Synthesis and polymerization of benzoxazine molecules with electron-withdrawing group substitution and ring-opening polymerization

Sankar Rajasekar¹,² and Natarajan Hari³

Abstract
The synthesis of strong electron-withdrawing group substituted aromatic amine and phenol-based benzoxazines is hampered due to the poor solubility of the reactant. In this article, a simple methodology is presented to synthesize the strong electron-withdrawing groups substituted benzoxazine monomers from a solution method using a low-boiling polar solvent. In order to achieve this, we used formaldehyde as a reactant as well as a solvent, and the reaction was carried out for a longer time. Also, benzylaniline derivatives were successfully prepared through benzoxazine. The monomers were polymerized by using solution polymerization method using lithium bromide as a catalyst. The structure of the monomers and polymers was confirmed by Fourier transform infrared and nuclear magnetic resonance spectroscopy. The thermally activated polymerization of the monomers was evaluated by differential scanning calorimetry, and thermal properties of polymers were analyzed by thermogravimetric analysis.

Keywords
Benzoxazine, bifunctional benzoxazine, polybenzoxazine, ring-opening polymerization

Introduction
High-performance polymers are widely applicable in automobile, aerospace, and electrical and electronic industries due to their excellent mechanical properties. The mechanical properties of high-performance polymers must be retained over a wide range of temperature and also for a long period of time. Phenolic resins are one of the important classes of high-performance polymers, and among them, polybenzoxazine has great attention due to its excellent mechanical properties, thermal stability, near zero shrinkage, and low flammability.¹⁻⁷

In 1944, the preparation of benzoxazine monomer was reported by Holly and Cope.⁸ Generally benzoxazine is prepared by condensation of phenol and primary amine with formaldehyde.⁹⁻¹¹ The purification of benzoxazine monomers is very difficult, and it depends on substitution of phenol, amine, and reaction medium.¹²,¹³ Several structural modifications and ring-opening behaviors were reported for benzoxazine monomer.¹⁴⁻¹⁸ Polybenzoxazine is prepared by either thermal or cationic ring opening of benzoxazine monomer. The solution polymerization was carried out by using different initiators like cationic, anionic, or radical which were used to polymerize the benzoxazine monomers.¹⁹⁻⁻²¹ For the preparation of polybenzoxazine, in general, a two-step process is involved with cationic polymerization. The first step is opening of oxazine ring due to cation attack on either –O– or –N– of the oxazine ring followed by the formation of iminium ion. The second step is an electrophilic substitution of iminium ion on either ortho or para position of phenol. Further the hydroxyl group of the phenol provides different polymeric structures, such as phenolic and phenoxy, usually combined with the polymer backbone, that

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is, cross-linked polymeric structure. The phenoxy and phenolic structures of the polymer backbone are highly dependent on the substitution of benzoxazine monomer. The para-substituted benzoxazine monomers yielded linear polymers with phenolic and phenoxy structures. The ring-opening behavior is highly dependent on the electronegativity of the benzoxazine ring. Several benzoxazine monomers are synthesized with para-substituted phenols and primary amines in order to study the electronic effects during the thermal polymerization, and it has been reported that high-electronegative-substituted benzoxazine ring opened at low temperature. Ishida reported the synthesis of benzoxazine from strong electronegative para-substituted amine with unsubstituted phenol.

The benzoxazine monomers are generally synthesized in solution method which has some limitations. One such limitation is the formation of oligomers while using polar solvents, which highly decreases the yield of the benzoxazine monomers. The nonpolar solvents are supposedly better choices to get high yield. Ishida reported that nonpolar high boiling solvents were preferable compared to polar high boiling solvents due to the side reaction. The nonpolar low boiling solvents are not favorable for electron-withdrawing substituted benzoxazine monomers due to the poor solubility of aromatic amines. The synthesis of strong electron-withdrawing group substituted aromatic amine and phenol-based benzoxazines was hampered due to the poor solubility of the reactants. To overcome these difficulties, we here used a polar low boiling solvent such as formaldehyde.

In this work, we prepared benzoxazine from strong electronegative-substituted aromatic amines and phenols by a solution method. The preparation of high-purity disubstituted benzoxazine monomers with high yield was accomplished using strong electron-withdrawing group substituted aromatic amines and phenols. The polymerization reaction was carried out using the solution method.

**Materials**

4-nitroaniline, 4-nitrophenol, 4-hydroxy benzoic acid, 3-nitroaniline, 4-amino acetophenone, 4-hydroxy acetophenone, and paraformaldehyde were procured from Sigma-Aldrich (Bengaluru, Karnataka, India) and used as received. N,N-dimethylformamide (DMF) was purified by distillation under reduced pressure and stored over 4 Å molecular sieves which were procured from HiMedia Laboratories (Mumbai, Maharashtra, India).

**Measurements**

Infrared spectra were recorded on a Spectrum100 Fourier transform infrared (FTIR) instrument (Perkin Elmer, Waltham Massachusetts, USA). Proton nuclear magnetic resonance (1H-NMR) and carbon-13 nuclear magnetic resonance (13C-NMR) spectra were recorded on an AVANCE-II 300 MHz NMR instrument (Bruker Biospin, Bayern, Germany).

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**Figure 1.** Reaction mechanism of benzoxazine ring opening.
Fallanden, Switzerland). The inherent viscosities of the polymers were measured with an Ostwald viscometer at 0.5 dL g\(^{-1}\) concentration. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using SDT Q600 and DSC Q20 instruments (TA Instruments, New Castle, Delaware, USA), respectively.

**Methods**

**Synthesis of benzoxazines**

3-(4'-Nitrophenyl)-6-nitro-3,4-dihydro-2H-1,3-benzoxazine (M1). Bifunctional strong electron-withdrawing group substituted benzoxazine was synthesized by solution method (shown in Figure 1). One hundred milliliters of formaldehyde, 4-nitrophenol (1.39 g, 0.01 mol), and 4-nitroaniline (1.38 g, 0.01 mol) were added into a 250-mL round-bottomed (RB) flask. The mixture was stirred at 100°C for 48 h. Initially, reaction mixture was homogenous and the product was phase separated after completion of the ring formation. After completion of 48 h, the reaction mixture was filtered in hot condition and washed with hot water. Finally, yellow-colored dinitrobenzoxazine monomer was dried in vacuum. Yield: 94%. \(^1\)H-NMR (dimethyl sulfoxide (DMSO)-d\(_6\)) ppm: 4.98 (s, 2 H, Ar–CH\(_2–N\)), 5.77 (s, 2 H, O–CH\(_2–N\)), and 6.97–8.19 (7 H, Ar). \(^1\)3C-NMR (DMSO-d\(_6\)) ppm: 47.64, 77.93, 115.65, 117.33, 121.85, 123.64, 124.02, 125.53, 139.80, 140.66, 152.33, and 159.23. FTIR (cm\(^{-1}\)) 1117, 1259, 981, and 1550.

3-(3'-Nitrophenyl)-6-nitro-3,4-dihydro-2H-1,3-benzoxazine (M2). The above mentioned method was adopted to prepare 3-(3'-nitrophenyl)-6-nitro-3,4-dihydro-2H-1,3-benzoxazine. The 250-mL RB flask was filled with 100 mL of formaldehyde, 4-nitrophenol (1.39 g, 0.01 mol), and 3-nitroaniline (1.38 g, 0.01 mol). Yield: 95%. \(^1\)H-NMR (DMSO-d\(_6\)) ppm: 4.97 (s, 2 H, Ar–CH\(_2–N\)), 5.78 (s, 2 H, O–CH\(_2–N\)), and 6.97–8.19 (7 H, Ar). \(^1\)3C-NMR (DMSO-d\(_6\)) ppm: 47.64, 77.93, 115.65, 117.33, 121.85, 123.64, 124.02, 125.53, 139.80, 140.66, 152.33, and 159.23. FTIR (cm\(^{-1}\)) 1115, 1280, 944, 1550, and 1345.

3-(4'-Nitrophenyl)-6-carboxy-3,4-dihydro-2H-1,3-benzoxazine (M3). Similar method was adopted to prepare 3-(4'-nitrophenyl)-6-carboxy-3,4-dihydro-2H-1,3-benzoxazine. The 250-mL RB flask was filled with 100 mL of formaldehyde, 4-hydroxy benzoic acid (1.38 g, 0.01 mol), and 4-nitroaniline (1.38 g, 0.01 mol). Yield: 93%. \(^1\)H-NMR (DMSO-d\(_6\)) ppm: 4.92 (s, 2 H, Ar–CH\(_2–N\)), 5.68 (s, 2 H, O–CH\(_2–N\)), and 6.86–8.13 (7 H, Ar), and 12.71 (–OH). \(^1\)3C-NMR (DMSO-d\(_6\)) ppm: 47.16, 77.12, 115.2, 116.54, 120.91, 123.29, 125.53, 129.16, 129.45, 139.35, 157.31, 159.35, and 166.81. FTIR (cm\(^{-1}\)) 1114, 1251, 984, 1550, and 1350.

<table>
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<th>Amine substitution</th>
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<th>Yield (%)</th>
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<td>p-NO(_2)</td>
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Table 1. FTIR and yield of the benzoxazine monomers.

FTIR: Fourier transform infrared.
Figure 3. $^1$H-NMR spectra of the benzoxazine monomers. $^1$H-NMR: proton nuclear magnetic resonance.
Figure 4. $^{13}$C-NMR spectra of the benzoxazine monomers. $^{13}$C-NMR: carbon-13 nuclear magnetic resonance.
formaldehyde, 4-nitrophenol (1.39 g, 0.01 mol), and 4-hydroxy acetophenone (1.35 g, 0.01 mol). Yield: 94%.

1H-NMR (DMSO-d$_6$) ppm: 4.93 (s, 2 H, Ar–CH$_2$–N), 5.70 (s, 2 H, O–CH$_2$–N), and 6.97–8.19 (7 H, Ar).

13C-NMR (DMSO-d$_6$) ppm: 26.12, 47.34, 77.28, 115.35, 117.48, 121.85, 123.24, 124.02, 125.53, 139.78, 140.37.

Figure 5. (A) $^{13}$C, (B) $^1$H, and (C) D$_2$O exchange NMR spectra of benzylaniline derivatives. NMR: nuclear magnetic resonance.

formaldehyde, 4-nitrophenol (1.39 g, 0.01 mol), and 4-hydroxy acetophenone (1.35 g, 0.01 mol). Yield: 94%.

$^{13}$C-NMR (DMSO-d$_6$) ppm: 26.12, 47.34, 77.28, 115.35, 117.48, 121.85, 123.24, 124.02, 125.53, 139.78, 140.37.
Figure 5. (continued)
3-(4′-Nitrophenyl)-6-acetyl-3,4-dihydro-2H-1,3-benzoxazine (M5). Similar method was adopted to prepare 3-(4′-nitrophenyl)-6-acetyl-3,4-dihydro-2H-1,3-benzoxazine. The 250-mL RB flask was filled with 100 mL of formaldehyde, 4-nitrophenol (1.36 g, 0.01 mol), and 4-nitroaniline (1.38 g, 0.01 mol). Yield: 92%, \( ^1H \)-NMR (DMSO-\( d_6 \)) ppm: 2.47 (s, 3 H), 4.98 (s, 2 H, Ar–CH\( _2 \)–N), 5.77 (s, 2 H, O–CH\( _2 \)–N), and 6.79–8.15 (7 H, Ar). \( ^{13}C \)-NMR (DMSO-\( d_6 \)) ppm: 26.35, 47.88, 77.27, 115.33, 116.53, 120.92, 125.53, 128.63, 136.72, 139.43, 152.59, 157.63, and 196.28. FTIR (cm\(^{-1}\)) 1097, 1274, 957, 1659, 1550, and 1350.

**Synthesis of 2-phenylaminomethylphenol**

2-(4′-Nitrophenyl)aminomethyl-4-nitrophenol. One hundred milliliters of aqueous ethanol (90%) and 500 mg of 3-(4′-nitrophenyl)-6-nitro-3,4-dihydro-2H-1,3-benzoxazine monomer (M1) were added into a 250-mL RB flask. The reaction mixture was stirred at 100°C for 48 h. The homogeneous reaction mixture was poured into water and the precipitated 2-(4-nitrophenyl)aminomethyl-4-nitrophenol was collected by filtration, washed with deionized water, and dried under vacuum. Yield 94%, \( ^1H \)-NMR (DMSO-\( d_6 \)) ppm: 4.31 (s, 2 H, Ar–CH\( _2 \)–N) and 6.87–8.19 (7 H, Ar). \( ^{13}C \)-NMR (DMSO-\( d_6 \)) ppm: 40.48, 114.65, 116.33, 121.65, 122.64, 123.02, 125.33, 139.80, 140.66, 152.33, and 159.63.
Synthesis of polybenzoxazine

The polybenzoxazine was prepared by the following procedure. The reaction was carried out in a 100-mL RB flask, and 10 mL of dry DMF, 1 g of benzoxazine monomer, and 0.1 g of lithium bromide (LiBr) were added into the flask. The reaction mixture was heated to 150°C for 12 h under nitrogen atmosphere. The polymer was precipitated by pouring the homogenous reaction mixture into distilled water and was later collected by filtration. The polymer was dried under reduced pressure.

Results and discussion

The synthesis of disubstituted benzoxazines is shown in Figure 1. The purification of benzoxazine molecules is very difficult due to the formation of oligomers which is due to the usage of high boiling polar and nonpolar solvents. To overcome this difficulty, low boiling (91–101°C) polar solvent such as formaldehyde (37% aqueous) was used as solvent for the strong electron-withdrawing group substituted benzoxazine synthesis. The strong electron-withdrawing substituted aromatic amine was added to formaldehyde solution, and the reaction was maintained at 50°C for 1 h to form dimethylol aniline. Then the strong electron-withdrawing substituted phenol was added to dimethylol aniline, and the temperature was raised to 100°C for 48 h. Disubstituted benzoxazine monomers were filtered under hot conditions. The product was washed several times with hot water to remove the unreacted amine and alcohol. Different strong electron-withdrawing groups (nitro, carboxylic acid, and ketone) substituted benzoxazine monomers were accordingly prepared. The yield of all monomers has occurred in the range of 95–86% (Table 1).

The structure of benzoxazine monomers was confirmed by 1H-NMR, 13C-NMR, and FTIR spectrum. The FTIR spectra show characteristic absorbance peaks of oxazine ring due to C–O–C symmetric stretching at 1117, 1115,
1114, 1112, and 1097 cm\(^{-1}\) and asymmetric stretching at 1259, 1280, 1251, 1268, and 1274 cm\(^{-1}\). The peaks at 981, 944, 984, 964, and 957 cm\(^{-1}\) are due to the out-of-plane bending of benzene ring (attached to the oxazine ring). The peak of keto group of 3-(4-nitrophenyl)-6-acetyl-3,4-dihydro-2H-1,3-benzoxazine peaks appeared at 1659 cm\(^{-1}\). The nitro group of benzoxazine compounds has peaks at 1550 and 1350 cm\(^{-1}\). The FTIR spectra confirm the presence of oxazine ring and the functional group of substituted benzoxazine monomers (Table 1 and Figure 2).

In the \(^1\)H-NMR spectra, the oxazine ring consists of two different methylene (Ar–CH\(_2\)–N and O–CH\(_2\)–N) protons, which appeared in the range of 4.78–4.92 and 5.47–5.77 ppm, respectively. The aromatic protons, ortho to oxazine ring, appear in the range of 6.86–7.51 ppm. The strong downfield signals 7.79–8.20 are attributed to the aromatic protons flanked at ortho position to strong electron-withdrawing group substituents nitro, carboxy, and keto carbonyl groups. The \(^1\)H-NMR spectra of the benzoxazine monomers are shown in Figure 3.

The \(^{13}\)C-NMR spectra of benzoxazine monomers clearly confirm the presence of oxazine ring. The corresponding spectra show carbon resonances in the range of 47.7–49.2 ppm and 77.1–79.1 ppm for two different methylene group carbons of oxazine ring. The carbon of keto carbonyl and methyl groups of the monomer M4 shows peaks at 196 and 26 ppm, respectively. The carbonyl carbon of monomer M3 appears at 169 ppm. The \(^{13}\)C-NMR spectra of the benzoxazine monomers are shown in Figure 4. The \(^1\)H and \(^{13}\)C spectra reveal highest level of purity of benzoxazine monomers.

The strong electron-withdrawing substituted benzoxazine monomers were refluxed in water in order to isolate the 2-phenylaminomethyl phenol derivatives. The electron-withdrawing substituent enhanced the oxazine ring-opening ability with increasing electronegativity of the substituent. Based on the position and the electron-withdrawing nature of the substituent, the electronegativity of the benzene ring attached on the oxazine ring plays a unique role in the oxazine ring-opening behavior. The ring-opening behavior was highly dependent on the substituent of benzoxazine ring. The ring-opening ability increases with the increase in the electron-withdrawing nature of the substituent on the oxazine ring-substituted phenyl moiety. The ring-opening temperature of the monomers decreases with increasing electronegativity of the substituent either on oxazine ring containing benzene or on oxazine (N–) substituted phenyl moiety. The structure of 2-phenylaminomethyl phenol-based derivatives was confirmed by \(^1\)H-NMR and \(^{13}\)C-NMR. The \(^1\)H, \(^{13}\)C, and the deuterated water (D\(_2\)O) exchange NMR spectra confirm the presence of N–H and O–H protons (Figure 5). In all of the five monomeric components, the signals observed as doublets at 4.33 ppm. The triplet at 7.20 ppm is attributed to N–CH\(_2\)–Ar and C–NH–Ar. The methylene proton coupled with amine proton appeared as a doublet and amine proton coupled with methylene protons appeared as a triplet. These were further confirmed by deuterium exchange experiment. The \(^{13}\)C-NMR spectrum confirms the presence of methylene carbon around 40.0 ppm.

The solution polymerization was performed in the presence of 1.0 mol\% LiBr and DMF as solvent. The polymerization mechanism has been studied in detail, and the mechanism for the generation of phenoxy and phenolic type structures is shown in Figure 6. The resulting polymers were soluble in polar aprotic solvents at room temperature. The molecular structure of the polymers was confirmed by \(^1\)H-NMR and FTIR spectroscopic techniques. The \(^1\)H-NMR spectra of the resulting polymers revealed the presence of phenolic and phenoxy structures in polymer backbone. The ring-opening polymerization of benzoxazine monomer was also confirmed by the disappearance of bands in FTIR spectra at 1225 cm\(^{-1}\) due to C–O–C stretching, at 1190 cm\(^{-1}\) due to C–N–C stretching, and at 950 cm\(^{-1}\). The FTIR spectra of the polymers are shown in Figure 7. Due to the electron-withdrawing nature of oxygen and nitrogen atoms, the \(^1\)H-NMR signal of the methylene group in the phenoxy structure appears downfield than that of the methylene group in phenolic structure. The \(^1\)H-NMR spectra of the polymers are shown in Figure 8.

The ring-opening polymerization and melting behavior of electron-withdrawing group substituted benzoxazine
monomers were analyzed using DSC, as shown in Figure 9. The monomer M1 (192°C) shows higher melting temperature than M2 (173°C) and this is attributed to meta substitution of nitro group in M2. The monomer M4 shows sharp melting temperature at 166°C. Compared to all monomers, the monomer M3 has the highest melting temperature (222°C) which is due to the presence of carboxylic acid. The monomer M1 shows maximum exothermic shift of which occurred at 219°C. The exothermic peak started from the melting temperature due to the opening of benzoxazine ring. The endothermic peak appeared at 256°C due to the formation of benzylaniline derivative. The monomer M2 (286°C) shows much higher ring-opening temperature when compared to M1 (237°C) and M4 (249°C). The exothermic (ring opening) of M2 and M4 started from the melting temperature of the monomers. Monomers M3 and M5 did not show any melting endotherm due to the strong molecular interaction of carbonyl group. The monomer M5 shows the highest exothermic peak at 344°C.

Figure 8. $^1$H-NMR spectra of polymers. $^1$H-NMR: proton nuclear magnetic resonance.
The thermal stability of the benzoxazine polymers was evaluated by TGA. The results of the monomers and polymers are shown in Figures 10 and 11, respectively. Thermal polymerization and weight loss were studied by using TGA and later compared with the monomers and polymers. The initial weight loss of M1 began at 200°C. At 280°C, it lost 24% of its own weight due to the formation of benzylaniline intermediate and continued throughout the polymerization process. The degradation continued up to 420°C and which revealed the decomposition of polymer. The weight loss of polymer (P1) derived from M1 through solution polymerization occurred between 250 and 450°C, which confirms that the ring opening occurred before 250°C. Similarly, monomers M2, M3, M4, and M5 also show sharp weight loss characteristics, as shown in Table 2. The monomer M4 shows initial degradation at 150°C and completely degrades around 200°C due to the presence of moisture. The maximum weight loss of the polymers occurred in the range of 220–480°C (Table 3). The char yield of the polymers was in the range of 52–66%. The char yield, when compared to the thermally polymerized monomers char yield (32-45%), indicates higher level of conversion of monomers into polymer by solution polymerization.

**Conclusion**

The strong electron-withdrawing group substituted benzoxazine monomers were successfully prepared by using solution method. The low boiling polar solvent gave high yield. The structure of all the monomers was confirmed by FTIR, ¹H-NMR, and ¹³C-NMR spectroscopic techniques. The benzylaniline derivatives were successfully prepared from the monomers and the method gave a way to prepare novel benzylaniline derivatives. The thermal ring-opening polymerization of all monomers was evaluated by DSC which revealed low ring-opening temperature due to the presence of strong electron-withdrawing group in benzoxazine monomers. The benzoxazine monomers were polymerized by a convenient

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**Table 2. Thermal properties of monomers.**

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<th>$T_{exo}$ (°C)</th>
<th>$T_i$ (°C)</th>
<th>$T_{max}$ (°C)</th>
<th>Char yield* (%)</th>
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</table>

$T_i$: initial decomposition temperature; $T_{max}$: maximum decomposition temperature; $T_{exo}$: exothermic temperature; $T_m$: exothermic temperature.

*Char yield at 800°C.

**Table 3. Thermal properties of polymers.**

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>$T_i$ (°C)</th>
<th>$T_{max}$ (°C)</th>
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$T_i$: initial decomposition temperature; $T_{max}$: maximum decomposition temperature.

*Char yield at 800°C.
solution polymerization method using LiBr as a catalyst. The structure of polymers was confirmed by FTIR and $^1$H-NMR spectroscopic techniques. The polymers showed good thermal stability and high char yield. The efficacy of the solution method for polymerization leads to the conclusion that the solution method can successfully be applied to synthesize variety of polymers.

**Declaration of Conflicting Interests**

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