

**AN INVESTIGATION OF THE EFFECTS OF METHOXY SUBSTITUTION
ON THE THERMOMECHANICAL PROPERTIES OF LIGNIN-BASED
BISPHENOL DERIVED POLYMERS**

by

Dakota Hanemann-Rawlings

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Honors Degree in Chemical Engineering with Distinction

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BISPHENOL DERIVED POLYMERS**

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ABSTRACT

Bisphenol A-based methacrylate resins and composites are used for many medical applications such as dental fillings and medical adhesives. Recent information regarding adverse health effects of BPA, however, has initiated interest in safer and more environmentally friendly alternatives. This work focuses on assessing the feasibility of utilizing lignin-derived bisguaiacols as alternative monomers for dental resins. Three different lignin based bisguaiacol monomers, bisguaiacol F, bisguaiacol P, and bisguaiacol S, are investigated, with each monomer differing in the number of methoxy groups. The bisguaiacol monomers are synthesized and functionalized with methacrylates capable of free radical polymerization. Ultraviolet light-activated radical polymerization is then used in the production of copolymer systems with the medically relevant reactive diluent Triethyleneglycol dimethacrylate (TEGDMA) for each respective monomer. The conversion of the polymerizations are studied using in situ FTIR analysis. Additionally, the thermomechanical properties of each respective polymer system are investigated using DMA analysis. The thermomechanical properties of the polymer systems derived from each monomer are compared and the effect of methoxy substitution is analyzed. The applicability of these monomers in dental resins is then assessed by comparing the resulting polymer properties with those of bis-GMA/TEGDMA systems.

Chapter 1

INTRODUCTION

1.1 Bisphenol A

Bisphenol A (BPA) is an extremely versatile industrial monomer that is commonly employed in the production of polycarbonate plastics, epoxy resins, and methacrylate dental resins. The increase in demand for high performance plastics in the materials and medical industries has resulted in a high demand for this versatile monomer, reaching 2.2 million tons in 2009.¹ Recent studies, however, have shown that BPA has various adverse health effects that make it dangerous for human use and environmental exposure.¹ BPA is classified by the FDA as an endocrine disrupting chemical (EDC) because it has particular chemical similarities to estrogen that allow it to bind to estrogen receptors. This results in a host of different potential health effects such as various cancers, behavioral changes, brain development issues in infants and fetuses, and reproductive issues. Consequently, there is significant interest in the development of a monomer that lacks the adverse health and environmental effects but retains the high performance properties of BPA.

The high performance thermal, mechanical, optical, and electronic properties of BPA based polymers are commonly attributed to the high aromaticity and the diol nature of the monomer.¹ Consequently, current efforts to develop a possible substitution for the BPA have focused on synthesizing monomers with a similar bisphenol structural skeleton.¹

1.2 Dental Resins

Composite dental restorative materials are an immensely useful and versatile class of biomaterials. This novel class of compounds has largely replaced metal fillers in the past few years due to their superiority in terms of convenience and aesthetics. Modern dental composites are comprised of two main components; a polymerizable organic resin and an inorganic filler.⁹ The filler consists of a high surface area particulate material that serves to improve several properties including the modulus, thermal expansion behavior, and polymerization induced shrinkage of the polymer resin. The resin is often composed of two or more polymerizable monomers that can be cured using visible light in the presence of photoinitiators. While there are a host of different resins that have been successfully utilized in dental restoration, there is still a great demand for composite restorative materials with improved properties. As with many biomaterials, dental composites require a specific set of high performance properties including low polymerization shrinkage, thermal expansion similar to that of bone, resistance to fracture, abrasion, and wear, high conversion, low toxicity, marginal chemical leakage, high modulus and high glass transition temperature.⁹ One of the common methacrylate monomer systems that is employed in dental resins is 2,2 bis[4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl]propane (bis-GMA) and triethylene glycol dimethacrylate (TEGDMA), where bis-GMA offers high aromaticity which lends to high modulus and glass transition temperature and TEGDMA serves as a reactive diluent that reduces viscosity and improves the maximum achievable conversions. This resin system is often cured using a visible light initiated radical photoinitiator.¹⁰ This study will focus on the evaluation of several alternative polymerizable dental resin materials. The glass transition temperature, monomer

conversion, and storage and loss modulus of the materials will be compared to test their applicability in dental materials.

While the bis-GMA/TEGDMA system offers many beneficial properties, there are several concerns that remain regarding this particular monomer mixture. bis-GMA is derived from BPA, and many works have shown that bis-GMA based dental composites leach BPA resulting in adverse health effects.¹⁷ It is also desired to develop monomers that are derived from more sustainable sources.

1.3 Lignin Model Compounds

In an effort to develop sustainable alternatives to useful industrial aromatic compounds such as styrene and BPA, recent work has focused on the development of small molecule aromatic compounds derived from lignin.⁴ Lignin is the second most abundant naturally occurring organic compound. It is produced in industrial quantities as a waste product in various industries including the timber and pulp manufacturing.⁴ The molecular structure of lignin consists of a complex network of aromatic compounds and can be readily processed, for example with pyrolysis, to produce a host of small molecule aromatic hydrocarbons with various functional groups including methoxy, alkene, aldehyde, and hydroxyl groups.⁴ A select few of these compounds are currently purified and sold in the chemical industry, however, the wide variety of aromatic compounds that can be produced from lignin have been largely unexplored as potential feedstocks for bio-based chemical production. One notable exception is the use of methacrylated lignin-based monomers in block copolymer compounds.¹¹

A majority of the aromatic compounds that are derived from lignin contain one or more methoxy moieties. Furthermore, there is little understanding on how methoxy

groups in lignin based monomers effect the properties of the overall polymer. In assessing the feasibility of using lignin derived molecules in polymer materials, it is important to have an understanding of how methoxy substitution effects the properties of resulting polymers. The lignin model compounds that are used in this work differ solely in the number of methoxy groups they contain. One of the main focuses of this study is to evaluate the effects that the methoxy substitution of monomers have on the resulting polymer systems.

1.4 Thesis Overview

While recent years have witnessed an increase in the development of polymers derived from bio-based resources, little work has concentrated on the development of renewable, highly aromatic monomers that could potential replace BPA. This study investigates the synthesis and characterization of several bisguaiacol compounds that are derived from lignin model compounds. These bisguaiacols have unique promise in their practicality as industrial monomers because their synthesis utilizes industrially relevant processes, including the use of widely available catalysts and industrial processes. Additionally, due to their bisaromatic structure, it is expected that these lignin based bisguaiacols will impart favorable thermomechanical properties when incorporated into polymer resins.² To fully understand the industrial utility of these promising monomers, however, it is important to have a detailed understanding of how the chemical structure of these monomers effects the properties of the resulting polymer networks. This thesis concerns the development of synthesis, functionalization, polymerization, and characterization methods for three lignin derived bisguaiacol monomers. In particular, three lignin derived bisguaiacols are synthesized with each differing in the number of methoxy groups. These monomers

are cured in medically relevant systems and the differences in conversion and thermomechanical properties are evaluated.

Hydroxyl groups and aldehyde groups, which are common to lignin derived aromatics, serve as functional handles allowing for many possible functionalization schemes. Industrially, hydroxyl containing chemicals such as BPA can be functionalized readily with epoxides, methacrylates, and acrylates. Holmberg *et al.* demonstrated the ability to functionalize lignin derived phenols with polymerizable methacrylate groups through facile esterification reactions with methacrylic anhydride.⁴ Since lignin derived bisguaiacols contain two hydroxyl groups, they can be functionalized with two polymerizable methacrylate groups, allowing them to be used as a cross linker in thermoset resins. Such crosslinkers are analogous to the petroleum derived dimethacrylated bisphenol monomers currently used in medical applications, the most common of which is 2,2-bis[p-(3-methacryloxy-2-hydroxypropoxy)phenyl]propane (bis-GMA). These compounds can be readily copolymerized with a reactive diluent and cured using a photoinitiator. Photocured bis-GMA/TEGDMA resins are favorable for dental applications due to their high modulus, high polymerization conversion, and high glass transition temperature as discussed by Bowman *et al.*⁵ Accordingly, the lignin-based dimethacrylate monomers copolymerized with TEGDMA in this study are compared to analogous bis-GMA copolymerized with TEGDMA to serve as a point of comparison.

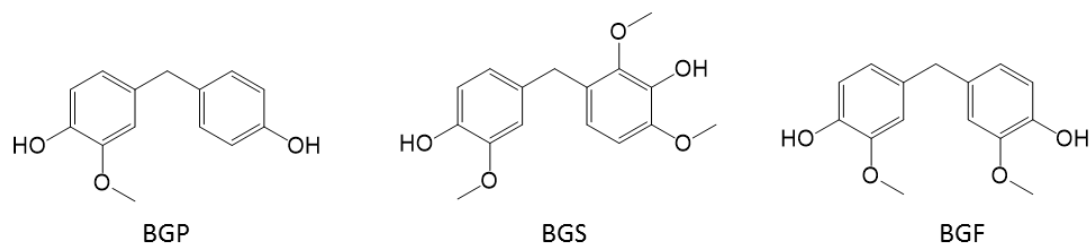


Figure 1.1 Structures of lignin derived bisguaiacol monomers

This thesis focuses on three particular lignin based bisguaiacols; bisguaiacol F (BGF), bisguaiacol P (BGP), and bisguaiacol S (BGS). The structures of these compounds are shown in Figure 1.1. Following functionalization, BGS and BGP are copolymerized with the medically relevant reactive diluent triethylene glycol dimethacrylate (TEGDMA). Photopolymerization methods are then utilized to synthesize a methacrylate thermoset. The thermomechanical properties of the resulting thermoset are evaluated. Dynamic mechanical analysis (DMA) is used to determine the glass transition temperature (T_g) of the polymer networks, along with the elastic storage and loss moduli. The monomer conversion is investigated using in situ FTIR analysis. The properties of each respective polymer network are then compared to evaluate the effect of aromatic methoxy substitution on the thermomechanical properties and the conversion. These polymers are also compared to the petroleum based analogue, bis-GMA, to gain information on the feasibility of using lignin derived bisguaiacol dimethacrylates for dental applications.

Chapter 2

TECHNIQUES

2.1 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) is used in this study to evaluate the thermomechanical properties of the various cured resins that are synthesized. In general, most polymeric materials exhibit stress-strain behavior that is both viscous and elastic in nature. Polymer materials can vary greatly in the degree of viscosity and elasticity that they exhibit, and a detailed characterization of a material with respect to these parameters can reveal a great deal of information about the thermal, structural, and mechanical nature of a polymer.¹¹ The most common method of analysis for these polymeric properties involves the application of an oscillatory stress and the measurement of the resulting strain, or the application of an oscillatory strain and the measurement of the resulting stress, along with the measurement of the lag that occurs between the stress and the strain due to the viscoelastic nature of the material.¹¹ An oscillatory strain on a material can be expressed as a function of time as follows:

$$\gamma = \gamma_0 \sin(\omega t)$$

In which γ is the strain, γ_0 is the strain amplitude, ω is the frequency, and t is time.

The force, F , exerted by an elastic material is known to be proportional to strain. In the presence of an oscillatory strain, this can be expressed as:

$$F = F_0 \sin(\omega t)$$

For a fluid material, the force exerted in response to a strain is proportional to the time derivative of the strain and can be expressed as follows for an oscillatory strain:

$$F = F_0 \cos(\omega t)$$

The modulus of a viscoelastic material, which is a measure of the overall force divided by the strain, can thus be determined with an addition of the fluid and elastic force components as follows:

$$E^* = E' \sin(\omega t) + E'' \cos(\omega t)$$

In which E^* is referred to as complex modulus, E' is referred to as the elastic, or storage, modulus and E'' is referred to as the viscous, or loss modulus. A useful output of DMA testing is the tangent of the loss modulus over the storage modulus, expressed as $\tan(\delta)$.¹¹

One important method in DMA analysis is the temperature sweep, in which the complex modulus is determined over a range of temperatures. Since polymers exhibit glassy behavior at low temperatures and rubbery behavior at high temperatures, temperature ramps in DMA can be used to sweep through the glassy and the rubbery regions for a material and this can in turn be used to determine the rheological glass transition temperature, corresponding to the maximum in the $\tan(\delta)$ value.¹¹ In this study, DMA measurements are used to determine rheological glass transition temperature of each synthesized polymer along with the complex modulus at relevant temperatures.

2.2 Neutron Magnetic Resonance Spectroscopy

Neutron Magnetic Resonance spectroscopy (NMR) is a robust molecular characterization technique that is commonly employed in the determination of molecular structure, mixture compositions, reaction conversions, and in several other applications. In this study, NMR is utilized to confirm the molecular structures of reaction products. Additionally, NMR is used to determine the purities of synthesized reactants.¹³

NMR relies on magnetic properties of an atomic nucleus to deduce information about particular atoms in molecules. Atoms with odd atomic masses (e.g. ^1H , ^{13}C , ^{15}N) possess spin, resulting in the presence of a magnetic field. A magnetic nucleus can possess either an “up” spin or a “down” spin depending on the spin axis orientation. In the absence of an external magnetic field, both the up spin and the down spin are degenerate and are at thermal equilibrium, and accordingly, half the population of magnetic nuclei will be in the “up” state and half will be “down” state. When a strong external magnetic field is applied, however, the “up” state has a lower energy because it is aligned with the direction of the magnetic field.¹³ A photon of electromagnetic energy can be used to promote a nuclei in the lower energy state to the higher energy state given that the energy of the photon matches the energy of the gap between the up and down states. Upon changing from an up state to a down state, a nuclei will exhibit a precession due to the angular momentum of the nucleus and the torque exerted by the external magnetic field. The frequency of this precession is proportional to the strength of the external magnetic field and to the strength of the magnetic moment of the nucleus.

The resonant frequency of the nucleus can be measured by the application of a varying radio frequency to the sample until an energy is detected from a nuclear resonance. After this resonance state energy is pulsed to the NMR sample, the pulse can be stopped and the absorbed energy is released from the nucleus as a transient wave representing the nuclear precession. An NMR spectrometer measures the decay of this wave emission over time, and this decay data can then be Fourier transformed into a spectrum. The x axis of the spectrum corresponds to the energy of the resonant frequency.¹³ The resonant frequency of an atom depends on the electronic

environment of an atom in a molecule because the bonding electrons in a molecule possess a small magnetic field that modifies the magnetic character of a nucleus slightly. This small variation is termed the chemical shift and it is displayed in units of parts per million (ppm).¹³ The chemical shifts of peaks in a spectrum can be used to gain information about the identity and structure of atoms in a molecule. Additionally, since ^1H is the most abundant isotope of hydrogen, in ^1H NMR the integration of a peak can be approximated as being proportional to the molar quantity of an atom. Among other things, this phenomenon can be used to determine purities and concentrations in a sample.¹³

2.3 Infrared Spectroscopy

Infrared (IR) spectroscopy is an extremely important tool in molecular characterization and can be used for a multitude of different applications such as reaction dynamics, compositional characterization, determination of molecular structure, etc. IR spectroscopy generally involves radiation between 7000 and 400 cm^{-1} .¹⁴ This energy range is on the order of the vibrational energies of intermolecular bonds. Accordingly, particular frequencies of IR radiation will be absorbed by intermolecular bonds with the corresponding energy.¹⁴ The vibrational energy of an intermolecular bond is dependent on the atoms involved in the bond, the chemical environment of the atoms in the bond, and the type of bond (e.g. double, single, triple, etc.). Thus, in an IR spectrum, which shows the absorbance of a sample over a range of frequencies, certain frequencies at which IR radiation is absorbed can be correlated to particular bonds in a compound. Furthermore, molecules have several modes of vibration including stretching, bending, etc. As a result, each individual bond may absorb more than one frequency of IR radiation.¹⁴

In an IR spectrum, the absorbance can be correlated to the concentration of a compound. Absolute concentrations can be determined using Beers law. More relevant, however, is the determination of relative concentrations between the same molecules in different spectra, which can be used to determine the percent increase or decrease in the molar concentration of a bond. In this work, monomer resins containing methacrylate functional groups are polymerized using photoinitiated radical polymerization.¹⁵ The polymerizations are conducted in situ in an IR spectrometer and spectra for the sample are collected at set time intervals during the curing process. The absorbance of the peak for the double bond in the methacrylate group is recorded as a function of time, and this is used to determine the conversion of the monomer as a function of time. The double bond in the methacrylate has several frequencies of absorption, however, in this work the peak in the near IR region is used as shown in the example spectrum below. Since the polymer samples used in this study are relatively thick, the near IR peak is ideal because it has a low absorbance. This follows the work of Lovell et. al.¹⁵

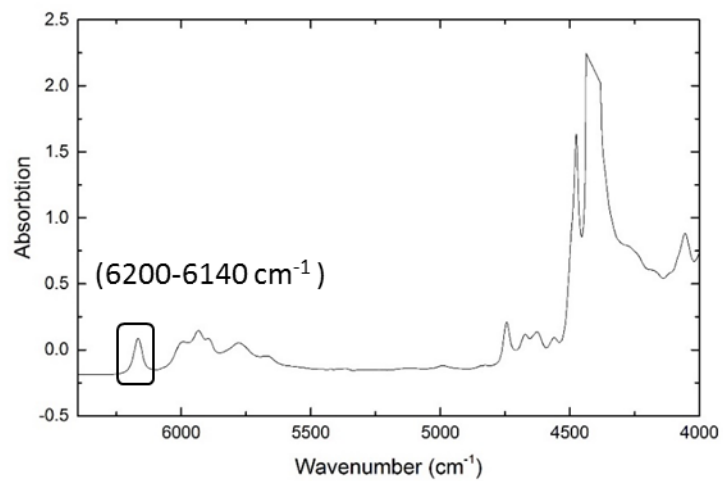


Figure : Example FTIR spectrum of bis-GMA/TEGDMA sample displaying near IR peak used in determining double bond conversion

Chapter 3

MONOMER SYNTHESIS

The main focus of this work is to synthesize novel bisguaiacol monomers using readily available lignin model compounds, and to subsequently incorporate these bisguaiacol monomers into thermoset polymer networks. The method for synthesis of bisguaiacol compounds involved an electrophilic aromatic substitution reaction in which vanillyl alcohol, an aromatic compound derived from lignin, is protonated using an acid catalyst and subsequently acts as a nucleophile which can then substitute a hydrogen on an aromatic ring. In this study, vanillyl alcohol was catalytically reacted with three lignin-derived aromatic compounds; phenol, guaiacol, and syringol. This results in the production of the majority products shown in Figure 1.1. Since these bisguaiacols do not contain any functional groups that can be readily polymerized via radical polymerization, the bisguaiacol monomers were functionalized with methacrylate groups capable of radical polymerization as detailed by Stanzion et al.⁶ Phenolic hydroxyl groups can be reacted with either methacrylic anhydride or methacryloyl chloride through esterification reactions to result in a polymerizable methacrylate functional group. These techniques were applied in the methacrylation of each bisguaiacol to form the monomer products shown below.

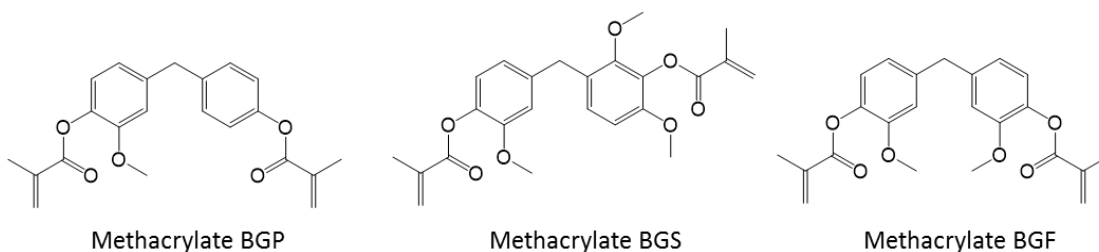


Figure 3.1: Chemical structures of dimethacrylated bisguaiacol monomers synthesized and polymerized in this study.

3.1 Reagents

Vanillyl alcohol (98+%), guaiacol (99+%), syringol (99+%), methacryloyl chloride (97%, contains 200 ppm monomethyl ether hydroquinone as stabilizer), bisphenol A (99+%) and trimethylamine (99+%) were purchased from Sigma Aldrich and used as received. Amberlyst ion exchange resin catalyst (15 hydrogen form) was purchased from Sigma Aldrich. Phenol (99+%) was purchased from Fischer Scientific. Compressed argon was obtained from Keen Compressed Gas Co. (99.998%).

3.2 Methods

In synthesizing polymerizable lignin-based bisguaiacol monomers, the diaromatic diol was first synthesized via the reaction of two aromatic lignin model compounds, and this was then functionalized with polymerizable methacrylate groups.

3.2.1 Bisguaiacol Synthesis

BGP, BGF, and BGS were synthesized in a neat reaction via an electrophilic aromatic substitution reaction involving vanillyl alcohol and guaiacol, phenol, or syringol. Hydroxyl and methoxy substituents are *ortho* and *para* directing in electrophilic aromatic substitution, where the *para* position is preferred, with hydroxyl

groups being stronger directing groups than methoxy groups. Therefore, the product in which the vanillyl alcohol substitutes the hydrogen *para* to the hydroxyl group dominates for reactions with phenol and guaiacol. For reactions with syringol, however, the product in which the vanillyl alcohol substitutes *meta* to the hydroxyl group dominates because of the *ortho para* directing nature of the two methoxy groups.

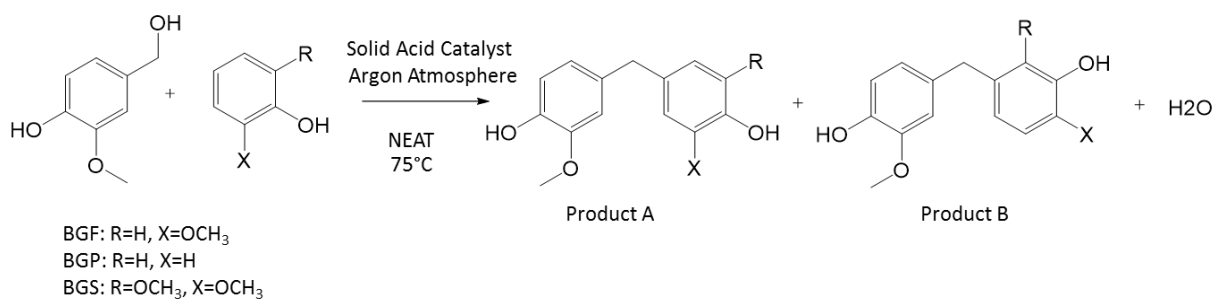


Figure 3.2: Reaction scheme for reaction of vanillyl alcohol with phenol, guaiacol, or syringol to form bisguaiacol. Product B is favored in reactions that involve syringol while Product A is favored in reactions that involve guaiacol or phenol

Bisguaiacol F, as displayed in Figure 1.1, was synthesized via an acid catalyzed electrophilic aromatic substitution reaction of vanillyl alcohol and guaiacol. A 500 mL round bottom flask was equipped with a magnetic stir bar, a catalytic amount of Amberlyst solid acid exchange resin (10 wt% of vanillyl alcohol), 50 g of vanillyl alcohol, and an excess of guaiacol (4.5 molar equivalents of vanillyl alcohol). The reaction vessel was sealed with a septum and sparged for 40 minutes with argon gas. The flask was then placed in a 75 °C oil bath for 30 minutes. The reaction mixture was then allowed to cool and the solid catalyst was filtered using a Buchner funnel. The excess guaiacol in the reaction mixture was then removed using a single step

batch distillation at 100 °C and reduced pressure. Recrystallization was then utilized to remove the additional guaiacol along with the other reaction byproducts by mixing the concentrated reaction product with 1L of heptane and heating to approximately 70 °C in a 2 L beaker. The heptane phase was then decanted into a second beaker and allowed to cool to approximately 4 °C for one day resulting in the precipitation of crystalline BGF. The crystalline BGF was then removed and dried using an oven under reduced pressure at 60 °C. The resulting BGF product was then characterized using ^1H NMR (400.13 MHz, 16 scans at 298.2 K) on a Bruker AV-600 spectrometer. The resulting spectrum showed chemical shifts that are consistent with the expected chemical structure. Additionally, the NMR spectrum was used to determine a compound purity of 85 mol%.

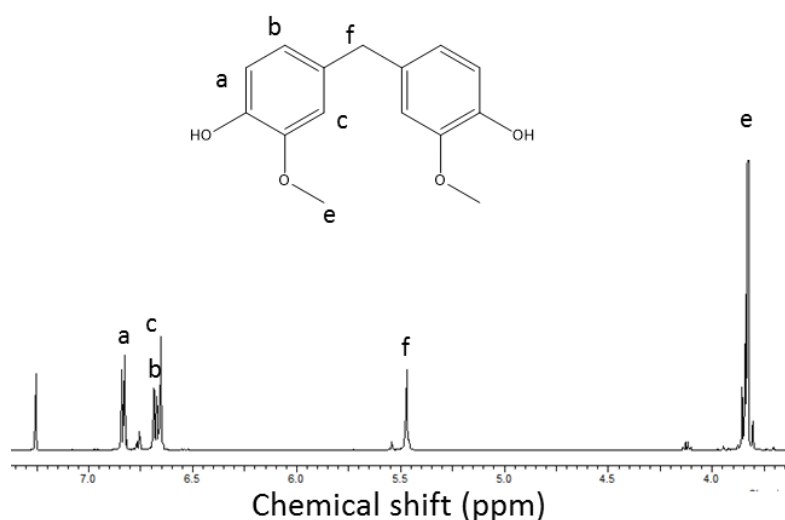


Figure 3.3: ^1H NMR of purified BGF using Bruker AV-600 spectrometer (400.13 MHz, 16 scans at 298.2 K in CDCl_3)

BGP and BGS were synthesized using methods similar to those used in the synthesis of BGF by replacing the guaiacol with phenol for BGP and syringol for BGS. A 500 mL round bottom flask was equipped with a magnetic stir bar, a catalytic amount of Amberlyst solid acid exchange resin (30 wt% of vanillyl alcohol), 10 g of vanillyl alcohol, and an excess of phenol or syringol (4.5 molar equivalents of vanillyl alcohol). The reaction vessel was sealed with a septum and purged for 40 minutes with argon gas. The flask was then placed in an 80 °C oil bath for 50 minutes. The reaction mixture was then allowed to cool and the solid catalyst was filtered using a Buchner funnel. The excess phenol or syringol in the mixture was then removed using a single step batch distillation at 80 °C and reduced pressure. The resulting mixture was then further purified using flash column chromatography with a binary solvent system of ethyl acetate and hexane. The resulting product was then characterized using ¹H NMR (400.13 MHz, 16scans at 298.2 K) using a Bruker AV-600 spectrometer. The spectrum agreed with the expected chemical structure and a purity of 99% by mole was estimated using peak integration for both BGS and BGP. The spectrum for BGP is shown in Figure 3.4 and the spectrum for BGS is shown in Figure 3.5.

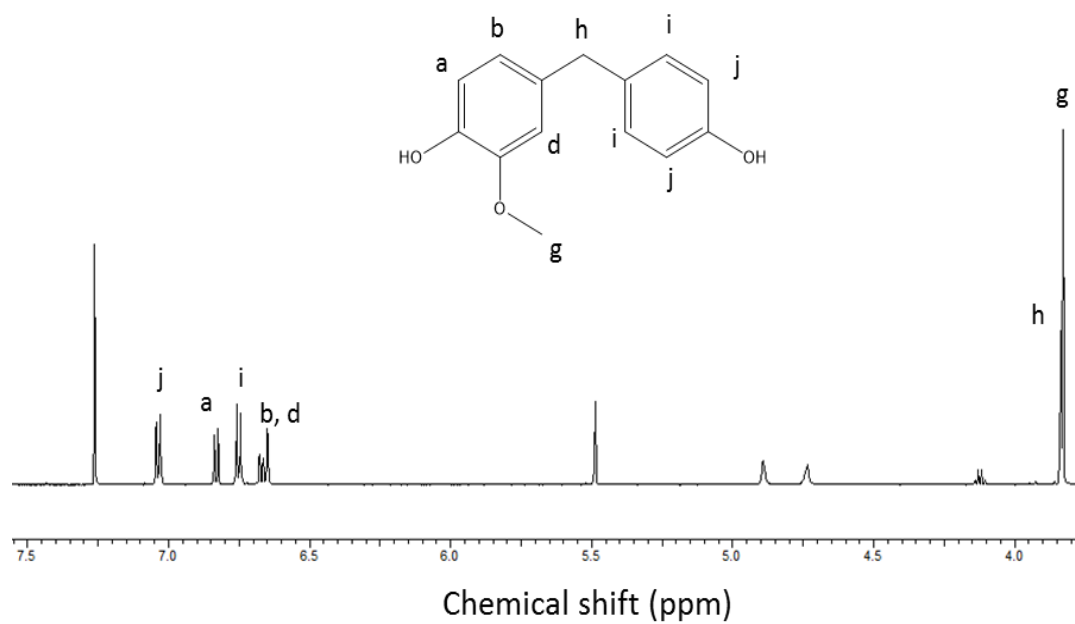


Figure 3.4: ¹H NMR of purified BGP using Bruker AV-600 spectrometer (400.13 MHz, 16scans at 298.2 K in CDCl₃)

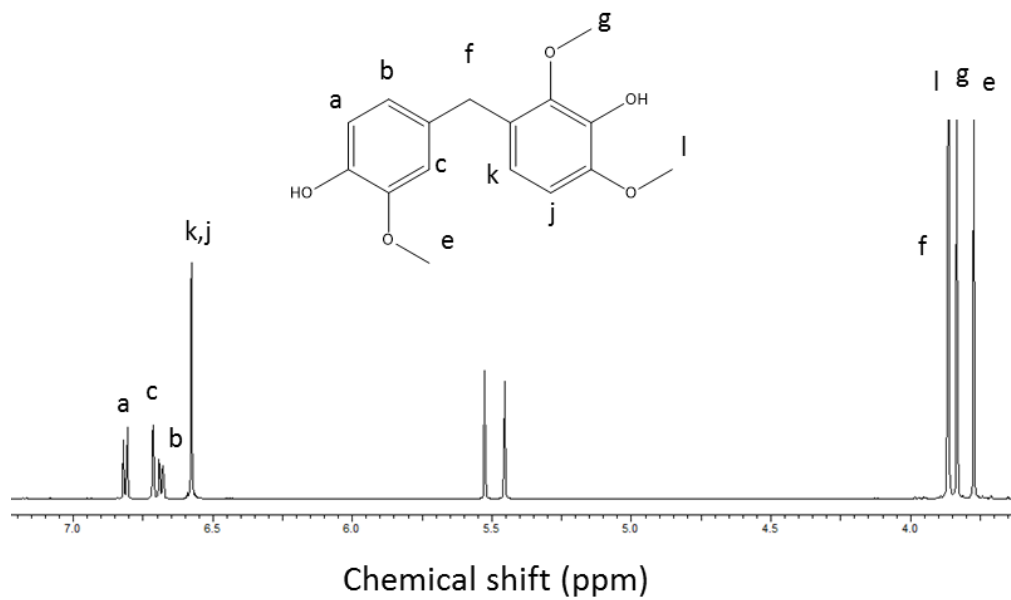


Figure 3.5: ¹H NMR of purified BGS using Bruker AV-600 spectrometer (400.13 MHz, 16scans at 298.2 K in CDCl₃)

As discussed above, the majority product that was observed from the reactions involving phenol and guaiacol resulted from the vanillyl alcohol substituting the hydrogen para to the hydroxyl group on the aromatic ring of phenol and guaiacol. This is expected because hydroxyl groups are known to be para directing. For the reaction involving syringol, however, the majority product resulted from vanillyl alcohol substituting the hydrogen atom *meta* to the hydroxyl group on the aromatic ring of syringol. This can may be attributed to the *ortho para* directing nature of the methoxy groups, which may have outweighed the strong *para* directing nature of the hydroxyl group.

3.2.2 Bisguaiacol Functionalization

Since the bisguaiacol monomers synthesized above do not contain any readily polymerizable functional groups, the monomers were difunctionalized with methacrylate groups to allow for radical polymerization. This functionality was chosen because it is easily applied to hydroxyl moieties and it is commonly used in dental materials. Along with the three lignin based bisguaiacols, BPA was also methacrylated to serve as a control. The methacrylation technique used in this study utilizes an esterification reaction involving methacryloyl chloride. While there are greener methods for methacrylation, for example via reaction with methacrylic anhydride, this method was chosen for convenience. Esterification with methacryloyl chloride results in high reaction conversions with minimal side products. This resulted in easier purifications.

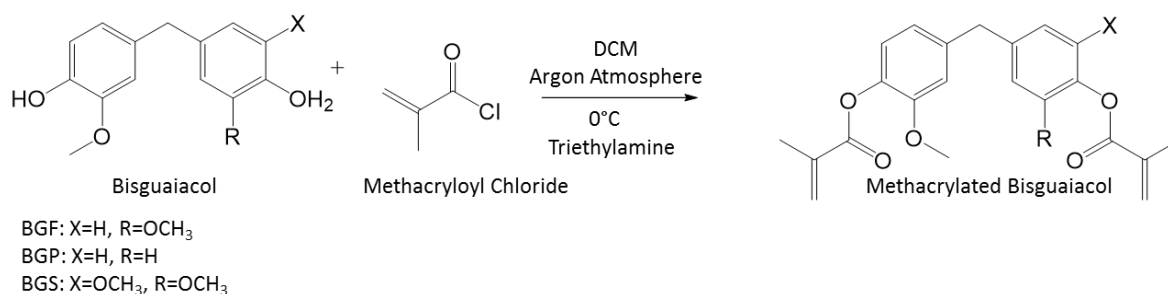


Figure 3.8: Reaction scheme for the reaction of lignin based bisguaiacol with methacryloyl chloride to form dimethacrylated bisguaiacol

A bisguaiacol monomer (10 g) was added to a 500 mL round bottom flask with triethylamine (2 bisguaiacol equivalents). The mixture was then diluted with 150 mL of dichloromethane (DCM). The flask was then placed in an ice water bath and subsequently sealed with a septum and sparged with argon for an hour to remove moisture and oxygen from the mixture. Methacryloyl chloride (2.5 bisphenol equivalents) was diluted to 50 vol% in DCM then added to the reaction mixture over the course of two hours using a separatory funnel. After all of the methacryloyl chloride was added to the mixture, the reaction was stirred for 24 hours and the temperature of the mixture was slowly increased to room temperature. This follows the work of Koz et al.⁷

Upon completion of the reaction, the mixture was dissolved in DCM (500 mL). The mixture was then washed with a saturated solution of sodium bicarbonate (500 mL) repeatedly. This was then followed by washes with 1.0 M NaOH in water and subsequently 1.0 N HCl (500 mL) and finally water (500 mL). The resulting products were then concentrated under reduced pressure after the addition of 400 ppm hydroquinone as a radical inhibitor. The product was characterized using ¹H NMR (400.13 MHz, 16scans at 298.2 K) with a Bruker AV-600 spectrometer. The major

peaks in the spectrum agreed with the expected structure of the dimethacrylated bisguaiacols.

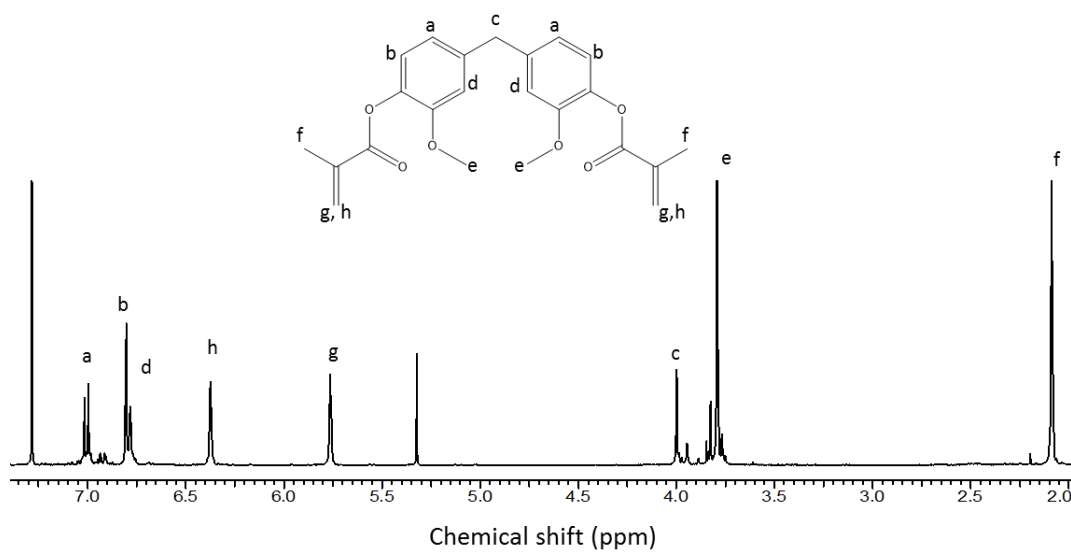


Figure 3.9: ^1H NMR of washed dimethacrylated BGF synthesized using methacryloyl chloride. Spectrum taken using Bruker AV-600 spectrometer (400.13 MHz, 16scans at 298.2 K in CDCl_3)

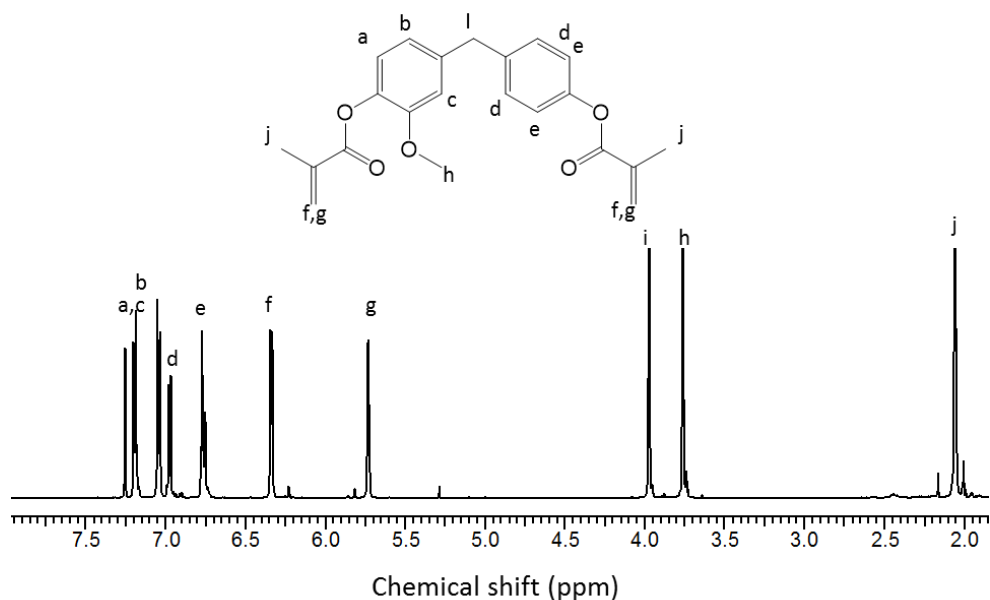


Figure 3.10: ^1H NMR of washed dimethacrylated BGP synthesized using methacryloyl chloride. Spectrum taken using Bruker AV-600 spectrometer (400.13 MHz, 16scans at 298.2 K in CDCl_3)

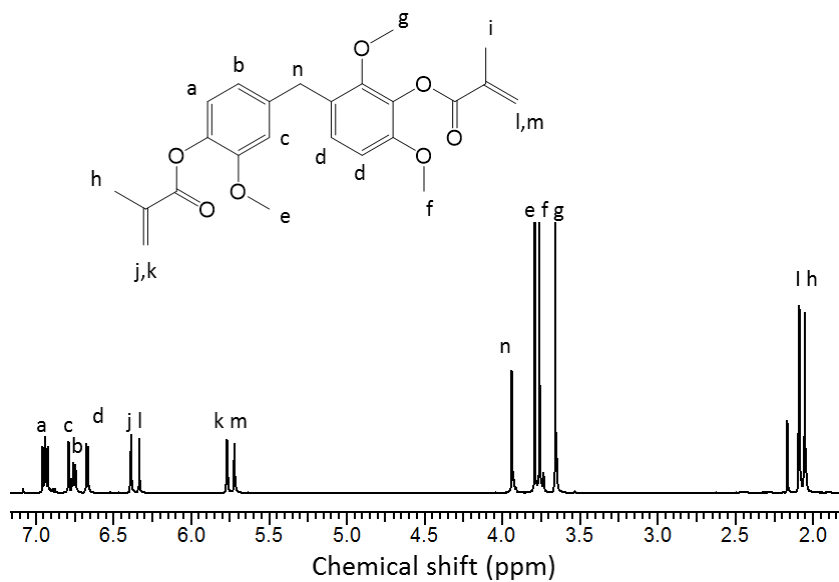


Figure 3.11: ^1H NMR of washed dimethacrylated BGS synthesized using methacryloyl chloride. Spectrum taken using Bruker AV-600 spectrometer (400.13 MHz, 16scans at 298.2 K in CDCl_3)

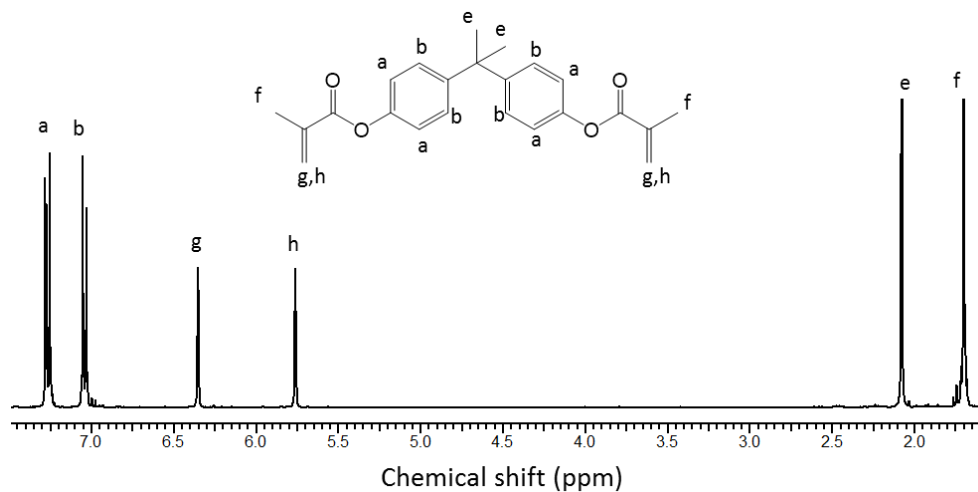


Figure 3.12: ^1H NMR of washed dimethacrylated BPA synthesized using methacryloyl chloride. Spectrum taken using Bruker AV-600 spectrometer (400.13 MHz, 16scans at 298.2 K in CDCl_3)

Chapter 4

POLYMER SYNTHESIS AND CHARACTERIZATION

4.1 Photocuring of Polymer Resins

The goal of this work is to cure each of the lignin based monomers with the reactive diluent Triethyleneglycol dimethacrylate (TEGDMA) and to evaluate the thermomechanical properties and conversion of the resulting polymers. The dimethacrylated BPA and bis-GMA were also cured with TEGDMA for comparison. Systems incorporating bis-GMA were used to determine representative properties of current resins used in dental practice. The polymer systems with dimethacrylated BPA were used to directly compare the properties of the bisguaiacol monomers with the properties of BPA. Dimethacrylated BGF was not cured because it was found to be insoluble in TEGDMA.

The conversion of the monomers in the sample were monitored using real time IR spectroscopy in which the near IR peak of the methacrylate =C-H peak was measured over time. The near IR peak was chosen because it has a relatively low absorptivity, allowing for thicker specimens to be measured.¹⁵

4.1.1 Materials

Triethyleneglycol dimethacrylate (TEGDMA) was purchased from Polysciences and used as received as a reactive diluent. 1-hydroxycyclohexyl phenyl ketone (Irgacure 184) was purchased from Ciba-Geigy. 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane (bis-GMA) was obtained from Esstech, Inc. All materials were used as received.

4.1.2 Methods

Each lignin based bisguaiaicol along with the dimethacrylated BPA were mixed with the reactive diluent TEGDMA at a mass ratio 50/50. The cleavage type UV-light photoinitiator Irgacure184 was used as the radical initiator for the system at a mass ratio of 0.5 wt%. In addition to the dimethacrylated bisphenols, samples of 50/50 wt% bis-GMA and TEGDMA were similarly prepared. The monomer and initiator were well mixed prior to curing until a homogeneous resin was achieved. For the bisguaiaicol resins, the monomers and initiators were first mixed with 10 mL of DCM. The DCM was then removed using a rotary evaporator and NMR was used to confirm that the solvent was fully removed with a tolerance of .05% mole purity. The specimen mold was constructed from two parallel transparent glass slides treated with Rain-X® as a releasing agent, separated by a rubber gasket, and secured with binder clips. The gasket contained a rectangular cutout for the specimen with the dimensions 21.00x4.61x0.80 mm. A schematic of this setup is shown in the figure below. A pipette was used to inject the solution into the open slot of the mold.

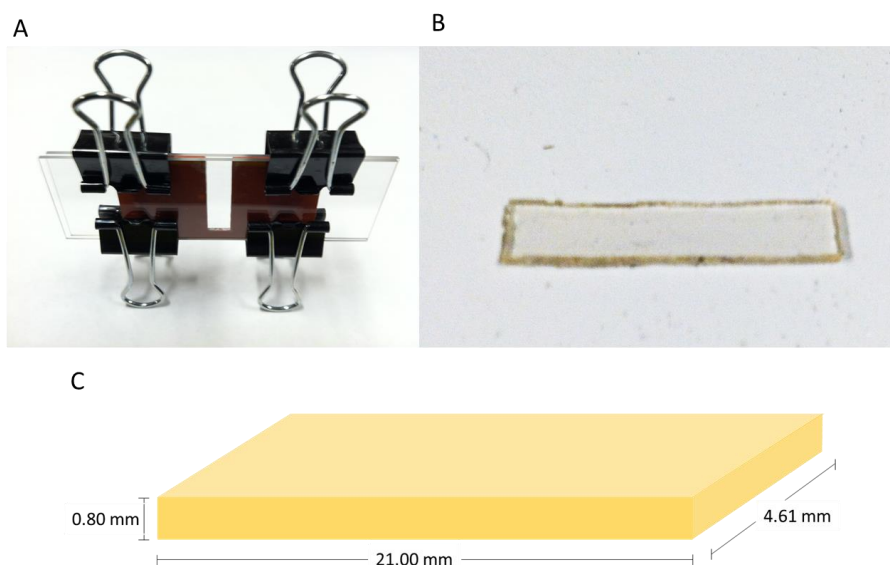


Figure : (A) Image of specimen mold constructed from glass slides, rubber gasket, and binder clips. (B) Image of example specimen following curing procedure. (D) Schematic of sample with sample dimensions

For the investigation of the conversion of the monomers in the resin sample, the resins were photopolymerized inside a Fourier transform infrared spectrometer (FTIR) chamber (Thermo Scientific Nicolet iS50 FTIR). An Omnicure series 2000 ultraviolet light source with a 365nm filter and with an intensity of 5 mW/cm^2 was used to cleave the Irgacure 184 and initiate polymerization. A near IR spectrum ($4000\text{--}7000 \text{ cm}^{-1}$) of the monomer mixture in the mold was collected prior to each cure and the area of the methacrylate =C-H peak ($6200\text{--}6140 \text{ cm}^{-1}$) was recorded (KBr beam splitter and MCTA detector cooled with liquid N_2). Real time near IR spectroscopy was then used to monitor the photopolymerization under constant UV IR-radiation with 4 scans per spectrum and 16 wavenumber resolution over a 30 minute curing time with an acquisition rate of 50 spectrum per minute. The UV light was turned on at 1 minute and normalized to time $t=0$ minutes. The area of the methacrylate =C-H

peak ($6200\text{-}6140\text{ cm}^{-1}$) was monitored over time using a series run. For each monomer, the above procedure was repeated in triplicate. The curing procedures follow the work of Lovell et. al.¹⁵

4.1.3 Results

Figure 4.1 - 4.4 show the near-IR series curves with standard error bars for each sample cured inside the FTIR chamber. The plots depict the conversion, which was calculated using the intensity of the methacrylate =C-H peak as a function of time. To obtain the conversion, the peak intensity at each given time was normalized by the peak intensity in the uncured sample, and this value was then subtracted from one to obtain the fractional conversion of the C=C double bonds over time.¹⁵ For each monomer, three sets of conversion data were obtained and the conversion values were averaged to determine a mean conversion and a standard deviation as a function of time. The standard deviation for every fiftieth data point is displayed by an error bar in the figures below.

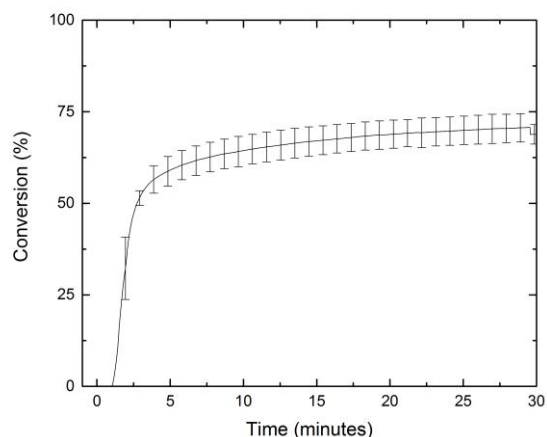


Figure 4.1: Double bond conversion as a function of time for bis-GMA/TEGDMA measured using IR spectroscopy tracing the methacrylate =C-H peak ($6200\text{-}6140\text{ cm}^{-1}$). Data points represent the average of three samples and error bars display the standard deviation in conversion for every fiftieth data point. The samples reached an average final conversion of 70.1 % with a standard deviation of $\pm 3.9\%$.

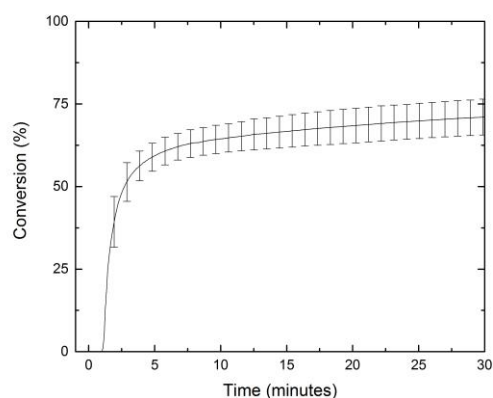


Figure 4.2: Double bond conversion as a function of time for dimethacrylated BPA/TEGDMA measured using IR spectroscopy tracing the methacrylate =C-H peak ($6200\text{-}6140\text{ cm}^{-1}$). Data points represent the average of three samples and error bars display the standard deviation in conversion for every fiftieth data point. The samples reached an average final conversion of 71.1 % with a standard deviation of $\pm 5.4\%$.

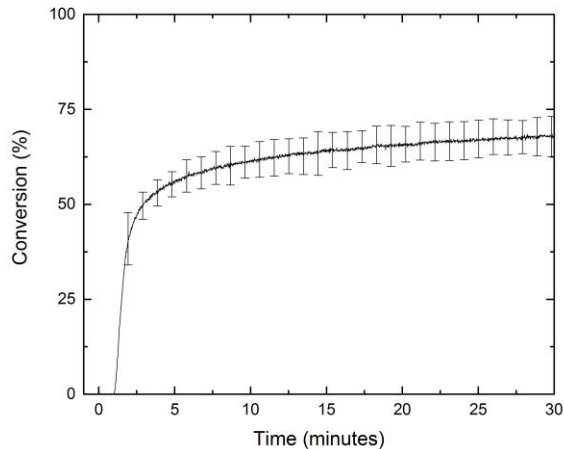


Figure 4.3: Double bond conversion as a function of time for dimethacrylated BGS/TEGDMA measured using IR spectroscopy tracing the methacrylate $=C-H$ peak ($6200-6140\text{ cm}^{-1}$). Data points represent the average of three samples and error bars display the standard deviation in conversion for every fiftieth data point. The samples reached an average final conversion of 68.7 % with a standard deviation of $\pm 7.0\%$

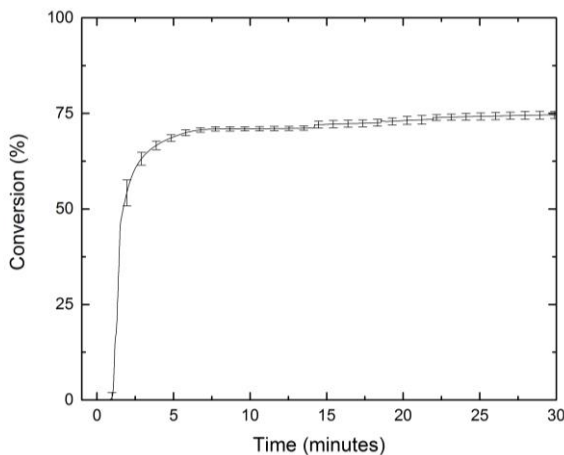


Figure 4.4: Double bond conversion as a function of time for dimethacrylated BGP/TEGDMA measured using IR spectroscopy tracing the methacrylate $=C-H$ peak ($6200-6140\text{ cm}^{-1}$). Data points represent the average of three samples and error bars display the standard deviation in conversion for every fiftieth data point. The samples reached an average final conversion of 74.8 % with a standard deviation of $\pm 0.7\%$

The data for double bond conversion as a function of time was also used to construct a plot of the polymerization rate. This is shown in the figure below.

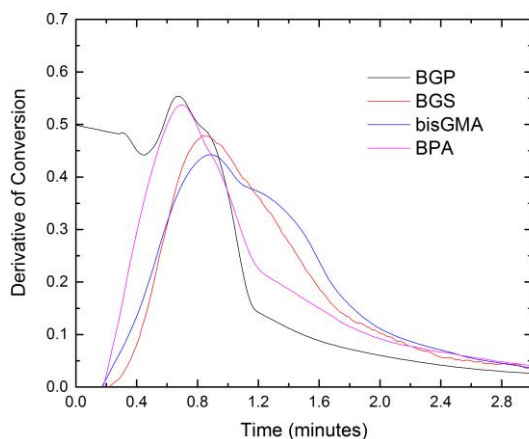


Figure : Reaction rate as a function of time found by approximating the derivative of the conversion data using Origin Labs software. The data is smoothed using the Savitzky-Golay method every 20 data points to aid in analysis

4.2 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was used to determine the storage modulus (E'), the loss modulus (E''), and the loss tangent ($\tan\delta$, the tangent of the ratio of the loss to storage modulus) at a fixed frequency over a specified temperature range. The rheological glass transition temperature (T_g) was taken as the maximum of the loss tangent curve. These parameters served as measures of the thermomechanical properties for the materials and allowed for a point of comparison.

4.2.1 Methods

A TA instruments Q800 dynamic mechanical analyzer was used to conduct all DMA experiments. All polymer samples were cured in rectangles with average dimensions of 21.00x4.61x0.80 mm. A tension film clamp was used for all tests. A temperature sweep was utilized with a constant frequency of 1 Hz with a maximum strain of 0.05 % to 0.1 %, depending on the sample. A heating rate of 3 °C/min was employed over a temperature range of -30 °C to 200 °C. The sample was kept under tension during experiments, with a static preload force of 0.01 N.

For each sample, the above procedure was repeated three times. This is because during the first heating trace, in the higher temperature region where the sample is rubbery, unreacted monomer in the sample cures and the sample reaches a higher conversion during the testing. Accordingly, only the third heating trace was used in data analysis.

4.2.2 Results

Figures 4.5 - 4.8 show the third heating trace DMA results for a bis-GMA/TEGDMA sample, a dimethacrylated BPA/TEGDMA sample, a dimethacrylated BGS/TEGDMA sample, and a dimethacrylated BGP/TEGDMA sample, respectively. The storage modulus and the loss modulus are shown as a function of temperature from -30 °C to 200 °C. For each sample, as the temperature is increased the storage modulus decreases rapidly as the thermoset transitions from a glassy state to a rubbery state, also known as the glass transition. The loss tangent as a function of temperature is shown in blue. The loss tangent goes through a clear maximum representing the rheological glass transition temperature. The loss tangent curve for the samples containing BPA, BGS, and BGP display a shoulder, or a slight

bump, at a temperature below the main T_g . This shoulder may indicate that the samples are slightly heterogeneous, and that upon polymerization, phase separation of the TEGDMA and respective bisguaiacol occurred, resulting in a lower T_g associated with the heterogeneous TEGDMA regions.

In running DMA for certain samples, temperature control issues were experienced, resulting in signal noise in some of the data. To aid in the analysis of the data, the Savitzky-Golay smoothing method was used to improve the appearance of the data using Origin Labs software.

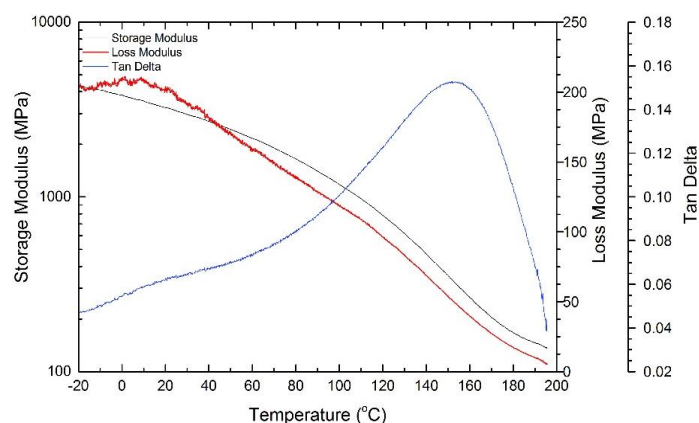


Figure 4.5: DMA data for cured bis-GMA/TEGDMA sample. The data was obtained with a maximum strain of 0.1%. The sample was heated at a rate of 2°C/min from -30°C to 200°C.

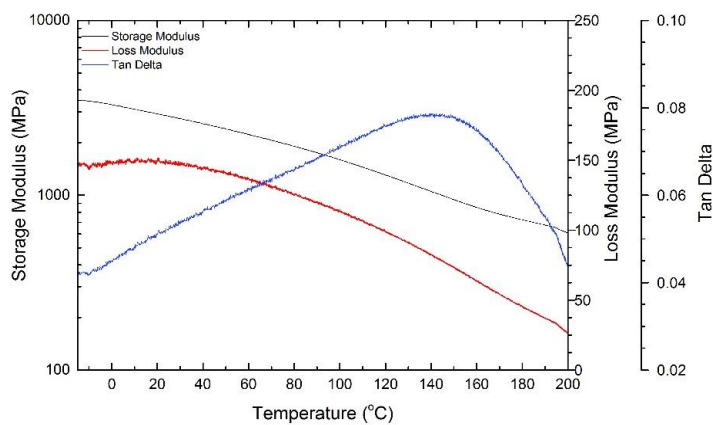


Figure 4.6: DMA data for dimethacrylated BPA/TEGDMA sample. A maximum strain of 0.05% was utilized. The sample was heated at a rate of 2°C/min from -30°C to 200°C.

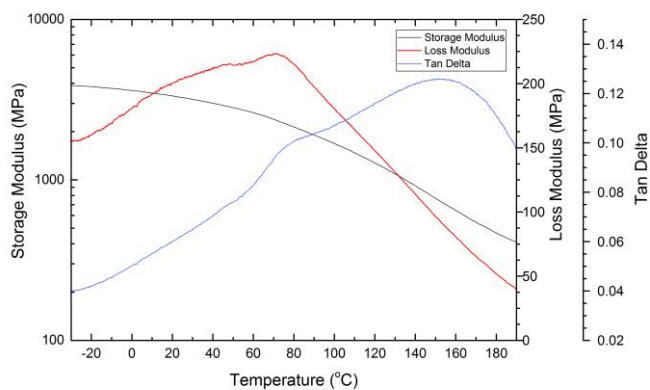


Figure 4.7: DMA data for dimethacrylated BGS/TEGDMA sample. A maximum strain of 0.1% was utilized. The sample was heated at a rate of 5°C/min from -30°C to 200°C.

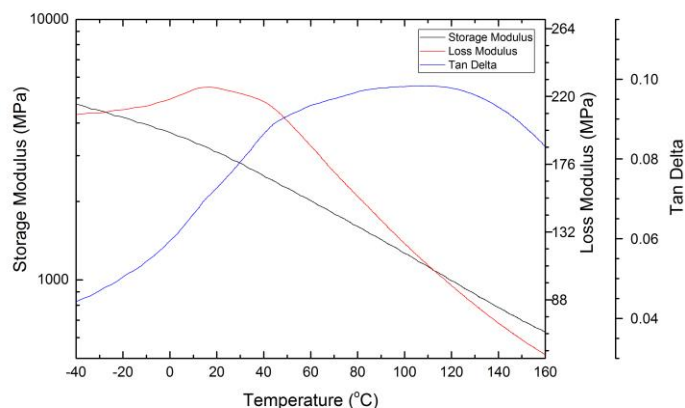


Figure 4.8: DMA data for dimethacrylated BGP/TEGDMA sample. A maximum strain of 0.05% was utilized. The sample was heated at a rate of 3°C/min from -30°C to 200°C. The loss tangent data is smoothed using the Savitzky-Golay method every 100 data points.

Table 4.1: Summary of T_g , conversions, and storage moduli at room temperature for each monomer sample

Sample	% Conversion	T_g (°C)	Storage Modulus at 20 °C (GPa)
bis-GMA/TEGDMA	70.1 ± 3.9	152	3.2
Dimethacrylated BPA/TEGDMA	71.1 ± 5.4	145	2.9
Dimethacrylated BGP/TEGDMA	74.8 ± 0.7	110	3.1
Dimethacrylated BGS/TEGDMA	68.7 ± 7.0	151	3.3

4.3 Discussion

Each novel bisguaiacol monomer exhibited polymerization behavior similar to that of bis-GMA/TEGDMA systems. In the neat photopolymerization of dimethacrylate monomers such as bis-GMA and TEGDMA, the propagation and the

termination reaction steps are known to be diffusion controlled.⁹ Termination reactions involve two radicals coming together to result in termination of both radical species. This process is known to be diffusion limited throughout the entirety of the polymerization reaction.⁶ As the network formation proceeds, the mobility of radicals decreases and consequently the rate of termination decreases. The resulting effect of this phenomenon is an increase in the rate of polymerization as the reaction proceeds.⁹ Radical propagation reactions, by contrast, only display diffusion limiting character at higher conversions since these reactions involve mobile methacrylate groups reacting with polymeric radicals.⁹ As higher polymerization conversions are reached, the polymer undergoes vitrification, resulting in decreased mobility of methacrylate groups and a shift to diffusion controlled kinetics. The vitrification of the network decelerates the rate of polymerization and limits the final conversion of the material.¹⁸ The two distinct kinetic regimes for propagation results in two regions of kinetic behavior, which were clearly exhibited in the conversion plots of each system. In each plot of conversion vs. time, at low conversions an exponential polymerization rate is displayed, as indicated by the large slope. When higher conversions are reached, however, each plot displays a distinct region with a low polymerization rate, indicating that the kinetics have been slowed by vitrification. One notable deviation in kinetic behavior is the initial polymerization rate displayed by dimethacrylated BGP systems. As shown in Figure 4.4, dimethacrylated BGP/TEGDMA samples reached high conversions considerably faster than bis-GMA/TEGDMA and the other dimethacrylated bisphenol/TEGDMA resins. Compared to BGS, BGP has a lower number of aromatic methoxy groups. Methoxy groups are electron donating, and accordingly the aromatic ring of BGS is most likely more nucleophilic than that of

BGP. The higher electrophilicity of BGP when compared to BGS may explain the higher relative reaction rate in the first kinetic regime in which propagation is not diffusion limited. Additionally, compared to BPA, BGS also has more rotational freedom due to the lack of methyl groups on the alkane bridge between the two aromatic groups. This increased rotational freedom of BGP may account for the faster kinetics associated with dimethacrylated BGP when compared to the kinetics of systems derived from BPA.

The differences in final conversions between the dimethacrylated bisguaiacols, dimethacrylated BPA, and the bis-GMA are within error of each other and therefore are not statistically significant. This may indicate that neither the number of methoxies nor the nature of the polymerizable methacrylate group effect final conversion when compared to BPA derived monomers. It may be expected that more flexible glycidyl methacrylate groups, such as those found in bis-GMA, allow for increased radical propagation and higher final conversions compared to the more ridged methacrylate groups of the bisguaiacol dimethacrylates. This behavior, however, was not observed in the conversion studies presented here and therefore may be attributed to a higher mobility of the methacrylated monomers themselves due to their smaller size and molecular weight.

The T_g of the bisguaiacol dimethacrylate monomer systems displayed a significant deviation from each other and from the dimethacrylated BPA and bis-GMA systems. The highest T_g was displayed by dimethacrylated BGS/TEGDMA systems, followed by the dimethacrylated BPA, bis-GMA, and dimethacrylated BGP in decreasing order. The dimethacrylated BPA monomer synthesized in this study exhibited a T_g 10 °C higher than that of bis-GMA. This is expected because bis-GMA

contains glycidyl methacrylate moieties, which increase chain mobility and therefore decrease the T_g compared to the dimethacrylates that contain shorter and less flexible methacrylate groups. The dimethacrylated BGS/TEGDMA sample exhibited a particularly high T_g of 151 °C, 41 °C higher than dimethacrylated BGP systems and 21 °C higher than dimethacrylated BPA systems. Dimethacrylated BGS contains three methoxy groups compared to dimethacrylated BGF (two methoxy groups) and dimethacrylated BGP (one methoxy group). Side groups, such as methoxys, have the potential to increase the free volume in the polymer sample which increases the molecular motion of the chains in the polymer network and thus decreases the T_g . Contrarily, an increased number of methoxy groups may also have the effect of restricting the bond rotation in the polymer sample, which increases the stiffness of the sample and results in a higher T_g . The high T_g of polymers incorporating dimethacrylated BGS may indicate that the decreased bond rotation caused by the methoxy groups has a more significant effect on the glass transition than the increase in free volume. Furthermore, this hypothesis is supported by the low T_g of polymer systems incorporating BGP.

Chapter 5

SUMMARY

In this study, novel lignin based bisguaiacol monomers were synthesized via acid catalyzed electrophilic aromatic substitution reactions involving vanillyl alcohol and either guaiacol, syringol, or phenol. This resulted in three bisguaiacol compounds designated BGF, BGS, and BGP respectively. Each bisguaiacol monomer differs solely in the number of aromatic methoxy groups they contain, where BGP contains one, BGF contains two, and BGS contains three methoxy groups. As expected, vanillyl alcohol primarily substituted *para* to the hydroxyl of phenol and guaiacol during electrophilic aromatic substitution reactions, however, in reactions with syringol, vanillyl alcohol primarily substituted *meta* to the hydroxyl group. This is attributed to the two *ortho*, *para* directing methoxy groups on syringol, which appear to dominate over the strong *para* directing nature of the hydroxyl group.

One application of interest for the lignin based bisguaiacols synthesized in this work is in dental resins for restorative composites. Accordingly, each monomer was difunctionalized with methacrylate moieties, which are commonly used in medical and dental materials because they are readily photopolymerizable. Dimethacrylated BPA was also synthesized for use as a direct comparison to the bisguaiacol monomers.

Following the synthesis of the lignin based dimethacrylate monomers, the dimethacrylated BGP and dimethacrylated BGS were photopolymerized using TEGDMA as the reactive diluent. The polymerization conversion of each of the monomers was monitored using in situ FTIR spectroscopy. Each dimethacrylated bisguaiacol monomer, along with bis-GMA and dimethacrylated BPA, had no statistically significant difference in final conversion, ranging from 68.7 % to 71.1 %.

Dynamic mechanical analysis testing was completed for polymer samples incorporating BGP, BGS, BPA, and bis-GMA and the T_g of the samples, determined from the peak of the loss tangent, were compared. Polymer samples incorporating dimethacrylated BGS were found to have considerably higher T_g compared to the other methacrylated bisguaiacols and BPA derived methacrylates. It is postulated that this increase in T_g is a result of decreased backbone rotational freedom and increased chain stiffness imparted by the three methoxy side groups.

The lignin based bisguaiacol monomers in this study display considerable promise in their applicability for dental composite resins when reacted with TEDGMA. While the bisguaiacol based polymer systems exhibited slightly lower storage moduli, these monomers displayed high T_g and high degrees of conversion when compared to currently used bis-GMA/TEGDMA systems. These characteristics are highly favorable in dental resin systems. Further testing in the practicality of these materials may include an investigation of the polymerization induced shrinkage and the chemical stability.

Chapter 6

FUTURE WORK

6.1 Additional Parameters for Dental Resins

One aim of this study was to evaluate the applicability of novel lignin based bisguaiacols in dental resin systems. In this work, DMA was used to calculate the T_g of the samples along with the storage and loss moduli. FTIR was also used to track the monomer conversion. While these are important parameters in the characterization of a dental resin material, there are several other parameters that are important to evaluate in assessing a material's efficacy as a dental resin. One additional relevant parameter is the polymerization shrinkage upon curing. Polymer systems such as bis-GMA/TEGDMA exhibit a shrinkage stress, which can deform dental structures in teeth and cause adhesive failure.⁹ Polymerization shrinkage can be measured with a tensometer, in which the sample is cured in situ and the shrinkage caused by curing is measured by the increase in tension. Another important parameter is the flexural strength of the material. A three-point bending flexural test can be used to obtain additional mechanical properties that help to compare the properties of the resin to that of bone. Chemical degradation analysis is also important in determining a material's suitability for dental materials. This helps to ensure that the resin will remain stable in biological conditions.¹⁶

6.2 Additional Functionalities

In this work, methacrylate functionality is used in the synthesis of bisguaiacol monomers for dental resin applications, and these monomers are compared to bis-GMA, with glycidyl methacrylate groups. It is somewhat insufficient to compare the dimethacrylated monomers in this study to bis-GMA because they have different

functionality. To conduct a more thorough evaluation of the lignin based bisguaiacol monomers as potential dental resins, it is desired to also use glycidylmethacrylate functionality for the bisguaiacol monomers.

6.3 Additional Polymer Systems

While the lignin based bisguaiacol monomers synthesized in this study have shown some promise as dental materials, there are a wide variety of other polymer and chemical applications in which these monomers may be applicable. The feasibility of using these monomers for applications similar to that of BPA can be further evaluated by incorporating the bisguaiacol monomers in additional polymer systems. Current work is focusing on synthesizing epoxy resins from the bisguaiacol monomers and comparing these resins to similar BPA based products. The novel lignin based bisguaiacols may also be incorporated into polycarbonate polymers.

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