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Strategy to Prepare 4-Hydroxylphenyl Propargyl Ether-based Benzoxazine from Bisphenol A

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ABSTRACT

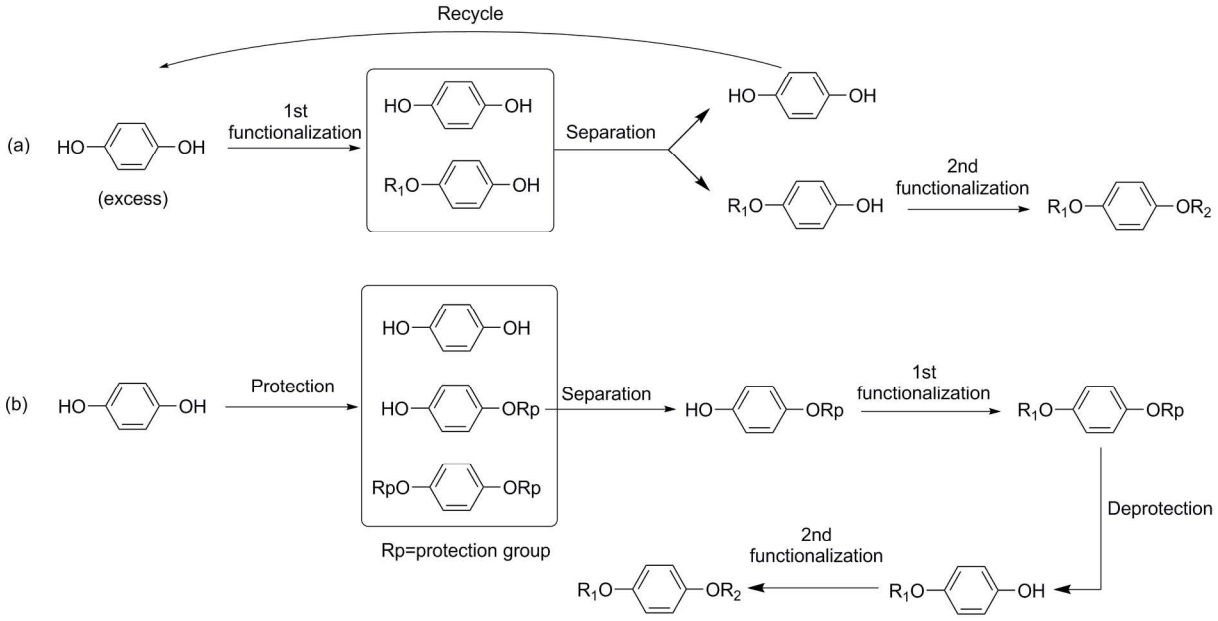
4-Aminophenyl propargyl ether/phenol-based benzoxazine **(P-appe)** has been reported by many authors. However, to the best of our knowledge, its isomer: 4-hydroxylphenyl propargyl ether/aniline-based benzoxazine **(HPPE-a)** has never been prepared in the literature. The precursor for **HPPE-a**, the 4-hydroxylphenyl propargyl ether, is difficult to prepare from hydroquinone without tedious separation because the reactivity of the two hydroxyls in hydroquinone is the same. In this study, we report a straightforward strategy to prepare **HPPE-a** from bisphenol A by a four-step process including thermolysis, nucleophilic substitution, oxidation, and Mannich-type condensation. The structure of was well characterized by NMR, IR, and high resolution mass spectra. Two exothermic peaks at 228 °C and 249 °C were observed in the DSC thermogram of **HPPE-a**. According to IR analysis, the first exotherm is related with the ring opening of the oxazine, and the second exotherm is related with Claisen rearrangement of propargyl ether. Since **P-appe** and **HPPE-a** are structural isomers, the structure-property relationship of these two benzoxazines was discussed. We found that thermal properties of thermoset of **HPPE-a** are slightly lower or comparable to those of thermoset of **P-appe**, but much higher than that of phenol/aniline-based benzoxazine (**P-a**).

KEYWORDS: benzoxazine; propargyl ether; synthesis; thermal properties; hydroquinone

INTRODUCTION

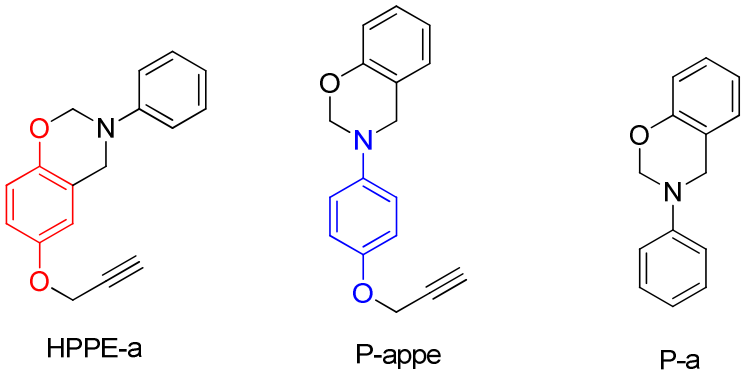
Recently, thermosetting polymers introducing a propargyl ether group have been reported showing high-temperature resistance.[1-3] Therefore, the introduction of a cross-linkable group should be effective to enhance thermal stability of polybenzoxazines. It is known that aryl propargyl ether undergoes Claisen type rearrangement to benzopyran after thermal treatment, and subsequently polymerizes through the curing of the C=C bond in the benzopyran structure.[2, 4-10] Syntheses of propargyl ether-containing benzoxazine have been reported independently by Takeichi et al.,[11] Yagci et al.,[12] Ishida et al,[13, 14] and Lin et al.[15] For example, the preparation of 4-aminophenyl propargyl ether/phenol-based benzoxazine **(P-appe)** has been reported by Takeichi et al.,[11] Yagci et al.,[12] and Ishida et al.[13, 14] The starting material of Takeichi's work and Ishida's work is 4-nitrophenol, and that of Yagci's work is acetic acid-protected aminophenol, acetaminophen. 4-Aminophenyl propargyl ether was the common precursor for benzoxazine preparation in these cases. Lin et al. used 4-aminophenol as the starting material, and a phosphinated hydroxylbenzoxazine was synthesized as an intermediate. Then, the propargyl ether-containing benzoxazine was obtained by nucleophilic substitution of the hydroxylbenzoxazine with propargyl bromide. The common characteristic of these propargyl ether-containing benzoxazines is that the benzoxazine moiety comes from the Mannich-type condensation of aminophenyl linkage with phenol and formaldehyde. However, to the best of our knowledge, the structure isomer of **P-appe**: the 4-hydroxylphenyl propargyl ether/aniline-based benzoxazine **(HPPE-a)** has never been prepared in the literature. The precursor for **HPPE-a**, the 4-hydroxylphenyl propargyl ether, is difficult to prepare from hydroquinone without tedious separation because the reactivity of the two hydroxyls in hydroquinone is the same.

Historically, syntheses of asymmetrical hydroqinone diethers, R_2O-Ph-OR_1, have not been achieved easily in a straightforward manner. They generally undergo multiple-step processes involving both synthesis and separation tasks, as shown in Scheme 1a. This method encounters intricate synthetic problems such as low conversions to avoid contaminating di-substitution products with mono-substitution products in the first functionalization. Thereafter, the process had to go through cumbersome separation procedures to ensure isolation of mono functional intermediates from the mixtures prior to the second functionalization.[16-20] Another common strategy based on protection/de-protection processes of hydroquinone (Scheme 1b). The first step is the protection of hydroquinone, making mixed products consisting of un-, mono- and di-protected hydroquinone products. The second step is the isolation of mono-protected product from the mixture. The third step is the first functionalization to the mono-protected product. The forth step is the de-protection, and the final step is the second functionalization.



Scheme 1. Known synthetic strategies to prepare asymmetrical hydroquinone diethers, R_2O-Ph-OR_1.

Therefore, it would be attractive if a strategy can be applied to prepare a hydroquinone monether (HO-Ph-OR_1) such as 4-hydroxylphenyl propargyl ether without tedious separation processes. Many years ago, Dai et al.[21-23] have published a straightforward precedure for preparing hydroqinone monoethers from bisphenol A. Taking advantage of this synthetic strategy, we prepared 4-hydroxylphenyl propargyl ether from bisphenol A, and then prepared **HPPE-a** (Scheme 2) based on the Mannich condensation of 4-hydroxylphenyl propargyl ether, aniline and formaldehyde. Detailed synthetic procedures and curing chemistry of **HPPE-a** were presented in this work. **HPPE-a**, simultaneously with a propargyl ether and benzoxazine structure, is an isomer of **P-appe** that has been prepared previously. It would provide insightful structure-property relationship of through study of these two benzoxazines.



Scheme 2. Structure of benzoxazines **HPPE-a**, **P-appe** and **P-a**.

EXPERIMENTAL

Materials. Bisphenol A (BPA), paraformaldehyde, tetra-n-butylammonium bromide (TBAB) and hydrochloric acid were purchased from Alfa aesar. Potassium carbonate and hydrogen peroxide aqueous (35%) were purchased from SHOWA. Propargyl bromide and sodium hydroxide was purchased from Aldrich. The solvents used are commercial products and were

without further purification. They were all used without purification unless specified in the experimental procedures.

Preparation of 4-isopropenyl phenol. BPA (115 g, 0.5 mol) and traced $NaOH_{(s)}$ (0.2 g) was added to a reaction flask as a catalyst, and then the pyrolysis was carried out at 230-250 °C under reduced pressure (15 mm of Hg pressure). The resulting mixed products of 4-isopropenyl phenol and phenol were then collected together in a receiving flask. After the thermolysis step, traced $NaOH_{(s)}$ (0.2 g) was again added to the mixed products of phenol and 4-isopropenyl phenol. The mixture immediately underwent a fractionation at 80-90 °C under 20 mmHg of vacuum to remove phenol. This was followed by heating the remaining 4-isopropenyl phenol and oligomers at temperatures of 230-250 °C under the reduced vacuum pressure (15 mmHg). This second pyrolysis was performed in a short span of time preferably less than one-hour, over a distillation head, which is equipped with a warm-water condenser for ensuring a fast and continuous flow of 4-isopropenyl phenol**.** The 60.0 g (90% of yield) of isolated 4-isopropenyl phenol was obtained.

Synthesis of 4-isopropenylphenyl propargyl ether (1). The solution of 4-isopropenyl phenol (24.1 g, 0.18 mol 4-isopropenyl phenol in 50 mL DMAc), propargyl bromide 53.16 g (0.36 mol), TBAB 3.22 g (0.01 mol), and potassium carbonate 32.73 g (0.24 mol) were added into a 250 mL three-neck flask with condenser and a magnetic stirrer. The mixed solution was heated to 85°C with stirring under a dry nitrogen purge for 3 hours with FTIR monitoring. After the disappearance of hydroxyl absorption, we separated out the catalyst and salt by filtration, then purified the reaction products by distillation at 130 °C (under 15 mmHg) and obtained a colorless liquid (21.1 g, 68% of isolated yield). FTIR (KBr): ν= 3292 (CH of propargyl ether), 2122 (C≡C of propargyl ether), 1626, 1607 (C=C of isopropenyl) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6), δ: 2.05 (s, 3H, CH_3), 3.55 (s, 1H, CH), 4.79 (s, 2H, OCH_2), 4.99(s, 1H, C=CH^a), 5.33 (s, 1H,

C=CH[b]), 6.93-6-96 (m, 2H, Ar-H), 7.43-7.45 (m, 2H, Ar-H). ^{13}C-NMR (400 MHz, DMSO-d_6), δ: 21.59, 55.47, 78.17, 79.28, 111.02, 114.65, 126.47, 133.58, 141.83, 156.79. HRMS (EI, *m/z*): $[M+H]^+$ Calcd for $C_{12}H_{12}O$, 172.0888; Found, 172.0882.

Synthesis of 4-hydroxylphenyl propargyl ether (2). Hydrogen peroxide$_{(aq)}$ 3.30 g (0.034 mol), 2-propanol (15 mL) and hydrochloric acid$_{(aq)}$ (0.5 mL) were added into a 100mL three-neck flask with condenser and a magnetic stirrer. Then, the 5.47 g (0.031 mol) of **(1)** dissolved in 2-propanol (40 mL) to dropwise into reaction slowly at 60 °C. After addition, the reaction was continued for another 4 hours with FTIR monitoring, The reaction solution was then cooled and quenched with 2N NaOH$_{(aq)}$. After a quick removal of 2-propanol by a rotary evaporator, the product was extracted into 80 mL of ethyl ether. As a result, we obtained a deep brown liquid (4.4 g, 95% of isolated yield). FTIR (KBr): *v*= 3381 (OH of phenol), 3290 (CH of propargyl ether), 2122 (C≡C of propargyl ether) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6), δ: 3.48 (s, 1H, CH), 4.64 (s, 2H, OCH2), 6.66-6.69 (m, 2H, Ar-H), 6.78-6.81 (m, 2H, Ar-H), 8.99 (1H, Ar-OH).

Synthesis of HPPE-a. 8.15 g (0.055 mol) of **(2)**, 3.60 g (0.12 mol) of paraformaldehyde and 5.12 g (0.055 mol) of aniline were added into a 100 mL three-neck flask with condenser and a magnetic stirrer in the presence of toluene as the solvent. As a result, we separated the surplus paraformaldehyde by filtration and removed solvent to obtain a brown viscous liquid (13.1 g, 90% of yield). FTIR (KBr): *v*= 3288 (CH of propargyl ether), 2121 (C≡C of propargyl ether), 1359 (C-N stretch), 1254 (Ar-O-C asymmetric stretch), 960 (N-C-O stretch) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6), δ: 3.51 (s, 1H, CH), 4.61 (s, 2H, OCH_2), 4.68 (s, 2H, CH_2 of oxazine), 5.37 (s, 2H, CH_2 of oxazine), 6.65-6.85 (m, 5H, Ar-H), 7.09-7.11 (m, 2H, Ar-H), 7.20-7.24 (m, 2H, Ar-H). ^{13}C-NMR (400 MHz, DMSO-d_6), δ: 48.99, 55.86, 77.87, 78.53, 79.46, 113.15, 114.63,

116.76, 117.30, 120.42, 121.72, 129.02, 147.80, 148.33, 150.93. HRMS (EI, *m/z*): $[M+H]^+$ Calcd for $C_{17}H_{15}NO_2$, 265.1103; Found, 265.1098.

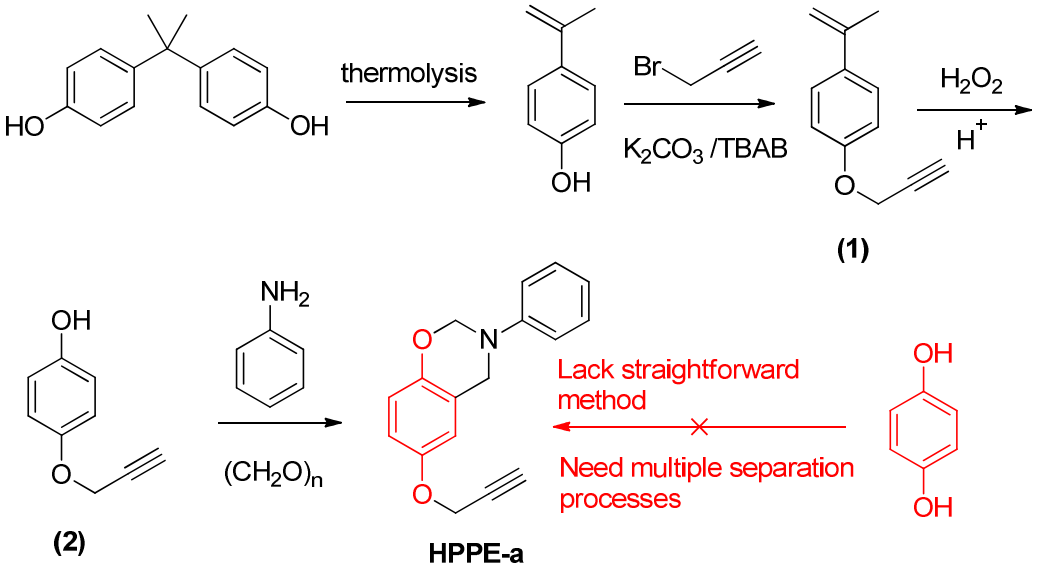
Curing Procedure. HPPE-a was stirred in a temperature-controlled hot plate at 160 °C for 20 min, and then transferred to an aluminum mold. The samples were cured at 180 °C (2 h), 200 °C (2 h), 220 °C (2 h), and 240 °C (1 h) in an air-circulating oven. Thereafter, samples were allowed to cool slowly to room temperature to prevent cracking. The thermoset of **HPPE-a** is named P**(HPPE-a),** and compared with P**(P-appe)**[11] and P**(P-a)**[11, 24].

Characterization. Fourier transform infrared (FTIR) were recorded over the range from 4000-450 cm^{-1} using a Perkin-Elmer Spectrum One FTIR spectrometer. NMR spectra were recorded using a Varian Inova 400 NMR in DMSO-d_6 and the chemical shift was calibrated by setting the chemical shift of DMSO-d_6 at 2.49 ppm. Melting points were measured using a BÜCHI B-540 melting-point apparatus operated at a heating rate raising 3 °C/min. Electron ionization (EI) mass spectra were recorded using a Finnigan/Thermo Quest MAT 95XL apparatus. Differential scanning calorimetry (DSC) scans were obtained using a Seiko SII model SSC/6200 in a nitrogen atmosphere at a heating rate of 10 °C/min. Thermal gravimetric analysis (TGA) was performed with a Seiko SII model SSC/5200 at a heating rate of 10 °C/min in an atmosphere of nitrogen or air. 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 δ 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 μm. Thermal mechanical analysis (TMA) was performed with a Perkin-Elmer Pyris Diamond TMA at a heating rate of 5 °C/min.

RESULTS AND DISCUSSION

Synthesis and Characterization of HPPE-a. As shown in Scheme 3, **HPPE-a** was prepared from bisphenol A by a four-step process including: (a) Thermolysis of BPA to 4-isopropenyl phenol; (b) Nucleophilic substitution the hydroxyl of 4-isopropenyl phenol with propargyl bromide; (c) Oxidation of the isopropenyl to phenol (d) Mannich-type condensation with aniline and paraformaldehyde. The preparation of 4-isopropenyl phenol has been reported previously in the literature by Schnell et al.[25] However, we prepared 4-isopropenyl phenol with an extra pyrolysis at temperatures of 230-250°C under the reduced vacuum pressure (15 mmHg). Without this modified distillation set-up, 4-isopropenyl phenol tends to freeze on the condenser thereby retarding the flow of 4-isopropenyl phenol into the receiving flask. As a result, the yield of 4-isopropenyl phenol suffers greatly. In addition, it is known that 4-isopropenyl phenol is a rather labile compound and can dimerize rapidly or polymerize slowly in a weak acidic solution with the presence of phenol or phenolic compounds. For purposes of safe and long-term storage, it is essential that 4-isopropenyl phenol be combined with a polar solvent such as DMAc[26, 27] during the distillation. Through this procedure, the 4-isopropenyl phenol solution can be stored at 0 °C for weeks without any appreciable changes. The yields of the 4-isopropenyl phenol in solution was generally in the range of 85-95% using this new procedure, while phenol recovery in this cracking step is about 95~98%. Etherification of phenol was accomplished with conventional Williamson synthesis. Propargyl bromide was added into a 4-isopropenyl phenol/DMAc solution in the presence K_2CO_3 and TBAB to obtain **(1).** The oxidation of the isopropenyl group of **(1)** was carried out with 35 wt% of H_2O_2 aqueous. The crude products were extracted and dried to give **(2)** with a yield of 95%. Then, **HPPE-a** was synthesized through Mannich-type condensation[28] by treating **(2)** with aniline and paraformaldehyde at 80 °C in a yield of 90%.

Figure 1 shows the ^{1}H-NMR spectra of **(2)** and **HPPE-a .** The disappearance of the phenolic OH signal of **(2)** at 8.99 ppm, and the appearance of oxazine signals of **HPPE-a** at 4.68 (H^{3}) and 5.37 (H^{4}) ppm indicate the transformation of phenolic OH to benzoxazine.



Scheme 3. Synthesis of benzoxazine **HPPE-a**

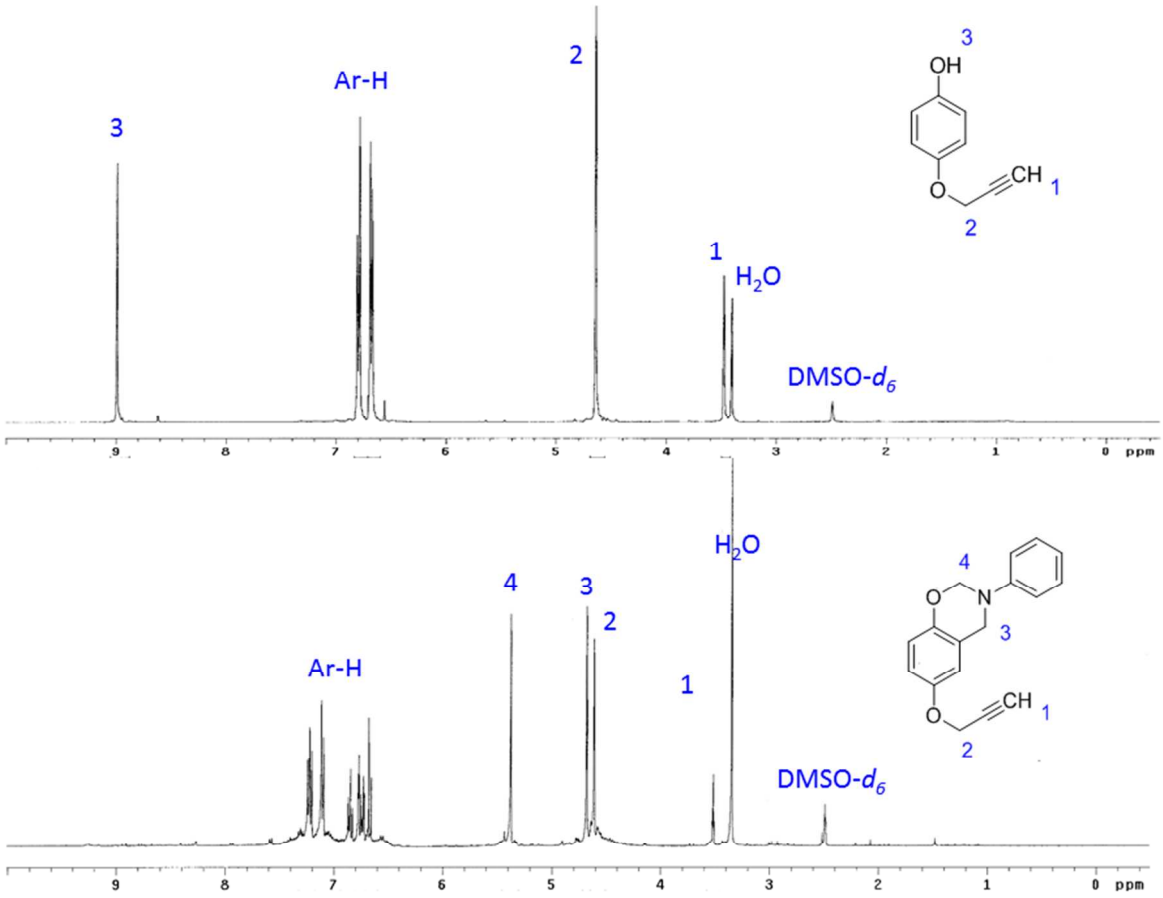


Figure 1. ^{1}H-NMR spectra of **(2)** and **HPPE-a**

DSC and IR Analysis of HPPE-a. DSC of thermograms of **(2)** and **HPPE-a** were shown in Figure 2. An exothermic peak at 253 °C corresponding to the polymerization of propargyl ether were observed for **(2).** Two exothermic peaks at 228 °C and 249 °C, with an exothermic enthalpy of 1059 and 780 J/g, respectively, were observed for **HPPE-a**. Through comparison of the two exotherms, we thought that the first exotherm at 228 °C is related with the ring-opening polymerization of benzoxazine, and the second exotherm is related with the polymerization of propargyl ether.

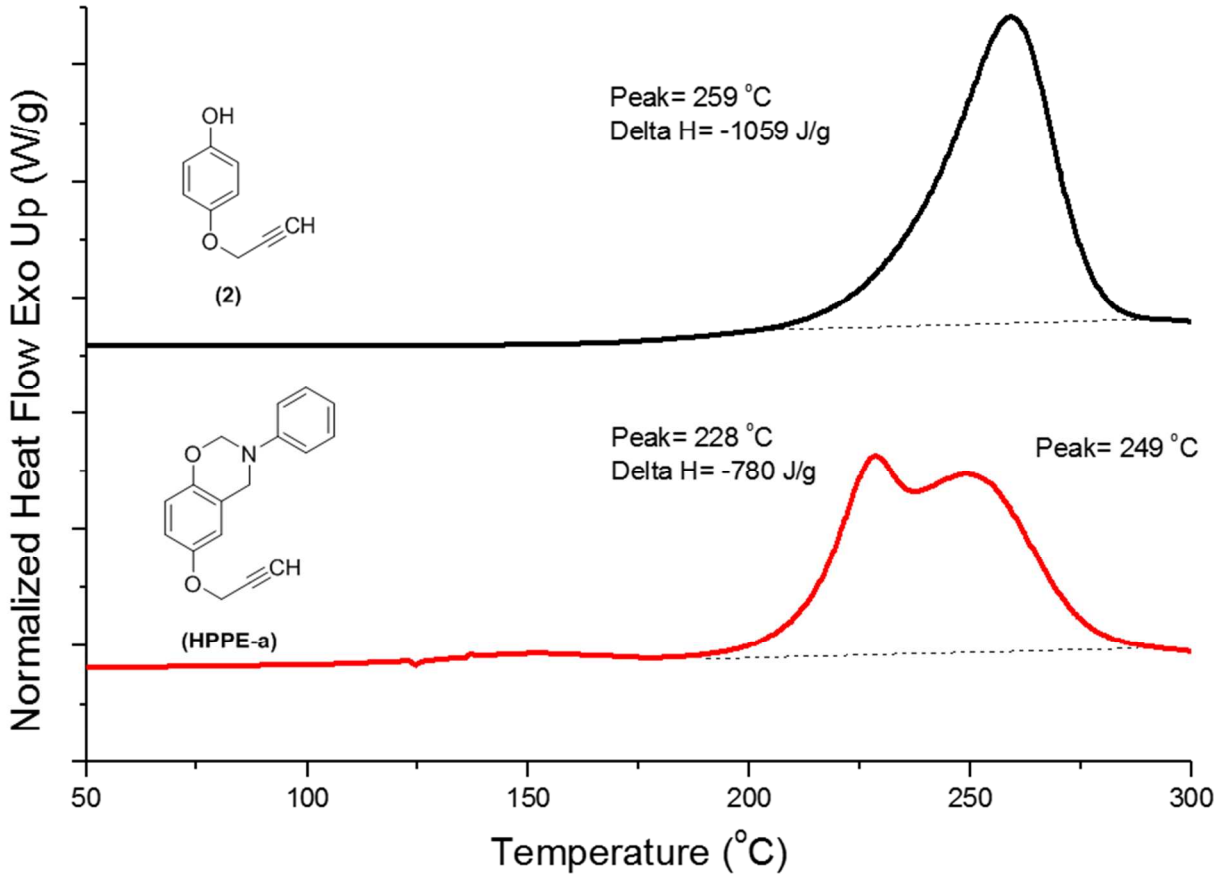


Figure 2. DSC thermograms of **(2)** and **HPPE-a**

Figure 3 shows the IR spectra of **HPPE-a** after accumulative curing at various temperatures for 30 min. The absorptions of oxazine at 960 cm^{-1} decreased apparently after curing at 180 °C. The C≡**C-H** absorption of propargyl ether at 3285 cm^{-1} decreased slightly after curing at 180 °C, but almost disappeared after curing at 220 °C. A C=C absorption appeared after curing at 180 °C, indicating the formation of the benzopyran structure (the product of Claisen type rearrangement of propargyl ether). However, the intensity of C=C bond remained after curing at 260 °C. This result suggests that the curing C=C bond of benzopyran did not occur in this system. In addition, an unknown absorption at 1710 cm^{-1} was observed, which was not observed in previous

studies.[11-15] We initially cure **HPPE-a** in an air oven, so we thought that the absorption is related with the oxidation product with quinone structure. However, we re-cure **HPPE-a** in a nitrogen atmosphere, and a similar result was observed. At this moment, we cannot interpret the origin of this absorption. A further analysis is required to understand this phenomenon.

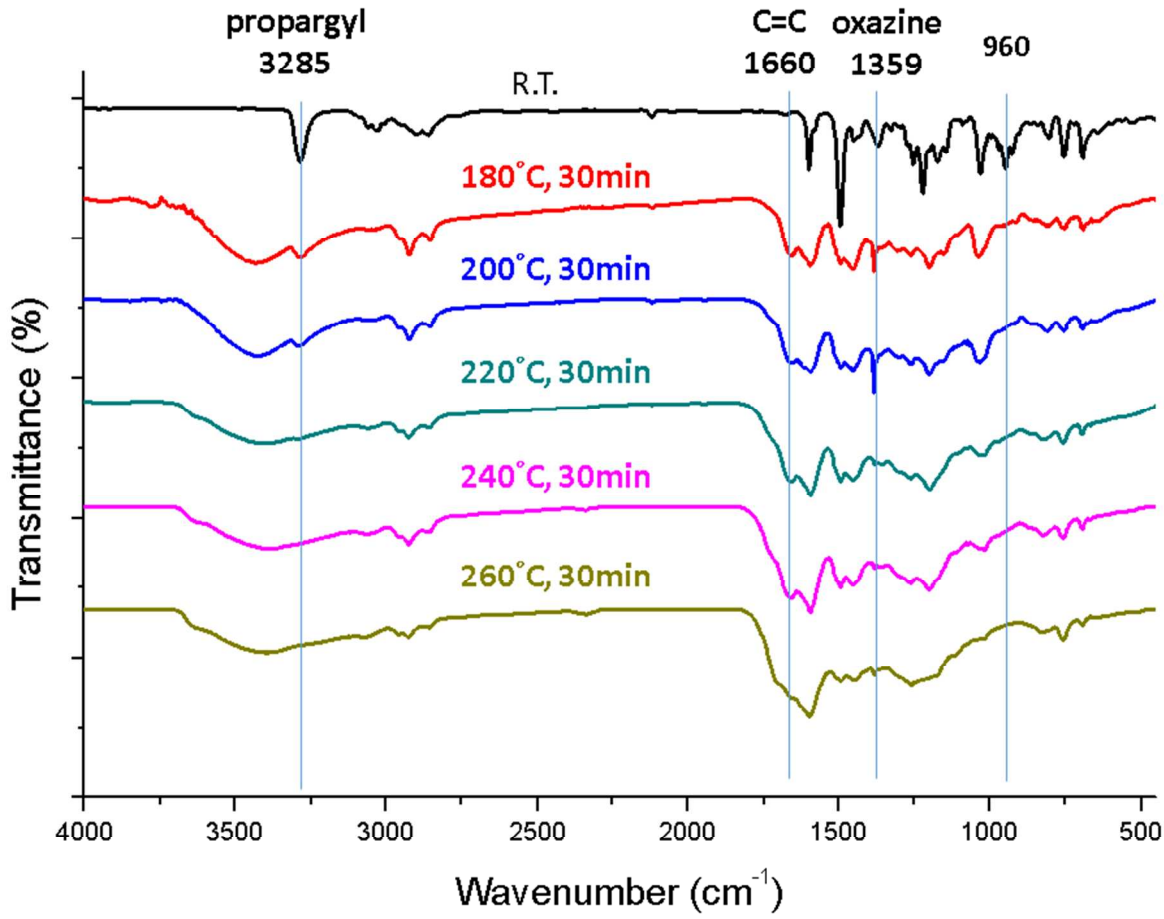


Figure 3. IR spectra of **HPPE-a** after accumulative curing at various temperatures for 30 min in a nitrogen atmosphere.

Figure 4 shows the DSC thermogram of **HPPE-a** after accumulative curing at various temperature for 30 min (the same thermal history as in Figure 3). The exothermic enthalpy corresponding to the ring-opening polymerization of oxazine and polymerization of propargyl

group decreased after each curing cycle. There is no exothermic enthalpy after curing at 240 °C, suggesting that the curing program (240 °C (1 h) for the final curing condition) we applied for preparing thermoset of **HPPE-a, P(HPPE-a),** is adequate. As shown in Figure 4, the intensity of first exothermic peak decreased obviously, while the second exothermic peak decreased slightly after curing at 180 °C for 30 min. IR analysis in Figure 3 shows that ring-opening polymerization of benzoxazine occurred after curing at 180 °C, further supporting that the first exotherm is related with the ring-opening polymerization of benzoxazine. According to the data in Figures 2-4, we proposed a two-stage polymerization mechanism of **HPPE-a** in Scheme 4. The first stage is related with the ring-opening polymerization of the oxazine, and the second stage is related with the Claisen rearrangement of propargyl ether. However, as shown in Figure 3, part of the propargyl ether polymerized along with the ring-opening polymerization of oxazine, so the boundary between two stages is blurry. As to the curing of C=C of benzopyran, it is not observed in this system.

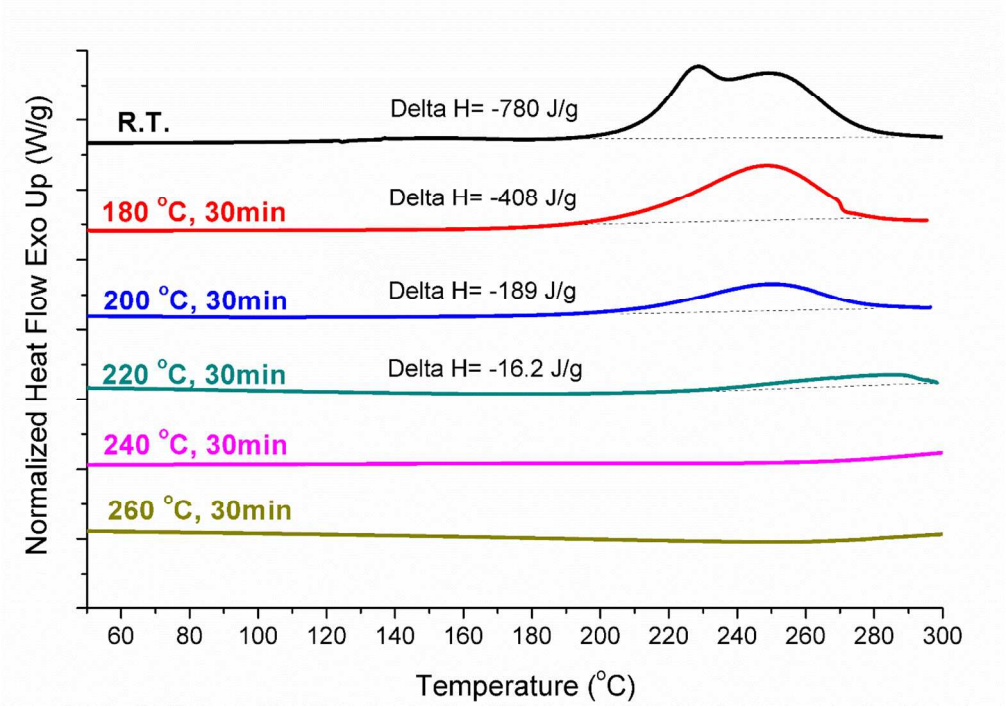
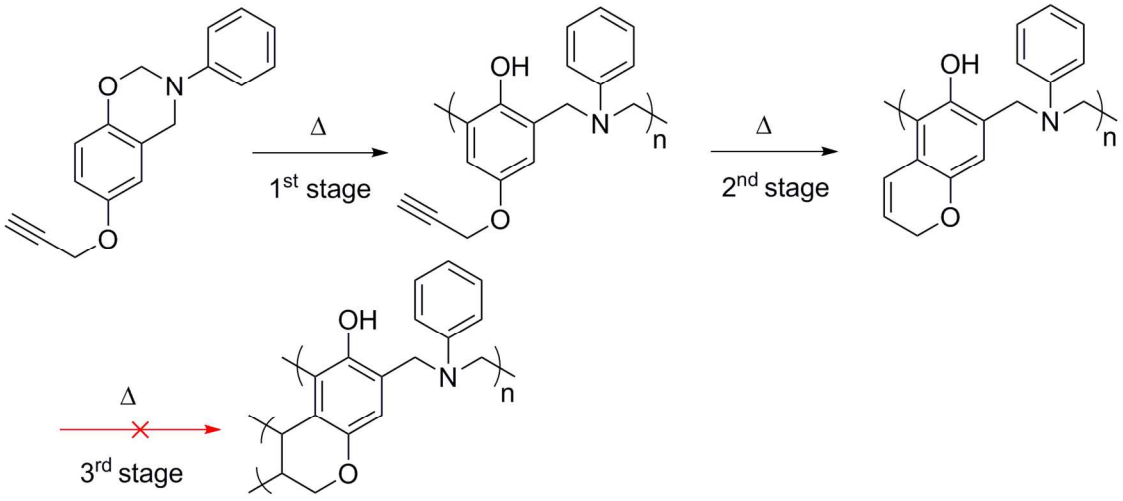


Figure 4. DSC thermogram of **HPPE-a** after accumulative curing (the same thermal history as in Fig.3).



Scheme 4. Proposed polymerization mechanism of **HPPE-a.**

Properties of P(HPPE-a). Figure 5(a) shows the DSC thermogram of P**(HPPE-a).** The T_g value of P**(HPPE-a)** is 230 ^oC with a ΔC_p of 0.178 J/g ^oC. Figure 5(b) shows that the DMA thermogram of P**(HPPE-a)**. T_g determined from the peak temperature of tanδ is 235 ^oC. Although the value is slightly lower than the value (251 ^oC) of P(**P-appe**),[11] probably due to the uncured characterization of C=C bond of benzopyran in this system, but is much higher than other thermosets of monobenzoxazines such as P(**P-a**) (T_g= 161 ^oC)[11, 24] that does not exhibit propargyl ether linkage. TMA measurement shows P**(HPPE-a)** exhibits a T_g value of 200 ^oC with a coefficient of thermal expansion of 43 ppm/^oC (Figure 5c). TGA measurement shows the 5% decomposition temperature of P**(HPPE-a)** is 372 ^oC (Figure 5d), which is slightly higher than the value (362 ^oC) of P(**P-appe**).

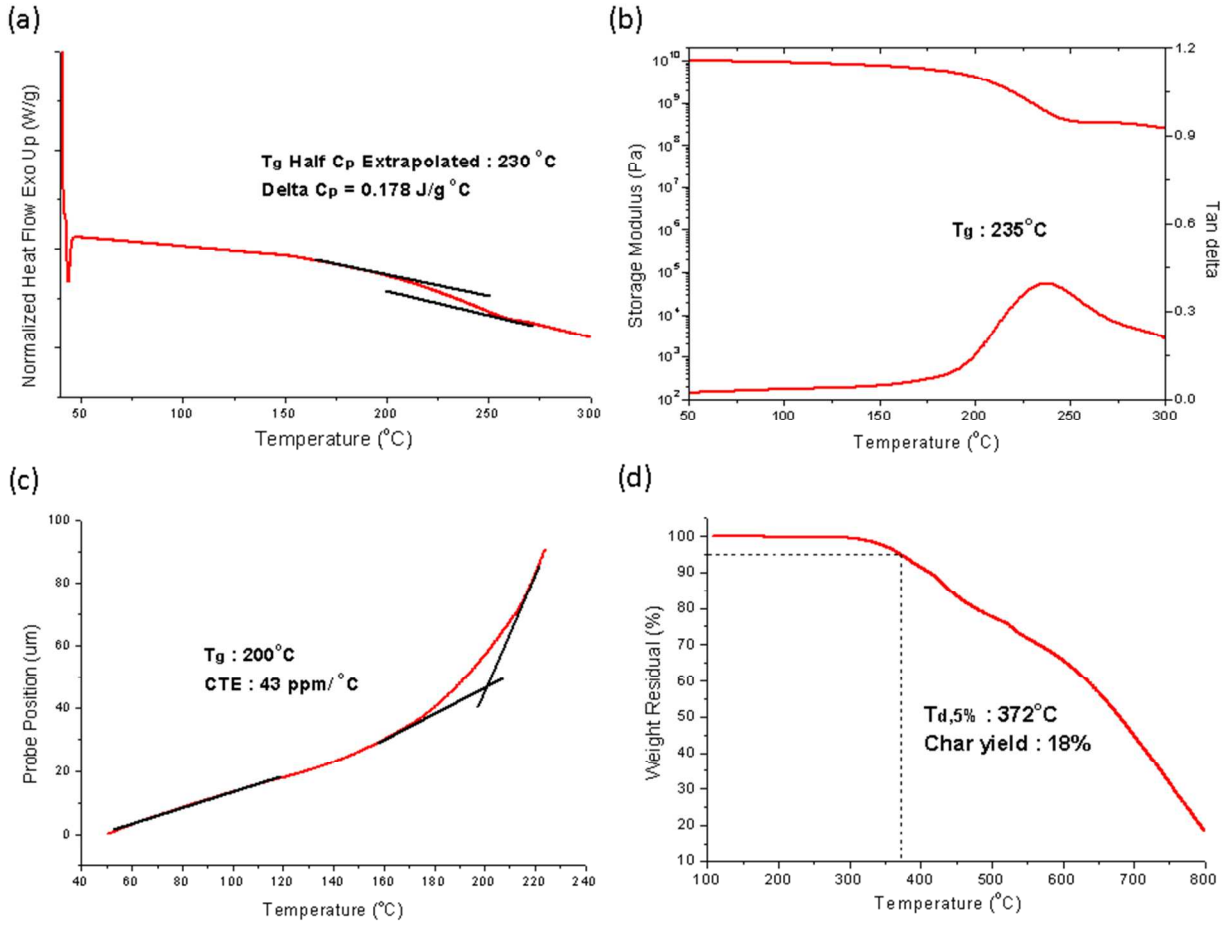


Figure 5. (a)DSC (b) DMA (c) TMA, and (d)TGA thermogram of P**(HPPE-a)**.

CONCLUSIONS

A 4-hydroxylphenyl propargyl ether/aniline-based benzoxazine **(HPPE-a)**, which is a structural isomer of 4-aminophenyl propargyl ether/phenol-based benzoxazine **(P-appe)** reported by Takeichi et al.,[11] and Yagci et al., [12] was successfully prepared from bisphenol A by a straightforward strategy. According to IR and DSC analyses in Figures 2-4, we proposed a two-stage polymerization mechanism of **(HPPE-a)**. The first stage is related with the ring-opening polymerization of the oxazine, and the second stage is related with the Claisen rearrangement of propargyl ether. However, part of the propargyl ether polymerized along with the ring-opening

polymerization of oxazine, so the boundary between two stages is blurry. As to the curing of C=C of benzopyran, it is not observed in this system. Thermal analyses show that the T_g of P**(HPPE-a)** is 235 ^oC by DMA, the coefficient of thermal expansion is 43 ppm/^oC, and T_d 5% (N_2) is 372 ^oC. These values are slightly lower or comparable with those of the thermoset of **(P-appe)**, probably due to the uncured characterization of C=C bond of benzopyran in this system, but are much higher than other thermosets of monobenzoxazine such as P(**P-a)** that does not exhibit propargyl ether linkage.

ACKNOWLEDGEMENTS

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GRAPHICAL ABSTRACT

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Strategy to Prepare 4-Hydroxylphenyl Propargyl Ether-based Benzoxazine from Bisphenol A

Due to the same reactivity of the two hydroxyls of hydroquinone, the 4-hydroxylphenyl propargyl ether/aniline-based benzoxazine **(HPPE-a)** is difficult to prepare from hydroquinone without tedious separation. In this study, we report a straightforward strategy to prepare **HPPE-a** from bisphenol A by a four-step process.