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# Advanced Polymers from Simple Benzoxazines and Phenols by Ring-Opening Addition Reactions

Zeynep Deliballi, Baris Kiskan,* and Yusuf Yagci*

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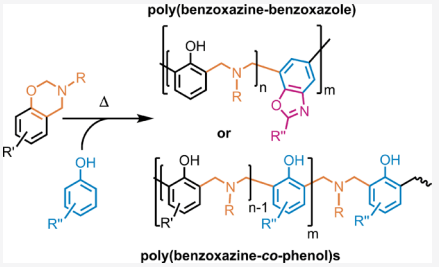
**ABSTRACT:** Simple benzoxazines were mixed and reacted with various phenolics such as phenol, *p*-nitrophenol, *p*-cresol, 1,3-dihyroxybenzene (resorcinol), 1,3,5-trihydroxybenzene (phloroglucinol), and *N*-(2-hydroxyphenyl)benzamide. The influence of these phenolic compounds on ring-opening polymerization temperature of benzoxazines was examined by DSC analysis. The cresol-based benzoxazine (C-a) and phenolics yielded polymers with molecular weight of around 1500 Da. Interestingly, for C-a/resorcinol- and C-a/phloroglucinol-based polymers, a second GPC trace was observed that corresponds to a few million daltons for mixing ratios of 4:1 and 5:1. Moreover, the mixtures of C-a and *N*-(2-hydroxyphenyl)benzamide gave poly(benzoxazine−benzoxazole)s through a new methodology eliminating the need of synthesis of *ortho*-amide benzoxazines. The obtained polymers were soluble and characterized in detail by $^{1}$H NMR, $^{13}$C NMR, GPC, DSC, and TGA analyses.

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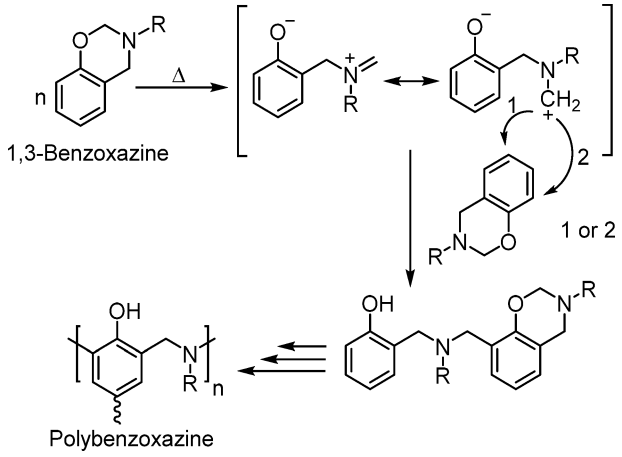
## INTRODUCTION

Polybenzoxazines as phenolic polymers resembling Novolac resin have attracted significant attention from both academia and industry because of their unique advantages. Typically, these polymers exhibit high glass transition temperatures, mechanical strength, and a high decomposition temperature and are therefore well suited for high-temperature applications.[1−6] Moreover, polybenzoxazines have additional useful properties such as minor amounts of water sorption, hydrolytic stability even in hot water, chemical resistance, low dielectric constants, and limited shrinkage during production from their monomers.[1,7−9] Therefore, polybenzoxazines are comparable to bismaleimides and superior to classical phenol−formaldehyde resins for many applications.[10] On the other hand, unmodified polybenzoxazines exhibit some deficiencies including high curing temperature, as much as 260 °C depending on the functionalities and purity of the corresponding benzoxazine monomer, and low fracture toughness.[11−16] These disadvantages can be overcome by monomer design, synthesizing curable polymeric benzoxazine precursors, or blending benzoxazine monomer with toughening agents and other resins prior to curing.[17−30] In the latter approach, benzoxazine monomers can also react with the added components forming a network possessing whole system in the structure. Thus, the reactive nature of benzoxazine monomers tolerates the use of various compounds in benzoxazine resin formulations.[31] The benzoxazine monomers polymerize through a cationic pathway containing two major stages. Initially, the ring-opening reaction of oxazine occurs to form zwitterionic species, and then, the carbocation, therefrom, reacts with the aromatic moiety of the benzoxazine in a fashion of Friedel−Crafts reaction (Scheme 1).[32−37] Accordingly, the generated carbocation also has the ability to give similar Friedel−Crafts reaction with other aromatic compounds, especially with those bearing an activating substituent such as −OH and having free *ortho*- and/or *para*-positions.[38,39]

**Scheme 1. Simplified Mechanism for Ring-Opening Polymerization of a Benzoxazine Monomer to Produce a Polybenzoxazine**

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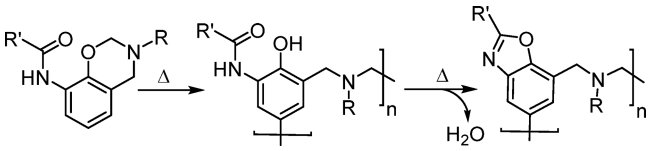
These ring-opening addition reactions of benzoxazines with suitable aromatic compounds are highly interesting in terms of synthesizing novel compounds and to develop polymers containing a high amount of phenolic −OH groups. Actually, this approach was first reported in 1965 by Burke et al. by reacting 1,3-benzoxazines and phenols to obtain amino-alkylated phenols.[40] And then, by applying this procedure as an alternative method, the reaction of benzoxazine and phenol dimers, trimers, and tetramers gave several azacalixarenes with different ring sizes.[41] This concept was extended to polymer synthesis by Endo et al., and the ring-opening addition reaction of a monofunctional benzoxazine with 2-methylresorcinol (2-MR) gave an adduct containing four hydroxyls. In this reaction, 2-MR acted as a bifunctional reagent to react with 2 equiv of the monofunctional benzoxazine. Additionally, 2-methylresorcinol was also used as cross-linker for side-chain polybenzoxazine precursors.[42] In the case of bifunctional benzoxazines, the same reaction produced ring-opened main-chain polybenzoxazines having molecular weights between 0.8 and 3.9 kDa with broad dispersity ($Đ$).[43] In another study, a similar concept was applied by using a trifunctional benzoxazine and different phenolics to obtain cross-linked polymers with good thermal properties such as 78% char yield at 500 °C.[44]

In the past decade, benzoxazines containing amide groups in the structure are an emerging class of monomers as additional properties may be imparted to the resulting networks. Several synthetic strategies ensuing different accomplishments were reported. Initially, primary amine functional benzoxazine monomers were synthesized as a useful intermediate for the production of various amide and polyamides.[45,46] Alternatively, an amide linkage containing mono- and difunctional benzoxazine monomers and main-chain polybenzoxazine precursor was synthesized starting from commercially available and relatively cheap 3,4-dihydrocoumarin (DHC). Besides, DHC was also used to synthesize a similar main-chain polybenzoxazine in a one-pot approach.[47,48] Apart from these syntheses, *ortho*-amide functional benzoxazines were designed to utilize benzoxazole formation that takes place at ca. 250 °C between the phenolic −OH and *ortho*-amide moiety with water elimination (Scheme 2). This reaction transforms

**Scheme 2. Curing of *ortho*-Amide Benzoxazine to Produce Polybenzoxazine and Subsequent Benzoxazole Formation**




polybenzoxazines into poly(benzoxazine−benzoxazole)s, resulting in a high-performance thermoset with improved mechanical performance and an apparent thermal stability compared to classical polybenzoxazines.[49−55] However, this approach requires the synthesis of *ortho*-amide functional benzoxazines, starting from the reaction of 2-aminophenols with acid halides to obtain 2-hydroxyphenyl amides. Subsequently, these molecules are used in classical benzoxazine monomer synthesis by reacting with formaldehyde (or paraformaldehyde) and a suitable primary amine that tolerates the synthesis conditions.

It seemed appropriate to take advantage of the reactive nature of benzoxazines toward phenols which is expected to provide the possibility to synthesize advanced polybenzoxazines by selecting proper phenol additives during curing of classical benzoxazine monomers. This way, the requirement of complicated benzoxazine monomer synthesis could be avoided. We herein report a simple method to obtain an alternative poly(benzoxazine−benzoxazole) system by using various additive phenols.

## EXPERIMENTAL SECTION

**Materials.** Aniline (Merck, 99.5%), *p*-cresol (Sigma-Aldrich, ≥99.0%), paraformaldeyhde (Sigma-Aldrich, 95.0−100.5%), toluene (Aldrich, 95.0−100.5%), ethanol (Sigma-Aldrich, 95.0−100.5%), sodium hydroxide (Sigma-Aldrich, 95.0−100.5%), diethyl ether (VWR Chemicals, ≥99.5%), resorcinol (Sigma-Aldrich, ≥99.0%), phloroglucinol (Carlo-Erba, 98%), phenol (Sigma-Aldrich, ≥99.0%), 4-nitrophenol (Merck, ≥99.5%), 2-aminophenol (Sigma-Aldrich, 99.0%), benzoyl chloride (Sigma-Aldrich, ≥99.0%), *N*,*N*-dimethylacetamide (DMAc, Sigma-Aldrich, anhydrous, 99.8%), acetone (Alfa Aesar, 99+%), and distilled water were used as received.

**Characterization.** FTIR spectra were recorded on a PerkinElmer FTIR Spectrum One spectrometer. Differential scanning calorimetry (DSC) was performed on PerkinElmer Diamond DSC from 30 to 320 °C with a heating rate of 10 °C $min^{-1}$ under nitrogen flow. A typical DSC sample was 2−5 mg in a 30 μL aluminum pan. Thermal gravimetric analysis (TGA) was performed on a PerkinElmer Diamond TA/TGA with a heating rate of 10 °C $min^{-1}$ under nitrogen flow. Gel permeation chromatography (GPC) measurements were performed on a TOSOH EcoSEC GPC system equipped with an autosampler system, a temperature-controlled pump, a column oven, a refractive index (RI) detector, a purge and degasser unit, and a TSKgel superhZ2000, 4. 6 mm ID × 15 cm × 2 cm column. Tetrahydrofuran was used as an eluent at flow rate of 1.0 mL/min at 40 °C. The refractive index detector was calibrated with polystyrene and poly(methyl methacrylate) standards having narrow molecular weight distributions. Data were analyzed by using Eco-SEC Analysis software.

**Synthesis of Monofunctional Benzoxazine Monomers from *p*-Cresol (C-a) or Phenol (P-a).** A typical solventless method was used.[56] Aniline (17.2 g, 0.185 mol), *p*-cresol (20.0 g, 0.185 mol) (or phenol, 17.4 g, 0.185 mol), and paraformaldehyde (11.1 g, 0.370 mol) were placed in a round-bottom flask, and the mixture was stirred at 100 °C for 2 h. After cooling the contents of the flask to room temperature, the sticky product was dissolved in diethyl ether (250 mL) and extracted with 0.5 M sodium hydroxide (3 × 100 mL). Then, the diethyl ether solution was washed with distilled water (3 × 100 mL). The ether solution was dried with anhydrous $MgSO_4$ and filtered. Diethyl ether was evaporated by using a rotary evaporator. The product was dried under vacuum at 45 °C for 24 h (yield ≈ 56%, mp = 51 °C for C-a, and ≈49%, mp = 91 °C for P-a).

**Synthesis of *N*-(2-Hydroxyphenyl)benzamide (2HPB).** A modified procedure was used.[53] 2-Aminophenol (5.41 g, 49.65 mmol) was dissolved in 70 mL of DMAc, and then the solution was cooled to 0 °C. With vigorous stirring, benzoyl chloride (13.96 g, 99.3 mmol) was added dropwise into the solution. The reaction content was stirred at 0 °C for 4 h and then at room temperature for 14 h. Afterward, the mixture was poured in distilled water to precipitate the product. After filtering, the obtained solid was washed with a copious amount of cold water. The final product was dried under vacuum at 40 °C for 24 h, giving a light-brown solid (yield ≈ 90%, mp = 136 °C).

**Polymerization Process.** Benzoxazine monomer synthesized from *p*-cresol (C-a) or phenol (P-a) was dissolved in acetone (the volume of acetone was ca. 1.5 mL for 100 mg of monomer) and mixed with resorcinol and pholoroglucinol in mole ratios of 1:1, 2:1, 3:1, 4:1, and 5:1 and also with phenol, *p*-cresol, 4-nitrophenol, and *N*-(2-hydroxyphenyl)benzamide in a ratio of 5:1. The samples were placed in a Teflon mold, and acetone was removed in a vacuum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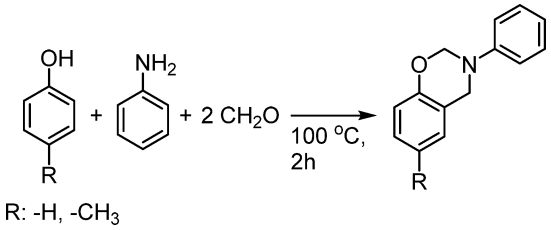
chamber at ambient temperature. Then, the molds were heated gradually as 100 °C for 15 min, 150 °C for 15 min, and 220 °C for 1 h in an open-air oven. After cooling, the obtained poly(benzoxazine-*co*-phenol)s were removed from the molds by using a spatula. Moreover, C-a and 2HPB were mixed in 2:1 and 5:1 mole ratios and molded; then the same gradual heating was applied in an oven for ring-opening polymerization, and thereafter a post-heat treatment was also applied at 300 °C for 15 min to obtain poly(benzoxazine−benzoxazole)s.

## RESULTS AND DISCUSSION

Phenolic compounds are potential candidates for the ring-opening addition reaction of benzoxazines as mentioned in the Introduction. Several commercially available phenols, namely *p*-nitrophenol, *p*-cresol, 1,3-dihyroxybenzene (resorcinol), and 1,3,5-trihydroxybenzene (phloroglucinol), were selected for the purpose. *N*-(2-Hydroxyphenyl)benzamide was synthesized according to a modified procedure.[53] Although many structurally different benzoxazine monomers are accessible, two different simple monofunctional benzoxazine monomers were synthesized from phenol and *p*-cresol, aniline, and formaldehyde abbreviated as P-a and C-a (Scheme 3) and characterized by $^1$H NMR spectral and DSC thermal analyses (see the Supporting Information, Figures S1−S3).

**Scheme 3. Synthesis of C-a (R: $-CH_3$) and P-a (R: $-H$) Monomers**




To prepare poly(benzoxazine-*co*-phenol)s, monofunctional benzoxazines and phenolics (C-a or P-a/phenolics) were mixed in various mole ratios starting from 1:1 to 5:1 and heated (Scheme 4). The obtained polymers from C-a/phenolics were soluble, therefore facilitating their spectral (Figure S4) and molecular weight characterization. Even though the P-a monomer is monofunctional as the C-a monomer, cross-linked polybenzoxazine is formed due to the vacant *para*-and *ortho*-positions on the benzene ring (see Scheme 1). The observed solubility for the polymer from C-a monomer is due to the presence of a methyl blocking group on the *para* position of the benzene ring. The GPC analysis for thermally treated C-a/phenolics gave molecular weights mostly around 1500 Da. It is interesting to note that especially for C-a/resorcinol and C-a/phloroglucinol mixtures a second GPC trace corresponding to a few million daltons for mixing ratios of 4:1 and 5:1 was observed (Table 1). The observed high molecular weight indicates the bridging role of added phenolics between C-a-based polybenzoxazine chains. This effect is pronounced only at lower phenolic and higher C-a moles. It is likely that the formation of such large structures requires long polybenzoxazine chains that have ability to react with a phenolic having vacant carbons at both *ortho*- and *para*-positions (Scheme 5). This hypothesis was further confirmed by conducting similar experiments using C-a monomer with *p*-cresol and *p*-nitrophenol as the *para*-position blocked phenolics in 4:1 and 5:1 mole ratios (see Figure S5). In contrast to the usage of a low amount of phenolics, for higher phenolic mole ratios, in for example 1:1, 2:1, and 3:1 C-a/phenolics, only polymers with low molecular weights ($M_n$: 1090 and 1450 Da) were obtained because a higher amount of phenolics reduced the probability of the self-reaction of C-a to form long polybenzoxazine chains. On the other hand, pholoroglucinol and resorsinol gave high molecular weight polymers even at low C-a mole amounts due to their highly reactive nature in the Friedel−Crafts reaction (Scheme 5). It is worth mentioning that the amount of low molecular weight poly(benzoxazine-*co*-phenolics) is much higher than that of high molecular weight polymers as calculated by the related area of the GPC traces (see Figure S6). Accordingly, the area ratios of the bands of low and high molecular weight polymers vary between 9 and 107 depending on the phenolics used and mole ratios (Table 1). Moreover, the polydispersity index ($Đ$) of the all soluble samples is quite high. This could be expected since the polymerization takes place via uncontrolled multi-stage reactions, and these $Đ$ results are also typical for such a polymerization process. Besides, the nature of reaction may also lead to the formation of branched and/or hyperbranched structures, especially when pholoroglucinol and resorsinol are used as the phenolic reagent.

**Scheme 4. Curing of Benzoxazines with Added Phenols**

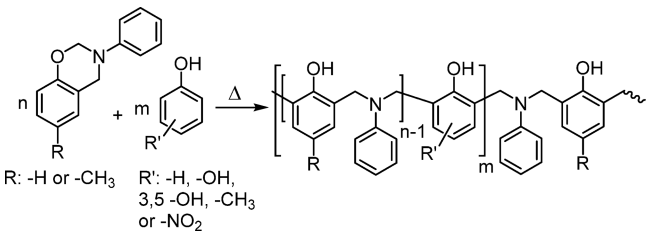



**Table 1. GPC Analyses of C-a/Phenolics-Based Polymers**

| polymer[a] | $M_n$ (kDa) first trace ($Đ$)[b] | $M_n$ (kDa) second trace ($Đ$) | ratio[c] |
|---|---|---|---|
| C-a/*p*-cresol (5:1) | 1.099 (2.38) | | |
| C-a/*p*-nitrophenol (5:1) | 1.450 (2.56) | | |
| C-a/phenol (5:1) | 1.465 (2.51) | 182.930 (2.62) | 29 |
| C-a/phenol (3:1) | 2.390 (5.77) | | |
| C-a/resorcinol (5:1) | 1.535 (2.55) | 5472.400 (1.48) | 107 |
| C-a/resorcinol (3:1) | 1.541 (2.19) | | |
| C-a/resorcinol (1:1) | 1.300 (1.88) | | |
| C-a/phloroglucinol (5:1) | 1.319 (2.11) | 1180.760 (3.35) | 9 |
| C-a/phloroglucinol (4:1) | 1.523 (3.0) | 4508.966 (1.68) | 8.4 |
| C-a/phloroglucinol (3:1) | 1.288 (2.13) | 3457.028 (2.01) | 13.5 |
| C-a/phloroglucinol (2:1) | 1.102 (2.47) | 574.879 (3.92) | 32.6 |
| C-a/phloroglucinol (1:1) | 1.414 (2.36) | 176.028 (1.45) | 41.3 |

[a]Heated at 180 °C for 30 min. [b]Dispersity index ($M_w/M_n$). [c]The area ratio of the second and first traces in GPC.

It is well established that, except for photoinitiated polymerizations,[57] the ROP temperatures ($T_{ROP}$) of benzoxazines are between 180 and 260 °C, and these temperatures are strictly dependent on the structure and the purity of the monomer. In general, the ROP takes place without using any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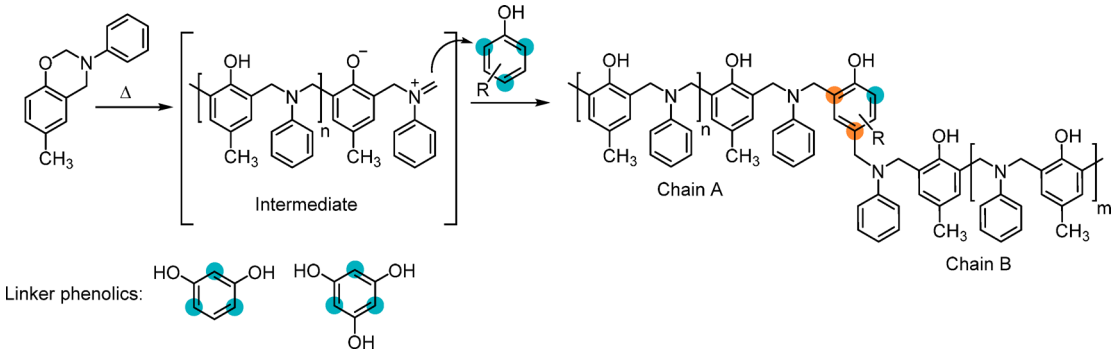
**Scheme 5. Formation of High Molecular Weight Polybenzoxazines from Highly Active Phenols**




catalyst and additive; thus, the process seems like noncatalytic reaction. However, in fact, the traces of phenolic impurities that remained from benzoxazine monomer synthesis initiate the polymerization. Highly pure monomers have ROP temperatures higher than 260 °C.[12] Certainly, such high curing temperatures can cause side reactions such as degradation and destructing the hydrogen-bonding interactions that may affect the properties of polybenzoxazines adversely. Therefore, reducing the $T_{ROP}$ is crucial in the production of polybenzoxazine-related materials in industry.[58−60]

It seemed therefore appropriate to study thermal behavior of C-a and C-a/phenolics at different mixing ratios and types of phenolics by DSC. In Figure 1 and Table S1, the catalytic

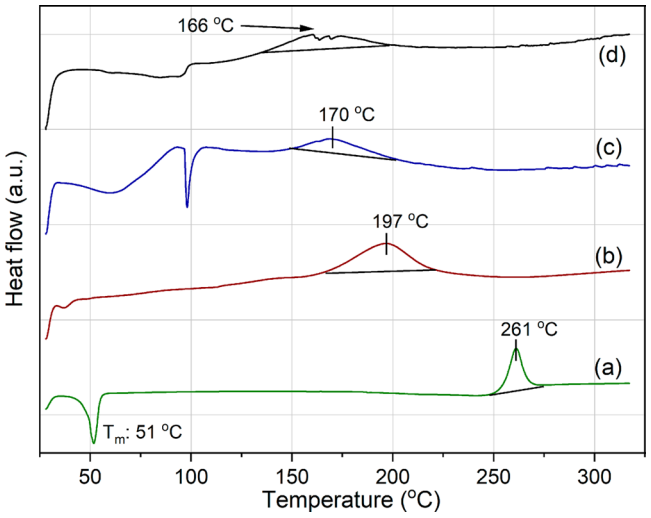



**Figure 1.** DSC thermograms of C-a (a) and C-a/phloroglucinol (5:1) (b), C-a/phloroglucinol (3:1) (c), and C-a/phloroglucinol (1:1) (d).

effect of phloroglucinol is clearly visible, and the $T_{ROP}$ temperatures are reduced with high phenolic content in the formulations. A similar effect is also observed for resorcinol (Figure S7). On the other hand, the type of phenol has a vast impact on the $T_{ROP}$ of benzoxazines as can be observed from Figure 2 and Table S2. Accordingly, simple phenols such as phenol and *p*-cresol has limited influence on maximum $T_{ROP}$, and only 10 °C reduction for phenol and 27 °C for *p*-cresol were monitored. Similarly, large enthalpy values are observed for C-a/phloroglucinol and C-a/resorcinol mixtures. The curing enthalpy values of DSC peaks in Figure 1 and 2 are between 88 and 370 J/g (Tables S1 and S2), indicating that

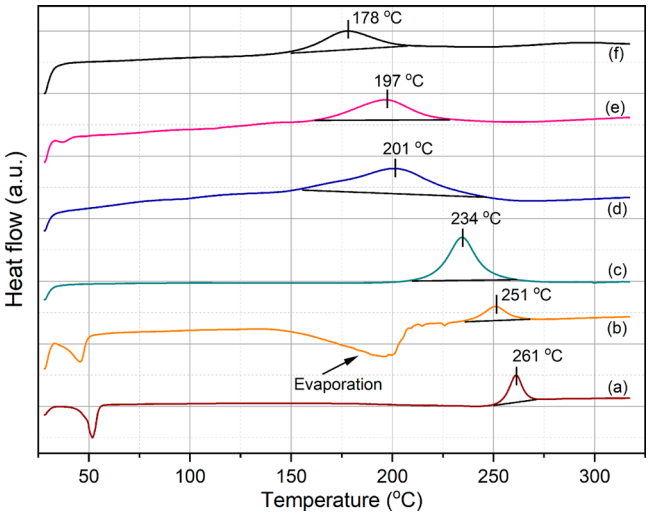



**Figure 2.** DSC thermograms of C-a (a) and C-a/phenol (5:1) (b), C-a/*p*-cresol (5:1) (c), C-a/resorcinol (5:1) (d), C-a/phloroglucinol (5:1) (e), and C-a/*p*-nitrophenol (5:1) (f).

the reactions of C-a with the phenols are exothermic, but the activation energies differ depending on the used phenol. The minor catalytic effect of phenol can be due to the sublimation related evaporation of phenol before curing of benzoxazine (Figure 2b). Although *p*-nitrophenol is another simple phenol, it exhibited the best catalytic performance among the phenolics used arising from the strong electron-withdrawing effect of the $-NO_2$ group that increases the acidity of the phenol. Highly acidic phenolics as Brønsted−Lowry acids were previously reported as good catalysts for the ROP of benzoxazines.[59,61,62] The DSC studies also revealed that the increased number of hydroxyl groups has a positive impact on the catalytic behavior of the phenols. The better performance of the multihydroxyl phenols observed could be due to the less evaporation and high reactivity in electrophilic aromatic substitution reaction. To clarify the effect of the −OH group, a control experiment was conducted by using anisole instead of phenols. Expectedly, anisole did not display any catalytic property, and the ROP temperature remained the same for C-a (see Figure S8). Moreover, C-a/anisole (5:1) gave only dimers, trimers, and so on after curing, pointing out the necessity of −OH groups for polymer formation in the proposed system.

It was recently reported that polybenzoxazines from *ortho*-functional benzoxazines exhibit unique physical properties compared to *para*- and *meta*-based counterparts.[52] These findings led to the development different benzoxazines with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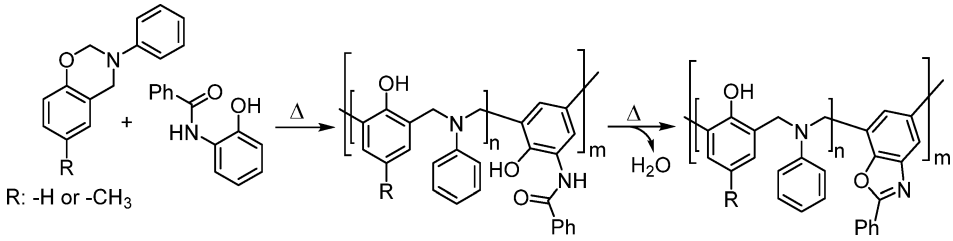
**Scheme 6. Synthesis of Poly(benzoxazine−benzoxazole) from Monofunctional Benzoxazines and *N*-(2-Hydroxyphenyl)benzamide**




amide and imide groups at the *ortho*-position. The existence of intramolecular hydrogen bonding in *ortho*-amide benzoxazines accelerated the ROP and lowered the curing temperatures.[50] Besides, these polybenzoxazines exhibited an additional thermal conversion after curing to form benzoxazoles from *ortho*-hydroxylamides (see Scheme 2). In most examples, benzoxazole formation took place around 300 °C for *ortho*-amide benzoxazines, while a similar ring-forming reaction for *ortho*-imide benzoxazines was at about 400 °C. Moreover, converting *ortho*-hydroxylamides into benzoxazoles significantly reduced the polarizability of the final polybenzoxazines, which is beneficial to obtain materials with low dielectric constants.[51] The proposed strategy in the present work has eliminated the need of synthesis of *ortho*-amide benzoxazines, and related materials were obtained simply by mixing classical benzoxazines with *N*-(2-hydroxyphenyl)benzamide (2HPB) in various mole ratios (Scheme 6). The DSC thermogram of 2HPB (see Figure S9) reveals a large endotherm starting ca. 210 °C and ending at ca. 300 °C possibly due to water loss during benzoxazole formation supporting the proposed idea.

The polymers from C-a/2HPB were soluble, and the molecular weights were determined to be 1400 and 1900 Da for 2:1 and 5:1 mixing ratios, respectively. A two-step thermal treatment was applied for those mixtures. At the first step, the mixtures were exposed to 180 °C for ROP of benzoxazines, and then the temperature was raised to 300 °C for benzoxazole formation. The final soluble product was analyzed by $^{1}$H NMR and FTIR analyses. Accordingly, the $^{1}$H NMR spectra of C-a, 2HPB, and C-a/2HPB (5:1, cured at 300 °C) are overlaid in Figure 3 to trace both amide NH and oxazine N−$CH_2$−O protons after the thermal treatment. The disappearance of NH proton can be considered as an evidence for the transformation of *ortho*-amide phenolic to benzoxazole structure. Moreover, the disappearance of N−$CH_2$−O protons clearly confirms the complete ring-opening of benzoxazines. In addition, in the $^{13}$C NMR spectrum of the soluble polymer, the typical peak belongs to the N=C−O carbon of benzoxazole appearing at 167 ppm (see Figure S10). The comparative FTIR spectra of the 2NHB and C-a/2NHB (2:1) sequentially heated at 180 and 300 °C presented in Figure 4 also gave evidence for the formation of a benzoxazole ring. The stretching vibration of the aromatic amide C=O of 2NHB appearing at 1645 $cm^{-1}$ is still visible after the first curing of the mixture at 180 °C. However, this band disappears after the second thermal treatment at 300 °C. Besides, the C=N stretching vibration band of benzoxazole at ca. 1642 $cm^{-1}$ is detectable.[63] Moreover, in Figure 4b,c, the presence of broad hydroxyl bands confirms the successful ring-opening polymerization of benzoxazine. It is also deduced from the shape of the hydroxyl bands that the hydroxyl groups have more hydrogen-bonding interactions before the second thermal treatment. This was

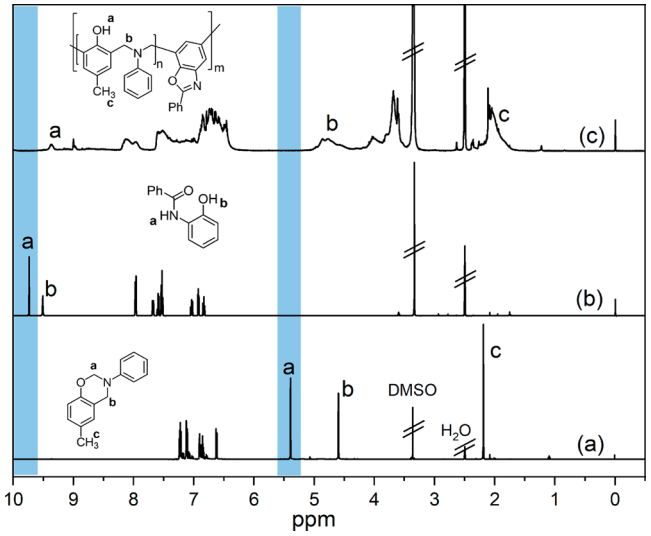



**Figure 3.** $^{1}$H NMR spectra of C-a (a), 2HPB (b), and thermally treated C-a/2HPB 5:1 (c).

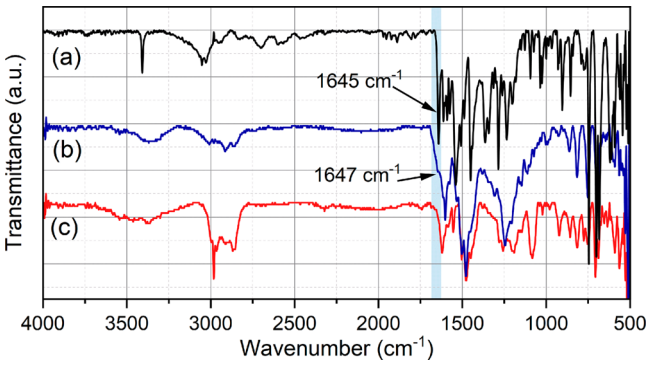



**Figure 4.** FTIR spectra of 2HPB (a), C-a/2HPB (2:1) preheated at 180 °C (b), and C-a/2HPB (2:1) preheated at 300 °C (c).

further supported by the shift of hydroxyl bands over 3500 $cm^{-1}$ as a consequence of benzoxazole ring formation.

To gain more insight into the overall mechanism of the two-step procedure, further detailed DSC studies were conducted on the mixtures of C-a/2HPB (5:1) and C-a/2HPB (2:1) (Figure 5). The thermograms showed a typical ring-opening polymerization exotherm at 214 and 219 °C, respectively. After these exotherms, irregular endotherms at 262 and 231 °C for C-a/2HPB (5:1) and C-a/2HPB (2:1), respectively, appeared. As known, when *ortho*-amide phenols are exposed to higher temperatures, they generate water through intramolecular cyclization between the neighboring hydroxyl and amide groups to form oxazole rings.[64] Accordingly, these endotherms can be attributed to the dehydration and formation of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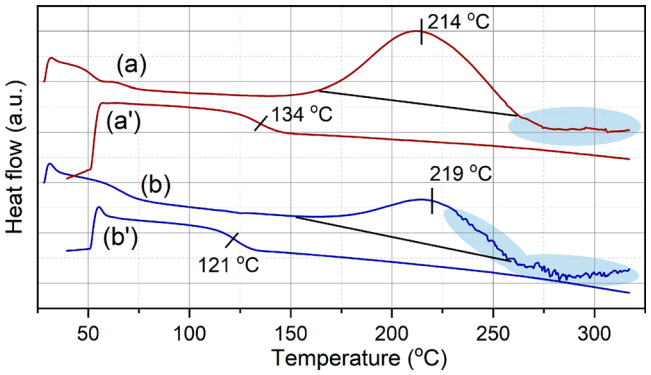


**Figure 5.** DSC thermograms of C-a/2HPB (5:1) first run (a) and second run (a′) and of C-a/2HPB (2:1) first run (b) and second run (b′).

polybenzoxazole as presented in Scheme 6 (*vide ante*), in a similar manner to that described for poly(*o*-hydroxyamide)s.[65,66] To confirm that the observed thermograms were not related to the degradation of the formed polymers, second DSC runs were also performed. The only observed thermal transitions in the second runs are associated with the glass transition temperatures ($T_g$) of the poly(benzoxazine−benzoxazole) polymers. The $T_g$ value of postheated C-a/2HPB (5:1) and C-a/2HPB (2:1) are 134 and 121 °C. Notably, the polymer with higher molecular weight and more hydrogen bondings exhibited a higher $T_g$ value.

The dehydration phenomenon has also been supported by TGA thermograms shown in Figure 6, which indicates the

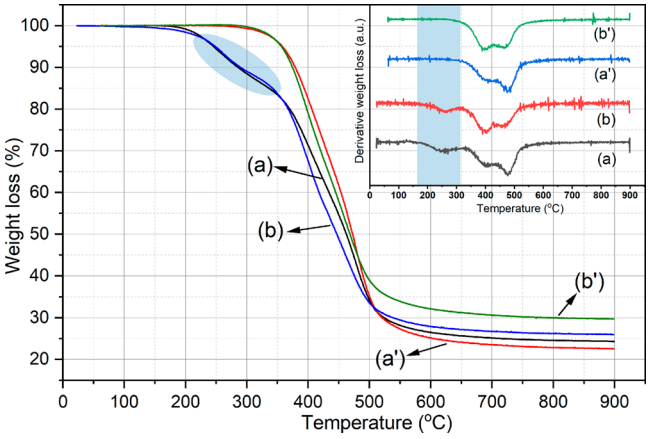


**Figure 6.** TGA traces and derivative weight loss (%) of TGA of C-a/2HPB (2:1) thermally treated at 180 °C (a) and thermally treated at 300 °C (a′) and of C-a/2HPB (5:1) thermally treated at 180 °C (b) and thermally treated at 300 °C (b′).

presence of weight loss at an earlier temperature from the samples heated at 180 °C. The TGA traces and derivative of weight loss are in accordance with the endothermic transition temperatures observed in DSC analysis. On the contrary, early weight loss is not detectable for the postheated samples. To further verify the benzoxazole formation via TGA, another analysis was devised by holding the temperature of TGA furnace at ca. 300 °C for 10 min to amplify the dehydration based weight loss and related derivative weight loss (Figure 7). In the resulting TGA thermogram, the water removal can clearly be seen approximately at the similar temperature ranges observed in the previous DSC and TGA analyses.

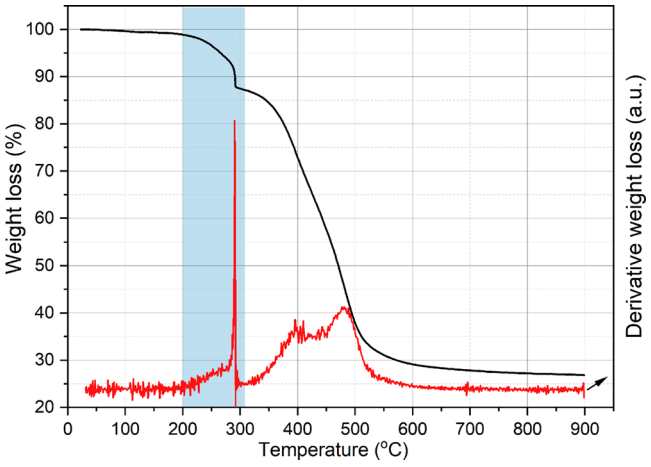


**Figure 7.** TGA trace and derivative weight loss of C-a/2HPB (2:1) thermally treated at 180 °C.

## CONCLUSION

A polyaddition system based on the use of different phenols as both additive and curative for benzoxazines is proposed. The obtained polybenzoxazines were soluble after curing favored by the selected benzoxazine monomer and therefore enabling spectral and molecular weight analyses. It was shown that for specific mixing ratios and phenols very high molecular weight polybenzoxazines can be obtained. Especially, multihydroxy-containing phenols as additives gave polymers with molecular weights up to millions of daltons due to the high reactivity of these phenols toward benzoxazines. This approach has also led to synthesize poly(benzoxazine−benzoxazole) by using *N*-(2-hydroxyphenyl)benzamide (2HPB) as the phenolic additive. *ortho*-Amide phenols are known to transform to benzoxazole structure under heat exposure with water release. In this work, we combined the affinity of phenols toward benzoxazines and benzoxazole generation from 2HPB for the fabrication of advanced polymers by curing and subsequent thermal treatment.

The benzoxazine/phenol system described herein constitutes an inventive approach to synthesize thermally stable poly(benzoxazine−benzoxazole)s without synthesizing complicated benzoxazine monomers. Also, it is anticipated that many novel polybenzoxazole precursors can be produced by using the large benzoxazine monomer library, which cannot be found in the traditional concept for polybenzoxazole formation.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c00225.

NMR spectra of C-a, P-a, and C-a/phloroglucinol; DSC thermograms of P-a, C-a, C-a/resorcinol, C-a/anisole, and 2HPB; DSC results of C-a, C-a, and several phenol mixtures; GPC traces of thermally treated C-a/phloroglucinol and C-a/p-cresol (PDF)

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### Notes

The authors declare no competing financial interest.

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