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Cationic Ring-Opening Polymerization of 1,3-Benzoxazines: Mechanistic Study Using Model Compounds

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ABSTRACT: The benzoxazine monomer is used to simplify the study of the benzoxazine initiation mechanism. The HPLC retention time and the ^{1}H NMR spectra of crude products from the benzoxazine reaction are compared with the results from a vast number of pure model compounds, which are synthesized based on the hypothesized mechanisms. Products involved in the process are identified, with species having benzoxazine structures, Mannich base and other components (acetal, nonacetal phenoxy structures, and methylene bridge structure). Initiation mechanisms of benzoxazine, e.g., the oxygen protonation and the nitrogen protonation, are proposed.

1. Introduction

Many thermosetting polybenzoxazines have been developed because they possess excellent properties[1] and overcome many of the disadvantages of traditional phenolic resins.[2] The advantages of benzoxazines near-zero shrinkage polymerization, high char yield, high thermal and chemical resistance, excellent electrical properties, and superb molecular design flexibility make them attractive to a wide range of applications. Moreover, polybenzoxazines having oxazine rings in the main chain[3] have also been synthesized in order to obtain further flexibility in benzoxazine system design. In addition to the above advantages of monomeric benzoxazine resins, these main-chain type polybenzoxazines exhibit excellent mechanical properties so that films of thermosetting resin can be manufactured. Guth and Schwob[4] used benzoxazine oligomers as cross-linking agents for epoxy resins, resins for the preparation of laminates based on glass and carbon fibers, antioxidant and complexing agents, and modifiers for carbon black and carbon fiber surfaces.

Despite years of study, the polymerization mechanism of benzoxazines has remained elusive. Spectroscopic observation of active species has been difficult. Thus, it is the purpose of this study to further the fundamental understanding of the benzoxazine polymerization mechanism. Upon successful elucidation of the mechanism, this knowledge can be applied to both thermosetting and thermoplastic polybenzoxazines to tailor the desired structures, such as to control the molecular weight and improve the properties.

In 1968, McDonagh and Smith[5] proposed that 3,4-dihydro-2*H*-1,3-benzoxazines would exhibit ring/chain tautomerism when protonated by migration of the proton from the oxygen to the nitrogen atom, thereby producing iminium ions in the chain form. In 1985, Riess et al.[6] proposed two mechanisms occurring for the reaction of benzoxazine with various kind of phenols (Scheme 1). They suggested the existence of an intermediary complex in the ortho reaction, resulting from the formation of an intermolecular hydrogen bond. Another possible mechanism involves an initial ring-opening step via protonation by the phenol followed by a condensation reaction of iminium species and the phenolate. Expanding on this later mechanism in 1999, Dunkers and Ishida[7] proposed that the ring-opening polymerization of benzoxazines occurs via by protonation of the oxygen atom to form an iminium ion and then electrophilic aromatic substitution as shown in Scheme 2. It has been shown that protonated benzoxazines can exhibit ring chain tautomerism with the iminium species under acidic conditions.[5] On the basis of this mechanism it can be expected that Lewis acids could be used to enhance the rate of initiation of such benzoxazine polymerizations. Nevertheless, it has proven quite difficult to obtain a high molecular weight polybenzoxazine using such catalysts with monofunctional benzoxazine monomers.[3] It has been reported that using less acidic cationic initiators that benzoxazine monomers polymerize to a phenylether (*N*,*O*-acetal linkage) repeat unit[8] which can then rearrange to the phenolic (Mannich-type) structure upon further heating at an elevated temperature.[9] The focus of this paper is restricted to the study of the thermally activated polymerization, thus studying the mechanism to form the phenolic and symmetric Mannich bridge structures.

Hayakawa et al.[10] studied the reaction pathways of 3,4-dihydro-6,8-dimethyl-3-phenyl-2*H*-1,3-benzoxazine with 2,4-xylenol. They studied the reaction products and compared the spectroscopic information obtained from a few model compounds they synthesized. Their early reaction products were reported to be 6-({[(2-hydroxyl-3,5-dimethylphenyl)methyl]phenylamino}methyl)-2,4-dimethylphenol and 2,4-dimethyl-6-[(phenylamino)methyl]-phenol. Heating was reported to result in structural rearrangement into more thermally stable structures which contain benzene rings that are bridged by a methylene linkage in a manner similar to traditional phenolic resins.

In order to investigate the mechanism of benzoxazine polymerization, the polymerization of benzoxazine was simplified by targeting benzoxazine dimer model systems. Blocking the ortho and para positions of the benzoxazine monomers with methyl groups simplified the chemical reactions and made the interpretation of the results easier than the unblocked systems reported by Hayakawa et al.'s study.[10] Furthermore, the studies have been systematically designed, allowing for a facile qualitative and quantitative analysis of the crude products. The crude products from the model systems were studied using high performance liquid chromatography (HPLC). Nearly 40 possible reaction

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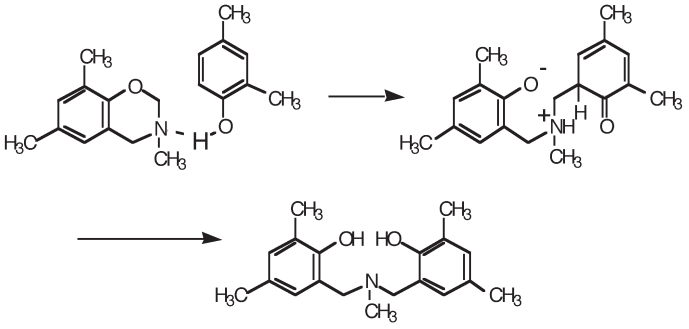
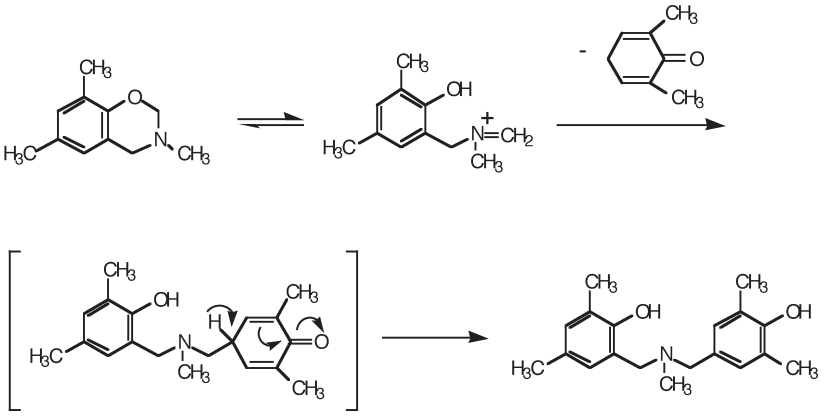
Scheme 1. Mechanism Proposed by Riess et al.

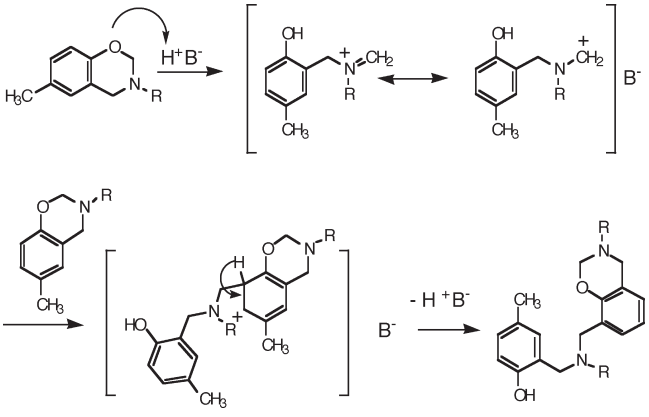
Intermolecular hydrogen-bonding (ortho reaction)



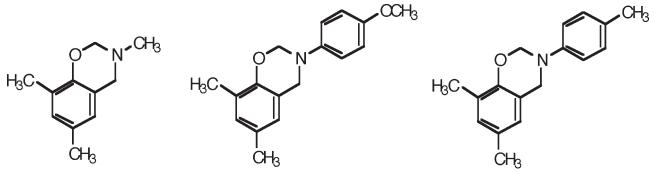
Partial phenol dissociation (para reaction)



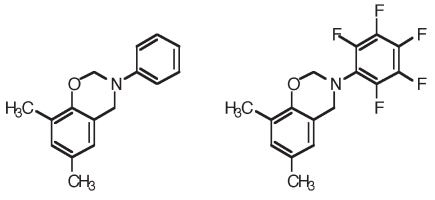
Scheme 2. Proposed Initiation Mechanism of Benzoxazine Monomer by Dunkers and Ishida



Scheme 3. Structure of Benzoxazine Monomers



24DMP-m 24DMP-pma 24DMP-pt



24DMP-a 24DMP-pfa

products from the hypothesized reaction mechanisms were separately synthesized as purified model compounds whose chromatograms and NMR spectra formed the basis for the later comparison with the results of the final crude product. In addition to the polymerization mechanism, the studies on structural rearrangements are also included in this paper.

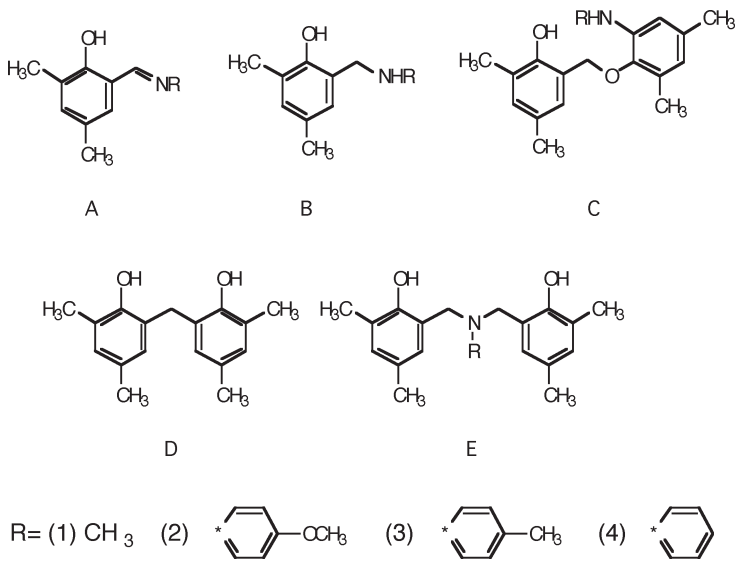
2. Experimental Section

2.1. Starting materials. All reagents were purchased from Aldrich Chemical Co. and used as received, except for 37% formaldehyde, which was purchased from Fluka Chemical Company. Dichloromethane, tetrahydrofuran, and dimethylformamide were carefully dried by the conventional method[11] before use.

2.2. Synthesis of Monomers. The structures of all synthesized benzoxazine monomers are shown in Scheme 3. Because of very long IUPAC names, benzoxazine monomers have historically used short acronyms using a hyphenated names representing the phenolic compound used in capital letters and primary amine compounds in lower case letters, each representing their abbreviated names.[1a] Therefore, the acronyms are not the abbreviated IUPAC names of the final benzoxazine compound.

2.2.1. 3,6,8-Ttrimethyl-2H,4H-benzo[e]1,3-oxazine (*24DMP-m*)[12]. The mole ratio of amine: formaldehyde: phenol was 1:2:1. A solution of 0.200 mol (16.2 g) of formaldehyde in 50 mL of 1,4-dioxane was stirred with 0.078 mol (7.8 g) of 40% methylamine solution in 20 mL of 1,4-dioxane while being chilled in an ice

Scheme 4. Proposed Products from Dimerization of Various Benzoxazine Monomers



bath for 20 min. To this mixture was added 0.103 mol (12.6 g) of 2,4-dimethylphenol in 50 mL of dioxane. The mixture was then heated, stirred, and allowed to reflux for 5 h. After the mixture was allowed to cool to room temperature, the solvent was removed by a rotary evaporator. The resulting yellowish oil was dissolved in 200 mL of ethyl ether and washed with 5×40 mL of 1.5 N aqueous sodium hydroxide solution to remove any unreacted −OH groups. The ethereal solution was dried over anhydrous sodium sulfate overnight. After filtration, the ether was removed using a rotary evaporator. The benzoxazine monomer was obtained as a very pale yellow liquid. Yield: 70%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.15 (3H, Ar−CH_3), 2,21 (3H, Ar−CH_3), 2.58 (3H, N−CH_3), 3.90 (2H, Ar−CH_2−N), 4.77 (2H, O−CH_2−N), 6.61−6.80 (2H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.1 (1C, Ar−CH_3), 20.0 (1C, Ar−CH_3), 39.1 (1C, N−CH_3), 51.7 (1C, Ar−CH_2−N), 83.4 (1C, O−CH_2−N), 119.0−149.3 (6C, Ar).

All aromatic benzoxazine monomers shown below were synthesized from 2,4-dimethylphenol, formaldehyde, and amine by a solventless method.[13]

2.2.2. 6,8-Dimethyl-3-phenyl-2H,4H-benzo[e]1,3-oxazine (*24DMP-a, Scheme 3*). This was obtained as a pale yellow liquid. Yield: 78%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.14 (3H, Ar−CH_3), 2.21 (3H, Ar−CH_3), 4.57 (2H, Ar−CH_2−N), 5.35 (2H, O−CH_2−N), 6.68−7.30 (7H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.5 (1C, Ar−CH_3), 20.5 (1C, Ar−CH_3), 50.3 (1C, Ar−CH_2−N), 79.3 (1C, O−CH_2−N), 118.0−150.3 (12C, Ar).

2.2.3. 6,8-Dimethyl-3-(4-methylphenyl)-2H,4H-benzo[e]1,3-oxazine (*24DMP-pt, Scheme 3*). This was obtained as white flake-like crystals. Yield: 83%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.37 (3H, Ar−CH_3), 2.45 (3H, Ar−CH_3), 2.50 (3H, N—Ar—CH_3), 4.77 (2H, Ar−CH_2−N), 5.56 (2H, O−CH_2−N), 6.89−7.50 (6H, Ar−H). ^{13}C NMR(50.3 MHz, $CDCl_3$, 298 K): δ 15.5 (1C, Ar−CH_3), 20.3 (1C, Ar−CH_3), 21.0 (1C, Ar−CH_3), 50.1 (1C, Ar−CH_2−N), 79.1 (1C, O−CH_2−N), 118.0−150.3 (12C, Ar).

2.2.4. 1-(6,8-Dimethyl(2H,4H-benzo[e]1,3-oxazin-3-yl))-4-methoxybenzene (*24DMP-pma, Scheme 3*). This was obtained as flake-like pale brown crystals. Yield: 80%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.16 (3H, Ar−CH_3), 2.23 (3H, Ar−CH_3), 3.76 (3H, OCH_3), 4.51 (2H, Ar−CH_2−N), 5.29 (2H, O−CH_2−N), 6.78−7.10 (6H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.5 (1C, Ar−CH_3), 20.3 (1C, Ar−CH_3), 50.1 (1C, Ar−CH_2−N), 53.4 (1C, O−CH_3), 79.1 (1C, O−CH_2−N), 118.0−151.0 (12C, Ar).

2.2.5. 6,8-Dimethyl-3-(2,3,4,5,6-pentaluorophenyl)-2H,4H-benzo[e]1,3-oxazine (*24DMP-pfa, Scheme 3*). This was obtained as white crystals. Yield: 80%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.16 (3H, Ar−CH_3), 2.24 (3H, Ar−CH_3), 4.49 (2H, Ar−CH_2−N), 5.10 (2H, O−CH_2−N), 6.66−6.84 (2H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.3 (1C, Ar−CH_3), 20.3 (1C, Ar−CH_3), 50.5 (1C, Ar−CH_2−N), 79.1 (1C, O−CH_2−N), 115.0−152.0 (12C, Ar).

2.3. Synthesis of 2,4-Dimethylphenol-Based Benzoxazine Dimers (Scheme 4E). The synthesis of 2,4-dimethylphenol-based benzoxazine dimers followed the previous synthesis method.[14] They were separated from dimerization model systems by gradient solvent column chromatography (hexane:ethyl acetate).

2.3.1. 6-({[(2-Hydroxy-3,5-dimethylphenyl)methyl]phenylamino}-methyl)-2,4-dimethylphenol (*Scheme 4, E3*). 2,4-Dimethylphenol (47.5 mg, 0.39 mmol) with 6,8-dimethyl-3-(4-methylphenyl)-2*H*,4*H*-benzo[*e*]1,3-oxazine (0.1 g, 0.39 mmol) and 5% by mole of sebacic acid (3.9 mg, 0.0095 mmol) were melted together at 140 °C for 1 h. The orange mixture was cooled. Subsequently, purification was done by gradient solvent column chromatography (hexane:ethyl acetate) to give a white solid. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.20 (3H, CH_3), 2.24 (3H, CH_3), 2.27 (3H, CH_3), 4.33 (4H, CH_2), 6.75 (2H, Ar−H), 6.80 (2H, Ar−H), 6.90 (2H, Ar−H), 7.05 (2H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.3, 20.1, 20.3 (5C, Ar−CH_3), 58.8 (2C, Ar−CH_2−N), 119.0 −152.6 (18C, Ar).

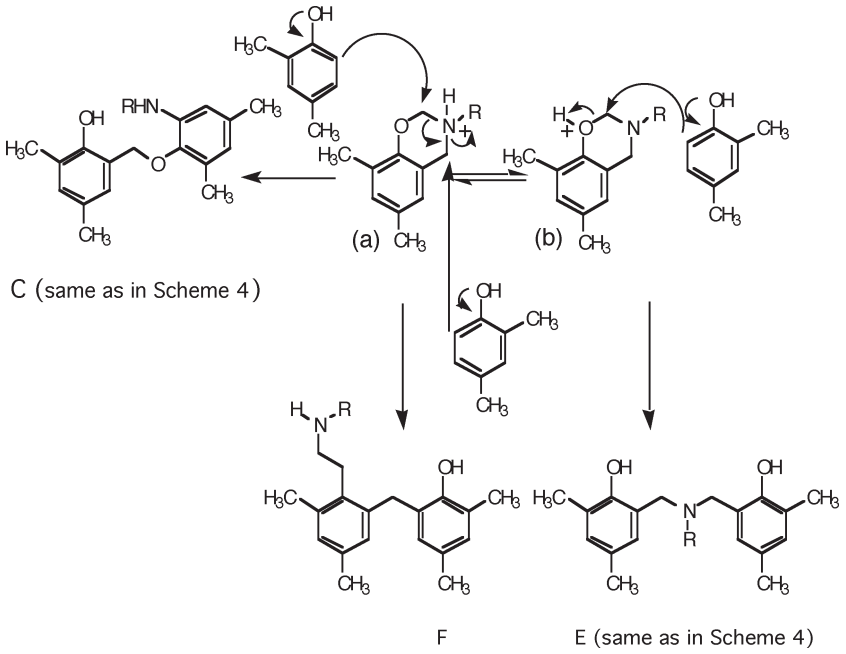
All dimers were synthesized in the same manner as above.

2.3.2. 6-({[(2-Hydroxy-3,5-dimethylphenyl)methyl]methylamino}-methyl)-2,4-dimethylphenol (*Scheme 4, E1*). White solid; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.24 (6H, CH_3), 2.26 (6H, CH_3), 3.66 (4H, CH_2), 6.75 (2H, Ar−H), 6.88 (2H, Ar−H); ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.7, 20.5 (4C, Ar−CH_3), 41.1 (1C, N−CH_3), 59.3 (2C, Ar−CH_2−N), 121.8 −152.0 (12C, Ar).

2.3.3. 6-({[(2-Hydroxy-3,5-dimethylphenyl)methyl](4-methoxyphenyl)amino}methyl)-2,4-dimethylphenol (*Scheme 4, E2*). White solid; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.17 (12H, CH_3), 3.74 (3H, CH_3−O-Ar), 4.16 (4H, CH_2), 6.64 (2H, Ar−H), 6.78 (2H, Ar−H), 6.82 (2H, Ar−H), 7.15 (2H, Ar−H) ; ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.3, 20.3 (4C, Ar−CH_3), 58.8 (2C, Ar−CH_2−N), 60.2 (1C, CH_3−O), 118.2 −152.6 (18C, Ar).

2.3.4. 6-({[(2-Hydroxy-3,5-dimethylphenyl)methyl]phenylamino}-methyl)-2,4-dimethylphenol (*Scheme 4, E4*). This was obtained as a white solid. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.24 (6H, CH_3), 2.27 (6H, CH_3), 4.36 (4H, CH_2), 6.80−7.00 (8H, Ar−H), 7.27 (1H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.8, 20.5 (4C, Ar−CH_3), 55.7 (2C, Ar−CH_2−N), 121.6 −152.0 (18C, Ar).

Scheme 5. Proposed Mechanism for 24DMP-R (R = Amine Substituent) Dimerized with 24DMP: (a) Nitrogen Protonated; (b) Oxygen Protonated



2.4. Other Model Compound Synthesis (Scheme 4, A−D). *2.4.1. 2-Hydroxy-3,5-dimethylbenzaldehyde as a Precursor*[15]. To a fresh Grignard reagent, CH_3−MgBr (100 mL of 300 mmol/100 mL ether), was added dropwise 40 mL of THF solution of 2,4-dimethylphenol (300 mmol, 36.6 g) at room temperature. After the phenoxide had completely precipitated, 300 mL of toluene was added. The ether and most of the THF were removed by distillation until the temperature reached 80 °C. Then additional toluene was added to bring the total volume to 300 mL. After the solution was cooled, triethylamine (450 mmol, 45.45 g) and parafomaldehyde (750 mmol, 22.5 g) were added at once. The reaction mixture was then poured into 500 mL of 10% by mole of HCl. The toluene and aqueous phases were separated and the aqueous phase was subsequently extracted with ether. The organic phases were combined and dried over sodium sulfate. After removal of the solvent under vacuum, the residue was distilled in vacuo to give the corresponding 2-hydroxy-3,5-dimethyl benzaldehyde in 75% yield; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.19 (3H, CH_3), 2.26 (H, CH_3), 7.12 (1H, Ar−H), 7.16 (1H, Ar−H), 9.77 (1H, CH aldehyde), 11.05 (1H, CH aldehyde); ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.0, 20.1 (2C, Ar−CH_3), 130.3 −153.5 (6C, Ar) 187.2 (1C, CH aldehyde).

2.5. Synthesis of Model Compounds A1−A4 in Scheme 4[16]**.** 2-Hydroxy-3,5-dimethyl-benzaldehyde (1.0 g, 7.14 mmol) was mixed with various amine (7.14 mmol) at 135 °C in a toluene solution, using Dean and Stark trap to remove water. After 5 h, the toluene was removed using a rotary evaporator. The yellow products were then dissolved in dichloromethane, washed with water, and dried over sodium sulfate.

2.5.1. 6-((1E)-2-Azaprop-1-enyl)-2,4-dimethylphenol (*Scheme 4, A1*). This was obtained as a yellow liquid; yield 70%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.24 (6H, CH_3), 3.44 (3H, CH_3), 6.85 (1H, Ar−H), 6.99 (1H, Ar−H), 8.28 (1H, Ar−CH=N). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.0, 20.1 (2C, Ar−CH_3), 31.3 (1C, N−CH_3), 130.3−153.5 (6C, Ar), 158.2 (1C, Ar−CH=N).

2.5.2. 6-[(1E)-2-Aza-2-(4-methoxyphenyl)vinyl]-2,4-dimethylphenol (*Scheme 4, A2*). This was obtained as a yellow liquid; yield 85%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.31 (6H, CH_3), 3.84 (3H, CH_3), 6.93−7.92 (6H, Ar−H), 8.55 (1H, Ar−CH=N). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.0, 20.1 (2C, Ar−CH_3), 60.5 (1C, O−CH_3), 131.8−153.5 (12C, Ar), 158.2 (1C, Ar−CH=N).

2.5.3. 6-[(1E)-2-Aza-2-(4-methylphenyl)vinyl]-2,4-dimethylphenol (*Scheme 4, A3*). This was obtained as a yellow crystal; yield 70%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.30 (6H, CH_3), 2.39 (3H, CH_3), 7.04−7.26 (6H, Ar−H), 8.58 (1H, Ar−CH=N). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.0, 20.1, 20.3 (3C, Ar−CH_3), 131.5−154.0 (12C, Ar), 158.4 (1C, Ar−CH=N).

2.5.4. 6-((1E)-2-Aza-2-phenylvinyl)-2,4-dimethylphenol (*Scheme 4, A4*). This was obtained as a yellow liquid; yield 80%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.29 (6H, CH_3), 7.03−7.48 (7H, Ar−H), 8.56 (1H, Ar−CH=N). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.0, 20.1 (2C, Ar−CH_3),131.0−153.5 (12C, Ar), 158.0 (1C, Ar−CH=N).

2.6. Synthesis of Model Compounds B1−B4 in Scheme 4[17]**.** The imine (**A1−A4**, Scheme 4) was reduced by using sodium borohydride. Then, the imine was dissolved in dichloromethane: methanol (50:50), cooled to 0 °C, mixed with sodium borohydride and stirred for 1 h at room temperature. The residue, separated by pouring the solution into cold water, was further crystallized from ethanol to furnish the following compounds.

2.6.1. 2,4-Dimethyl-6-[(methylamino)methyl]phenol (*Scheme 4, B1*). This was obtained as a white crystal; yield 80%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.23 (6H, CH_3), 2.26 (3H, CH_3), 3.89 (2H, CH_2), 6.75 (H, Ar−H), 6.88 (H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.2, 20.1 (2C, Ar−CH_3), 41.3 (1C, Ar−CH_2−N),130.0 −152.5 (6C, Ar).

2.6.2. 2,4-Dimethyl-6-{[(4-methoxyphenyl)amino]methyl}phenol (*Scheme 4, B2*). This was obtained as a white solid; yield 90%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.22 (3H, CH_3), 2.25 (3H, CH_3), 3.77 (3H, OCH_3), 4.32 (2H, Ar−CH_2−N), 6.78−6.92 (6H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.2, 20.1 (2C, Ar−CH_3), 58.6 (1C, Ar−CH_2−N), 60.2 (1C, CH_3−O),120.0 −152.5 (6C, Ar).

2.6.3. 2,4-Dimethyl-6-{[(4-methylphenyl)amino]methyl}phenol (*Scheme 4, B3*). This was obtained as a white crystal; yield 95%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.22 (3H, CH_3), 2.26 (3H, CH_3), 2.28 (3H, CH_3), 4.34 (2H, Ar−CH_2−N), 6.75−7.08 (6H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.2, 20.1, 20.3 (3C, Ar−CH_3), 58.8 (1C, Ar−CH_2−N), 120.0 −152.5 (6C, Ar).

2.6.4. 2,4-Dimethyl-6-[(phenylamino)methyl]phenol (*Scheme 4, B4*). This was obtained as a white crystal; yield 90%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K):δ 2.17 (3H, CH_3), 2.21 (3H, CH_3), 4.30 (2H, Ar−CH_2−N), 6.86−7.28 (7H, Ar−H). ^{13}C

NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.2, 20.1 (2C, Ar−CH_3), 55.6 (1C, Ar−CH_2−N), 60.2 (1C, CH_3−O),120.6 −152.5 (6C, Ar).

2.7. Synthesis of Model Compounds C1−C4 in Scheme 11. Compounds C (Scheme 4) were used as a representative to verify proposed nitrogen protonation initiation (Scheme 5a).

2.7.1. Step 1: Synthesis of 3,5-Dimethyl-2-prop-2-enyloxybenzaldehyde (*Scheme 11,* ***I*** ⇒ ***II***)[18]. Potassium hydroxide (12.0 g, 0.18 mol) was dissolved in dimethylformamide. 2-Hydroxy-3,5-dimethyl-benzaldehyde (6.7 g, 0.045 mol) and allyl bromide (13.1 g, 0.110 mol) were added to the solution. After 5 h, water was added to the solution. The resulting mixture was extracted with dichloromethane, washed with water, and dried over sodium sulfate. Dichloromethane was evaporated using a rotary evaporator. Further purification was carried out by column chromatography using gradient solvent (hexane:ethyl acetate). The product was obtained as a yellow liquid; yield 60%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 2.30 (6H, CH_3), 4.41−4.47 (2H, CH_2), 5.28−5.45 (2H, CH_2), 6.00−6.20 (1H, CH), 7.28 (1H, Ar−H), 7.50 (1H, Ar−H), 10.32 (1H, CH aldehyde). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.0, 20.2 (2C, Ar−CH_3), 75.6 (1C, O−CH_2), 110.8 (1C, CH_2), 130.2 (1C, CH), 125.6−160.5 (6C, Ar), 187.2 (1C, CH aldehyde).

2.7.2. Step 2: Synthesis of (*3,5-Dimethyl-2-prop-2-enyloxyphenyl*)*methan-1-ol* (*Scheme 11,* ***II*** ⇒ ***III***)[19]. Sodium borohydride (2.52 g, 0.067 mol) and potassium carbonate (2.3 g, 0.017 mol) were mixed with methanol at room temperature. Then, *3,5-dimethyl-2-prop-2-enyloxybenzaldehyde* ((8.3 g, 0.044 mol), from step 1) was added dropwise and reacted overnight. The solution was dissolved in 20 mL dichloromethane and washed with 20 mL water, followed by drying over sodium sulfate. The product was obtained as a colorless liquid; yield 98%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.26 (6H, CH_3), 4.33−4.36 (2H, CH_2), 4.65 (2H, CH_2), 5.25−5.48 (2H, CH_2), 6.00−6.20 (1H, CH), 6.90 (1H, Ar−H), 6.97(1H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.1, 20.2 (2C, Ar−CH_3), 55.4 (1C, CH_2−OH), 75.5 (1C, O−CH_2), 110.8 (1C, CH_2), 130.2 (1C, CH), 125.6−160.5 (6C, Ar).

2.7.3. Step 3: Synthesis of (*3,5-Dimethyl-2-prop-2-enyloxyphenyl*)*methyl methylsulfonate and 3-*(*Chloromethyl*)*-1,5-dimethyl-2-prop-2-enyloxybenzene* (*Scheme 11,* ***III*** ⇒ ***IV*** + ***V***)[20]. Product from step 2 (4.0 g, 0.02 mol) was added into a triethylamine (3.2 g, 3.13 mmol) and dimethyl-4-pyridilamine (0.12 g, 1.00 mmol) solution of dichloromethane at −78 °C. Chloromethylsulfone (3.64 g, 3.12 mmol) was added via syringe. After 3 days at −30 °C, the suspension was diluted with additional dichloromethane (40 mL), and the resulting solution was washed successively with 1 N HCl, water, and 1 N NaOH. Then, the solution was dried over sodium sulfate and was evaporated after drying overnight. The product was obtained as a white solid; yield 70%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.27 (6H, CH_3), 4.39−4.42 (2H, CH_2), 4.63 (2H, CH_2), 5.25−5.52 (2H, CH_2), 6.02−6.22 (1H, CH), 6.98 (1H, Ar−H), 7.05 (1H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.1, 20.3 (2C, Ar−CH_3), 30.1 (CH_3−S), 41.2 (1C, Ar−CH_2−Cl), 55.4 (1C, Ar−CH_2−O), 75.5 (1C, O−CH_2), 110.8 (1C, CH_2), 130.2 (1C, CH), 125.3−160.0 (6C, Ar).

2.7.4. Step 4: Synthesis of 2-[(*3,5-dimethyl-2-prop-2-enyloxyphenyl*)*methoxy*]*-3,5-dimethylbenzaldehyde* (*Scheme 11,* ***IV*** + ***V*** ⇒ ***VI***)[21]. Under nitrogen, the substance from step 3 (3.3 g, 0.016 mol) and 2-hydroxy-3,5-dimethylbenzaldehyde (3.6 g, 0.024 mol) in the presence of NaI (4.8 g, 0.030 mol) in dimethylformamide were added dropwise at −30 °C to a well stirred mixture of fine KOH powder (4.3 g, 0.064 mol) in dimethylformamide. The reaction mixture was stirred at −30 °C for 30 min and 1 h at −20 °C. The mixture was then allowed to warm to room temperature and was stirred at room temperature for overnight. The product was obtained as a white solid; yield 76%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.26 (6H, CH_3), 2.31 (6H, CH_3), 4.28−4.31 (2H, CH_2), 4.92 (2H, CH_2), 5.19−5.41 (2H, CH_2), 5.92−6.10 (1H, CH), 7.00 (1H, Ar−H), 7.10 (1H, Ar−H), 7.28(1H, Ar−H), 7.50 (H, Ar−H), 10.28 (1H, CH aldehyde). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.1, 20.3 (4C, Ar−CH_3), 58.4 (1C, Ar−CH_2−O), 75.4 (1C, O−CH_2), 110.8 (1C, CH_2), 130.2 (1C, CH), 124.4−161.0 (12C, Ar), 187.6 (1C, CH).

2.7.5. Step 5: Synthesis of Model Compound VII in Scheme 11 (***VI*** ⇒ ***VII***)[16]. The substances **VI** were mixed with various amines in a mole ratio of 1:1. The reactions were carried out in toluene at 140 °C for 12 h. The solvent was then evaporated. Gradient solution column chromatography (hexane:ethyl acetate) was performed for purification of the product.

2.7.5.1. ***VII*** (*Amine = Methylamine*) *3-*((*1Z*)*-2-azaprop-1-enyl*)*-2-*[(*3,5-dimethyl-2-prop-2-enyloxyphenyl*)*methoxy*]*-1,5-dimethylbenzene*. The product was obtained as a yellow liquid; yield 70%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.35 (12H, CH_3), 3.50 (3H, CH_3), 5.20 (2H, CH_2), 4.92 (2H, CH_2), 5.23 (2H, CH_2), 5.89 (1H, CH), 6.67−7.20 (4H, Ar−H), 8.56 (1H, CH_2−N). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 11.6, 20.1 (4C, Ar−CH_3), 31.0 (1C, CH_3), 58.7 (1C, Ar−CH_2−O), 75.4 (1C, O−CH_2), 110.8 (1C, CH_2), 130.2 (1C, CH), 123.4−161.0 (12C, Ar), 171.6 (1C, CH).

2.7.5.2. ***VII*** (*Amine = 4-Methoxyphenylamine*) *1-*((*1Z*)*-1-aza-2-*{*2-*[(*3,5-dimethyl-2-prop-2-enyloxyphenyl*)*methoxy*]*-3,5-dimethylphenyl*}*vinyl*)*-4-methoxybenzene*. The product was obtained as a yellow liquid; yield 95%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.35 (12H, CH_3), 3.75 (3H, CH_3), 5.20 (2H, CH_2), 4.90 (2H, CH_2), 5.23 (2H, CH_2), 5.90 (1H, CH), 6.60−7.15 (8H, Ar−H), 8.56 (1H, CH_2−N). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.2, 20.1 (4C, Ar−CH_3), 58.7 (1C, Ar−CH_2−O), 56.0 (1C, CH_3−O), 75.4 (1C, O−CH_2), 110.8 (1C, CH_2), 130.2 (1C, CH), 120.6−160.5 (18C, Ar), 171.6 (1C, CH).

2.7.5.3. ***VII*** (*Amine = 4-Methylphenylamine*) *3-*[(*1Z*)*-2-Aza-2-*(*4-methylphenyl*)*vinyl*]*-2-*[(*3,5-dimethyl-2-prop-2-enyloxyphenyl*)*methoxy*]*-1,5-dimethylbenzene*. The product was obtained as a yellow liquid; yield 90%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.35 (15H, CH_3), 5.20 (2H, CH_2), 4.92 (2H, CH_2), 5.23 (2H, CH_2), 5.89 (1H, CH), 6.67- 7.14 (8H, Ar−H), 8.56 (1H, CH_2−N). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 11.6, 20.1 (5C, Ar−CH_3), 60.2 (1C, Ar−CH_2−O), 75.4 (1C, O−CH_2), 110.8 (1C, CH_2), 130.2 (1C, CH), 123.0−160.2 (18C, Ar), 171.6 (1C, CH).

2.7.5.4. ***VII*** (*Amine = Aniline*) *3-*((*1Z*)*-2-Aza-2-phenylvinyl*)*-2-*[(*3,5-dimethyl-2-prop-2-enyloxyphenyl*)*methoxy*]*-1,5-dimethylbenzene*. The product was obtained as a yellow liquid; yield 80%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.35 (12H, CH_3), 5.20 (2H, CH_2), 4.92 (2H, CH_2), 5.22 (2H, CH_2), 5.90 (1H, CH), 6.67- 7.50 (9H, Ar−H), 8.56 (1H, CH_2−N). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 11.6, 20.1 (4C, Ar−CH_3), 60.5 (1C, Ar−CH_2−O), 75.4 (1C, O−CH_2), 110.8 (1C, CH_2), 130.2 (1C, CH), 123.0−165.0 (18C, Ar), 171.6 (1C, CH).

2.7.6. Step 6: Synthesis of Model Compounds VIII in Scheme 11 (***VII*** ⇒ ***VIII***)[17]. The various amine based phenoxy model compounds (0.1 g) from step 5 were reduced by using sodium borohydride (1.5 equiv) in the presence of potassium carbonate (0.38 equiv), dissolved in methanol and dichloromethane solution (50:50).

2.7.6.1. ***VIII*** (*Amine = Methylamine*) ({*2-*[(*3,5-Dimethyl-2-prop-2-enyloxyphenyl*)*methoxy*]*-3,5-dimethylphenyl*}*methyl*)*methylamine*. The product was obtained as a brown liquid, yield 80%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.35 (15H, CH_3), 3.66 (2H, CH_2), 5.20 (2H, CH_2), 4.92 (2H, CH_2), 5.23 (2H, CH_2), 5.89 (1H, CH), 6.67−7.14 (4H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 11.6, 20.1 (4C, Ar−CH_3), 33.0 (1C, CH_3), 48.0 (Ar−CH_2−N), 58.9 (1C, Ar−CH_2−O), 75.4 (1C, O−CH_2), 110.8 (1C, CH_2), 130.2 (1C, CH), 123.0−160.0 (12C, Ar).

2.7.6.2. ***VIII*** (*Amine = 4-Methoxyphenylamine*) ({*2-*[(*3,5-Dimethyl-2-prop-2-enyloxyphenyl*)*methoxy*]*-3,5-dimethylphenylmethyl*)(*4-methoxyphenyl*)*amine*. The product was obtained as a dark brown liquid, yield 95%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.35 (12H, CH_3), 3.75 (3H, CH_3), 4.32 (1H, CH_2−N),

5.20 (2H, CH_2), 4.90 (2H, CH_2), 5.23 (2H, CH_2), 6.10 (1H, CH), 6.32−6.70 (8H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.2, 20.1 (4C, Ar−CH_3), 58.7 (1C, Ar−CH_2−O), 56.0 (1C, CH_3−O), 58.6 (Ar−CH_2−NH), 75.4 (1C, O−CH_2), 110.8 (1C, CH_2), 130.2 (1C, CH), 120.6−160.5 (18C, Ar).

2.7.6.3. ***VIII*** *(Amine = 4-Methylphenylamine) ({2-[(3,5-dimethyl-2-prop-2-enyloxyphenyl)methoxy]-3,5-dimethyl}methyl)(4-methylphenyl)amine.* Brown liquid, yield 90%; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.35 (15H, CH_3), 4.32 (2H, CH_2−N), 5.20 (2H, CH_2), 4.92 (2H, CH_2), 5.23 (2H, CH_2), 5.90 (1H, CH), 6.65- 7.14 (8H, Ar−H); ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 11.6, 20.1 (5C, Ar−CH_3), 60.2 (1C, Ar−CH_2−O), 58.5 (1C, Ar−CH_2−NH), 75.0 (1C, O−CH_2), 110.8 (1C, CH_2), 130.2 (1C, CH), 123.0−160.2 (18C, Ar).

2.7.6.4. ***VIII*** *(Amine = Aniline) ({2-[(3,5-Dimethyl-2-prop-2-enyloxyphenyl)methoxy]-3,5-dimethylphenyl}methyl)phenylmine.* The product was obtained as a brown liquid, yield 90%. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.35 (12H, CH_3), 4.32 (1H, CH_2−N), 4.90 (2H, CH_2), 5.20 (2H, CH_2), 5.22 (2H, CH_2), 5.90 (1H, CH), 6.67- 7.50 (9H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 11.6, 20.1 (4C, Ar−CH_3), 58.6 (1C, Ar−CH_2−NH), 60.5 (1C, Ar−CH_2−O), 75.4 (1C, O−CH_2), 110.8 (1C, CH_2), 130.2 (1C, CH), 123.0−165.0 (18C, Ar).

2.7.7. Step 7: Synthesis of Model Compounds IX in Scheme 11

2.7.7.1. (***VIII*** ⇒ ***IX*** (***C3****, Scheme 4*))[22]. In a one-necked round-bottom flask which is equipped with a magnetic bar and nitrogen balloon was placed $ZrCl_4$ (1 equiv). Dried THF was syringed into the flask, and immediate formation of a red brown solution was observed. The contents were cooled to 0 °C, and $NaBH_4$ (4 equiv) was added to the above solution. The red brown solution slowly turned to a pale pink. To this reagent system at 0 °C the allylated compound (1 equiv) in dried THF was added. After complete addition of the allylated alcohol, the flask was removed from the ice bath and contents were brought to room temperature. The contents were again cooled to 0 °C and quenched by the dropwise addition of 5% aqueous HCl solution. From the reaction mixture, THF was evaporated under vacuum and the remaining aqueous layer was extracted with ethyl acetate. The organic fractions were combined and washed successively with brine and water and dried over anhydrous sodium sulfate. Evaporation of solvent was followed by purification of the crude product by silica gel column chromatography using a gradient solvent (hexane and ethyl acetate). ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.35 (15H, CH_3), 5.20 (2H, CH_2), 4.32 (2H, CH_2−N), 6.31−6.84 (8H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 11.6, 20.1 (5C, Ar−CH_3), 60.2 (1C, Ar−CH_2−O), 58.5 (1C, Ar−CH_2−NH), 75.0 (1C, O−CH_2), 110.8 (1C, CH_2), 130.2 (1C, CH), 123.0−160.2 (18C, Ar).

C1, C2, and **C4** (Scheme 4) were synthesized in the same manner;

2.7.7.2. 6-({2,4-Dimethyl-6-[(methylamino)methyl]phenoxy}methyl)-2,4-dimethylphenol (Scheme 4, C1). Yellowish solid; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.20, 2.35 (15H, CH_3), 3.67 (2H, CH_2), 5.20 (2H, CH_2), 6.52−6.60 (4H, Ar−H); ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 11.6, 20.1 (4C, Ar−CH_3), 32.8 (1C, N−CH_3), 48.0 (Ar−CH_2−N), 58.9 (1C, Ar−CH_2−O), 122.5−160.0 (12C, Ar).

2.7.7.3. 6-[(6-{[(4-Methoxyphenyl)amino]methyl}-2,4-dimethylphenoxy)methyl]-2,4-dimethylphenol (Scheme 4, C2). Yellowish solid; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.35 (12H, CH_3), 3.75 (3H, OCH_3), 5.20 (2H, CH_2), 4.30 (2H, CH_2−N), 6.20−6.60 (8H, Ar−H); ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 15.2, 20.1 (4C, Ar−CH_3), 56.0 (1C, CH_3−O), 58.6 (Ar−CH_2−NH), 64.2 (1C, Ar−CH_2−O), 120.6−155.5 (18C, Ar).

2.7.7.4. 6-({2,4-Dimethyl-6-[(phenylamino)methyl]phenoxy}methyl)-2,4-dimethylphenol (Scheme 4, ***C4****).* Yellowish solid; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.34 (12H, CH_3), 5.20 (2H, CH_2), 4.32 (2H, CH_2−N), 6.40−7.10 (9H, Ar−H); ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 11.6, 20.1 (4C, Ar−CH_3), 58.6 (1C, Ar−CH_2−NH), 63.5 (1C, Ar−CH_2−O), 123.0−162.0 (18C, Ar).

Table 1. HPLC Results from 24DMP-R (R = m = Methylamine) Dimerization Model Experiment at 150 °C

		% of peak area at each retention time (min)			
time (min)	catalyst (mol %)	7.1	13.0	15.2	21.0
60	5	46		7	45
	10	26		9	65
	20	33		13	54
120	0	18		15	67
	5	22		22	56
	10	27		24	49
	20	32		30	38

	retention time (min)		retention time (min)
methylamine	4.3	**A1** (Scheme 4)	13.3
2,4-dimethylphenol	7.1	**D** (Scheme 4)	15.2
24DMP-m (Scheme 3)	11.9	**E1** (Scheme 4)	21.0
B1 (Scheme 4)	13.0	**C1** (Scheme 4)	27.5

2.8. Synthesis of 6-[(2-Hydroxy-3,5-dimethylphenyl)methyl]-2,4-dimethylphenol[23,24]**.** 2,4-dimethylphenol (3.1 g, 25 mmol) was refluxed with 5% w/w aqueous sodium hydroxide (25.0 g, 31 mmol) and 37% w/w aqueous formaldehyde (4.14 g, 51 mmol) for 4 h. The dark brown mixture was cooled and neutralized with glacial acetic acid (3 cm^3). The pale precipitates were washed with water and dried in vacuum to give a mustard yellow powder (4.3 g, 67%). Recrystallization from chloroform/petroleum ether resulted in a pale yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 2.12 (6H, Ar−CH_3), 2.23 (6H, Ar−CH_3), 3.85 (2H, CH_2), 6.02 (2H, OH), 6.80 (2H, Ar−H), 6.94 (2H, Ar−H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 298 K): δ 16.0, 20.4 (4C, Ar−C), 31.2 (1C, Ar−CH_2), 123.8−148.8 (12C, Ar).

2.9. Dimerization. The monomer (24DMP-R, Scheme 3) was dimerized (Scheme 5) with and without 2,4-dimethylphenol in the ratio of 1:1 by mole. Sebacic acid was used to increase the rate of the reaction. Conditions used are shown in Tables 1-4.

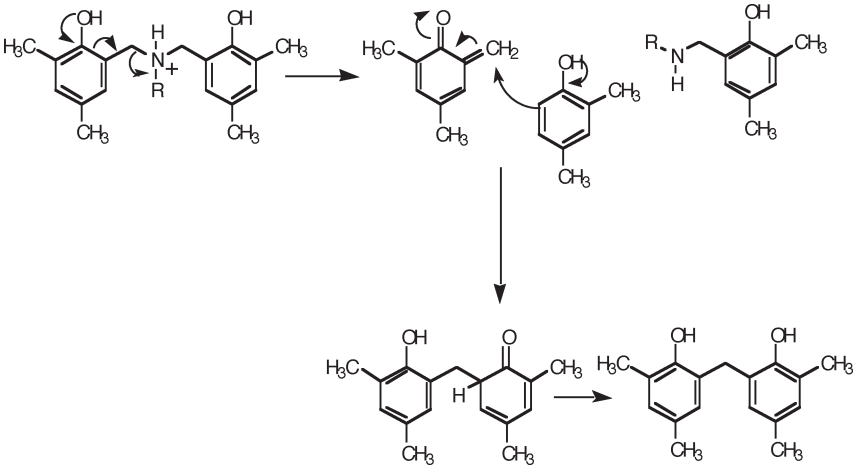
2.10. Characterization. The proton and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were taken using Varian 200 MHz Gemini NMR spectrometer at the proton frequency of 200 MHz and the corresponding carbon frequency of 50.3 MHz using trimethylsilane (TMS) as internal standard. The purity was examined by a Hewlett-Packard 6890 gas chromatography-5973 mass selective detector. High performance liquid chromatography (HPLC) was performed on a Varian Prostar with a UV detector model 320 and RI detector model 350. Gradient HPLC analyses were carried out using a Varian pump equipped with a Lichrospher RP18 (Octadecylsilane-covered spherical silica, 5 μm partical size, 10 nm pore size, 25 cm × 4.6 mm) and a UV detector at 254 nm. The gradient program was as follows: step 1, 50−100% acetonitrile over 25 min; step 2, 100% acetonitrile over 5 min; step 3, 100−50% acetonitrile over 5 min; (recycle). The mobile phase was a mixture of acetonitrile and water.

3. Results and Disscussion

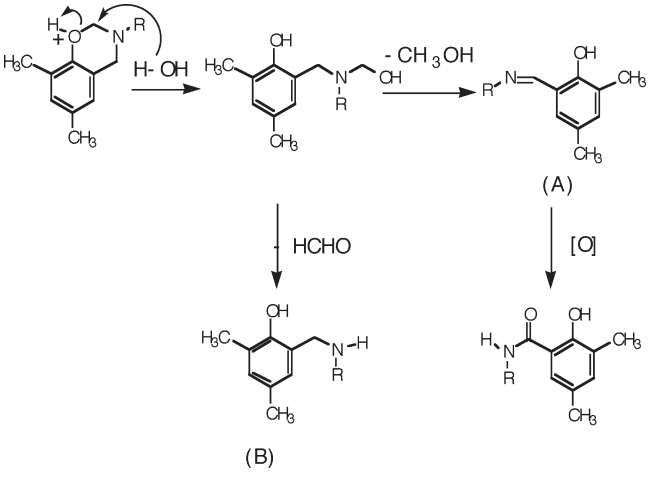
The study began with the synthesis of a series of substituted benzoxazines (Scheme 3) which will be reacted with 2,4-dimethylphenol in the model reaction. In addition a range of possible products (Scheme 4), were also separately synthesized in order to allow identification of the products from the model reaction. Schemes 5−9 show possible mechanistic routes to a number of these possible products.

Protonation of the benzoxazine can either at the more basic nitrogen atom (Scheme 5a) or the oxygen atom (Scheme 5b). If protonation occurs at the nitrogen atom, then either compound **C** or **F** (Scheme 4) will be the likely products. If protonation takes

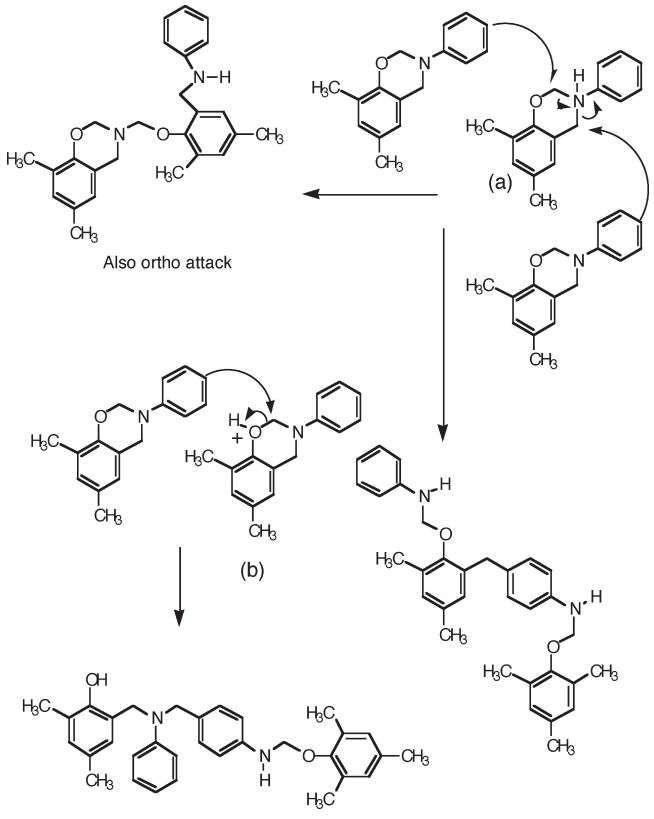
Scheme 6. Proposed Mechanism for 24DMP-R Dimer Mannich Bridge (*R* = Amine Substituent) Exchange to Methylene Bridge Structure



Scheme 7. Proposed Mechanism for A and B



Scheme 8. Proposed Mechanism for DMP-a, Para-Position of Aromatic Ring Attack: (a) Nitrogen Protonated; (b) Oxygen Protonated

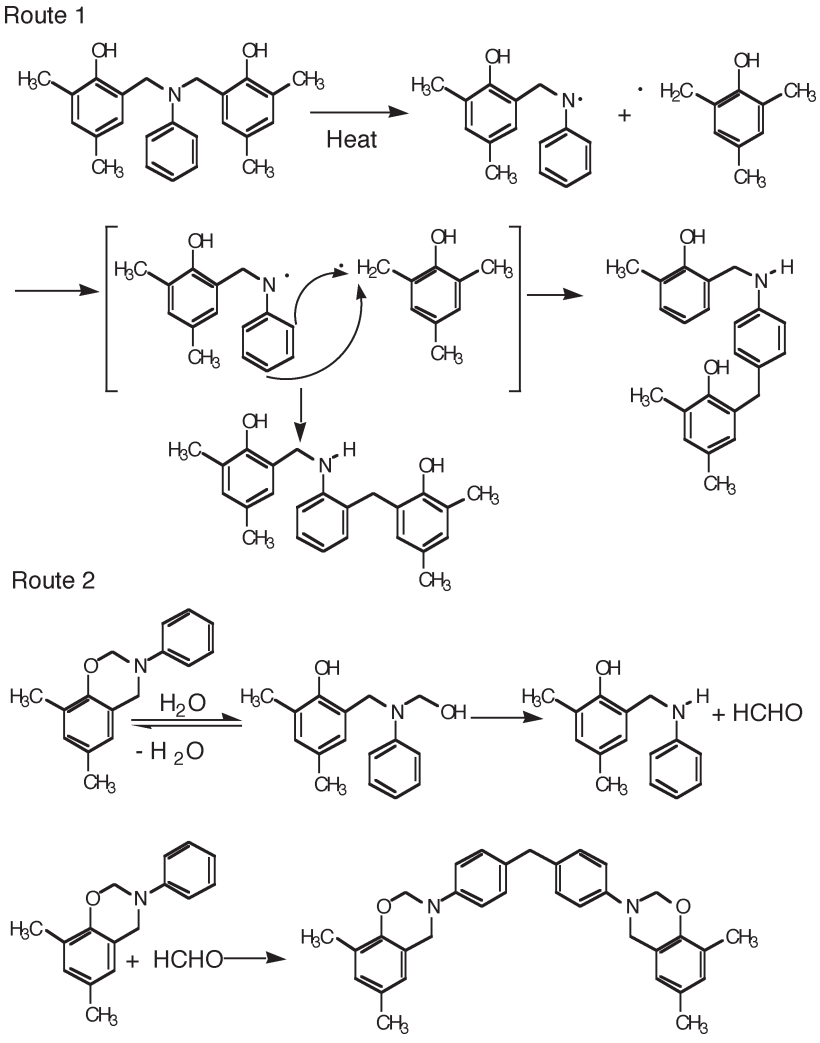


place at the oxygen atom then compound **E** (Scheme 4), which is the commonly observed Mannich base product from the previous studies of benzoxazine polymerization, would be the likely result.[7] Alternatively the Mannich base structure can also occur via protonation of the nitrogen, tautomerism to the iminium species which then reacts with the phenolate. Once the Mannich base product **E** is formed it is possible for it to be converted in to the methylene bridge structure **D** as shown in Scheme 6. In addition to this other side reactions can occur, for example, the oxygen protonated species can react with water to yield **A** after elimination of methanol, or eliminate formaldehyde to form **B** as is shown in Scheme 7. In the case of the aniline-based benzoxazine monomer, the ortho and para positions of the aromatic rings of aniline can be the nucleophile that attacks the protonated species (Scheme 8). Scheme 9 proposes the other potential pathways and products for aniline-based benzoxazine monomer. The propagation mechanism is also proposed in Scheme 10 by intramolecular hydrogen bonding activation to undergo the polymerization.

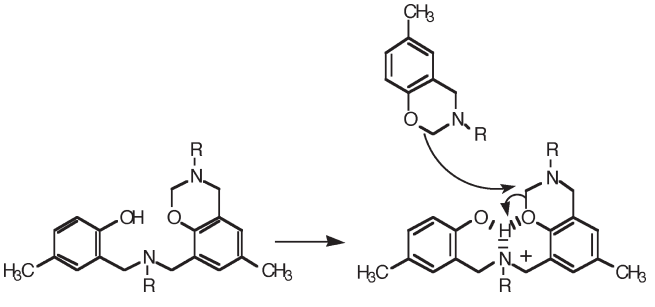
The monomers used in this study are not expected to form high molecular weight materials because two of the reactive sites on the phenolic ring have been blocked by methyl groups. Therefore, all reaction products are soluble, making it possible to carry out solution-state NMR and HPLC analyses. By comparison of the retention time of the crude reaction products with the retention of those of separately synthesized model compounds, we can investigate the proposed initiation mechanism.

It is common for resonances around 8.00−10.0 ppm to be observed in the NMR spectra of the polymerization of benzoxazines derivatives. . The peaks were also observed in the model reactions. Peaks in this general resonance range suggest the presence of Schiff bases, which might be the cause of coloration in poly(benzoxazine)s. NMR spectrum of the aromatic imine compound (**A**, Scheme 4) has the methine proton resonance between the nitrogen and aromatic ring at 8.58 ppm (Figure 1S of the Supporting Information). Moreover, the color of these imine model compounds is yellow, consistent with structures similar to compound **A** (Scheme 4) occurring in the benzoxazine polymerizations. In addition, one should notice that there is a difference in retention time between the 4-methylphenylamine based imine and the other amine-based imine. Exceptionally, the methine

Scheme 9. Proposed Potential Pathways and Products from Aniline-Based Benzoxazine



Scheme 10. Proposed Propagation Mechanism of Benzoxazine Monomer



proton in **A** (Scheme 4) shifts from 8.58 to 4.34 ppm (Figure 2S of the Supporting Information) of the methylene proton in **B** (Scheme 4) after reducing the imine to an amine. All the other HPLC chromatograms and NMR spectra of other compounds, e.g. 2,4-dimethylphenol, amine, monomer, dimer, phenoxy acetal, crude dimerization have been carried out and are summarized in Tables 1−4.

Methylamine-based benzoxazine monomer (24DMP-m, Scheme 3) is one of the simplest of the benzoxazine systems. Therefore, the possible product of the monomer from dimerization with 2,4-dimethylphenol is fewer than other aromatic amine-based benzoxazines, which have additional reactive sites, e.g. the ortho and para positions. From Table 1, we could not observe any monomer, which has retention time around 12 min left in the system. Hence, DMP-m is quite reactive. However, the concentration of the expected product (**E1**, Scheme 4) decreases when the catalyst concentration increases or time increases. The retention time at 21.0 min corresponds to the expected dimer of DMP-m monomer. The retention time at 15.2 min corresponds to compound **D** (Scheme 4) and it increases with reaction time and catalyst concentration. It is proposed that the cause of the formation of this molecule is an internal rearrangement, as shown in Scheme 6. Without a catalyst, e.g., sebacic acid, dimer is also obtained, meaning that a proton from hydroxyl group of 2,4-dimethylphenol can also be a catalyst for this system.

As expected, more products were observed in 24DMP-pma. Table 2 shows that when the catalyst concentration and the time are increased, the yield of the desired dimer (**E2**, Scheme 4) decreases. The methylene bridge linkage phenolic compound **D** was not observed in this case but two other compounds appeared at 18.3, and 25.0 min. The retention time of this compound was not matched with the product from the nitrogen protonation (**C2**, Scheme 4), which has a retention time at 27.5 min. Therefore, these products might come from either the rearrangement or degradation of the Mannich dimer. The degradation of the Mannich dimer has been reported elsewhere where ease of amine evaporation was reported to be the function of the amine structure, such as conjugation and steric hindrance.[25]

Surprisingly, only a small amount of the desired dimer (**E3**, Scheme 4), whose retention time is around 16.2 min, was hardly

Scheme 11. Synthesis of *O*-(2-Hydroxy-3,5-dimethyl-benzyl)-7-(*N*-*substituted*-methyl) 3,5-Dimethylphenoxide (C1−C4 in Scheme 4)

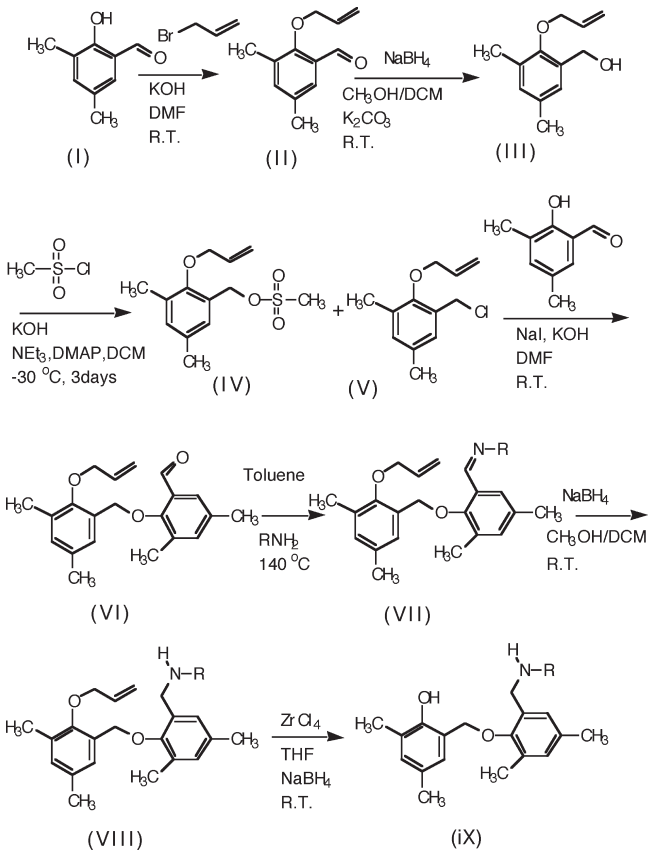


Table 2. HPLC Results from 24DMP-R (*R* = pma = *p*-Methoxyaniline) Dimerization Model Experiment at 150 °C

		% of peak area at each retention time (min)					
time (min)	catalyst (mole %)	4.4	17.7	18.3	20.4	21.1	25.0
60	5	2	2		62	23	12
	10	2	3		64	17	14
	20	2	6		48	16	28
120	0	4	1		56	38	1
	5	3	-		51	34	12
	10	2	1		40	26	30
	20	3	24	15	29	28	1

	retention time (min)		retention time (min)
p-anisidine	4.4	24DMP-pma (Scheme 3)	17.7
2,4-dimethylphenol	7.1	**E2** (Scheme 4)	20.4
B2 (Scheme 4)	13.7	**A2** (Scheme 4)	21.1
D (Scheme 4)	15.2	**C2** (Scheme 4)	27.5

obtained from the reaction of 24DMP-pt dimerization (Table 3). However, a large amount of 24DMP-pt monomer (retention time = 20.5 min) was evident along with two unexpected products (retention time = 22.0 and 25.0 min). One of these was speculated to be **C3** (Scheme 4), which would provide evidence of an N protonation initiation mechanism (Scheme 5). However neither of these peaks corresponds to **C3**, which has a retention time at 28.0 min. Thus, N protonation is unlikely. Again, the two unexpected products can be either from the rearrangement or degradation of the Mannich dimer. In addition, upon an increase in the amount of catalyst and the reaction time, the percentage of the peak that appears at 24.0 min increases and the peak at 25.0 min decreases.

Table 3. HPLC Results from 24DMP-R (*R* = pt = *p*-toluidine) Dimerization Model Experiment at 150 °C

		% of peak area at each retention time (min)					
time (min)	catalyst (mol %)	5.0	16.2	20.5	22.0	24.0	25.0
60	5	4		63	2	26	4
	10	6		65	1	23	4
	20	2	2	57	12	13	13
120	0	5		52		32	11
	5	1	2	44	4	21	28
	10	1	3	8	25	9	53
	20	17		63		20	

	retention time (min)		retention time (min)
p-toluidine	5.0	**B3** (Scheme 4)	20.4
2,4-dimethylphenol	7.1	24DMP-pt (Scheme 3)	20.5
D (Scheme 4)	15.2	**A3** (Scheme 4)	24.0
E3 (Scheme 4)	16.2	**C3** (Scheme 4)	28.0

Table 4. HPLC results from 24DMP-R (*R* = a = aniline) dimerization model experiment at 150°C

		% of peak area at each retention time (min)					
time (min)	catalyst (mol %)	14.8	19.1	21.5	22.7	23.7	26.0
60	5	19	20	1	34	9	17
	10	33	25	8	16	8	9
	20	27	22	3	24	9	15
120	0	4	17	1	34	13	32
	5	13	20	3	24	14	26
	10	7	19	1	31	12	30
	20	7	13	1	25	10	26

	retention time (min)		retention time (min)
aniline	4.9	**E4** (Scheme 4)	14.8
2,4-dimethylphenol	7.1	**D** (Scheme 4)	15.2
24DMP-a (Scheme 3)	11.9	**A4** (Scheme 4)	21.5
B4 (Scheme 4)	14.2	**C4** (Scheme 4)	27.5

Table 4 shows a more complicated system of 24DMP-a, e.g., a larger number of unexpected species (retention time = 22.7, 23.7, and 26.0 min). The retention time of **E4** and **D** are very close. However, we observed from ^{1}H NMR that a resonance appears at 3.80 ppm, corresponding to the proton of methylene linkage of compound **D**, instead of proton of Mannich bridge linkage of compound **E**, which appears at 4.32 ppm. In addition, there is no monomer left in the reaction to be changed to other compounds.

More evidence of O protonation is shown in Figure 3S of the Supporting Information. Two different types of products were separated (Figure 3S (iii) and 3S (iv) of the Supporting Information) from dimerization of 24DMP-pma with 2,4-dimethylphenol. At first, it was thought that spectrum **iv** (Figure 3S of Supporting Information) corresponded to the nonacetal structure (**C**, Scheme 4), due to the four different resonance positions at 2.00−2.30 ppm and resonance centered at 4.20 and 4.75 ppm of methylene groups. However, these positions were not observed in the model compound (**C2**, Scheme 4). Because of the closeness of the polarity of the side products, it is hard to obtain the pure compound from crude dimerization via column chromatography. The resonance centered at 4.75 ppm corresponds to protons of the methylene group of a triaza compound, which was proposed before as a side product in benzoxazine polymerization.[26] A resonance at 3.85 ppm was observed and is believed to belong to the protons of a methylene bridge structure (**D**, Scheme 4. The resonance peak at 8.25 ppm corresponds to **A2** (Scheme 4). The dimer compounds

Table 5. Electronegativity[a] of Nitrogen and Oxygen of Benzoxazine Monomer

monomer	N	O
24DMP-m	−0.128	−0.234
24DMP-pma	+0.163	−0.272
24DMP-pt	+0.181	−0.220
24DMP-a	+0.196	−0.218
24DMP-pfa	+0.077	−0.235

[a] Partial charge values were calculated from CS Chem3D Pro, Hückel method, Cambridgesoft.

Table 6. Relationship between pK_b of Various Amine-Based Benzoxazine Monomer and the Percentage of Desired Mannich Base Structure Formed

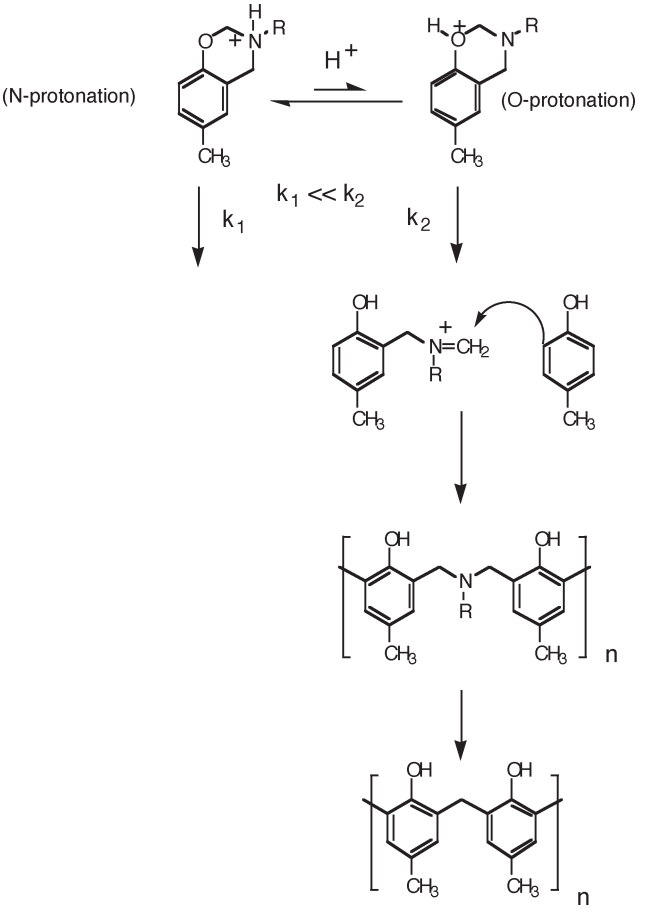
compound	pK_b	Mannich bridge dimer content (%)
24DMP-a	9.4	4.0
824DMP-pt	8.9	5.0
24DMP-pma	8.7	56
24DMP-m	3.4	67

(**E2**, Scheme 4) were heated longer and their spectra are the same as 6-[(2-hydroxy-3,5-dimethylphenyl)methyl]-2,4-dimethylphenol shown in Figure 4S (ii) of the Supporting Information. The resonance centered at 4.20 ppm decreases while the resonance at 3.85 ppm intensifies. 24DMP-pfa (Scheme 3) was also reacted with 24DMP (Figure 4S (iii) of the Supporting Information) and the crude product is bisphenol as the spectrum of this pure compound is shown in Figure 4S (iv) of the Supporting Information. From this result, we can summarize that the Mannich bridge structures can be rearranged to the methylene bridge structure. In other words, the Mannich bridge phenolic structure is less stable than methylene bridge structure.

The electronegativity of the nitrogen and oxygen were calculated in order to obtain a better idea of the initiation site. Admittedly, the calculation performed in this paper is less rigorous than the specialized papers on this subject; however, it was our interest to obtain a qualitative comparison. The partial charge results are shown in Table 5. As expected, the oxygen atom has higher electronegativity than the nitrogen atom. This result is consistent with results of the partial charge calculation reported by Liu and Gu.[27] They calculated the partial charge of the oxygen and nitrogen atoms of nine 1,3-benzoxazine compounds. While the absolute values differ from our results, both studies consistently obtained the partial charge of the oxygen atom to be always more electronegative than the nitrogen atom of the oxazine ring. The pK_b of various amine with the percentage of Mannich base product from the reaction between 2,4-dimethylphenol (24DMP) coupled with different amine-based benzoxazine compounds (24DMP-R) is shown in Table 6. It was found that the higher the basicity of amine, the higher the Mannich base product concentration.

Accordingly, the initiation mechanism of benzoxazine is proposed in Scheme 12. The protonation can take place at either the nitrogen atom or the oxygen atom. However, from observation of the final product in this study, there is no evidence of compound **C** (Scheme 4), which is the proposed product from the nitrogen protonation. This means that the nitrogen protonation specie is more stable than the oxygen protonation specie. In other words, k_2 is greater than k_1. Therefore, we expected to see higher amounts of the desired dimer (E, Scheme 5) in the following order: aniline (**E4**) > 4-methylphenylamine (**E3**) > 4-methoxyphenylamine (**E2**) > methylamine (**E1**). However, we observed the opposite order: methylamine (**E1**) > 4-methoxyphenylamine (**E2**) > 4-methylphenylamine (**E3**) > aniline (**E4**). This result can be explained by understanding that the nitrogen protonation species is more stable in methylamine-based benzoxazine than in the aromatic amine-based benzoxazine, which makes the methylamine-based benzoxazine reaction proceed more slowly than the aromatic amine-based benzoxazine. Moreover, the aromatic amine-based benzoxazine has more reactive sites at the ortho- and para-positions allowing it to form the other compounds (Schemes 8 and 9). Consequently, we obtained high amount of desired structure from methylamine-based benzoxazine.

Scheme 12. Benzoxazine Monomer Initiation Mechanism



4. Conclusions

The polymerization initiation mechanism of benzoxazine system was proposed based on the evidence obtained by ^{1}H NMR spectroscopy and HPLC. The assignment of retention time was based on a model compound study. A detailed analysis of the final products provided information about the reaction mechanism. By combining experimental results with the basicity of amine substituent in benzoxazine monomer, the initiation mechanism of benzoxazine system has been proposed. The protonation initiation can take place at either the nitrogen atom or the oxygen atom. The nitrogen protonated specie is stable but the oxygen protonated specie is reactive. It is easier to obtain the desired product from methylamine-based benzoxazine. The benzoxazine structure breaks down via the cleavage of the O−C bond of the six-membered ring and forms a Mannich linkage dimer (E, Scheme 4). Nitrogen-containing structures, such as amine and imine and methylene bridge linkage phenol, were also found.

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Supporting Information Available: Figures showing HPLC chromatograms and ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Ning, X.; Ishida, H. *J. Polym Sci., Chem. Ed.* **1994**, *32*, 1121–1129. (b) Ishida, H.; Low, H. Y. *Macromolecules* **1997**, *30*, 1099–1106. (c) Ishida, H.; Ohba, S. *Polymer* **2005**, *46*, 5588–5595. (d) Ghosh, N. N.; Kiskan, B.; Yagci, Y. *Prog. Polym. Sci.* **2007**, *32*, 1344–1391.

(2) Knop, A.; Pilato, L. A. *Phenolic Resins: Chemistry, Applications and Performances, Future Directions*; Springer-Verlag: Berlin, 1985,; Chapter 9.

(3) (a) Chernykh, A.; Liu, J. P.; Ishida, H. *Polymer* **2006**, *47*, 7664–7669. (b) Takeichi, T.; Kano, T.; Agag, T. *Polymer* **2005**, *46*, 12172–12180. (c) Chernykh, A.; Liu, J. P.; Ishida, H. *Polymer* **2006**, *47*, 7664–7669. (d) Agag, T.; Takeichi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1878–1888. (e) Kiskan, B.; Yagci, Y.; Ishida, H. *J. Polym. Sci.; Part A: Polym. Chem.* **2008**, *46*, 414–420. (f) Nagai, A.; Kamei, Y.; Wang, X. S.; Omura, M.; Sudo, A.; Nishida, H.; Kawamoto, E.; Endo, T. *J. Polym. Sci.; Part A: Polym. Chem.* **2008**, *46*, 2316–2325. (g) Velez-Herrera, P.; Doyama, K.; Abe, H.; Ishida, H. *Macromolecules* **2008**, *41*, 9704–9714. (h) Chou, C. I.; Liu, Y. L. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6509–6517. (i) Chernykh, A.; Agag, T.; Ishida, H. *Polymer* **2009**, *50*, 382. (j) Chernykh, A.; Agag, T.; Ishida, H. *Polymer* **2009**, *50*, 3153–3157. (k) Chernykh, A.; Agag, T.; Ishida, H. *Macromolecules* **2009**, *42*, 5121–5127.

(4) (a) Guth, G. Ph.D. Thesis, University of Mulhouse, **1981**., (b) Schwob, M. J., Ph.D. Thesis, University of Mulhouse, **1983**.

(5) McDonagh, A. F.; Smith, H. *J. Org. Chem.* **1968**, *33*, 8–12.

(6) Riess, G.; Schwob, M. J.; Guth, G.; Roche, M.; Lande, B., *Advances in Polymer Synthesis*; Culbertson, M. B., Mcgrath, E. J., Eds.; Plenum: New York, 1985; pp27−49. This mechanism was first proposed by Burke (Burke, W. J. *J. Am. Chem. Soc.* **1949**, *71*, 609–612. Burke, W. J.; Bishop, J. L.; Glennie, E. L.; Bauer, W. N., Jr. *J. Org. Chem.* **1965**, *30*, 3423–3427) but later refined by Riess et al.

(7) Dunkers, J.; Ishida, H. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1913–1921.

(8) Wang, Y. X.; Ishida, H. *Polymer* **1999**, *40*, 4563–4570.

(9) Sudo, A.; Kudoh, R.; Nakayama, H.; Arima, K.; Endo, T. *Macromolecules* **2008**, *41*, 9030–9034.

(10) Hayakawa, T.; Osanai, Y.; Niizeki, K.; Haba, O.; Ueda, M. *High Perform. Polym.* **2000**, *12*, 237–246.

(11) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Boston, MA, 1998.

(12) Dunkers, J.; Ishida, H. *Spectrochim. Acta* **1995**, *51A*, 855–867.

(13) Ishida, H. U.S. Patent 5,543,516, **1996**.

(14) Ishida, H.; Roduriguez, Y. *J. Appl. Polym. Sci.* **1995**, *58*, 1751–1760.

(15) Wang, R. X.; You, X. Z.; Meng, Q. J.; Mintz, E. A.; Bu, X. R. *Synth. Commun.* **1994**, *24*, 1757–1760.

(16) Yudin, L. G.; Blokhin, A. V.; Bundel, Yu. G.; Simkin, B. Ya.; Terenin, V. I. *Zh. Org. Khim.* **1983**, *19*, 2361–2366.

(17) Joglekar, S. J.; Samant, S. D. *J. Indian Chem. Soc.* **1988**, *65*, 110–111.

(18) Li, C.; Lobkovsky, E.; Porco, J. A., Jr *J. Am. Chem. Soc.* **2000**, *122*, 10484–10485.

(19) Wan, X.-H.; Zhou, H.-B.; Xie, R.; Zhang, D.; Feng, X.-D.; Zhou, Q.-F. *Chem. Res. Chin. Univ.* **1999**, *15*, 182–187.

(20) Norte, M.; Rodriguez, M. L.; Fernandez, J. J.; Eguren, L.; Estrada, D. M. *Tetrahedron* **1988**, *44*, 4973–4980.

(21) Wolfrom, M. L.; Koos, E. W.; Bhat, H. B. *J. Org. Chem.* **1967**, *32*, 1058–1060.

(22) Chary, K. P.; Mohan, G. H.; Iyengar, D. S. *Chem. Lett.* **1999**, *11*, 1223–1224.

(23) Pethrick, R. A.; Thomson, B. *Br. Polym. J.* **1986**, *18*, 171–180.

(24) Dargaville, T. R.; De Bruyn, P. J.; Lim, A. S. C.; Looney, M. G.; Potter, A. C. *J. Polym. Sci. Part A: Polym Chem.* **1997**, *35*, 1389–1398.

(25) Hemvician, K.; Laobuthee, A.; Chirachanchai, S.; Ishida, H. *Polym. Degrad. Stab.* **2002**, *76*, 1–15.

(26) Brunovska, Z.; Liu, J. P.; Ishida, H. *Macromol. Chem. Phys.* **1999**, *200*, 1745–1752.

(27) Liu, X.; Gu, Y. *Sci. Chin., Ser. B* **2001**, *44*, 552–560.