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A deoxybenzoin-based 1,3-benzoxazine resin with unique catalyzed cationic polymerization mechanism was developed to afford high flame-retardant thermosets.

н Self-Catalyzed Cationic Ring-Opening Polymerization Deoxybenzoin Based High Thermal Stability **Benzoxazine Resin** Low Flammability

Unique Self-Catalyzed Cationic Ring-Opening Polymerization of a High

Performance Deoxybenzoin-based 1,3-Benzoxazine Monomer

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ABSTRACT: An asymmetric bis(1,3-benzoxazine) monomer based on deoxybenzoin has been synthesized through Mannich condensation. The chemical structure of this deoxybenzoin-based monomer has been confirmed using ¹H NMR, ¹³C NMR, FT-IR and elemental analysis. The assignments for the oxazine protons and carbon atoms in the asymmetric structure have also been confirmed using two-dimensional (2D) NMR techniques, including ¹H-¹H nuclear Overhauser effect spectroscopy (NOESY) and ¹H-¹³C heteronuclear multiple quantum coherence spectroscopy (HMQC). In addition, the effect of incorporation of deoxybenzoin on the mode of polymerization of benzoxazine has been investigated using differential scanning calorimetry (DSC), in situ FT-IR and ¹H NMR spectroscopy. This deoxybenzoin containing bis(benzoxazine) exhibits a low polymerization temperature resulting from a unique self-catalyzed cationic polymerization mechanism. Furthermore, the thermal stability of the resulting polybenzoxazine has been studied using thermogravimetric analysis (TGA). This deoxybenzoin-based polybenzoxazine exhibits high thermal stability and low flammability, with a T_{d5} temperature of 403 °C, a high char yield value (68%) and low total heat release (THR of 11.4 KJ/g).

Keyword: Benzoxazine; deoxybenzoin; Polybenzoxazine; low flammability.

1. Introduction

Composites based on polymeric matrices are useful for a wide range of industrial applications that require high performance but light-weight, such as in construction, transportation and electronic materials. However, the inherent flammability of many polymeric materials poses a societal threat, especially in enclosed or isolated spaces. Halogenated molecules, such as brominated aromatics, are widely used as flame retardants by inhibiting gas phase combustion [1]. Unfortunately, while such halogen-containing organic structures are effective flame retardants, they have also been revealed as unfriendly and harmful to human health [2-4]. Nonhalogenated flame retardants, such as phosphorus-containing compounds and hydrated metal oxides, inhibit flammability through various mechanisms [5-9]. In general, the trade-off between polymer flammability and flame retardant toxicity has to be addressed, and halogen-free polymers that combine the desirable properties of excellent processability and low flammability are desired.

Benzoxazine resin, as a relatively new type of thermoset, has attracted strong attention from both academia and industry in recent years [10-15]. Specifically, this class of polymers offers significant advantages compared with other traditional thermosets, such as high thermal resistance [16,17], good mechanical properties [18], low dielectric constant [19-21], low surface free energy [22-24], and low flammability [25]. These desirable properties originate from the excellent flexible molecular structure of benzoxazines. By taking advantage of molecular design flexibility, various bis(benzoxazine) monomers synthesized from bisphenols, primary monoamines and formaldehyde have been widely reported since 1994 (Scheme 1) [26-28].

Scheme 1. Synthesis of bis(benzoxazine)s through a one-pot modified Mannich reaction based on the flexible molecular design capability of benzoxazines.

The introduction of deoxybenzoin into polymers has been reported to significantly decrease the possibility to undergo combustion [29-32]. The first use of 4,4'-bishydroxydeoxybenzoin (BHDB) in polycondensation chemistry has been described. Calorimetric methods has been used to demonstrate exceedingly low heat release for BHDB-containing polymers undergoing combustion [33,34]. Since BPA-based polymers are moderately flammable and used with flame-retardant additives, BHDB could be used as a replacement for BPA. Surprisingly, deoxybenzoin-based bis(benzoxazine) monomer has not been reported. The synthesis and properties of main chain type bishydroxydeoxybenzoin-based benzoxazines has recently been reported [35].However, the structure of most benzoxazine polymers is poorly defined. A detailed structural characterization for these materials has not been reported. In addition, the mode of polymerization for deoxybenzoin-based benzoxazines has not been detailed.

An asymmetric bis(benzoxazine) monomer based on deoxybenzoin from BHDB, aniline and paraformaldehyde has been prepared. The temperature for ring-opening polymerization of deoxybenzoin-based benzoxazine is significantly lower than that for traditional bis(benzoxazine)s. Furthermore, the polybenzoxazine derived from this new benzoxazine monomer shows higher thermal stability and lower flammability than many traditional benzoxazine resins. Unexpectedly, the thermal properties of the BHDB based polybenzoxazine is comparable to those of BHDB based main chain type benzoxazines. This reveals an exception since it is well-known that thermosets derived from main chain type benzoxazines shows higher thermal stability than ones from monomers. Detailed synthetic methodology, a proposed polymerization mechanism and the kinetics of deoxybenzoin-based benzoxazine monomer, and the properties of the resulting polybenzoxazine are presented.

2. Experimental

2.1. Materials

Desoxyanisoin, pyridine hydrochloride, and paraformaldehyde (99%), were used as received from Sigma-Aldrich. Aniline was purchased from Aldrich and purified by distillation. Hexanes, xylenes, ethyl acetate, and sodium sulfate were obtained from Fisher scientific and used as received. Bisphenol-A and aniline derived benzoxazine monomer, 6,6'-(propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine) (hereinafter abbreviated as BA-a), was synthesized according to a previously reported procedure [11].

2.2. Characterization

One dimensional ¹H NMR spectra were recorded using a Bruker AVANCE II 400 MHz nuclear magnetic resonance (NMR) spectrometer at a proton frequency of 400 MHz and solutions in CDCl₃/DMSO-d₆ containing tetramethylsilane as an internal reference. Two dimensional ¹H-¹H nuclear Overhauser effect spectroscopy (NOESY) and ¹H-¹³C Heteronuclear multiple quantum coherence (HMQC) were also used. A Fourier transform infrared (FT-IR) spectrophotometer (Bomem, model Michelson MB 110) was used to acquire FT-IR spectra. The spectrometer was equipped with a deuterated triglycine sulfate (DTGS) detector and dry air purge unit and was operated at a resolution of 4 cm⁻¹ in the frequency range of 4000-400 cm⁻¹. A TA Instruments differential scanning calorimeter (DSC) model 2920 was used with a temperature ramp rate of 10°C/min and a nitrogen flow rate of 60 mL/min for all tests of DSC study. All samples were sealed in hermetic aluminum pans with lids. Thermomechanical analysis (TMA) was measured by a NETZSCH TMA/402F4 at a heating rate of 5°C/min, and the coefficient of thermal expansion was calculated in the range from 50 to 250°C. Dynamic mechanical analysis (DMA) was conducted on a NETZSCH DMA/242E applying controlled strain tension mode with amplitude of 10 µm and a temperature ramp rate of 3°C/min from room temperature to 400°C. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 thermogravimetric analyzer that was purged with nitrogen at a flow rate of 40 mL/min. A heating rate of 10°C/min was applied. Specific heat release rate

(HRR, W/g), heat release capacity (HRC, J/g.K) and total heat release (THR, kJ/g) were measured on a microscale combustion calorimeter (MCC). MCC thermograms were measured from 100 to 750°C at a heating rate of 1°C/s in an 80 mL/min stream of nitrogen. The anaerobic thermal degradation products in the nitrogen gas stream were mixed with a 20 mL/min stream of oxygen prior to entering the combustion furnace (900°C). Heat release is quantified by standard oxygen consumption [36], and HRR is obtained by dividing dQ/dt at each time interval, by the initial sample mass, and HRC is obtained by dividing the maximum value of HRR by the heating rate.

2.3. Methods

Synthesis of 4,4'-bishydroxydeoxybenzoin (abbreviated as BHDB).

4,4'-Bishydroxydeoxybenzoin (BHDB) was prepared by demethylation of desoxyanisoin (1,2-bis(4-methoxyphenyl)ethanone), as previously described [30]. Desoxyanisoin (5.0 g, 19.5mmol) and pyridine hydrochloride (9.0 g, 78.1mmol) were added to a round-bottom flask equipped with a condenser. The mixture was kept stirring for 5 h at 200°C, then cooled to room temperature, and poured into water. The precipitate was filtered and recrystallized from acetic acid to give a yellow crystal (yield ca. 81%). ¹H NMR (400 MHz, DMSO-*d*₆), ppm: δ = 4.10 (s, 2H, Ar-CH₂-CO-Ar), 6.67-7.92 (8H, Ar-H), 9.27 (s, OH-Ar-CH₂), 10.38 (s, OH-Ar-CO). FT-IR spectra (KBr), cm⁻¹: 3457 and 3344 (O-H stretching), 1666 (carbonyl stretching), 759 (C=O bending).

Synthesis of 1,2-bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)ethanone (abbreviated as BHDB-a).

Into a 100 mL round-bottom flask were added 35 mL of xylenes, aniline (1.09 g, 0.012 mol), BHDB (1.33 g, 0.006 mol), and paraformaldehyde (0.76 g, 0.025 mol). The mixture was stirred at 120°C for 8 h. After cooling to room temperature, the reaction solution was washed with deionized water for three times. Then column chromatography was used afterward to purify benzoxazine monomer with mixed solvents of hexane and ethyl acetate in 4:1 ratio. The purified products were further recrystallized from

acetone/toluene mixtures (1:1). After recrystallization, needle like crystals were obtained (yield ca. 72%). ¹H NMR (400 MHz, CDCl₃), ppm: δ = 4.12 (s, 2H, Ar-CH₂-CO-Ar), 4.62-4.68 (d, 2H, Ar-CH₂-N, oxazine), 5.36-5.44 (d, 2H, O-CH₂-N, oxazine), 6.79-7.83 (16H, Ar). FT-IR spectra (KBr), cm⁻¹: 1676 (carbonyl stretching), 1498 (stretching of trisubstituted benzene ring), 1238 (C-O-C asymmetric stretching), 924 (benzoxazine related band), 781 (C=O bending). Anal. Calcd. for C₃₀H₂₆N₂O₃: C, 77.90; H, 5.67; N, 6.06. Found: C, 77.84%; H, 5.70%; N, 6.02%.

Polymerization of benzoxazine monomers.

Solution of 30% solid content of BHDB-a and BA-a in DMF was prepared, respectively. Then, each solution was cast on a dichlorodimethylsilane-pretreated glass plate. The films were dried in an air-circulating oven at 100°C for 2 days to remove the solvent. At last, the films of BHDB-a and BA-a as coated on the glass plates were polymerized stepwise at 160, 180, 200, 220 and 240°C for 1 h each to obtain poly(BHDB-a) and poly(BA-a), respectively.

3. Results and discussion

3.1. Synthesis of Deoxybenzoin-Based Benzoxazine Monomer.

The new deoxybenzoin-based benzoxazine monomer (BHDB-a) was synthesized successfully by the traditional Mannich condensation reaction between 4,4'-bishydroxydeoxybenzoin (BHDB), aniline and paraformaldehyde using xylenes at 120°C as shown in Scheme 2. Similar to the most reported bis(benzoxazine)s, a further purification, such as column chromatography and/or recrystallization, has to be applied for obtaining pure compound due to the existence of phenolic byproducts in the synthesis of bis(benzoxazine) monomers.



Scheme 2. Synthesis of deoxybenzoin-based benzoxazine monomer.

The structure of BHDB-a was confirmed by ¹H NMR, ¹³C NMR, and FT-IR analyses. In general, the characteristic benzoxazine ¹H NMR resonance pair for O-C H_2 -N and the Ar-C H_2 -N consists of singlets with frequency separation of around 0.8-0.9 ppm [10,11]. However, as seen in Fig. 1, the characteristic proton resonance due to the O-C H_2 -N and the Ar-C H_2 -N groups in the oxazine ring of BHDB-a exhibits two sets of doublets at 5.36 and 5.44 ppm and 4.62 and 4.68 ppm, respectively. Furthermore, two sets of doublets at 79.42 and 80.22 ppm and 50.43 and 50.54 ppm for the characteristic carbon resonances of the O-C H_2 -N and the Ar-C H_2 -N and the Ar-C H_2 -N groups can also be observed as shown in Fig. 2. One goal of the current study is to assign ¹H and ¹³C NMR resonances of BHDB-a as this asymmetric monomer is much more complex compared with symmetric benzoxazine ring, it must be noticed that there is no isomerism involved in BHDB-a due to the characteristic resonance of the methylene in -OC-C H_2 - bridge exhibiting a singlet at 4.12 ppm as shown in Fig. 1. In addition, Fig. 2 also shows a singlet at 44.23 ppm for the corresponding carbon resonance of -OC-C H_2 - group.



Fig. 1. ¹H NMR spectrum of BHDB-a.



Fig. 2. ¹³C NMR spectrum of BHDB-a.

Complementary spectroscopic studies were then performed. Fig. 3a shows the 2D 1 H- 1 H nuclear Overhauser effect spectroscopy (NOESY) of BHDB-a. There are many possible manners and different order to follow the NOE interactions to analyze the spectrum. Nevertheless, the most important information is obtained from the NOE interaction observed by H_D. H_D is a characteristic aromatic proton resonance with singlet peak as assigned in Fig. 3a. Clearly, only one interaction with a proton H_A['] is detected for H_D. Since H_A['] is much closer through space to H_D than H_A, it strongly suggests that the

 $H_{A'}$ should be in the oxazine ring attached to the H_D containing benzene ring. Therefore, the proton signals could now be assigned unambiguously as shown in the inset structure in Fig. 3a. In addition, the assignments for the carbons of the oxazine ring and methylene bridge in the structure of BHDB-a are supported by the ¹H-¹³C HMQC spectrum as seen in Fig. 3b.



Fig. 3. (a) 2D ¹H-¹H NOESY NMR spectrum of BHDB-a and NOE interactions observed. (b) 2D ¹H-¹³C HMQC NMR spectrum of BHDB-a.

FT-IR spectroscopy was further used to monitor the effectiveness of the reaction to form benzoxazine. There are a number of infrared absorption bands, highlighted in Fig. 4, that are used to verify the existence of deoxybenzoin and oxazine ring formation in BHDB-a. The observed strong band at 1676 cm⁻¹, attributed to the C=O stretching, shows that the deoxybenzoin nuclei is present in the molecule. Besides, the band for tri-substituted benzene that appears at 1495 cm⁻¹ indicates the combination of deoxybenzoin with benzoxazine structures. Moreover, the presence of the benzoxazine ring aromatic ether in the monomer is indicated by the band centered at 1238 cm⁻¹, which is due to the C-O-C antisymmetric stretching modes [37]. The characteristic oxazine related mode, which includes the vibration of O-C₂ vibration with a minor contribution

from the phenolic ring is located at 924 cm⁻¹ [38]. All the above information is consistent with the successful synthesis of the target bis(benzoxazine) compound.



Fig. 4. FT-IR spectrum of BHDB-a.

3.2. Thermal Behavior and Ring-Opening Polymerization Mechanism of BHDB-a.

The polymerization behavior of BHDB-a was studied by DSC as depicted in Fig. 5. The thermogram of BHDB-a exhibits two obvious thermal events. The first one is a very sharp endothermic process with its minimum at 134°C, which is associated with the melting of the bis(benzoxazine) resin's needle-like crystal. This sharp endothermic peak further indicates the high purity of BHDB-a. Additionally, an exotherm, attributed to the ring-opening polymerization, is observed with its maximum at 217°C and an onset temperature at 198°C. In order to better understand the polymerization behavior of BHDB-a, the DSC thermogram of another bis(benzoxazine) monomer, BA-a, has also been performed as shown in Fig. 5. Similarly, BA-a exhibits the melting endotherm with its minimum at 111°C and the polymerization exotherm with its maximum at 258°C. The pure BA-a crystalizes and the onset of exotherm becomes very high. Obviously, BHDB-a shows a much lower polymerization temperature compared with BA-a, although the structural difference is simply in the middle bridge structure of both compounds. These DSC result implies the existence of the self-catalytic polymerization possibly caused by the interaction of deoxybenzoin and oxazine ring in BHDB-a.



Fig. 5. DSC thermogram of BHDB-a.

Fig. 6 shows a comparison of TGA and DSC thermograms of BHDB-a. As shown in Fig. 6, the initial weight loss of BHDB-a occurs around 180°C, which reflects that almost no evaporation can take place before its polymerization. A further ~5.3% of weight loss can be observed during the polymerization at the range from the onset temperature to 300°C. This weight-loss stage has been determined to be the cleavage of the zwitterionic intermediate, forming unstable phenolic species and *N*-methyleneaniline during the ring-opening polymerization of benzoxazines [16,39]. The degradation in this temperature range mostly occurs for the monomer-based polybenzoxazines rather than from main-chain type polybenzoxazines, due to the degradation from the chain ends and/or side groups, rather than from the middle of the main chain [40]. Additionally, the weight-loss during the polymerization of BHDB-a is much lower compared with other reported bis(benzoxazine)s [16,41]. The unique polymerization behavior resulting from the interaction of oxazine ring and deoxybenzoin seems to significantly improve the thermal stability of BHDB-a during the polymerization process.



Fig. 6. TGA vs DSC plots of of BHDB-a (heating rate: 10 °C/min, under a N₂ atmosphere).

To gain deeper understanding, the qualitative study of the polymerization behavior for BHDB-a was performed by in situ FT-IR analyses as shown in Fig. 7. The characteristic absorption bands around 1238 cm⁻¹ (C-O-C antisymmetric stretching mode) and 924 cm⁻¹ (benzoxazine related mode) can be used to study the ring-opening polymerization of the oxazine ring in BHDB-a by observing the gradual decrease of those bands as a function of the temperature and finally complete disappearance at 240°C. This result suggests that BHDB-a completes polymerization by heating stepwise at 160, 180, 200, 220 and 240 °C for 1 h each. In addition, the characteristic band for carbonyl absorption at 1676 cm⁻¹ gradually decreases as the ring-opening polymerization of oxazine ring proceeds, and meanwhile the multiple broadband of -OH around 3400 cm⁻¹, gradually appears. The very broad background ranging typically from 3400 to 2200 cm⁻¹ is due to the so-called chelated phenolic OH groups that are forming intramolecular 6-membered hydrogen bonding with the nitrogen atom of the main chain [10,11]. However, the polybenzoxazine derived from deoxybenzoin-based monomer shows additional rather strong and broad band in the region between 3600 and 3200 cm⁻¹, implying different source of hydroxyl groups as proposed in a later section that discusses the polymerization mechanism. This

variation from *in situ* FT-IR spectra strongly suggests the structural evolution of deoxybenzoin in BHDB-a should be a key factor for lowering the polymerization temperature of benzoxazine.



Fig. 7. FT-IR spectra of BHDB-a after various thermal treatments at the designated temperature for 1 h.

In order to further investigate the structural evolution of BHDB-a during the polymerization, the ¹H NMR analyses in deuterated DMSO (DMSO-_{d6}) were also carried out. Fig. 8 shows the ¹H NMR spectra of the thermally treated BHDB-a at different temperatures, where ¹H NMR spectrum of BHDB-a after polymerization at 180°C presents complicated signals due to the different types of -CH₂- units in polybenzoxazine chains. Doublet resonances apart from ones around 5.4 and 4.6 ppm attributed to the benzoxazine structure may be ascribed to the residual oxazine rings at the chain ends of some oligomers or polybenzoxazines with low molecular weight. In addition, a broad signal with multiple resonances between 4.5 and 3.7 ppm is probably due to the presence of -CH₂- in deoxybenzoin and phenolic -CH₂- groups, which are associated with the Mannich bridge after ring-opening polymerization. Moreover, a new signal at 5.0 ppm can also be observed at the ¹H NMR spectrum of BHDB-a after polymerization at 180°C, which seems to be the presence of new –OH group.



Fig. 8. ¹H NMR spectra of BHDB-a in DMSO-_{d6} after various thermal treatments.

The above DSC, in situ FTIR and ¹H NMR analyses show that the deoxybenzoin group exhibits additional autocatalytic ring-opening polymerization of benzoxazine beyond the usual autocatalytic activities caused by the formed phenolic OH groups upon oxazine ring opening. The remarkable difference in reactivity of BHDB-a over BA-a suggests a mechanism where the deoxybenzoin has an important role to promote the ring-opening polymerization. The proposed polymerization mechanisms for BA-a and BHDB-a are shown in Scheme 3. As the purity of both BA-a and BHDB-a synthesized in this work is high, both bis(benzoxazine)s do undergo polymerization induced only by heat without any impurity participating in or during the reaction, which is consistent with the reported study on intrinsic ring opening polymerization of oxazine ring [42]. However, BHDB-a shows a polymerization exotherm maximum at 217°C, which is rather unusual for ordinary benzoxazine monomers with such high purity without added initiators. We, therefore, hypothesize a self-catalyzed polymerization mechanism. The deoxybenzoin structure in BHDB-a can be activated to form enolic structure by the electron transfer reaction as shown in Scheme 3b. Afterward, the ionization of enolic structure leads to the polymerization of BHDB-a into a traditional cationic ring-opening polymerization mechanism. This built-in intramolecular catalytic feature can be considered a smart







(b) Self-catalyzed cationic ring-opening polymerization mechanism of BHDB-a



Scheme 3. Proposed polymerization mechanism of benzoxazine monomers.

Thermal behavior of products obtained by the polymerization of BHDB-a was also studied by DSC as shown in Fig. 9 after cumulative thermal treatments at 160, 180, 200, 220 and 240°C for 1 h at each temperature. Interestingly, BHDB-a can be made into a more processing-friendly state simply by partially polymerized at 160°C for 1 h. After this simple thermal treatment, the endothermic peak of BHDB-a can be eliminated and the exothermic maximum appears at a lower temperature (206°C). Besides, it is observed that the exothermic peak temperature gradually decreases after each thermal treatment. After the treatment at 240°C, completion of the ring-opening polymerization has been observed. Moreover, a glass transition temperature (T_g) as high as 298°C was observed

after the end of the heat cycle at 240°C of BHDB-a, which indicates the excellent thermal property of the final thermoset.



Fig. 9. DSC thermograms of BHDB-a after various thermal treatments.

3.3. Activation Energy of Polymerization of BHDB-a.

The activation energy of polymerization of BHDB-a was also investigated with nonisothermal DSC at different heating rates of 2, 5, 10, 15 and 20 °C/min. Fig. 10 shows the DSC thermograms of BHDB-a at different heating rates, respectively.



Fig. 10. DSC curves of BHDB-a at various heating rates.

The apparent activation energy of polymerization process was determined using the well-known Kissinger and Ozawa methods [43,44]. Based on the Kissinger method, the activation energy can be calculated by Eq. (1) as follows:

$$\ln(\frac{\beta}{T_p^2}) = \ln(\frac{AR}{E_a}) - \frac{E_a}{RT_p}$$
(1)

where the heating rate is represented by β , the frequency factor is represented by A. Besides, T_p is the temperature of the exothermic peak, E_a is the activation energy, and R is the gas constant. Another theoretical treatment, namely, the modified Ozawa method, can also be applied to the thermal data using Eq. (2) as follows:

$$\ln\beta = -1.052\frac{E_a}{RT_p} + C \tag{2}$$

where C is a constant.

Alternatively, if the plot of $\ln(\beta/T_p^2)$ and $\ln(\beta)$ against $1/T_p$ are linear, a single process can be assumed, and the corresponding E_a can be obtained from the slope of the straight lines. Fig. 11 shows the plot of $\ln(\beta/T_p^2)$ or $\ln(\beta)$ against $1/T_p$ for BHDB-a according to the Kissinger and Ozawa methods. The E_a value was estimated to be as low as 91.2 (Kissinger) and 93.1 (Ozawa) kJ/mol. Generally, the activation energy reported for difunctional benzoxazines showed higher values compared with monofunctional benzoxazines [45]. However, the E_a value of BHDB-a is even lower than those reported values for monobenzoxazines [46]. This result suggests that BHDB-a is easy to be activated to polymerize possibly due to the existence of self-catalyzed polymerization system.



Fig. 11. Plots generated by the Kissinger and Ozawa methods for determination of the activation energy of BHDB-a.

3.4. Thermal Properties of polybenzoxazines.

The thermomechanical properties of poly(BHDB-a) were studied by TMA. Fig. 12 shows the TMA curve of poly(BHDB-a) thermosetting film. The coefficient of thermal expansion (CTE) is obtained from TMA as 48.4 ppm/°C which compares favorably with the reported thermal expansion coefficient of bisphenol A epoxy resin of 70 ppm/°C [47]. Besides, a T_g of 301°C is observed, which is in accordance with the result from DSC. Notably, poly(BHDB-a) shows a much higher T_g temperature compared with poly(BA-a), which was reported as around 152°C [27]. Moreover, dynamic mechanical analysis (DMA) was utilized to further confirm the T_g value of poly(BHDB-a). As shown in Fig. 13, the T_g determined by the peak temperature of tan δ is as high as 311 °C, which is in relatively good agreement with that measured by DSC and TMA with the expected discrepancy amongst the three different techniques.



Fig. 12. Thermomechanical analysis of thermoset film of poly(BHDB-a).



Fig. 13. Dynamic mechanical spectra of poly(BHDB-a).

The thermal stability of polybenzoxazines has been studied by TGA under nitrogen atmosphere and the result is shown in Fig. 14. The decomposition temperatures of 5 % and 10% weight losses (T_{d5} and T_{d10}) for poly(BHDB-a) and poly(BA-a) are 403 and 440°C and 302 and 324°C, respectively. As anticipated, the incorporation of deoxybenzoin into the benzoxazine backbone structure significantly improved thermal stability as compared to typical BA-a resin. Besides, poly(BHDB-a) exhibits a high char yield (Yc) value of 68 % at 800°C. Particularly noteworthy is the nearly complete lacking

of the low temperature degradation events, as seen around 300 and 400°C for poly(BA-a). The high thermal stability of poly(BHDB-a) is thought to be attributed to the formation of diphenylacetylene as other BHDB related polymers [35]. Much more detailed study is required to verify this hypothesis, though it is not the main goal of the current paper. The thermal property data of poly(BHDB-a) and poly(BA-a) are summarized in Table 1, which demonstrates a high thermal stability of poly(BHDB-a).



Fig. 14. Thermogravimetric analysis of poly(BHDB-a) and poly(BA-a).

Sample	T _{d5}	T_{d10}	Yc	HRC	THR
	(°C)	(°C)	(wt.%)	(Jg ⁻¹ K ⁻¹)	(KJg ⁻¹)
poly(BHDB-a)	403	440	68	96	11.4
poly(BA-a)	302	324	32	328	35.3

 Table 1
 Thermal and heat release properties of poly(BHDB-a) and poly(BA-a).

Microscale combustion calorimetry (MCC) was also applied to quantitatively evaluate the flammability of polybenzoxazines. Typically, the specific heat release rate (HRR) is obtained by dividing dQ/Dt at each time interval, by the initial sample mass. In addition, the heat release capacity (HRC) can be obtained by dividing the maximum value of HRR by the heating rate. In General, HRC is regarded as an effective evaluation of thermal

combustion that is one of the best single predictors of the flammability of a material [48]. Herein, milligram size samples of poly(BHDB-a) and poly(BA-a) were tested at a constant heating rate of 1 K/s over the temperature range 100-750°C. As shown in Fig. 15, MCC characterization of poly(BHDB-a) and poly(BA-a) reveals HRC values of 96 and 328 Jg⁻¹K⁻¹, respectively. Besides, poly(BHDB-a) shows a low THR value of 11.4 KJg⁻¹ whereas poly(BA-a) exhibits that of 35.3 KJg⁻¹. In general, the lower the values of HRC and THR, the higher the flame resistance. The HRC less than 300 J/g.K is considered self-extinguishing whereas materials with values less than 100 J/g.K are considered non-ignitable [49]. Therefore, introduction of deoxybenzoin into polybenzoxazine network leads to a substantial HRC reduction and improved flame retardancy, which makes this material attractive for application in high thermal requirement without the need of flame-retardant additives.



Fig. 15. Microscale combustion calorimetric curves of poly(BHDB-a) and poly(BA-a).

4. Conclusion

A deoxybenzoin based asymmetric bis(benzoxazine) monomer has been successfully synthesized, and the chemical structures of this monomer have been analyzed in detail by 1D and 2D NMR techniques. The benzoxazine resin was shown to undergo a unique

self-catalyzed cationic ring-opening polymerization without adding any initiators or catalysts and formed cross-linked polymeric networks. This self-catalyzed reaction takes place beyond the usual autocatalytic reaction caused by the phenolic OH formed as a result of oxazine polymerization. The activation energy for the polymerization was measured to be as low as 91.2 (Kissinger) and 93.1 (Ozawa) kJ/mol. Moreover, the polybenzoxazine derived from bis(benzoxazine) monomer exhibited high thermal stability with the glass transition temperature of 301 °C and a char yield of 68%. Furthermore, the polybenzoxazine also showed low heat release capacity (HRC of 96 Jg⁻¹K⁻¹) as well as the low total heat release (THR of 11.4 KJg⁻¹). The thermal properties of the deoxybenzoin-based bis(benzoxazine) resin is comparable to deoxybenzoin based main-chain type benzoxazine polymers. Therefore, the combination of above excellent properties makes this new deoxybenzoin based benzoxazine resin as an attractive candidate for high-performance applications.

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References

- F. Rahman, K. H. Langford, M. D. Scrimshaw, J. N. Lester, Polybrominated diphenyl ether (PBDE) flame retardants, Sci. Total. Environ. 275 (2001) 1–17.
- B. A. Howell, W. Sun, Biobased flame retardants from tartaric acid and derivatives, Polym. Degrad. Stabil. 157 (2018) 199-211.
- [3] R. C. Hale, M. J. La Guardia, E. P. Harvey, M. O. Gaylor, T. M. Mainor, W. H. Duff,

Flame retardants-persistent pollutants in land-applied sludges, Nature 412 (2001)140-141.

- [4] A. Blum, The fire retardant dilemma, Science 318 (2007) 194–196.
- [5] R. N. Rothon, P. R. Hornsby, Flame retardant effects of magnesium hydroxide, Polym. Degrad. Stab. 54 (1996) 383–385.
- [6] K. A. Salmeia, S. Gaan, G. Malucelli, Recent advances for flame retardancy of textiles based on phosphorus chemistry, Polymers 8 (2016) 319.
- [7] P. R. Hornsby, The application of hydrated mineral fillers as fire retardant and smoke suppressing additives for polymers, Macromol. Symp. 108 (1996) 203–219.
- [8] R. N.Rothon, C. M. Liauw, G. C. Lees, W. C. E. Schofield, Magnesium hydroxide filled EVA: The effects of filler surface modification on the strength of filler/matrix adhesion and the consequences for composite structure and properties, J. Adhes. 78 (2002) 603–628.
- [9] S. Levchik, Non-Halogenated Flame Retardant Handbook, 2014, pp. 17–74.
- [10] H. Ishida., T. Agag, Handbook of Benzoxazine Resins, Elsevier, Amsterdam, 2011.
- [11]H. Ishida., P. Froimowicz, Advanced and Emerging Polybenzoxazine Science and Technology, Elsevier, Amsterdam, 2017.
- [12] N. N. Ghosh, B. Kiskan, Y. Yagci, Polybenzoxazines-new high performance thermosetting resins: synthesis and properties, Prog. Polym. Sci. 32 (2007) 1344-1391.
- [13] S. Ohashi, D. Iguchi, T. R. Heyl, P. Froimowicz, H. Ishida, Quantitative studies on the p-substituent effect of the phenolic component on the polymerization of benzoxazines, Polym. Chem. 9 (2018) 4194-4204.
- [14]B. Kiskan, Y. Yagci, Benzoxazine resins as smart materials and future perspectives, in: Q. Guo (Ed.), Thermosets: Strucutre, Properties, and Applications, Second, Elservier, Amsterdam, 2018, pp. 543-576.
- [15] G. Kaya, B, Kiskan, Y. Yagci, Phenilic naphtoxazines as curing promotes for

benzoxazines, Macromolecules 51 (2018) 1688-1695.

- [16] N. K. Sini, T. Endo, Toward elucidating the role of number of oxazine rings and intermediates in the benzoxazine backbone on their thermal characteristics, Macromolecules 49 (2016) 8466-8478.
- [17]Z. Deliballi, B. Kiskan, Y. Yagci, Main-chain benzoxazine precursor block copolymers, Polym. Chem. 9 (2018) 178-183.
- [18] T. Agag, J. Liu, R. Graf, H. W. Spiess, H. Ishida, Benzoxazole resin: A novel class of thermoset polymer via smart benzoxazine resin, Macromolecules 45 (2012) 8991-8997.
- [19]K. Zhang, L. Han, P. Froimowicz, H. Ishida, A smart latent catalyst containing o-trifluoroacetamide functional benzoxazine: precursor for low temperature formation of very high Performance polybenzoxazole with low dielectric constant and high thermal stability, Macromolecules 50 (2017) 6552–6560.
- [20] P. Velez-Herrera, K. Doyama, H. Abe, H. Ishida, Synthesis and characterization of fluorinated polybenzoxazine material with low dielectric constant, Macromolecules 41 (2008) 9704-9714.
- [21] J. Wu, Y. Xi, G. T. McCandless, Y. Xie, R. Menon, Y. Patel, D. J. Yang, S. T. Lacono, B. M. Novak, Synthesis and characterization of partially fluorinated polybenzoxazine resins utilizing octafluorocyclopentene as a versatile building block, Macromolecules 48 (2015) 6087-6095.
- [22] C. F. Wang, Y. C. Su, S. W. Kuo, C. F. Huang, Y. C. Sheen, F. C. Chang, Low-surface-free-energy materials based on polybenzoxazines, Angew. Chem. Int. Ed. 45 (2006) 2248-2251.
- [23] S. W. Kuo, Y. C. Wu, C. F. Wang, K. U. Jeong, Preparing low-surface-energy polymer materials by minimizing intermolecular hydrogen-bonding interactions, J. Phys. Chem. C. 113 (2009) 20666-20673.

- [24] C. S. Liao, C. F. Wang, H. C. Lin, H. Y. Chou, F. C. Chang, Tuning the surface free energy of polybenzoxazine thin films, J. Phys. Chem. C. 112 (2008) 16189-16191.
- [25]K. Zhang, Z. Shang, J. C. Evans, L. Han, H. Ishida, S. Yang, Benzoxazine atropisomers: Intrinsic atropisomerization mechanisms and conversion to high performance thermosets, Macromolecules 51 (2018) 7574-7585.
- [26]X. Ning, H. Ishida, Phenolic materials via ring-opening polymerization: Synthesis and characterization of bisphenol-A based benzoxazines and their polymers, J. Polym. Sci., Part A: Polym. Chem. 32 (1994) 1121-1129.
- [27] N. K. Sini, M. Azechi, T. Endo, Synthesis and properties of spiro-centered benzoxazines, Macromolecules 48 (2015) 7466-7472.
- [28] S. Zhang, Q. Ran, Q. Fu, Y. Gu, Preparation of transparent and flexible shape memory polybenzoxazine film through chemical structure manipulation and hydrogen bonding control, Macromolecules 51 (2018) 6561-6570.
- [29] B. Y. Ryu, T. Emrick, Bisphenol-1,2,3-triazole (BPT) epoxies and cyanate esters: synthesis and self-catalyzed curing, Macromolecules 44 (2011) 5693-5700.
- [30] B. Y. Ryu, S. Moon, I. Kosif, T. Ranganathan, R. J. Farris, T. Emrick, Deoxybenzoin-based epoxy resins, Polymer 50 (2009) 767-774.
- [31] T. Ranganathan, P. Cossette, T. Emrick, Halogen-free, low flammability polyurethanes derived from deoxybenzoin-based monomers, J. Mater. Chem. 20 (2010) 3681-3687.
- [32] T. Ranganathan, B. C. Ku, J. Zilberman, M. Beaulieu, R. J. Farris, E. B. Coughlin, Poly(arylate-phosphonate) copolymers with deoxybenzoin in the backbone: Synthesis, characterization, and thermal properties, J. Polym. Sci., Part A: Polym. Chem. 45 (2007) 4573-4580.
- [33] T. Ranganathan, J. Zilberman, R. J. Farris, E. B. Coughlin, T. Emrick, Synthesis and characterization of halogen-free antiflammable polyphosphonates containing 4,4'-bishydroxydeoxybenzoin, Macromolecules 39 (2006) 5974-5975.

- [34]K. A. Ellzey, T. Ranganathan, J. Zilberman, E. B. Coughlin, R. J. Farris, T. Emrick, Deoxybenzoin-based polyarylates as halogen-free fire-resistant polymers, Macromolecules 39 (2006) 3553-3558.
- [35] C. H. Chen, C. H. Lin, J. M. Hon, M. W. Wang, T. Y. Juang, First halogen and phosphorus-free, flame-retardant benzoxazine thermosets derived from main-chain type bishydroxydeoxybenzoin-based benzoxazine polymers, Polymer 154 (2018) 35-41.
- [36] R. E. Lyon, R. N. Walters, Pyrolysis combustion flow calorimetry, J. Anal. Appl. Pyrol. 71 (2004) 27-46.
- [37] T. Agag, T. Takeichi, Synthesis and characterization of novel benzoxazine monomers containing allyl groups and their high performance thermosets, Macromolecules 36 (2003) 6010.
- [38]L. Han, D. Iguchi, P. Gil, T. R. Heyl, V. M. Sedwick, C. R. Arza, S. Ohashi, D. J. Lacks, H. Ishida, Oxazine ring-related vibrational modes of benzoxazine monomers using fully aromatically substituted, deuterated, ¹⁵N isotope exchanged, and oxazine-ring-substituted compounds and theoretical calculations, J. Phys. Chem. A. 121 (2017) 6269-6282.
- [39]K. Zhang, X. Yu, Catalyst-free and low temperature terpolymerization in a single-component benzoxazine resin containing both norbornene and acetylene functionalities, Macromolecules 51 (2018) 6524–6533.
- [40] A. Chernykh, T. Agag, H. Ishida, Synthesis of linear polymers containing benzoxazine moieties in the main chain with high molecular design versatility via click reaction, Polymer 50 (2009) 382.
- [41] Y. Liu, R. Yin, X. Yu, K. Zhang, Modification of solventless-synthesized benzoxazine resin by phthalonitrile group: An effective approach for enhancing thermal stability of polybenzoxazines, Macromol. Chem. Phys. 2018, 1800291.

- [42] L. Han, M. L. Salum, K. Zhang, P. Froimowicz, H. Ishida, Intrinsic self initiating thermal ring-opening polymerization of 1, 3-benzoxazines without the influence of impurities using very high purity crystals, J. Polym. Sci., Part A: Polym. Chem. 55 (2017) 3434-3445.
- [43]H. E. Kissinger, Reaction kinetics in differential thermal analysis, Anal. Chem. 29 (1957) 1702–1706.
- [44] T. Ozawa, Kinetics of non-isothermal crystallization polymer 12 (1971) 150–158.
- [45]K. Zhang, H. Ishida, Thermally stable polybenzoxazines via ortho-norbornene functional benzoxazine monomers: Unique advantages in monomer synthesis, processing and polymer properties, Polymer 66 (2015) 240-248.
- [46] W. Zhang, P. Froimowicz, C. R. Arza, S. Ohashi, Z. Xin, H. Ishida, Latent catalyst-containing naphthoxazine: Synthesis and effects on ring-opening polymerization, Macromolecules 49 (2016) 7129-7140.
- [47] J.A. Dudek, J.A. Kargol, Linear thermal expansion coefficients for an epoxy/glass matte-insulated solid cast transformer, Intern. J. Thermophys. 9 (1988) 245-253.
- [48] R. E. Lyon, N. Safronava, J. G. Quintiere, S. I. Stoliarov, R. N. Walters, S. Crowley, Materials properties and fir test results, Fire. Mater. 38 (2014) 264-278.
- [49] R. N. Walters, R.E. Lyon, Molar group contributions to polymer flammability, J. Appl. Polym. Sci. 87 (2003) 548–563.

Highlights

- 1. A novel asymmetric bis-benzoxazine monomer based on deoxybenzoin has been successfully synthesized.
- 2. This deoxybenzoin-based benzoxazine shows a unique self-catalyzed cationic ring-opening polymerization mechanism.
- 3. Deoxybenzoin-based benzoxazine possesses much higher thermal stability compared with BA-a resin.
- 4. The polybenzoxazine derived from deoxybenzoin-based benzoxazine also exhibits low flammability.