Synthesis and Characterization of Structurally Uniform Model Oligomers of Polybenzoxazine

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ABSTRACT: The controlled synthesis of a series of polybenzoxazine model oligomers is described. A synthetic strategy is developed in which bromine is used as an ortho position blocking group allowing a stepwise synthesis of structurally uniform compounds. Debromination and subsequent hydrogenation is achieved in high yields by using activated Raney nickel catalyst in a methanol/aqueous base reaction medium. An effective hydrogenation procedure that does not require the addition of hydrogen gas is described. Polybenzoxazine oligomers as large as the model tetramer are synthesized. Applications for these strategies and procedures toward the synthesis of a variety of polybenzoxazine structures are described. Model oligomeric compounds of polybenzoxazines have been characterized by Fourier transform infrared spectroscopy (FT-IR), UV−visible spectroscopy, nuclear magnetic resonance spectroscopy (NMR), high performance liquid chromatography (HPLC), and size exclusion chromatography (SEC). Those oligomers used are the dimer, trimer, and tetramer of a monofunctional benzoxazine resin. Additional model compounds have also been synthesized. They are 2,6-bis(dimethylaminomethyl)-4-methylphenol and 2,6-bis(*N*-ethyl-*N*-methylaminomethyl)-4-methylphenol, which were used as model compounds to aid infrared band assignments.

Introduction

In the characterization of complex, high molecular weight polymer systems, much insight can be gained by analyzing oligomeric model compounds. We have synthesized a series of model oligomers of polybenzoxazine: a novel phenolic-type resin that has demonstrated excellent mechanical and physical properties. Although there has been great progress in our laboratory in understanding the physical properties,[1] processability,[2] chemical structure, reaction mechanisms, and vibrational spectra,[3,4] of many of these polybenzoxazines, there is a need for a deeper understanding of the correlation between the chemical structures and the physical properties. Exhaustive studies have been done on model oligomers of the traditional phenol−formaldehyde structures[5] in which the repeating unit is of the form [−Ph(OH)−CH_2−]. These oligomers have been thoroughly characterized in terms of their melting points,[6,7] hydrogen bonding,[8,9] acidity,[10−12] crystal structure,[13−16] conformation in solution,[17,18] and ability to complex metals and cations,[19,20] as well as their kinetics and reactivity toward electrophilic bromination.[8,21−24]

Similar oligomers have never been synthesized for the polybenzoxazine analogues. A direct comparison of the traditional phenolic oligomers and polybenzoxazine oligomers has limited validity. Polybenzoxazines have a repeating unit of the form [−Ph(OH)−CH_2−NR−CH_2−], a Mannich bridge structure which offers the polymer more flexibility than traditional phenolics as well as the obvious dimensional differences. Phenol−formaldehyde oligomers have shown both intra- and intermolecular hydrogen bonding among the hydroxyl groups which strongly affects many of its properties and conformations.[8] Similarly, polybenzoxazine oligomers have demonstrated such hydrogen bonding. It has been proposed that the hydroxyls are also able to hydrogen bond to the nearby hydroxyl groups[25] or the nitrogen lone pair of the Mannich bridge.[26] Both linear and cyclic phenol-formaldehyde oligomers have been shown to chelate metal cations because their acidic −OH groups can ionize when they are stabilized by intramolecular hydrogen bonds.[26,27] Polybenzoxazine oligomers will undoubtedly have similar interesting properties, which is further motivation to synthesize and study these model compounds.

A rational, stepwise synthesis of model oligomers with specific structures often requires some type of protective or blocking groups. In most of the work done in preparing traditional phenolic oligomers, linear or cyclic, halogens were used to block or protect ortho- or para-positions from undergoing substitution. The stepwise synthesis of cyclic phenolic oligomers, called calixarenes, was first developed by Hayes and Hunter[29] and thoroughly studied and extended by Kämmerer, Happel et al.[30] Many dehalogenation routes have been performed successfully under very mild conditions, at room temperature and atmospheric pressure.[31,32] Other stepwise synthetic strategies include the use of bromomagnesium salts and stereospecific coordination reaction mechanisms.[13−15] Although these procedures proved to be effective in traditional phenol/formaldehyde oligomer systems, many of these reactions are not directly applicable to polybenzoazine chemistry. In this work, many of the same strategies have been modified and developed for the polybenzoxazine system. A generalized strategy for a controlled, stepwise synthesis utilizing a protection/deprotection approach was taken. Bromine was used as a protecting group, and dehalogenation was performed with activated Raney nickel as a catalyst in a methanolic solution of sodium hydroxide. This debromination procedure produced reasonable yields even without the addition of hydrogen gas, making our procedure even simpler than those reported by Kammerer et al. Pojer also reported[33] successful catalytic hydrogenation of alkenes, alkynes, and aromatics using only Raney nickel and a hydrogen donor such as alcohol or sodium hypophosphite. For this initial study, we have synthesized oligomers based on *p*-cresol and methylamine as shown in Scheme 1. The strategies and

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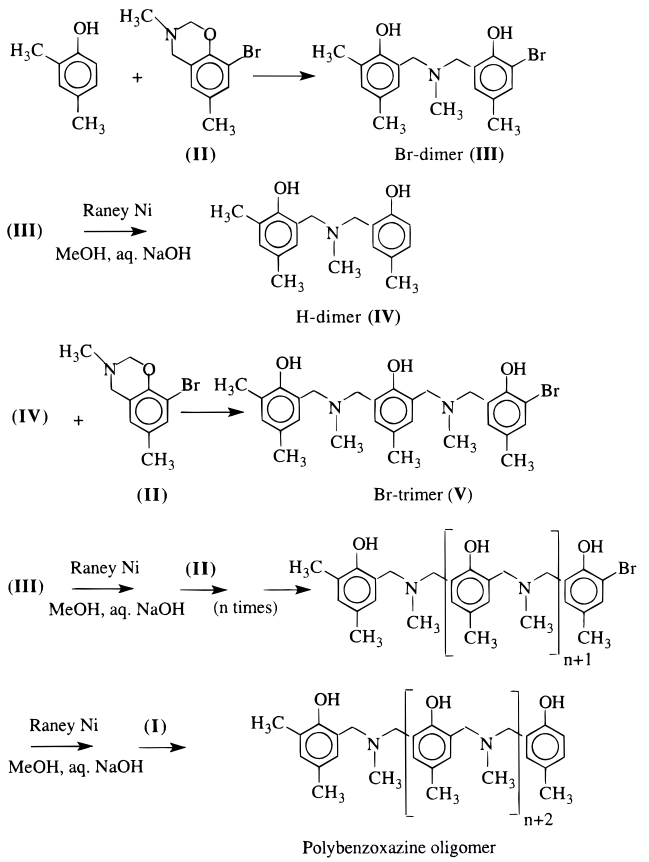
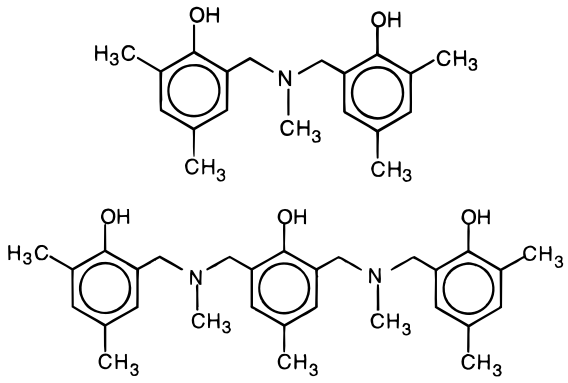
Scheme 1



procedures described here, however, can be used to build a variety of polybenzoxazine architectures—linear, cyclic, or branched.

Dunkers and Ishida synthesized the model dimer of polybenzoxazine based on 2,4-dimethylphenol and methylamine.[3] Their study included the crystal structure, nuclear magnetic resonance (NMR) analysis, and vibrational band assignments of both this dimer and its deuterated analogue. As a logical extension of that work, we have begun a series of higher oligomers also based on *p*-cresols and methylamine that can be characterized similarly.

Although the information derived from the characterization of the model dimer can certainly be applied to the trimer and tetramer compounds characterized in this work, differences arise due to the increased length of the model oligomer chain. The dimer represents two "end" groups of the polymer chain, while the higher oligomers contain internal phenolic groups that are joined by two bridge units via *ortho* substitution.



Characterization of a series of model oligomers of increasing size can provide a better understanding of the relationships between the structures and the properties of the final polymer.

Structurally uniform phenolic model oligomers have been characterized in a few different ways. The melting points of a series of linear phenolic oligomers, analyzed by Kämmerer and Niemann,[6] increase with increasing oligomer length, but show a dramatic melting point minimum at the pentamer structure. Linear oligomers rarely possess melting points above 250 °C, while cyclic phenolic oligomers, commonly called calixarenes, exhibit significantly higher melting points, as high as 412 °C.[7]

Many of the studies conducted on structurally uniform phenolic oligomers have been concerned with the effect that hydrogen bonding has on their physical properties. Böhmer et al. studied the acidity of a series of phenolic oligomers and found evidence with UV/visible spectroscopy that a chain of intramolecular hydrogen bonds can stabilize a monoanion in the oligomer.[11] Several studies have also shown[23] that intramolecular hydrogen bonding has a strong effect on the reactivity of the growing polymeric chain toward electrophilic bromination. Intramolecular hydrogen bonding has also been reported[8] as the reason phenolic oligomers conform into a pseudocyclic or pseudohelical shape. A phenolic chain that is curled into a ring will have a sterically hindered growing end, so polymerization reactivity and kinetics are affected.

Although a thorough characterization of the model dimer has already been accomplished,[3] a deeper understanding of the polybenzoxazine structure can be reached through the analysis of higher oligomers, such as the model trimer and tetramer. The FT-IR spectra of the trimer and tetramer are, understandably, more complex than that of the model dimer. A larger compound has a larger number of vibrational degrees of freedom, and therefore produces more vibrational bands. Additionally, the trimer and tetramer compounds have the "internal" phenolic units: the phenol groups attached to two Mannich bridges. To aid in the interpretation of these spectra, model compounds were synthesized and analyzed. These model structures will elucidate many of the "bridge modes" that were difficult to resolve even in the dimer.

Experimental Section

Synthesis. 2,4-Dimethylphenol, 99%, was purchased from Fluka Chemicals. All other reagents were purchased from Aldrich. The formaldehyde was 37 wt % in water, and the methylamine was 40 wt % in water. Raney Nickel (Ni/Al alloy, activity 2W) was purchased as a suspension in aqueous sodium hydroxide, pH 9. 2-Bromo-4-methyl phenol, 96%, was purified by vacuum distillation and *N*-ethylmethylamine (94%) was distilled before it was used; all other chemicals were used as received. The chemical structures were verified by ^{1}H nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FT-IR) spectroscopy. Oligomer purity was verified using high-performance liquid chromatography (HPLC).

Preparation of Benzoxazine Monomers: 3-Methyl-3,4-dihydro-6,8-dimethyl-2*H*-1,3-benzoxazine (I) and 3-Methyl-3,4-dihydro-6-methyl-8-bromo-2*H*-1,3-benzoxazine (II). For these reactions, the mole ratio of the reagents, amine: formaldehyde:phenol, was 1:2:1. The procedure described by Dunkers and Ishida[3] for the synthesis of monofunctional benzoxazines was followed with a few modifications:

I. A solution of 0.4 mol (32.5 g, 30.0 mL) of formalin in 50 mL of 1,4-dioxane was stirred with 0.2 mol (15.5 g, 17.2 mL) of methylamine solution in 20 mL of 1,4-dioxane while being

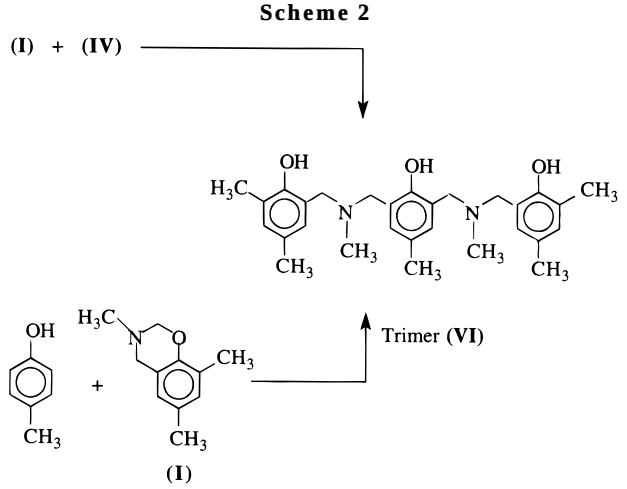
chilled in an ice bath for 20 min. To this mixture, 0.2 mol (24.4 g, 23.8 mL) of 2,4-dimethyl phenol in 50 mL of dioxane was added. The mixture was then heated, stirred, and allowed to reflux for 5 h. After the mixture was allowed to cool to room temperature, the solvent was removed by rotary evaporation. The resulting yellow oil was dissolved in 200 mL of ethyl ether and washed with 4 × 50 mL of 3 N aqueous sodium hydroxide solution to remove any unreacted −OH groups. The ethereal solution was dried over anhydrous sodium sulfate overnight. After the ether was removed by a rotary evaporator, the benzoxazine monomer was a very pale yellow liquid. Further purification was done by vacuum distillation (78−79 °C/0.5 mmHg) which produced a clear, colorless liquid at room temperature. With only slight chilling, **I** easily crystallizes into large spherulites that melt just below room temperature. Yield: 27.9 g, 79%. ^{1}H NMR ($CDCl_3$): δ 2.25 (Ar−CH_3), 2.59 (N−CH_3), 3.92 (Ar−CH_2−N), 4.79 (O−CH_2−N), 6.67−6.79 (Ar−H).

II. Formalin (0.2 mol of formaldehyde in 80 mL of dioxane) and methylamine solutions (0.1 mol of methylamine in 20 mL of dioxane) were mixed as before with chilling in an ice bath for 20 min. A solution of 0.1 mol (18.7 g) 2-bromo-4-methylphenol in 100 mL dioxane was added with continuous stirring. This mixture was heated to 70−75 °C and stirred for more than 48 h. After the solvent was removed under reduced pressure, a red-orange oil remained. After usual washing and purification, the brominated benzoxazine (**II**) easily crystallized from ethyl ether. After recrystalization in ethyl ether, clear, colorless cubic crystals formed: mp 50−51 °C. Yield: 18.9 g, 78%. ^{1}H NMR ($CDCl_3$): δ 2.24 (Ar−CH_3), 2.59 (N−CH_3), 3.92 (Ar−CH_2−N), 4.89 (O−CH_2−N), 6.80 (Ar−H).

Preparation of *N*-(2-Hydroxy-3-bromo-5-methylbenzyl)-*N*-(3,5-dimethyl-2-hydroxybenzyl)methylamine (III, Scheme 1, Br-Dimer). In a 50 mL round-bottomed flask, 8.17 g (0.0317 mol) of **II** was reacted with 3.87 g (0.0317 mol) of 2,4-dimethylphenol under argon. With magnetic stirring, the mixture was heated in an oil bath at 135−140 °C for 1.5 h. Near the end of the reaction, the increased viscosity often prevented the magnetic bar from stirring. After cooling to a hard, orange glassy resin, the mixture was slowly dissolved in ethyl ether. Almost immediately, a yellowish white powder formed. After filtration, recrystallization in 80:20 hexane/tetrahydrofuran produced white crystals. Yield: 80−85%. ^{1}H NMR ($CDCl_3$): δ 2.21 (−CH_3), 3.64 (−CH_2), 6.73−6.89 (Ar−H).

Debromination of III to Yield *N*-(3,5-Dimethyl-2-hydroxybenzyl)-*N*-(2-hydroxy-5-methylbenzyl)methylamine (IV, Scheme 1, H-Dimer). The brominated dimer, **III** (3.643 g, 0.01 mol), was dissolved in 30 mL of methanol with vigorous mechanical stirring. A solution of 0.9 g (0.016 mol) of sodium hydroxide in 5 mL of water was added. Approximately 4 g of wet Raney nickel was added with vigorous stirring. The hydrogenation was carried out at atmospheric pressure and room temperature for 8 h, during which additional Raney nickel and sodium hydroxide pellets were added occasionally. After the reaction was complete, the metal was removed by careful filtration. The filtrate was then acidified with dilute aqueous hydrochloric acid while stirring until the pH was between 5 and 6. Approximately 100 mL of aqueous solution was added. Much of the excess methanol was removed slowly by rotary evaporation until a white, gummy solid formed in the mainly aqueous solution. The entire mixture was transferred to a separatory funnel, and the hydrogenated phenolic product was extracted with 4 × 50 mL of chloroform. The gummy solid easily dissolved into the organic phase. The organic solutions were combined, and the chloroform was removed under reduced pressure. The remaining yellowish oil was dissolved in 15 mL ethyl ether with a few drops of ethanol and then dried over anhydrous sodium sulfate overnight. After filtration, the solution was slowly concentrated to half the volume. From this yellow solution, yellowish crystals formed. After recrystalization in THF/hexane, colorless, cubic crystals formed, mp 122−123 °C. Yield: 2.426 g, 85%. ^{1}H NMR confirmed the structure of a completely debrominated product (**IV**). ^{1}H NMR ($CDCl_3$): δ 2.22 (−CH_3), 3.65 (−CH_2−), 6.86−6.89 (Ar−H).

Scheme 2



Preparation of *N*,*N*-Bis(3-bromo-2-hydroxy-5-methylbenzyl)methylamine (VII, DiBr-Dimer). Preparation of the DiBr-Dimer is similar to Scheme 1 except for the ortho positions to the hydroxyl groups are symmetrically substituted by the Br atom. A 25 mL round-bottomed flask was filled with 1.751 g (6.79 mmol) of brominated benzoxazine **II**, 1.312 g (7.00 mmol) of 2-bromo-4-methylphenol, and 5 mL of methanol. The mixture was stirred and heated to a gentle reflux for 5 h. After the methanol was removed under rotary evaporation and the mixture was cooled, a yellow-orange hard resin remained. The resin was slowly dissolved with ethyl ether and a few drops of ethanol. The solution was cooled in a freezer, and large, white, cubic crystals formed. Several batches of crystals were collected by further concentrating the mother liquor after each crystallization, mp 117 °C. Total yield: 1.872 g, 61%. ^{1}H NMR ($CDCl_3$): δ 2.23 (−CH_3), 3.69 (−CH_2−), 6.84−7.21 (Ar−H).

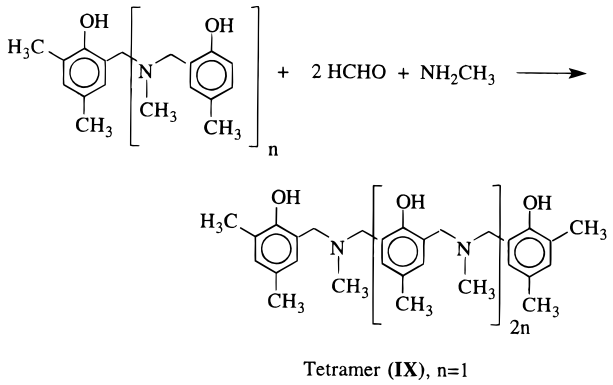
Preparation of 2-[*N*-(3-Bromo-5-methyl-2-hydroxybenzyl)-*N*-methylaminomethyl]-6-[*N*-(3,5-dimethyl-2-hydroxybenzyl)-*N*-methylaminomethyl]-*p*-cresol (V, Scheme 1, Br-Trimer). Br-Trimer was synthesized by combining 0.2062 g (0.722 mmol) of **IV** with 0.2010 g (0.830 mmol) of brominated benzoxazine (**II**) under argon. The mixture was warmed and stirred magnetically to melt the crystals. The fluid mixture was then heated to 135 °C with stirring for 2 h until a yellow viscous oil formed, which then cooled to a hard resin. Ethyl ether was added to slowly dissolve the mixture which produced a white chalky powder almost immediately. The precipitate was filtered, washed with ether, and then redissolved into warm THF. A fine white powder slowly reprecipitated, which was collected. ^{1}H NMR confirmed an asymmetric trimer structure, **V**, mp 126−127 °C. Yield: 0.247 g, 67%. ^{1}H NMR ($CDCl_3$): δ 2.19−2.23 (−CH_3), 3.66 (−CH_2−), 6.81−6.90 (Ar−H).

Preparation of 2,6-Bis[*N*-(3,5-dimethyl-2-hydroxybenzyl)-*N*-methylaminomethyl]-*p*-cresol (VI, Scheme 2, Trimer). Two different routes were followed.

Route A. A 0.2573 g (0.902 mmol) sample of **IV** was dissolved in 5 mL of dioxane, to which a small excess of benzoxazine **I** was added (0.1980 g, 1.1 mmol). One drop of concentrated HCl was added to the mixture, which was then stirred and refluxed for 48 h. A white precipitate had formed, which was collected and washed with ethyl ether. Size exclusion chromatography (SEC) and HPLC analysis implied a trimer, but with impurities. The sample was purified on silica gel with ethyl acetate/chloroform (70:30) as a mobile phase. Chromatographically pure trimer was confirmed by HPLC and ^{1}H NMR, mp 141−142 °C. Yield: 0.217 g, 52%. ^{1}H NMR ($CDCl_3$): δ 2.20 (Ar−CH_3), 2.23 (N−CH_3), 3.65 (−CH_2−), 6.66−6.88 (Ar−H).

Route B. An excess of benzoxazine **I** (11.35 g, 0.064 mol) was added to 1.52 g (0.016 mol) of *p*-cresol in 10 mL of 1,4-dioxane and one drop of concentrated HCl. The yellow mixture

Scheme 3



Tetramer (**IX**), n=1

was stirred and heated to reflux for 48 h. Most of the dioxane was then removed under reduced pressure, and the remaining oil was dissolved in ethyl ether. Over 3 days at room temperature, a white precipitate slowly formed which was collected by filtration and washed with ethyl ether and then chilled chloroform. HPLC analysis showed a trimer of greater purity than the original product in route A, but still with some impurity. The sample was purified on silica gel with ethyl acetate/chloroform (70:30) as a mobile phase to produce a fine white powder, mp 141−142 °C. NMR and FT-IR spectra imply a structure identical to that from route A. Yield: 5.155 g, 69.7%. ^{1}H NMR ($CDCl_3$): δ 2.20 (Ar−CH_3), 2.23 (N−CH_3), 3.65 (−CH_2−), 6.66−6.88 (Ar−H).

Preparation of *N*,*N*-Bis{2-hydroxyl-5-methyl-3-[(*N*-3,5-dimethyl-2-hydroxylbenzyl)-*N*-methylaminomethyl]}-methylamine (IX, Scheme 3, Tetramer). A mixture of 2 mmol of formaldehyde, 1 mmol of methylamine, and 0.5 mL of methanol was chilled in an ice bath with magnetic stirring for 20 min. The dimer compound **IV** (0.650 g, 2.25 mmol) was added along with an additional 0.5 mL of methanol. Once the phenolic compound dissolved, the solution was heated and refluxed for 12 h until a chalky precipitate was visible. The white powder was filtered and washed with ethyl ether and then cold chloroform. Purity was determined by HPLC, and the tetramer structure was confirmed by ^{1}H NMR; mp 190−191 °C. Yield: 0.444 g, 71%. ^{1}H NMR ($CDCl_3$): δ 2.21 (−CH_3), 3.66 (−CH_2−), 6.79−6.92 (Ar−H).

Preparation of 2,6-Bis(dimethylaminomethyl)-4-methylphenol (Model Compound A). Aqueous 40% dimethylamine (23.67 g, 0.21 mol) was added dropwise to 17.04 g (0.21 mol) of formalin in a three-necked flask equipped with a cold-water-cooled condenser, a thermometer, and a magnetic stir bar. The flask was chilled in a cold water bath to maintain a temperature of less than 30 °C. After the dimethylamine was added, the solution was stirred for 20 min. To this mixture was added 10.81 g (0.10 mol) of *p*-cresol. The mixture became milky as the aqueous and organic phases separated. After 15 min of thorough stirring, the mixture was heated over an oil bath until a reflux began at 92 °C. Reflux was maintained for 2 h. The solution was cooled, and the aqueous layer was separated from the light pink organic product. The remaining water was removed under vacuum with slight heating. Finally, the crude product was vacuum distilled using 0.5 mmHg vacuum. After a small amount of unreacted *p*-cresol was removed, a second small fraction distilled at 91−92 °C (0.5 mm) as a clear liquid. This was later analyzed by ^{1}H NMR as the monoaminomethylated product, 2-(dimethylaminomethyl)-4-methylphenol. The third large fraction distilled at 114 °C as a clear liquid. The purity and structure of the desired product, a diaminomethylated phenol, was confirmed by ^{1}H NMR ($CDCl_3$), δ 2.22 (Ar−CH_3), 2.27 (12H, N−CH_3), 3.48 (4H, Ar−CH_2−), 6.82 (2H, Ar−H).

Preparation of 2,6-Bis(*N*-ethyl-*N*-methylaminomethyl)-4-methylphenol (Model Compound B). The procedure was similar to that for the dimethylamine compound, but using once-distilled *N*-ethyl-*N*-methylamine instead. After 2 h of heating, both the aqueous and the organic phases were yellowish. The two phases were separated, and the crude product was dried slowly under vacuum with warming. The monoaminoalkylated product distilled at 124−125 °C/0.5 mm while the desired product distilled at 142 °C/0.5 mm as a yellowish viscous liquid. The purity and structure was confirmed by ^{1}H NMR ($CDCl_3$), δ 1.12 (6H, CH_2−CH_3), 2.22 (3H, Ar−CH_3), 2.24 (6H, N−CH_3), 2.50 (4H, CH_2−CH_3), 3.60 (4H, Ar−CH_2−), 6.80 (2H, Ar−H).

Characterization. The infrared spectra were taken on a Biorad FTS 60/896 Fourier transform infrared spectrometer which was equipped with a liquid nitrogen cooled, linearized MCT (mercury−cadmium−telluride) detector with a specific detectivity, D^*, of 1×10^{10} cm Hz$^{1/2}$ W^{-1}. After a 20 min dry nitrogen purge, 256 coadded scans were taken at a resolution of 1 cm^{-1}. The samples were either thin liquid films between two KBr plates or finely ground powder dispersed in KBr and pressed into pellets.

The ^{1}H nuclear magnetic resonance (NMR) spectra were collected on a Varian XL-200 NMR spectrometer with a proton frequency of 200 MHz. Typically, 100 scans were coadded in the final spectrum. The ^{13}C NMR spectra were acquired on a Varian Gemini-200 with proton decoupling. Because the polybenzoxazine oligomers are sparingly soluble in many of the solvents typically used for NMR, dilute samples were analyzed. To achieve a high signal-to-noise ratio in the ^{13}C NMR experiment, it was necessary to collect nearly 9500 scans of the dilute solutions. In both sets of experiments, deuterated chloroform was used as the solvent and tetramethylsilane (TMS) was used as an internal standard.

The UV/visible spectra were taken with a Hewlett-Packard HP8450A diode-array spectrophotometer. A deuterium lamp was used as a light source for typical integration times of 5 s. Quartz cuvettes with the dimensions 1 cm × 1 cm × 5 cm held sample solutions made with high-performance liquid chromatography (HPLC) grade tetrahydrofuran (THF).

Size exclusion chromatography (SEC) was performed with a Waters 510 HPLC pump, U6K universal injector, Waters 440 UV detector fixed at 254 nm, and a Waters 410 refractive index detector. Three columns, μ-styragel 1000, 100, and 50 nm, were connected in series and used with HPLC grade chloroform as the eluent. The flow rate was maintained at 1 mL/min throughout the experiment.

High-performance liquid chromatography (HPLC) was similarly done with a Waters 510 HPLC pump, U6K universal injector, and a Waters 484 tunable UV detector tuned to 290 nm to best detect phenolic groups. The column used was Whatman Partisil 5, a silica gel column, with a surface area >350 m^2/g and an average pore diameter of 8.5 nm. A chloroform/ethyl acetate mixture of 3-to-1 volume ratio was used as the eluent, and the flow rate was maintained at 1 mL/min throughout the experiment.

Results and Discussion

Synthesis. After about 12 h of reaction time, high yields can be found of 2-methylaminomethyl-4-methyl-6-bromophenol, which is a Mannich base and a probable precursor to the benzoxazine structure. Only after 48 h do we find high concentrations of benzoxazine in the reaction mixture. Although brominated benzoxazine formation is less facile than that of some of the alkyl-substituted benzoxazines, the advantage lies in the fact that benzoxazines derived from halogenated phenols are very reactive and will easily add to a second phenolic unit. Synthesis of **III**, a brominated dimer, produces extremely low yields when **I**, an alkyl-substituted benzoxazine, is reacted with 2-bromo-4-methylphenol. The reason for this is an electronic effect: bromine on the phenolic substrate deactivates the aromatic ring toward attack by the carbonium ion electrophile. The use of the more reactive brominated benzoxazine and 2,4-dimethylphenol, by contrast, produces better yields,

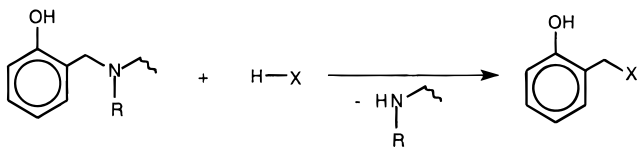
because the dimethylphenol is much more receptive to electrophilic substitution.

The debromination reactions produced surprisingly good yields even without the addition of hydrogen gas as it is done in traditional hydrogenolysis. Attempts to debrominate/hydrogenate the brominated oligomers using hydrogen gas produced yields similar to those found with the simpler method reported in this paper. We propose that traditional hydrogenolysis over Raney nickel may be too effective of a hydrogenating method: it is possible for the Mannich bridge itself to be substituted by a hydrogen. The reaction mixture in these hydrogen gas experiments smelled very strongly of methylamine, which would be released in a reverse Mannich reaction. Activated Raney nickel contains hydrogen directly adsorbed onto the metal. Hydrogen gas can also be released by the oxidation of residual aluminum from the nickel−aluminum alloy that is used to make the Raney catalyst:

$$2Al + 2OH^- + 2H_2O \rightarrow 2AlO_2^- + 3H_2$$

An additional source of hydrogen is the reaction solvents, methanol and water, which can act as proton donors in the presence of Raney nickel.[33] Attempts to reduce brominated benzene to brominated cyclohexane by adding hydrogen gas over Raney nickel often produce debrominated cyclohexane as side product.[34] This unwanted "over-hydrogenation" is generally avoided by using low pressures of hydrogen gas. For the polybenzoxazine structures, using only the hydrogen provided by the catalyst and the reaction system has proven to be effective in the substitution of bromine for hydrogen.

In studying this debromination reaction, lower yields were found when the reaction was conducted in aqueous base solution, which is a reaction condition popular in traditional phenolic oligomer literature. Low yields of the brominated starting material were found, which would suggest that the Mannich bridge structure of these oligomers cannot withstand the aqueous alkaline conditions. Water is a powerful nucleophile, and it can possibly deaminate the Mannich bridge structure of polybenzoxazine oligomers. A hydrogen-active substrate, H−X, can attack the amino group of the Mannich bridge which would result in a nucleophilic substitution reaction:[35]



Best results were found when the reaction was conducted in methanol, a less effective nucleophile, and either sodium or potassium hydroxide. A few milliliters of water was added to aid in dissolving the base and the salts produced in the substitution. An additional drawback of using a completely aqueous solution for debromination is the oligomers' limited solubility in even strongly basic water.

Several different strategies were adopted that use the protection/deprotection technique to build oligomers in a stepwise manner. These strategies are depicted in Schemes 1, 2, and 3. Scheme 1, synthetic strategy A, describes the controlled oligomer growth in one direction. In other words, the oligomer becomes one repeat unit longer with every protection/deprotection cycle. On the other hand, similar to Scheme 1 but in an attempt to synthesize unsubstituted ortho positions at both terminal groups, oligomers can be grown in two directions with two repeat units being added to each side of the molecule with each step. Thus, oligomers with even numbered units are synthesized, and larger molecules can be grown in fewer reaction procedures.

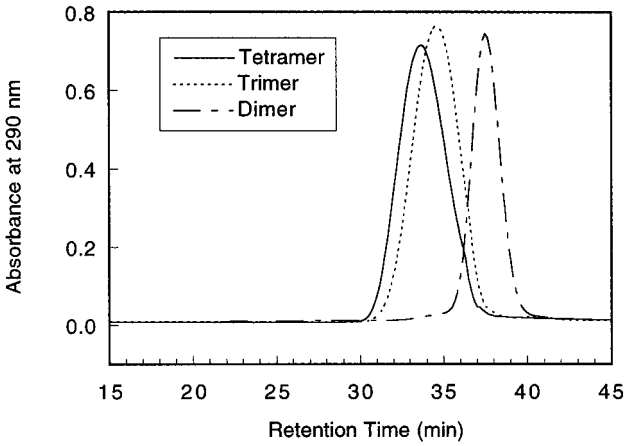


Figure 1. SEC chromatograms of polybenzoxazine model dimer (37.50 min), trimer (34.67 min), and tetramer (33.67 min).

The structurally uniform model trimer was produced by two different methods as shown in Scheme 2. One approach involves the debromination of Br-Dimer and the addition of benzoxazine (**I**). After three reaction steps, the final yield of trimer has an average value of 35%. The second, more direct approach involves the addition of two equivalents of **I** to *p*-cresol. Both methods produce trimer, but the second approach involves only one reaction step and a higher final yield of about 70%.

Scheme 3 describes a slight variation on benzoxazine chemistry. Two phenolic substrates with open ortho positions may be joined with a Mannich bridge via a direct Mannich reaction using formaldehyde and a primary amine. In order for the resulting oligomer to be structurally uniform, identical phenolic substrates must be coupled, and that phenolic unit must only have one open ortho position. In other words, in every reaction, there must only be one possible resulting structure, resulting in smaller amount of side products or unreacted starting material which are relatively easy to separate from the desired product. Synthesizing a distribution of molecular weights with every step would require tedious and often difficult separation techniques. Due to the strong inter- and intramolecular hydrogen bonding of these types of compounds, fractional crystallization of the various compounds poses a formidable challenge.

Characterization. HPLC and SEC. The purity of the model trimer and tetramer were first confirmed with size exclusion chromatography (SEC). For the sake of comparison, the trimer, tetramer, and model dimer chromatograms are shown together in Figure 1. As expected, the model tetramer has the shortest retention time since it has the highest molecular weight of the three. The retention times were 33.67 min for the tetramer, 34.67 min for the trimer, and 37.50 min for the model dimer. Chloroform is used in these experiments because the higher oligomers are very sparingly soluble in THF.

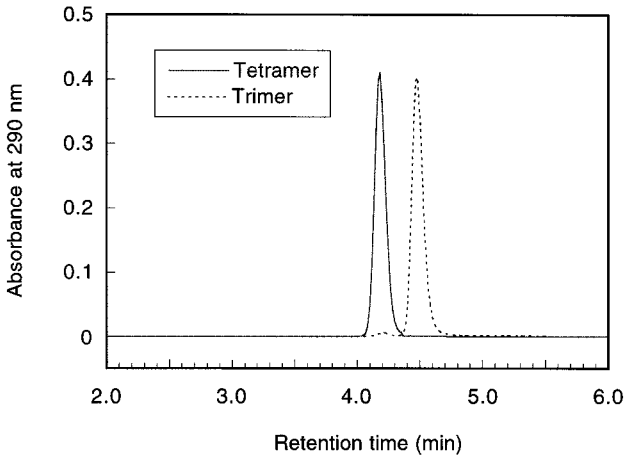


Figure 2. HPLC chromatograms of polybenzoxazine model trimer (4.5 min) and tetramer (4.2 min).

Most SEC experiments use a molecular weight calibration curve based upon polystyrene standards. Polystyrene is not an appropriate molecular weight standard for polybenzoxazines or other phenolic compounds because their hydrogen-bonding behavior will strongly affect the hydrodynamic volume of the phenolic chain. The concentration of the polybenzoxazine sample solution will also influence the shape of the resulting chromatogram because intramolecular hydrogen bonding will dominate at low sample concentations, while intermolecular hydrogen bonding will come into play at higher concentrations. A more accurate and useful SEC analysis would require the hydrogen bonds to be broken by changing one or all of the hydroxyl groups to a non-hydrogen-bonding functionality. This hydrogen bonding is also responsible for the broadening of the chromatograms as a result of a distribution of similarly hydrogen-bonded species. Structurally uniform oligomers can, in this way, serve as molecular weight standards for the SEC analysis of unknown polybenzoxazine samples.

A better separation of the oligomers can be obtained from high performance liquid chromatography (HPLC), shown in Figure 2. The silica gel columns used in these experiments separate the components according to their interaction with the acidic adsorbent. The tetramer elutes at 4.2 min, while the trimer elutes at 4.5 min. These short retention times, as well as the reported hyperacidity of traditional phenolic oligomers, imply that these oligomers are acidic and do not have a strong association with the silica gel column. As expected, the tetramer would be more acidic because the additional benzoxazine unit can help stabilize a labile proton via a longer chain of intramolecular hydrogen bonds.

^{1}H and ^{13}C NMR Spectra. The proton NMR spectra of the model trimer and tetramer are displayed in Figures 3 and 4, and a summary of their assignments are found in Table 1. The ^{1}H NMR resonances for the model dimer were assigned by Dunkers and Ishida,[3] and these assignments are fully supported by the spectra of the trimer and tetramer compounds. In both the trimer and the tetramer, the different methyl protons, the aminomethyls and the aromatic methyls, produce different peaks. The methyl groups on the aromatic rings produce a proton resonance at 2.19 ppm, while the methyls attached to the nitrogen of the bridge structure produce a easily discernible peak at 2.22 ppm. The theoretically calculated shifts[36] for these two types of methyl groups predict that the N−CH_3 protons would

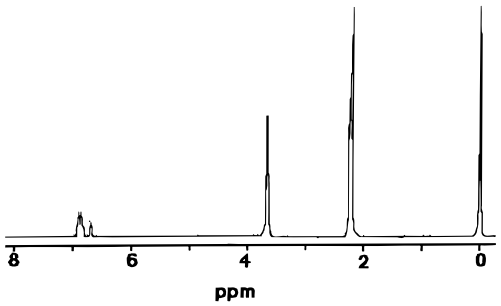


Figure 3. ^{1}H NMR spectrum of polybenzoxazine model trimer.

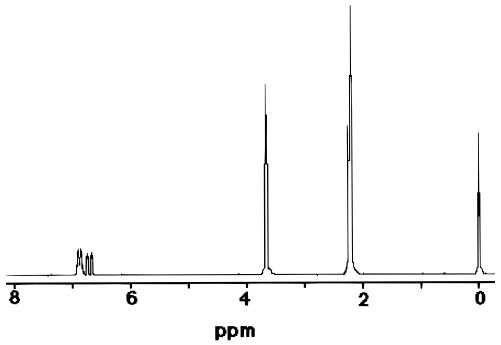
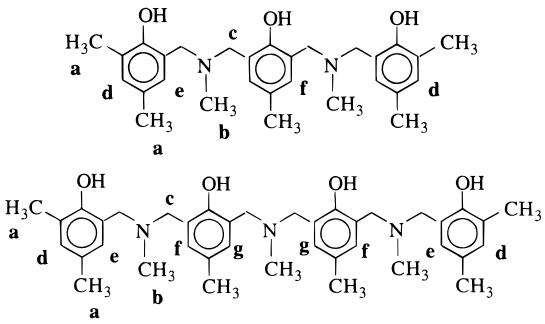


Figure 4. ^{1}H NMR spectrum of polybenzoxazine model tetramer.

Table 1. ^{1}H NMR Assignments of Model Polybenzoxazine Trimer and Tetramer



proton	trimer, ^{1}H (ppm)	tetramer, ^{1}H (ppm)
a	2.19	2.19
b	2.22	2.22
c	3.66	3.65
d	6.67	6.68
e	6.88	6.74
f	6.88	6.85
g		6.92

appear upfield from the aromatic methyl protons; the integral of these peaks, however, imply the above assignment. The methylenes of the Mannich bridge structures, [−CH_2−NR−CH_2−], give rise to a resonance at 3.65 ppm in both compounds.

The model trimer contains three sets of magnetically inequivalent aromatic protons which should produce three peaks, while the model dimer contains only two magnetically distinguishable protons. In the trimer spectra, however, only two peaks are clearly resolved at 6.67 and 6.88 ppm. The latter peak, which is relatively broad, produces an integral that implies four protons. It is possible that two different pairs of protons are buried under this peak at 6.88 ppm. The model tetramer produces four sets of magnetically inequivalent aromatic protons which appear at 6.68, 6.74, 6.85, and

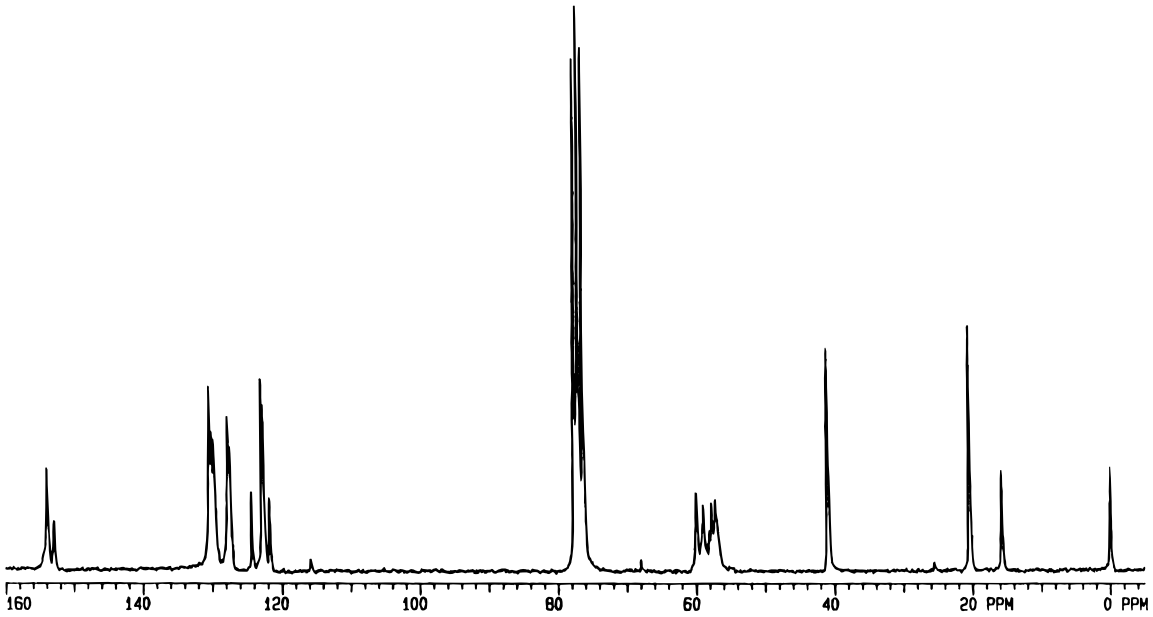
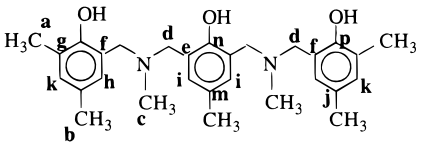


Figure 5. ^{13}C NMR spectrum of polybenzoxazine model trimer.

Table 2. ^{13}C NMR Assignments for the Model Polybenzoxazine Trimer



carbon	trimer, ^{13}C (ppm)	carbon	trimer, ^{13}C (ppm)
a	15.8	**h**	127.7
b	20.4	**i**	127.7
c	41.0	**j**	129.7
d	58.0 (center)	**k**	130.0
e	122	**m**	130.3
f	123	**n**	153
g	124	**p**	154

6.92 ppm. The assignments were made based on those of the dimer and trimer and on the calculated chemical shifts. The integral of these peaks suggests a total of eight aromatic hydrogens.

The ^{13}C NMR spectra of the model trimer shown in Figure 5 also contains many of the same peaks found in the spectra of the model dimer. Some of the differences appear because the longer oligomers give rise to slightly different magnetic environments, especially for the atoms of the internal phenolic units. A summary of the carbon assignments is found in Table 2. The methyl carbon on the end of the trimer, carbon **a**, appears at 15.8 ppm, in the same position as in the model dimer. The *para* methyls and the amine methyls, carbons **b** and **c**, give rise to peaks at 20.4 and 41.0 ppm, respectively. Again, these resonances are supported by the assignments made for the model dimer.

The carbons of the trimer Mannich bridges produce several peaks centered around 58 ppm, whereas the Mannich bridge carbons of the model dimer produced only one resonance at 59.3 ppm. Many peaks appear in this region because, unlike the model dimer, the trimer and higher oligomers can assume many different conformations in solution due to increased chain length and the possibility for rotation about C(Ar)−C(methylene) bond. Preliminary molecular modeling results as well as FT-IR data imply that the most energetically favorable trimer conformation is one in which the first and last C(Ar)−O bonds are pointing in opposite directions which permits strong intramolecular −OH- - -N hydrogen bonding. Other conformations are possible, however, which is evident by the appearance of a tetrad of peaks in this area of the spectrum. The ^{13}C NMR spectra of linear ortho-connected phenolic oligomers also showed an increasing number of peaks with increasing chain length.[37] Similarly, because of the different polybenzoxazine conformations, many of the nuclei that were magnetically equivalent in the more "linear" model dimer are no longer equivalent in the trimer or tetramer. The aromatic region of the ^{13}C NMR spectrum of the model trimer contains twice as many peaks as there were in the spectra of the dimer. Conformational effects can also affect the magnetic environments of the aromatic carbons. Because there are a variety of similar carbons in the aromatic region, many of the peaks are overlapped. Theoretical ^{13}C shifts were calculated by adding shielding constants of the appropriate groups to the carbon of interest.[36] Using the calculated values and the assignments made by Dunkers and Ishida for the model dimer, assignments were made for the aromatic carbons of the model trimer.

On the basis of ^{13}C NMR assignments made for the model benzoxazine monomer and dimer[3,4] and on a calculated shift value of 121.8, the resonance at 122 ppm was assigned to carbon **e**. Carbon **f**, which appears on the terminal phenolic units, appears at 123 ppm. These two carbons were differentiated and assigned accordingly because carbon **e** should appear slightly upfield from carbon **f**. This is because carbon **e** is influenced by two alkylamine substituents (the Mannich bridges) in the C1 and C3 positions, which will have the effect of a slight upfield shift.[36] The resonance at 124 ppm was assigned to carbon **g**, the "end" carbon, since that peak matches both the calculated shift and the dimer assignment. Carbons **h** and **i** have calculated shifts of 127.4 and 127.7 ppm, and their peaks are nearly indistinguishable in the spectrum. The peak at 127.7 ppm was assigned to these two carbons, and the analogous dimer carbon was found at 128 ppm. The relatively large intensity of the peak further supports its assignment

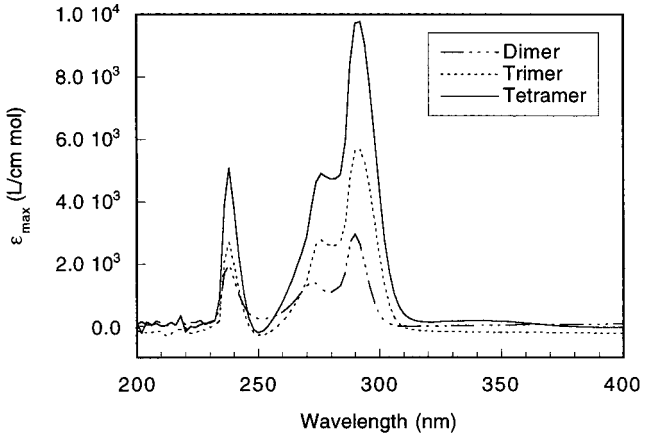


Figure 6. UV/visible spectra of polybenzoxazine model dimer, trimer, and tetramer, plotted as molar absorptivity vs wavelength. All solutions are 0.025 g/L in THF.

to an unsubstituted carbon: aromatic carbons with substituents suffer from longer T_1 times and diminished nuclear Overhauser effect (NOE) which produces lower peak intensities. The third unsubstituted carbon, carbon **k**, also produces a peak of relatively high intensity at 130 ppm. This value is also in good agreement with the calculated shift, 129.9 ppm, and the dimer analogue.

The carbons *para* to the hydroxyl group, carbons **j** and **m**, produce two different peaks because of the effect of the two Mannich bridge units attached to the central phenolic ring. On the basis of this slight structural difference, the calculated shifts for **j** and **m** are 130.4 and 130.5 ppm, respectively. For this reason, the resonances appearing at 129.7 and 130.3 ppm are assigned to carbons **j** and **m**. The difference between the calculated and experimental chemical shifts for carbon **j** was larger than of the other differences.

Finally, the carbons attached to the hydroxyl groups, carbons **n** and **p**, appear at 153 and 154 ppm, respectively. They were assigned based on calculated shifts of 152.2 and 153.4 ppm. Carbon **n** of the central phenolic unit has two alkylamine substituents in both C2 positions; this will cause the carbon **n** resonance to appear slightly upfield from that of carbon **p** for the same reasons as explained above.

Ultraviolet/Visible (UV/Vis) Spectra. The UV/vis spectra of the model dimer, trimer, and tetramer are shown in Figure 6, and a list of the band wavelengths, λ_{max}, and their molar absorptivities, ϵ_{max}, are found in Table 3. Although these spectra were taken from solutions of THF, a relatively nonpolar solvent, the electronic transitions occur at higher wavelenths than those expected for phenolic compounds. Phenol is characterized by three aromatic $\pi \rightarrow \pi^*$ transitions: an allowed ethylenic (E_1) transition around 180 nm, an allowed ethylenic (E_2) transition at approximately 210 nm, and a benzenoid (B) transition near 270 nm.[38] In the following UV/vis experiments, we were concerned only for the transitions occurring above 200 nm. In the polybenzoxazine oligomers, the E_2 transition is shifted to 238 nm, and the B transition occurs at 291 nm. Bathochromic shifts, or red shifts, can occur in polar solvents or when the phenol is substituted with a chromophore, such as a carbonyl or nitro group. Large red shifts are seen in phenols that are converted to the corresponding anion in alkaline solutions. In this case, both the E_2 and the B bands increase in intensity, a hyperchromic effect, because the anion offers an additional pair of nonbonding electrons to interact with the π-electron system. This same effect is seen in phenolic oligomers that are known to intramolecularly hydrogen bond very strongly.[11] The more dissociated the proton is from the phenolic oxygen, the stronger the bathochromic shift.

A phenolic hydrogen which is "shared" evenly with the nitrogen of the Mannich bridge would create a

Table 3. UV/Visible Spectra λ_{max} Values, Molar Absorptivities (e_{max}) and Absorptivities (a_{max}) for Polybenzoxasine Dimer, Trimer, and Tetramer[a]

	λ_{max} (nm)	assignt	e_{max} (L/(cm mol))	a_{max} (L/(cm g))
dimer	238	E_2	1990	6.65
	272		1440	4.81
	290	B	2960	9.89
	232	$n \rightarrow \pi^*$	75.5	0.202
trimer	238	E_2	2700	5.83
	266	(shoulder)	839	1.81
	276		2770	5.99
	291	B	5680	12.3
	340	$n \rightarrow \pi^*$	96.6	0.209
tetramer	238	E_2	5090	8.12
	266	(shoulder)	1930	3.08
	276		4910	7.84
	291	B	9780	15.6
	340	$n \rightarrow \pi^*$	190	0.303

[a] All samples are THF solutions at a concentration of 0.025 g/L.

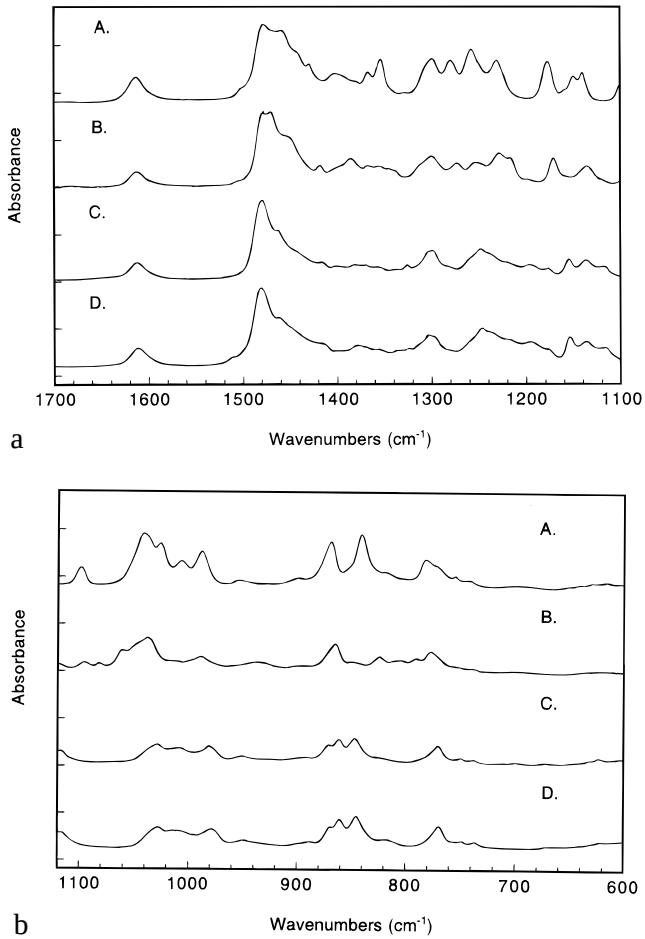
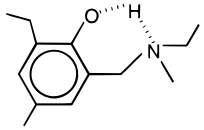


Figure 7. FT-IR spectra of model compound A (A), model compound B (B), polybenzoxazine model trimer (C), and model tetramer (D): (a) 1700−1100 cm^{-1} region; (b) 1100−600 cm^{-1} region.

Table 4. Infrared (cm^{-1}) Assignments of Model Compound A (Based on Dimethylamine), Model Compound B (Based on Ethylmethylamine), and the Polybenzoxazine Model Trimer and Model Tetramer

dimethylamine	ethylmethylamine	trimer	tetramer	assignment
	2875 m			CH_2–CH_3 stretch
2856 s	2838 m	2830 m	2830 m	CH_2 stretch
2814 m	2815 m			N−CH_3 stretch
	2790 s	2797 m	2796 m	CH_2 stretch
2776 s				CH_2−N−$(CH_3)_2$ stretch
1501 sh	1505 sh	1510 sh	1510 sh	C−N−$(CH_3)_2$
1469 vs	1470 vs	1461 s	1462 s	CH_2 asymmetric deformation
1430 m	1418 w	1417 w	1417 w	N−CH_3 asymmetric deformation
1354 m	1355 w	1357 vw	1356 vw	CH_2 scissors
	1345 w	1337 vw	1335 vw	
1299 m	1300 m	1298 m	1298 m	CH_2 twist
1280 m	1273 w	1282 vw		
1258 s	1253 w	1259 w	1259 w	N−CH_3 symmteric deformation
		1236 w	1235 m	
	1217 m			C−N−C asymmetric deformation
	1200 vw	1196 vw	1196 w	C−N−C asymmetric deformation
1177 m	1171 m	1177 vw	1176 vw	C−N−C asymmetric deformation
1159 sh	1159 sh			C−N−C asymmetric stretch
1119 vw	1118 sh	1117 vw	1117 w	C−N stretch, N−CH_3 rock
1099 w	1096 vw			
	1082 vw	1078 vw	1078 vw	
		1028 w	1028 w	
988 m	989 w	988 w	995 vw	N−CH_3 rock
	975 vw	981 w	986 vw	N−CH_3 rock
949 vw	944 vw			
	937 vw		938 vw	
900 vw	897 vw	895 vw	899 vw	bridge
		891 vw	889 vw	bridge
855 m		861 m	861 m	bridge
841 s	848 vw	847 m	845 m	C−N−C symmetric stretch
	824 w	828 vw		
818 vw	812 vw		817 vw	
	805 vw			
782 w	791 w	785 vw	784 vw	
755 vw	755 vw	754 vw	757 vw	bridge
		750 vw	748 vw	bridge
742 vw	739 vw	737 vw	737 vw	bridge
		717 vw	716 vw	
		673 vw	672 vw	

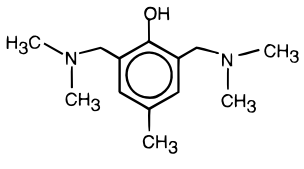
system that can be thought of as a six-membered ring. This would have the same effect as other fused aromatic or heteroaromatic ring systems: electronic transitions of longer wavelengths and higher intensities.



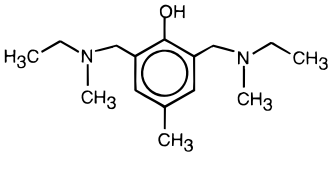
These same bathochromic and hyperchromic shifts are seen in the UV/vis spectra of phenolic oligomers of increasing chain length, but not to the extent seen in the polybenzoxazine oligomers. In polynuclear phenolic compounds, these λ_{max} and ϵ_{max} changes are due to an increase in n−π conjugation with increasing oligomer length[36] and, in part, to intramolecular hydrogen bonding.[11] In polybenzoxazines, the nitrogen of the Mannich base allows very strong intramolecular hydrogen bonding and provides an auxochromic heteroatom with a lone pair of electrons, both of which profoundly affect the compound's electronic transitions.

Fourier Transform Infrared Spectra of Model Oligomers. A complete infrared analysis and band assignment of the model trimer and tetramer is not entirely necessary since many of the bands have already been discussed and assigned in the analysis of the model dimer. However, the trimer and tetramer structures give rise to several unique bands due to their increased chain length. The higher oligomers will obviously contain several Mannich bridge structures. Even in the model dimer, the vibrational bands that were due to the single bridge structure were difficult to analyze and many of the assignments were questionable. As the spectra of the higher oligomers are inspected, the vibrational bands from the end groups will be less prominent, and the vibrations from the "chain" structure will become easier to decipher.

To aid further in the analysis of the bridge modes, model compounds were synthesized and characterized. These model compounds are 2,4,6-trisubstituted phenols that have [−CH_2−NR_2] substituents in the two positions *ortho* to the hydroxyl. Model compound A is 2,6-(dimethylaminomethyl)-4-methylphenol, and model compound B is 2,6-bis(*N*-ethyl-*N*-methylaminomethyl)-4-methylphenol whose structures are shown as follows.



(A)



(B)

The fingerprint region of the FT-IR spectra of the two model compounds, the trimer, and the tetramer are displayed in parts a and b of Figure 7.

When the four spectra are compared, there are many similar spectral features. This is expected since all four

compounds are similarly substituted phenols. A discussion of the various aromatic vibrational modes would be redundant due to a previous work, and the spectra of the model compounds do support the aromatic assignments made by Dunkers and Ishida.[3] Many of the C−N−C stretching modes and N−CH_3 modes that were found in the spectra of the model phenols can be attributed to bands in the dimer, trimer, and tetramer. These are summarized in Table 4.

Conclusions

The synthesis of structurally uniform oligomers of polybenzoxazine has been made possible by modifying many of the synthetic methods used for similar phenol−formaldehyde model oligomers. A controlled, stepwise synthesis is achieved by protecting the desired open ortho positions during the addition of each consecutive monomer units. Deprotection, in the form of debromination, is very effective when activated Raney nickel is used in alkaline methanolic solution, even without the addition of hydrogen gas. This simple and gentle hydrogenation method removes the bromine protecting group without attacking the Mannich bridge structure. With each step of the synthesis, it is crucial that there be only one phenolic structure possible so that tedious separations may be avoided. With the procedures developed here, many different structurally uniform compounds may be synthesized to aid in the characterization and deeper understanding of this new class of resin, polybenzoxazine.

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