# Deprotection-Free Preparation of Propargyl Ether-Containing Phosphinated Benzoxazine and the Structure–Property Relationship of the Resulting Thermosets

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**ABSTRACT**: Generally, protection and deprotection procedures of amino groups are required in preparing propargyl ether-containing benzoxazines. In this study, we report a facile, deprotection-free preparation of a propargyl ether-containing phosphinated benzoxazine **(2)** from the nucleophilic substitution of a phenolic OH-containing phosphinated benzoxazine **(1)** and propargyl bromide in the catalysis of potassium carbonate. The structure of **(2)** was characterized and confirmed by a high-resolution mass spectrum, $^1$H, $^{13}$C, $^1$H-$^1$H, $^1$H-$^{13}$C nuclear magnetic resonance (NMR) spectra, and X-ray single crystal diffractogram. infrared (IR) and differential scanning calorimetry were used to monitor the ring-opening of benzoxazine and crosslinking of propargyl ether. The microstructure and the structure–property relationship of the resulting homopolymers and copolymers are discussed. The $T_g$ of homopolymer of **(2)** is 208 °C by dynamic mechanical analysis, the coefficient of thermal expansion is 43 ppm/°C, and $T_d$ 5% ($N_2$) is 393 °C, respectively, which are higher than those of the homopolymer of **(1)**. Similar trends were observed in the copolymerization system. The results demonstrate the beneficial effect of crosslinking afforded by the propargyl ether group is higher than that by the phenolic OH group. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1008–1017, 2012

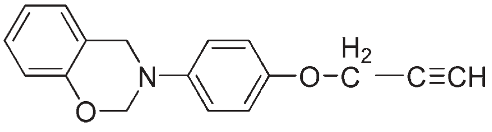
**KEYWORDS**: benzoxazine; flame retardance; phosphinated; propargyl ether; protection; synthesis; thermal properties; thermosets

**INTRODUCTION** The demand for flame-retardant polymers is high due to their wide applications in electronic industries, such as in printed circuit boards or encapsulation. Brominated compounds have been widely used to reduce flammability, but they are considered as carcinogens and face restriction in some area due to health and environmental concerns.[1–6] Some halogen-free, environment-friendly flame-retardant structure or element, such as alkyne,[7–9] deoxybenzoin,[10–12] triazole,[1,13] and phosphorus,[14–22] have been incorporated into polymers to enhance flame retardancy, and promising results have been achieved.

Benzoxazines are resins that can be polymerized to thermosets via the thermally activated ring-opening of oxazine linkage. Epoxy/benzoxazine systems have recently been used in the field of copper clad laminates due to the characteristics of higher $T_g$, better adhesion to glass fiber, and better toughness than the epoxy/phenol novolac system. Although carbon fiber reinforced polybenzoxazine P(B-a) shows improved flame retardancy,[23] neat polybenzoxazines cannot meet the flame-retardancy standard, UL-94 V-0. Thus, the research on flame-retardant polybenzoxazines is interesting for electronic industries. Recently, flame-retardant benzoxazines based on phenylphosphine oxide-containing biphenol,[24] phosphinated trisphenol,[25] phosphinated triamine,[26] aromatic amines,[20,27–30] and phosphazine[31] have been reported, and the flame retardancy of resulting thermosets has been proven.

Aryl propargyl ether is known to undergo Claisen type rearrangement to benzopyran with thermal treatment, and subsequently polymerize via the curing of the C=C bond in the benzopyran structure.[32–39] Agag and Takeichi prepared a propargyl ether-containing benzoxazine (P-appe, Fig. 1) from *p*-nitrophenol by a three-step procedure including (1) nucleophilic substitution with propargyl bromide, (2) reduction of nitro group, and (3) formation of benzoxazine.[40] Yagci and coworkers prepared the same compound from 4-aminophenol by a four-step procedure including (1) protection of the amino group by acetic acid, (2) nucleophilic substitution with propargyl bromide, (3) deprotection of amino from acetamide, and (4) formation of benzoxazine.[41] Propargyl ether containing benzoxazines have also been prepared by

Additional Supporting Information may be found in the online version of this article.



P-appe

**FIGURE 1** Structure of P-appe.

Ishida and coworkers by a similar approach.[42,43] In these strategies, protection form of amine (in nitro or acetamide form) is required to prevent side reactions from amino and propargyl bromide. After the nucleophilic substitution of phenolic OH and propargyl bromide is complete, regenerating of amino group, no matter from reduction of nitro group or deprotection from acetamide, is needed. Therefore, it would be of interest if propargyl ether-containing benzoxazines could be prepared by an alternative approach without any reduction or protection–deprotection procedure.

Herein, we report a deprotection-free synthesis of a propargyl ether-containing benzoxazine **(2)** via the nucleophilic substitution of a phenolic OH-containing benzoxazine **(1)** with propargyl bromide in the catalysis of potassium carbonate. In this work, the amino group is protected in a benzoxazine form, so no reduction or deprotection procedure is required after the nucleophilic substitution. To the best of our knowledge, no propargyl ether containing-benzoxazines have been prepared via this facile approach. We also demonstrate that copolybenzoxzines based on the propargyl ether benzoxazine **(2)** show better thermal properties than those based on the phenolic OH benzoxazine **(1)**. The detailed synthesis, curing behavior, the microstructure of **(2)**, and the structure–property relationship of the resulting thermosets are reported in this work.

## EXPERIMENTAL

### Materials

Phenolic OH-containing benzoxazine **(1)** was prepared by the procedure in our previous work.[44] Potassium carbonate and propargyl bromide were purchased from Acros. Bis(4-(2H-benzo[e][1,3]oxazin-3(4H)-yl)phenyl)methane (**P-d**) was kindly supplied by the Shikoku Corporation, Japan. *N*,*N*-Dimethyl acetamide (DMAc) was purchased from Tedia and purified by distillation under reduced pressure over calcium hydride (Acros) and stored over molecular sieves. The other solvents used are commercial products and were used without further purification.

### Synthesis of Benzoxazine (2)

A total of 4.41 g (0.01 mol) of **(1)**, 2.07 g (0.015 mol) of potassium carbonate, and 10 mL of DMAc were introduced into a 100-mL round-bottom glass flask equipped with a condenser and a magnetic stirrer. Also 1.78 g (0.012 mol) of 80% propargyl bromide in toluene was added. The mixture was stirred at 80 °C for 24 h. After that, the mixture was filtered and the filtrate was poured into water (250 mL). The precipitate was filtered and dried (88% yield). As the phosphorus and the adjacent aliphatic carbon are both chiral centers, two diastereomers were formed in the preparation. The ratio of two diastereomers, calculated from nuclear magnetic resonance (NMR) spectra, is around 4:1. After crystallization in methanol, the minor of the two diastereomers was removed (70% yield). A melting point at 174 °C with enthalpy of 180 J/g and an exothermic peak at 255 °C with enthalpy of 499 J/g were observed in the differential scanning calorimetry (DSC) thermogram.

HR-MS (FAB+) *m*/*z*: calcd. for $C_{29}H_{22}O_4NP$ 479.1286; anal. 479.1288, $(M)^+$ C29, H22, O4, N, P. Fourier transform

**TABLE 1** Thermal Properties of P(2), (1)/P-d, and (2)/P-d Copolymers

| | | | | | Thermal Stability | | Flammability | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample ID | Phosphorus Content (wt %) | $T_g$ (°C)[a] | $T_g$ (°C)[b] | CTE (ppm/°C)[c] | $T_d$ (°C)[d] | Char Yield (wt %)[e] | $t_1$ | $t_2$ | UL-94 Grade |
| P(**P-d**) | 0 | 208 | 180 | 50 | 412 | 45 | >60 | – | Burning |
| P(**2**) | 6.4 | 208 | 194 | 43 | 393 | 48 | 1.2 | 0.5 | V-0 |
| P(**2**)-0.5 | 0.5 | 220 | 201 | 40 | 440 | 56 | 11.1 | 1.8 | V-1 |
| P(**2**)-0.75 | 0.75 | 224 | 204 | 39 | 435 | 56 | 6.1 | 0.6 | V-0 |
| P(**2**)-1.0 | 1.00 | 225 | 206 | 39 | 420 | 57 | 3.4 | 1.2 | V-0 |
| P(**2**)-1.25 | 1.25 | 230 | 208 | 38 | 418 | 53 | 2.0 | 1.0 | V-0 |
| P(**2**)-1.5 | 1.50 | 237 | 211 | 37 | 425 | 57 | 1.2 | 0.8 | V-0 |
| P(**1**)-0.75 | 0.75 | 194 | 163 | 49 | 382 | 46 | 6.3 | 1.7 | V-0 |
| P(**1**)-1.0 | 1.00 | 187 | 156 | 48 | 378 | 47 | 3.7 | 1.1 | V-0 |
| P(**1**)-1.25 | 1.25 | 187 | 162 | 49 | 368 | 47 | 2.8 | 1.1 | V-0 |
| P(**1**)-1.5 | 1.50 | 180 | 160 | 47 | 367 | 45 | 2.1 | 0.5 | V-0 |

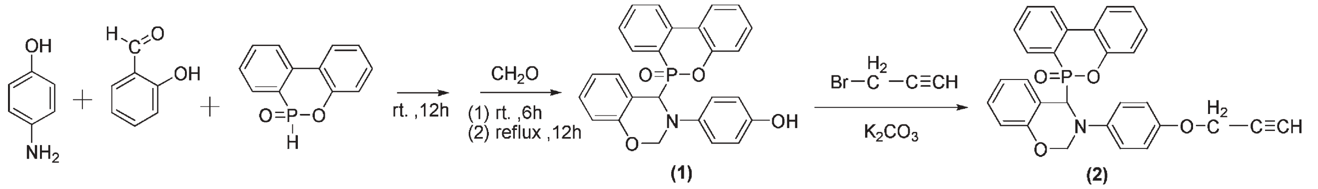
[a] Peak temperature of tan $\delta$, measured by DMA at a heating rate of 5 °C/min.

[b] Measured by TMA at a heating rate of 5 °C/min.

[c] Coefficient of thermal expansion before $T_g$.

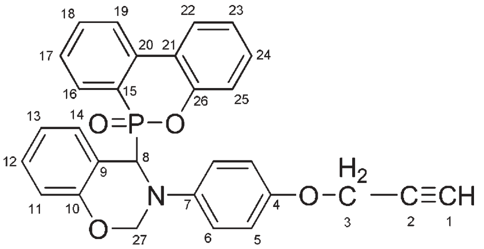
[d] 5% decomposition temperature in nitrogen.

[e] Residual weight percentage at 800 °C in nitrogen.



**SCHEME 1** Synthesis of benzoxazine **(2)**.

infrared spectroscopy (FTIR) absorption (KBr): sp-hybridized C—H at 3295 cm$^{-1}$, symmetric Ar—O—C at 1041 cm$^{-1}$, a characteristic mode of benzene with an attached oxazine ring at 956 cm$^{-1}$. $^{1}$H NMR (ppm, CDCl$_3$), $\delta$ = 2.43 (1H, H$^{1}$), 4.51 (2H, H$^{3}$), 4.72 (1H, H$^{8}$), 4.91–5.33 (2H, H$^{27}$), 6.61 (1H, H$^{6}$), 6.67–6.69 (1H, H$^{5}$), 6.85 (1H, H$^{11}$), 6.98 (1H, H$^{13}$), 7.18 (1H, H$^{12}$), 7.23–7.26 (2H, H$^{23}$and H$^{25}$), 7.38 (1H, H$^{24}$), 7.40–7.43 (2H, H$^{14}$ and H$^{18}$), 7.69 (1H, H$^{17}$), 7.86–7.89 (1H, H$^{19}$), 7.96 (1H, H$^{22}$), 7.99–8.01 (1H, H$^{16}$). $^{13}$C NMR (ppm, CDCl$_3$), $\delta$ = 55.8 (C$^{3}$), 60.1 and 60.8 (C$^{8}$,$^{1}J_{\text{P—C}}$ = 111.8 Hz), 75.4 (C$^{1}$), 77.7 (C$^{27}$), 78.4 (C$^{2}$), 114.8 (C$^{9}$), 115.3 (C$^{5}$), 117.5 (C$^{11}$), 119.9 (C$^{25}$), 121.1 (C$^{13}$), 121.4 and 121.7 (C$^{15,}$ $^{1}J_{\text{P—C}}$ = 39 Hz), 121.8 (C$^{6}$), 122.4 (C$^{20}$), 123.4 (C$^{16}$), 124.5 (C$^{23}$), 125.0 (C$^{22}$), 128.1 (C$^{14}$), 128.3 (C$^{18}$), 128.8 (C$^{12}$), 130.7 (C$^{24}$), 132.6 (C$^{19}$), 133.8 (C$^{17}$), 136.2 (C$^{21}$), 143.6 (C$^{7}$), 149.8 (C$^{4}$), 159.6 (C$^{26}$), 154.7 (C$^{10}$). Single crystal data: C$_{29}$H$_{22}$O$_4$NP, 0.48 × 0.44 × 0.42 mm$^3$, monoclinic with $a$ = 9.8242 (8) Å, $b$ = 13.0353 (9) Å, $c$ = 17.9252 (15) Å, $\alpha$ = 90°, $\beta$ = 93.002 (10)°, $\gamma$ = 90° with $D_c$ = 1.389 mg/m$^3$ for $Z$ = 4, $V$ = 2292.38 (4) Å$^3$, $T$ = 297 (2) K, $\lambda$ = 0.71073 Å, $F$(000) = 1000, final $R$ indices: $R1$ = 0.0378, $WR2$ = 0.1104.



## Curing Procedure

For copolymerization systems, **(1)/P-d** and **(2)/P-d** with various weight ratios were melted, stirred homogeneously in a temperature-controlled hot plate at 160 °C for 20 min, and then transferred to an aluminum mold. The samples were cured at 180 °C (2 h), 200 °C (2 h), 220 °C (2 h), and 240 °C (1 h) in an air-circulating oven (The reason for 240 °C curing will be explained in "Microstructure" section.). Thereafter, samples were allowed to cool slowly to room temperature to prevent cracking. For **(1)/P-d** and **(2)/P-d** copolymers, the relation between the sample ID and the content of phosphorus is listed in Table 1. The number after P is the phosphorus content in the copolymer. For example, P**(1)**-1.25 means the **(1)/P-d** copolymer with a phosphorus content of 1.25 wt %, and P**(2)**-1.5 means the **(2)/P-d** copolymer with a phosphorus content of 1.5 wt %. Homopolymer of **(2)**, P**(2)**, was cured by the same curing program as copolymers.

## Characterization

DSC was performed with a Perkin-Elmer DSC 7 in a nitrogen atmosphere at a heating rate of 10 min/°C. Thermal gravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris1 at a heating rate of 20 °C/min in a nitrogen atmosphere. Dynamic mechanical analysis (DMA) was performed with a Perkin-Elmer Pyris Diamond DMA with a sample size of 5.0 × 1.0 × 0.2 cm$^3$. The storage modulus $E'$ and tan $\delta$ were determined as the sample was subjected to the temperature scan mode at a programmed heating rate of 5 °C/min at a frequency of 1 Hz. The test was performed by a bending mode with an amplitude of 5 $\mu$m. Thermal mechanical analysis (TMA) was performed with a Perkin-Elmer Pyris Diamond TMA at a heating rate of 5 °C/min. NMR

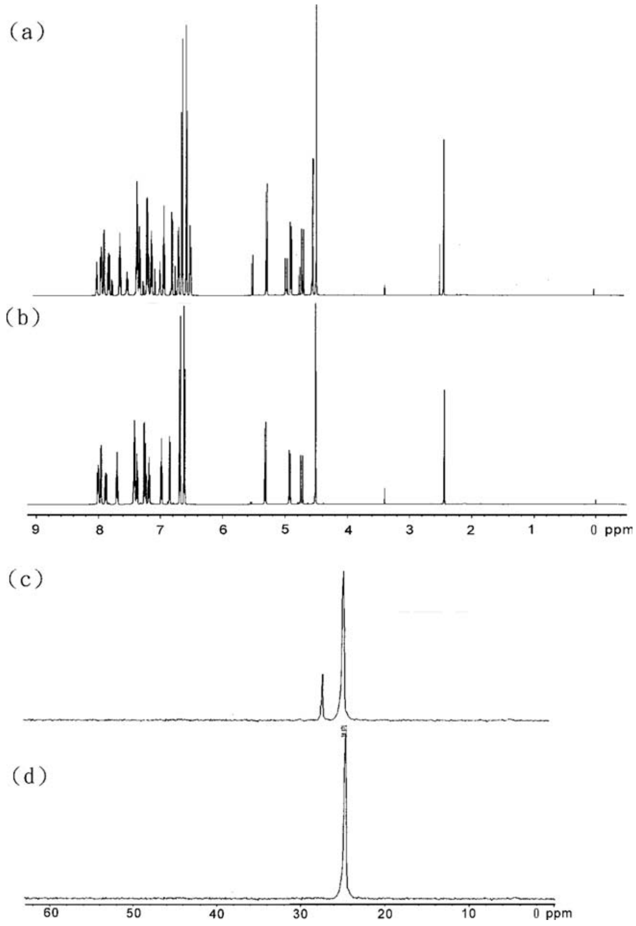


**FIGURE 2** (a) $^{1}$H NMR (as prepared), (b) $^{1}$H NMR (methanol-recrystallized), (c) $^{31}$P NMR (as prepared), and (d) $^{31}$P NMR (methanol-recrystallized) spectra of **(2)**.

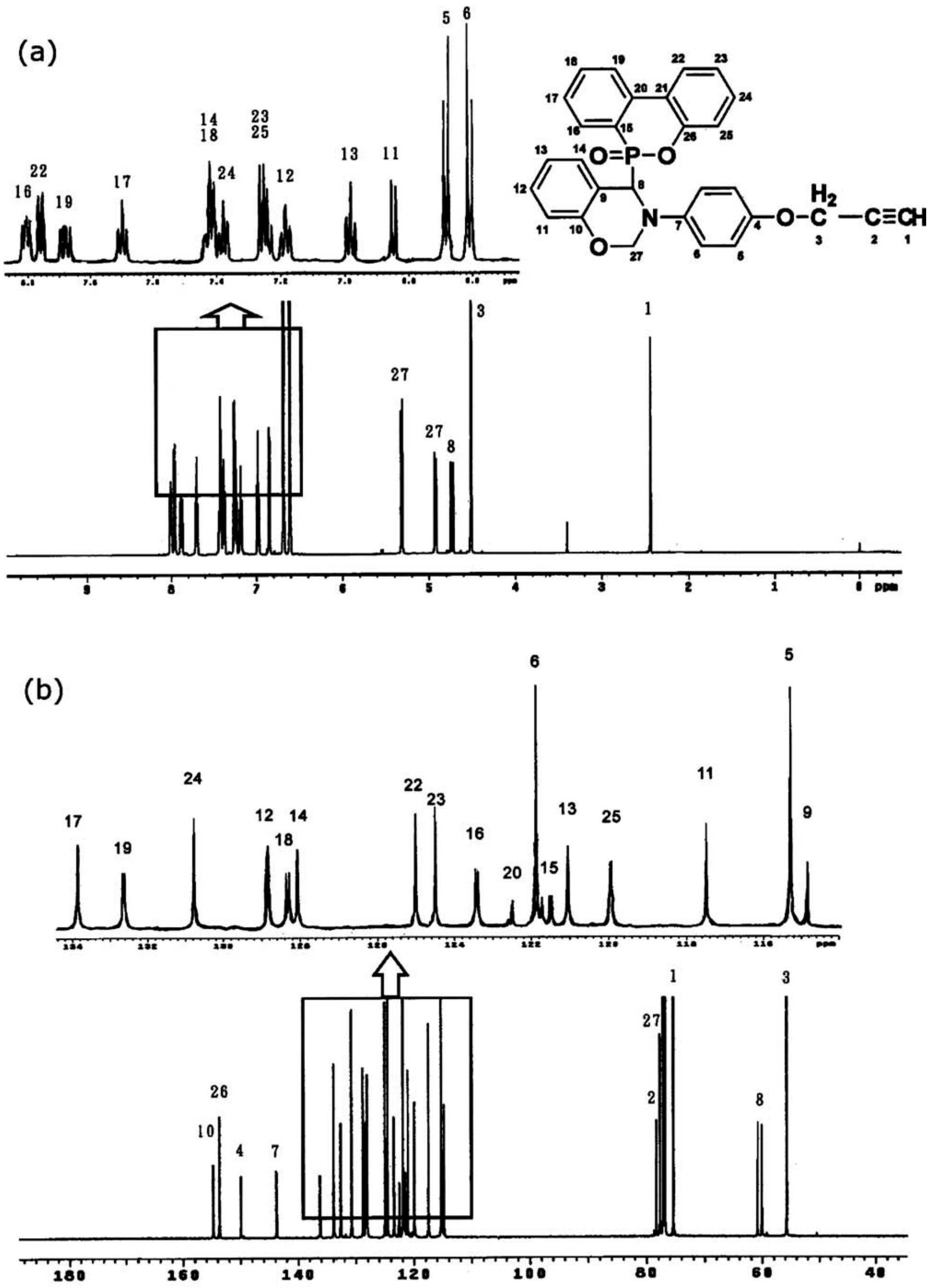


**FIGURE 3** (a) $^1$H NMR and (b) $^{13}$C NMR spectra of **(2)**.

measurements were performed using a Varian Inova 600 NMR in DMSO-$d_6$, and the chemical shift was calibrated by setting the chemical shift of DMSO-$d_6$ as 2.49 ppm. Infrared (IR) spectra were measured by a Perkin-Elmer RX1 infrared spectrophotometer in KBr powder form. High-resolution mass spectra were obtained by a Finnigan/Thermo Quest MAT 95XL mass spectrometer. The UL-94 vertical test was performed according to the testing procedure of FMVSS 302/ZSO 3975 with a test specimen bar of 127 mm in length, 12.7 mm in width, and about 1.27 mm in thickness. The height of the burner flame was 25 mm and the height from the top of the burner to the bottom of the test bar was 10 mm. During the test, the polymer specimen was subjected to two 10 s ignitions. After the first ignition, the flame was removed and the time for the polymer to self-extinguish ($t_1$) was recorded. Cotton ignition was noted if polymer dripping occurred during the test. After cooling, the second ignition was performed on the same sample. The self-extinguishing time ($t_2$) and dripping characteristics were again recorded. Five specimens were measured and the average burning time was recorded. If $t_1 + t_2$ was less than 10 s with no dripping, it

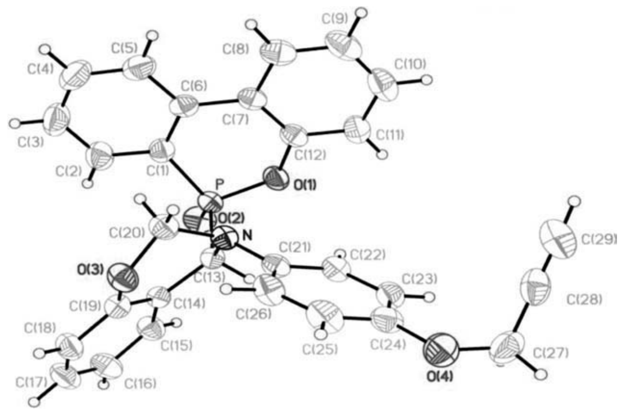


**FIGURE 4** X-ray single crystal diffractogram of **(2)**.

was considered to be a V-0 grade, an industrial standard for flame-retardancy. If $t_1 + t_2$ was in the range of 10–30 s without any dripping, the polymer was considered to be a V-1 material. If $t_1 + t_2$ was in the range of 10–30 s with dripping that ignited a cotton indicator located below the sample, the polymer was considered to be a V-2 material.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of (2)

In our previous work, we reported a facile synthesis of a phenolic OH-containing benzoxazine **(1)** by the reaction of 4-aminophenol, 2-hydroxybenzaldehyde, and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO).[44] In this work, based on the nucleophilic substitution of **(1)** with propargyl bromide in the catalysis of potassium carbonate, we prepared a propargyl ether-containing benzoxazine **(2)** (88% yield, Scheme 1). In this work, the amino group is protected in a benzoxazine form, so no deprotection procedure is required after the nucleophilic substitution.

Figure 2 shows the NMR spectra of as-prepared **(2)**; therefore, the crude product before crystallization. Because the phosphorus and the adjacent aliphatic carbon are both chiral centers, two diastereomers were formed in the preparation. This can be supported by the complicated peak patterns at 4.5–5.5 ppm in Figure 2(a), and the two $^{31}$P NMR peaks in Figure 2(c). The ratio of two diastereomers, calculated from NMR spectra, is around 4:1. After recrystallization in methanol, the minor of the two diastereomers was removed (70% yield, note that removing the minor diastereomer is not necessary for practical application). This can be supported by the simplified patterns in Figure 2(b) and the single $^{31}$P peak in Figure 2(d), respectively.

Figure 3 shows the (a) $^{1}$H and (b) $^{13}$C NMR spectra of methanol-recrystallized (2). The signals of propargyl ether were observed at 4.51 (H$^{3}$) and 2.43 (H$^{1}$) in Figure 3(a), and at 78.4 (C$^{2}$), 75.4 (C$^{1}$), and 55.8 (C$^{3}$) ppm in Figure 3(b), respectively. The signals of oxazine linkage were observed at 4.72 (H$^{8}$) and 4.91 and 5.33 (H$^{27}$) in Figure 3(a), and at 60.1 and 60.8 (C$^{8}$, $^{1}J_{\mathrm{P-C}} = 111.8$ Hz) and 77.7 (C$^{27}$) ppm in Figure 3(b), respectively. The intact of oxazine linkage indicates the stability of oxazine linkage in the alkaline-catalyzed reaction condition. It should be noted that carbon C$^{8}$ is a chiral center, so the two hydrogens of $OCH_2N$ (H$^{27}$) are not magnetic equivalent. The detailed assignment of each peak,

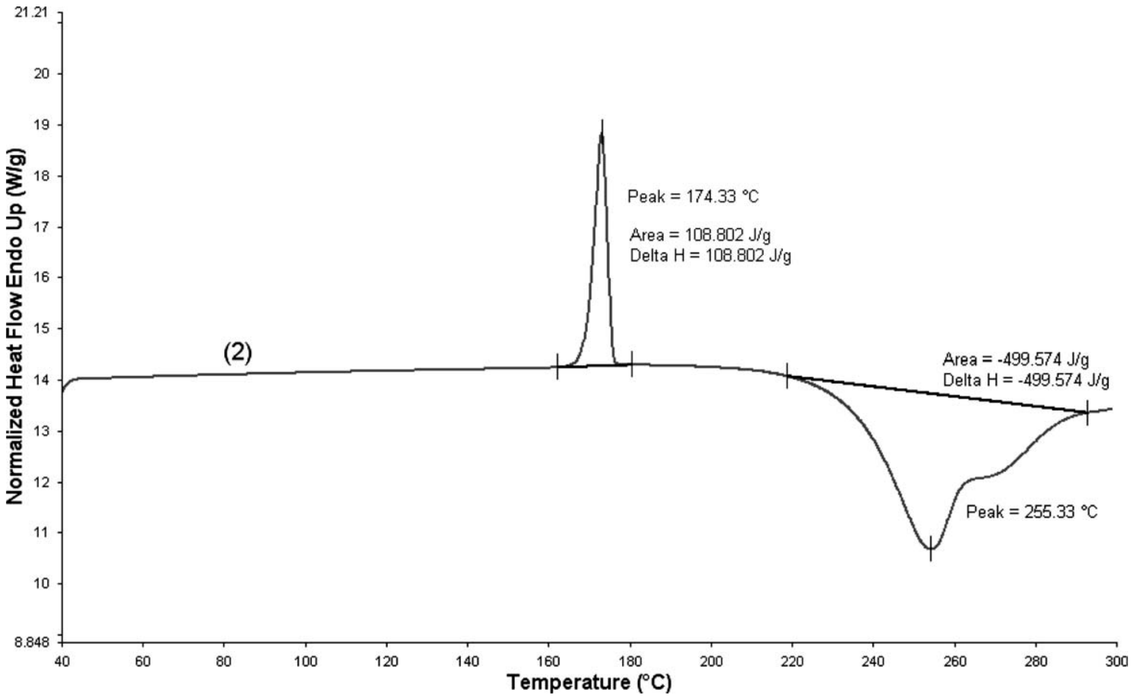


**FIGURE 5** DSC thermogram of benzoxazine **(2)**.

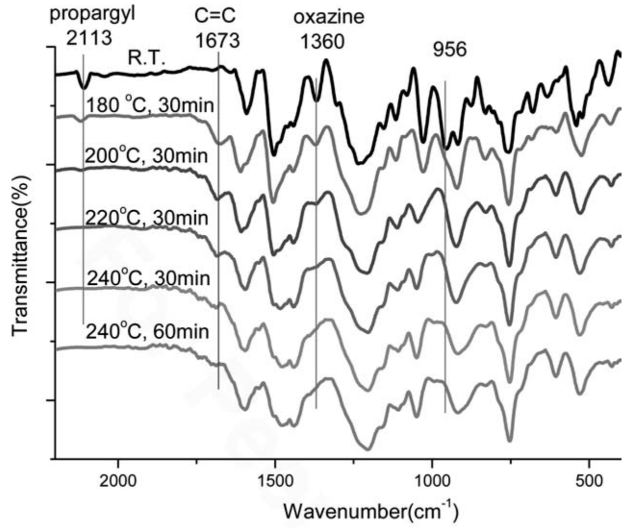


**FIGURE 6** IR spectra of **(2)** after accumulative curing. The curing temperature and curing time are marked in the Figure 5.

assisted by the correlation in $^1$H—$^1$H, and $^1$H—$^{13}$C spectra (Supporting Information Figs. S1 and S2), confirms the structure of **(2)**. The structure of **(2)** can further be confirmed by the X-ray single crystal diffractogram, as shown in Figure 4. The crystal is monoclinic, with $a$ = 9.8242 (8) Å, $b$ = 13.0353 (9) Å, $c$ = 17.9252 (15) Å, $\alpha = 90°$, $\beta$ = 93.002 (10)°, and $\gamma = 90°$.

## DSC Thermogram

Figure 5 shows the DSC thermogram of a single crystal of benzoxazine **(2)**. A melting point at 174 °C, an exothermic peak at 255 °C, and a shoulder at around 260 °C were observed. When compared with the value (230 °C and 237 °C) of **(1)**,[44] the melting point of **(2)** is reduced remarkably due to the disappearance of hydrogen bonding resulting from phenolic OH. The reduction in melting point leads to a reasonable processing window for **(2)**. The enthalpy of the exothermic peak is as high as 499 J/g, which is much higher than that of benzoxazine without propargyl ether, in which propargyl ether is replaced by a methyl group.[29] Surprisingly, in units of kJ/mol, the exothermic enthalpy (239 kJ/mol) of **(2)** is even higher than the value (188 kJ/mol) of P-appe,[40] probably because the DSC thermogram of **(2)** was measured by a high-purity single crystal.

## Microstructure

Supporting Information Figure S3 shows the IR spectra of **(2)** after accumulative curing at 180 °C for various periods of time. The absorptions of the characteristic mode of benzene with an attached oxazine ring[45] at 956 cm$^{-1}$ and propargyl ether at 2113 cm$^{-1}$ decreased gradually, and almost disappeared after curing for 60 min. A C=C absorption, which resulted from the benzopyran (the product of Claisen type rearrangement of propargyl ether), appeared after curing for 15 min. Supporting Information Figure S4 shows DSC thermograms of **(2)** after accumulative curing at 180 °C for various periods of time (the same thermal history as in Supporting Information Fig. S3). The first exotherm decreased apparently after each curing cycle. The second exotherm seemed not to be as obviously affected by the curing time as

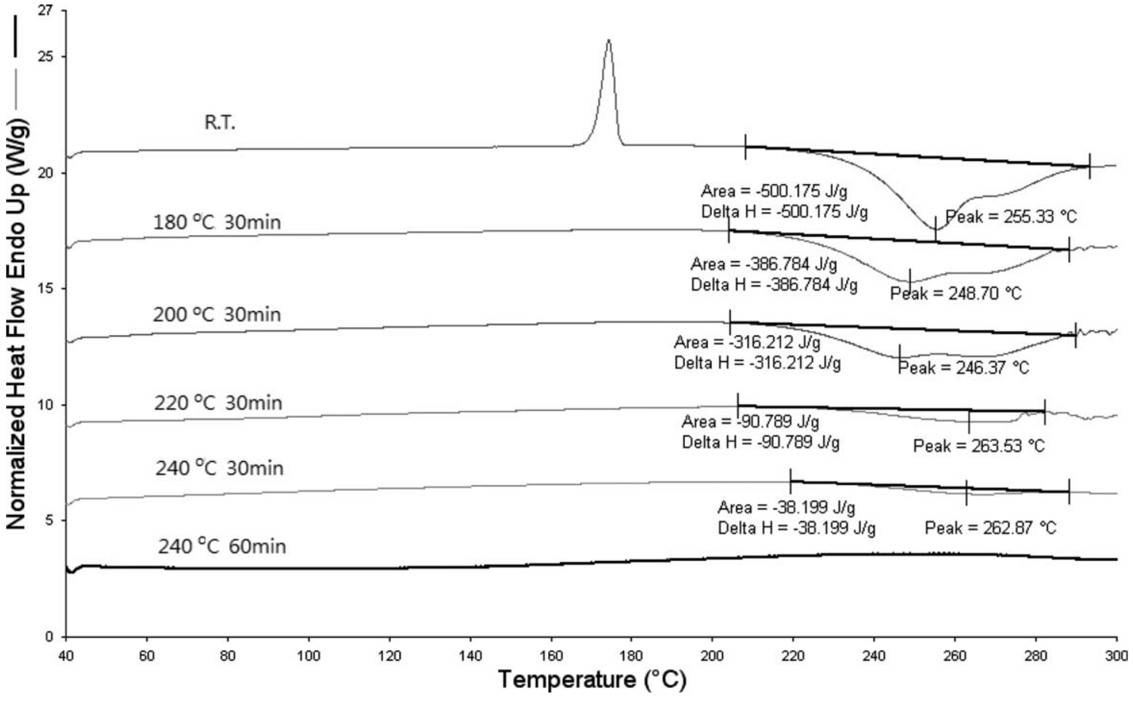
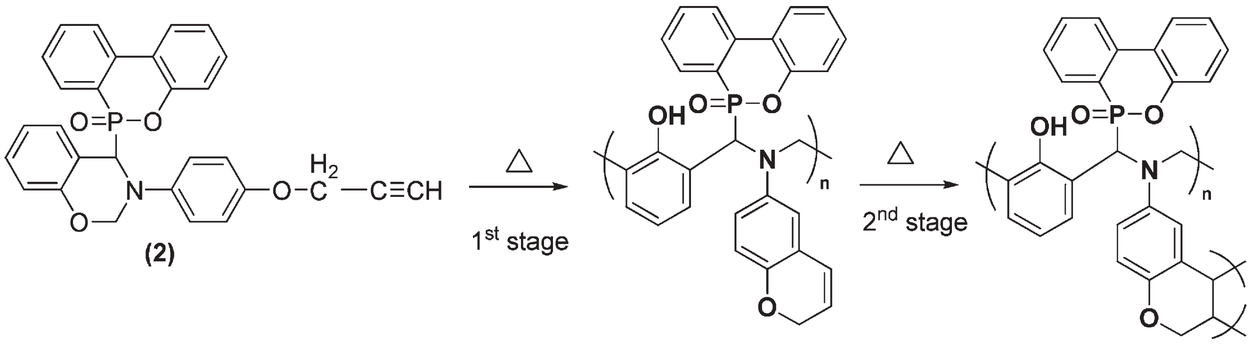


**FIGURE 7** DSC thermograms of **(2)** after accumulative curing (the same thermal history as in Fig. 6).



**SCHEME 2** Polymerization mechanism of **(2)**.

the first exotherm. IR and DSC data suggest that the ring opening of oxazine and the first-stage crosslinking of propargyl ether (the formation of benzopyran) are correlated with the first DSC exotherm.

Figure 6 shows the IR spectra of **(2)** after accumulative curing, and the curing temperature and curing time are marked in the figure. The absorption of C=C of benzopyran at 1,673 cm$^{-1}$ decreased gradually after curing at 220 °C for 30 min, and disappeared after curing at 240 °C for 60 min. Figure 7 shows the DSC profiles of **(2)** after accumulative curing (the same thermal history as in Fig. 6). The exothermic enthalpy corresponding to the ring opening of oxazine and crosslinking of propargyl group decreased after each curing cycle. The second exothermic peak decrease obviously after curing at 240 °C for 30 min, and disappeared after curing for 60 min. From IR and DSC data, the second exotherm is related with the polymerization of C=C bond in the benzopyran structure, and the final curing temperature for homopolymer and copolymers are set to 240 °C, 1 h. According to the data in Supporting Information Figures S3–S4 and Figures 5 and 6, a two-stage polymerization mechanism of **(2)** was proposed in Scheme 2. This first stage is related

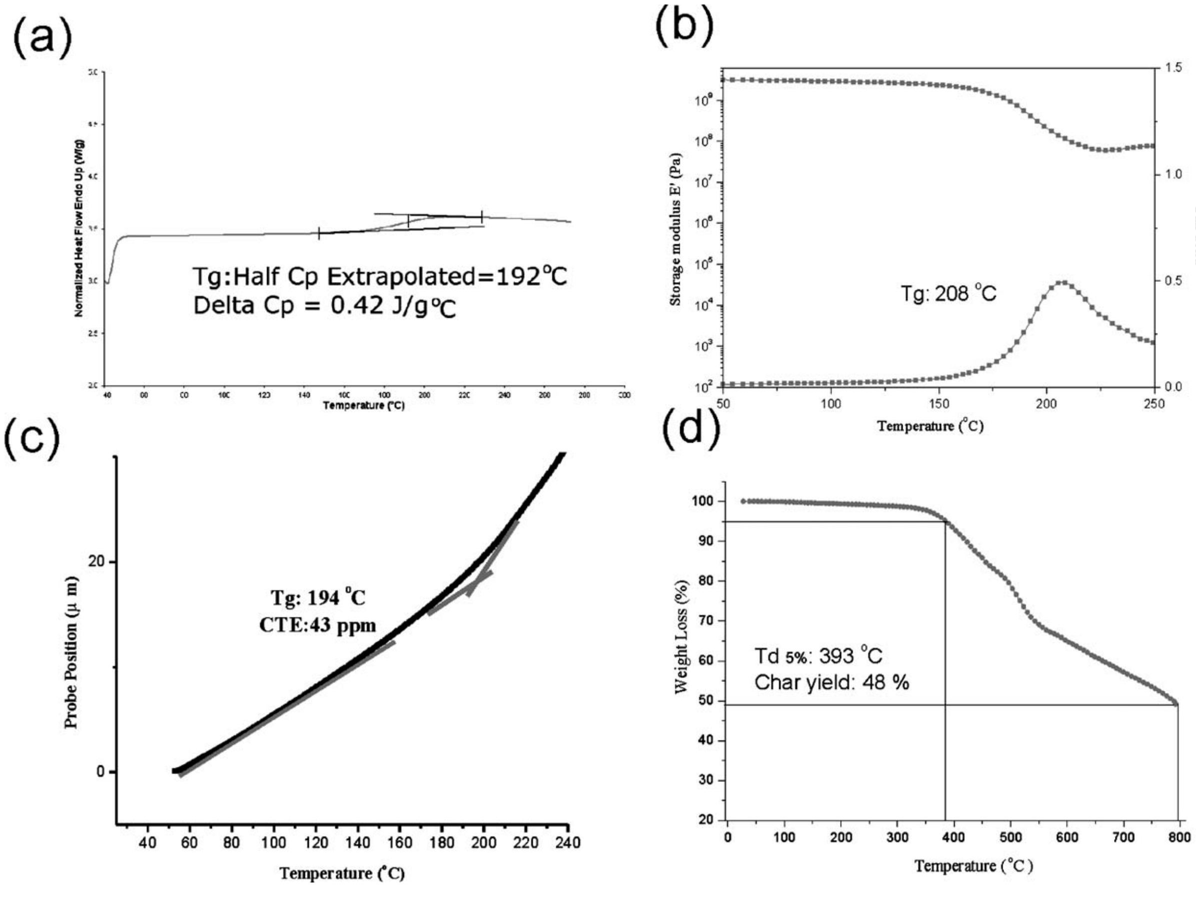


**FIGURE 8** (a) DSC, (b) DMA, (c) TMA, and (d) TGA thermograms of P**(2)**.

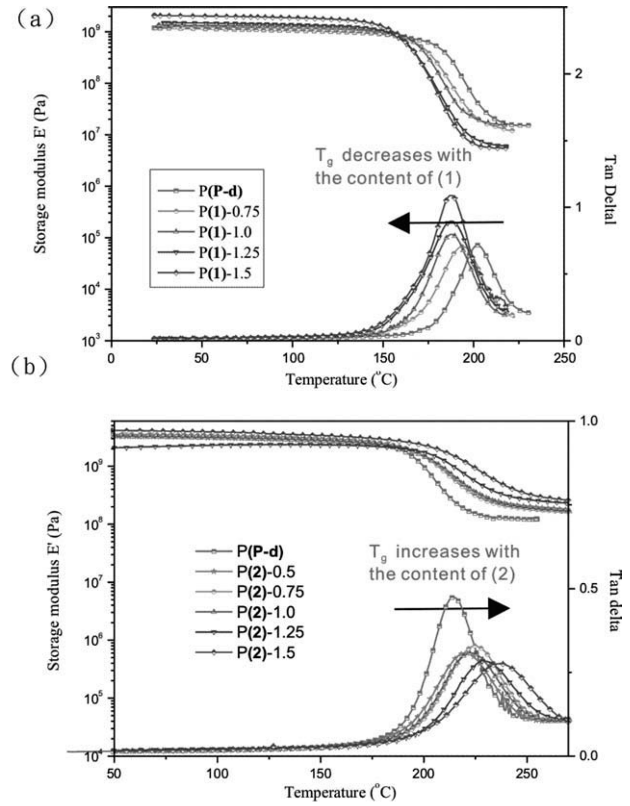


**FIGURE 9** DMA thermograms of (a) **(1)/P-d** and (b) **(2)/P-d** copolymers.

with the ring opening of the oxazine and Claisen rearrangement of propargyl ether, and the second stage is the curing of benzopyran. This observation is consistent with data reported in previous studies.[32–40]

### Properties of Homopolymers

Figure 8(a) shows the DSC thermogram of P**(2)**. The DSC scan shows the $T_g$ value of P**(2)** is 192 °C, which is higher than the value (161 °C) of P**(1)**, and much higher than the value (124 °C) of polybenzoxazine in which propargyl ether is replaced by a methyl linkage.[29] It is known that the free ortho position of a phenolic OH can react with oxazine linkage,[29,46–48] making P**(1)** a crosslinking polymer. From the $T_g$ data, the beneficial effect of crosslinking afforded by the incorporation of the propargyl ether group is higher than that by the phenolic OH group. Figure 8(b) shows the DMA thermogram of P**(2)**. $T_g$ is 208 °C from the tan $\delta$ peak. Although the value is lower than the value (251 °C) of P(P-appe),[40] probably due to the steric hindrance induced by the bulky phosphinate pendant, the value is much higher for other thermosets of mono-benzoxazines. TMA measurement shows P**(2)** exhibits a $T_g$ value of 194 °C, and a coefficient of thermal expansion of 43 ppm/°C [Fig. 8(c)]. TGA measurement shows the 5% decomposition temperature of P**(2)** is 393 °C [Fig. 8(d)], which is comparable with the value (362 °C) of P(P-appe). According to the previous studies,[49,50] the release of aniline fragments is responsible for the low thermal stability of polybenzoxazines, so the 5% degradation temperatures of common polybenzoxazines are not high. Therefore, introduction of a crosslinkable site into aniline moiety, such as allyl,[51] nitrile group,[52,53] and maleimide,[54,55] has been proved as an effective way to enhance the thermal stability of polybenzoxazines. In this case, the aniline linkage in P**(2)** is bonded to the other repeating unit via the crosslinking of propargyl ether, which makes P**(2)** thermally stable.

### Thermal and Flame-Retardant Properties of Copolymers

Figure 9 shows the DMA thermograms of (a) **(1)/P-d** and (b) **(2)/P-d** copolymers, and the detailed data are listed in Table 1. For the **(1)/P-d** copolymers, $T_g$s decrease with the content of **(1)**. In contrast, $T_g$s increase with the content of **(2)** in the **(2)/P-d** copolymers. For example, $T_g$ decreases from 208 °C for P**(P-d)** to 180 °C for P**(1)**-1.5), but increases to 237 °C for P**(2)**-1.5. The height of tan $\delta$ peak increases with the content of **(1)** in the **(1)/P-d** copolymers, suggesting the crosslinking density decreases with the content of **(1)**. However, opposite trend was observed in the **(2)/P-d** copolymers, suggesting the crosslinking density increases with the content of **(2)**. The observation is consistent with the $T_g$ data. A very interesting phenomenon in $T_g$ value was observed. In Figure 8, we report the $T_g$ of P**(2)** is 208 °C. However, the $T_g$ of **(2)/P-d** copolymers increases with the content of **(2)**. A $T_g$ value as high as 237 °C, which is much higher than both P**(P-d)** and P**(2)**, can be achieved for P**(2)**-1.5). A similar result was observed in our previous work, in which a benzoxazine with bulky trifluoromethyl pendants showed low $T_g$.[56] However, $T_g$ increased significantly when it was copolymerized with bis(3,4-dihydro-2H-3-phenyl-1,3-benzoxazinyl)methane (F-a, a benzoxazine based on bisphenol F/aniline/formaldehyde). It was thought that incorporating a benzoxazine without bulky pendant into a benzoxazine with bulky pendants can dilute the steric hindrance caused by the bulky pendants, leading to thermosets with a higher crosslinking density and consequently a higher $T_g$. In this case, the bulky phosphinate pendant might hinder the curing of P**(2)**, so the $T_g$ of P**(2)** is limited to 208 °C. When **P-d** was copolymerized with **(2)**, the steric hindrance caused by the bulky pendants was diluted, leading to copolymers with higher $T_g$ than neat P**(2)**. The dimensional stability of the copolymers was measured by TMA, and the data are listed in Table 1. A similar $T_g$ trend is observed in the TMA measurement. The dimensional stability of **(2)/P-d** is improved slightly with the content of **(2)**. The coefficient of thermal expansion (CTE) of **(2)/P-d** copolymers range from 37 to 40 ppm/°C, which are smaller than those (47–49 ppm/°C) of **(1)/P-d** copolymers. The results further demonstrate the beneficial effect of crosslinking afforded by the propargyl ether group is higher than that by the phenolic OH group. The 5 wt % degradation temperatures of **(2)/P-d** copolymers range from 418 to 440 °C. The values are relative high when compared with other polybenzoxazines. As to the flame retardancy, a thermoset with an UL-94 V-0 grade can be achieved with a phosphorus content as low as 0.75 wt %

for both **(1)/P-d** and **(2)/P-d** systems. This result demonstrates the good flame retardancy of the phosphinate pendant. Interesting, with the same phosphorus content, **(2)/P-d** copolymers show shorter burning time than **(1)/P-d** copolymers. The phenomenon might be probably related with the difference in microstructure and crosslinking density.

## CONCLUSIONS

We have provided an alternative approach to prepare a propargyl ether-containing benzoxazine by the nucleophilic substitution of a phenolic OH-containing precursor with propargyl ether in the catalysis of potassium carbonate. Four findings are reported in this work. First, we report the benzoxazine structure is stable in an alkaline condition for nucleophilic substitution. Second, because the amino group is protected in a benzoxazine form, no procedure of reduction or deprotection of the amino group is required. This approach demonstrates a facile synthesis of propargyl ether-containing benzoxazines. To the best of our knowledge, no propargyl ether containing-benzoxazines have been prepared by this approach. This finding will increase the design flexibility of benzoxazine-containing derivatives. Third, homopolymer of **(2)** shows better thermal properties than homopolymer of **(1)**. In addition, **(2)/P-d** copolymers exhibit better thermal properties than **(1)/P-d** copolymers. The data suggest that the beneficial effect of crosslinking afforded by the propargyl ether group is higher than that of the phenolic OH. Fourth, the flame retardancy and the thermal properties of the resulting copolymers increase simultaneously with the content of **(2)**. Generally, incorporating phosphorus element usually leads to decreased thermal properties, so the result of this work is rarely seen in the literature. These properties make **(2)** attractive for industrial application, especially in the field of copper clad laminates.

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