Benzoxazole Resin: A Novel Class of Thermoset Polymer via Smart Benzoxazine Resin

5 **AUTHORS**, INCLUDING:

Jia Liu
Case Western Reserve University

14 PUBLICATIONS **66** CITATIONS

SEE PROFILE

Robert Graf
Max Planck Institute for Polymer Research

140 PUBLICATIONS **3,837** CITATIONS

SEE PROFILE

Hatsuo Ishida
Case Western Reserve University

450 PUBLICATIONS **12,912** CITATIONS

SEE PROFILE

Benzoxazole Resin: A Novel Class of Thermoset Polymer via Smart Benzoxazine Resin

Tarek Agag,*[,†] Jia Liu,[†] Robert Graf,[‡] Hans W. Spiess,[‡] and Hatsuo Ishida*[,†]

[†]Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106-7202, United States

[‡]Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany

ABSTRACT: Among the wide list of known high performance polymers, polybenzoxazoles (PBOs) have gained a prominent position as the most heat-resistant polyheterocyclic polymer. Nonetheless, PBOs have found applications in a rather restricted variety of technologies, mainly in the form of fibers. Herein, we report our pioneering work for producing cross-linked polybenzoxazole via a novel route using recently developed smart class of benzoxazine resins as precursors. This class of benzoxazines incorporates multiple smart features all in one molecule. The most attractive feature is its structural transformation into a more thermally stable cross-linked polybenzoxazole without the harmful consequences of traditional polybenzoxazole synthesis, such as the use of poly(phosphoric acid) as solvent. By this smart conversion, the flame-retardant oxazole moieties are successfully incorporated into the network structure. Further advantages of this new route for cross-linked polybenzoxazoles include outstanding flexibility in molecular design, cost effectiveness, and easy processability.
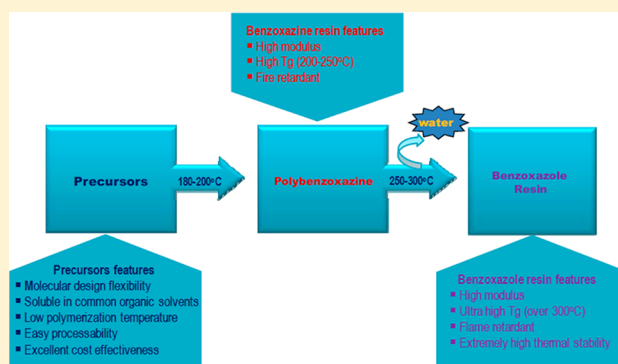
1. INTRODUCTION

There is a growing interest for the next generation of materials to meet recent demands by the space and electronics technologies. Polymers of outstanding performance are a crucial requirement for such applications. Aromatic polybenzoxazoles (PBOs) as a class of heterocyclic polymers are ranked as materials of superb thermal stability, extremely high tensile strength, and good chemical resistance. The excellent performance of PBOs makes them attractive for many applications; in particular, PBOs are suitable for ballistic applications.[1] The commercial applications of PBO fibers include protective garments such as firefighter clothing, ballistic vests and helmets, and reinforcing fibers for heat-resistant conventional and molecular composites. Also, photosensitive PBOs are attractive materials for microelectronics technology because of their remarkable thermal and mechanical properties and lower dielectric constants and loss factors than photosensitive polyimides.[2] There are two traditional methods for the synthesis of aromatic PBOs. The first method is one-step synthesis in which a direct polycondensation reaction takes place between bis(o-aminophenol)s and aromatic diacids using poly(phosphoric acid) (PPA),[3] phosphorus pentoxide/methanesulfonic acid (PPMA),[4] or trimethylsilyl polyphosphate (PPSE)/o-dichlorobenzene[5] as the reaction medium. The only successful commercial application of PBO produced by this method is ultrahigh strength PBO fibers that possess superior properties to other ultrahigh performance fibers, such as polyaramids (e.g., Kevlar, Twaron) and ultrahigh modulus

polyethylene fibers (Spectra). The major disadvantage of this method is the long-term instability of PBO fibers due to the residual acid when exposed to moisture at moderate to elevated temperatures, causing a hydrolytic degradation of the benzoxazole ring.[6] As a result, a premature failure in ballistic performance of body armor containing the PBO fiber has been reported.[7]

The second method is two-step condensation reaction of an aromatic diacid chloride with a bis(o-aminophenol)s in solution at room temperature to form poly(o-hydroxyamide), followed by sequential thermal intramolecular cyclodehydration reaction in the bulk state or in solution with loss of water to yield the final aromatic polybenzoxazole.[8−11] A chlorine-free synthetic method is also applied to prepare poly(o-hydroxyamide)s using aromatic dicarboxylic active diester and bis(o-aminophenol). Recently, Mathias and others reported the possible thermal conversion of α-hydroxypolyimides into polybenzoxazoles with loss of carbon dioxide at temperatures over 400 °C.[12−17] More recently, however, Hodgkin et al. questioned this proposed mechanism and reported that it actually yields cross-linked polyimide containing biphenylene structure.[18]
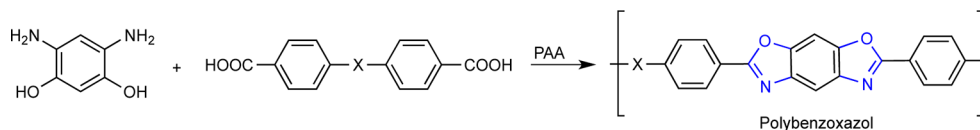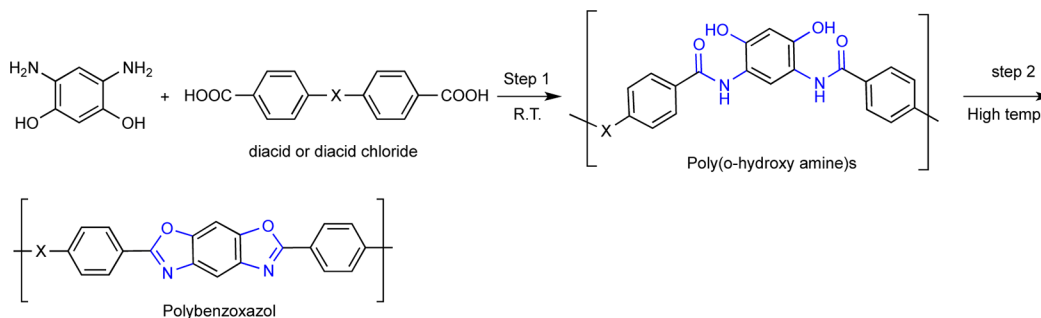
While the very high rigidity of PBO molecules is responsible for the outstanding performance, it also leads to difficulties in synthesis and fabrication. The wholly aromatic PBOs suffer

Scheme 1. Direct Polycondensation Synthesis of Polybenzoxazol

Scheme 2. Two-Step Condensation Synthesis of Polybenzoxazole via Intermediate Poly(o-hydroxyamine)


from various associated difficulties: (i) they are soluble only in harsh acids, such as sulfuric, methanesulfonic, triflic, and polyphosphoric acids, and complex-mediated Lewis acid/solvent systems, such as $AlCl_3$/nitromethane; (ii) the decomposition temperature of PBOs is below their melting points, which impedes the melt processing of PBOs; and (iii) bis(o-aminophenol)s used as the main starting materials for most synthesis approaches of PBOs are extremely expensive.[19,20] All of these shortcomings limit the application of this highly useful class of high performance polymers. The drawbacks of the aforementioned methods for polybenzoxazole synthesis motivated us to develop a new route to solve, if not all, many of the disadvantages of the traditional approaches.

Polybenzoxazines are a new class of high performance polymers that have boundless potential for growth in research and industrial applications.[21] Compared with other classes of polymers, polybenzoxazines exhibit high chemical and thermal stability as well as low flammability. In addition, polybenzoxazines possess low dielectric constants and dissipation factors, low water absorption, and unusually high glass transition temperatures. Their polymerization through a thermally accelerated ring-opening mechanism generates no reaction byproducts; furthermore, the presence of very stable intramolecular 6-membered-ring hydrogen bonding in the main chain of polybenzoxazine leads to near-zero shrinkage upon polymerization. The most interesting and unique characteristic of this class of polymers is their extraordinarily rich molecular design flexibility that allows designing a variety of molecular structures of any desired properties.

2. EXPERIMENTAL SECTION

2.1. Materials. o-Aminophenol (>98%), p-aminophenol (98%), isophthaloyl dichloride (98%), triethylamine (99%), paraformaldehyde (99%), sodium borohydride (>98%), sodium carbonate (99.8%), and trifluoroacetic anhydride (>99%) were used as received from Sigma-Aldrich. Aniline (98%), sodium sulfate anhydrous (99%), sodium chloride (>99%), ethyl acetate, 1,4-dioxane, chloroform, tetrahydrofuran, dimethylacetamide (DMAc) hexane, 2-propanol, methanol, xylenes, and sodium sulfate were obtained from Fisher Scientific.

2.2. Preparation of N_1,N_3-Bis(2-hydroxyphenyl)-isophthalamide (Compound 1). As shown in Scheme 3, N_1,N_3-bis(2-hydroxyphenyl)isophthalamide (**1**) was synthesized by reacting o-aminophenol with isophthaloyl dichloride and triethylamine in DMAc. o-Aminophenol (10.84 g, 99.3 mmol) was dissolved in 100 mL

Scheme 3. Preparation of N_1,N_3-Bis(2-hydroxyphenyl)isophthalamide (Compound 1)
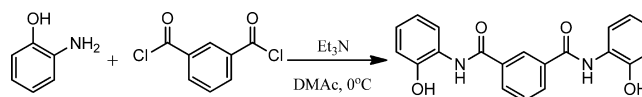
of DMAc. Triethylamine was added into the system afterward. The solution was then cooled to 0 °C, and isophthaloyl dichloride (10.08 g, 49.7 mmol) was added dropwisely with stirring. The solution was kept at 0 °C for 4 h at room temperature. After confirming the structure of the product by ^{1}H NMR, the reaction mixture was poured into cold water to eliminate extra DMAc. The precipitate was filtered and dried afterward under vacuum. Light pink crystal was obtained (yield: 85%); mp 175 °C. ^{1}H NMR (DMSO-d_6), ppm: δ = 5.35 (s, OH), 6.80–8.50 (12H, Ar), 9.15 (s, NH). ^{13}C NMR (DMSO-d_6), ppm: δ = 125.8 (s, Ar–C–NH–), 148.4 (s, Ar–C–OH) and 164.7 (s, C=O).

2.3. Preparation of Difunctional o-Amide Benzoxazine. Difunctional o-amide benzoxazines were synthesized via a solvent synthesis method (as shown in Scheme 4). The as-synthesized amide containing biphenol, Compound **1**, aniline, and paraformaldehyde were added to a round-bottom flask in stoichiometric amounts (1:2:4). The reactants were mixed with 1,4-dioxane and further refluxed for 5 h. After cooling, the reaction mixture was poured into 100 mL of cold water to give a powder-like precipitate. The product was further purified by washing with 3 N NaOH solution and water to eliminate the residual starting materials. The purified products were dried over sodium sulfate, followed by filtering and drying under vacuum to obtain a white fine powder (yield 82%). ^{1}H NMR (DMSO-d_6), ppm: δ = 4.61 (s, Ar–CH$_2$–N), 5.54 (s, –O–CH$_2$–N), 6.62–8.57 (20H, Ar), and 9.15 (s, NH). ^{13}C NMR (DMSO-d_6), ppm: δ = 47.84 (Ar–C–N), 77.68 (O–C–N), and 124.31 (C–NH) and 164.74 (Ar–C=O–NH). FTIR (KBr), cm^{-1}: 3320 (N–H stretching), 1664 (carbonyl stretching), 1466 (stretching of trisubstituted benzene ring), 1226 (asymmetric stretching of C–O–C), 1164 (asymmetric stretching of C–N–C), 952 (out-of-plane C–H of benzene ring to which oxazine ring is attached).

2.4. Preparation of 3-Phenyl-3,4-dihydro-2H-benzo[e][1,3]-oxazin-6-amine (P-a-NH$_2$) by Deprotection of 2,2,2-Trifluoro-N-(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)-acetamide (Compound 2). P-a-NH$_2$ was prepared according to methods reported elsewhere.[22] Into a 50 mL round flask was dissolved compound **1** (2.034 g, 9 mmol) in a mixture of ethyl acetate and methanol at a ratio of 100:1 (100 mL:1 mL), followed by addition of NaBH$_4$ (1.7024 g, 45 mmol). The resulting mixture was stirred for 6 h at room temperature under a nitrogen atmosphere. Then the reaction mixture was washed carefully four times with brine and one time with
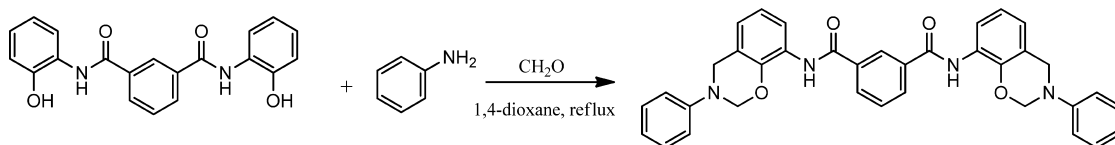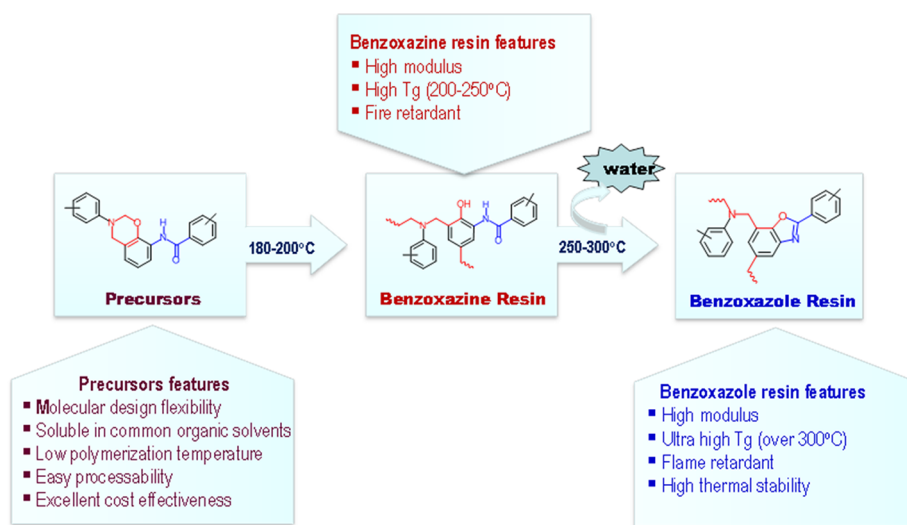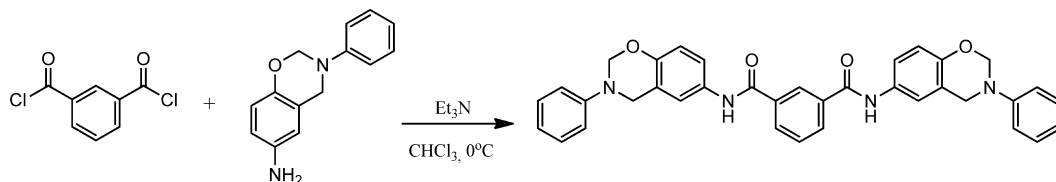
Scheme 4. Preparation of Difunctional *o*-Amide Benzoxazine

Scheme 5. Preparation of Difunctional *p*-Amide Benzoxazine

Figure 1. Smart features for easy synthesis of benzoxazole resin.

deionized water. The ethyl acetate solution was dried over sodium sulfate anhydrous. After filtering and removal of the excess solvent by a rotary evaporator under reduced pressure afforded a colorless viscous material (yield 85%). ^{1}H NMR (DMSO-d_6), ppm: δ = 4.50 (s, CH$_2$ oxazine), 4.59 (s, NH$_2$), 5.29 (s, CH$_2$ oxazine), 6.32–7.26 (8H Ar). ^{13}C NMR (DMSO-d_6), ppm δ = 48.93 (Ar–C–N, oxazine), 78.18 (O–C–N, oxazine). FT-IR (KBr), cm^{-1}: 3353 (N–H stretching), 1500 (stretching of trisubstituted benzene ring), 1224 (asymmetric stretching of C–O–C), 1180 (asymmetric stretching of C–N–C), 950 (out-of-plane C–H of benzene ring to which oxazine ring is attached).

2.5. Preparation of Difunciton al *p*-Amide Benzoxazine. As shown in Scheme 5, difunctional para-amide benzoxazine was prepared by a reaction between P-a-NH$_2$ and isophthaloyl dichloride in the presence of triethylamine as reported in our previous work.[1] Into a 25 mL flask were dissolved P-a-NH$_2$ (2.26 g, 10 mmol) and triethylamine (4.8 mL) in 50 mL of chloroform and cooled in an ice bath. The solution was stirred for 15 min, followed by dropwise addition of the 50 mL of chloroform solution of isophthaloyl chloride (1.015 g, 5 mmol). The mixture was stirred for 1 h in the ice bath and another 5 h at room temperature. The solution was washed with 0.5 N Na$_2$CO$_3$ aqueous solution and then with deionized water. The solution was dried over sodium sulfate anhydrous, followed by concentration and precipitation in 200 mL of hexane. The precipitate was removed by filtration and dried to give a white powder (yield: 90%). ^{1}H NMR (DMSO-d_6), ppm: δ = 4.67 (s, AR-CH$_2$–N), 5.44 (s, –O–CH$_2$–N), 6.72–8.47 (20H, Ar), and 9.35 (s, NH). ^{13}C NMR (DMSO-d_6), ppm: δ = 48.98 (Ar–C–N, oxazine), 78.71 (O–C–N, oxazine), 130.31 (C–NH), and 164.58 (Ar–CdO–NH). FTIR (KBr), cm^{-1}: 3288

(N–H stretching), 1646 (carbonyl stretching), 1496 (stretching of trisubstituted benzene ring), 1226 (asymmetric stretching of C–O–C), 1186 (asymmetric stretching of C–N–C), and 954 (out-of-plane C–H of benzene ring to which oxazine ring is attached).

2.6. Measurements. ^{1}H and ^{13}C NMR spectra were acquired on a Varian Oxford AS600 at a proton frequency of 600 MHz and its corresponding carbon frequency of 150.9 MHz. The average number of transients for ^{1}H and ^{13}C MNR measurement was 64 and 1024, respectively. A relaxation time of 10 s was used for the integrated intensity determination of ^{1}H NMR spectra. Fourier transform infrared (FTIR) spectra were obtained using a Bomem Michelson MB100 FTIR spectrometer, which was equipped with a deuterated triglycine sulfate (DTGS) detector and a dry air purge unit. Coaddition of 32 scans was recorded at a resolution of 4 cm^{-1}. Transmission spectra were obtained by casting a thin film on a KBr plate for partially cured samples. Elemental analysis was performed by MHW Laboratories. A TA Instruments DSC model 2920 was used with a heating rate of 10 °C/min and a nitrogen flow rate of 60 mL/min for all tests. All samples were crimped in hermetic aluminum pans with lids.

Dynamic mechanical analyses were done on a TA Instruments Q800 DMA applying controlled strain tension mode with amplitude of 10 μm and a ramp rate of 3 °C/min. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 TGA with a heating rate of 10 °C/min in a nitrogen atmosphere at a flow rate of 40 mL/min.

3. RESULTS AND DISCUSSION

An attractive class of multiple smart polybenzoxazine precursors, known as *o*-amide functional benzoxazines, has been developed and has potential for use as precursors for benzoxazole resin. Figure 1 summarizes the exceptional features of this class of polymers that is regarded as a unique class, not only among traditional polybenzoxazines but also among all commonly known classes of high performance polymers. The precursors can be easily synthesized in various molecular architecture forms, including monomers, oligomers, and main-chain-type as well as side-chain-type polymers that allow performance and processability control.

Interestingly, this class of benzoxazines is shown to polymerize via cationic ring-opening polymerization at much lower temperatures than any other known class of benzoxazines without added initiators and/or catalysts to form amide-containing polybenzoxazines. The presence of intramolecular hydrogen bonding between an amide linkage and the adjacent oxazine ring acts as an internal incentive to stimulate the ring-opening polymerization in a smart way, like a self-complementary initiator (Figure 2). As a result, a novel class
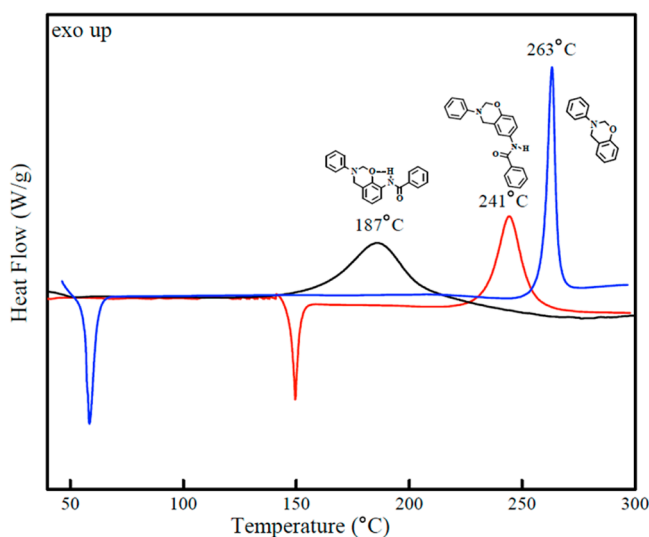
of amide-functional polybenzoxazines is produced that can also be coined as poly(*o*-hydroxyamide)s or poly(*o*-amidephenol)s, owing to the presence of amide linkages next to the triggered phenolic moieties upon ring-opening polymerization.

Furthermore, when this smart class of polybenzoxazines is exposed to higher temperatures via postcuring above 200 °C or catching fire, it generates water through intramolecular cyclization between the neighboring hydroxyl and amide groups to form oxazole rings as a repeating units in the new network structure. As a result, the new polymeric network structure becomes even more thermally stable by converting into a new class of polymer thermosets. Such materials have never been reported and are now collectively termed benzoxazole resins, representing a new class of thermosetting resins.

The concept has been initially demonstrated by designing two examples of monomeric amide-functional benzoxazine isomers (ortho and para) based on isophthaloyl chloride, as shown in Scheme 6. Upon polymerization at 200 °C, the ortho-isomer is expected to give cross-linked polybenzoxazine of poly(*o*-hydroxyamide) structure, which is very similar to poly(*o*-hydroxyamide)s as a typical polybenzoxazole precursor. Thus, it is believed that such precursors can be structurally rearranged into a thermosetting polybenzoxazole. On the other hand, the para-isomer gives a polybenzoxazine of poly(*p*-hydroxyamide) structure that has no possibility for structural rearrangement to oxazole structure before degradation.

The thermal stability of the *o*- and *p*-benzoxazine isomers has been studied by thermogravimetric analysis (TGA) (Figure 3) after thermal treatment at 200 °C. It is well-established that the polymerization of benzoxazines occurs through oxazine ring-opening without producing any byproduct and the thermal degradation of polybenzoxazines starts over 300 °C. *p*-Benzoxazine isomer (line B, Figure 3) shows degradation similar to typical polybenzoxazine; however, *o*-benzoxazine isomer shows a bimodal degradation profile (line A, Figure 3) in which the first step of weight loss occurs at lower temperature than polybenzoxazine degradation and in the same temperature range of the typical cyclodehydration of poly(*o*-hydroxyamide)s to give polybenzoxazole.

Using the advantage of tremendous flexibility in molecular design of this novel class of polybenzoxazines, another series of *o*-amide functional benzoxazine monomers of different

Figure 2. DSC polymerization behavior of monomers.

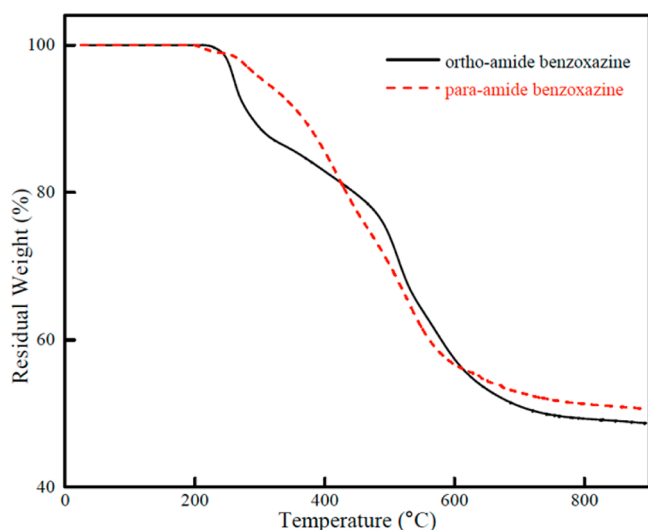**Scheme 6. Polymerization of Amide-Functional Benzoxazine Isomers**
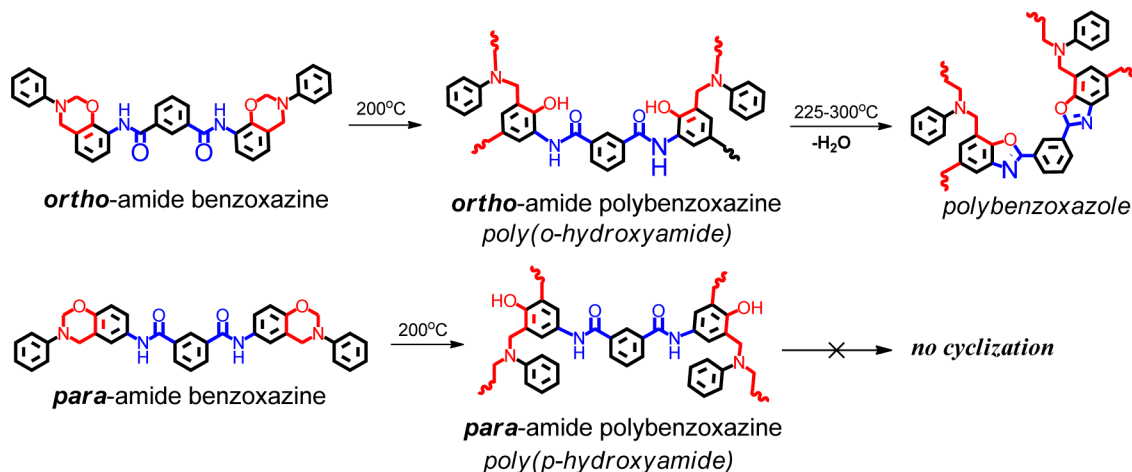
Figure 3. Thermogravimetric analysis of amide-functional benzoxazine monomers after thermal polymerization at 250 °C.

molecular structure (Figure 4, series X_1) have been synthesized, using various aromatic diamines and N-(2-hydroxyphenyl)-benzamide. The polymerization behavior of this series has been compared with various traditional aromatic amine based-benzoxazine monomers (series X_2, Figure 4). Detailed information about the synthesis of these monomers will be published elsewhere. Expectedly, the TGA thermograms of phenol/diamine based benzoxazine monomers treated at 200 °C shows typical features for polybenzoxazine degradation in which the degradation starts above 300 °C. On the contrary, o-amide benzoxazine monomers, treated also at 200 °C, show an early stage of weight loss, which is attributed to the loss of water and a formation of polybenzoxazole.

A detailed example to support the conversion of this class of polybenzoxazines into polybenzoxazole resin has been studied using main chain-type benzoxazine polymers containing amide functionalities (Figure 5). The polymerization behavior of the benzoxazine resins has been studied by differential scanning calorimetry (DSC), and the results showed a typical polymerization exotherm at 212 and 259 °C for ortho and para polymers, respectively. The benzoxazine with o-amide has a lower polymerization temperature than the para-isomer and much lower than the traditional benzoxazine monomer as described earlier. For the ortho-isomer polybenzoxazine, the exotherm is followed by an endotherm, which is attributed to the dehydration and formation of polybenzoxazole as shown earlier in Scheme 1, in a way similar to poly(o-hydroxyamide)s. This phenomenon has been supported by TGA thermograms

of both isomers shown in Figure 6, which indicates the presence of weight loss at earlier temperature from the ortho-isomer within the same temperature range.

The ring-opening polymerization of benzoxazine structure and the thermal cyclodehydration of o-amide polybenzoxazine have been monitored by Fourier transform infrared spectroscopy (FT-IR). For consistency, the sample has been prepared by casting a thin film on a KBr plate from a chloroform solution of o-amide benzoxazine main-chain polymer followed by stepwise heating process up to 300 °C. Arrows shown in Figure 7 indicate the characteristic vibrational modes which are useful for this study. The typical absorption band at 925 cm^{-1} which can be used to study the ring-opening reaction of benzoxazine structure gradually decreases and almost disappears by 200 °C, suggesting the formation of cross-linked o-amide polybenzoxazine. The cyclization to poly(o-hydroxyamide) was supported by the disappearance of the amide I mode at 1646 cm^{-1}. The formation of benzoxazole structure gives rise to a band at 1595 cm^{-1}.[24,25] The FTIR spectra of this novel o-amide-functional polybenzoxazine, cross-linked poly(o-hydroxyamide), is practically identical to those reported for polybenzoxazole synthesized through the traditional approach of linear poly(o-hydroxyamide) method, indicating that thermal cyclization has been completed.

Dynamic mechanical analysis (DMA) has been performed to further understand the effect of cyclization and polybenzoxazole thermoset formation on the thermomechanical properties with respect to the o-amide polybenzoxazine as a smart precursor. The spectrum in Figure 8 for the o-amide-functional polybenzoxazine which is heat-treated at 200 °C shows clearly that the storage modulus maintained a stable value and started decreasing in the glass transition region. Interestingly, the modulus tends to increase in the rubbery plateau as shown in Figure 8, implying the presence of restriction in the segmental mobility and, perhaps, the further structural rearrangement to further increase the rigidity of the molecules. The E'' of o-amide polybenzoxazine which is heat-treated at 200 °C, reveals one relaxation peak at 212 °C which is attributed to the T_g and less defined peak above 300 °C. Two clearly resolved relaxations have been observed from the tan δ peak, reflecting the cyclodehydration and formation of polybenzoxazole of rigid molecular structure of lower segmental mobility. The relatively low T_g of the o-amide polybenzoxazine allows a greater mobility of chain segments and thus assisted the cyclodehydration and the easy formation of polybenzoxazole. The DMA spectrum of the o-amide polybenzoxazine postcured at 300 °C for 1 h shows a stable storage modulus up to 300 °C due to the formation of polybenzoxazole of a stiffer molecular structure.
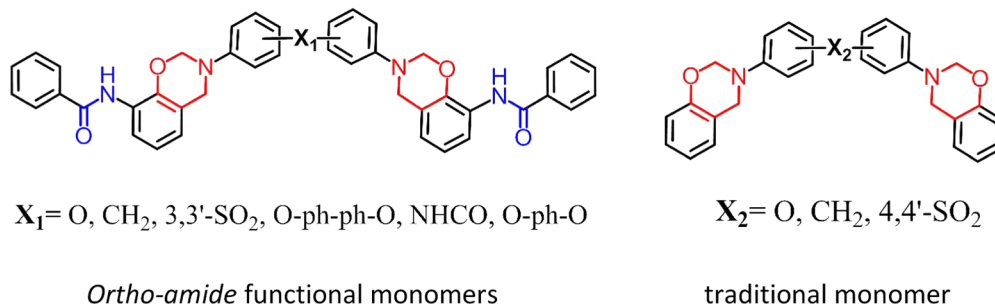

X_1 = O, CH$_2$, 3,3'-SO$_2$, O-ph-ph-O, NHCO, O-ph-O X_2 = O, CH$_2$, 4,4'-SO$_2$

Ortho-amide functional monomers traditional monomer

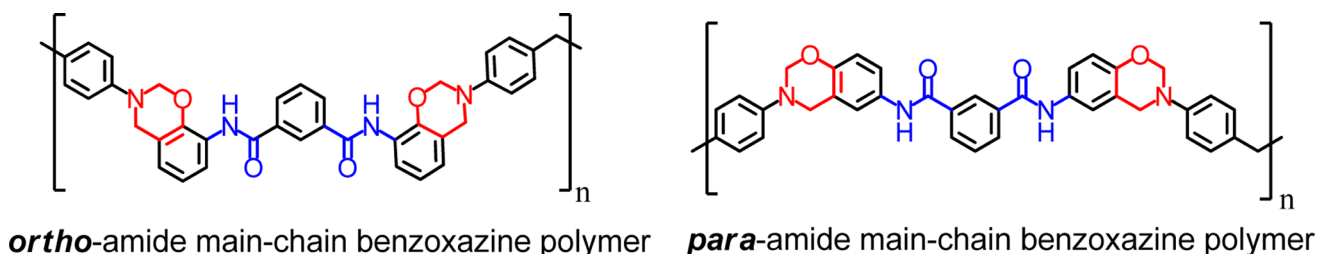**Figure 4.** Structure of bifunctional benzoxazines.

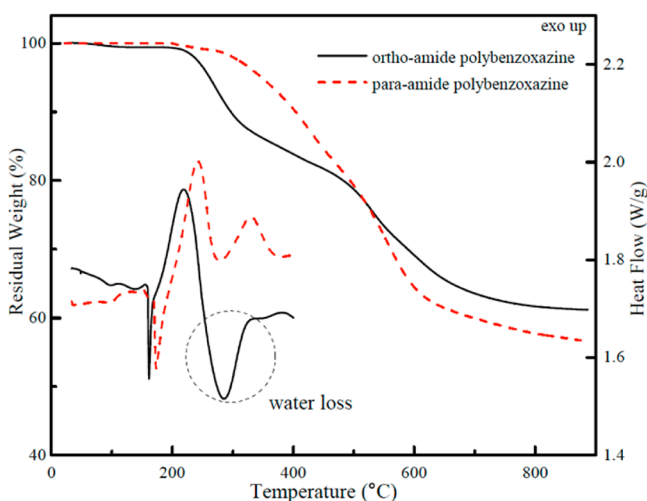**Figure 5.** Structure of ortho and para main-chain type.

Figure 6. TGA and DSC thermograms of ortho and para main-chain-type benzoxazine polymers.
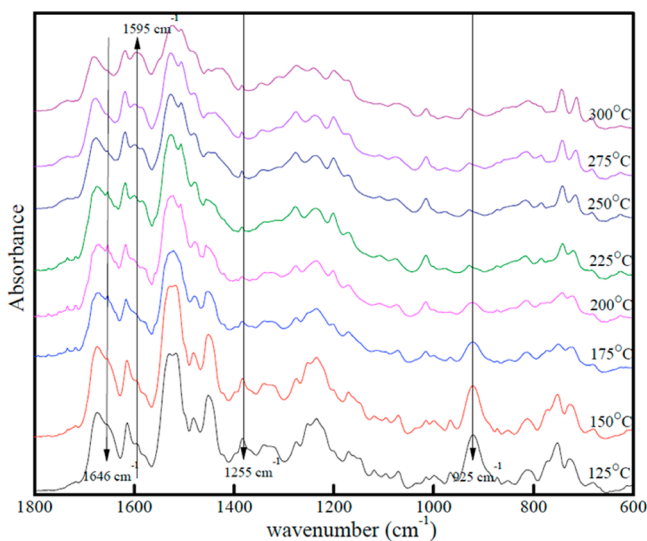

Figure 7. FT-IR spectra of ortho main-chain-type benzoxazine polymers after various thermal treatments.
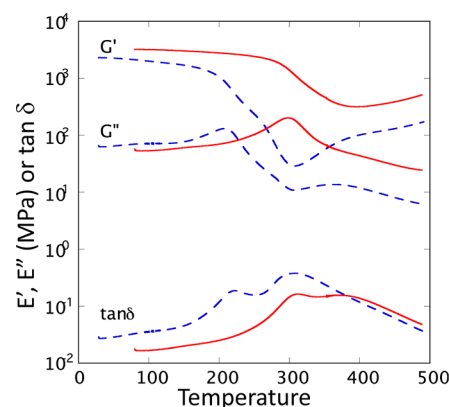

Figure 8. Dynamic mechanical spectra of *o*-amide benzoxazine with (solid line) and without (broken line) heat treatment at 200 °C for 1 h.

and magnetic-angle spinning (MAS) was also used as shown in Figures 9 and 10. After 1 h of heating at 220 °C, both orth- and
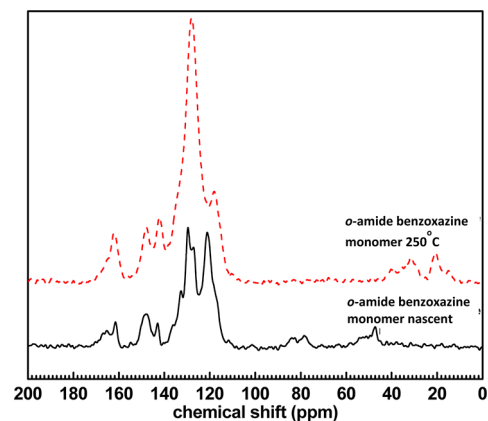

Figure 9. [13]C CP MAS spectrum of *o*-amide benzoxazine monomer at nascent and 250 °C for 1 h.

The maximum amplitude of the α-relaxation peak decreases with the rearrangement of *o*-amide polybenzoxazine resin into polybenzoxazole, suggesting a more severe restriction of the segmental mobility, due to the formation of rigid benzoxazole units in the polymer. This behavior implies that the cyclodehydration of the polybenzoxazine is successfully taking place.

In order to further confirm the occurrence of benzoxazole cyclization, solid state ^{13}C NMR with cross-polarization (CP)

para-model compounds showed similar spectra, though with expected minor differences due to the difference in substitution position. The similarity is due to the similar structural changes caused by oxazine ring-opening polymerization. However, when the heating condition was changed to 250 °C for 1 h, the spectra for the ortho- and para-model compounds showed drastic differences. The ^{13}C resonances at 163, ~148, and ~142 ppm, which can be assigned to the benzoxazole group, are well resolved. However, for the *p*-amide polybenzoxazine, at the same conditions, none of the above benzoxazole signals are observed, although broad resonances heavily overlap at 163 and 148 ppm. In fact, little changes in spectral feature were observed after this thermal treatment for *p*-amide polybenzox-
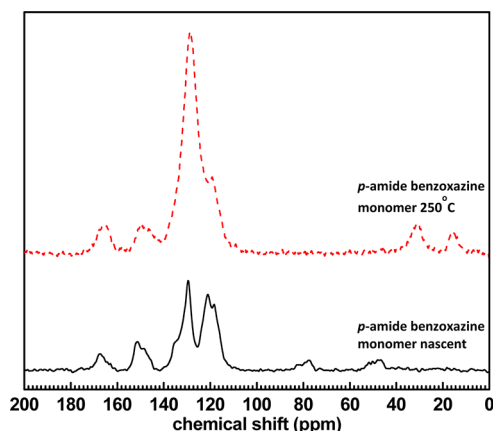
Figure 10. ^{13}C CP MAS spectrum of *p*-amide benzoxazine monomer at nascent and 250 °C for 1 h.

azine. This difference between the ortho- and para-model compounds is a strong support of the proposed benzoxazole formation in the *o*-amide-containing polybenzoxazine and in accordance with other aforementioned evidence by FTIR, DSC, and TGA analyses.

Heat release rate (HRR) is governed by the heat release capacity (HRC) which is the maximum amount of heat released by combustion per degree of temperature rise per unit mass of polymer in the mesophase. HRC is considered as a semi-quantitative predictor of fire performance and flammability of materials which is related to flame resistance. HRR and HRC for a set of polybenzoxazine derived from amide-functional benzoxazines have been evaluated to be ~92 J/(g K). In general, the lower the values of both HRC and HRR, the higher the flame resistance. The HRC value of polybenzoxazole thermoset was one of the lowest among 47 polymers studied by Lyon et al.[26] Furthermore, this new class of thermoset polymers is better than poly(ether imide) which shows HRC of 121 J/(g K) and UL-94 rating of V0. It has been concluded that this novel class of polymers has excellent flame resistance; a detailed study will be published elsewhere.

4. CONCLUSION

A new class of cross-linkable polybenzoxazole (PBO), namely benzoxazole resin, has been successfully developed. The in-situ thermal conversion of amide-functional benzoxazines as smart class of polybenzoxazine precursors has been proposed as an alternative approach to the traditional PBO formation. Using the tremendous molecular design flexibility of these novel polybenzoxazole precursors, which cannot be found in the traditional concept for polybenzoxazole formation, it has become possible to produce polybenzoxazoles through easily processable precursors. The water is produced due to the endothermic nature of cyclodehydration reaction of this class of smart polybenzoxazines when producing polybenzoxazole, which provides an additional advantage for fire retardancy. The greatest advantage of this concept is that the benzoxazole resin is obtained from a low molecular weight compound (resin) unlike the high molecular weight poly(*o*-hydroyamide)s.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: taa16@case.edu (T.A.); hxi3@cwru.edu (H.I.).

■ REFERENCES

(1) Holmes, G. A.; Rice, K.; Snyder, C. R. *J. Mater. Sci.* **2006**, *41*, 4105−4116.
(2) Fukukawa, K.; Ueda, M. *Macromolecules* **2006**, *39*, 2100−2106.
(3) Dotrong, M. H.; Evers, R. C.; Moore, G. J. *Polym. Prepr.* **1990**, *31*, 675−676.
(4) Ueda, M.; Sugita, H.; Sato, M. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1019−1026.
(5) Reinhardt, B. A. *Polym. Commun.* **1990**, *31*, 453−454.
(6) Walsh, P. J.; Hu, X.; Cunniff, P.; Lesser, AJ *J. Appl. Polym. Sci.* **2006**, *102*, 3517−3525.
(7) Park, E. S.; Sieber, J.; Guttman, C.; Rice, K.; Flynn, K.; Watson, S.; Homes, G. *Anal. Chem.* **2009**, *81*, 9607−9617.
(8) Kubota, T.; Nakanishi, R. *J. Polym. Sci., Part B* **1964**, *2*, 655−659.
(9) Moyer, W. W.; Cole, C.; Anyos, T. *J. Polym. Sci., Part A* **1965**, *3*, 2107−2121.
(10) Imai, Y.; Uno, K.; Iwakura, Y. *Makromol. Chem.* **1965**, *83*, 179−187.
(11) Ueda, M.; Ebara, K.; Shibasaki, Y. *J. Photopolym. Sci. Technol.* **2003**, *16*, 237−242.
(12) Tullos, G. L.; Powers, J. M.; Jeskey, S. J.; Mathias, L. J. *Macromolecules* **1999**, *11*, 3598−3612.
(13) Okabe, T.; Morikawa, A. *High Perform. Polym.* **2008**, *20*, 53−66.
(14) Park, H. B.; Jung, C. H.; Lee, Y. M.; Hill, A. J.; Pas, S. J.; Mudie, S. T.; Wagner, E. V.; Freeman, B. D.; Cookson, D. J. *Science* **2007**, *318*, 254−258.
(15) Schab-Balcezak, E.; Jikei, M.; Kamimoto, M. *Polym. J.* **2003**, *35*, 208−212.
(16) Guzman-Lucero, D.; Likhatcher, D. *Polym. Bull.* **2002**, *48*, 261−269.
(17) Chen, B. K.; Tsai, Y. J.; Tsay, S. Y. *Polym. Int.* **2006**, *55*, 93−100.
(18) Hodgkin, J. H.; Dao, B. N. *Eur. Polym. J.* **2009**, *45*, 3081−3092.
(19) Kim, S.; Pearce, E. M.; Kwei, T. K. *Polym. Adv. Technol.* **1990**, *1*, 49−73.
(20) Kim, S. S.; Pearce, E. M. *Makromol. Chem. Suppl.* **1989**, *15*, 187−218.
(21) Ishida, H. In *Handbook of Benzoxazine Resins*; Ishida, H., Agag, T., Eds.; Elsevier: Amsterdam, 2011; pp 3−81.
(22) Agag, T.; Arza, C. T.; Maurer, F. H. J.; Ishida, H. *Macromolecules* **2010**, *43*, 2748−2758.
(23) Hemvician, K.; Ishida, H. *Polymer* **2002**, *43*, 4391−4402.
(24) Hsiao, S. H.; Huang, Y. H. *Eur. Polym. J.* **2004**, *40*, 1127−1135.
(25) Yang, G.; Matsuzono, S.; Koyama, E.; Kokuhisa, H.; Hiratani, K. *Macromolecules* **2001**, *34*, 6545−6547.
(26) Lyon, R. E.; Janssens, M. L. Polymer Flammability. U.S. Department of Transportation, Federal Aviation Administration, Report #DOT/FAA/AR-05/14.