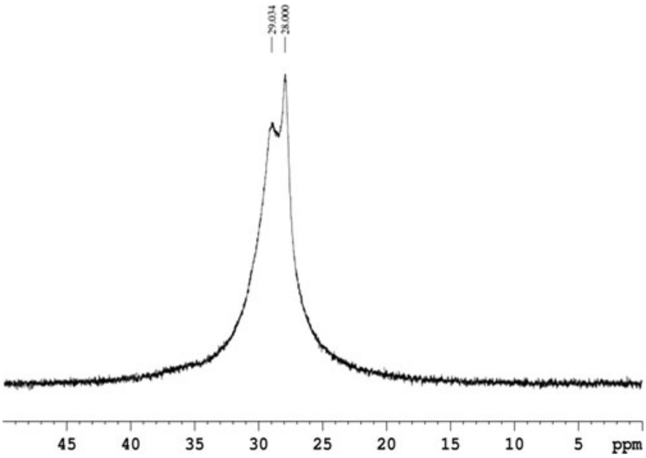
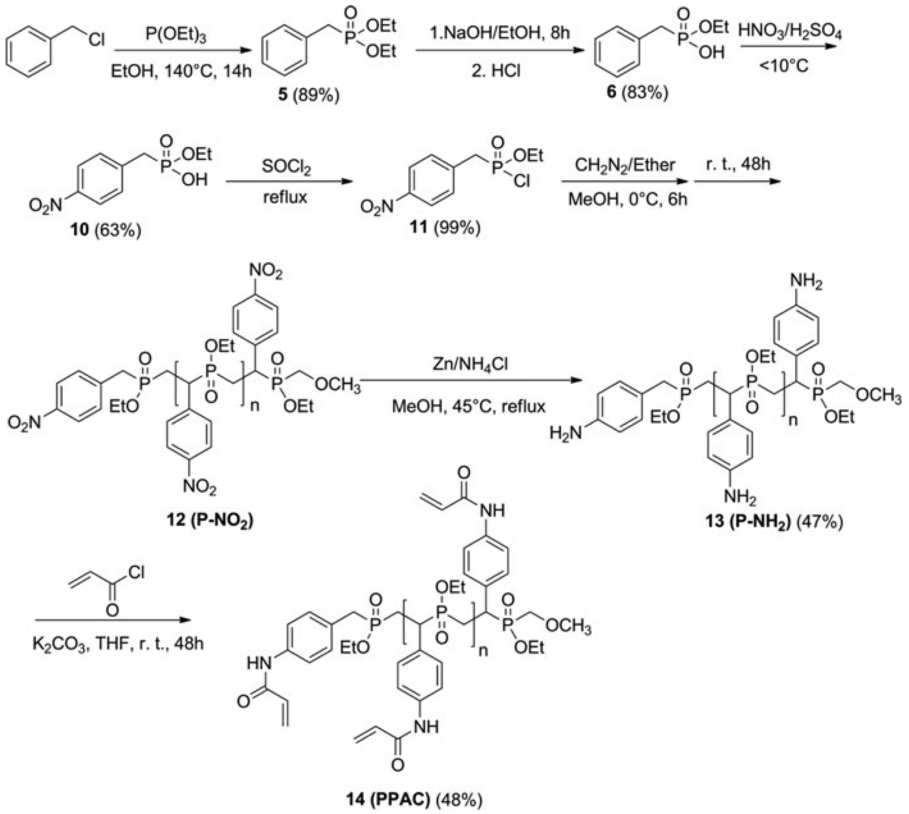


**Figure 1** $^{31}$P NMR spectrum of compound (8).



Scheme 4 Scheme of synthetic route 3.

due to the low yield of the transesterification and too many reaction steps. Hence, the route needs to be further improved to increase the yield.

**Route 3.** Route 2 is feasible, but the yield is very low. Therefore, route 3 was designed based on the above mentioned synthetic methods. Diethyl benzylphosphonate was synthesized by Arbuzov reaction, then, diethyl benzylphosphonate was partially hydrolyzed to obtain monoethyl benzylphosphonate. Nitryl was introduced into the aromatic ring of monoethyl benzylphosphonate by a nitration reaction, subsequently the carbene polymerization of the product was carried out. Finally, nitryls were reduced and amidated to introduce acryloyl groups into the prepolymer to obtain the target product (PPAC). The reaction process is shown in Scheme 4.

The $^{1}$H NMR and GPC spectra of intermediate products (10)–(13) are shown in Figures S12–17. The final product PPAC was characterized by IR, $^{1}$H NMR, $^{13}$C NMR, $^{31}$P NMR and GPC. The results are shown in Figures 2–5, Figure S18 and Table 2.

Table 2 Molecular weight and molecular weight distribution of PPAC

| Mn | Mw | Polydispersity |
|---|---|---|
| 1012 | 2149 | 2.12 |

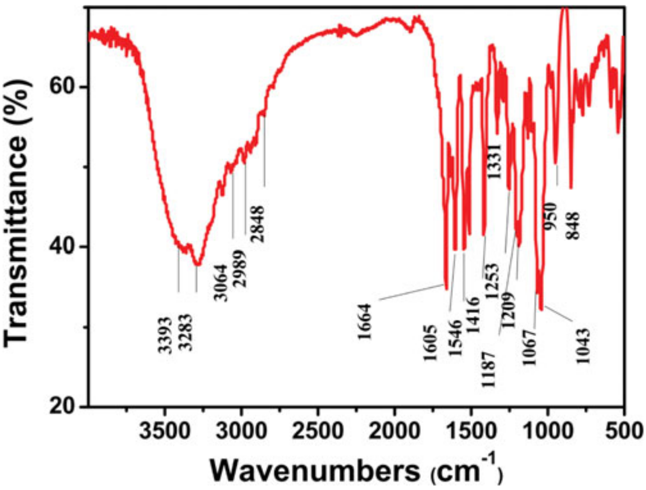


**Figure 2** IR spectrum of PPAC.

Mn and Mw of PPAC were 1012 and 2149, respectively. The chemical shift of aromatic hydrogen changed again in the $^{1}$H NMR spectrum, indicating that the p-amino group became an amide group. Similarly, there are two peaks at 21.3 and 21.4 ppm in the $^{31}$P NMR spectrum, demonstrating that PPAC is a syndiotactic prepolymer. The yield of PPAC was greatly enhanced through optimizing synthetic route and reached 48%.

## Photopolymerization Kinetics of PPAC

The photopolymerization ability of PPAC was investigated by real-time infrared (RTIR) spectroscopy. As shown in Figure 6, the photopolymerization systems containing PPAC and different monomers can rapidly polymerize under the irradiation of 365 nm UV light, and the final double bond conversions of the systems were more than 95% after the irradiation for 3 min, indicating that PPAC had great photopolymerization performance.

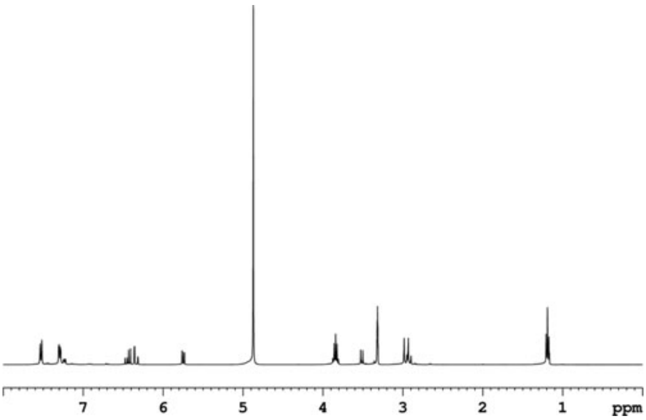


**Figure 3** $^{1}$H NMR spectrum of PPAC.

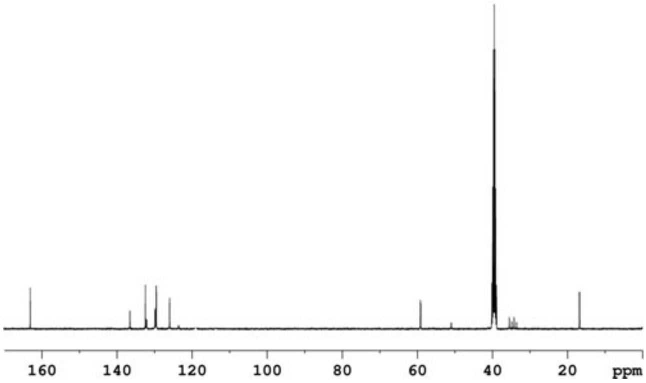


**Figure 4** $^{13}C$ NMR spectrum of PPAC.

In addition, the photopolymerization rate of the system with TMPTA was higher than that with HEA due to the high functionality of TMPTA. Furthermore,Figure 7 exhibits that the polymerization rate of the systems slightly increased with the increase of the photoinitiator content, while the final double bond conversion did not obviously change.

## Smoke Release

The cone calorimeter has been available for the bench-scale assessment of several reactions of fire and fire parameters, and many research groups have taken interest in quantitative material flammability analysis.[14–18] In this work, the cone calorimeter was employed to evaluate the flame resistance of PPAC during the combustion of UV-cured resin samples.

The SPR is the principal cause of death during fire. Therefore, the measure of SPR for a variety of polymer components will be useful in indicating the relative risk under well-ventilated conditions presented by these materials.[19] Incomplete combustion of the

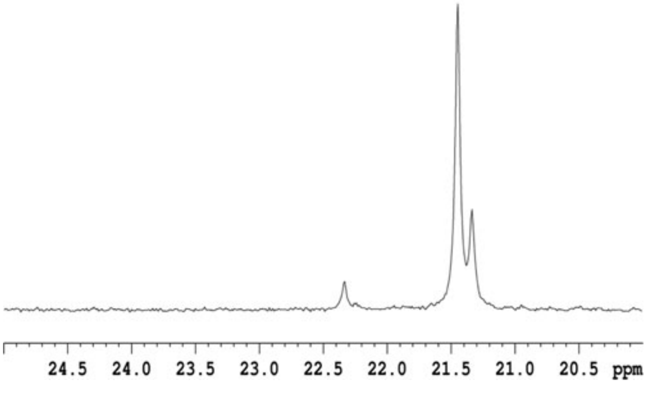


**Figure 5** $^{31}P$ NMR spectrum of PPAC.

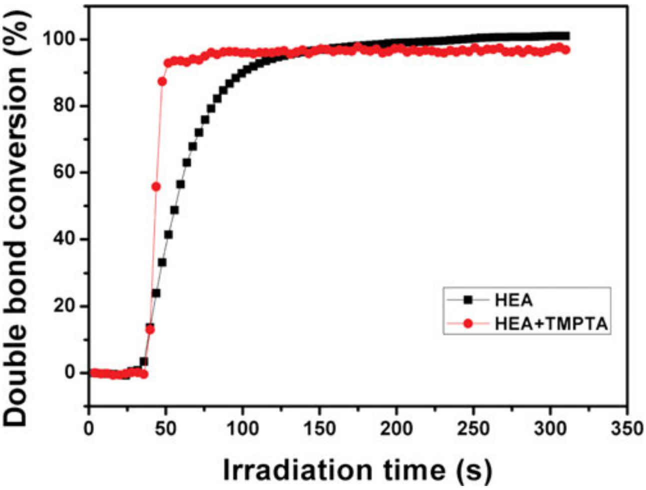


**Figure 6** Photopolymerization kinetics of PPAC. System composition: PPAC/monomer = 2/97 (wt%); photoinitiator 1173, 1 wt%; HEA/TMPTA = 5/1 (wt%).

pyrolyzed polymer volatile fuels causes the formation of CO, which occurs at low temperatures in early stages of fire development. When the fire develops, the high temperature avails the formation of $CO_2$, which is especially dependent on oxygen availability to the fire.[20]

The productions for $CO_2$ and CO are presented in Figures 8 and 9, respectively. The CO and $CO_2$ productions of the resin samples without PPAC were relatively high compared with those with PPAC. With the increase of PPAC content from 1 to 5 wt%, the production for CO decreased from 0.024 to 0.023 g/s, while the production for $CO_2$ decreased from 0.92 to 0.85 g/s. SPR curves of the resin samples are shown in Figure 10. SPR of the resin without PPAC was 0.31 $m^2$/s, while those with 1 and 5 wt% PPAC decreased to 0.27 and 0.24 $m^2$/s, respectively. These results proved that PPAC provided the smoke suppression and exhibited a flame retardant effect.

## EXPERIMENTAL

### Materials

Triethyl phosphite ($P(OEt)_3$) was purchased from Sinopharm Group Chemical Reagent Co. (Beijing, China). Acryloyl chloride was obtained from Ouhechem Co. (Beijing, China). Benzyl chloride, hydrochloric acid (HCl), concentrated sulfuric acid ($H_2SO_4$), nitric acid ($HNO_3$), sodium hydroxide (NaOH), potassium carbonate ($K_2CO_3$), ammonium chloride ($NH_4Cl$) and zinc powder (Zn) were all supplied by Beijing Chemical Works. Trimethylolpropane triacrylate (TMPTA), isobornyl acrylate (IBOA), and HEA were purchased from Eternal Specialty Chemical Co. (Zhuhai, China). The photoinitiator 2-hydroxyl-2-methyl-1-phenylpropane-1-one (Darocur 1173) was purchased from Ciba Geigy Co. Diazomethane ($CH_2N_2$) was synthesized by following previously reported processes.[21] The water in tetrahydrofuran (THF) and trichloromethane ($CHCl_3$) was removed by Na and $P_2O_5$, respectively, before use.

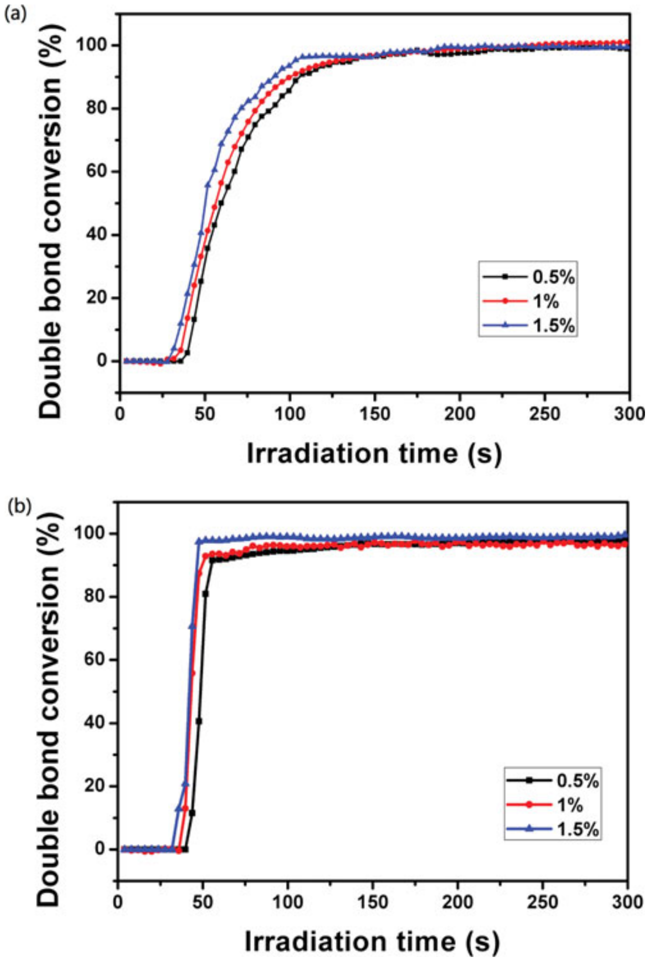


**Figure 7** Photopolymerization kinetics of PPAC with different contents of photoinitiator 1173. (a) HEA; (b) HEA/TMPTA = 5/1 (wt%). System composition: PPAC/monomer = 2/97 (wt%).

## Characterization

The Fourier transform infrared (FTIR) spectra were obtained on a Nicolet 50XC spectrometer (Nicolet, USA) and scanned between 400 and 4000 cm$^{-1}$.

The $^{1}$H NMR, $^{13}$C NMR and $^{31}$P NMR spectra were recorded on an AV400 unity spectrometer (Bruker, Germany).

The molecular weight of the prepolymer was determined by Water 515–2410 gel permeation chromatography (GPC, Water, USA). Tetrahydrofuran, 1.0 ml/L, was used as the mobile phase. Calibration was carried out by linear polystyrenes of known molecular weight and dispersity.

## Photopolymerization

The systems of TMPTA and HEA were employed as a range of concentration of poly acryloyl ethyl phosphinate (PPAC). All samples were investigated by real-time infrared

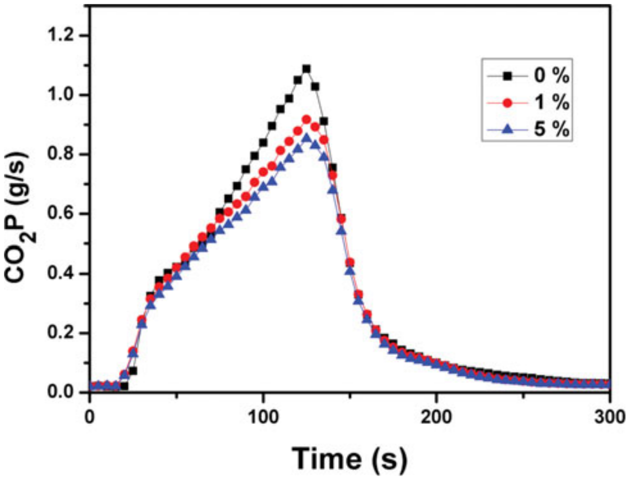


**Figure 8** $CO_2$ production ($CO_2P$) as a function of time. System composition: IBOA/photoinitiator 1173 = 100:1 (wt%).

(RTIR) spectroscopy (RT-IR; Nicolet 5700, Thermo Electron, USA, equipped with an extended range KBr beam splitter and an MCT/A detector) according to the procedures reported before.[22]

## Smoke Release

The cone calorimeter tests were conducted to research the fire performance on a FTT cone calorimeter according to ISO 5660–1. The samples with the dimension of 100 mm × 100 mm × 3 mm were exposed to a radiant cone at a heat flux of 40 kW/$m^2$.

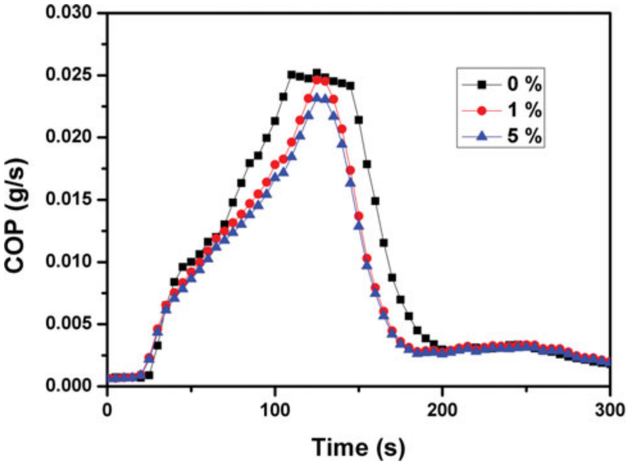


**Figure 9** CO production (COP) as a function of time. System composition: IBOA/photoinitiator 1173 = 100:1 (wt%).

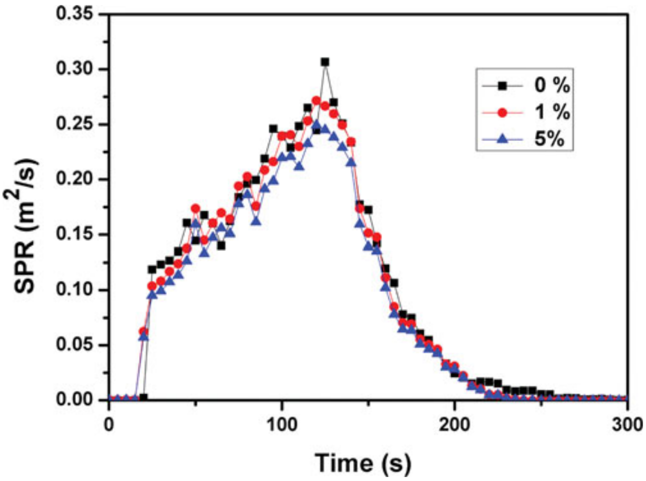


**Figure 10** SPR as a function of time. System composition: IBOA/photoinitiator 1173 = 100:1 (wt%).

## FT-IR and NMR Spectra of PPAC

$\nu_{max}$ (KBr)/cm$^{-1}$: 1603, 1546 and 848 (Ar), 1043 and 1067 (P-O-C), 1209 and 1289 (P = O), 3064 (C = CH), 2989 and 2848 ($CH_2CH_3$), 1664 (C = O), 1416 (CN).

$^1$H NMR (400 MHz, $CD_3OD$, $\delta$): 7.51–7.56 (m, 8H, $C_6H_4$), 7.26–7.32, (m, 8H, $C_6H_4$), 6.30–6.48 (m, 8H, $CH_2$ = CH), 5.70–5.80 (m, 4H, $CH_2$ = C*H*), 3.79–3.85(m, 8H, $POCH_2CH_3$), 3.48–3.54 (d, $J_{P,H}$ = 10.4 Hz, 3H, $POCH_2OCH_3$), 2.92–3.00 (d, $J_{P,H}$ = 20.4 Hz, 10H, $POCH_2$), 2.80–2.90 (m, 3H, PC*H*$CH_2$), 1.15–1.22 (t, $J_{H,H}$ = 7.0Hz, 12H, $POCH_2CH_3$).

$^{13}$C NMR (100 MHz, $CD_3OD$, $\delta$): 162.9 (*C* = O), 125.9–136.4 ($C_6H_4$, $CH_2$ = *C*H), 59.1 (d, $J_{P,C}$ = 5.5 Hz, PO*C*$H_2$), 50.8 (O*C*$H_2CH_3$), 33.5–35.4 (Ph-*C*$H_2$, P*C*H($CH_2$)Ph), 16.7 (O*C*$H_3$).

$^{31}$P NMR (162 MHz, $CD_3OD$, $\delta$): 21.3, 21.4.

## CONCLUSIONS

The optimal route to synthesize poly ethyl (4-acrylamidebenzyl) phosphinate (PPAC) was determined as route 3. The structures of all products were characterized by NMR, FT-IR and GPC. PPAC had good photopolymerization performance and the final double bond conversion of the system reached above 95% after the irradiation for 3 min. The results of the cone calorimeter demonstrated that the addition of PPAC decreased the SPR, $CO_2P$ and COP of the UV-cured resins, indicating that PPAC has flame retardant capability for UV-curable resins.

## FUNDING

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## SUPPLEMENTARY MATERIAL

Supplemental data for this article can be accessed on the publisher's website at http://dx.doi.org/10.1080/10426507.2015.1049741.

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