Synthesis of a Bisbenzylideneacetone-Containing Benzoxazine and Its Photo- and Thermally Cured Thermoset

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Supporting Information

ABSTRACT: A bis(4-hydroxybenzylidene)acetone/aniline-based benzoxazine (BHBA-a) was prepared from a bisbenzylidene-containing bisphenol, bis(4-hydroxybenzylidene)acetone (BHBA), aniline, and paraformaldehyde through Mannich condensation in a cosolvent of toluene/ethanol (2:1, v/v). The structure of BHBA-a was successfully confirmed by Fourier transform infrared and 1H and 13C NMR spectra. According to the differential scanning calorimetry (DSC) thermogram of BHBA, an immediate exothermic peak after the melting peak was observed, suggesting that BHBA is thermally active. NMR data of thermally treated BHBA confirm that the immediate exothermic peak after melting of BHBA in the DSC thermogram is resulted from the curing of a double bond. UV and 1H NMR spectra of BHBA-a show that the bisbenzylideneacetone moiety underwent dimerization through the [2π + 2π] cycloaddition. Therefore, two procedures were applied to cure BHBA-a. The first one was thermal curing of the double bond of bisbenzylideneacetone and oxazine moieties. The second one was photocuring of the bisbenzylideneacetone moiety, followed by thermal curing of the oxazine moiety. The thermal properties of thermosets were evaluated based on these two procedures. Thermosets of BHBA-a exhibit Ts as high as 318 °C for curing procedure 1 and 342 °C for curing procedure 2. These values are much higher than that of a traditional bisphenol/aniline-based benzoxazine thermoset. We conclude that the thermal curing of the double bond of bisbenzylideneacetone and oxazine moieties contributes to the good thermal properties.

1. INTRODUCTION

Polybenzoxazines feature for special characteristics such as a moderate-to-high thermal property,1−14 superior electrical properties,15 low water absorption,16 and low surface energy.17 Main-chain-type polybenzoxazine precursors18,19 and multifunctional benzoxazine20−25 have been developed to enhance the properties of traditional bifunctional benzoxazines. Introducing photosensitive moieties such as methacryloyl26,27 and coumarins28−30 is another strategy to enhance the properties of benzoxazine thermosets. For example, Ishida et al. prepared methacryloyl functional benzoxazine and studied its photopolymerization and thermally activated polymerization.26 They found that photopolymerization can be successfully carried out with and without a photoinitiator, but the thermally activated polymerization is compromised by low-temperature degradation. Kiskan and Yagci28 and Kuo et al.29,30 prepared coumarin-containing benzoxazines and found that polybenzoxazine with highly cross-linking networks can be obtained after photo- and thermal curing. Yagci et al. used benzoxazine as a hydrogen donor for photoinitiated free-radical polymerization of methyl methacrylate in the presence of 2-chlorothioxanthone as a sensitizer to prepare benzoxazine-containing poly(methylmethacrylate).31,32 A cross-linked structure is formed, which contains small domains of polybenzoxazine after ring-opening polymerization of benzoxazine.

Photo-cross-linkable liquid crystalline polymers with bis(benzylidene)cycloalkanone, such as pentanone, cyclohexanone, and cycloheptanone, have been prepared by Gangadhar and Kishore.33 They found that the photoreactivity decreases with the increase in the ring size of cycloalkanone. The chromophores with linear structure are likely to favor bimolecular reactions, leading to the cross-linking of the polymer chains. Murali and Samui have also reported bisbenzylidene cycloalkanone as a versatile building block for polymers.34 Some of the resulting polymers have a melting point at around 260 °C, indicating that the double bond of bisbenzylidene cycloalkanone is thermally stable at a temperature as high as 260 °C. On the basis of bis(4-hydroxybenzylidene)cycloalkanone, Alagar et al. synthesized bis(4-hydroxybenzylidene)cycloalkanone/aniline-based benzoxazine (Scheme 1a).35 However, the double bond of bisbenzylidene cycloalkanone is an exocyclic double bond, which is expected to be less photo- and thermal reactive because of the steric hindrance. If we replace the cycloalkanone moiety with the acetonel moiety, the steric hindrance is expected to be significantly reduced. In this work, bis(4-
hydroxybenzylidene)acetone (BHBA) was prepared, and a BHBA/aniline-based benzoxazine (BHBA-a) was prepared from BHBA, aniline, and paraformaldehyde (Scheme 1b). The differential scanning calorimetry (DSC) thermogram of BHBA (Figure 1, will be discussed later) shows that the double bond of bisbenzylideneacetone is thermally reactive. Because the double bond of bisbenzylideneacetone is thermally reactive, two procedures were applied to cure BHBA-a. The first one was thermal curing of the bisbenzylideneacetone moiety, followed by thermal curing of the oxazine moieties. The second one was photocuring of the bisbenzylacetone and oxazine moieties. The second one was photocuring of the bisbenzylideneacetone moiety, followed by thermal curing of the oxazine moiety. The thermal properties of thermosets were evaluated based on the two procedures. Detailed synthesis and analysis were reported.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of BHBA. BHBA was prepared from 4-hydroxybenzaldehyde and acetone in the presence of boron trifluoride diethyl etherate, a catalyst recommended by Narender et al. (Scheme 2). The characteristic peaks of CH\text{=}\text{CH} at 7.09 and 7.66 ppm and the signal of phenolic OH at 10.03 ppm were observed in the \text{H} NMR spectrum. The characteristic peaks of CH\text{=}\text{CH} at 142 and 123 ppm and the signal of carbonyl at 188 ppm were observed in the \text{C} NMR spectrum. Through the \text{H}−\text{H} correlation spectroscopy (COSY) and \text{H}−\text{C} heteronuclear correlation (HETCOR) (Figures S1 and S2), the signals of aromatic hydrogens and aromatic carbons were correctly assigned. A melting point at 204 °C with a delta enthalpy of 79 J/g, followed by an exothermic peak at 235 °C with a delta enthalpy of 175 J/g, was observed for BHBA-a in the DSC thermogram (Figure 1b). The processing window between the melting peak and the exothermic peak temperature was 31 °C.

2.2. Synthesis and Characterization of Benzoxazine (BHBA-a). BHBA-a was prepared by the Mannich condensation of BHBA, aniline, and formaldehyde (Scheme 2). Reaction in 1,4-dioxane, a common solvent for Mannich condensation, at 80 °C for 12 h leads to low conversion and some byproducts. However, BHBA-a can be successfully prepared using toluene/ethanol (2/1) as a solvent, a recommended medium for Mannich condensation in our previous work.36 Figure 2 shows the \text{H} NMR spectra of the product of the Mannich condensation in toluene/ethanol (2:1) at 80 °C for various reaction times. A signal of triazine, an intermediate for the Mannich condensation, was observed initially at 4.8 ppm after 1 h, and the triazine signal gradually transforms to benzoxazine. After 24 h, no phenolic OH and triazine signals were observed, suggesting that the reaction was complete. After washing the crude product by toluene, BHBA-a can be obtained with high purity (Figure 3).

Figure 3a shows the \text{H} NMR spectrum of BHBA-a. The characteristic peaks of oxazine at 4.71 and 5.53 ppm were observed. No signal of phenolic OH was observed, suggesting the purity of BHBA-a. Figure 3b shows the \text{C} NMR spectrum of BHBA-a. The characteristic peaks of oxazine were also observed at 48.7 and 79.3 ppm. Through the \text{H}−\text{H} COSY (Figure S3) and \text{H}−\text{C} HETCOR (Figure S4), the signals of aromatic hydrogens and aromatic carbons were correctly assigned. A melting point at 204 °C with a delta enthalpy of 79 J/g, followed by an exothermic peak at 235 °C with a delta enthalpy of 175 J/g, was observed for BHBA-a in the DSC thermogram (Figure 1b). The processing window between the melting peak and the exothermic peak temperature was 31 °C.

2.3. Thermal Properties of Thermally Cured Poly-(BHBA-a). Figure S5 shows the \text{H} NMR spectra of BHBA after thermal treatment at 240 °C for 2 h. The signals of C\text{=}\text{C} double bonds at 7.09 and 7.66 ppm disappeared, and new absorptions at 2.2 and 3.6 ppm appeared. It is known that a cyclobutane structure will be formed in the photodimerization of bisbenzylideneacetone and the signal of cyclobutane will be at around 4−5 ppm (4.19 and 4.58 ppm, as shown in Figure 6). However, there was no new absorption at around 4−5 ppm in Figure S5, suggesting that the reaction is resulted from the thermal curing of the double bond, not from the dimerization of bisbenzylideneacetone. The immediate exothermic peak after the melting of BHBA also supports the thermal curing of the double bond (Figure 1). Therefore, the double bond of bisbenzylideneacetone (marked in red in Scheme 3) and benzoxazine (marked in blue in Scheme 3) are both thermal...
curable moieties in BHBA-a. Figure 4 shows the dynamic mechanical analysis (DMA) thermograms of P(BHBA-a)-X. The $T_g$ taken from the peak temperature of tan $\delta$ is 276 and around 318 °C for P(BHBA-a)220 and P(BHBA-a)240, respectively. The high modulus at 300 °C (higher than 1 GPa) and the small height of tan $\delta$ intensity (less than 0.15) indicate the very high cross-linking density of P(BHBA-a)-X. Generally, thermosets of bisphenol-based benzoxazines such as bisphenol A/aniline-based poly(B-a) and bisphenol F/aniline-based poly(F-a) exhibit $T_g$ at around 150−160 °C.1,3 The very high $T_g$ value supports the cross-linking of the double bond of bisbenzylideneacetone in BHBA-a. As listed in Table 1, the $T_g$ values of thermosets of bis(4-hydroxybenzylidene)cyclopentanone/p-toluidine-based benzoxazine P(BHBP-T) and bis(4-hydroxybenzylidene)cyclohexanone/p-toluidine-based benzoxazine P(BHBH-T)35 are 202 and 189 °C, respectively. Although the $T_g$ values are measured by different instruments, the $T_g$ values of P(BHBP-T) and P(BHBH-T) are obviously lower than that of P(BHBA-a)-X. In the introduction part, we speculated that the exocyclic double bond of bisbenzylidene cycloalkanone is much less thermally reactive than the double bond of bisbenzylideneacetone because of the steric hindrance. This result supports our speculation.

According to rubber elasticity theory, the cross-linking density of P(BHBA-a)-220 was calculated by eq 1 suggested by Nielsen and Landel37

$$\log(E'_e/3) = 7.0 + 293(\rho_x)$$

where $E'_e$ is the storage modulus in the rubbery state (dyne cm$^{-2}$) and $\rho_x$ is the cross-linking density (mol cm$^{-3}$).

The value of $\rho_x$ is as high as $11.8 \times 10^{-3}$ mol cm$^{-3}$. This value is much higher than those of other benzoxazine
thermosets, demonstrating the high cross-linking density characteristic of P(BHBA-a)\(^{20,37}\).

Table 1 lists the thermal stability data on P(BHBA-X in a nitrogen atmosphere. P(BHBA-a)-X has the 5 wt % decomposition temperature higher than 405 °C and a char yield at 800 °C as high as 61%. Generally, the thermoset of bisphenol-based benzoxazines such as bisphenol F/aniline-based and bisphenol A/aniline-based benzoxazines exhibits 5 wt % decomposition temperature at around 300–350 °C.\(^1^{,3}\) The result demonstrates the high thermal stability characteristic of P(BHBA)-X. In addition, as listed in Table 1, the 5 wt % decomposition temperatures of thermosets of bis(4-hydroxybenzylidene)cyclopentanone and bis(4-hydroxybenzylidene)cyclohexanone-based benzoxazines\(^35\) are 259 and 247 °C, respectively, which are much lower than that of P(BHBA-a)-X. We think the reason for better thermal

Figure 3. (a) \(^1\)H NMR and (b) \(^{13}\)C NMR spectra of BHBA-a in DMSO-\(d_6\).
stability of P(BHBA-a)-X is the same as that discussed previously for \( T_g \) values.

### 2.4. Thermal Properties of UV- and Thermally Cured Poly(BHBA-a)

Figure 5 shows the UV absorption spectra of BHBA-a in DMAc at a concentration of 0.8 mg/40 mL after irradiation at 365 nm for various periods of time. An approximately 50% reduction of the \( \pi-\pi^* \) absorption was observed. This result indicates that one of the two double bonds remains after UV irradiation, and the structure of BHBA-a dimer is proposed in Scheme 4.

Figure 6 shows the \( ^1H \) NMR spectra of BHBA-a after irradiation at 365 nm for various periods of time. Two new absorptions at 4.19 and 4.58 ppm, corresponding to the cyclobutane structure of the BHBA-a dimer (Scheme 4), appear after irradiation for 15 min. The appearance of the new absorption of cyclobutane is consistent with the result of UV analysis (Figure 5). The signals for oxazine at 4.7 and 5.6 ppm are intact, suggesting that oxazines are stable under the UV irradiation that we have applied. The oxazines in the BHBA-a dimer can be thermally cured, leading to P(BHBA-a)-uv-X (Scheme 4).

Figure 7 shows the DMA thermograms of P(BHBA-a)-uv-X. The \( T_g \) taken from the peak temperature of tan \( \delta \) is 294, 318, and 342 °C for X as 200, 220, and 240, respectively. With the same curing temperature, the \( T_g \) value of P(BHBA-a)-uv-X is higher than that of P(BHBA-a)-X. This result indicates that the BHBA-a dimer, a tetrafunctional benzoxazine, contributes to a higher cross-linking density.

Table 1. Thermal Properties of the Resulting Polybenzoxazine

| sample ID   | tan \( \delta \) (°C) (DMA) | \( T_{\text{g,5\%}} \) (°C) | char yield (%) |
|-------------|----------------------------|-----------------|---------------|
| P(BHBA-a)-220 | 276                       | 408             | 61            |
| P(BHBA-a)-240 | 318                       | 405             | 61            |
| P(BHBP-T) | 202                       | 259             |               |
| P(BHBH-T) | 189                       | 247             |               |
| P(BHBA-a)-uv-200 | 294                | 340             | 58            |
| P(BHBA-a)-uv-220 | 318                | 349             | 58            |
| P(BHBA-a)-uv-240 | 342               | 376             | 60            |
| P(BHBH-T)-uv | 221                       | 280             | 38            |
| P(BHBH-T)-uv | 206                       | 267             | 32            |

“Measured by DMA at a heating rate of 5 °C/min; \( T_g \) values were determined from a peak temperature of the tan \( \delta \) curve. bTemperature corresponding to 5% weight loss by thermogravimetry at a heating rate of 20 °C/min in nitrogen. cResidual weight % at 800 °C in nitrogen. dThermoset of P(BHBP-T). e\( T_g \) (DSC) of P(BHBP-T) was determined after curing at 200 °C (2 h). f\( T_g \) (DSC) of P(BHBP-T)-uv was determined after UV irradiation for 30 min and curing at 200 °C (2 h). gValues were determined from a peak temperature of the tan \( \delta \) curve. hThermoset of P(BHBH-T). i\( T_g \) (DSC) of P(BHBH-T) was determined after curing at 200 °C (2 h). j\( T_g \) (DSC) of P(BHBH-T)-uv was determined after UV irradiation for 30 min and curing at 200 °C (2 h). kResidual weight % at 800 °C in nitrogen.
further demonstrating the high cross-linking density characteristic of P(BHBA-a). Table 1 lists the thermal stability data of P(BHBA-a)-uv-. However, the thermal stability of P(BHBA-a)-uv- is lower than that of P(BHBA-a)-X, probably because of the less thermal stability of cyclobutane moiety or the degradation from UV irradiation.

3. CONCLUSIONS

We have successfully prepared BHBA-a from BHBA, aniline, and paraformaldehyde in a cosolvent of toluene/ethanol (2:1, v/v). The DSC thermogram of BHBA shows an immediate exothermic peak after the melting peak (Figure 1), suggesting that BHBA is thermally active. The NMR data of thermally treated BHBA (Figure S5) confirm that the immediate exothermic peak after melting of BHBA in the DSC thermogram is resulted from the curing of the double bond. The UV absorption (Figure 5) and 1H NMR (Figure 6) spectra of BHBA-a show that the bisbenzylideneacetone moiety can be

Figure 6. 1H NMR spectra of BHBA-a after irradiation at 365 nm for various periods of time.

Figure 7. DMA thermograms of P(BHBA-a)-uv-X.
photocured to afford a tetrafunctional benzoxazine, BHBA-a dimer. Therefore, two curing procedures were applied for BHBA-a to afford thermosets. The first one was thermal curing of the bisbenzylideneacetone and oxazine moieties, forming thermoset P(BHBA-a)-X. The second one was photocuring of the bisbenzylideneacetone moiety, followed by thermal curing of the oxazine moiety, forming thermoset P(BHBA-a)-uv-X.

According to the DMA thermograms (Figure 4), P(BHBA-a)-X exhibits a very high \( T_g \) value (318 °C as \( X \) is 240). The cross-linking of the double bond of bisbenzylideneacetone might be responsible for the \( T_g \) being much higher than that of the thermoset of general bifunctional benzoxazines. According to the DMA thermograms (Figure 7), P(BHBA-a)-uv-X exhibits a higher \( T_g \) value (342 °C as \( X \) is 240) than that of P(BHBA-a)-X, indicating that the BHBA-a dimer, a tetrafunctional benzoxazine, contributes to a higher cross-linking density. In conclusion, we successfully demonstrate that incorporating bisbenzylideneacetone into benzoxazine appears to be a good strategy to afford high-performance benzoxazine thermosets, and this work contributes the structure–property relationship for the design of high-performance benzoxazine thermosets.

4. EXPERIMENTAL SECTION

4.1. Materials. 4-Hydroxybenzaldehyde (from Acros), acetone (from Acros), boron trifluoride diethyl etherate (from Alfa), aniline (from Acros), paraformaldehyde (from PanReac), and all solvents (high-performance liquid chromatography grade) were purchased from various commercial sources and were used without further purification.

4.2. Characterization. DMA was performed using a PerkinElmer Pyris Diamond DMA analyzer with a sample size of 5.0 cm \( \times 1.0 \text{ cm } \times 0.2 \text{ cm} \). 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 using a bending mode with an amplitude of 5 μm. UV spectra were obtained using UV WinLab Lambda 25. Thermogravimetric analysis was performed using a PerkinElmer Pyris 1 at a heating rate of 20 °C/min in an atmosphere of nitrogen or air. DSC scans were obtained using a PerkinElmer DSC 7 calorimeter in a nitrogen atmosphere at a heating rate of 10 °C/min. NMR measurements were recorded using a Varian Inova 600 NMR spectrometer in DMSO-\(d_6 \) and the chemical shift was calibrated by setting the chemical shift of DMSO-\(d_6 \) at 2.49 ppm. IR spectra were obtained from at least 32 scans in the standard wavenumber range of 667–4000 cm \(^{-1} \) using a PerkinElmer RX1 infrared spectrophotometer.

4.3. Synthesis of BHBA. A bisbenzylideneacetone-containing bisphenol, BHBA, was prepared according to the following procedure: Acetone (1.2 g) (20.5 mmol), 4-hydroxybenzaldehyde (5.0 g) (41 mmol), and 30 mL of methanol were introduced into a 250 mL round-bottom glass flask equipped with a condenser and a magnetic stirrer. After a homogeneous solution was obtained, boron trifluoride diethyl etherate (0.1 mL) was added and stirred at 50 °C for 4 h. After that, the solution was poured into methanol/water (1:1), yielding a yellow powder. After drying the powder at 60 °C, the yield was 81%. \(^1\)H NMR (DMSO-\(d_6 \)): \( \delta = 6.83 \) (4H, H\(^5 \)), 7.09 (2H, H\(^3 \)), 7.62 (4H, H\(^3 \)), 7.66 (2H, H\(^5 \)), 10.03 (2H, OH). \(^{13}\)C NMR (DMSO-\(d_6 \)): \( \delta = 115.84 \) (C\(^6 \)), 122.67 (C\(^3 \)), 125.84 (C\(^4 \)), 130.44 (C\(^5 \)), 142.39 (C\(^2 \)), 159.83 (C\(^7 \)), 188.04 (C\(^1 \)). A melting peak at 243 °C with an enthalpy of 64 J/g was observed in the DSC thermogram. FT-IR (KBr): 1601 cm \(^{-1} \) (C=C stretch), 1648 cm \(^{-1} \) (C=O stretch), 3325 cm \(^{-1} \) (OH stretch).

UV–vis \( \lambda_{\max } (C_2H_5OH) = 351 \text{ nm} \) (C=C–C–).

4.4. Synthesis of BHBA/Aniline/Formaldehyde-Based Benzoxazine (BHBA-a). BHBA (1.0 g) (3.76 mmol), aniline (0.7 g) (7.52 mmol), paraformaldehyde (0.451 g) (15.04 mmol), and toluene/ethanol (2:1) (30 mL) were introduced into a 250 mL round-bottom glass flask equipped with a condenser and a magnetic stirrer. The mixture was stirred at 80 °C for 24 h. The solvent was evaporated in vacuum, and the powder was washed with toluene and dried at 100 °C to afford a yellow powder with a yield of 73%. \(^1\)H NMR (DMSO-\(d_6 \)): \( \delta = 4.71 \) (4H, H\(^{10} \)), 5.53 (4H, H\(^{7} \)), 6.80 (2H, H\(^{6} \)), 6.88 (2H, H\(^{15} \)), 7.14 (6H, H\(^{3,13} \)), 7.24 (4H, H\(^{14} \)), 7.53 (2H, H\(^{5} \)), 7.58 (2H, H\(^{2} \)), 7.65 (2H, H\(^{7} \)). \(^{13}\)C NMR (DMSO-\(d_6 \)): \( \delta = 48.77 \) (C\(^{10} \)), 79.31 (C\(^{11} \)), 116.83 (C\(^{6} \)), 117.53 (C\(^{3} \)), 120.77 (C\(^{13} \)), 121.76 (C\(^{8} \)), 123.61 (C\(^{4} \)), 127.16 (C\(^{7} \)), 127.53 (C\(^{5} \)), 128.43 (C\(^{14} \)), 129.12 (C\(^{15} \)), 142.15 (C\(^{1} \)), 147.53 (C\(^{9} \)), 156.12 (C\(^{7} \)), 188.01 (C\(^{1} \)). FT-IR (KBr): 934 cm \(^{-1} \) (N–C–O stretch), 1032 cm \(^{-1} \) (Ar–O–C symmetric stretch), 1232 cm \(^{-1} \) (Ar–O–C asymmetric stretch), 1367 cm \(^{-1} \) (C–N stretch), 1601 cm \(^{-1} \) (C=C–C stretch), 1648 cm \(^{-1} \) (C=O stretch). A melting peak at 205 °C with an enthalpy of 76 J/g and an exothermic peak at 235 °C with an enthalpy of 176 J/g were observed in the DSC thermogram.

4.5. Sample Preparation and Curing Procedure.

4.5.1. Thermal Curing. BHBA-a (2.0 g) was melted, stirred on a hot plate, and then cured at 180 °C (2 h), followed by 200 °C (2 h), 220 °C (2 h), and 240 °C (2 h). The thermoset is named P(BHBA-a)-X, in which X is the final curing temperature. For example, if the curing procedure includes 180 °C (2 h), 200 °C (2 h), and 220 °C (2 h), the sample is named P(BHBA-a)-220.

4.5.2. Photocuring Followed by Thermal Curing. BHBA-a (1.0 g) was dissolved in DMAC (20 wt %) and irradiated by UV light (100 W, 365 nm) for 30 min. The solution was heated in an oven at 80 °C for 12 h to remove the solvent and then cured at 180 °C (2 h), followed by 200 °C (2 h), 220 °C (2 h), and 240 °C (2 h). The thermoset is named P(BHBA-a)-uv-X, in which X is the final curing temperature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00573.

\(^{1}\)H–\(^{1}\)H COSY NMR spectra of BHBA and BHBA-a in DMSO-\(d_6 \), \(^{1}\)H–\(^{1}\)C HETCOR NMR spectra of BHBA and BHBA-a in DMSO-\(d_6 \), and \(^{1}\)H NMR spectra of BHBA (PDF)
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**Notes**

The authors declare no competing financial interest.

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